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Handbook of Thermoplastic Elastomers

Jiri George Drobny

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To Mary Martha and Jirina

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Preface

The goal of this work is to compile in one place the current working knowledge of chemistry, processing, physical, and mechanical properties, as well as the applications of thermoplastic elastomers.

The introduction (Chapter 1) covers some general theoretical subjects applicable to all thermoplastic elastomers, such as principles of rubber elasticity, phase structure, and essential thermodynamics of phase separation in block copolymers, general methods of synthesis of thermoplastic elastomers, classification of thermoplastic elastomers, and advantages and disadvantages of thermoplastic elastomers in comparison to conventional vulcanized rubber materials. Following the introduction are a brief history of TPEs and a chapter on additives for thermoplastics in general.

A rather comprehensive review of processing methods applicable generally to thermoplastic elastomers is in Chapter 4. This chapter will be useful to the reader in that it provides a ready reference when reading sections dealing with processing of individual thermoplastic elastomers and needs additional and more detailed information about the particular process. In some cases processing conditions for individual thermoplastic elastomers are in corresponding chapters. Additional processing data for most commercial TPEs are in Appendix 4.

Because of the great number of thermoplastic elastomers, and the variety of chemistries involved, it appeared useful to create individual detailed chapters describing individual groups of TPEs containing specifics as to the industrial preparation, properties, processing methods, and conditions for each group. Applications form a separate chapter that includes ample illustrations for each group. Recent developments and trends conclude the main body of the work.

A significant part of this book is dedicated to engineering data useful to processors and users of these materials. We attempted to include as many of these as possible and to present information provided by the major manufacturers and they are included in respective appendices. It should be noted that with the very large number of different grades with constant development and/or replacement of current grades there is only a limited number of data sheets we could include. Yet, it is felt that even with these limitations they will be a valuable resource for the reader.

Additional appendices include bibliography, list of major manufacturers and respective trade names, ISO nomenclature, and recent patents. A rather comprehensive glossary concludes the work.

To make the work useful to readers anywhere in the world, both SI units and those common in the United States are used side by side as much as possible.

The focus is more on practical than on theoretical subjects. The goal has been to provide a useful reference and resource of learning the basics for those entering the field and updated references for those already involved in polymerization, processing, and part manufacture. The work is also intended to be a solid resource for end users as well as a comprehensive textbook for students specializing in polymer science and technology or material science. Each chapter includes ample references for in-depth study of the subjects. These references are listed at the end of each chapter. Bibliography, major symposia, and major review papers on thermoplastic elastomers are listed in Appendix 1.

My thanks are due to the team from the William Andrew Publishing, particularly to Dr. Sina Ebnesajjad, Valerie Haynes, Betty Leahy, Martin Scrivener, and Millicent Treloar for bringing this work to fruition, to Professor Nick Schott from the University of Massachusetts at Lowell, Professor Vratislav Ducháček from the Technical University in Prague, and Dr. Ivan Chodák from the Slovak Academy of Sciences for helpful comments during the preparation of the manuscript.

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May 2007

1 Introduction

1.1 Elasticity and Elastomers

Rubber-like materials consist of relatively long polymeric chains having a high degree of flexibility and mobility, which are joined into a network structure. The flexibility and mobility allow for a very high deformability. When subjected to external stresses, the long chains may alter their configuration rather rapidly because of the high chain mobility. When the chains are linked to a network structure, the system has solid-like features, where the chains are prevented from flowing relative to each other under external stresses. As a result, a typical rubber may be stretched up to 10 times its original length. On removal of the external forces, it is rapidly restored to its original dimensions, with essentially no residual or nonrecoverable strain.

When ordinary solids, such as crystalline or glassy materials, are subjected to external forces, the distance between two atoms may be altered by only a few angstroms for the deformation to be recoverable. At higher deformations, such materials either flow or fracture. The response of rubber is entirely intramolecular, that is, the externally applied forces are transmitted to the long chains through the linkages at their extremities, change their conformations, and each chain acts like an individual spring in response to the external forces [1].

High molecular weight polymers form *entanglements* by molecular intertwining (see Fig. 1.1a), with a spacing (in the bulk state) characteristic of the particular molecular structure. The spacing is expressed by *molecular weight between entanglements* (M_e). Some examples of values of the molecular weight M_e for several elastomers are listed in Table 1.1. Thus, a high molecular weight polymeric melt will show transient rubber-like behavior even in the absence of any permanent intermolecular bonds [2]. In a crosslinked elastomer, many of these entanglements are permanently locked in (see Fig. 1.1b), and at a high enough degree of crosslinking, they may be regarded as fully equivalent to crosslinks and as such they contribute to the elastic response of the material.

A *network* is obtained by the linking of polymer chains together, and this linkage may be either *chemical* or *physical*. Physical linking can be obtained by [1]

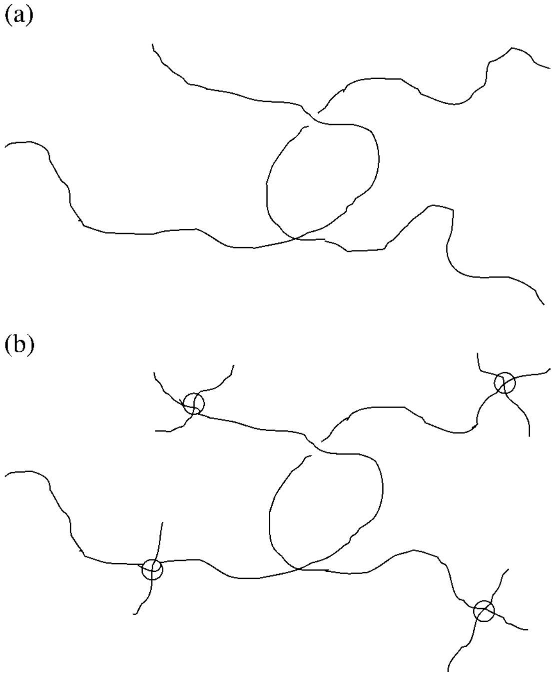


Figure 1.1. (a) Molecular entanglements in a high-molecular weight polymer. (b) Molecular entanglements locked by cross-linking. *Source*: Reference [2].

Table 1.1. Representative Values of the Average Molecular Weight between Entanglements (M_e) for Polymeric Melts

Polymer	M_e
Polyethylene	4,000
cis-1,4-Polybutadiene	7,000
cis-1,4-Polyisoprene	14,000
Poly(isobutylene)	17,000
Poly(dimethyl siloxane)	29,000
Polystyrene	35,000

Note: Obtained from viscosity measurements.
Source: Reference [2].

(1) absorption of chains onto the surface of finely divided particulate fillers;
(2) formation of small crystallites;

(3) coalescence of ionic centers; and
(4) coalescence of glassy blocks.

These physical crosslinks are, in general, not permanent and may disappear on swelling or increase in temperature. Physical, thermoreversible networks are present in most *thermoplastic elastomers* (TPEs). Materials of this kind are technologically very attractive because they can be processed as thermoplastics; yet they exhibit the behavior of rubber vulcanizates, when cooled down to a sufficiently low temperature.

1.2 Thermoplastic Elastomers

In the previous section, the concept of physical crosslinks was introduced and a statement was made that materials with thermoreversible crosslinks can be processed as thermoplastics (i.e., by melt processing) and that they exhibit elastic behavior similar to that of vulcanized (chemically crosslinked) conventional elastomers. Such materials represent a large group of polymers called thermoplastic elastomers.

1.2.1 Phase Structure

Most TPEs are essentially phase-separated systems. The only currently known exceptions are Alcryn® (registered trademark of Advanced Polymer Alloys), a single-phase melt-processible rubber (MPR) and materials based on ionomers. Usually, one phase is hard and solid at ambient temperature whereas the other is an elastomer. Often, the phases are bonded chemically by block or graft polymerization. In other cases a fine dispersion of the phases is apparently sufficient [3]. The hard phase gives these TPEs their strength and represents the physical crosslinks. Without it the elastomer phase would be free to flow under stress and the polymer would be practically unusable. On the other hand, the elastomer phase provides flexibility and elasticity to the system. When the hard phase is melted or dissolved in a solvent, the material can flow and can be processed by usual processing methods. Upon cooling or evaporation of the solvent, the hard phase solidifies and the material regains its strength and elasticity.

The individual polymers constituting the respective phases retain most of their characteristics so that each phase exhibits its specific glass transition temperature (T_g) or crystalline melting temperature (T_m). These two temperatures determine the points at which the particular elastomer goes through transitions in its physical properties. An example of this is in Fig. 1.2, which represents the measurement of flexural modulus over a wide range of temperatures. There are three distinct regions:

(1) At very low temperatures, that is, below the glass transition of the elastomeric phase, both the phases are hard, so the material is stiff and brittle.
(2) Above the T_g temperature, the elastomeric phase softens and the material is elastic, resembling a conventional vulcanized rubber.
(3) As the temperature increases, the modulus stays relatively constant (a region referred to as "rubbery plateau") until the point where the hard phase softens or melts. At this point the material becomes a viscous fluid.

From these findings, it is obvious that the service temperature range lies between the T_g of the elastomeric phase (lower service temperature) and the T_g or T_m of the hard phase (upper service temperature). The exact values depend on the service conditions of the final product, for example, the amount of hardening that will be tolerated in the final product or the amount of stress applied. Thus, often the actual lower service temperature will be higher than T_g of the elastomer and the actual upper service

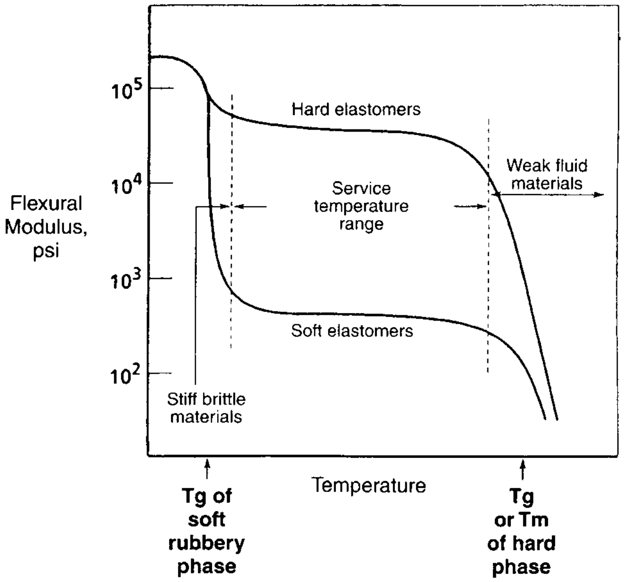


Figure 1.2. Stiffness of typical thermoplastic elastomers in dependence on temperature (Courtesy Hanser Publishers).

Table 1.2. Glass Transition and Crystalline Melt Temperatures of Major TPEs

Thermoplastic Elastomer Type	Soft, Rubbery Phase, T_g (°C)	Hard Phase, T_g or T_m (°C)
Styrenic block copolymers		
S–B–S	−90	95 (T_g)
S–I–S	−60	95 (T_g)
S–EB–S	−55	95 (T_g) and 165 (T_m)[a]
Multiblock copolymers		
Polyurethane elastomers	−40 to −60	190 (T_m)
Polyester elastomers	−40	185 to 220 (T_m)
Polyamide elastomers	−40 to −60	220 to 275 (T_m)
Polyethylene–poly(α-olefin)	−50	70 (T_m)
Poly(etherimide)–polysiloxane	−60	225 (T_g)
Hard polymer–elastomer combinations		
Polypropylene–hydrocarbon rubber[b]	−60	165 (T_m)
Polypropylene–nitrile rubber	−40	165 (T_m)
PVC–(nitrile rubber+DOP)	−30	80 (T_g) and 210 (T_m)

Notes:
[a] In blends containing polypropylene.
[b] EPDM, EPR, butyl rubber, and natural rubber.
Source: Reference [4] chapter 19.

temperature will be lower than the T_g or T_m of the hard phase. Glass transition and crystalline melt temperatures for major TPEs are given in Table 1.2.

1.2.2 Methods of Synthesis of Thermoplastic Elastomers

1.2.2.1 Methods of Synthesis of Block Copolymers

A substantial portion of industrially produced TPEs is represented by *block copolymers*, consisting of two or more polymer chains attached at their ends. A *linear block* comprises two or more polymer chains in sequence, whereas a *star block* copolymer comprises more than two linear blocks attached at a common branch point. Most block copolymers are prepared by controlled polymerization methods discussed below. Block copolymer architectures are shown in Fig. 1.3.

Anionic polymerization is a well-established method for the synthesis of tailored block copolymers. To prepare well-defined polymers, the technique is demanding, requiring high-purity starting reagents and the use of high-vacuum procedures to prevent accidental termination due to presence

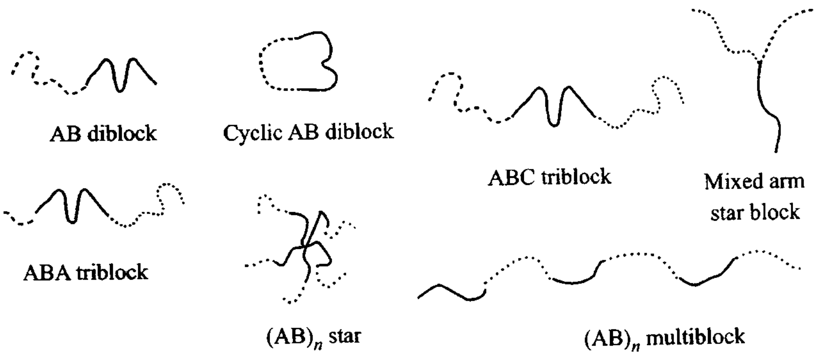


Figure 1.3. Block copolymer architectures.

of impurities. In the laboratory, it is possible to achieve polydispersities $M_w/M_n < 1.05$ via anionic polymerization. In industrial practice, this method is used to prepare several important classes of block copolymers including the SBS-type TPEs. Anionic polymerization is discussed in some detail in Chapter 5.

Cationic polymerization (sometimes referred to as *carbocationic polymerization*) is used to polymerize monomers that cannot be polymerized anionically, although it is used for only a limited range of monomers. More details on cationic polymerization used in the synthesis of styrenic TPEs with isobutylene monomer of the type (S–iB–S) are in Section 5.3.

Controlled/living radical polymerization (CLRP) is the most recently developed method that can be used for the synthesis of TPEs [5]. The principle of CLRP is to establish a dynamic equilibrium between a small fraction of growing free radicals and a large majority of dormant species. Generated free radicals propagate and terminate as in conventional free radical polymerization, although the presence of only a small fraction of radicals prevents premature termination [6]. More details are in Chapter 16.

Polymerization with Ziegler-Natta catalysts is used for the synthesis of several block polyolefin-based TPEs [7], which is described in Chapter 7.

Polyaddition is used for the synthesis of multiblock thermoplastic polyurethanes using diisocyanate, long-chain diol, and a chain extender [8]. A more detailed discussion of this subject can be found in Chapter 9.

1.2.2.2 Methods of Synthesis of Other Thermoplastic Elastomers

Other industrial methods used for the synthesis of TPEs with morphologies other then blocks are

- dynamic vulcanization—used for thermoplastic vulcanizates (TPVs) (Chapter 6);
- esterification and polycondensation—used for polyamide elastomers (Chapter10);
- transesterification—used for copolyester elastomers (COPEs) (Chapter 11);
- catalytic copolymerization of olefins—used for reactor thermoplastic polyolefins (RTPOs) (Chapter 7); and
- direct copolymerization, for example, copolymerization of ethylene and methacrylic acid leading to certain ionomeric TPEs (Chapter 12).

1.2.3 Phase Separation

In order to develop superior mechanical properties in a two-component polymeric system, the components should be neither so incompatible that they do not wet nor so mutually soluble that would they form one homogeneous phase [9]. Most of the currently known systems are compatible to the extent that a slight degree of mixing takes place or interfacial bonding is developed directly, such as in grafts or blocks [10].

Polymer incompatibility arises from the very small entropy gained by mixing different kinds of long chains. In fact, in the limit of high molecular weight, only polymer pairs with zero or negative heats of mixing form one phase.

Generally, materials mix to form a single-phase system if the free energy of mixing (ΔG_m) is favorable, that is, negative. This free energy can be expressed in terms of enthalpy of mixing (ΔH_m) and entropy of mixing (ΔS_m):

$$\Delta G_m = \Delta H_m - T\Delta S_m, \tag{1.1}$$

where T is the absolute temperature. The condition for domain formation (i.e., phase separation) is a positive value of the free energy of mixing. Thus,

$$\Delta H_m > T\Delta S_m. \tag{1.2}$$

ΔH_m for hydrocarbon polymers is almost always positive because there are no strongly interacting groups and increases as the structures of the two polymers forming the segments become less alike [11]. T and ΔS_m will always be positive and therefore the term $-T\Delta S_m$ will always be negative. However, this term will approach zero as the molecular weights of the segments become large and/or as the temperature decreases. The conditions favoring the phase separation (or domain formation) will be

- segments with highly different structures;
- segments with high molecular weight; and
- low temperature.

Unlike polyblends, where the constituting polymers separate at macroscopic scale, for block copolymers, only microhomogeneous scale separation is possible, due to the covalent bond linking the blocks of different polymers, which forces them to regroup in smaller domains. The reasons for demixing of two blocks of the copolymer are the same as those for demixing of low molecular weight liquids. However, it becomes predominant for mixtures of polymers or in a block copolymer when the chains are very long and/or the constituting polymers differ considerably (see above).

The two or more distinct and incompatible moieties provide unique solid state and solution properties to block copolymers, which in turn lead to various applications. The *microphase separation* in block copolymers gives rise to formation of different types of microdomains in the solid state, including spherical, cylindrical, lamellar, and others. In addition to this, they show micellization and adsorption characteristics in suitable solvents [12].

When a diblock copolymer is mixed with a homopolymer A, the mixture may exist as an ordered or disordered single phase or undergo *macrophase separation*. Thus, phase diagrams of mixtures containing a block copolymer and a homopolymer exhibit fascinating complexity involving macrophase or microphase separation [12].

The phase behavior of undiluted bulk $(A-B)_nx$ (branched) block copolymers is essentially determined by three experimentally controllable factors [13]:

(1) the overall degree of polymerization;
(2) architectural constraints and the composition (overall volume fraction of the component A); and
(3) the A–B segment–segment (Flory–Huggins) interaction parameter χ.

The first two factors are controlled by polymerization stoichiometry and affect the translational and configurational entropy, whereas the magnitude of the largely enthalpic χ is determined by the selection of the monomer A–B pair.

The issues of thermodynamics of block copolymers and of order–disorder transitions in block copolymers are discussed thoroughly in references [13] and [14], respectively.

1.2.4 Classification of Thermoplastic Elastomers

Currently known TPEs can be classified into the following seven groups:

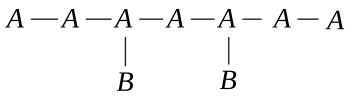
(1) styrenic block copolymers (SBCs);
(2) crystalline multiblock copolymers;
(3) miscellaneous block copolymers;
(4) combinations of hard polymer/elastomer;
(5) hard polymer/elastomer graft copolymers;
(6) ionomers; and
(7) polymers with core-shell morphologies.

Considering such a large variety of materials, it is clear that their properties will be within a wide range, from very soft rubbery to hard and tough, at which point they approach the ill-defined borderline between elastomers and flexible thermoplastics. Property ranges are shown in Table 1.3.

1.2.4.1 Nomenclature of Block Copolymers

The majority of TPEs are either *block* or *graft* copolymers, which are made up of sequences with different chemical and physical structures usually represented by capital letters—A, B, C, etc. These sequences are of such molecular weight, which would give them polymeric features, even when they were separated. The manner in which these sequences are arranged defines the type of block copolymer. Thus, a *diblock* copolymer is represented by A–B, indicating that a segment with composition A is connected to a segment with composition B. *Triblock* copolymers can be represented as A–B–A or A–B–C. Other possibilities are $(A–B)_n$ or $(A–B)_nx$. Triblocks of the A–B–A type have two terminal blocks A connected to a central block B; the A–B–C triblocks are composed of three blocks, each from a different monomer. $(A–B)_n$ is an alternating block copolymer A–B–A–B…, and $(A–B)_nx$ is a branched copolymer with n branches, where $n = 2, 3, 4, \ldots$, and x represents a multifunctional junction point. Branched block copolymers with $n = 3$ or more are referred to as *star-shaped* or *star-branched* block copolymers.

Using this terminology, a graft copolymer may be represented as



$$\begin{array}{ccccccccccccc} A & - & A & - & A & - & A & - & A & - & A & - & A \\ & & & & | & & & & | & & & & \\ & & & & B & & & & B & & & & \end{array}$$

In this copolymer one or more polymeric segments B are attached (grafted) to the chain backbone composed of polymeric species A.

It is common practice to use the first letter of the monomer unit to denote the polymeric block, for example, S for a styrene polymeric block, B for a polybutadiene polymeric block, and so on. Thus, the block copolymer poly(styrene-b-butadiene-b-styrene) is written as S–B–S. By the same token, if one of the block is itself a copolymer (ethylene-propylene copolymer), the block copolymer poly(styrene-b-ethylene-co-propylene-b-styrene) is written as S–EP–S [7, 14, 15].

Table 1.3. Property Ranges of Selected TPEs

Thermoplastic Elastomer	Specific Gravity	Durometer Hardness
Styrenic block copolymers		
S–B–S (pure)	0.94	65A–75A
S–I–S (pure)	0.92	32A–37A
S–EB–S (pure)	0.91	65A–71A
S–B–S (compounds)	0.9–1.1	40A–45D
S–EB–S (compounds)	0.9–1.2	5A–60D
Polyurethane/elastomer block copolymers	1.05–1.25	70A[a] –75D
Polyester/elastomer block copolymers	1.15–1.40	35D–80D
Polyamide/elastomer block copolymers	1.0–1.15	60A–65D
Polyethylene/poly(α-olefin) block copolymers	0.85–0.90	65A–85A
Polypropylene/EPDM or EPR blends	0.9–1.0	60A–65D
Polypropylene/EPDM dynamic vulcanizates	0.95–1.0	35A–50D
Polypropylene/butyl rubber dynamic vulcanizates	0.95–1.05	50A–80D
Polypropylene/natural rubber dynamic vulcanizates	1.0–1.05	60A–45D
Polypropylene/nitrile rubber dynamic vulcanizates	1.0–1.1	70A–50D
PVC/nitrile/DOP rubber blends	1.20–1.33	50A–90A
Halogenated polyolefin/ethylene interpolymers blends	1.10–1.25	50A–80A

Note:
[a] As low as 60A when plasticized.
Source: Modified from reference [3].

1.2.5 Advantages and Disadvantages of Thermoplastic Elastomers

TPEs offer a variety of *advantages* over conventional thermoset (vulcanized) rubber materials, such as the following:

(1) Simpler processing with fewer steps since TPEs use the processing methods for thermoplastics, which are typically more efficient and significantly less costly so the final cost of the finished part is lower.

(2) Shorter fabrication times, which also lead to lower finished part costs. Since molding cycles for TPEs are typically several seconds as opposed to minutes for thermoset rubbers, the productivity of the given equipment is greatly increased.

(3) There is little or no compounding. The majority of TPEs is supplied fully formulated and ready for fabrication.

(4) The possibility of reusing scrap in the same fashion as with thermoplastics. The scrap from thermoset rubbers is very often discarded. Its amount generated may be in some cases comparable to the weight of the molded part. The TPE scrap can be reused as a regrind frequently producing materials having the same properties as the virgin material.

(5) Lower energy consumption due to shorter molding cycles and simpler processing.

(6) Better quality control and closer tolerances of finished parts due to simpler formulations and process.

(7) Lower quality control costs because of greater reproducibility and consistency of properties of TPE resins.

(8) Since most TPEs have lower density than conventional rubber compounds, their volume cost is often lower.

The *disadvantages* of TPEs in comparison to conventional rubber materials include

(1) melting at elevated temperatures. This inherent property limits the use of parts from TPEs to service temperatures well below

Table 1.4. World Thermoplastic Elastomer Demand, Current and Forecast ('000 metric tons)

Item	2004	2009	2014	% Annual growth, 09/04
Thermoplastic elastomer demand	2300.0	3100.0	4200.0	6.2
By type				
Styrenic block copolymers (SBCs)	1081.0	1409.0	1847.0	5.4
Thermoplastic polyolefins (TPOs)	506.2	687.0	936.0	6.3
Thermoplastic polyurethanes (TPUs)	320.1	442.0	609.0	6.7
Thermoplastic vulcanizates (TPVs)	161.7	233.0	332.0	7.6
Copolyester elastomers (COPEs)	120.9	175.0	256.0	7.7
Other TPEs	110.1	154.0	220.0	6.9
By region				
North America	628.7	785.5	980.5	4.6
Western Europe	503.4	608.0	726.5	3.8
China	690.0	1052.0	1587.0	8.8
Japan	153.0	183.5	220.5	3.7
Other Asia/Pacific	237.0	342.5	497.5	7.6
Other regions	87.9	128.5	188.0	7.9

Source: Freedonia Group, Inc., Cleveland, Ohio.

their melting point. A thermoset rubber would be probably suitable for a brief exposure to that temperature;

(2) limited number of low hardness TPEs. Many TPEs are available at hardnesses about 80 Durometer A or higher. The number of materials softer than 50 Durometer A is still rather limited;

(3) drying prior to processing. This step is almost never used for conventional rubber materials but is quite common in fabrication of thermoplastics in general.

1.2.6 Demand for Thermoplastic Elastomers and Its Growth

Current global demand (apparent consumption) for TPEs reported in November 2005 (data from 2004) is 2,300,000 metric tons, with SBCs representing the largest volume, followed by thermoplastic polyolefins (TPOs) [16]. China represents the largest volume market in the world, mainly due its massive footwear industry. Through 2009, China's TPE market is predicted to expand and diversify rapidly based on the country's significant positions in the production of many of the key products manufactured with TPE parts and components. However, with the notable exception of China, global TPE sales will remain concentrated in the developed markets of the United States, Western Europe, and Japan, particularly for higher-performance materials such as COPEs and TPVs. Growth prospects through 2009, however, are predicted to be still strongest in the developing countries [13]. The current data and prognosis for the growth through 2014 overall, by type of TPE and by regions, are in Table 1.4.

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2 A Brief History of Thermoplastic Elastomers

The development of thermoplastic materials having more or less elastic properties started in the early 1930s with the invention of plasticization of PVC at the B.F. Goodrich Company [1]. This invention led to further interest in flexible plastics and eventually to the development of blends of PVC and NBR (butadiene-acrylonitrile rubber) [2, 3]. The PVC/NBR blends, when properly formulated, have a rubber-like look and feel and bridge the gap between liquid plasticized PVC and conventional cured elastomers. Thus, they can be considered as the precursors of thermoplastics elastomers, as we know them today.

A major breakthrough occurred with the discovery of the basic diisocyanate polyaddition reaction in 1937 [4], which was first applied to produce polyurethane fibers and then to the development of some elastomeric polyurethanes at DuPont and ICI [5–7]. The work at DuPont focused on elastic fibers and eventually led to the invention of elastic linear copolyesters, prepared by melt-ester interchange between two melt copolymerized polymers [8]. This synthetic elastomer had higher strength than vulcanized natural rubber and exhibited a rapid elastic recovery. It was used to make fibers by extrusion or spinning from solutions and can be considered to be the first thermoplastic elastomer. The DuPont patent dated 1954 [9] describes it as segmented polyurethane fiber with excellent elastic properties.

Further development of *thermoplastic polyurethanes* continued through the 1950s and 1960. In 1962 a group from the B.F. Goodrich Company presented an article on “Virtually cross-linked polymer, Polyurethane VC,” which was soluble, had high tensile strength, good elasticity, high abrasion resistance, and could be processed as a thermoplastic [10, 11]. Commercial polyurethane thermoplastic elastomers were introduced in the 1960s by B.F. Goodrich, Mobay and Upjohn in the United States, and by Bayer A.G. and Elastogran in Europe.

Styrene-diene block copolymers were first developed by Shell utilizing anionic block copolymerization of styrene with butadiene (S–B–S) and styrene with isoprene (S–I–S) and were introduced commercially in 1966 as Kraton®. Phillips Petroleum Co. entered this field in 1968 with radial styrenic block copolymers. In 1972 Shell added the S–EB–S copolymer, where EB is the ethylene-butylene copolymer segment. S–EB–S copolymer is prepared by hydrogenation of the polybutadiene center block thus eliminating the double bonds and improving resistance of the product to oxidative scission and ozone attack [12]. The product was introduced as Kraton G®.

Copolyetherester thermoplastic elastomers were developed during the 1960s and were commercialized by DuPont in 1972 as Hytrel®. The randomly segmented copolymer contains poly(tetramethylene oxide) terephtalate soft segments and multiple tetramethylene terephtalate hard segments. The attributes of this material were high strength, high elasticity, excellent dynamic properties, and creep resistance. Similar products were commercialized by the GAF Corporation in the late 1970s (Pelprene®), by Eastman Chemical Co. in 1983 (Ecdel®), and by the General Electric Corporation in 1985 (Lomod®).

Thermoplastic polyolefin blends (TPOs) were developed throughout the 1960s. The first patent on record is that of Hercules Inc. covering blends of crystalline polypropylene and ethylene-propylene copolymers (EPM), in which the propylene content was more than 50% [13]. Dynamically vulcanized blends of polypropylene and chlorinated butyl rubber were patented in 1962 [14]. Partially dynamically cured blends of EPM or ethylene-propylene-diene monomer with polypropylene using peroxide curing were the subject of two Uniroyal patents issued in 1974 [15, 16]. Uniroyal Inc. introduced TPR thermoplastic rubber materials consisting of blends of partially dynamically cured EPDM with polypropylene in 1972.

Thermoplastic vulcanizates (TPVs) are materials based on an extensive research done at the Monsanto Company during the 1970s and 1980s. These are mechanically mixed blends of an elastomer with a thermoplastic [17–30]. The first commercial product was Santoprene® based on a blend (or alloy) of EPDM and polypropylene introduced in 1981. A similar product based on a blend of butadiene-acrylonitrile rubber (ASTM designation NBR) and polypropylene, Geolast® was introduced in 1985 [31].

Polyamide thermoplastic elastomers were introduced in 1982 by ATO Chemie followed by Grilamid® and Grilon produced by Emser Industries and by Dow Chemical Company's Estamid® [32–34]. The properties of polyamide TPEs depend upon the chemical composition of the hard (polyamide) block and the soft (polyether, polyester, or polyetherester) block.

Single-phase melt-processable rubber (MPR) is based on work done at DuPont in the early 1980s and led to the commercialization of proprietary products under the name Alcryn® in 1985.

During the last two decades of the 20th century many new developments have taken place, such as functionalized styrenic TPEs [35, 36], new and improved TPVs, softer MPRs, and MPRs with improved physical properties, TPEs based on blends of natural rubber and polypropylene [37], thermoplastic fluoroelastomers [38], etc. Many more companies have developed new products and their applications. The above subjects will be discussed in chapters dealing with individual TPEs and their applications as well as in a chapter summarizing the newest developments and trends.

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3 Additives

Practically all thermoplastic resins contain essential stabilizers that are added during or immediately after polymerization to prevent their degradation during monomer recovery, drying, and compounding, and in some cases even during storage. The types and amounts vary depending on the type of the polymer. Other additives may be added during the different stages of processing and provide specific characteristics of the material during processing and/or application.

The following sections briefly describe the most common additives used in the majority of thermoplastics. The actual number of such additives is very large and the reader can find a more detailed coverage of this subject in several publications [1–3].

3.1 Antioxidants

Many organic materials, including polymers undergo reactions with oxygen. When polymers oxidize, they lose mechanical properties, such as tensile strength, may become rough or cracked on the surface, or discolor. These typical manifestations of oxidation are referred to as *aging*, and the effects of oxidation on the chemical structure of the polymers are called *degradation* [4]. Aging and degradation can be inhibited or retarded by chemical substances called *antioxidants*.

Most antioxidants are used in polyolefins and styrenics and impact-modified styrenics, and to a somewhat lesser degree in polycarbonates, polyesters, polyamides, and polyacetals. The type and amount of antioxidant used depend on the type of resin and application; typical levels range 0.05–1% by weight on the weight of the polymer [4].

The effectiveness of antioxidants under *processing conditions* has to be assessed on the polymeric melt. The usual procedure consists of multiple extrusions or prolonged residence times in a hot cylinder or in the injection molding machine. The properties evaluated are change in melt flow index, and possibly yellowing. The assessment of the effectiveness under *conditions of actual use* is done by measuring changes upon exposure to elevated temperatures in heat aging ovens below the melting point of the polymer. Accelerated aging test at temperatures much higher than service temperatures yield rapid results but these are generally not very significant in actual practice. Ideally, oven-aging tests should be carried out as close to the use temperature as practical [5].

In general, antioxidants inhibit the oxidation reaction by combining with free radicals or by reacting with hydroperoxides. *Primary antioxidants,* such as *hindered phenolics* and *secondary aromatic amines* are radical scavengers. The most common simple hindered phenolics antioxidant is butylated hydroxytoluene (BHT) or 2,6-di-t-butyl-4-methylphenol [6]. Higher molecular weight hindered phenolics antioxidants are less volatile and are used when high processing temperatures are necessary or for high temperature applications. The advantage of hindered phenolics antioxidants is that they do not discolor easily. Moreover, certain high molecular weight phenolics antioxidants are approved by the FDA [7]. Secondary aromatic amines are superior to phenolics for high-temperature applications, but they discolor easily and are therefore used only in combination with pigments or carbon blacks. In such a combination the discoloration is masked. These antioxidants are not approved for food-contact use [7].

Secondary antioxidants, also called peroxide decomposers [7], inhibit the oxidation of polymers by decomposing hydroperoxides. *Phosphites* and *thioesters* are the most common secondary antioxidants. Phosphites are the most widely used secondary antioxidants. They are nondiscoloring and FDA approved for many indirect food applications [7]. Secondary antioxidants are usually combined with primary antioxidants for a synergistic effect.

3.2 Light Stabilizers

In general, polymers deteriorate in the presence of sunlight, which results in cracking, embrittlement, chalking, discoloration, or loss of mechanical properties, such as tensile strength, elongation, and impact strength. *Photodegradation* occurs as a result to exposure to ultraviolet light at wavelengths 290–400 nm. Different wavelengths may produce different types of degradation, depending on the polymer [8]. Specialty chemicals, called *light stabilizers* or *UV stabilizers*, are used to interfere with the physical and chemical processes of light-induced polymer degradation. Stabilization of the polymer can occur by the use of additives that absorb UV radiation, preventing its absorption by the molecules of the polymers, by free radical scavengers, by the additives that decompose peroxides, or by quenchers that accept energy from the chromophore and convert it to heat [9].

3.2.1 UV Absorbers

UV absorbers act as optical filters; they absorb UV light and release the excess energy as heat. The most widely used UV absorbers are 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, organic nickel compounds, and sterically hindered amines (hindered amine light stabilizers, HALS). Other additives, such as carbon blacks and certain pigments (e.g., titanium dioxide, zinc oxide), may be used as UV absorbers in certain applications, where the color or loss of transparency does not matter [10].

3.2.2 Quenchers

Quenchers are molecules that accept the energy from an excited state chromophore. The chromophore, after transferring its energy, reverts to its ground state, a stable energy state. The quencher dissipates the energy as heat, fluorescence, or phosphorescence, that is, methods that do not result in the degradation of the polymer. Most widely used quenchers are organic nickel complexes, such as [2,2'-thiobis(4-octylphenolato)-n-butylamine nickel (II), nickel salts of thiocarbamate, and nickel complexes with alkylated phenol phosphonates [11]. Quenchers are often used in combination with UV absorbers.

3.2.3 Free Radical Scavengers

Free radical scavengers are similar to secondary antioxidants that are used to inhibit thermal oxidation. They react with free radicals in the plastic material, reducing them to stable, unreactive products. HALS function mainly as free radical scavengers, although they may also be made to work as quenchers and peroxide decomposers.

HALS are available in a wide variety of molecular weights. They display low volatility and good stability at high temperatures. They can provide surface protection and can be used alone or in combination with UV absorbers or quenchers. Use levels depend on the substrate thickness, pigmentation, and application requirements, generally ranging from 0.1% to 1.5% [12–14].

3.2.4 Evaluation of UV Stability

The most accurate test of UV stability is the use of the material in its intended end-use environment over a period of time. Because outdoor testing takes a very long time, accelerated testing using artificial light sources (xenon arc lamp, sunshine carbon lamp, mercury arc lamp) is common. Filtered xenon most accurately reproduces the spectral energy distribution of sunlight, whereas light sources with significant emission below 290 nm can produce different results than those obtained in long-term outdoor weathering. Accelerated tests may underestimate the effectiveness of HALS due to very high levels of UV radiation produced [14]. New types of artificial weathering devices have been developed in the past few decades, including those combining high UV intensity from fluorescent lamps with water condensation on the test samples (QUV, UVCON) [15].

3.3 Nucleating Agents

Polymers crystallize from a melt under the following conditions [16]:

(1) The molecular structure of the polymer must be regular enough to allow crystalline ordering.

(2) The crystallization temperature must be below the melting temperature, but not close to the glass transition temperature of the polymer.

(3) Nucleation must occur prior to crystallization.

(4) The crystallization rate has to be sufficiently high.

Because of chain connectivity, polymers crystallize in such a way that only a limited crystallinity is obtained. Polymers are, therefore, often referred to as semi-crystalline materials. This chain connectivity is also the main reason why polymers crystallize at significantly lower temperatures than they melt.

When polymers crystallize from the melt, the polymer crystals (lamellae) organize from a primary nucleus and form complex spherical macrostructures called spherulites. The spherulites contain lamellae as well as amorphous regions between the lamellae. The spherulites continue to grow into the melt until their growth fronts impinge on the growth fronts of the neighboring spherulites.

The onset of phase transformation is indicated by the appearance of very small particles of the new phase. Eventually primary nucleation will occur and the crystal growth will follow [17]. The rate of nucleation is strongly dependent on temperature.

The number and size of spherulites formed are determined by whether the nucleus formation is homogeneous or heterogeneous. The formation of nuclei is greatly enhanced by the addition of foreign substances—the *nucleating agents*. Since much more nuclei are formed in the presence of a nucleating agent, under the same cooling conditions the resulting spherulites will be considerably smaller than in a material to which no nucleating agents have been added. Nucleated polymers have, therefore, finer grain structure than unnucleated ones, and this is reflected in their physical and mechanical properties. Thus, plastics with coarse spherulites are more brittle and less transparent or translucent than ones with the same crystalline fraction but a fine spherulitic structure.

Nucleation increases the crystallization temperature and the rate of crystallization; as a result, parts can be removed from the mold at higher temperatures, and molding cycle times are reduced. Nucleated materials have higher tensile strength, stiffness, flexural moduli, and heat deflection temperatures (HDTs), but impact strength is in general lower. Clarity is enhanced by increased the cooling rate and reduced spherulite size, which reduces the scattering of light as it passes through the material [18].

Nucleating agents can be roughly classified as follows [19]:

(1) inorganic additives, such as talc, silica, clay;
(2) organic compounds, such as salts of mono- or polycarboxylic acids (e.g., sodium benzoate), and certain pigments;
(3) polymers, such as ethylene/acrylic ester copolymers.

The usual amounts of nucleating agents used in thermoplastics are up to 0.5%, higher amounts usually do not produce further enhancement. They are incorporated as powder/powder mixtures, as suspensions or solutions, or in the form of a master batch. Regardless of which method is used, a good predispersion of the nucleating agent is necessary for an optimum effect [19].

3.4 Flame Retardants

Many thermoplastics, particularly those with high carbon content are inherently flammable due to their petrochemical origin. Polyolefins ignite when in contact with a flame and burn with a faintly luminous flame even after the ignition source is removed. Melting occurs due to the high temperature of the flame, producing burning drips. Thermoplastics containing halogens tend not to burn easily; some of them do not burn at all, the main factor being the content of the halogen.

Additives used to retard or stop burning are referred to as *flame retardants*. Flame retardants generally impart their properties to polymers in the condensed or gaseous phase. In the condensed phase, the additive can remove thermal energy from the substrate by functioning as a heat sink or by participating in char formation to form a barrier heat and mass transfer. The additive can also provide flame retardancy by conduction, evaporation, or mass dilution or by participating in endothermic reaction.

Char forming systems, also called *intumescent* systems, form a foamy porous protective barrier on the polymeric material to shield it from further pyrolysis and combustion. Most intumescent systems require an acid source (catalyst), a char-forming compound (carbonific), and a gas-evolving compound (spumific). In a typical system, phosphorus compound promotes the charring of a substrate (typically a carbon–oxygen compound or an oxygen-containing polymer), and this char is foamed by gases released during the decomposition of a nitrogen compound. The acid is typically a phosphoric acid or a suitable derivative, such as ammonium polyphosphate. Typical carbonifics include pentaterythritol and other polyols. Common spumifics include urea, melamine, and dicyandiamide. Commercial intumescent systems containing catalyst, carbonific, and spumific are also available [20].

Other flame retardants acting in the condensed phase do so, not by forming an intumescent layer, but by depositing a surface coating that insulates the polymer from the heat source and retards the evolution of additional fuel. Some silicone flame retardants are thought to deposit silicon dioxide (sand) on the polymer surface [21].

The most widely used flame retardant alumina trihydrate (ATH) functions in the *condensed phase*, not by forming char or a protective layer, but by functioning as a heat sink and a source of a noncombustible gas (H_2O) for fuel dilution. ATH starts to decompose at 230°C and eventually loses 34.5% of its mass as water vapor. Magnesium hydroxide decomposes at 340°C and loses 31% mass.

Both ATH and magnesium hydroxide decompose endothermically and remove heat from the condensed phase, which decreases the rate of polymer decomposition. Substantial quantities of these additives are needed to impart flame retardancy to a combustible polymer. For example, a resin formulation containing 40–60% by weight of ATH is typical.

Flame retardants acting in the gas *phase* interrupt the combustion chemistry of the fire. During combustion, polymer fragments interact with oxygen and other highly reactive species in a chain reaction to form oxygen radicals, hydroxyl radicals, and hydrogen radicals. Certain additives, mainly those containing halogens or phosphorus, can chemically interact with these radicals to form less energetic species and interrupt the chain propagation necessary for fire initiation or continuation [22]. A typical example of such flame retardant systems is *antimony trioxide*, which is effective in halogenated polymer systems. Some *phosphorus* flame retardants can also be effective in the gas phase. *Zinc borate* has been used as a partial or complete replacement for antimony oxide mostly in olefins. Zinc borate is less expensive than antimony oxide and also functions as a smoke suppressant, afterglow suppressant, and antiarcing agent [23].

Organic compounds containing *halogens* (chlorine or bromine) function in the gas phase of the combustion reaction by scavenging free radicals formed during combustion. Antimony trioxide is generally added to halogenated flame retardants for *synergistic effect* [23].

Brominated flame retardants are subjected to increasing restrictions due to possible environmental and health risks of brominated diphenyl ethers, which can under some conditions form brominated dioxins and furans.

Recent research efforts in the field of nanocomposites have yielded flame retardant additives that are effective and environmentally friendly. Intercalated polymer clay nanocomposites have been used in several polymers and were found to have lower peak heat release rates than pure polymers [24]. The advantage of such systems is that only small loadings (3–6%) impart flame retardancy without affecting the physical properties of the resin used [25].

3.4.1 Flammability Tests

Flammability tests have been developed to measure the burning parameters, such as burning time, dripping, smoke emission, and flame spread, of a material under specific conditions, in order to predict its performance in an actual fire. Many applications require specific performance levels in particular tests.

The most common test is the Underwriters Laboratory UL-94. In this test, the specimen is suspended vertically over a Bunsen burner and surgical cotton. The specimen is ignited for 10 s with a defined gas flame from below. If the specimen extinguishes after the removal of the ignition flame, it is ignited once more for 10 s. The results are classified in the following way:

(1) V-0 rating
  - Afterflame time < 10 s
  - Sum of afterflames (10 flame applications) ≤ 50 s
  - No burning drips igniting the cotton
  - Specimens do not burn completely to the clamp
  - Afterglow after removal of ignition ≤ 30 s.

(2) V-1 rating
  - Afterflame time < 30 s
  - Sum of afterflames (10 flame applications) ≤ 250 s
  - No burning drips igniting the cotton
  - Specimens do not burn completely to the clamp
  - Afterglow after removal of ignition ≤ 60 s.

(3) V-2 rating
  - Afterflame time < 30 s
  - Sum of afterflames (10 flame applications) ≤ 250 s
  - Ignition of cotton by burning drips
  - Specimens do not burn completely to the clamp
  - Afterglow after removal of ignition ≤ 60 s.

Limiting oxygen index (LOI) test is based on determining the minimum concentration of oxygen necessary for candle-like burning of ≥3 min. Numerical data are obtained, and the LOI is generally directly proportional to the concentration of the flame retardants. A higher LOI indicates that more oxygen is needed to support combustion. Air contains ~21% oxygen, so a rating lower than this will usually support combustion under normal atmospheric conditions [26]. The LOI method has been standardized by the American Society for Testing Materials as ASTM D2863 and by the International Organization for Standardization as ISO 4589-2 [27].

In Europe, the German DIN 4102, the British BS 476 Part 7, and the French NF P 92-501 are used to test building materials and to assign flammability ratings [27].

3.5 Colorants

Colorants used in plastics are pigments or dyes. *Dyes* are organic compounds that are soluble in the plastic, forming a molecular solution. They produce bright, intense colors and are transparent and easy to disperse and process. *Pigments* are generally insoluble in the plastic; color results from the dispersion of fine particles (~0.01–0.1 μm) throughout the resin. They produce opacity or translucence in the final product. Pigments can be inorganic or organic compounds and are available in a variety of forms, such as dry powders, color concentrates, liquids, and precolored resins.

3.5.1 Optical Properties of Colorants

Pigment and dyes produce color in a resin from selective absorption of visible light with wavelength ranging from ~380 (violet) to 760 nm (red). The perceived color is the color of the light transmitted through the colorant and not the light that was absorbed. Complementary colors are red–green, blue–orange, and violet–yellow. The human eye can detect color differences of about 1 nm in wavelength. Absorption of all wavelengths will produce a black color; no absorption will appear colorless [28].

Because dyes are in solution, color is produced only from light absorption, and the material is transparent. A dispersion of pigment particles in a resin can also reflect or scatter light. If the refractive index of the pigment particle is different from that of spherulites in the polymer microstructure, light will be reflected, and the particle dispersion will scatter light in all directions. Light reflection and scattering produces opacity in an originally transparent resin. Resins can be colored and opaque if light was absorbed only at particular wavelengths, or white and opaque if all light was reflected (no absorption). The color shade is affected by the particle size of the pigment. Ultramarine blue pigments are nonreflective because of their refractive index being similar to that of the plastic [29].

3.5.2 Characteristics of Colorants

Pigments must be adequately dispersed in the polymer for optimum scattering; specks and uneven coloration can result from incomplete dispersion. If agglomerates are present they may adversely affect the mechanical properties of the resulting product, mainly tensile strength, impact strength, and flex fatigue.

Pigments should be compatible with the polymer; poor compatibility may be a cause of part failure. Some pigments may be partially soluble in the resin and may migrate through the polymer to the surface, where they rub off. Pigments must also be compatible with any other additives present in the formulation.

High temperature during processing can damage or destroy the pigment causing changes in shade or loss of color. Thermal sensitivity is related to both temperature and duration of exposure—long cycles in injection molding and rotational molding can have a more adverse effect than high-speed extrusion.

Some pigments can act as nucleating agents, altering the mechanical properties and improving the clarity of the resin [30].

3.5.3 Inorganic Pigments

The most common inorganic pigments include oxides, sulfides, hydroxides, chromates, and other complexes based on metals such as cadmium, zinc, titanium, lead, and molybdenum. They are generally more thermally stable than organic pigments and are more opaque and resistant to migration, chemicals, and fading. They can cause wear on the processing equipment, such as extrusion machine screws and barrels. The use of compounds of heavy metals (e.g., cadmium) has been restricted due to toxicity issues.

White pigments—titanium oxide (rutile) is the most widely used white pigment. It is used either alone or in combination with other colorants to control opacity and produce pastel shades. Other white pigments are zinc oxide, zinc sulfide, and lead carbonate (lead white).

Black pigments—carbon black, which is essentially pure carbon, is by far the most widely used black pigment. When combined with white pigments, it produces different shades of gray, depending on the particle size and tinting strength of the carbon black grade. Iron oxide, Fe_3O_4, is another black pigment, which has lower thermal stability and tinting strength.

Other colored pigments—a variety of inorganic compounds is used for coloring thermoplastics. Below is a listing of the most common ones:

(1) Yellow pigments: Chrome yellow; nickel-, chrome-titanium yellow; iron oxides; lead chromates.
(2) Orange pigments: Molybdate orange and cadmium orange.
(3) Brown pigments: Iron oxide or combination of chrome/iron oxides.
(4) Red pigments: Iron oxide; cadmium sulfide/selenide.
(5) Blue pigments: Ultramarine (aluminosilicate with sodium ion and ionic sulfur groups); mixed metal oxides, based primarily on cobalt aluminate.
(6) Green pigment: Chrome oxide; cobalt-based mixed oxides.

3.5.4 Organic Pigments

Organic pigments are usually brighter, stronger, and more transparent than inorganic pigments but are not as light resistant. They may be partially soluble in many thermoplastics, with a much greater tendency to migrate.

Azo pigments are the largest group of organic pigments; they contain one or more azo (—N=N—) chromophoric groups and form yellow, orange, and red pigments. Monoazo pigments, that is, with only one chromophore, exhibit low thermal and light stability and have a tendency to bleed; they are not usually used in plastics. Polyazos, with more than one chromophore, do not tend to bleed and have better thermal stability and excellent chemical stability.

Nonazo pigments have varied structures, usually polycyclic and sometimes complexed with metals. Phtalocyanine blues and greens, most of which are complexed with copper, are highly stable to light, heat, and chemicals and form highly transparent, intense colors with high tinting strength. Other organic pigments are *quinacridones* (red, violet, orange), dioxazines (violet), isoindolines (yellow, orange, red), and *perylenes, flavanthrones, and anthraquinones* [31].

3.5.5 Special Effect Pigments

Some colorants produce special effects in plastics, such as pearlescence or phosphorescence. The pigment must be well dispersed in the resin and must be carefully handled during processing. *Pearlescent pigments* produce pearly lusters and iridescence—the resin has a soft, silky, and/or multicolor appearance. Luster is produced by reflection of light by thin (<1 μm) platelets oriented in parallel layers. Pearlescent pigments include titanium dioxide coated mica (muscovite), ferric oxide coated mica, and bismuth oxychloride.

Metallic flakes are used to produce silvery lusters or gold bronze effects. Aluminum, copper, and alloys of copper and zinc (bronze) are commonly used. Aluminum can be processed up to 310–340°C (600–650°F) with loadings in the range 0.5–4%. Copper is susceptible to oxidation starting at ~120°C (250°F) and can tarnish, depending on temperature and duration of exposure. Slow discoloration occurs in outdoor applications [32, 33].

Fluorescent pigments appear to glow in daylight; they absorb visible and ultraviolet light, and then emit the light in longer wavelengths. A glow appears when this light combines with the reflected color of the plastic. *Phosphorescent pigments* also emit light at longer wavelengths than it was absorbed, but the yellow–green glow appears only in darkness. Phosphorescence is produced by the addition of doped zinc sulfide [34].

3.5.6 Colorant Forms

Colorant forms include dry color, color or pellet concentrates, liquid color, and precolored resins. A precolored resin contains the colorant already dispersed in the polymer; all other forms require dispersion by the resin processor.

Dry colorants are powders composed of one or more pigments or dyes. They are supplied in preweighed packets and must be compounded and dispersed into the resin. Dry colorants are the most economical form and provide the largest selection of colors and use a minimum of warehousing space. Their disadvantage is their tendency to dust and to cross-contaminate.

Color concentrates are colorants dispersed in a resin carrier that is formulated for use in a particular polymer family. Color concentrates can contain 10–80% colorant, depending on the application requirements, the pigment used, and the compounding equipment. Color concentrates are the most common form of in-house coloring. They are most frequently supplied in pellet form for easy flowing and metering.

Liquid colorants are composed of a pigment in a nonvolatile liquid carrier. Liquid carriers include mineral oils and complex fatty acid derivatives and can contain surfactants for improved dispersion and clean up. Their viscosities range from maple syrup to gel-like consistencies, and good dispersion can frequently be obtained with high pigment loading (10–80%). The carrier can affect polymer properties and its processing behavior.

A very comprehensive treatment of the subject of coloring additives, their types, their chemistry and technology can be found in references [1–3].

3.6 Antistatic Agents

In general, thermoplastics are good insulators, because of which, they do not conduct electricity and an electric charge can build up on the surface of a part, leading to problems with dust accumulation, static cling in films and fabrics, electric discharge that can produce shocks or fires, and damage to electronic components.

Static electricity or an electrostatic charge is a deficiency or excess of electrons, which occurs on ungrounded or insulated surfaces. It is produced by triboelectric charges, that is, charges generated by friction between two surfaces, such as, for example movement of paper through a copier or printer. The ability of a material to discharge static electricity is classified according to its surface resistivity, the ratio of direct current (DC) voltage to current passing across a square unit of area, in ohms/sq (see Table 3.1). Surface resistivity is independent of the size of the square or its unit.

A material with useful antistatic properties has a surface resistivity between 10^9 and 10^{12} ohms/sq. Static decay rate of insulating polymers measures the ability of grounded material to dissipate a charge induced on its surface. The decay rate of an insulated material is much slower than that of a material treated by dissipative materials.

3.6.1 Types of Antistatic Agents

Antistatic agents, commonly called *antistats*, can be ionic or nonionic. *Ionic* antistats include cationic compounds, such as quaternary ammonium, phosphonium, or sulfonium salts, and anionic compounds, usually sodium salts of sulfonates, phosphates, and carboxylic acids. Nonionic antistatic agents include esters, such as glycerol esters of fatty acids, and ethoxylated tertiary amines. Antistats are used usually at levels from 0.5% to <1%, and loading levels depend mainly on the resin processing temperatures, the presence of other additives, and application requirements, such as clarity, printability, and FDA compliance [35].

Table 3.1. Classification of Surface Resistivity

Surface Resistivity (Ohms/sq)	Classification
$\leq 10^5$	Conductive
$>10^5$ to $\leq 10^9$	Static dissipative
$>10^9$ to $\leq 10^{14}$	Antistatic
$>10^{14}$	Insulative

Source: Reference [35].

In general terms, antistatic agents can be divided according to the method of application into internal and external agents [36].

Internal antistats are incorporated into the polymer mass as surfactant additives, either before or during processing (e.g., molding). They have limited compatibility with the polymer and continuously migrate to the part surface. An antistat must exhibit the proper amount of compatibility with the given polymer for a controlled migration to the surface.

External antistats are applied directly to the surface of the finished article from an aqueous and/or alcohol solution (concentration typically 1–2%) as spray or dip. Internal and external antistatic agents can function lubricants and mold release agents [36, 37].

3.6.2 Electrically Conductive Materials

Static electricity can be dissipated by the addition of conductive fillers, such as special conductive grades of carbon black or graphite. In such a case electrons are then conducted through the polymer and resistivity values less than 10^8 ohm/sq [38] and often as low as 10^2–10^3 ohm/sq [37] are obtained with high loadings of conductive carbon black or graphite. Other conductive materials used less frequently are various metals (silver, copper, aluminum, iron, brass, steel fibers) and metal-coated particles (mica, glass flakes, and glass beads).

3.7 Slip Agents

Slip agents are used in plastic films and sheets to provide surface lubrication during and immediately after processing. They have limited compatibility with the polymer and exude to the surface, providing a coating that reduces the coefficient of friction. Slip agents reduce sticking of the plastic to itself by minimizing tack and facilitate processing on high-speed packaging equipment. They can also improve antistatic properties, lower plasticity, and act as mold release agents [37].

Slip agents are usually modified fatty acid esters, used in concentrations of 1–3 parts per hundred parts of polymer (phr) of fatty acid amines, especially erucamide and oleamide [37].

3.8 Antiblocking Agents

Antiblocking agents prevent plastic films from sticking together due to cold flow or a buildup of static electricity. They can be applied internally or externally. When incorporated internally, they must be partially incompatible with the polymer so that they can exude to the surface. Antiblocking agents include natural and manufacturing waxes, metallic salts of fatty acids, silica compounds, or polymers, such as polyvinyl alcohol, polyamides, polyethylene, polysiloxanes, and fluoroplastics [37].

3.9 Processing Aids

Processing aids is a general term that refers to several different classes of materials used to improve the processability and handling of high molecular weight polymers. The benefits are realized mainly in the melt stage of the host polymer [39]. Two main groups of processing aids are lubricants and fluoropolymer-based additives. Each has a distinct effect on the polymer melt and is used in a different way.

Lubricants are used in polymer processing to lower melt viscosity or to prevent polymers from sticking to metal surfaces. Internal lubricants act intermolecularly, making it easier for polymer chains to slip past one another. Lowering viscosity improves polymer flow. Materials used for lubricants include metal soaps, hydrocarbon waxes, polyethylenes, amide waxes, fatty acids, fatty alcohols, and esters [37].

Fluoropolymer-based processing aids are mostly copolymers of vinylidene fluoride and hexafluoropropylene. This material is commonly referred to as "fluoroelastomer," even though it is not crosslinked when used as a processing aid and, thus, has no elastomeric properties [40]. The most pronounced effect of fluoropolymer processing aids is the elimination of the melt fracture during polymer extrusion.

3.10 Fillers and Reinforcements

Fillers are relatively inexpensive, solid substances that are added in fairly large volumes to polymers to adjust volume, weight, cost, surface, color, processing behavior (rheology), shrinkage, expansion coefficient, conductivity, permeability, and mechanical properties. They can be roughly divided into inactive or extender fillers and active or functional or reinforcing fillers.

Inactive fillers are used mainly to reduce costs, whereas *active* fillers bring about a special change in properties so that the compound meets the requirements demanded of it; however, in reality, there is no filler that is fully inactive and reduces costs only [41].

Some reinforcing fillers function by forming chemical bonds with the polymer. Others produce enhancements in mechanical properties by taking up volume; they bind to nearby polymer chains, decreasing polymer chain mobility and increasing polymer orientation at the filler surface. The increased orientation results in increased stiffness, lower deformability, and increased strength. Reduced mobility results in higher glass transition temperature [42]. Another effect that some fillers have is on crystallinity by promoting nucleation [43].

Particle size and *shape* as well as derived properties like *specific surface* and *particle packing* are the most significant factors affecting the mechanical characteristics of a compound. In addition porosity and tendency to agglomeration (weak bonding) and/or aggregation can have important effects both on processing behavior and mechanical properties [44].

The true *density* of a filler depends on the chemical composition and morphology. Lightweight fillers, such as hollow glass spheres, reduce the density of a compound, whereas heavy fillers increase it and may be used, for example, for sound deadening applications. Most of the commercial fillers have densities between 1.5 and 4.5 g/cm^3. Because most fillers are used in powder form, the bulk or loose density significantly affects handling and feeding during processing. Fine fillers can have bulk densities below 0.2 g/cm^3 because of air entrapment and electrostatic charges, thus limiting their use on conventional processing equipment. These problems can be partially solved by split feeding, improved degassing, and surface treatment and/or compacting of the filler [44].

Specific surface area is defined as the total surface area per unit weight of the filler. The most widely used method of determining specific surface is by *nitrogen absorption* (BET) method. A simple method to get figures related to the specific surface area is to determine the *oil absorption*. The result is given as the quantity of the fluid in milliliters per gram of filler and provides a rough estimate of the minimum quantity of polymer needed to disperse the filler [45].

Other properties of fillers and reinforcement affecting the specific properties of a compound are

- optical properties
- hardness and abrasiveness
- electrical and magnetic properties
- acid solubility
- loss on ignition
- pH
- moisture content.

The reinforcing properties of fillers can be enhanced by *coupling agents*. Coupling agents, usually silanes and titanates, improve interfacial bond between the filler and the resin. They are bifunctional molecules, in which one end reacts with polar, inorganic materials, whereas the other end reacts with organic, nonpolar substrates. They function as molecular bridges between the filler and the resin. Commercially available coupling agents have different functional groups appropriate for the particular resin. The final effect is an improved adhesion between the filler and the polymer, which results in enhanced mechanical properties, such as tensile strength, flexural modulus, impact strength, and heat deflection temperature.

3.10.1 Fillers Commonly Used in Thermoplastic Polymers

3.10.1.1 Cubic and Spheroidal Fillers

Natural calcium carbonate depending on the raw material source is available in the form of chalk, limestone, or marble. Natural calcium carbonate reduces the cost of a compound without dramatic changes in its properties.

Precipitated calcium carbonate is most commonly prepared from calcined limestone (CaO) and carbon dioxide. Precipitated calcium carbonate is very pure and fine, but more expensive than the natural product, which limits its use. It is often offered surface treated with fatty acids. Because of its high specific surface (20–40 m^2/g) it has a major effect on rheological properties and adsorption properties (stabilizers, plasticizers) [46].

Barium sulfate is available both as a natural mineral (barite) and as a synthetic product (blanc fixe). It has the highest specific gravity among commercial fillers, is inert, very bright, and easy to disperse. Barium sulfate is most widely used for sound deadening applications (foams, piping), in carpet backing, floor tiles, sporting goods, brake and clutch linings, in radiation shielding, and as white pigment.

Glass and ceramic beads are widely used in resin systems. They are often treated by silanes to enhance the bonding between resin and particles or coated by metals (Ag, Cu) and used as conductive fillers. Spherical fillers impart tear and compressive strength, dimensional stability, scratch resistance, and stiffness to compounds. Hollow glass beads reduce specific gravity of the compound and are used in foams, syntactic foams, and in automotive parts. Solid spheres are used in bumper formulations, TV and computer housings, connectors, etc.

Synthetic silica is essentially amorphous silicone dioxide with primary particles having diameters ranging from 10 to 100 nm and forming aggregates (secondary particles) with 1–10 μm in size. Silica products are named after their production process: fumed, fused, and precipitated [47], and their surface area, depending on the process used, may vary from 50 to 800 m^2/g [48]. Synthetic silicas are used as semi-reinforcing fillers in thermoplastics, elastomers, as antiblocking additives for films, as viscosity regulators, and as matting agents. To enhance their reinforcing properties, synthetic silicas are treated by silane coupling agents. In summary, silicas perform the following functions in thermoplastics [49]:

- Reduction of shrinkage and crack formation
- Reinforcement
- Prevention of film blocking
- Improvement of dimensional stability under heat
- Reduction of the coefficient of linear expansion
- Improvement of electrical properties
- Increase of hardness
- Reduction of die swell
- Affecting rheological behavior.

Carbon black is predominantly used as reinforcement in elastomers. Its use in thermoplastics is limited to pigmentation, UV protection, and conductivity. Specific uses in thermoplastic elastomers are discussed in sections covering individual types of TPEs.

3.10.1.2 Platy Fillers

Talc, the softest of all minerals with a Mohs hardness of 1, is chemically magnesium silicate hydrate. Most talc goes into polypropylene compounds for automotive industry. Talc positively affects many properties, including HDT, creep resistance, shrinkage, and coefficient of linear thermal expansion (CLTE). Talc has an adverse effect on toughness, elongation at break, weld line strength, long-term thermal aging, and UV resistance [50].

Mica, like talc is a sheet silicate with an excellent platelet structure. The most important grades of mica are *muscovite* and *phlogopite*. Both these grades have aspect ratios of 20–40 and are used in thermoplastics to improve rigidity, dimensional stability, and HDT. Mica also exhibits good electrical properties and is acid resistant [51]. Muscovite appears white to virtually colorless, whereas phlogopite has a golden brown inherent color. Mica is relatively difficult to disperse, therefore, its surface is treated by aminosilanes, waxes, or aminoacetates. Another disadvantage of mica is its poor weld line strength.

Kaolin and clay, a variety of hydratized aluminum silicates, come in varying degrees of purity. The mineral has a hexagonal, sheet-like crystal structure with an aspect ratio of 10 maximum, is pale in color, and possess excellent chemical resistance and good electrical properties. The average particle size of commercial products ranges between 1 and 10 μm, and the surface areas range from 10 to 40 m^2/g [52].

The main application for kaolin is as a filler in the rubber industry, where distinction is made between hard and soft clay (according to its reinforcing effect). Kaolin is often used in calcined form and with special surface treatments (e.g., with silanes). In thermoplastics, it contributes to the improvement of chemical resistance, of electrical properties, and to the reduction of water absorption. It lowers the crack tendency in finish articles, improves shock resistance and surface quality. The lamellar structure results in improvement in the surface hardness of the finished products [53].

3.10.1.3 Fibrous Fillers

Glass fibers (chopped strand) are a frequently used reinforcement in thermoplastics. They are cost effective and a broad range of physical properties can be achieved for a large number of applications. Glass fiber reinforcements are strands of filaments drawn to different diameters between 3.8 and 18 μm. The number of filaments per strand, the configuration of the strand, and the fiber length-to-weight ratio can be varied, depending on the desired properties [54]. Chopped and continuous strands are used in injection molding, at loadings 5–30%. Mats can be made from chopped or continuous strands. Glass fiber reinforced resins have high tensile strength, high stiffness and flexural modulus, high creep resistance, impact resistance, and high HDTs. In addition, they exhibit excellent dimensional stability and low CLTE. The reinforcing efficiency of glass fibers can be further enhanced by the use of coupling agents (e.g., silanes). Because glass fibers orient in the flow directions during injection molding, shrinkage is greatly reduced in the direction of flow; in the transverse direction, the shrinkage reduction is not so great. Disadvantages of glass fibers are warpage, low weld line strength, and low surface quality. Because of their abrasiveness, they can damage machinery and tooling; hardened coatings on barrels, screws, and tooling can minimize abrasion [55].

Carbon fibers and *aramid fibers* have exceptional reinforcing properties, but because of their high cost, they are used only in specialized applications, such as aerospace, marine, military, and medical applications.

3.10.1.4 Nanofillers

Nanofillers are defined as fillers with particle sizes in the 1–100 nm range [56]. Such fillers, for example, carbon blacks, synthetic silicas, precipitated calcium carbonate, have been around for a long time; however, their primary particles form bigger, stable secondary particles through agglomeration, so that, ultimately, they cannot be classified as nanofillers.

Recently, different nanofillers, such as *nanoclays* (montmorrilonite, smectite) and needle-shaped nano-wiskers have become commercially available [57]. Nanoclays are *exfoliated* (separated into individual layers) and reinforcing primary particles with extremely high aspect ratios (greater than 200) are formed [57]. Exfoliation is enhanced by the surface treatment, so-called *intercalation*, by compounds containing ammonium or phosphonium functional groups. This converts the surface from hydrophilic to organophilic [58]. The advantage of such fillers is that they produce very good mechanical properties at low loadings, scratch resistance, superior barrier properties, enhanced fire resistant properties, and improved heat distortion performance when compared to neat polymers.

Major current applications are packaging films and rigid containers, automotive and industrial components [58].

3.11 Plasticizers

3.11.1 Types of Plasticizers

Plasticizers are defined as substances added to polymeric materials to improve their flexibility, extensibility, and processability. It is a characteristic of plasticizers that they lower the melting temperature, melt viscosity, glass transition temperature, and elastic modulus of polymers without altering their chemical nature [59]. Technologically, they fulfill several functions. They act as processing aids, enter into physical interaction with the polymer, and enable materials to be "tailormade," or very nearly so, to specific property requirements.

Commercial plasticizers are normally supplied in the form of low to high viscosity liquids and more rarely as solid products. Since many thermoplastics require high processing temperatures, plasticizers used for such materials must possess sufficient heat resistance to prevent discoloration, decomposition, or excessive evaporation rates during processing. Low volatility is also required for application, where the polymeric material is used at elevated temperatures for extended periods of times. Typical plasticizers meeting the requirement of low volatility are, for example, phtalates and adipates, prepared from C_{10}–C_{13} aliphatic alcohols and esters of trimellitic acid [60]. For articles exposed to complex effects of weathering, not only volatility, but also resistance to light, water extraction and fungal attack are required. It is not always easy to find a plasticizer or a combination of plasticizers, and often some compromise has to be made.

Migration problems can occur under unfavorable circumstances in multilayer articles, such as artificial leathers and films causing degradation or excessive tackiness of the layer that originally did not contain plasticizer. In such cases, a *polymeric plasticizer* could be the correct choice.

Flammability might be another issue in many applications. In such cases, phosphoric esters (e.g., tricresyl phosphate or trichloroethyl phosphate) and chlorinated paraffins with high chlorine content are used. Both these groups of plasticizers are irritants and may cause health problems when ingested or absorbed through skin. Therefore, adequate protection must be used when handling them.

For articles made from polar polymers (PVC, acrylonitrile and their copolymers) that are exposed to *low temperatures* (typically below −40°C or −40°F), special plasticizers, such as dibutyl phtalate, dioctyl phtalate, and dioctyl adipate, are suitable. The low temperature brittleness is reduced with increasing amount of plasticizer. Depending on the base polymer, the plasticizer content may be as high as 45% [61].

There are many types of plasticizers, each having a compatibility with a specific type of polymer. These can be grouped in the following manner [62]:

- Phtalic esters
- Phosphoric esters
- Adipic, azelaic, and sebacic esters
- Citric esters
- Trimellitic esters
- Halogenated hydrocarbons
- Hydrocarbons (aliphatic, naphtenic, and aromatic)
- Benzoic esters
- Fatty acid esters (oleates, stearates, ricinoleates), pentaerithrol
- Fatty esters, epoxidized
- Polyesters (polymeric plasticizers)
- Polymers, polycondensates.

3.11.2 Methods of Incorporation

Plasticized polyvinyl chloride compounds, *plastisols*, require relatively large amounts of plasticizers. They are prepared in planetary mixers, internal mixers, and dissolvers. Practically all thermoplastics and elastomers can be mixed with plasticizers and other compounding ingredients in batch and continuous mixers. Specialty or sensitive compounds prepared in small batches are usually mixed on roll mills. Plasticizers can be added in liquid form or as a dispersion (dry blend) on a carrier.

3.12 Other Additives

Other specialized additives have different functions in certain polymers and applications and include antimicrobials, fluorescent whitening agents, and PVC stabilizers.

Antimicrobials are natural or synthetic, mostly low molecular weight substances that kill or suppress the growth of viruses, bacteria, and/or fungi (i.e., yeasts and molds). Antiviral activity is only of minor interest to the polymer processing industry with the exception of medical devices, such as catheters. Major interest is in antimicrobials agents that control the growth of bacteria and fungi. Depending on the target organisms, this activity is described as *bacteriostatic* (inhibiting the growth of bacteria) or *fungistatic* (inhibiting the growth of fungi). In contrast, the activity of killing the bacteria or fungi is called *bactericidal* or *fungicidal* activity. Each antimicrobial substance has a specific spectrum of activity with susceptible microbial species [63].

Manifestations of deterioration of a plastic material due to a microbial attack are

- staining
- deterioration of electrical properties, particularly of insulation power
- deterioration of mechanical properties
- enhanced dirt uptake
- odor.

A detailed coverage of this subject and a comprehensive list of commercial antimicrobial agents can be found in reference [63].

Fluorescent whitening agents have the main effect of either improving or masking the initial color of plastics, which is often slightly yellowish. Moreover, they can produce a brilliant white color in certain articles or increase the brilliancy of colored and black pigmented articles.

Many thermoplastics absorb light in the blue spectral range of natural daylight, which is referred to as "blue defect," causing a more or less pronounced yellowish appearance. There are essentially three basic principles to compensate for it, namely bleaching, compensation for the blue deficit, and increase in reflection [64].

Only few of the known classes of fluorescent whitening agents have the properties required for mass whitening of plastics and fibers, namely *bis*-benzoxales, phenylcoumarins, and *bis*-(styryl) biphenyls [64].

The low thermal stability of PVC is well known. Despite this fact, processing of PVC and its blends at elevated temperatures is possible by adding specific *heat stabilizers* to stop the damage. When PVC is processed at high temperatures, it is degraded by dehydrochlorination, which is a chain scission and crosslinking of macromolecules. Free hydrogen chloride (HCl) evolves and discoloration of the resin occurs along with important changes in physical and chemical properties. This degradation can be controlled by the addition of stabilizers. A heat stabilizer must prevent the dehydrochlorination reaction, which is the primary process in degradation. Currently, the following commercially available classes of heat stabilizers for PVC are

- alkyltin stabilizers
- mixed metal stabilizers (K, Ca, Ba, Cd)
- organic phosphites
- β-diketone stabilizers
- epoxidized fatty acid ester stabilizers
- organotin mercaptides and organotin sulfides
- lead stabilizers
- metal-free stabilizers.

A detailed discussion of this subject is given in reference [65].

3.13 Selection of Additives

In the selection of additives by their function, it is important to consider not only the desirable properties it will confer on the compound, but also the side effects it may have on other properties and its effect on the overall processability of the whole compound.

Additives for thermoplastics are supplied in many varieties with frequent overlaps in properties [3]. Mineral fillers are increasingly offered with surface treatments to improve their bonding with the polymer matrix and give improved mechanical properties to the final products and at the same time, improved incorporation during mixing. Some pigments (e.g., titanium dioxide, carbon black, or zinc oxide) can provide shielding against the effects of UV radiation. Lubricants can not only plasticize the compound but also act as mold release agents and in some instances add antistatic properties to the product during its lifetime [3].

The current trend is to use multifunctional additives, or hybrid systems, or exploiting the synergistic effects of two or more additives. This development is evident in the development of technology for UV light stabilization and flame retardancy [3].

The form (liquid, powder, paste, pellets) and the microstructure of the additives are of importance because these may strongly affect the mixing process, particularly the sequence in which the individual ingredients are added to the mix.

The aspects of health, hygiene, and impact on environment are extremely important in the selection and use of any ingredient (see Section 3.14).

3.14 Health, Hygiene, and Safety

Health risks must be considered in all cases where human beings come in contact with chemicals. This, of course, also applies to additives for any polymeric material. Within the lifetime of an additive, the following phases are important [1]:

- Production
- Incorporation of the additive and processing of the polymeric material into its end use
- Use of the finished article
- Disposal of used articles.

The phases mainly applicable to this chapter are the selection, handling, and incorporation of additives into the compound; however, the way the individual additives affect the health, hygiene, and environment during the use and disposal of the finished article has to be also considered.

The manufacturers of additives are obliged to assess among other things the health and environmental impacts of their products during storage, handling, and fabrication by issuing specific documentation, such as Material Safety Data Sheets (MSDS), which has to be provided with the materials, including samples for laboratory work.

Because of the large number of additives with different molecular structures, their individual biological activity may rank from inactive to highly active, or nontoxic to toxic. Specific regulations exist for contact with food, for pharmaceutical devices and packaging, for toys, pipes for drinking water supply, etc. It is beyond the scope of this chapter to discuss details; only basic principles are addressed.

Product handling in production facilities requires a particular attention with the emphasis to avoid possible contamination that could be harmful to humans. Such possibility exists usually in filling facilities or where drums or other packages are opened and emptied.

When handling *solid additives*, the safest way is to store them in silos and use single-component dosing devices. In practice this system is less flexible than might be expected because the dosing systems must be individually adjusted to the solid flow properties of each component. Pellet form for polymers, color, and other additives is the best for such handling and weighing systems because they essentially eliminate dusting. If dusting occurs, adequate protective devices, such as masks or respirators, must be used.

Liquid additives, particularly toxic additives and volatile solvents, represent major hazards. The former can cause health problems, and the latter may be combustible, toxic, or both. Certain solvents, such as hexane and heptane, may cause explosions. Many liquid substances may be harmful to skin, eyes, and respiratory systems. Here again, sufficient protection, such as gloves, goggles, face shields, respirators, or protective clothing, is required.

Operating transportation conveying, mixing, and processing equipment represents another hazard leading to injury or in extreme situations even to death. Reasonable precautions including safety training minimize or eliminate such hazards.

In general, good housekeeping, ventilation, lighting, explosion-proof switches in areas where explosive solvents are used and a use of warning signs, floor, and wall markings reduce or entirely eliminate many hazards. Emergency showers and showers for flushing eyes are other important devices that can be used for safety and good hygiene.

More detailed coverage of this subject is in reference [1] (chapter 22) and reference [3] (chapter 21).

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4 Processing Methods Applicable to Thermoplastic Elastomers

4.1 Introduction

Polymeric materials come in a variety of forms. They may be solids of different hardness, liquids, or dispersed in water as latex or a suspension. Some are converted into finished products as received, that is, without modifications; others are modified, dissolved, blended, or mixed to produce desired processing and performance characteristics. Thermoplastics are generally processed by methods shaping them in the molten state to desired shapes and sizes. Such methods are often referred to as *melt-processing methods*. Most thermoplastics are not subjected to cross-linking, which means that they can be remelted and shaped again. Thus, production scrap or used parts can be utilized again, at least as a partial replacement of virgin materials.

Thermoplastic elastomers (TPEs) are materials, which can be generally processed by melt-processing methods used for plastics. The following sections will describe in some detail processing methods used for the fabrication of products from thermoplastic materials. Because of the large number of types of TPEs, these processing methods may be applicable only to some of them. On the other hand, there are some techniques, suitable specifically for TPEs. Specific processing methods and conditions used for individual TPEs and other relevant details are included in chapters discussing respective materials and in Appendix 4.

4.1.1 Properties Influencing Processing

4.1.1.1 Flow Properties

Thermoplastic elastomers, as any other thermoplastic materials are formed into articles almost exclusively by melt processes that rely on the flow of the melted material at elevated temperatures. Injection molding, blow molding, extrusion, and rotational molding/lining are all examples of melt processing. The most widely used melt-processing methods, their advantages and disadvantages are listed in Table 4.1. An understanding of melt flow is essential for success with these processes. The study of the flow of materials including that of polymers is known as *rheology*.

The rheology of a thermoplastics melt is complex, being very dependent on temperature and shear rate. This means that the melt viscosity—the characteristic that makes flow easy or difficult—can vary widely in the melt condition. The two key points about the flow of thermoplastics are that the behavior is non-Newtonian and that viscosities are very high. These characteristics are dictated by the long polymer chain molecular structure of the materials. One practical consequence is that considerable force is required to make a plastics melt flow into a mold or through a die. This explains why plastics processing machinery and molds must be very robust and are costly. Flow behavior pertaining to mixing is discussed in Section 4.2.1.2.

To understand and control melt processes, it is necessary to define the way in which melt viscosity changes with temperature and shear rate. The *shear rate* is a measure of how fast the melt passes through a channel or orifice. A simple fluid such as water has a constant viscosity value regardless of shear rate. This is known as *Newtonian behavior* in which the fluid can be described fully by a single constant—the viscosity. By contrast, the viscosity of a melt of a plastic at a constant temperature changes markedly as the shear rate changes. This is *non-Newtonian behavior*. There is no single viscosity value. The viscosity value for such a melt must always be related to the shear rate at which it was determined and strictly it should always be referred to as the *apparent viscosity*, although this qualification is usually assumed rather than explicitly stated. An important consequence follows: for a viscosity to be truly useful in determining how a process will turn out, it should be measured at about the same shear rate experienced in the process (see Table 4.2). Unfortunately, this is not true of the most popular and widely available measure of melt viscosity, the melt flow rate (MFR) or melt flow index (MFI).

The MFR test is performed at a low shear rate so MFR figures will be at their least inaccurate for medium to low shear rate processes like blow molding and thermoforming, and will be most inaccurate for injection molding. The quoted MFR value is the weight of polymer melt flowing through an orifice in specified conditions, so the higher the MFR value, the lower the melt viscosity and the easier

Table 4.1. Comparison of Molding Techniques and Extrusion for Thermoplastic Polymers

Process Technique	Advantages	Disadvantages
Injection Molding	The most precise control of shape and dimensions, highly automatic process, fast cycle times; the widest choice of materials	High capital cost; is only good for large numbers of parts; large mold pressures (typically 140 MPa or 20,305 psi)
Compression Molding	Lower mold pressures (typically 7 MPa, or 1,015 psi); does minimum damage to reinforcing fibers (in composites); large parts are possible	Requires more labor; longer cycle than injection molding; less shape flexibility than injection molding; each charge is loaded by hand
Transfer Molding	Good for encapsulating metal parts and electronic circuits	Some scrap with every part and each charge is loaded by hand
Blow Molding	Can make hollow parts (such as bottles); stretching action improves mechanical properties; fast cycle; requires low labor	No direct control over wall thickness; cannot mold small details with high precision; requires polymer with high melt strength
Rotational Molding and Rotolining	Labware that is shatterproof and will not contaminate samples; small to very large vessels; valve lining, bellows, items with complex geometry, containers	A slow process, requires labor, and involves numerous moving parts; a great deal of cleaning and surface conditioning is necessary
Extrusion	Used for films, sheets, wraps, or long continuous parts (i.e., pipes, wire, and cable insulation)	Must be cooled below its glass transition temperature to maintain stability

Source: Reference [63].

Table 4.2. Process Shear Rate Ranges

Process	Typical Process Shear Rate (s^{-1})
Injection Molding (Section 4.4)	1,000–10,000
Extrusion (Section 4.3)	100–1,000
Transfer Molding (Section 4.6)	1–100
Rotational Molding/Lining (Section 4.8)	<100
Compression Molding (Section 4.5)	<1
Blow Molding (Section 4.7)	—

Source: Reference [1].

the material will flow. Even though MFR values are measured at an unrealistically low shear rate, it might seem that the test would accurately rank different materials for comparative ease of flow. Unfortunately, not even this can be guaranteed because of the varying degree of shear dependency shown by different materials and grades. The MFR test owes its continued survival mostly to tradition and the fact that it is cheap and easy to perform [1].

More reliable viscosity measurements can be made with high-shear *rheometers*. Material testing is performed at shear rates similar to those experienced during extrusion or injection molding, so the resulting values have a direct bearing on process considerations (Fig. 4.1). Even then, it is not a simple matter to depict flow behavior. A number of viscosity models have been developed to describe this behavior, and while a detailed discussion is beyond the scope of this work, it is as well to be aware of some of these models because they are used in process simulation computer programs. These programs predict the effect of product and control parameters on the end product. The simplest version is known as the *Power Law Model*. More elaborate and accurate models are based on higher order versions of the power law, or on the *Carreau*, *Cross*, or *Ellis* models. Flow data corresponding to these models are still not widely published but can usually be obtained on request from materials suppliers. Developers of flow simulation software maintain extensive databases of plastics flow data but these are not freely accessible [1]. The situation has improved with the development of *Campus*, the free industry-standard materials database that includes rheological data (www.campusplastics.com).

A third type of flow measurement is sometimes available, although its popularity appears to be

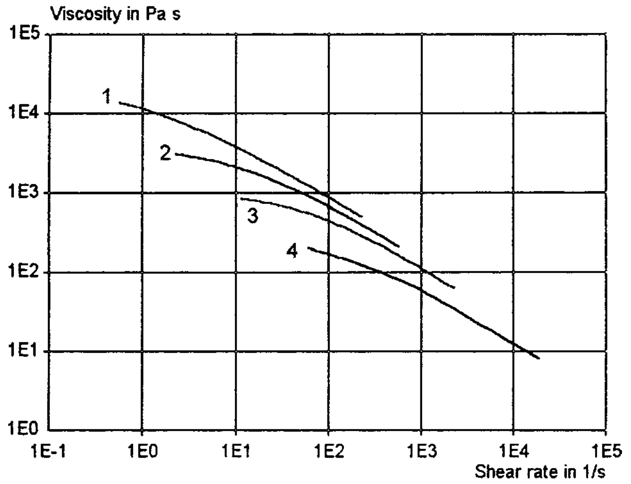


Figure 4.1. Example of viscosity curves at 260°C for polypropylene. 1—Blow molding grade (MFR=0.4); 2—Calenderfilm grade (MFR=1.1); 3—Block copolymer molding grade (MFR=5.0); 4—Thin wall molding grade (MFR=19.0). *Source*: Reference [1].

waning: *Spiral flow method* attempts to relate flow information directly to the injection molding process by using an industrial molding machine to run the tests, in conjunction with a test mold in which a long flow channel is arranged in a spiral. The disadvantage is that reproducibility between different presses and molds is low. The spiral flow behavior of thermoplastic is characterized simply by the flow length observed under prescribed conditions of temperature, pressure, and flow rate. Flow length measurements are specific to test conditions and cannot be extrapolated to other circumstances. However, because the test is performed at typical process shear rates, it will reliably rank materials for ease of flow at the test conditions. Another drawback is that the test is rather unwieldy and time consuming.

4.1.1.2 Thermal Properties

The melt processing of thermoplastics involves first heating the material to a point at which it can be made to flow, and then cooling it again to a temperature at which the formed object is stable. This requirement constitutes a major energy demand in the forming process, and is central to the efficiency and economy of the process. It is a common perception that thermoplastics are difficult to heat and even harder to cool, and that this is particularly true of TPEs. The perception is a sound one, and a study of thermal characteristics shows why this is so.

The heat energy or heat content of a system is a function of the mass of a material, its specific heat, and the temperature change. The quantity is often referred to as *enthalpy*. The heat energy to melt a thermoplastic is therefore proportional to the difference between its melt temperature and room temperature. Theoretically, the heat energy to be removed in cooling, in the case of a molding, is the difference between the melt temperature and the mold temperature. In practice, the component can usually be ejected at a higher temperature, and only a region near the surface needs to be at this temperature, so the heat to be extracted is considerably less.

The heat energy involved in heating and cooling varies considerably from one polymer to another (Table 4.3). An additional consideration is the fundamental difference between *amorphous* and *semi-crystalline* plastics. For semi-crystalline materials, the heat requirement for melting includes additional quantity for melting the crystalline structure. This is known as *latent heat of fusion* of the crystalline structure. For example, polypropylene (PP) has the heat of fusion 670 J/g and it is more than double of that of polystyrene and considerably greater than the energy requirement for materials with much higher

Table 4.3. Process Heat Requirements of Different Thermoplastics

Polymer	Melt Temperature (°C)	Mold Temperature (°C)	Heat Required to Melt (J/g)	Heat Removed on Cooling (J/g)
Polystyrene	200	20	310	310
ABS	240	60	451	369
PMMA	260	60	456	380
Polyamide 6	250	80	703	520
Polyamide 6/6	280	80	800	615
Polypropylene	260	20	670	670
HD polyethylene	260	20	810	810

Source: Reference [1], p.149.

melt temperatures, such as polycarbonate, polypropylene oxide (PPO) and polyether sulfone (PES). The cooling requirement for PP and high density polyethylene (HDPE) is even more demanding. These thermal characteristics have a direct bearing on processing. They mean for example that cooling for a PP mold must be much more efficient that for most other plastics. The need is often overlooked and it is responsible for the commonly experienced difficulty of overheating cores and pins.

The specific heat and thermal conductivity of plastics vary greatly with temperature. So indeed does density. These variations are not brought out in data sheets that deal only with solid properties, and are not widely appreciated by plastics processors. It is still difficult to obtain information about the thermal properties of plastics in the melt state, even though this is important for plastics process calculations. A plot of enthalpy against temperature shows the extent of the variation and also clearly differentiates between amorphous and semi-crystalline materials [2]. The enthalpy curve for the semi-crystalline polymers shows a distinct discontinuity or "knee." The rapid increase in enthalpy at this point corresponds to the latent heat of crystalline fusion. The curve for an amorphous material shows no such discontinuity. The enthalpy curves give a direct read-out of the approximate heat energy to be added or removed when heating or cooling a plastics material, and deserve to be more widely distributed. The Table 4.4 gives guideline spot values for the thermal properties of thermoplastics melts. In reality, the values for density, specific heat, and thermal conductivity are temperature-related variables. The latent heat of crystalline fusion is zero for amorphous polymers because the phenomenon is absent. *Freeze temperature* is the point at which the material becomes a solid. The *no-flow temperature* is not a fundamental property. Rather it is a useful concept that has been introduced in flow calculations to compensate for shortcomings in viscosity models at low temperatures near to the solidification. Effectively, it is the temperature at which the viscosity of a not quite frozen polymer is held to be infinite. Reinforcements and fillers tend to reduce the specific heat and enthalpy of PP but the effect is not very great [2]. If figures are not available for reinforced grades, it would be reasonable to use data for base grades which would then provide a small safety factor.

4.1.1.3 Shrinkage and Warping

Shrinkage and warping are complex consequences of melt processing. For semi-crystalline plastics such as PP the situation is particularly complicated. Crystalline regions exhibit a greater shrinkage than the surrounding amorphous regions, so semi-crystalline materials typically have a greater and more variable degree of shrinkage than amorphous materials.

Plastics melts are compressible, particularly at the high pressures used in injection molding and extrusion. The fundamental property is the relationship between pressure, volume, and temperature. Measurements describing this relationship for any material are known as PVT data, and are usually shown graphically in the form of a PVT plot. The plot for PP (Fig. 4.2) shows the now-familiar discontinuity or "knee" in the curve that corresponds to the region of crystalline fusion. For amorphous materials by

Table 4.4. Approximate Thermal Melt Properties of Different Thermoplastics

Polymer	Melt Density (g/cm^3)	Specific Heat of Melt (kJ/kg-K)	Thermal Conductivity of Melt (W/m-K)	No-Flow Temperature (˚C)	Freeze Temperature (˚C)	Latent Heat of Crystalline Fusion (kJ/kg)
Polystyrene	0.88	1.8	0.13	130	95	0
ABS	0.89	2.1	0.15	140	105	0
PMMA	1.01	2.0	0.15	140	110	0
PA 6	0.95	2.7	0.12	220	215	200
PA 6/6	0.97	2.7	0.13	250	240	250
Polypropylene	0.85	2.7	0.19	140	120	235
LD polyethylene	0.79	3.2	0.28	110	98	180
HD polyethylene	0.81	3.3	0.29	120	100	190

Source: Reference [2].

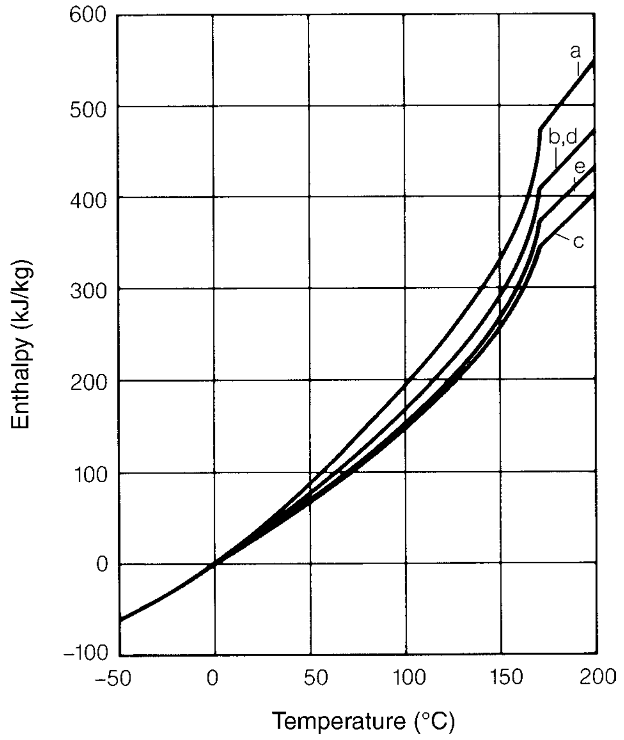


Figure 4.2. Example of a PVT plot for polypropylene homopolymers, measured during heating up. a—non-reinforced PP; b—PP with 20% talc; c—PP with 40% talc; d—PP with 20% glass fiber; e—PP with 30% coupled glass fiber. *Source*: Reference [2].

contrast PVT plots reveal a simple change of slope at a point corresponding to the glass transition temperature.

The PVT curves make it clear that shrinkage occurring as a result of melt processing is not just a function of thermal expansion and contraction but is also related to the compressibility of the melt. In practice, this relationship is made complex because process conditions will determine the extent to which the melt is compressed. Furthermore, process conditions are unlikely to be uniform throughout the part. For example, PP shrinkage is related to the degree of crystallinity in the material and hence to the cooling rate. A greater degree of crystallinity leads to a higher rate of shrinkage and also to a greater differential between shrinkage in the flow direction and shrinkage measured transversely to flow. The differential effect is another consequence of the viscoelastic property of long-chain molecules. During flow, the molecules are aligned to a limited extent in the flow direction and are extended to a degree proportional to shear rate. On cooling, a partial recovery of this extension gives rise to a higher shrinkage value. The effect is more pronounced in materials with a wide distribution of molecular weight. It is the differential shrinkage that is responsible for warping, the name given to the distortion of an apparently correctly formed part during and after cooling.

A further difficulty is that shrinkage takes place over a period of time. In the case of an injection molding, the greater part of total shrinkage is evident virtually immediately after ejection from the mold but shrinkage will continue for more than 24 hours. During this time, further crystallization and relaxation of internal stresses result in small dimensional changes. Thereafter, further changes take place very slowly but the effect is dependent on temperature and will occur more rapidly if the part is exposed to elevated temperatures. The sum of all these considerations is that it is impossible to state a simple and precise design figure for the shrinkage. Shrinkage can be minimized by using high viscosity, controlled rheology, or non-nucleated grade types. Warpage can be limited by using materials with a narrow molecular weight distribution, particularly the controlled rheology types. Although it is a volumetric phenomenon, shrinkage is usually expressed as a linear quantity either as a percentage or as a linear ratio (e.g., mm per mm) (Table 4.5).

The effect of fillers and reinforcements on shrinkage depends largely on the physical form of the additive. Particulate fillers such as talc or glass beads tend to counteract the effect of molecular orientation and so not only reduce shrinkage, but also reduce shrinkage differentials and hence the tendency to warp [3].

Fibrous reinforcements also reduce shrinkage but because the fibers become partially oriented during flow, the reduction is much greater in the flow direction than in the transverse direction [3]. This results in an increase in shrinkage differentials, although the increased tendency to warp is opposed to an extent by the greater stiffness of the reinforced material. In complex moldings, the varying flow patterns make it very difficult to anticipate shrinkage correctly by any means other than computer analysis. Even then, it is wise to design the product assembly to be tolerant of a degree of distortion and inaccuracy.

4.1.2 Pre-Processing

Before any thermoplastic is processed into semi-finished or end products, and irrespective of the process to be adopted, there are a number of prior considerations to be taken into account. For many

Table 4.5. Approximate Shrinkage Range of Different Thermoplastics

Polymer	Shrinkage (%)	Shrinkage (mm/mm)	Range (%)
SAN	0.4–0.6	0.004–0.006	0.2
ABS	0.4–0.7	0.004–0.007	0.3
Polystyrene	0.4–0.7	0.004–0.007	0.3
PVC-U	0.4–0.8	0.004–0.008	0.4
PET	1.6–2.0	0.016–0.020	0.4
PMMA	0.3–0.8	0.003–0.008	0.5
Polyamide 6	0.2–1.2	0.002–0.012	1.0
Polyamide 6/6	0.8–2.0	0.008–0.020	1.2
Polypropylene	1.2–2.5	0.012–0.025	1.3
HDPE	1.5–3.0	0.015–0.030	1.5
LDPE	1.0–3.0	0.010–0.030	2.0

Source: Reference [3].

thermoplastic materials, the principal questions are those concerning drying and coloring.

4.1.2.1 Drying

Most TPEs have a low tendency to absorb water and will not normally require drying before processing. If any moisture is present, it will be as water condensed or adsorbed on the polymer surface. This can occur, for example, if the material is moved from a relatively cool store to a warm and humid environment in the processing shop. Because the effect is purely a surface one, the moisture can be easily removed by conventional dryers but of course it is better to avoid the problem by attending to the storage conditions. Some TPEs tend to absorb moisture and these require thorough drying (see processing details for the individual materials).

A simple hopper dryer will usually be sufficient to remove surface moisture from the granules. However, if the material is in the form of powder, the problem will be more severe, simply because of the greatly increased surface area available for adsorption. Powdered materials constitute an explosion hazard and should not be dried in conventional equipment intended for granules. Instead, the problem should be circumvented by storing producer-dried powders in sealed containers at equable temperatures.

4.1.2.2 Coloring

Most of the TPEs are essentially colorless materials, ranging from milky white to near transparent depending on form and type. This characteristic means that it is possible to color the material to almost any desired shade by the inclusion of suitable dyes or pigments. The quality of the end result depends crucially on the even and thorough dispersion of the colorant throughout the melt, and processors have a variety of means at their disposal for achieving this. Coloring operations can be broadly divided into those that are coincidental with the forming process (in-process coloring) and those that precede it (pre-process coloring).

Pre-process coloring involves a separate coloring operation that takes place before the primary forming process. The method gives very good results but is relatively costly and adds to the heat history of the material. *In-process coloring* methods are, as the name implies, carried out during and as an integral part of the primary forming process. These processes—injection molding, blow molding, extrusion—involve the use of an extruder screw as a melt plasticizer, and in this case it is pressed into service for the additional duty of dispersing a colorant additive throughout the melt. The process screws are not designed expressly for this duty and cannot be optimized for it. Instead, the machine designer has to compromise to produce a screw and barrel that will work well enough with a range of polymers, while providing a reasonable balance between the conflicting requirements of throughput, heat transfer, mixing, pressure, and cost. Process conditions too, must be a compromise between what is best for dispersion and what is best for the physical product.

Consequently, the principal worry with in-process coloring is how to achieve widespread, uniform, and repeatable dispersion of color additives. Mixing can be improved by the addition of simple static mixers such as screen packs or flow-divider nozzles, but at the cost of greater process pressure drops and perhaps reduced throughput. On the plus side, no additional heat history is imparted to the material, and the equipment, energy, and time is effectively free. The processor also has no need to hold large inventories of bulk colored material, and can respond rapidly to changing needs and specifications. The most common method of in-process coloring is the use of color concentrate and to a lesser degree liquid color and dry color.

Color-compounded polymers come to the processor already colored in standard or custom colors. A custom compounder can prepare batches in desired colors from base polymer and color concentrates. The color is added in a melt process, generally a continuous process using an extruder or a screw-based mixer. Batch processes can also be performed in internal mixers or on roll mills but are less convenient and less uniform for thermoplastics. The color compounding process concludes with a pelletizing operation that results in colored pellets or granules ready for use in injection molding, extrusion, and other forming processes (for details see Section 4.2.5.2.1).

The compounding equipment can be optimized for mixing, so the colorants are uniformly and widely dispersed throughout the material. Together with the availability of specialist color formulation and color measuring equipment, this gives consistent and high quality results but there are a number of disadvantages. Certain TPEs are prone to oxidation at melt temperatures and must be stabilized to counteract this. By imposing an extra melt operation, the color compounding process adds to the thermal strain or as it is often known, the *heat history of the material*. The additional operation also adds an extra cost, which is partially offset by the efficiency gains of a dedicated business. Standard color ranges are necessarily limited, and the minimum order quantity for custom colors may be high.

The processor uses color-compounded materials in exactly the same way as natural grades of the TPEs. Color dispersion is already complete, so process conditions and equipment need take no account of this consideration. The color shade of the finished article can be taken for granted, provided quality checks are performed on the incoming compound. Minor process parameter adjustments may be necessary when changing from natural to color-compounded material but this is just a function of the minor rheological and thermal effects of the color additive on the polymeric matrix.

Color concentrate or masterbatch combines some of the advantages of pre-process and in-process coloring. The color concentrate is a thermoplastic compounded in the pre-process manner with a very high loading of colorant. It is then added in a minor proportion to natural (uncolored) polymer, and the process plasticizing screw has the task of mixing and distributing the colored polymer proportion throughout the mass of natural material. This requirement is relatively unexacting because the primary task of dispersion has already been performed during manufacture of the color concentrate. Consequently, there should be no chance of color agglomerates forming, even if the process screw is a relatively inefficient mixer.

The degree of dilution, or in other words the proportion of concentrate added to the polymer to be colored, is known as the *let-down ratio*. The concentrate manufacturer will aim to get the ratio as large as possible, but it is limited by the mixing efficiency of the conversion machinery and by the practicalities of concentrate compounding. Color concentrate is now the most widely used method of coloring PP. The processor requires only simple metering equipment to control the let-down ratio, and the added heat history is negligible. On the downside, the carrier polymer used in production of the color concentrate may have a minor effect on processing and on the properties of the finished part. This is because the carrier for a PP color concentrate is unlikely to have exactly the same characteristics as the grade being colored. Indeed, the carrier may well be of polyethylene rather than PP. These differences arise from the economic and logistical need to produce a near-universal color concentrate. The effects are usually insignificant provided the let-down ratio remains large.

4.2 Mixing and Blending

In many cases materials used to manufacture products from thermoplastics are used as received. However, some of them need to be prepared for further processing by the addition of other ingredients to attain specific processing characteristics and/or physical and mechanical properties. This process often referred to as *compounding* is essentially preparing a uniform mixture by blending and/or mixing. The method of preparing a uniform mixture depends on the nature of the components. If all components are solids, they are blended in a blender using paddles, screws, ribbons, or propellers and the process is referred to as *dry blending*. If they are all liquids, the blending is done by simple mixing with the use of some sort of propeller. If both liquid and solid components are in the mixture, the choice of method depends on the component that is largest in volume. Although in polymer processing all the above mixing and blending methods are used, the main focus in the following sections will be on polymeric melts.

In many cases polymeric solids are melted and blended or mixed in the molten stage. Frequently, various additives, such as powders, waxes, resins, pigments, reinforcing agents, liquid or solid plasticizers, antidegradants, colorants, or other specialty chemicals are added in the mixing process. Mixing in the molten stage requires specialized equipment, such as batch mixers or continuous mixers and consumes a large amount of energy. The finished mix is often called a *compound* or *formulation* and can be in the form of pellets, sheets, slabs, or ropes, depending on the form required for the next step in the manufacturing process.

In combining together different materials to form a mixture, there are two major concerns. One of them is to produce a homogeneous mixture. The compositional homogeneity of the mixture in a mixing process is achieved through *distributive mixing*. The second concern is to produce as fine and uniform dispersion of the ingredients as possible. The reduction of disperse phase during mixing is described as *dispersive mixing*. Another consideration regarding the mixing process is whether the substances being mixed are fully miscible, partially miscible are totally immiscible. They can be all liquids (e.g., molten polymers) or combinations of particulates that is, solids and liquids. If the mixtures are liquids, it is important to know the relative viscosities (or viscosity ratios) and the interfacial tensions between the phases [4].

4.2.1 Basic Concepts Pertaining to Mixing

4.2.1.1 Melting

Melting occurs when a solid polymer turns fluid as it is heated. Many polymers have crystalline molecular structure, and therefore a distinct melting point (*crystalline melting point*, frequently denoted as T_m). Materials that are "rubbery" and without crystallinity are called *amorphous*. When these polymers melt, their transition from glassy to molten state occurs at the *glass transition temperature* (T_g). Since this transition is gradual, the exact value of the glass transition temperature may not always be well defined. Some polymers are semi-crystalline, that is, partly crystalline and partly amorphous, and do not display a distinct melting temperature.

4.2.1.2 Rheology and Flow Pertaining to Mixing

Rheology, in general, is a scientific discipline that concerns the flow of fluids. The rheology of polymeric fluids (mainly melts) is rather complex because these materials exhibit many unusual features related mainly to their molecular structure. Polymers are usually *viscoelastic*, which means that they exhibit both *viscous* and *elastic* features. These features are apparent when a polymeric fluid is displaced slightly and then all forces acting upon it are removed. The fluid flows back slightly, but not completely. *Elasticity* of a material is its ability to retract to its original dimensions. If elasticity is not exhibited then the fluid is totally viscous.

A purely elastic material (*Hookean elastic*) behaves in such a way that its deformation is directly proportional to the applied stress, that is, follows Hooke's law. If elasticity is not exhibited then the material is totally *viscous*. Polymers are usually *viscoelastic*, which means that they exhibit both viscous and elastic features. These features are apparent when a polymeric fluid is displaced slightly and then all forces acting upon it are removed. The fluid flows back slightly, but not completely.

Flow of a fluid can be imposed by either shear or elongational forces. *Shear* forces are applied when a fluid is placed between two parallel plates and one of the plates is moving faster than the other. Purely *elongational* flow occurs when a fluid descends from an orifice and thins down to a smaller diameter.

The quantity providing the measure of deformation of a fluid (i.e., changes in its shape or movement) is the shear strain. *Newtonian* fluids exhibit a linear dependence of shear rate (measure of its flow) on the imposed shear stress. Thus the plot of shear stress versus shear rate (referred to as *flow curve*) for a Newtonian fluid is a straight line passing through the origin and having a slope expressing its resistance to flow, that is, its *viscosity*, μ (see Fig. 4.3). *Non-Newtonian* fluids are broadly classified as time-independent fluids, time-dependent fluids, and viscoelastic fluids [5].

Time-independent non-Newtonian fluids are those, for which the shear rate at any point is a function

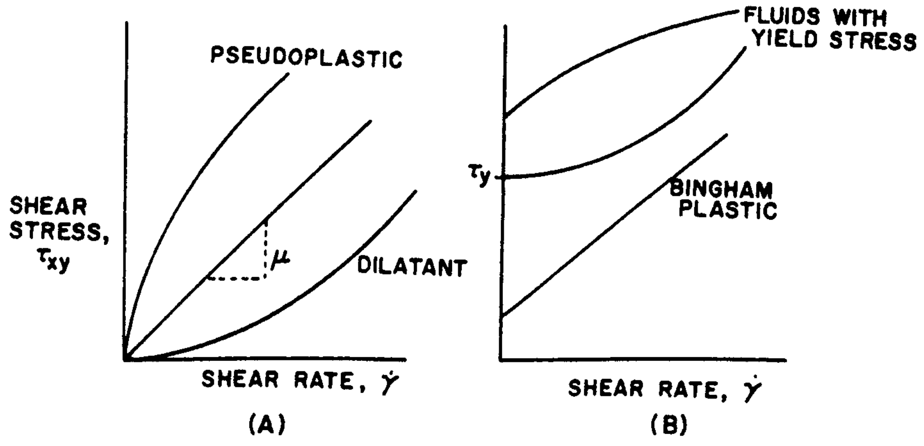


Figure 4.3. Flow curves for non-Newtonian, time-independent fluids (Courtesy Taylor & Francis) [5].

of only the instantaneous shear stress (Fig. 4.3). *Time-dependent* non-Newtonian fluids are those for which the shear rate depends on both the magnitude and duration of the applied shear. Such fluids also show a relationship between shear rate and the time lapse between consecutive applications of shear stress (Fig. 4.4). *Viscoelastic* fluids display the behavior of partial plastic recovery upon the removal of a deforming shear stress.

Time-dependent non-Newtonian fluids can exhibit *yield stress*, denoted as τ_y, which can be thought of as a minimum stress value that must be exceeded for deformation to occur. Flow curves of such fluids are shown in Fig. 4.3B. Also shown in that illustration is an idealized time-dependent fluid that is often referred to as *Bingham Plastic.*

Many industrial fluid-like materials can be described as being *pseudoplastic*. The flow curve of a pseudoplastic fluid is depicted in Fig. 4.3A. The *apparent viscosity* of a pseudoplastic fluid decreases with increasing shear rate and such a fluid is referred to as a *shear thinning* fluid. *Dilatant fluids* are time-independent materials exhibiting an increase in apparent viscosity with increasing shear rate. The flow curve for a dilatant fluid is also shown in Fig. 4.3A.

Time-dependent non-Newtonian fluids can be classified as thixotropic and rheopectic. *Thixotropic* fluids display a reversible decrease in shear stress with time at a constant shear rate (Fig. 4.4A). *Rheopectic* fluids (Fig. 4.4B) are sometimes called *antithixotropic* fluids because they exhibit a reversible increase in shear stress over time at a constant rate of shear under isothermal conditions [4].

Examples of non-Newtonian materials are shown in Table 4.6.

When a polymeric melt is forced through a circular opening (e.g., through an extrusion die), the emerging strand has frequently a considerably larger diameter than the opening. While a contraction may sometimes occur, most polymeric melts expand under these circumstances, sometimes as much as eight times [6]. This phenomenon is referred to as die *swell.*

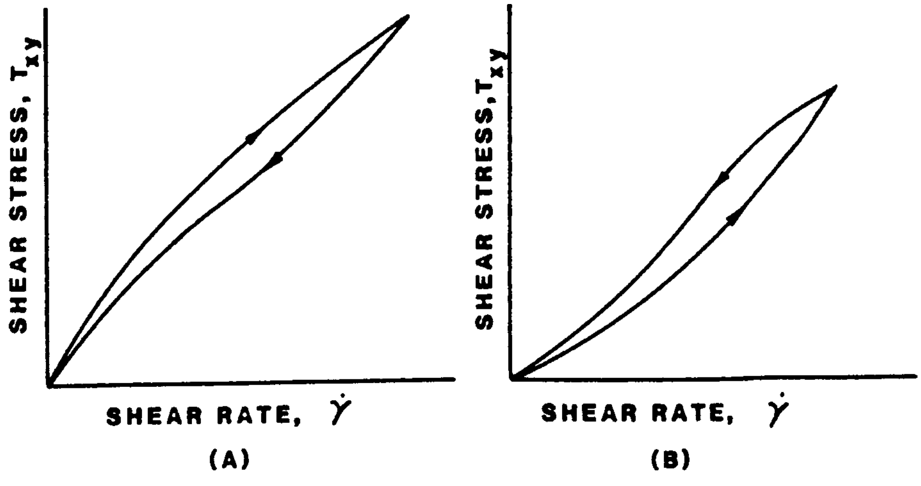


Figure 4.4. Hysteresis loops for time-dependent fluids, (A) thixotropic hysteresis, (B) rheopectic hysteresis (Courtesy Taylor & Francis) [5].

Table 4.6. Examples of Non-Newtonian Fluids

Type of Fluid	Examples
Time-Independent Fluids	
Fluids With a Yield Stress	Various plastic melts, oils, sand suspensions in water, mayonnaise, shortening, greases, toothpaste, soap, detergent slurries, paper pulp
Pseudoplastic Fluids (Without Yield Stress)	Rubber solutions, adhesives, polymer solutions and melts, starch suspensions, cellulose acetate, mayonnaise, paints, various biological fluids
Dilatant Fluids (Without Yield Stress)	Aqueous dispersions of titanium dioxide, corn flour/sugar solutions, gum arabic in water, wet beach sand, iron powder suspended in low-viscosity liquids
Time-Dependent Fluids	
Thixotropic Fluids	Melts of high-molecular weight polymers, various greases, margarine and shortening, printing inks, paints, various food substances
Rheopectic Fluids	Bentonite clay suspensions, gypsum suspensions, various oils, dilute suspensions of ammonium oleate
Viscoelastic Fluids	Bitumen, flour dough, napalm, various jellies, polymers and polymer melts (e.g., polyamide), various polymer solutions

Source: Reference [5].

During the melt mixing of polymeric compounds, flow in the mixing equipment may be caused by drag (drag flow) or by positive displacement. While one or the other may predominate, a combination of the two usually takes place [5].

Drag flow can be viewed in its simplest form as one plate sliding on top of another with polymer between them [7]. If there is no pressure, the velocity profile is linear and referred to as *pure drag flow*. If pressure is forcing the melt to move in the same direction or in the opposite direction it is flowing, the velocity profile becomes curved [7].

Positive displacement occurs by mechanically enclosing and transporting a pocket of a melt. Such pockets can be formed in mixing equipment with two intermeshing screws (see Section 4.2.3.3.2). The polymer is forced along the screw axis [7].

4.2.1.3 Residence Time

Residence or dwell time is the amount of time that an arbitrarily selected, small volume element in the feed stream spends inside the mixing equipment. Frequently, for an efficient mixing the entire residence time distribution has to be known. It can be roughly estimated by dropping several black pellets into the mixer while a white material is being mixed. At first, there is no change at the exit, after that the material blackens and eventually turns white again. If the intensity of the black color is directly proportional to the concentration of the black colorant, this intensity can be plotted as a function of time providing the residence time distribution [8].

4.2.1.4 Specific Mechanical Energy

The amount of energy required for mixing a polymeric compound is usually dictated by the amount of mixing needed. While better mixing is desirable, there are limitations set by the amount of exposure a polymer can tolerate. Knowing how much energy is required for an optimum mixing determines the size of the mixer and drive and the energy consumption while the equipment is in operation [9].

To compare different mixing machinery and for scale-up, the concept of *specific mechanical energy (SME)* is used. It is essentially the drive energy consumption per unit weight of polymer mixed by the specific equipment. The energy consumption is usually determined by measuring the current (I) in amps through the electric motor. For direct-current (DC) motors, the power (P) in watts is calculated using the well-known relation:

$$P = I \cdot V \tag{4.1}$$

where I is the current in amps and V is the voltage in volts.

The SME is obtained by dividing the power by the mass flow rate $\dot{m}_r$ (in kg/h) and multiplying by the motor efficiency η:

$$SME = \eta \cdot P/\dot{m}_r = \eta \cdot V \cdot I/\dot{m}_r \qquad (4.2)$$

For both DC and alternating-current (AC) drives, the torque is proportional to the current exerted on the drive. The power can be calculated by multiplying the torque by the rotational speed [9].

4.2.2 Polymer Blends

The development of new types of commercial polymers has decreased with considerably more interest directed to polymer blends, where synergies of properties are exploited to meet new application needs [10]. In fact, commercial blends were developed before the use of pure polymers, because early polymers did not provide desired properties [10]. Recent statistics indicate that blends represent more than 30% of all polymers used with an annual growth rate estimated at about 9% [11].

Only few polymers are miscible, that is, mutually soluble. The measure of compatibility in general is the magnitude of *interfacial tension* between the two materials. Ideally, when the interfacial tension is zero, they dissolve in each other. As the interfacial tension increases, the two materials are increasingly incompatible and immiscible with each other, in a thermodynamic sense. An example of values of interfacial tension for different polymer melt pairs is in Table 4.7. Interfacial tensions between two homopolymers melts have been found to be largely determined by the differences in polarity of the structural units. The larger the polarity difference is, the larger the interfacial tension. Thus the greatest interfacial tension between polymer melts listed in Table 4.7 is between polyethylene and polyamide 6 [12].

When immiscible polymers are combined in the mixing process, separate phases are formed. If only two immiscible polymers are blended, droplets may form in the final product [11]. As the relative volume of each polymer increases, a co-continuous morphology may form instead of droplets. Phase co-continuity may provide the best balance of properties in a blend of polymers. For example, a lamellar structure is preferred when barrier properties are desired [11].

In the early stages of mixing, the polymer of the minor phase is sheared into sheets that gradually disintegrate by forming cylindrical shapes or developing holes. In the next stage, the holes grow until they coalesce and the material from the original sheets forms ribbons and irregular fragments [13]. With additional flow these fragments may turn into droplets, which may break up further into smaller droplets. These may finally combine (coalesce) into larger droplets. A dynamic interchange between drop coalescence and breakage may occur and after a sufficient amount of time equilibrium will be established [14].

Table 4.7. Examples of Values of Interfacial Tensions for Different Melt Pairs

Polymer Melt Pair	Melt Temperature (˚C)	Interfacial Tension (dyne/cm)
Polyethylene-polypropylene	—	1.2
Polyethylene-polystyrene	180	4.1
	290	4.0–5.0
Polyethylene-polysulfone	290	6.5–7.0
Polyethylene-polyphenylene sulfide	290	7.2–7.9
Polyethylene-polymethylmethacrylate	180	9.0
Polyethylene-polyethylene terephtalate	290	9.2–9.4
Polyethylene-polycarbonate	290	12.5–13.0
Polyethylene-polyamide 6	290	12.8–13.2
Polypropylene-polystyrene	220	5.8
	250	3.7
Polystyrene-polymethylmethacrylate	180	1.2

Source: Reference [4].

The major factor determining the droplet size is its *surface tension*, which depends not only on the nature of the polymer within the droplet but also on the nature of the material that surrounds the droplet [15].

Interfacial tension is essentially the force that holds the droplet together. At the same time, the droplet is entrained in the melt flow inside the mixing equipment, subject to viscous forces that try to pull the droplet apart. The ratio of the two forces is called the *Weber Number*. If the droplet is in such a condition where the Weber Number is greater than some critical value, it will break up. This critical value is related to the viscosity ratio of the dispersed phase to that of the matrix [16]. The diameter of the dispersed particles has been shown to pass through a minimum value when the viscosities are matched [16]. A reduction in the interfacial tension generally leads to a smaller particle size and better physical properties of the mixed material.

In general, the miscibility of polymers, essentially a reduction of interfacial tension is improved by the use of *compatibilizing agents* in the mixture. Compatibilizing agents have a similar effect as surfactants in liquid systems (e.g., oil/water mixtures). These agents do not impart thermodynamic compatibility, which would cause the polymers to exist in a single molecularly blended, homogeneous phase [17]. Instead, they anchor themselves to both polymers across their interface. The molecules of compatibilizers have segments, which are soluble in each of the phases. They may have either block or graft structure [18–20]; the former is held to be more efficient; however, graft compatibilizers are used more frequently for cost reasons.

4.2.3 Mixing Equipment

Mixing machines are used to prepare materials with a minimum possible concentration gradient, that is, with a high uniformity. In some cases this might be accompanied by a decrease in the thermal gradient in processes involving heat generation and/or transfer. As pointed out earlier, the design of mixing machine suitable for a given system depends on the physical properties of components to be mixed. The mixing of non-Newtonian materials is essentially done by mechanical devices that combine the ingredients and provide intensive agitation. Common devices are sigma-blade mixers; roll mills, anchor agitators, centrifugal disk-type mixers, and others. Batch mixing is in general suitable if relatively short cycles are required [21].

Heavy pastes and polymeric melts require heavy machinery to achieve satisfactory mixing. Such materials are mixed in either batch of continuous operations. A *batch* mixing process is most frequently performed in a closed volume of the mixing device. Over the course of the mixing cycle, the properties of the mixture may change considerably and the material is completely discharged at the end of the mixing cycle.

A *continuous* mixing operation requires continuous loading and unloading of the components. There is a drastic variation in the concentration of components at the inlet. When properly performed, continuous mixing decreases these variations to the desired minimum. The main advantage of continuous mixing is that it provides a stable process. Moreover the power consumption is both lower and more constant than in the batch process. The major disadvantage of continuous mixing is a relatively long mixing time compared to batch technology [21].

4.2.3.1 Batch Mixers

The batch mixer is the oldest and conceptually simplest mixing machine and as pointed out earlier, the mixing occurs within a single isolated volume; the homogenization and dispersion of different phases is accomplished by rotating *agitators* or *rotors*. Certain technologies, such as mixing of rubber and certain plastics are still carried out in mixers of this design. Batch mixers can be divided into machines open to the atmosphere (e.g., a roll mill) and machines with enclosed mixing chambers (e.g., the Banbury mixer).

4.2.3.1.1 Roll Mills

The roll mill is the simplest batch mixing equipment. The principal design consists of two horizontal rolls, usually of equal size, arranged side by side and rotating toward each other at different speeds. The ratio of the peripheral speeds of the rolls, known as *friction ratio*, ranges from 1 to 2 but is usually around 1.2. The higher friction ratio leads to a higher heat generation in the processed material. Friction, speed, and the sizes of the rolls influence the cooling of the material mass and the intensity of its treatment. Depending on the properties of the process material and its desired temperature the rolls may be internally cooled or heated by using circulating cooling water or a suitable heating medium.

The basic mixing operation is illustrated in Fig. 4.5. The material is charged between the rolls in the form of lumps, pellets, chunks, or powder. As a

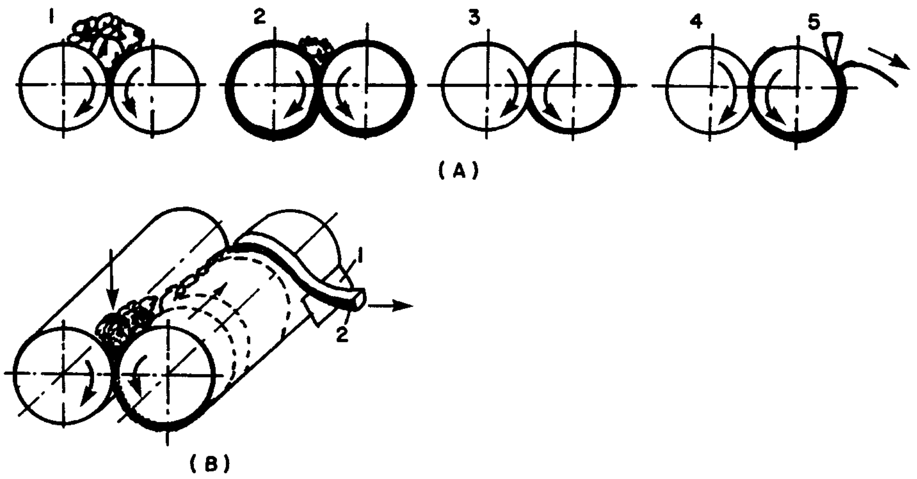


Figure 4.5. Operation of mixing rolls: (a) Batch operation. (1—loading; 2—rolling; 3—end of rolling; 4—mass shear; 5—knife); (b) Continuous operation (1—knife, 2—continuous removal of the material) (Courtesy Taylor & Francis) [5].

result of rotation, adhesion, and friction, the material is entrained into the gap between the rolls, and upon discharge it sticks to one of the rolls, depending on their temperature difference and velocities. Another factor is the gap between the rolls. In batch mixing the material after loading passes through the gap between the rolls several times and the mixing action is due to the different speeds of the rolls. Both the shearing action and entrainment of the material into the gap are very important in the mixing process and transporting of the material through the unit. The gap between the rolls can be adjusted by a massive screw mechanism. During the operation, cutting of the sheet of the material ("blanket"), folding, and rolling are carried out, which increases the uniformity of the composition. If additives, often in the powder, liquid, or paste form, are to be incorporated they are added into a rolling "bank" formed between the rolls.

Roll mills are also used for warming up materials for calendering or extrusion. In such cases the warm material is cut into strips that are fed into the calender or extruder often continuously. Another application of roll mills is to cool materials discharged from an internal batch mixer in a form of large lumps (see Section 4.2.3.1.2). The resulting blanket is then transported in form of strips to the calender or extruder or removed from the rolls as thick sheets.

A thorough theoretical analysis of mill mixing is in references [22] and [23].

Two-rotor mixers with open mixing chambers have been developed and manufactured by Werner & Pfleiderer of Germany.

4.2.3.1.2 Internal Mixers

An internal mixer consists usually of two rotors enclosed in a mixing chamber. One of the most widely used designs is the *Banbury*® *mixer* shown in Fig. 4.6. In this design, the massive rotors (1) rotate toward each other at slightly different speeds. Each rotor has a blade that extends along the length of the rotor roughly in the form of a spiral. Each rotor is

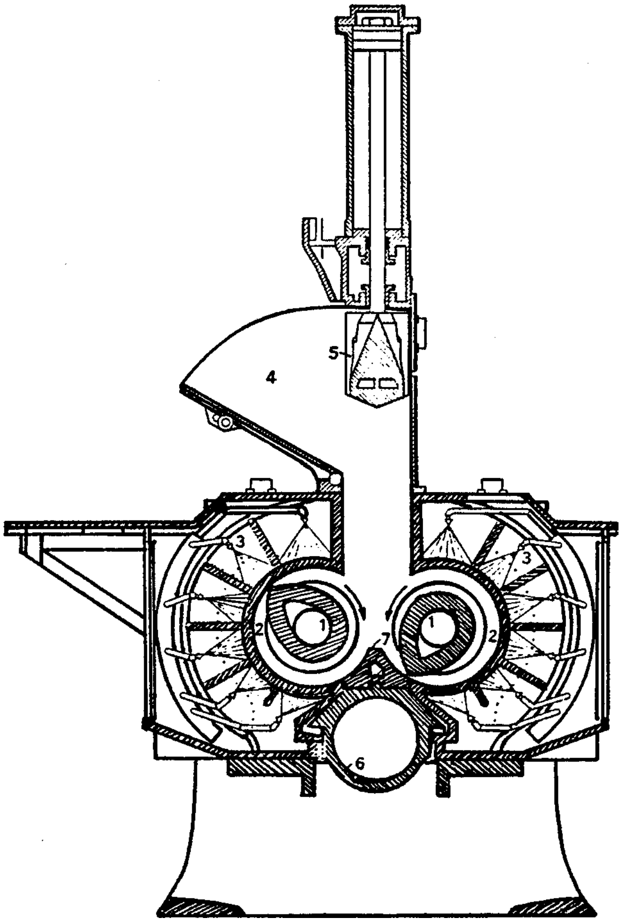


Figure 4.6. Schematic drawing of a Banbury® Mixer (Courtesy Farrel Corporation). 1—rotors; 2—mixing chamber; 3—cooling sprays; 4—feed hopper; 5—floating weight; 6—discharge slide; 7—saddle.

cored to permit cooling or heating by the passage of water or of an appropriate heating agent. Example of a two-wing rotor widely used in a Banbury design is shown in Fig. 4.7. The mixing chamber (2) may also be cooled or heated by means of sprays (3). The materials to be mixed are fed into the mixing chamber through the feed hopper (4). A floating weight (5) is operated by compressed air and rests on top of the feed, serving to confine the material to the mixing space and to exert pressure on it. The mixed material is discharged by a slide discharge mechanism (6) shown in this illustration. The saddle (7) between the rotors, which is attached to the sliding mechanism, slides from underneath the rotors, leaving an opening through which the mix discharges. Newer machines use a *drop door* for the discharge of the mixed compound, which assures a faster discharge that in turn increases the mixing capacity of the equipment by shortening the mixing cycle. The mixed batch is always dropped onto a two-roll mill or into a large single- or twin-screw extruder to partially cool it and to convert it into a desired shape for further processing, such as sheets, pellets, or chunks. Production-scale mixers of this design can process batches weighing 1,000 lbs (450 kg) or more with drives 4,000 hp (2,985 kW) and rotor diameter 29 in. (74 cm) [24]. Power draw on the motor during a mixing cycle in an internal mixer is depicted by Fig. 4.8.

Other designs of batch internal mixers include those with single mixing chambers containing single rotor or two rotors. The rotors may be separated, tangential, or intermeshing and with different directions of rotation (counter-rotating and co-rotating). These alternatives to the Banbury design are discussed in detail in reference [25].

4.2.3.2 Continuous Mixers

There are many designs of mixing machines operating continuously. Essentially, they consist of roughly elongated cylindrical or rectangular prismatic steel chambers into which feeders monitor the addition of various ingredients. They contain one or more rotating members that are capable of pumping and mixing. Such members are often of screw or screw-like shape.

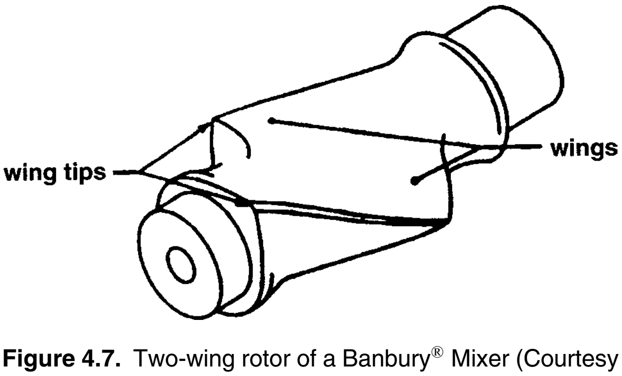


Figure 4.7. Two-wing rotor of a Banbury® Mixer (Courtesy Farrel Corporation).

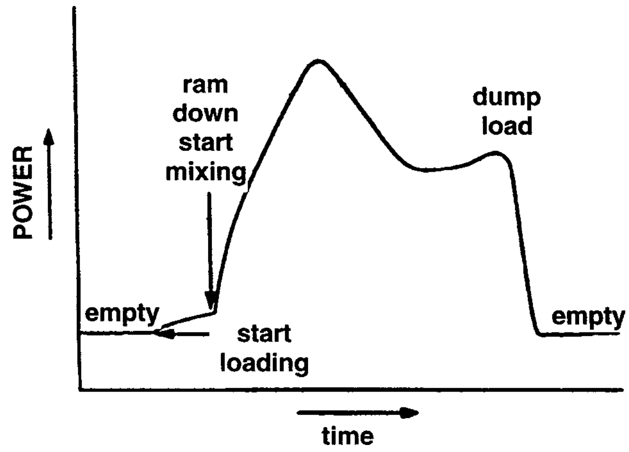


Figure 4.8. Power draw on the motor of the internal mixer during a production cycle (Courtesy Farrel Corporation).

Many continuous mixers, particularly single- and twin-screw extruders, are pressurized machines with dies that extrude strands. The strands are then continuously cut into pellets. Other continuous mixing machines are not pressurized at their exits. Examples are the single-screw KoKneter (or Kneader) manufactured by Buss AG, and various machines consisting of nonintermeshing, counter-rotating shafts with screw and mixing rotor sections. An example of the latter is Farrel Continuous Mixer (FCM®) and similar machines manufactured by Japan Steel Works, Kobe Steel, and Techint Pomini. The molten compound is discharged through doors or other connecting members into a second pressurized screw extruder with a pelletizing die [26].

The different continuous mixers differ in their internal operation. They may contain a single rotating and pumping member with the general configuration of a screw, but with the incorporation of special mixing sections. The Buss KoKneter (Kneader) contains a screw member that rotates and reciprocates in a barrel containing pins [26]. Other designs may use co-rotating or counter-rotating modular screws, intermeshing or tangential screws. Discussion of design and operating details of these machines is beyond the scope of this book and the reader is advised to obtain this information from reference [27].

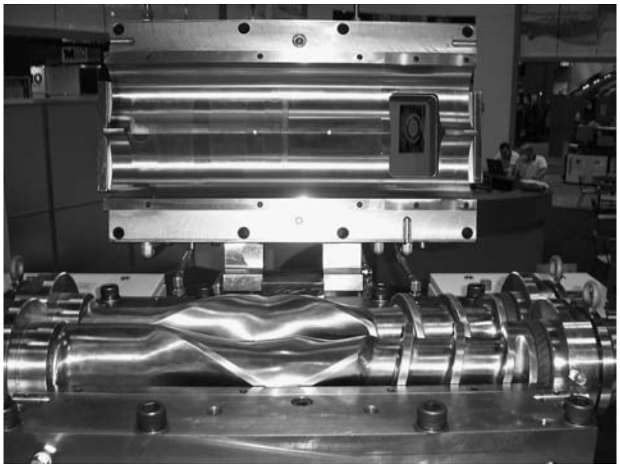


Figure 4.9. Farrel Continuous Mixer (Courtesy Farrel Corporation).

Farrel Continuous Mixer (FCM®) is a non-intermeshing counter-rotating machine (Fig. 4.9). Its distinctive feature is that the clearance between the screw flights and the barrel is much less than in a twin-screw extruder. This leads to increased shearing between screw flight tips and the machine barrel [28]. A sectional view of an FCM in operation is shown in Fig. 4.10.

The Farrel Continuing Mixer was originally developed for the continuing mixing of powdered/pelletized rubber [29]. Since the commercial introduction, there have been few applications of this kind; however it found use for post-polymerization processing of polyolefins and for mixing of compounds with high content of fillers [30].

KoKneter, Ko-Kneader, or Kneader is a reciprocating single-screw mixer made by the Swiss company Buss AG. Its screw rotates and reciprocates with one complete forward and return stroke for every rotation. The reciprocating action of the screw makes it completely self-wiping in the mixing section.

In the barrel wall of the machine, there are three rows of pins running from the main feeding port to the discharge (see Fig. 4.11). The rows of the mixing pins are spaced 120 degrees apart. These pins impart enhanced mixing to the screw, but also make each pin location a possible port to the mixing chamber. The Buss Kneader is manufactured in sizes ranging from 46 mm (1.7 in.) to 200 mm (7.4 in.) in diameters suitable for the processing of polymeric compounds and blends [31] with typical throughputs ranging from 10 kg/h (22 lb/h) to 6,000 kg/h (13,215 lb/h). It is used in applications where both dispersive and distributive mixing is required. Machines used specifically for engineering plastics are designed with electrical heating and twin-screw side feeding [32]. An overall view of a typical Buss Kneader is in Fig. 4.12.

4.2.3.3 Other Mixing Machinery

The machinery discussed in the previous sections is designated to mixing only. Other equipment that has a primary function to extrude melts into different shapes can be and at times is also used for continuous mixing. Single-screw and twin-screw extruders are pressurized machines having dies that extrude strands, which can be continuously cut into pellets if desired.

4.2.3.3.1 Single-Screw Extruders

Single-screw extruders are the most widely used polymer extrusion machines. Although their utility as mixing equipment is somewhat limited, many compounding operations have at least one [33]. Their key advantage is a relatively low cost,

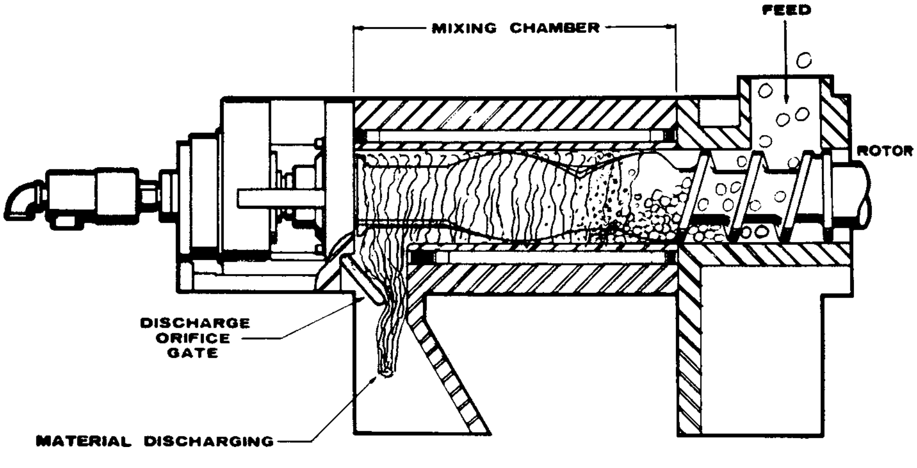


Figure 4.10. Sectional view of typical FCM in operation (Courtesy Farrel Corporation).

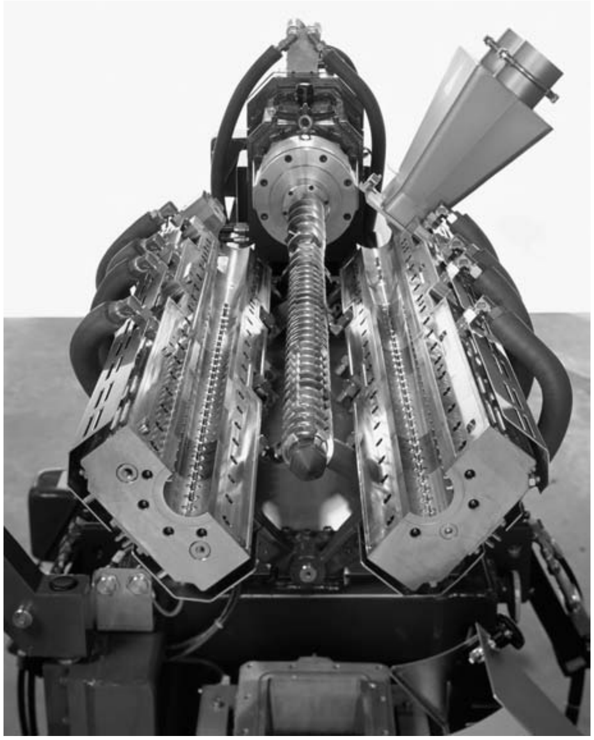


Figure 4.11. Cross-section of the Buss Kneader (Courtesy Buss AG).

straightforward design, ruggedness, and favorable performance/cost ratio.

The single-screw extruder is primarily a drag pump designed to work with highly viscous fluids such as polymeric melts. The usual screw configuration has twenty or more turns with a pitch similar to the diameter giving a long slender machine in which substantial longitudinal temperature gradients can be maintained and controlled. An appreciable residence time permitting a degree of end-to-end mixing is also provided. In addition to this *distributive* mixing, high shear stresses over flight lands give a degree of *dispersive* mixing for breaking up agglomerates such as pigments, waxes, and other similar additives [34].

Typical single-screw extruder is shown in Fig. 4.13. Its main components are:

- Barrel and feed section
- Barrel heating and cooling mechanism
- Barrel and die temperature control systems
- Motor and drive
- Gear Box
- Thrust bearing
- Feedscrew.

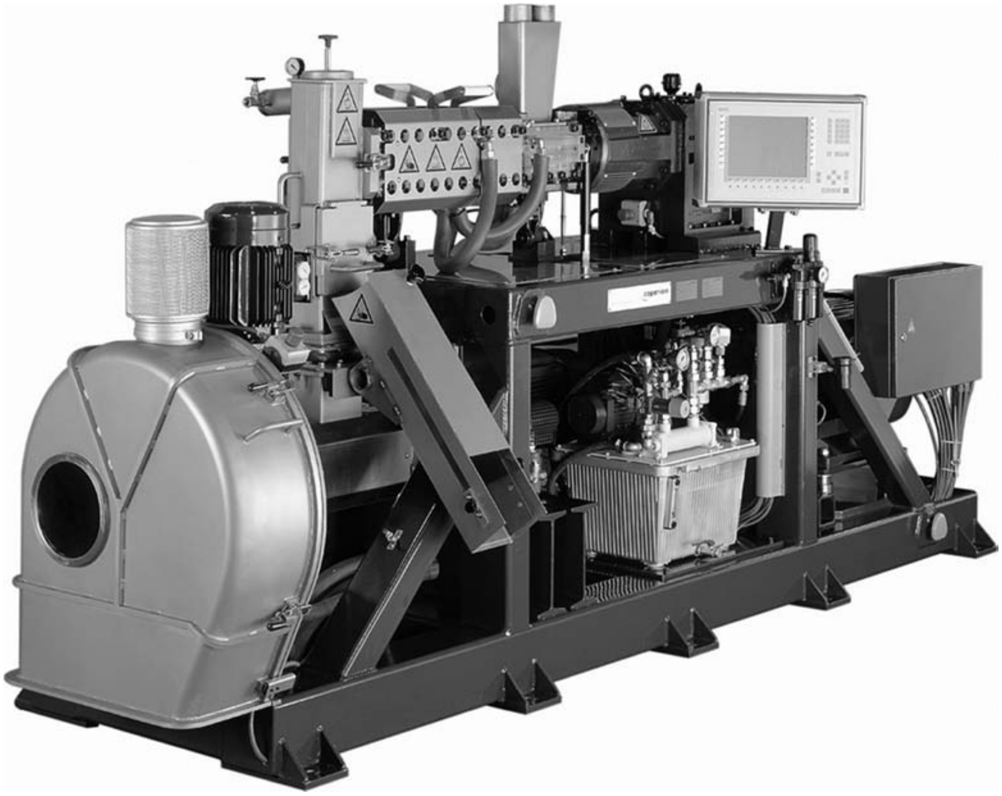


Figure 4.12. Buss Kneader, overall view Buss (Courtesy Buss AG).

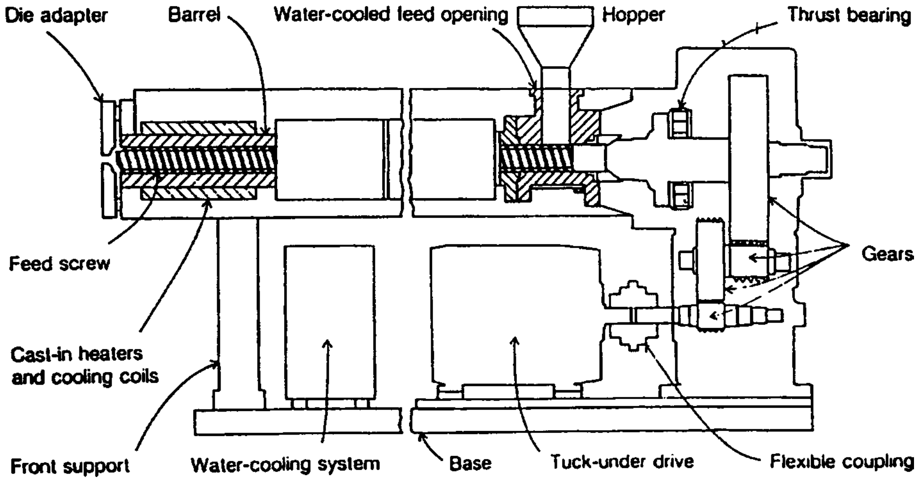


Figure 4.13. Typical single screw extruder (Courtesy Hanser Publishers).

The barrel houses the feedscrew and provides a transfer medium for heating, cooling, and venting and is made from a special bimetallic hardened liner to withstand wear and high pressures occurring during the operation of the extruder.

Inside diameter of the barrel (*D*) and barrel length (*L*) to barrel diameter ratio (*L*/*D*) are the principal dimensions used to express the size of the extruder. The (*L*/*D*) measurement is arrived at by dividing the barrel length from the downstream edge of the feed throat to the end of barrel by the barrel diameter. The (*L*/*D*) ratio has an important relation to available barrel surface area and residence time of the material within the extruder [35].

The feed opening is located at the end of the barrel, near the gearbox. The material to be processed is usually fed from a hopper that is bolted over the feed opening. In general, the opening is round and of the same diameter as the screw [36]. The material flows in most cases by gravity from the feed hopper down into the barrel and into the annular space formed between the extruder screw and barrel.

Most extruder screws have a single metal ridge (flight) wrapped like a large screw thread around a cylindrical root. The screw nomenclature is shown in Fig. 4.14 and the specific geometrical attributes in Fig. 4.15. The majority of single-screw extruders have single-flighted screws, which means that the screw has a single helical flight. Some screws are of multi-flight design, that is, they have more than one helical flight, typically two or three. The screw flights may *be right handed* or *left handed* when the screw rotation is in the clockwise direction, as viewed from the end of the screw (see Fig. 4.16). Almost all single-screw extruders have right-handed screw threads and rotate in the clockwise direction when viewed from the end of the screw [37].

The barrel is stationary and the screw is turning. The result is that the frictional forces act on the material and cause a forward movement. The output rate is controlled by the intake capacity of the feedscrew. The flights in the feed section are full in most cases. This case is referred to as *flood feeding*. As the material moves forward, it heats up as a result of the heat generated by and by heat conducted from the

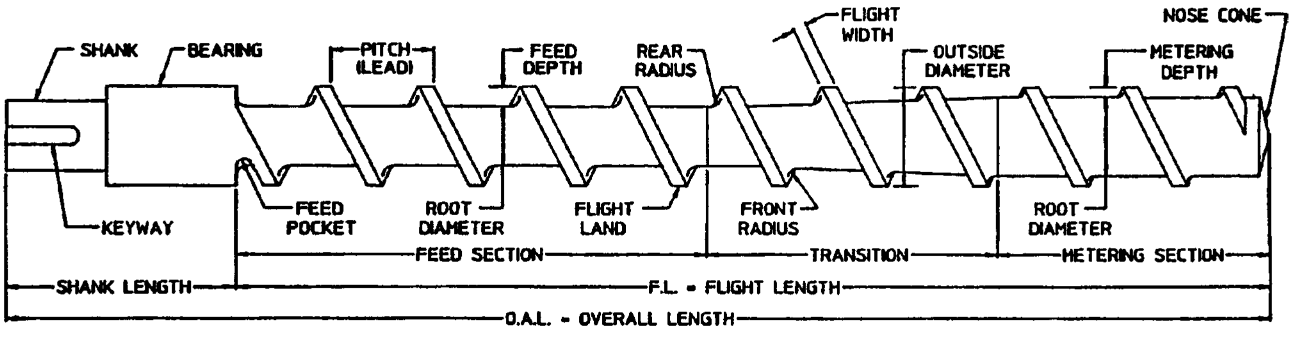


Figure 4.14. Feedscrew nomenclature (Copyright Spirex Corporation, 1979–2006).

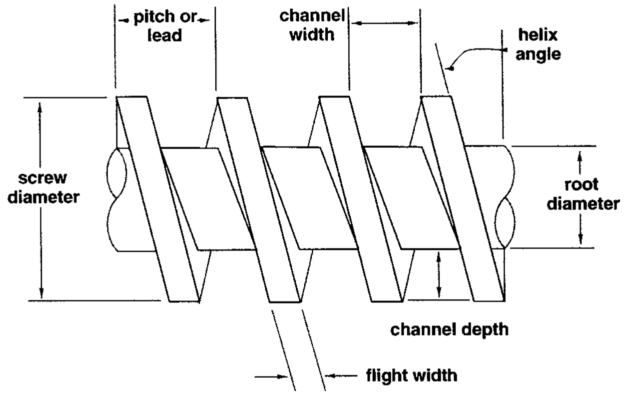


Figure 4.15. Geometrical attributes of a screw (Courtesy Hanser Publishers).

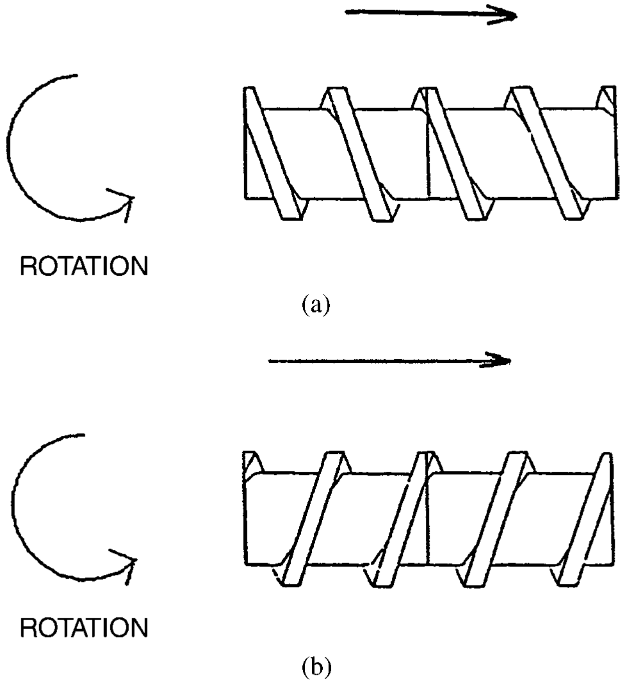


Figure 4.16. (a) Right-handed screw. (b) Left-handed screw.

barrel heaters. When the material exceeds its melting point, a melt film forms at the barrel surface. During the forward movement the amount of melted component increases and at one point all of it is melted. In the last part of the extruder, the *pumping section*, the polymer melt is pressurized and pumped into the die.

Although a single-screw extruder provides a degree of end-to-end mixing, the residence time of the melt is of the order of only 10 s. On the other hand, it is quite effective, especially at high back pressure, as a distributive mixer on a small scale, thus forming a useful compounding device when fed with a blend containing masterbatch (a premix), or following an intensive high-speed mixer for powders [38].

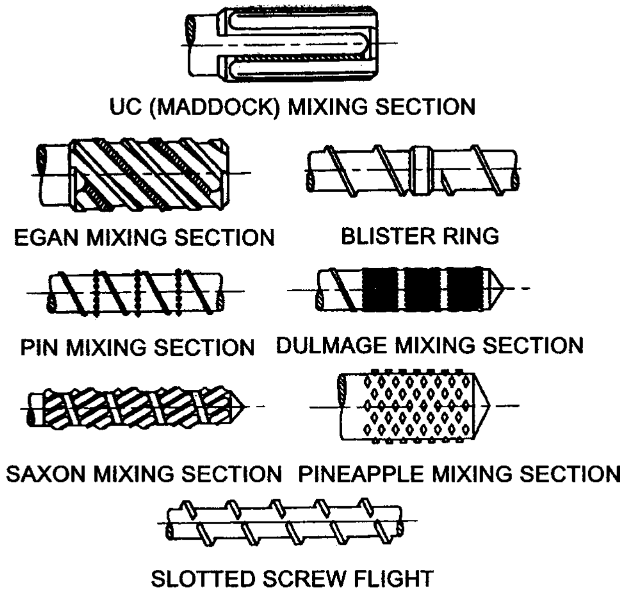


Figure 4.17. Various local screw modifications to enhance mixing.

Feed screw mixing devices, such as *mixing pins*, *Dulmage section*, *Dray Mixer*, and *Maddock Mixer* have been developed to overcome problems inherent in the design of single-screw extruders [38]. They mostly represent different modifications of the screw. Examples of such local screw modifications are in Fig. 4.17.

4.2.3.3.2 Twin-Screw Extruders

There are many different designs of twin-screw extruders being used in mixing of thermoplastic and elastomeric materials. Essentially, they can be grouped into two basic designs, namely *modular co-rotating* twin-screw extruders and *modular counter-rotating* twin-screw extruders.

Modular Co-rotating Twin-Screw Extruders. Modular co-rotating twin-screw extruders have become the most important commercial machine for continuous mixing of compounds based on thermoplastics. They also are the most studied and understood of the equipment developed in the period after the Second World War [39].

The machine contains two shafts mounted with various screw and mixing element modules each having a specific function. These are usually right-handed and left-handed screw elements, kneading disc blocks, distributive mixing elements, rotor and polygonal elements, and valves.

Modular co-rotating twin-screw extruders are widely used for blending of polymers and incorporation of fillers, pigments, oils, and other additives into the polymeric base. Moreover, they are used for removal of liquids (devolatilization), for reactive extrusion, polymerization, and grafting [40].

Modular Counter-rotating Twin-Screw Extruders. Modular counter-rotating twin-screw machines with modular construction are used for mixing, blending, devolatilization, and reactive extrusion. Two classes of these machines have been commercialized, namely *tangential screw* and *intermeshing screw* machines [41]. The intermeshing screw machines have been used for difficult mixing problems involving pigments, fillers, and lubricants that are difficult to disperse. The machines with tangential screws provide the processed material with a milder stress history and consequently are much less able to break up difficult particle agglomerates than the intermeshing screw machines. Therefore, they found their major applications in devolatilization and reactive extrusion [42].

4.2.4 Material Feeding and Feeders

Bulk raw materials are most frequently stored in large storage bins or tanks. Some liquids, such as highly viscous oils require heating in order to facilitate their flow into the feeding system. Other raw materials, such as waxes and certain chemicals have to be melted before being introduced into the mixer and are often stored in heated tanks.

All mixing machines must have some device or system to feed the material into the process. Their design depends on the type of machine and on the type of materials processed, their physical properties, and flow behavior. Such devices or systems are referred to as *feeders*.

There are many types of feeders, such as single- and twin-screw feeders, rotary feeders, belt feeders, vibratory feeders. They can discharge the raw materials by volume (volumetric feeders) or by weight (gravimetric feeders). The latter require weighing system and accurate and dependable controls.

Feeding systems for batch mixing are relatively simple. They may include scales, simple conveyor belts, or weigh belts. Liquids can be introduced directly into the mixing chamber from a volumetric or gravimetric feeder. Feeding systems for continuous mixers are considerably more sophisticated, often with complex controls.

The subject of feeding and feeders is covered in great detail in reference [43].

4.2.5 Finishing Operations

The mixed compound is often not in a form to be delivered to the user. Thermoplastic materials are most widely reduced in size to be suitable for the manufacture into semifinished or finished products.

4.2.5.1 Filtration

For certain applications the compounds must be clean, without solid contaminants, such as particulates, gels, unconverted polymer, carbonized polymers, agglomerated additives, and debris such as metal particles, dirt, or dust. These must be subjected to melt filtration. Machines with mixing screws almost always have a built-in filter, consisting of a breaker plate and a screen pack (see Fig. 4.18). In order to maintain continuous melt flow, *screen changers* of various designs are used. An example of a screen changer is in Fig. 4.19.

Compounds mixed by batch mixing equipment must be cleaned in down-stream equipment, which can be a simple single-screw extruder with a filtering device described above or a specialized strainer with a screen changer.

4.2.5.2 Size Reduction

In general, mixed compounds can emerge from the mixing equipment as lumps, strips, and slabs. In some cases the shapes and dimension are not suitable for use in such manufacturing equipments, as injection molding machines, extruders, blow molding

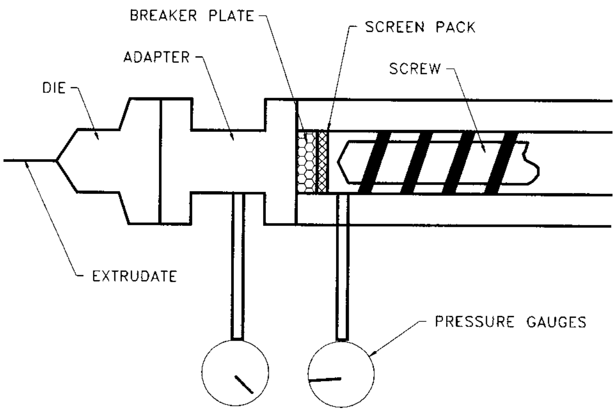


Figure 4.18. Location of screen pack and breaker plate in an extruder.

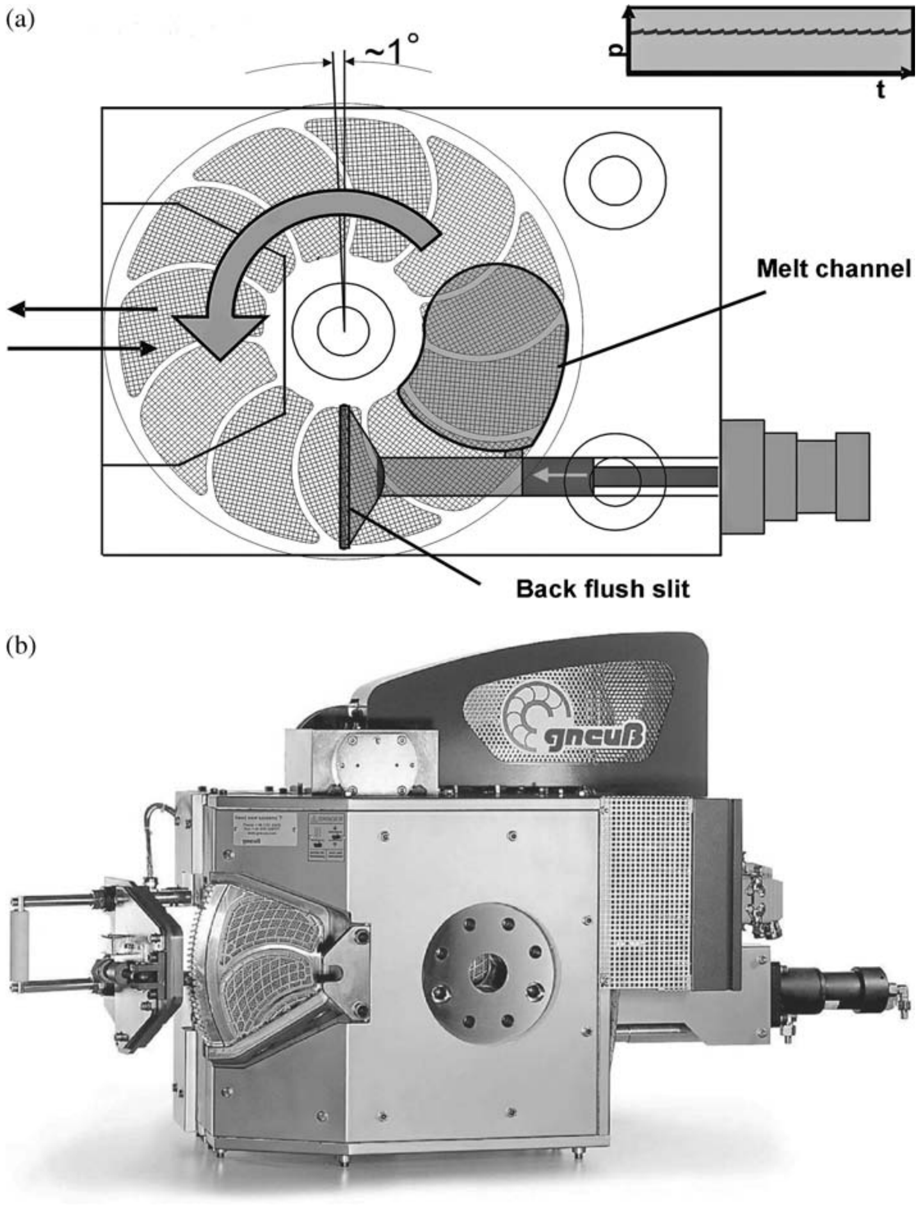


Figure 4.19. An example of a screen changer (Courtesy Gneuβ Kunststofftechnik, GmbH).
(a) Schematic diagram;
(b) overall view.

and rotomolding equipment. In order to prepare the mixed compounds for the next manufacturing step, they have to be reduced in size. The size reduction methods include pelletizing, dicing, and granulation. The processes and equipment used for pelletizing and dicing are listed in Table 4.8.

Below is the description of the most common processes and machines used for the production of reduced sizes of thermoplastic compounds after they are mixed or prepared for recycling.

4.2.5.2.1 Pelletizing

Pelletizing is the most widely used process for size reduction of many thermoplastic materials, including

Table 4.8. Processes and Equipment Used for Pelletizing and Dicing

Quenching, Solidifying, and Cutting	Cutting, Quenching, and Solidifying
Dicers	Die-face pelletizers
Strand Pelletizers	Dry face pelletizers
	Wet ring pelletizers
	Underwater pelletizers
	Rotary knife pelletizers
	Centrifugal pelletizers

raw polymers and mixed compounds. The process involves extrusion through a die. The extrudate is cooled to solidification and then cut into pellets, or the molten extrudate is cut as it emerges from the extrusion die and the pellets are subsequently cooled. In the latter case both cutting and cooling can be done in air or water, or cutting may be done in air, followed by quenching in water [44]. Cutting thermoplastics as a melt rather than as solid generates fewer fines and less knife wear [45].

The pelletizing device, which converts the product into pellets of different shapes and sizes, is frequently attached to an extruder or a gear pump. The pellet form offers several processing advantages over other forms. It can be easily weighed, uses simple feeding systems with fewer feeders, and allows homogeneous and uniform free-flowing feed for the subsequent end uses.

The product viscosity, heat history, product uniformity, required throughput, and other factors will generally determine the cutting method that can be successfully employed. Below are the most widely used pelletizing machines for thermoplastics.

Strand pelletizers have been most widely used for pelletizing thermoplastic polymers and compounds [46] in the past, but the current trend is to use the underwater machines. The strands emerging from the die of an extruder or a gear pump are conveyed through cooling water bath with grooved rollers that keep them separate until they solidify. Then they are air dried and fed into nip rolls to a multi-knife-blade rotor operating against fixed blades. The cross-section of the pellets can be round, oval, or nearly square [47] with typical diameter of 2–4 mm (0.08–0.16 in.) and length of 1–5 mm (0.04–0.2 in.). There are several methods of cooling and drying the pellets; these are discussed in some detail in [48]. A schematic diagram of a strand pelletizer is in Fig. 4.20.

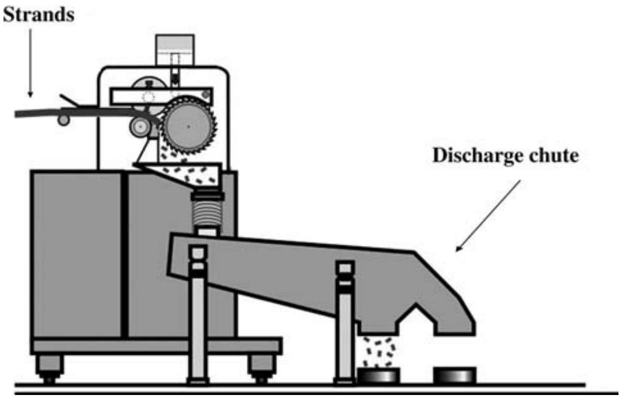


Figure 4.20. Schematic drawing of a strand pelletizer (Courtesy Rieter-Automatik).

Die-face pelletizers produce pellets by the use of knives rotating rapidly across a multiple-hole die plate. The pellets are quenched in air alone with a water mist, or by subsequent immersion into a water bath [49]. A schematic diagram of a hot die-face pelletizer is in Fig. 4.21.

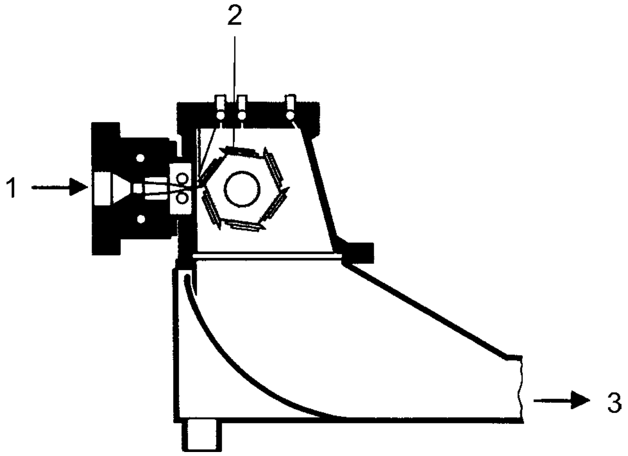


Figure 4.21. Schematic diagram of a hot die-face pelletizer. 1—Polymer melt; 2—Rotary knife; 3—Discharge chute.

Dry-cut eccentric pelletizers have an excentrically mounted cutter with multiple arms rotating at speeds up to 2,500 rpm.

Underwater pelletizers are probably the most versatile equipment for a wide viscosity range, higher outputs, and pellet size capability. They operate with the die face and rotating cutter fully immersed in water. The produced pellets are carried away as slurry in water for further cooling in transit, to the dewatering, screening, and drying equipment [50]. An example of an underwater pelletizing head is in Fig. 4.22 and the detail of cutting knives is shown in Fig. 4.22a.

In the *water ring pelletizer* the molten strands emerging from the die are cut with a centrally mounted cutter. The freshly cut pellets are thrown into a spirally rotated water, about 20 mm (0.8 in.) deep. The pellets are cooled down in the water, then screened and dried. A schematic of this type of pelletizer is in Fig. 4.23 and an example of the arrangement of die knives in such a device in Fig. 4.23a.

In *centrifugal pelletizers* the melt is fed into a rotating die chamber at atmospheric pressure.

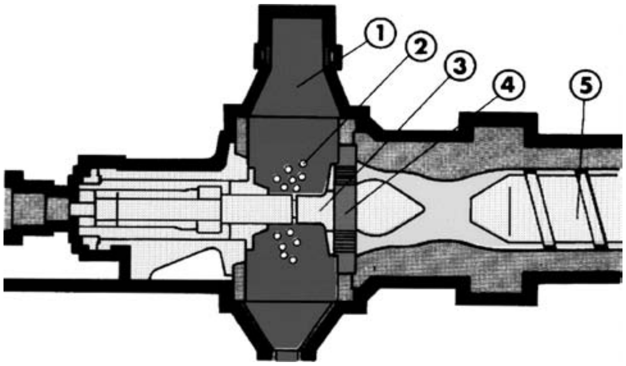


Figure 4.22. Schematic drawing of an underwater pelletizing head (Courtesy Pomini). 1—Water chamber; 2—Pellets; 3—Knife holder; 4—Die Plate; 5—Extruder feed screw.

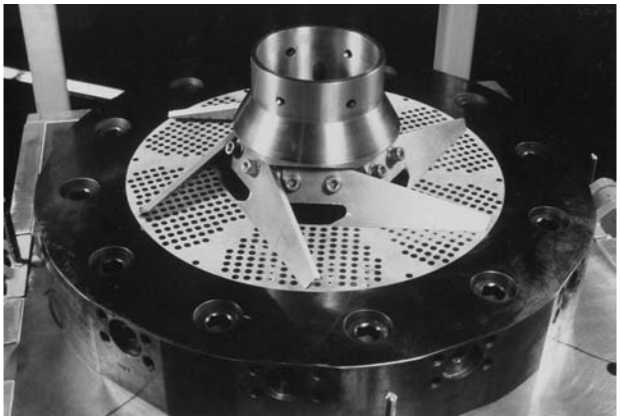


Figure 4.22a. Detail of the cutting head of an underwater pelletizer (Courtesy Dazvis-Standard LLC, Black Clawson Converting Machinery).

The pressure to extrude the polymer through the die holes is generated by the centrifugal force within the die rather than by an extruder or gear pump. The emerging strands are cut by single stationary knife [50]. This type of machine was offered at one time but is no longer being made.

Rotary knife pelletizers operate with a die similar to the strand die, but with the rotary cutter operating in close proximity to the emerging strands. The cutter is completely enclosed [51].

Thermoplastic elastomers can be processed essentially by any of these machines; the selection depends mainly on the apparent viscosity of the melt of the given material. The layout of a typical pelletizing system for most TPEs is in Fig. 4.23b.

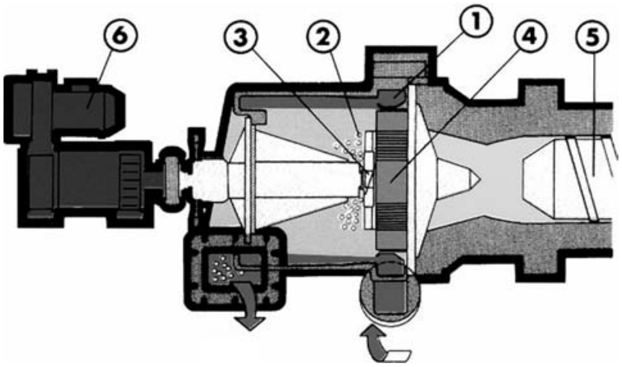


Figure 4.23. Schematic drawing of a water-ring pelletizer (Courtesy Pomini). 1—Water ring chamber; 2—Pellets; 3—Knife holder; 4—Die plate; 5—Extruder feed screw; 6—Motor.

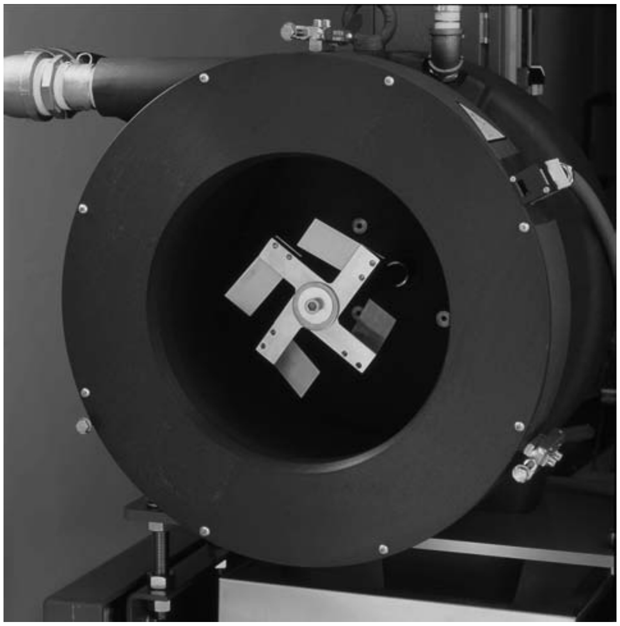


Figure 4.23a. Detail of the cutting head of a water ring pelletizer (Courtesy Xaloy Extrusion).

4.2.5.2.2 Dicing

Dicers are used to produce square, rectangular, parallelogram, or octahedral pellets [52]. The strip from an extruder or a sheet from a calender or a roll mill is quenched before entering the dicer and is then fed at a constant rate through nip rolls into the rotating knives operating against stationary-bed knife. The configuration of the knives, the strip feed rate, rotor speed, and the number of rotating knives determine the pellet size, configuration, and output.

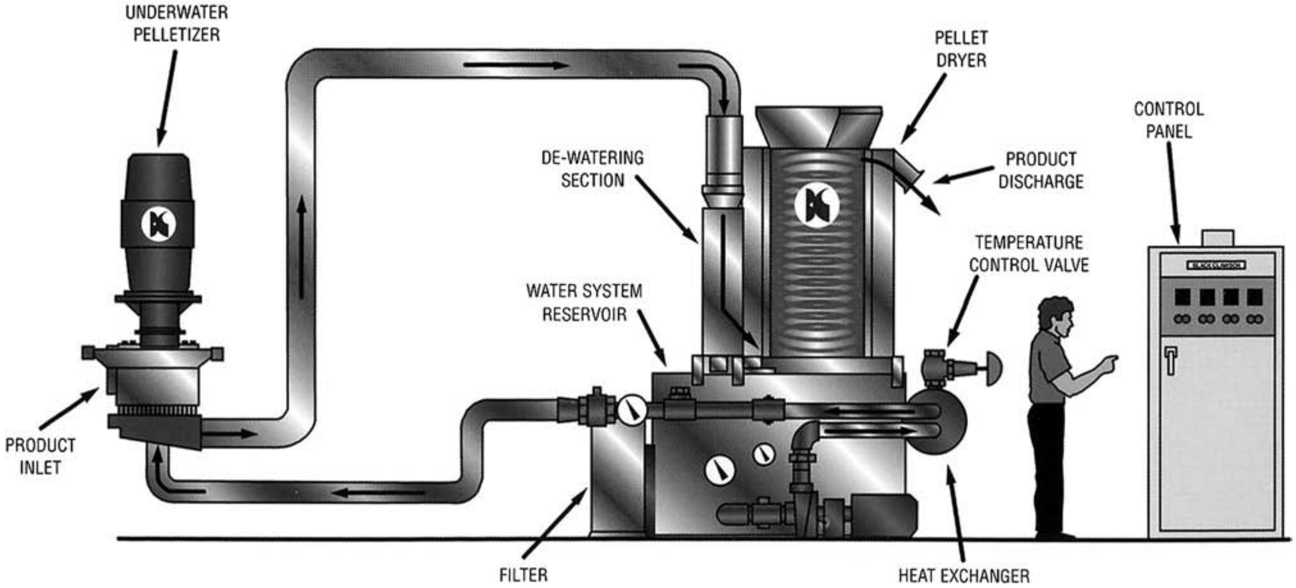


Figure 4.23b. Typical layout of a system for pelletization of thermoplastic elastomers (Courtesy Davis-Standard LLC, Black Clawson Converting Machinery).

4.2.5.2.3 Granulation

Although granulation is mostly used for reclaiming and recycling of thermoplastics, granulators can be useful for short runs or for compounds that are difficult to pelletize. They have two or more rotary knives inside a chamber, where stationary knives are mounted. Granulators are used in very limited applications to pelletize hot melt directly from the extrusion die; cooling for solidification is achieved in the granulator [53]. A schematic of a granulator is in Fig. 4.24.

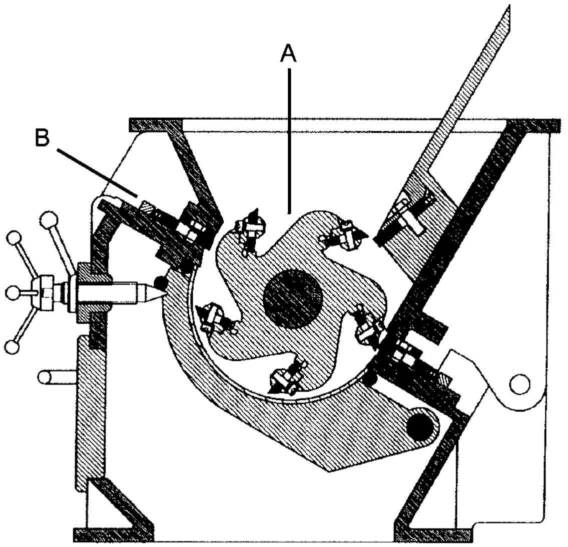


Figure 4.24. Schematic drawing of a granulator (Courtesy Neue Herbold GmbH).

4.3 Extrusion

Extrusion is one of the widely used processes for fabricating parts from TPEs. Unlike injection molding (Section 4.4), extrusion usually results in a semifinished or intermediate article that needs further processing to arrive at an end product. The principal end products made by extrusion are wire insulation, tubing, profiles, film, and sheet.

The flow behavior of the molten polymer is of critical importance in the extrusion of most thermoplastics. Thermoplastic elastomers, and generally thermoplastic materials, must be processed below the velocity at which *melt fracture* occurs, referred to as the *critical shear rate*. Melt fracture in molten plastics takes place when the velocity of the resin in flow exceeds the critical velocity, the point where the melt strength of the polymer is surpassed by internal stresses. Parts extruded in a process that exceeds the critical shear rate have poor quality. Typical symptoms of melt fracture include a rough surface (*shark skinning*), and frosty or cloudy surface.

4.3.1 Fundamentals of Extrusion Processes

Extrusion is a continuous process that involves forming a product *(extrudate)* in two dimensions. These *x*–*y* dimensions determine the cross-sectional form of the extrudate, and this can be almost unlimited in scope, ranging from a simple tube to a very complex extruded profile. The third (z) dimension is the length of the extrudate. In principle it can be infinite. In fact, it is limited by practical considerations governing winding, reeling, storage, and transport. The essential point is that extrusion always produces an object of constant cross-section.

The product cross-section is formed in a die; the extrusion process consists of heating a thermoplastic above its melt temperature and forcing it through the die. The heating and pressurizing device involves one or more screws operating in a heated barrel, and is known as an *extruder*. Downstream of the die, the extrudate is calibrated, cooled, and packaged by an array of ancillary devices including vacuum calibrators, air cooling chamber, water tanks, cooling rolls, haul-offs, cutters, and winders. Upstream of the die, a melt pump (Fig. 4.25) may be interposed between the extruder and the die [54]. The exact selection and arrangement of these components of an extrusion system will depend on the end product. The specific processes for production of different extruded products will be discussed in detail later in this chapter. The principle of extrusion is common to all these processes and will be discussed first.

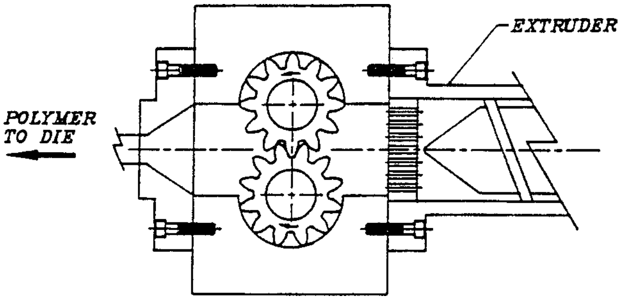


Figure 4.25. Schematic diagram of a melt pump.

4.3.2 The Extruder

The function of the extruder is to heat the plastics material to a homogeneous melt and to pump it through the extrusion die at a constant rate. Because the extrusion of plastics is a continuous process, the melt preparation device must be capable of a constant output. Thermoplastic extrusion depends almost entirely on the rotating screw as a melt delivery device. Thermoplastics are generally characterized by low thermal conductivity, high specific heat, and high melt viscosity, so the preparation of a uniform melt and its delivery at adequate pressure and a constant rate pose considerable challenges. These have been countered by the introduction of various types of extruders.

The principal variants are the single-screw and the twin-screw types. Of these, the single-screw extruder (Fig. 4.26) is by far the most popular. The twin-screw extruder may have parallel or conical screws, and these screws may rotate in the same direction (*co-rotating*) or in opposite directions (*counter-rotating*) (see Fig. 4.27). Extruders with more than two screws are known, for example, the quad-screw extruder, but are not widely used [54]. Twin-screw extruders are normally used when mixing and homogenization of the melt is very important, and in particular where additives are to be incorporated. Thermoplastic elastomers are normally extruded using a single-screw machine.

The single-screw extruder consists essentially of a screw that rotates in an axially fixed position within the close-fitting bore of a barrel. The screw is motor-driven through a gear reduction train, and is supported by a thrust bearing that opposes the force exerted on the plastic melts. A helical flight on the screw provides the drag-induced conveying motion that develops this force. The barrel is equipped with both heating and cooling means, and its

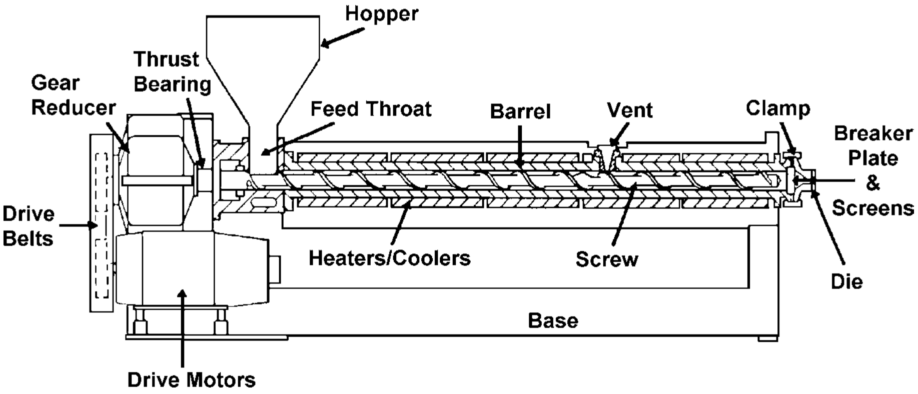


Figure 4.26. Typical single-screw extruder with a vented barrel.

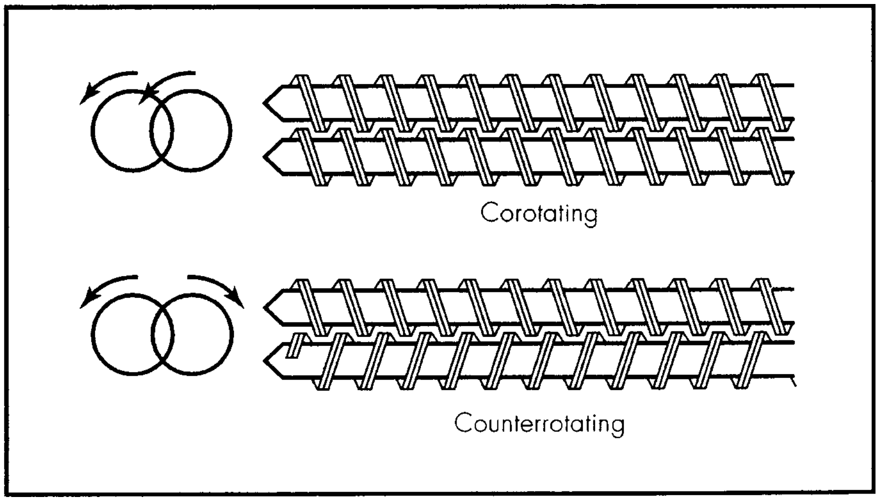


Figure 4.27. Co-rotating and counter-rotating twin screws.

downstream end is provided with an attachment device for a shaping die that determines the cross-section of the extruded product. The upstream or inlet end of the barrel is equipped with a feed throat or an aperture in the barrel wall where a plastics material is input, generally in the form of granules or pellets. During its passage along the helical screw flight, this material is heated by a combination of conducted heat received from the barrel and mechanical shear heat derived from the mixing and kneading action of the screw. The output rate of the extruder is a function of screw speed, screw geometry, and melt viscosity. The pressure developed in the extruder system is a function of melt viscosity, screw design, and barrel and die resistance. Extrusion pressures are lower than those encountered in injection molding, and are typically less than 35 MPa (5,000 psi) [55].

The key determinant of extruder performance is the screw. The screw has three functions to perform: feeding and conveying the solid thermoplastic feed (most frequently pellets); melting, compressing, and homogenizing the material; and metering or pumping the melt to the die. The typical extruder screw (Fig. 4.28) takes the form of a single constant-pitch flight that decreases in depth from the input end to the output end. The pitch is usually equal to the screw diameter. This is sometimes known as a square pitch screw; the resulting helix angle is 17.8°. The screw features three sequential zones, corresponding to the three functions of feeding, compression, and metering.

Flight depth is usually constant in the feeding and metering zones, and decreases at a constant rate over the compression zone. The feed zone occupies about 50% of the screw length; the compression zone takes up 25–30%, and the metering zone accounts for the balance. The ratio of the flight depths in the feeding and metering zones is known as the compression ratio, and it affects the mixing and shear-heating

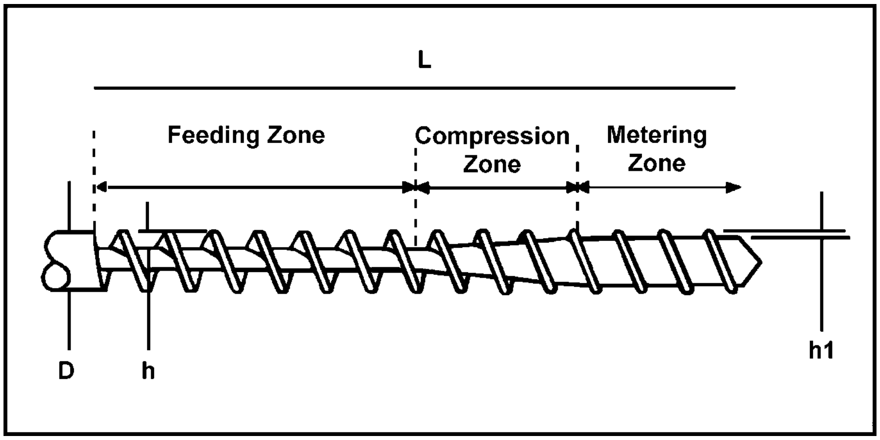


Figure 4.28. Features of a typical extrusion screw: L=screw length; D=diameter; h=initial Length; h_1= final flight depth; h/h_1= compression ratio.

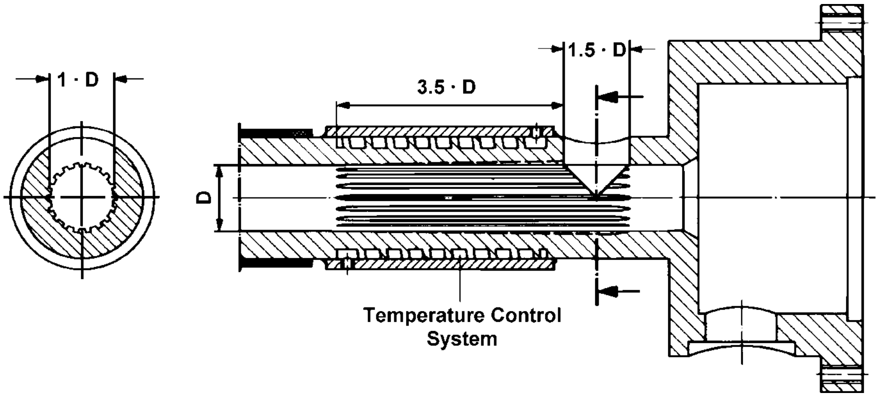


Figure 4.29. Grooved feed section of barrel.

characteristic of the screw. The ratio of the screw length to its diameter is known as the *L*/*D* ratio; this has a bearing on mixing and uniformity of output. Most conventional screw designs perform satisfactorily for TPEs. Extrusion screws for wire insulation should have an *L*/*D* ratio in the range of 24:1 to 30:1. A screw with a long feed section with approximately a 3:1 compression ratio (core progressive profiles that do not subject the resin to excessive shear) is preferable.

The mixing performance of a single screw can be improved by the addition of mixing elements in the metering zone as shown earlier in Fig. 4.17. These are sometimes teamed with or replaced by static elements such as pins in the barrel. Attention to the barrel can also improve the material conveying performance at the inlet, stepping up the output rate. A series of axial grooves in the barrel wall (Fig. 4.29), extending for at least three screw diameters, is effective.

Variants on the single screw include the *barrier* or *melt extraction screw* (Fig. 4.30) and the *vented screw*. Barrier screws have separate input and output flights that overlap in the midsection of the screw where the plastics material is only partially melted. The barrier flights are slightly smaller in diameter than the main flights. Molten material passes through this clearance and proceeds to the metering zone while solids are retained for further heating. The barrier screw offers the potential for lower melt temperatures or higher output rates, but is difficult to design and optimize. Vented screws, sometimes known as decompression screws or two-stage screws are effectively two screws placed in series, with the second or downstream screw having a higher transport rate than the first. The upstream end of the screw is provided with conventional feeding, compression, and metering zones, but these are followed by a sudden increase in flight depth, and then by further compression and metering zones. The mid-screw increase in flight depth causes a sudden pressure drop in the molten plastic, and this allows any dissolved volatile matter to boil out. The lack of compression at this point, coupled with the differential transport rates of the two screw sections, makes it possible to extract the volatile material through a port in the extruder barrel without the plastics melt emerging at the same time. Vented screws typically have an *L*/*D* ratio of greater than 30:1 and suffer from some instability in pumping output. Operating conditions are also constrained by the need to ensure that the vent does not plug with plastics melt. For these reasons, the use of vented screws is usually confined to materials likely to contain moisture, volatile matter, or entrained air. Thermoplastic elastomers are not usually prone to these problems, so vented screws are not normally used in their processing.

Figure 4.30. Section of a barrier screw.

4.3.3 Extrusion Methods

Depending on the intended use, the corresponding extrusion method is used. Each method requires specific tooling and process conditions. Often the method and the polymer grade have to be matched to assure a satisfactory product. The most common extrusion methods are film and sheet extrusion, pipe and tube extrusion, wire coating, and profile extrusion.

4.3.3.1 Film and Sheet Extrusion

Films from thermoplastics can be produced either by extrusion casting or extrusion blowing processes. Each has its advantages and disadvantages. These basic processes result in film with a molecular orientation predominantly in the machine direction. Regardless of process, film production lines include common downstream equipment such as haul-off, tensioning, and reeling stations. A high purity melt, free of inclusions, is essential for film production. This is achieved by filtering the melt through a *screenpack* located upstream of the die.

4.3.3.1.1 Cast Film Extrusion

Cast film is produced by extruding the melt from a slit die and cooling it either by contact with a *chill roll* or by quenching in a *water bath*. Both processes are characterized by relatively high melt temperatures and rapid rates of film cooling. This results in films with low haze, good clarity, and high gloss. Cast film grades typically have a melt flow index in the range 5.0–12.0 g per 10 min.

In the *chill roll cast film process*, a plastics web is extruded from a slit die (Fig. 4.31) against the surface of a water-cooled chill roll. The die is arranged to extrude vertically or obliquely downwards so that the film web is delivered approximately tangentially to the roll surface. The die is similar in principle to a sheet die but will usually not include a restrictor bar. Film thickness is partially regulated by the gap between the die lips but also by the rotational speed of the chill roll which is arranged so as to draw down and thin the melt web. Consequently, the die gap is set in excess of the desired film thickness. Typical die gap settings for most thermoplastics are 0.4 mm for films up to 0.25 mm (0.01 in.) thick, and 0.75 mm (0.03 in.) for film gauges in the range 0.25–0.6 mm (0.01 to 0.024 in.). Die lip adjusters should allow the die gap to be varied at each adjustment point across the die width in order to allow control of the transverse film thickness. Film reel quality will suffer if the transverse thickness tolerance exceeds ±5% of target thickness. A constant temperature should be maintained across the die so that film draw-down rates and physical properties remain constant across the film web. Attempts to control film thickness by varying the temperature profile across the die will disturb these factors and reduce film quality. When the process is correctly regulated, the thickness uniformity of chill roll cast film is substantially superior to blown film.

The die is maintained in close proximity (typically 40–80 mm or 1.6–3.2 in.) to the chill roll so that the low-strength melt web remains unsupported for a minimal distance and time (Fig. 4.32). If the die is too close, there is insufficient space for thickness draw-down and widthwise neck-in to take place in a stable manner. The web flows on to the water-cooled chill roll with a wraparound of 240° or more before passing to a second chill roll, and then proceeding to edge trimming, tensioning, and win-up stations. The first chill roll is critical to process quality. The cooling capacity must be sufficient to chill the film at high output rates, and the temperature gradient across the width of the roll should not exceed ±1°C (1.8°F). The actual roll temperature depends on film gauge, line speed, and roll diameter. The chill roll drive speeds must be very precisely regulated to control film draw-down and finished thickness.

At line speeds greater than 30 m/min (98 ft/min), there is a tendency for a thin cushion of air to become trapped between the film and the chill roll. This

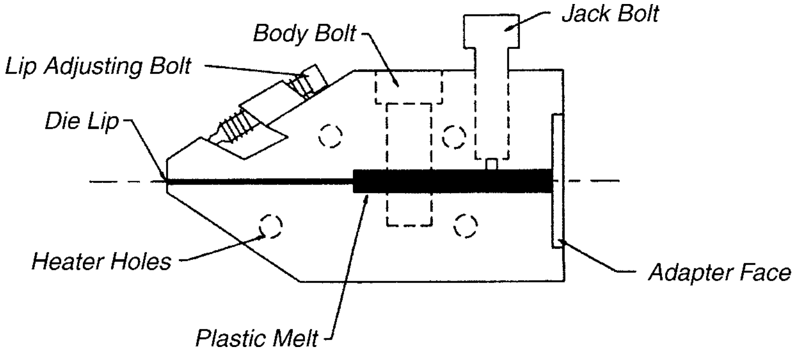


Figure 4.31. Typical slit die for cast film.

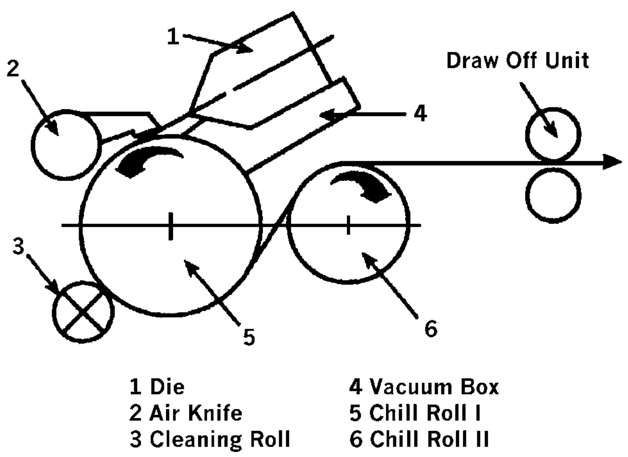


Figure 4.32. Detail of chill roll process.

results in slow and uneven cooling, affecting the appearance and properties of the film. Two measures are adopted to counteract the problem (Fig. 4.32). An air knife delivers a streamline jet of filtered air that impinges on the film just beyond the point of first contact with the chill roll and presses it against the roll. The air is supplied through a narrow slit of about 1.5 mm (0.06 in.) gap, and controlled at a low differential above atmospheric pressure. An optimum air knife setting improves film clarity and gloss, but excessive pressure induces melt vibration and mars the film surface. The second measure is the provision of a vacuum box, associated with the die, and operating close to the chill roll surface just ahead of the extruded melt web. The vacuum box removes any condensates that have been deposited on the roll by the film, and tends to draw air out of the interface between film and roll.

The film temperature should be close to ambient at the film windup station; otherwise the reel will continue to shrink after cooling, causing stretch marks and corrugations, and accentuating any variations in thickness. Winding tension should be sufficient to ensure the integrity of the reel but otherwise should be kept low to allow for a small amount of post-winding shrinkage that will tighten the reel. A typical line for chill roll cast film is in Fig. 4.33.

As in other plastic processes, the cast film process depends on many interactive variables, so that any defect may have one of several causes. A remedy for one defect may introduce another, so process problem solving is not straightforward. With these provisos, the troubleshooting chart (Table 4.9) provides a useful guide for problem solving.

The *water quench cast film process* (Fig. 4.34) is similar in concept to the chill roll process and uses similar downstream equipment. A water bath takes the place of the chill roll for film cooling, and by cooling both sides of the film equally, it produces a

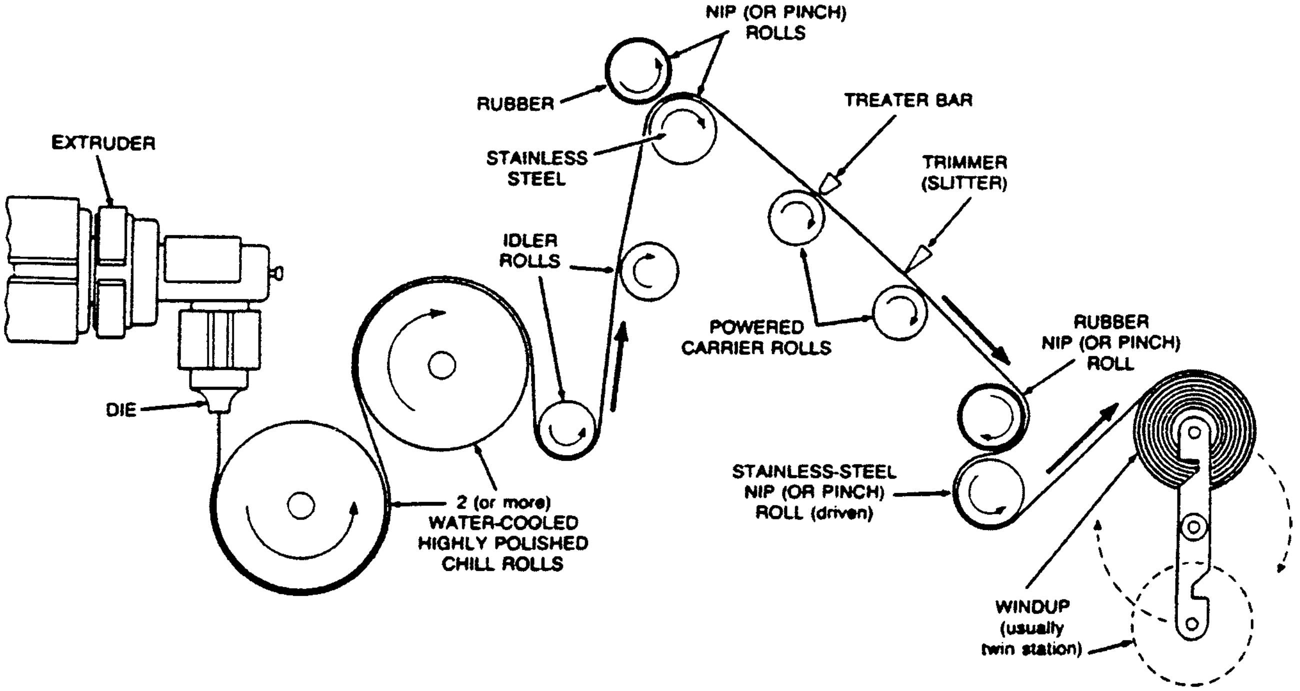


Figure 4.33. Typical line for chill roll cast film.

Table 4.9. Chill Roll Troubleshooting Chart

Problem	Possible Cause	Suggested Remedy
Poor Clarity	Cooling rate too low	Increase melt temperature Reposition air knife Increase air knife pressure Reduce chill roll temperature
Variable Optical Properties	Temperature gradient across the chill roll	Adjust chill roll coolant supply Check chill roll cooling circuits
Pleateout	Poor chill roll contact	Increase chill roll wrap-around Adjust air knife
Flow Defects	Melt temperature too low	Increase die and adapter temperatures
Brittle and Fibrous Heat Seals	Melt temperature too high	Decrease die and adapter temperatures

Source: Ebnesajjad, S., *Fluoroplastics, Vol.2*, William Andrew Publishing, 2003, p. 200.

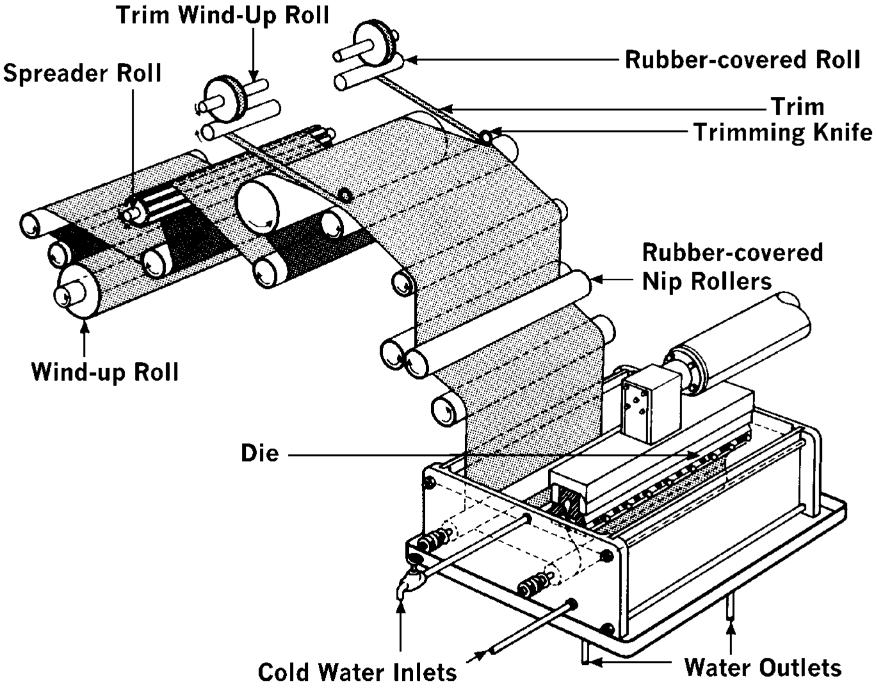


Figure 4.34. Typical water quench film line.

film with slightly different properties compared to chill roll cast film. The extruder's slit die is arranged vertically and extrudes a melt web directly into the water bath at close range. The film passes under a pair of idler rollers in the bath and, for any given rate of extrusion, it is the rate of downstream haul-off that regulates film draw-down and finished thickness.

The speed of the process is limited by the tendency of the film to carry over water from the quench bath. Surface defects can also arise from rippling in the water bath. The very rapid quenching induced by the water bath reduces crystallinity and produces a tough film.

4.3.3.1.2 Blown Film Extrusion

The blown film process involves extruding a relatively thick tube, which is then expanded or blown by internal air pressure to produce a relatively thin film. The air-cooled blown film process is in very widespread use mainly for polyolefin films. The process needs a melt strength greater than that required by cast film processes; so lower melt temperatures are used.

The die should be designed for constant output rates and thickness at every point around the annular die gap. This requires streamlined internal melt flow paths and precise multipoint means of centering the mandrel within the die ring. The die gap is typically about 0.4 mm (0.015 in.), with a short land length and a die entry angle of about 10°. Close thickness tolerances are difficult to achieve with the blown film process; variations around the bubble can belimited to perhaps $\pm 10\%$ of the target film thickness. To distribute these variations evenly, blown film lines may include rotating or oscillating motions applied either to the die, the extruder, or the haul-off.

As it emerges from the die, the tube passes through an air ring that lays a large volume of low velocity cooling air over the external surface. At the same time, the tube is pressurized internally by air supplied through the die mandrel. The air is confined by downstream nip rollers, so it inflates the still soft tube to form an enlarged bubble. The amount that the bubble is extended is called the *blow-up ratio* (BUR) and is typically in the range 2:1 to 4:1. The distance that the tube travels upward before its diameter increases is called the *stalk height*. Most materials are blown with a short stalk, with the bubble diameter being increased to the final size shortly after leaving the die lips [56]. The line speed is effectively limited by the bubble length available for cooling. Downstream equipment includes bubble calibration, a collapsing frame, and haul-off, tensioning, and reeling stations. Film thickness and process control is a balance between cooling rate, bubble length, blowup ratio, and film tension.

After the bubble is cooled and collapsed into a flat shape, the product (*layflat*) is rolled up on a high-speed winder. In some cases the layflat is slit to form two separate sheets and wound onto individual rolls, requiring two independent winding shafts (Fig. 4.35).

The *water-quench blown-film* process is also known as the tubular water quench process, and uses a tube die that is arranged to extrude vertically downwards (Fig. 4.36). The bubble size is limited and calibrated by an annular water cooling weir that covers the outer bubble surface with a stream of cooling water. The water contact is directed and controlled by an annular flexible skirt [55]. The rapid bubble cooling induced by the water

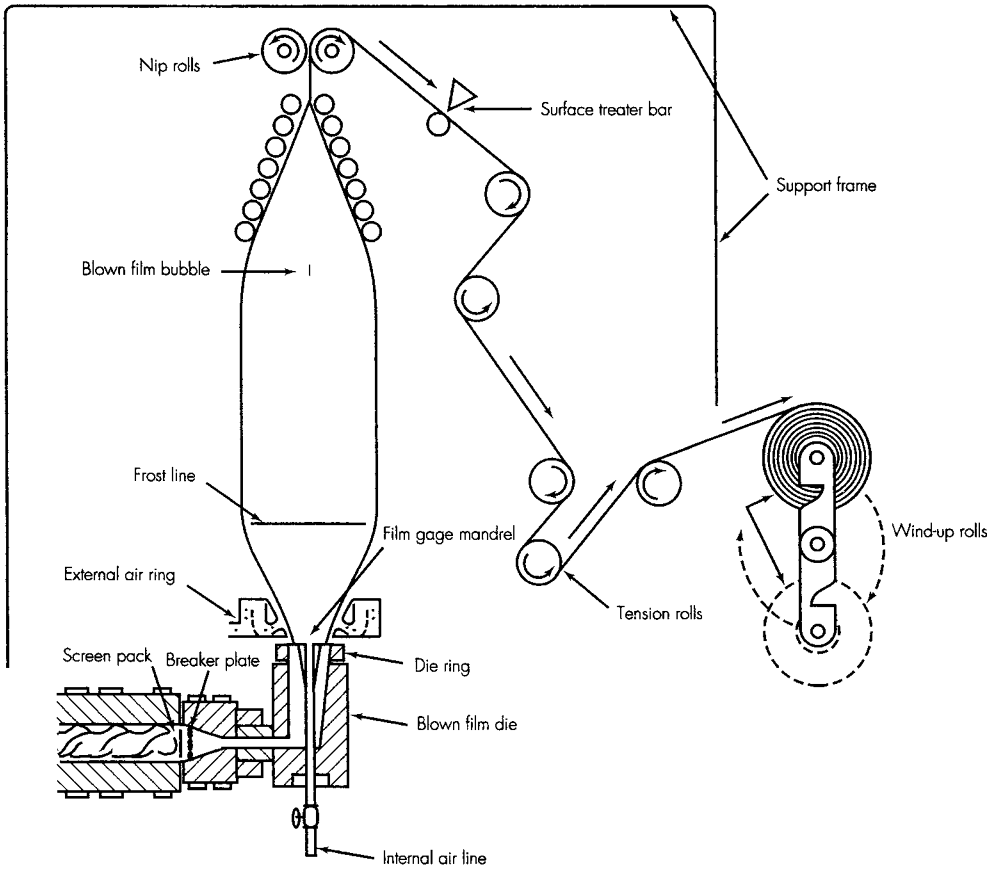


Figure 4.35. Air-cooled blown film process.

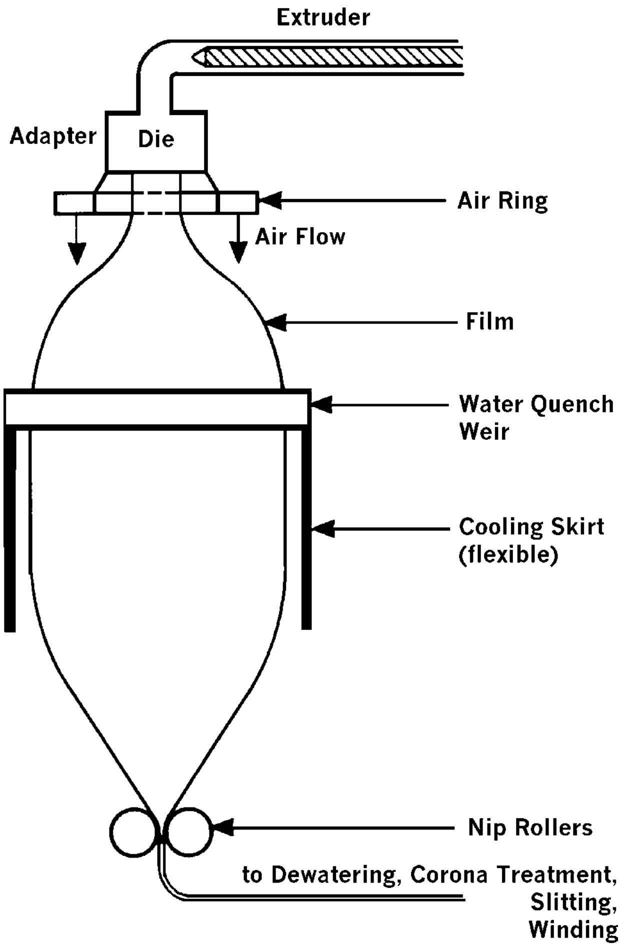


Figure 4.36. Water-quench process for blown film.

stream limits crystallinity and produces a clearer film than is possible by the air-cooled blown process.

After cooling, the film passes through a collapsing frame and proceeds through de-watering, haul-off, and winding stations.

4.3.3.1.3 Sheet Extrusion

A *sheet* is usually defined as thicker than 0.25 mm (0.01 in.); anything thinner is classified as *film*. Many thermoplastic sheets are extruded up to 30 mm (1.18 in.) thick and in widths up to 2,500 mm (100 in.). The sheet material can be thermoformed, or fabricated by blanking, punching, machining, and welding.

Extruded sheet is produced with a die having a wide slit-like outlet. The internal flow geometry is designed to transform the cylindrical melt flow received from the extruder to this slit form, while at the same time ensuring that the melt flow velocity at the slit exit is constant at all points across the slit width. This is difficult to achieve, particularly in wide sheet dies, and a number of solutions have been devised to deal with the problem. The usual approach is known as the *coat hanger* die, so called because the internal flow passage tapers from the die center to the edges (Fig. 4.37) [57]. By offering a greater resistance to flow in the die center, this tends to equalize flow rates across the die. Most sheet dies include two other regulating devices. An internal adjustable dam known as a *restrictor bar* or *choker bar* is positioned in the flow path of the die exit and acts as a coarse regulator. Fine regulation is achieved by adjustment of the *die lips* at the die exit slot. The gap is formed by two flat metal plates and is called the *land area*. The upper die lip includes a thin section that can be flexed elastically by the action of manual or automatic adjuster bolts, so that the die exit gap can be varied across the die width [58]. The die gap should be set in the range of 0–10% greater than the desired sheet thickness.

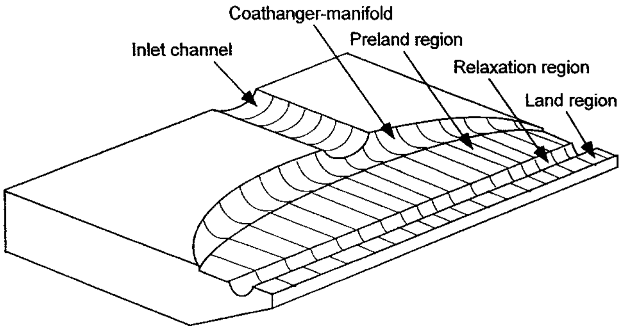


Figure 4.37. Coathanger die (Courtesy Hanser Publishers).

From the die, the sheet passes immediately to a cooling and finishing device in the form of a roll cooling stack. The usual configuration is a three-roll vertical stack with the sheet entering at the nip between the upper two rolls. Variations include up-stack working where the sheet enters between the lower two rolls, a horizontal roll stack used with a vertical die for low viscosity melts, and a two-roll stack for thinner sheet gauges. The function of the stack is to cool and polish the sheet. Alternatively, an embossed roll may be used to impart a texture to the sheet surface. Close temperature control of the rolls is critical; the temperature variation across the roll should be no more than 1.5°C (2.7°F) Roll temperatures depend on sheet thickness and production rate, and on whether a gloss surface is required. If so, the appropriate sheet surface must be maintained at least at 110°C (230°F) until it contacts the polishing roll. Table 4.10 summarizes the effect of die and roll variables on sheet characteristics.

Table 4.10. Influence of Die and Roll Stack Variables on Sheet Characteristics

Variable	Orientation	Transparency	Gloss	Stiffness	Impact Resistance
Die Gap	>	—	—	—	—
Melt Temperature	<	—	>	—	—
Roll Temperatures	—	<	>	>	<
Roll Speeds	>	<	>	>	<

Source: Reference [55].

4.3.3.2 Coextrusion

Coextrusion is the process of forming an extrudate composed of more than one thermoplastic melt stream. The process came about because some service demands, particularly from the packaging industry, could not be satisfied by a single polymer although they could be met by a combination of polymers. Coextrusion was first practiced in the production of cast film and is now also used in blown film and sheet extrusion. The intention is normally to produce a laminar structure in which each layer contributes a key property to the overall product performance. Coextruded films may be very complex structures composed of many different functional layers, including tie layers whose purpose is to bond neighboring layers of limited compatibility. Five layers are not uncommon. However, side-by-side coextrusion is also possible.

Separate extruders are required for each distinct material in the coextrusion. The process has two variations, depending on the point at which the separate melt streams are brought together. In feed block coextrusion, the streams are merged into a single laminar melt flow in a feedblock (Fig. 4.38) which is positioned immediately upstream of the extrusion die. The process depends on the high viscosity of plastics melts to prevent intermingling of the layers as they pass through the extrusion die. The flow rate of each component layer can be controlled by valves in the feedblock and the capital cost is relatively low. The alternative, die coextrusion, uses a complex die construction in which separate melt path manifolds are arranged to merge at a point close to the die exit (Fig. 4.39). The thickness and flow rate of individual layers can be independently controlled, and it is also possible to handle polymers with substantially differing viscosities and melt temperatures. The capital and maintenance costs of such multi-manifold coextrusion dies are high.

Coextrusion of blown film is accomplished by multi-manifold dies. The distribution of melt along the circumference of these dies is accomplished by a spiral mandrel [57]. An example of a die for the coextrusion of a three-layer film is in Fig. 4.40 and an arrangement for the coextrusion of a nine-layer blown film is in Fig. 4.41.

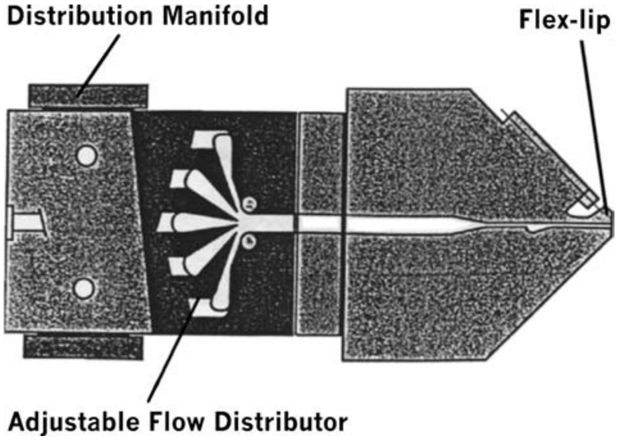


Figure 4.38. Schematic of coextrusion feedblock.

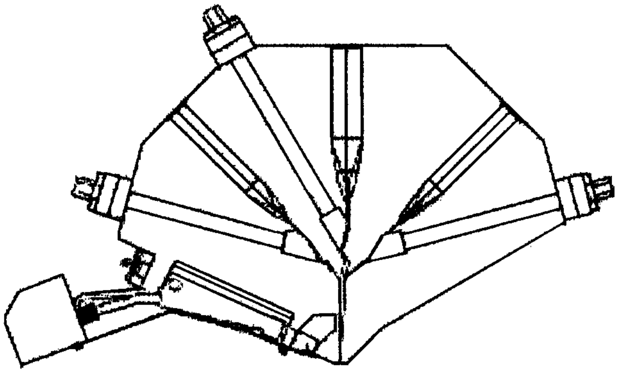


Figure 4.39. Three-layer multi-manifold coextrusion die.

4.3.3.3 Wire Coating

The process of coating wire and cable by extrusion has been around for quite some time. Molten

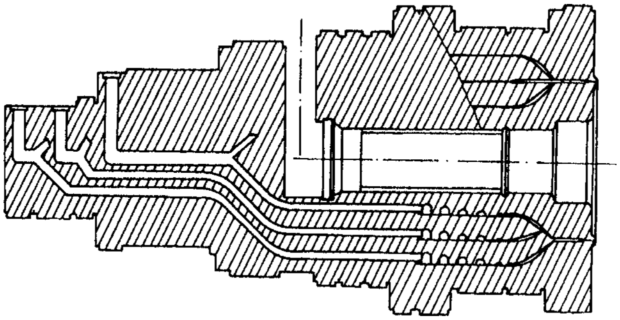


Figure 4.40. Three-layer coextrusion die for blown film (Courtesy Hanser Publishers).

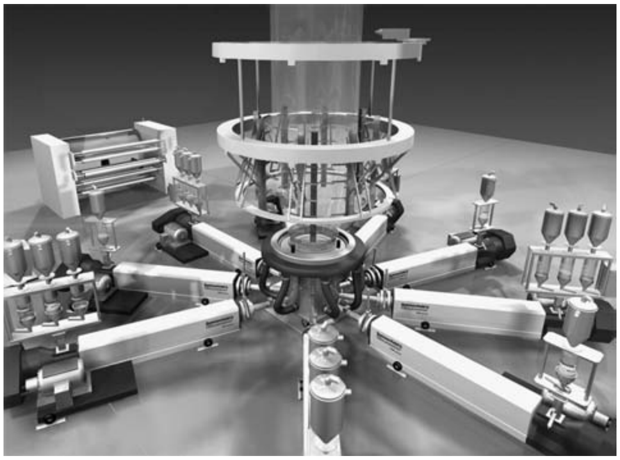


Figure 4.41. Equipment for coextrusion of nine-layer blown film (Courtesy Battenfeld Gloucester Engineering Company).

plastic is extruded into a crosshead die through which the wire being coated is passed. After leaving the die, the coated wire is cooled in air and/or water bath while it is continuously tested for spark and *concentricity* (roundness of the coating). In this process, *primary insulation* is defined as a metal wire directly coated with a plastic to isolate the metal electrically. *Jacketing* (or *sheathing*) is referred to covering one wire or a group of wire with a plastic coating or jacket for nonelectrical protection. Jackets are usually put on primary wires.

Typical wire coating line has several pieces of equipment as summarized in Table 4.11. A standard thermoplastic extruder design, built using special materials of construction, with a length to diameter (*L*/*D*) ratio of 20:1 to 30:1 can be used to extrude most TPEs. High *L*/*D* machines are required to obtain sufficient contact surface area for heat transfer to melt the resin. Lower *L*/*D* results in a lower output, and barrel temperatures would have to be raised, which can lead to an increase in the polymer degradation. Table 4.12 shows the relationship between diameter, output, and motor size for different extruders. Restriction of flow imposed by the sizing die usually reduces the extruder capacity.

Table 4.11. Wire Insulation Line Equipment and Components

Equipment/Component	Function
Hopper (feed of material)	Dry and feed resin to the extruder
Unwind	Feed uncoated wire to the cross-head die
Tension control device	Regulates tension in the feed wire
Preheater	Heats up the uncoated wire
Extruder	Melts, heats up the resin, and feeds the cross-head die
Cross-head die	Redirects the molten resin 90° to coat the wire
Cooling trough	Quenches the coated wire
Capstan	Drives the wire to the line speed
Spark tester	Detects faults in the coated wire
Take-up	Winds up the coated wire

Source: Reference [55].

Moisture should be avoided during the extrusion because it can form bubbles in the insulation, which can form points of dielectric breakdown failure. Most TPEs are hydrophobic but can pick moisture due to condensation (pigments in color concentrates can be hygroscopic). The best way to dry the resin is to blow warm air into the feed hopper in a concurrent manner to the flow of the pellets. Blowing air at a temperature in the range of 120–160°C (248–320°F) for 1–2 hr at a velocity of <1 cm/s is sufficient for drying the resin [11]. It is also possible to dry the resin in an oven prior to charging it to the hopper. More details on drying are found in sections on the processing of individual TPEs.

Polymer melt travels from the extruder to the head through an adapter. The internal design of the adapter should be streamlined to allow smooth flow. Conical reductions should, thus, be made at

Table 4.12. Relationship Between Extruder Output and Motor Size

Extruder Diameter	Output (kg/hr)	Motor Size (kW)
30	15	3.7–7.5
50	45	11.1–18.6
65	75	26.1–37.3

Source: Reference [55].

a maximum angle of 30°. The adapter should be equipped with a heater band to prevent cooling of the melt and also alleviate the need for overheating the melt in the extruder. Melt viscosity is a strong function of the melt temperature. Extrusion rate (the volume of the resin extruded per unit time) varies with viscosity so any variation in melt viscosity will be reflected in the extrusion rate. It is important to preheat the adapter by using the heater band to prevent solidification of the initial melt on its interior surface, which can result in excessive pressure buildup.

A crosshead die is the transition piece that usually alters the direction of the melt flow by 90° to coat the wire. Design of the crosshead should be streamlined with minimum melt residence time. Figures 4.42 and 4.43 show two designs of crosshead dies. In one design (Fig. 4.42), the die is manually adjusted for concentricity while in the other design the die is fixed and concentricity adjusts automatically. The most common type of die for thermoplastic extrusion is a tube die (Fig. 4.44a) that extrudes a thin wall tube around the wire. The tube is drawn by vacuum onto the wire after it leaves the die. The vacuum is pulled through the clearance between the conductor and its passageway through the crosshead. Another type is pressure die in which the melt comes in contact with the wire prior to leaving the die while the melt is under pressure (Fig. 4.44b).

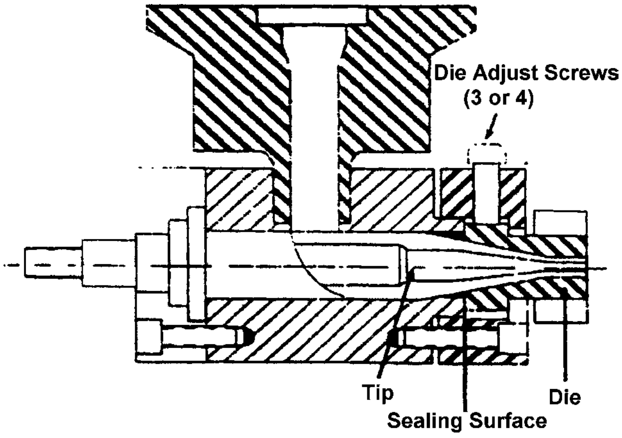


Figure 4.42. A conventional cross-head design.

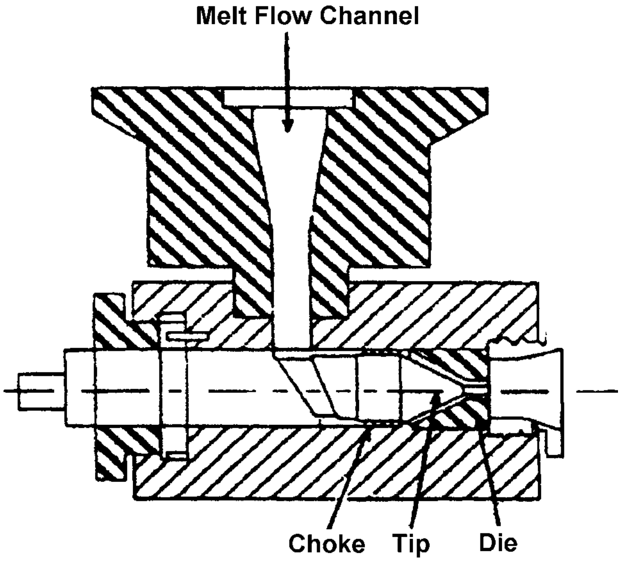


Figure 4.43. A self-centered die cross-head design.

4.3.3.4 Extrusion of Pipe and Tubing

Dies for pipe and tubing production consist essentially of a female die ring that shapes the pipe outside diameter, and a male mandrel that shapes the inside diameter. The difficulty is to support the mandrel in rigid and accurate alignment with the die ring without compromising the product. The spider type (Fig. 4.45) uses three or four spider legs (ribs) to support the mandrel but these legs cause axial weld lines as the melt flows around them [55]. An alternative is the breaker plate design in which the mandrel is supported by a disc pierced by a multitude of small holes. A better solution, particularly for larger pipe dies is the spiral mandrel. Here the mandrel is rigidly supported and the melt flow is directed around it in an initially helical pattern, which is converted to axial flow by the geometry of the flow channels and lands. Weld lines are eliminated but the difficulty is to ensure an even flow rate at all points of the die outlet [55].

As the melt exits the die, it swells slightly. Therefore it requires a size adjustment namely *calibration*. The outside diameter of a pipe or tube may

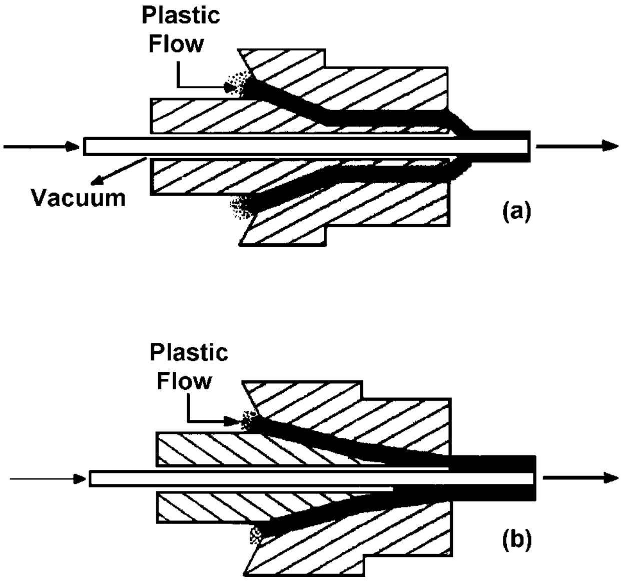


Figure 4.44. Schematic diagrams of (a) tube and (b) pressure die.

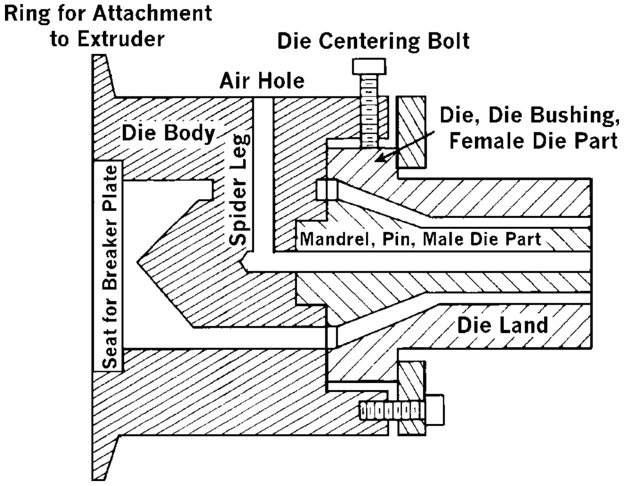


Figure 4.45. Typical spider-type tube die for pipe and tube extrusion.

be calibrated either by an internal air pressure of 1.3–2.0 bar (19–29 psi), or by external calibration in a vacuum sizing tank (Fig. 4.46) operating at a pressure of 0.3–0.5 bar (4.5–7 psi). For calibration by internal pressure, the diameter of the die ring is made approximately equal to the internal diameter of the finished pipe. For vacuum tank calibration, the die ring is made up to 25% larger and the haul-off is set for a wall thickness draw-down of up to 30%. Below is a more detailed description of the pipe and tube sizing methods.

Thermoplastics tube and pipe size is set by one of four techniques: the vacuum trough, the extended (internal) mandrel, the sizing sleeve, and the sizing plates (Fig. 4.47). Vacuum trough and extended mandrel are the more common techniques for holding the size of the tubes and pipes in a quench bath. These two methods are described in detail below. In the sizing sleeve method, the outside diameter of the tube is fixed as it comes in contact with a water-cooled metal sleeve (usually brass). This contact takes place by air pressure inside the tube or by drawing a vacuum through the perforated internal surface of the sleeve. The sizing-plate method predates the vacuum trough technique. In this method, the tube takes its size as it is pulled through a series of brass or stainless steel plates, similar to the way that metal wire is drawn from a metal rod. The tube is forced through the plates by a positive internal air pressure.

In the *vacuum trough method* illustrated in Fig. 4.47a, the tube (or pipe) enters into one end of a closed long trough and is extruded out of the other end. The trough is filled with water, which directly contacts and surrounds the tube, providing efficient cooling. Inside the trough, vacuum is drawn over the water, reducing the pressure in the trough, thus allowing the soft tube to expand against the collars or rings at the entrance and exit. This mechanism prevents tube collapse and ensures well-rounded sizing of the outside of the tube. The pressure difference between the outside (under vacuum) and the inside of the tube that is open to the atmosphere generates the expansion force. The tube moves through fixed metal collars or rings, which give it its size. The first collar at the trough entrance is the most important one. A small stream of water is directed at the pipe just before entrance as a lubricant. The number and positions of the rings and sleeves are usually adjustable. They become slightly smaller as the pipe passes through the trough, taking into account shrinkage that results from cooling and crystallization of the polymer.

The vacuum trough method provides excellent cooling with little frictional drag acting against the tube. There are no theoretical limitations to the production rate. The trough has to be longer for higher output rates, which has a bearing on the available space. Large pipes (>100 mm or 4 in. outside diameter) are hard to keep submerged under the water without distorting them or marring their surface. On these occasions, the trough is not filled, but water is sprayed and cascaded all around the pipe

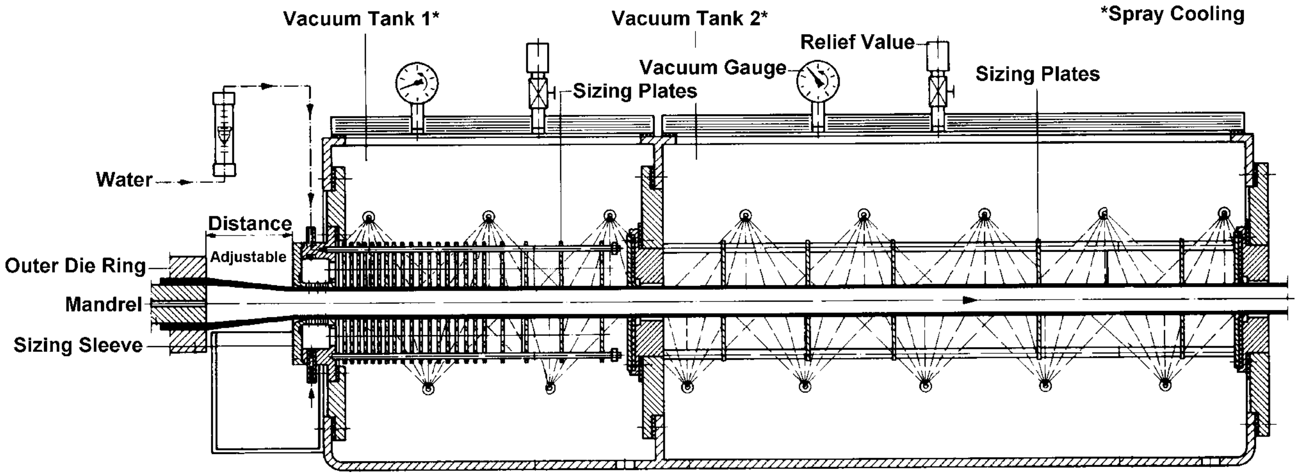


Figure 4.46. Vacuum sizing tank used for pipe and tube extrusion.

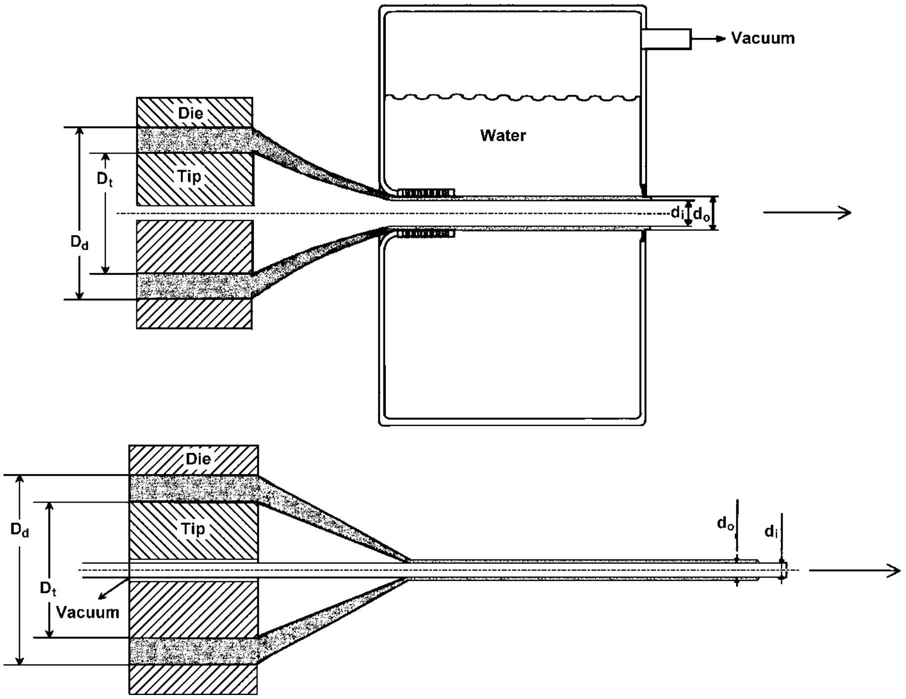


Figure 4.47. Methods for pipe and tube sizing: (a) vacuum trough (top), (b) extended mandrel method (bottom).

while it is passing through. The entire inside space of the trough is maintained under vacuum. Smaller pipes and tubing (OD 0.5 in. or 12.5 mm) are usually sized without the use of vacuum [56].

The *extended mandrel technique*, illustrated in Fig. 4.47b, provides internal cooling and support to the tube. The shrinkage of the plastic as a result of cooling causes a tight contact between the tube and the metal mandrel that can extend up to 30 cm (12 in.) beyond the die. Longer mandrels have been difficult to use due to mechanical difficulties [55]. The mandrel is tapered with the larger end closer to the die. The diameter difference between the large and small ends is a function of the polymer type in addition to the variables related to the tube type and size. The end of the mandrel is slightly larger than the final pipe size to allow additional shrinkage. There is a passage for cooling water inside the mandrel. To ensure a constant temperature, the passage must be uniform. Water cascades accomplish additional cooling over the tube. A small split ring is placed around the tube just as it leaves the die to prevent oscillation of the water, which could otherwise cause water marking. Water cascades further cool the tube after it leaves the mandrel. It finally enters a water trough equipped with sizing plates.

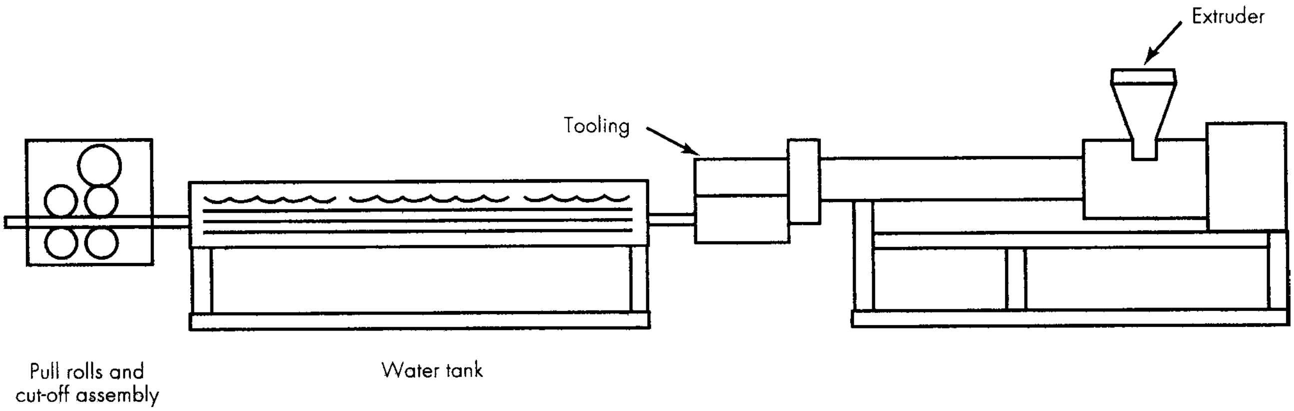


Figure 4.48. Schematic drawing of a profile extrusion line.

Pipe and tubing can also be made by extrusion through a crosshead die, similar to that used for wire and cable coating, described in Section 4.3.3.3 [56].

4.3.3.5 Extrusion of Profiles

Profile shapes, from simple tubing or rods to complex custom shapes can be readily produced by extrusion. Methods of cooling and shaping of the final products vary with the type of profile. It may be a simple water trough to a complex vacuum sizing equipment that holds the outer surface fixed during the melt solidification. The melt temperatures for profile extrusion are lower than those for the extrusion of films and sheets, where lower melt viscosities aid in forming the product [56]. A schematic of a simple profile extrusion line is in Fig. 4.48.

4.3.3.6 Extrusion Coating

The extrusion of melt through a flat sheet die also can be used to produce a thin film coating on paper, fabric, foils, or other substrates. The substrate to be coated is unwound off a feeder roll and passed through the first nip of the roll stack (Fig. 4.49). Sometimes the substrate is treated prior to coating for enhanced adhesion [56].

4.3.4 Process Control in Extrusion

It is important to equip the extrusion line with sufficient instrumentation to produce a high quality product. Process variables that are routinely controlled and/or monitored are various temperatures, melt pressure inside the extruder, and motor drive speed. Table 4.13 contains a list of process variables, the location of each variable, the impact of each variable, and the methods of its control.

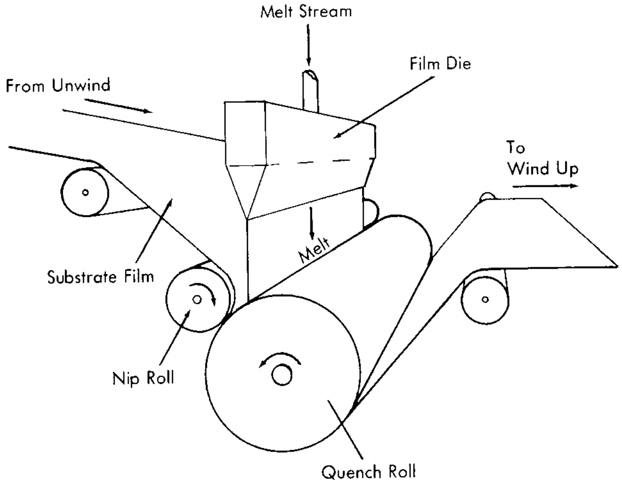


Figure 4.49. Schematic of the extrusion coating process.

Temperature control is critical because of the sensitivity of viscosity to temperature. Thermowells (encasements to place a thermocouple) can be built into the barrel wall to measure the temperature. Melt temperature should be measured directly to avoid dependence on the barrel temperature, which could significantly differ from the melt. A thermocouple is placed in the barrel in a manner that its tip is immersed in the melt, extending to the middle of the flow channel. Temperature controllers should be equipped with limit switches or other mechanisms to detect the failure of thermocouples, the heater, or the controller itself. An ammeter can detect a full-on failure that could lead to degradation of the resin. In cases where more than one band heater is controlled by a controller, all units should have the same power flux.

Pressure measurement is both important to the quality of the product and safety of the

Table 4.13. Extrusion Process Control Variables

Variable	Location	Impact	Control Method
Temperature	Extruder barrel; 3–4 zones Heater bands	Melt viscosity Resin degradation	PID[a] control of the barrel zones On–off control is less desirable
Pressure	Inside the barrel	Consistent flow requires consistent pressure	Melt temperature Screw speed Breaker plate A rupture disk relieves overpressure
Motor Drive	Extruder Take-up capstan	Extruder output Line tension	Solid state controllers Electronic controllers

Note:
[a] PID is abbreviation for *Proportional-Integral-Differential c*ontroller.
Source: Reference [55].

extrusion process. The most preferred sensor is a pressure transducer. High backpressure can damage the equipment, particularly when screenpacks or high-pressure drops are present. Similar to the melt thermocouple, pressure transducers should also be constructed from corrosion-resistant materials.

A variety of AC and DC drives are available for extruders. Direct-current motors with solid-state controllers and power supplies provide the most flexible scenario for control. A speed control feedback loop on the drive will minimize variation in the extruder output.

4.4 Injection Molding

A significant portion of TPE consumption is processed by means of injection molding. The process produces a complex finished part in a single rapid and automatic operation. This distinguishes plastics injection molding from most other manufacturing processes, although there are parallels with metal casting, particularly with die-casting. Generally speaking, a whole series of forming, joining, and finishing operations would be needed to replicate an injection molded article in other materials using different manufacturing methods. It is the single operation that makes injection molding economically viable despite the high cost of machinery and molds. Injection molding machines and molds are very costly because of the high pressures required when injecting most TPE melts (thermoplastics, in general) and the complexity of the process controls. The ability to produce a completely finished part at high speed balances the equation with high machine and mold costs and makes injection-molded articles highly cost effective.

4.4.1 General Considerations

As mentioned earlier, several factors affect any type of the processing of thermoplastics including injection molding. They include viscosity, heat, temperature, thermal stability, thermal conductivity, crystallinity, and moisture.

Viscosity is a measure of flow of a plastic, that is, how fast a given mass of the plastic will flow as a result of applying a force to it. Flow of plastics is inversely proportional to viscosity. Viscosity decreases with an increase in temperature. Lower viscosity is helpful to injection molding in that it reduces the flow time of the plastic, resulting in higher production rates and good geometric definition. Temperature must be increased beyond the melting point of the material to allow flow of the plastic. Above the melting point, viscosity reduction should be balanced against thermal degradation of the plastic. In practice, viscosity is replaced by the melt flow rate of the polymer, which is measured under standard conditions. The lower the melt flow rate, the higher the viscosity of the polymer.

Heat has to be delivered to the plastic to increase its temperature and melt it. The molding equipment should be able to deliver sufficient heat to melt the polymer being processed. *Thermal conductivity*, the speed by which heat is transferred through a material, of the plastic is usually the controlling step for the delivery of heat to the material.

Crystallinity is an important consideration in injection molding because of the impact of a part's crystalline content on its properties and appearance.

Most polymers are semi-crystalline, meaning that there is a relatively large volume increase as the polymer melts and becomes entirely amorphous. After a part has been molded, the rate at which it is cooled (the speed of cooling the part) will determine the extent of its recrystallization. For example, flex fatigue life and transparency increase when crystallinity decreases. Mechanical strength and various moduli increase with higher crystallinity.

Finally, the polymer should be free of moisture before molding begins; it should be dried before charging the machine. Moisture evaporates during the melting process and forms defects in the part. It appears as bubbles if it is trapped or as voids if it escapes from the part. Both types of defects are unacceptable quality problems.

4.4.2 Basic Technology

Injection molding is one of the most important processes for mass-production of objects from thermoplastics, usually without additional finishing being required. Today, most injection molding machines are the universal types, which can accept all types of molds, within limits. The economics of this process is excellent for articles with complex geometry, giving this process an advantage over other techniques. Cost per molding improves with scale, despite the sizable initial cost of injection molding machines.

The principle of injection molding is very simple. The plastic material is heated until it becomes a viscous melt. It is then forced into a closed mold that defines the shape of the article to be produced. There the material is cooled until it reverts to a solid, then the mold is opened and the finished part is extracted. Although the principle may be simple, the practice of injection molding is anything but simple. This is a consequence of the complex behavior of plastics melts and the ability of the process to encompass complicated products. The essential mechanisms of injection molding are heat transfer and pressure flow. The essential equipment is an injection molding machine, sometimes known as a *press*, and a mold which may also be referred to as a *tool* or sometimes a *die*. The product of the process is a *molded part* or *molding*, which confusingly and inaccurately is sometimes called a mold.

Injection molding is a process in which a thermoplastic polymer is heated above its melting point, resulting in the conversion of the solid polymer to a molten fluid with a reasonably low viscosity. This melt is mechanically forced, that is, *injected*, into a mold in the shape of the desired final object. The low viscosity of the molten polymer allows complete filling of the mold where the article resides until it is cooled below the freezing point of the polymer. In the case of semi-crystalline polymers, the crystallinity of the object (which governs its mechanical and appearance properties) is usually controlled by in-mold cooling of the object at a defined cooling rate. In the last step, the mold is opened and the part is ejected and recovered.

4.4.3 The Process

An injection molding machine (Fig. 4.50) can be divided into six components: plastification/injection section, clamping unit, mold including the runner system, control system, and tempering devices for the mold [59]. The most important part of the process is the mold, which is made of at least two parts to allow ejection (demolding) of the molded part. The injection molding process can be divided into six steps. Table 4.14 presents the main function of each step.

4.4.4 Injection Molding Machinery

There are many varieties of injection molding machines, but they all perform the same essential functions. They include melting or plastificating the plastic, injecting it into the mold, holding the mold closed, and cooling the injected material. It is convenient to think of an injection molding machine as consisting of two units. The plasticating and injection requirements are combined in the *injection unit* while the mold handling is performed by the *clamp unit*. The two units are mounted on a common machine base and are integrated by power and control systems. The convention is that the injection unit shall be on the right of the operator, with the clamp unit on the left (Fig. 4.50).

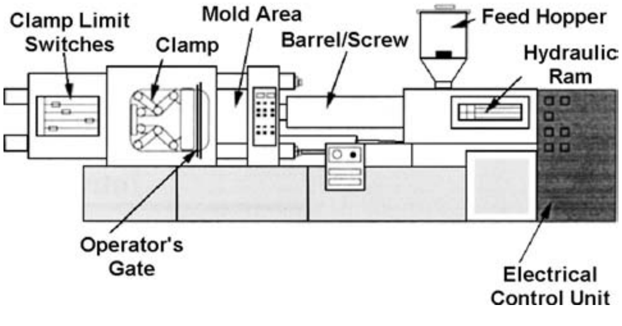


Figure 4.50. Typical injection molding machine.

Table 4.14. Processing Steps in Injection Molding

Step	Function
Beginning of Plastification	Screw transports the melt to the reservoir where it is heated
End of Plastification	The screw is switched off after the reservoir is filled
Closing the Mold	Clamping unit actuates closure of the mold
Beginning of Injection	Forward axial motion of the screw starts the flow of the melt into the mold until it is filled
Mold Cooling and End of Injection	The mold begins to cool and additional melt is injected to compensate for the part shrinkage
Ejection of the Molded Part	The part is ejected and the screw retracts for a new cycle

Source: Ebnesajjad, S., *Fluoroplastics, Vol.2*, William Andrew Publishing, 2003, p. 162.

4.4.4.1 Clamp Unit

The function of the clamp unit is to open and close the mold halves and particularly to hold the mold closed during injection of the plastic melts. High injection pressures are necessary, due to the high viscosity of plastic melts, so the force needed to hold the mold closed is very great. The melt pressure inside the mold is exerted over the entire area of cavities and feed systems at the mold parting line. The significant figure is the extent of this area when projected on to a plane perpendicular to the opening axis of the clamp system. This is known as the *projected area* of the mold. The clamp force needed to hold the mold shut during injection is a function of the injection pressure and the projected area, but this is not a simple function. The injection pressure varies throughout the cavities and feed systems and is also a complex function of process parameters such as melt and mold temperature, and injection rate. The cavity pressure is also a function of part thickness, which is completely independent of the projected area, so attempts to determine clamp force on the basis of the projected area by itself are going to be inaccurate. This means that the old rule-of-thumb method of allotting *x* units of clamp force per unit of projected area should be seen as a last resort. It is one that is likely to lead to under utilization of machines due to the need for a large safety factor to cover the deficiencies of the method. The rule-of-thumb clamp figure for fluoropolymer is 0.79 tons/cm^2 of projected area should be sufficient for all polymers in this group.

The force requirements ensure that the clamp unit must be engineered very robustly, but this conflicts with the need to open and close the mold rapidly to minimize production time. A variety of clamp mechanisms has evolved in the search for a suitable compromise. The two most common types are the direct hydraulic clamp (Fig. 4.51) and the toggle clamp (Fig. 4.52). Other variants include hybrid toggle/hydraulic types, lock-and-block systems, and electromechanical systems.

Whatever the variation, the clamp unit always features a stationary or fixed platen and a moving platen on which the mold halves are bolted or otherwise attached. The fixed platen is mounted rigidly on the machine base and is positioned adjacent to the nozzle of the injection unit. The injection half of the mold is attached to the fixed platen while the moving platen carries the ejection half of the mold.

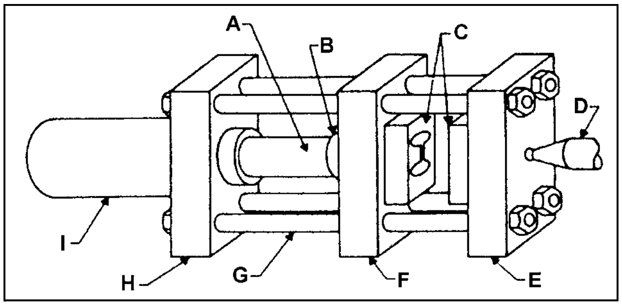


Figure 4.51. Typical direct hydraulic clamp unit: A—Actuating plunger; B—Removable spacer; C—Mold; D—Injection nozzle; E—Fixed platen; F—Movable platen; G—Tie bar; H—Cylinder base Plate; I—Clamping cylinder.

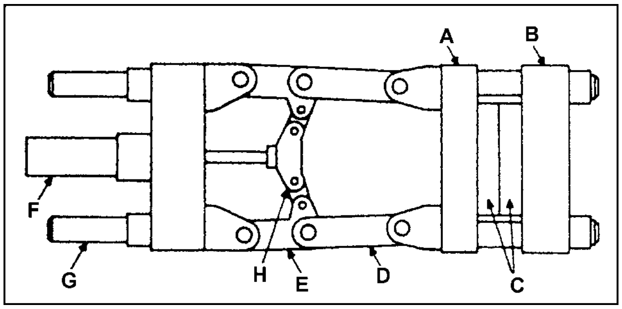


Figure 4.52. Typical toggle clamp unit: A—Movable platen; B—Fixed platen; C—Mold; D—Front link; E—Rear link; F—Actuating cylinder; G—Tie bar; H—Crosshead link.

These terms may, in the case of some sophisticated molds, cease to be literally true, and the expressions *fixed* and *moving* mold halves are often used instead.

The clamp also includes a tailstock platen or equivalent unit that the pressure means reacts against in order to clamp the mold halves together between the moving and fixed platens. For this purpose, the fixed and tailstock platens are united by tiebars (tie rods) that also serve as guides for the moving platen. The tiebars are stretched elastically when the clamp unit locks the mold shut under pressure. Since the tiebars limit access to the mold area and impede mold changing, tiebarless machines have been intensively developed in recent years. The tiebarless machine uses the same clamp concepts but employs a greatly strengthened machine base to tie the fixed and tailstock platens together. The result is a completely unencumbered mold area with free access for automation, ancillaries, and mold changing operations. Under clamp pressure, the machine frame and platens flex elastically. Tiebarless machines use a variety of means to counteract this tendency and keep the platens parallel. However, the effect limits the clamp force that can be designed into tiebarless machines although the figure is gradually being pushed upward.

Another development, particularly in large injection molding machines, is a move towards two-platen clamp systems. These systems do away with the tailstock platen and use a variety of mechanisms to lock the tiebars to the moving platen in the closed position. The advantage of a two-platen clamp is a considerable saving of up to 35% in floor space.

Clamp units are rated according to the maximum closing force they can apply to the mold. The figure may be expressed as kiloNewtons (kN), metric tonnes (tonne), or U.S. tons (ton) [60].

4.4.4.2 Injection Unit

The function of the injection unit is to heat the plastics material to a uniform and homogeneous melt and to inject it into the mold under controlled conditions of pressure and flow rate. Given the low thermal conductivity, high specific heat, and high melt viscosity of TPEs, these are exacting tasks. Once again, many variants have been devised to solve the difficult problems involved. The variants can be grouped roughly into four principal injection unit concepts:

- Single-stage ram or plunger
- Two-stage ram
- Single-stage screw
- Two-stage screw/ram.

The single-stage ram unit is inefficient in heating, mixing and pressure transmission and is largely obsolete although the form survives in very small machines and some specialized equipment. It has the merit of simplicity and low cost. The two-stage ram is also all but obsolete. It was an attempt to improve on the single-stage ram by separating the functions of heating and pressure flow, but the ram remains an inefficient mixer and heater. The two-stage screw/ram unit also separates the functions of heat and flow, using a screw for heating and mixing, and a ram for injection. Both are relatively efficient devices for their respective duties so the concept is attractive. However, the unit cost is higher, and it is difficult to devise an ideal melt flow path between the stages. The single-stage screw concept is by far the dominant form. A screw capable of both rotational and axial movement combines heating and mixing function with the function of injection. For this reason, the form is frequently referred to as a *reciprocating screw injection unit* (Fig. 4.53).

The extruder-like screw operates within a heated barrel and has axial zones that are concerned successively with feeding, melting, and metering the plastic material. Many different screw forms have been designed in the search for the best compromise between plasticating and throughput, particularly since CNC machining has made it possible to cut shapes that were previously impractical. The design process has been accelerated by extrusion simulation software that makes it possible to predict how a screw design will perform. Ideally, the screw should be optimized for use with a particular fluoropolymer, but this can only happen if it is known that the injection molding machine will be dedicated throughout its life to a narrow range of uses. Instead, virtually all injection molding machines are supplied with a screw that is designed as a compromise between the requirements for the majority of thermoplastics. This is known as a general-purpose screw. It is usual for a machine to be offered with additional screw options. Other options may include a vented screw, which includes a decompression zone and an associated exhaust port for the removal of water vapor or other volatile species.

Most general-purpose screws take the form of a single constant-pitch flight that decreases in depth from the input or upstream end to the output or downstream end (see Fig. 4.54). The flight pitch is

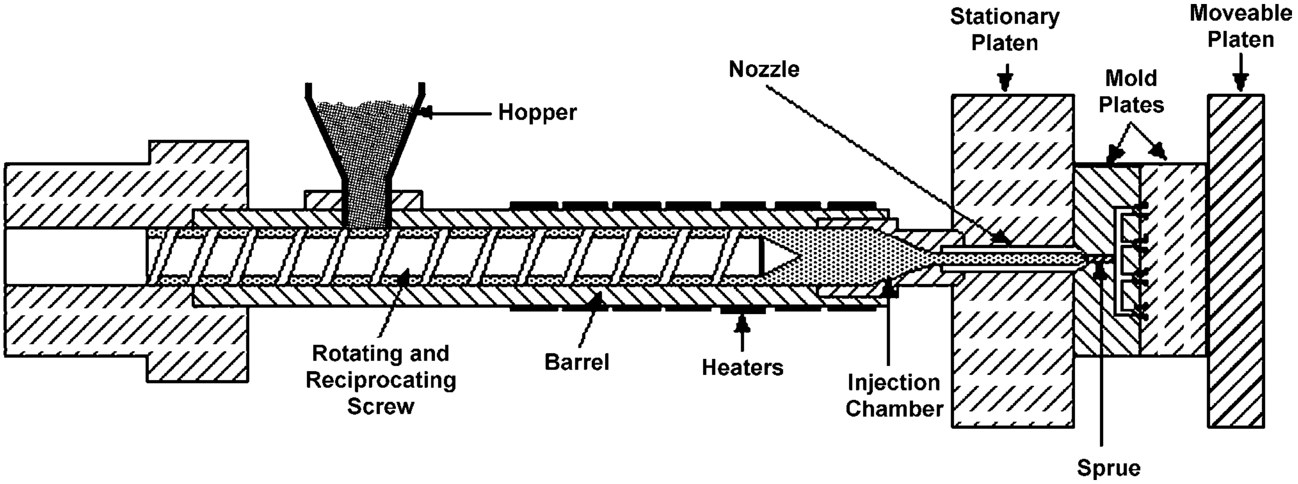


Figure 4.53. Typical reciprocating screw injection unit.

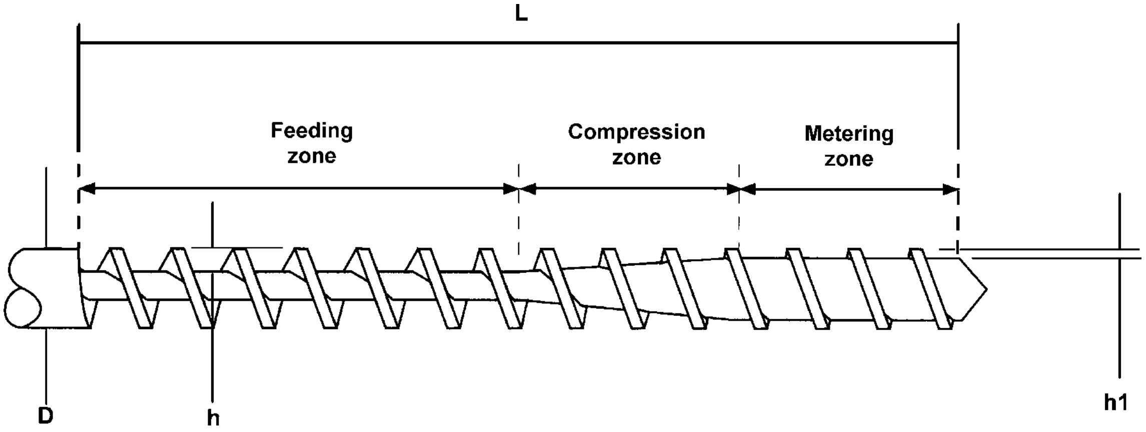


Figure 4.54. An example of a screw design for the injection molding of thermoplastics.

usually equal to the screw diameter, giving a helix angle of 17.8°. Flight depth is usually substantially constant in the feed and metering zones and decreases at a constant rate over the compression zone. The feed zone typically occupies half the screw length, with the compression and metering zones each making up a quarter of the length. The key parameters of such a screw are the ratio of length to diameter (the *L*/*D* ratio), and the compression ratio. The *L*/*D* ratio affects mixing and melts uniformity, higher values giving better results. An *L*/*D* ratio of 20:1 is regarded as a minimum for injection molding. Long screws with the *L*/*D* ratio as high as 28:1 are offered by some manufacturers. The compression ratio has a bearing on mixing and shear heating. Typical values range from 2:1 to 3:1 or greater. The real difference is between semi-crystalline and amorphous polymers. On heating to melt temperature, semi-crystalline materials undergo a greater volume increase than amorphous materials and so require a lower compression ratio.

The basic sequence of events in the injection unit is:

- The screw rotates, thereby heating and melting the material, which is conveyed along the screw flights to the downstream end of the screw. The barrel nozzle is closed by means of a thermal or a mechanical valve, or by the presence of a previous molding. The accumulating melt presses the still-rotating screw back against a controlled resistance (the back pressure) until sufficient melt has accumulated to make the next molding. At this point, screw rotation stops. This is the melt preparation phase.
- The barrel nozzle is opened and the screw performs the action of a ram by moving forward in the axial direction without rotating.

This forces (injects) the melt that has accumulated ahead of the downstream end of the screw through the nozzle and into the mold. The downstream end of the screw may be equipped with a valve arrangement to prevent melt flowing back down the screw flights. This is the mold filling or injection phase.

- After the mold is filled, screw pressure is maintained for a short period to compensate for volumetric shrinkage of the cooling melt contained in the mold. This is the packing or holding phase.
- At the conclusion of the holding phase, and while the mold remains closed for the molding to cool to ejection temperature, the injection unit cycle recommences with the resumption of screw rotation and melt preparation.

Injection units are rated in terms of the maximum injection pressure and injection volume available. Injection pressure is the theoretical maximum available at the downstream end of the screw. This is a function of the screw diameter and the force acting on it. It should not be confused, as it often is, with the hydraulic line pressure acting on the injection cylinder that supplies the force to the screw, nor should it be taken as the pressure available to fill the mold cavities. This is much less because of pressure losses in the nozzle and mold feed systems. Injection pressures are normally quoted in megapascals (MPa), atmospheric pressures (bar), or pounds per square inch (psi) [60].

The maximum injection volume or swept volume is the product of the screw diameter and its maximum retraction stroke during plasticating. The value is expressed in cubic centimeters (cm^3), cubic inches ($in.^3$), and sometimes as the weight in ounces (oz) or grams (g) of plastic material that can be injected. The weight rating is a less accurate measure and is relative to the density of the plastic material in question. The figure used to make the conversion should be the density in the melted state rather than in the solid state.

In principle, the entire theoretical shot volume is available for injection. In practice, the volume is limited by the concept of *residence time*. This is the time that an element of plastic material takes to pass through the screw and barrel system. It is a function of cycle time and injection stroke. The significance of residence time rests on the fact that a plastic material may begin to degrade if exposed too long to process temperatures normally regarded as safe. Residence time itself is independent of material, but the sensitivity of materials to residence time varies and is at its greatest with materials that are processed at a point close to the degradation temperature. It is especially unwise to expose such polymers to lengthy residence times in the injection unit. Small shots produced from big machines are likely to lead to trouble, especially if the cycle time is long.

Figure 4.55 shows residence times for a range of cycle times. Injection strokes are expressed in terms of D, the screw diameter. If, for example, we wish to limit residence time to five minutes, this means that the injection stroke should not be less than about $1D$ for a fifty-second cycle, or not less than about $0.6D$ for a thirty-second cycle. The two values equate to about 25% and 15% of maximum shot volume, respectively. The maximum injection stroke for a typical injection molding screw is about $4D$. The preferred shot volume is in the range of $1D$ to $3D$, or 25–75% of the maximum available.

Allowable residence times for TPEs depend on the material temperature. Temperature should be decreased as residence time is increased.

The European Committee of Machinery Manufacturers for the Plastics & Rubber Industries has developed a standard classification for injection molding machines. This is known as the Euromap international size classification and it consists of two numbers in the format xxx/xxx. The first number indicates the clamp force in kiloNewtons (kN). The second number is an injection unit rating derived by multiplying the maximum injection pressure (bar) by the shot volume (cm^3) and dividing by 1,000. This figure is useful for classifying injection molding machines that are supplied, as most are, with a choice of screw diameters. The maximum injection force exerted by the machine on the screw remains constant because only the screw and barrel assembly is interchanged. This means that shot volume is proportional to screw diameter but the maximum injection pressure is inversely proportional. The Euromap injection unit rating is unaffected by screw diameter. In other words, it returns the same figure for each of the alternative screw and barrel assemblies for a particular machine and so simplifies the task of classification. This rating is not much help in specifying an injection molding machine; maximum shot volume and injection pressure figures are indispensable for that purpose [60].

Major pressure drops occur in forcing the plastic melt through the injection nozzle and hence through the mold feed system and cavities. These pressure

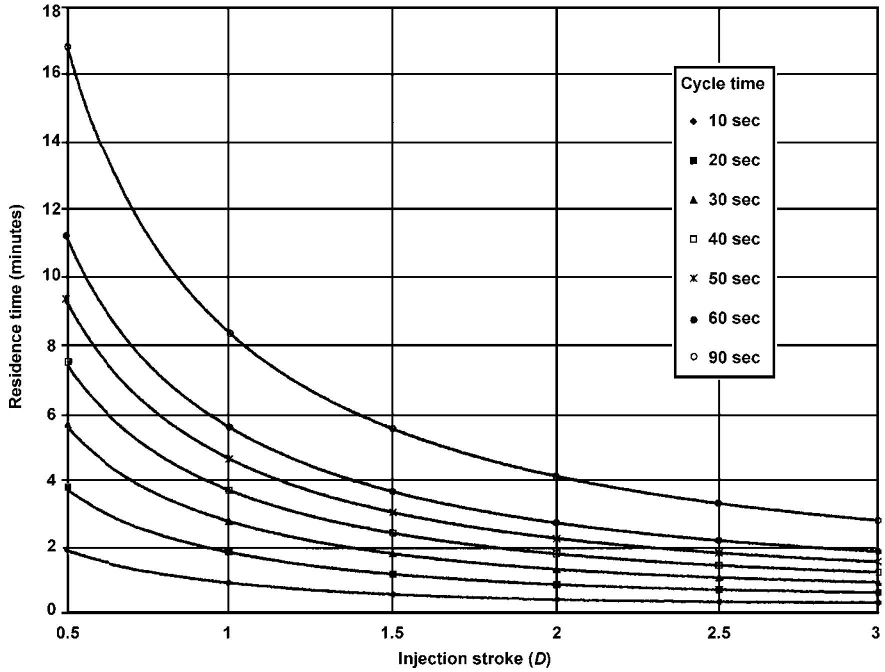


Figure 4.55. Material residence times.

losses cannot be quantified by simple rules. They are a function of the physical form of the flow path, the condition of the plastic melts, the rate of heat exchange, the type of polymer, and the rate and pressure of injection. Specific figures can be calculated with adequate accuracy by computer simulations of the molding process [61].

4.4.4.3 Power Systems

Injection molding machines perform a wide range of mechanical movements with differing characteristics. Mold opening is a low-force high-speed movement, and mold closing a high-force low-speed movement. Plasticating involves high torque and low rotational speed, while injection requires high force and medium speed. The modern injection molding machine is virtually always a self-contained unit incorporating its own power source. Early machine frequency ran from a centralized source serving an entire shop or factory. In this respect, injection molding machines have undergone the same metamorphosis as machine tools.

Oil hydraulics has become firmly established as the drive system for the vast majority of injection molding machines and until recently was almost unchallenged as the power source. Put at its simplest, the injection molding machine contains a reservoir of hydraulic oil which is pumped by an electrically driven pump at high pressure, typically at up to 14 MPa (2,030 psi), to actuating cylinders and motors. High and low pressure linear movements are performed by hydraulic cylinders, and rotary movements for screw drive and other purposes are achieved by hydraulic motors. Hybrid machines, in which the screw is driven by electric motor while the linear movements remain hydraulically powered, are not uncommon.

In recent years, the supremacy of the hydraulic machine has been challenged by all-electric machines. These use new brushless servomotor technology to power the various machine movements. The capital cost of all-electric machines is higher than that of conventional machines but the energy consumption in production is much lower. This is because the electric motors run only on demand, and there are no losses due to energy conversion, pipelines, or throttling. The elimination of hydraulic oil makes the all-electric machines inherently cleaner, so these machines are attractive for sterile or clean room use. There is also evidence that all-electric machine movements can be resolved with a higher degree of precision and repeatability than hydraulic systems.

4.4.4.4 Control Systems

The full sequence of operations and necessary options in a modern injection molding machine is very complex (Fig. 4.56). So too, is the range of parameters and adjustments needed to control the process accurately and automatically (Table 4.15).

	Unbalanced cavity in multi-cavity mold	Adjust runner or gate size
	Excessively thin region	Redesign part
Sink marks	Melt temperature too high	Reduce barrel temperatures
	Insufficient material injected	Increase feed Raise barrel temperatures Increase mold temperature Enlarge gates

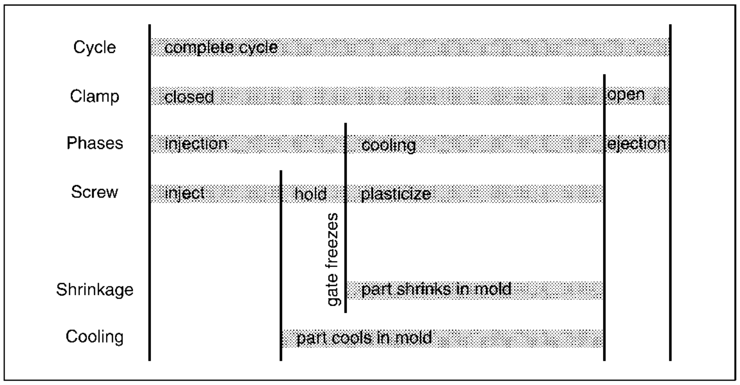


Figure 4.56. Principal elements of the injection molding cycle.

Table 4.15. Some Injection Molding Process Factors

Temperature	Time	Distance	Speed	Pressure or Force	Profile
Melt	Hold changeover	Hold changeover	Screw rotation	Hold changeover	Injection pressure
Mold	Open	Fast open	Injection stroke	Injection	Injection speed
Nozzle	Carriage forward delay	Slow open	Carriage	Peak	Holding pressure
Barrel Zones	Hold	Eject	Slow break	Holding	
Feed Throat	Carriage back delay	Sprue break	Fast open	Back	
Pellets	Screw start delay	Suck back	Slow open	Nozzle hold-on	
	Cooling	Shot	Eject	Clamp close	
	Eject	Cushion		Clamp open	
	Cycle delay				

Source: Maier, C., and Calafut, T., *Polypropylene*, William Andrew Publishing, 1998, p. 167.

Control is ultimately exercised by valves, regulators, and switches but it is rare now for these to be under individual manual control. The norm now is electronic control of varying degrees of sophistication ranging from simple partial control by programmable logic controller up to fully centralized computer control. It is usual for an injection molding machine to be offered with a choice of control options to suit a variety of end uses and budgets.

The precision and repeatability of injection molding machines has been much improved by the introduction of closed loop control to critical features like the injection screw sequence. The closed loop principle uses sensors to measure an important parameter—speed, position, pressure—of the element to be controlled. The readings are processed by the control system which generates control signals to a servo valve that regulates the element.

The process is often known as *feedback*. In effect, the system monitors itself to check whether it is performing as instructed and if not, it makes an adjustment based on the discrepancy.

4.4.5 The Injection Mold

The injection mold performs two vital functions: It defines the shape of the molded part, and it acts as a heat exchanger to cool the plastic material from melt temperature to ejection temperature. It must be very robustly engineered to withstand injection and clamping forces, it must operate automatically at high speed, and it must be built to very high standards of precision and finish. The mold also has other less obvious influences on the finished part. The dimensions and properties of the molding are greatly affected by shear rates, shear stresses, flow patterns, and cooling rates. Some of these are affected by both mold and machine; others are almost exclusively a function of the mold. These factors combine to make the injection mold a costly item. Modern technologies in the form of concurrent engineering, computer-aided analysis of flow and cooling, and high-speed and computer-controlled machining can help to keep the cost down. So too can the use of standard mold components that enjoy economies of scale and specialization. Even so, mold costs frequently dismay purchasers of moldings and there can be pressure to cut costs by reducing mold quality. This is false economy and will almost always result in a more expensive molding. There is no substitute for a quality mold [62].

4.4.5.1 Injection Mold Components

Figure 4.57 illustrates the principal components used in the construction of an injection mold.

The sequence of operations (Fig. 4.58) for a typical mold is:

- Plastics material is injected into the closed mold.
- The mold remains closed while the molding cools. The mold temperature is controlled by a coolant fluid (generally water or oil) which is pumped through cooling channels. Even if the mold is heated relative to ambient temperature, it is still cool in relation to the plastics melt temperature.
- The mold opens, leaving the molding attached by shrinkage to the core. During opening, the side action is retracted by a cam to release an undercut on the molding.
- The ejector plate is moved forward, causing ejector pins and stripper bars to push the molding off the core.
- The ejector plate returns and the mold closes, ready for the next cycle.

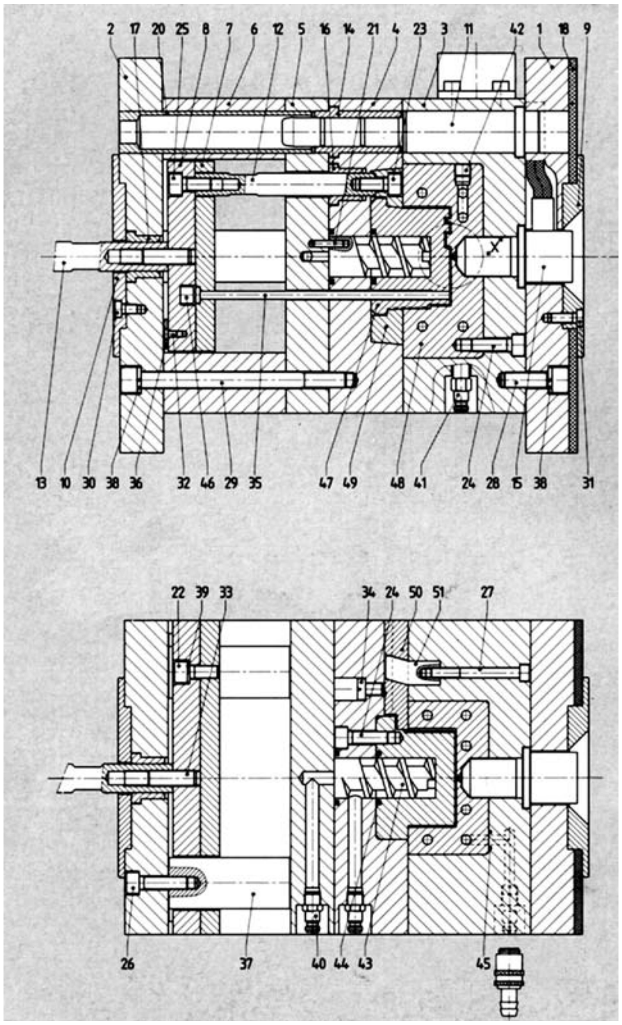


Figure 4.57. Example of an injection mold, illustrating principal component parts.

4.4.5.2 Injection Mold Types

Every molded part is different and so every mold is unique. Nevertheless, it is possible to distinguish some standard features and types. All are generally suitable for use with TPEs. The principal types are two-plate, three-plate, and stack molds. A further distinction concerns the feed system, which can be either the cold or hot type. These classifications overlap. A three-plate mold will have a cold runner feed system, and a stack mold will have a hot runner system. Two-plate molds can have either feed system [60].

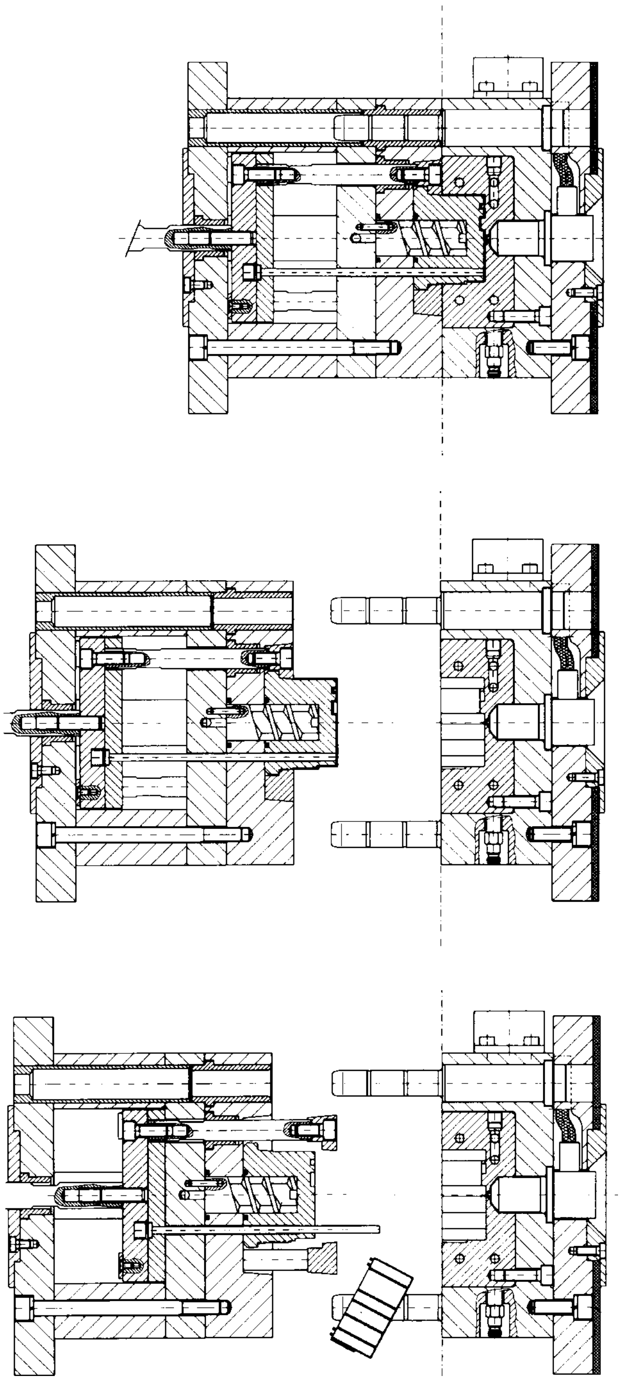


Figure 4.58. Sequence of mold operation: (a) plastic material is injected into the closed mold, (b) the mold opens, leaving the molding attached by shrinkage to the core, (c) the ejector plate is moved forward, causing ejector pins and stripper bars to push the molding off the core.

4.4.5.2.1 Two-Plate Molds

The two-plate mold has more than two plates in its construction. The description means that the mold opens or splits into two principal parts (Fig. 4.59).

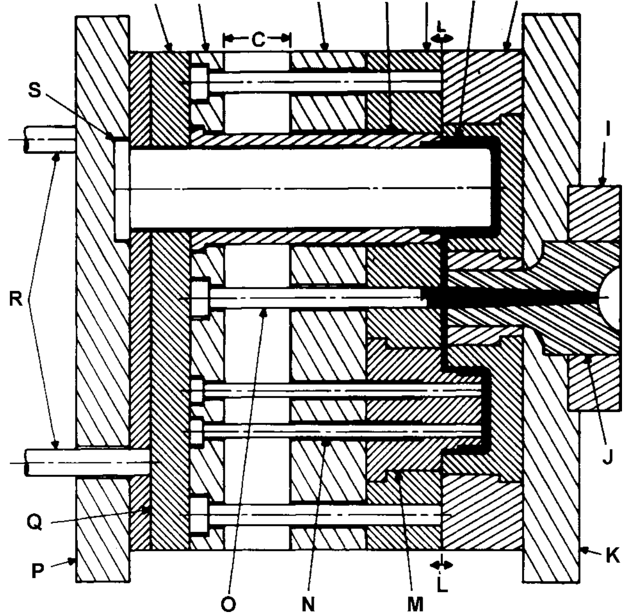


Figure 4.59. Schematic drawing of a two-plate mold: A—Knockout plate; B—Ejector retainer plate; C—Ejector travel; D—Support plate; E—Sleeve-type ejector; F—Rear cavity plate; G—Cavity; H—Front cavity plate; I—Locating ring; J—Sprue bushing; K—Clamping plate; L—Parting line; M—Core or force; N—Ejector pin; O—Sprue puller; P—Clamping plate; Q—Retainer plate; R—Knockout pins; S—Core or force pin.

These are known as the *fixed* or *injection half*, which is attached to the machine's fixed platen, and the *moving* or *ejection half*, which is attached to the moving platen. This is the simplest type of injection mold and can be adapted to almost any type of molding. The cavities and cores that define the shape of the molding—these are sometimes known as the *impressions*—are so arranged that when the mold opens, the molding remains on the ejection half of the mold. In the simplest case, this is determined by shrinkage that causes the molding to grip on the core. Sometimes it may be necessary to adopt positive measures such as undercut features or cavity air blast to ensure that the molding remains in the ejection half of the mold.

4.4.5.2.2 Three-Plate Molds

The three-plate mold is so called because it splits into three principal linked parts when the machine clamp opens (Fig. 4.60). As well as the fixed and moving parts equating to the two-plate mold, there is an intermediate floating cavity plate. The feed system is housed between the fixed injection half

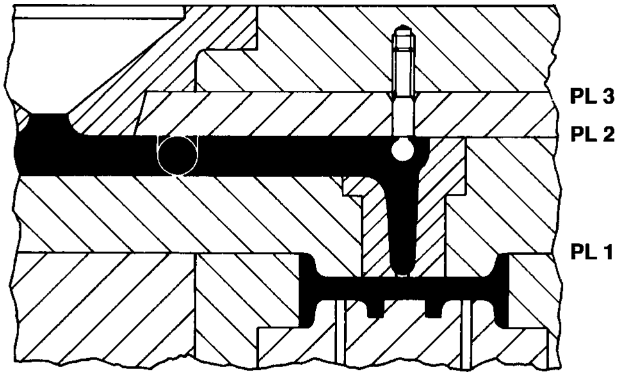


Figure 4.60. Schematic drawing of a three-plate mold (PL-Plate).

and the floating cavity plate. When the mold opens, it is extracted from the first daylight formed by these plates parting. The cavity and core is housed between the other side of the floating cavity plate and the moving ejection part of the mold. Moldings are extracted from the second daylight when these plates part. The mold needs separate ejection systems for the feed system and the moldings. Motive power for the feed system ejector and the movement of the floating cavity plate is derived from the clamp-opening stroke by a variety of linkage devices. The molding ejection system is powered normally by the injection machine ejection system.

The three-plate mold is normally used when it is necessary to inject multiple cavities in central rather than edge positions. This is done for flow reasons: to avoid gas traps, ovality caused by differential shrinkage, or core deflection caused by unbalanced flow. This type of mold also has the advantage of automatically removing (degating) the feed system from the molding. The disadvantages are that the volume of the feed system is greater than that of a two-plate mold for the same component, and that the mold construction is more complicated and costly.

4.4.5.2.3 Stack Molds

The stack mold also features two or more daylights in the open position. Two daylights are normal (Fig. 4.61) but up to four are known. The purpose of the stack mold is to increase the number of cavities in the mold without increasing the projected area and hence the clamp force required from the injection molding machine. This is done by providing cavities and cores between each of the daylights. Provided the projected area at each daylight is the same, opposed components of opening thrust from each daylight cancel out, leaving the total mold opening force no greater than that developed in a single daylight. The cavities are fed by a hot runner system deployed in the floating cavity plate. Separate ejection systems are required for each daylight. The mold engineering and hot runner control systems are complicated and become much more so when there are more than two daylights present. Stack molds are normally used for high volume production of relatively small and shallow components such as closures for packaging applications.

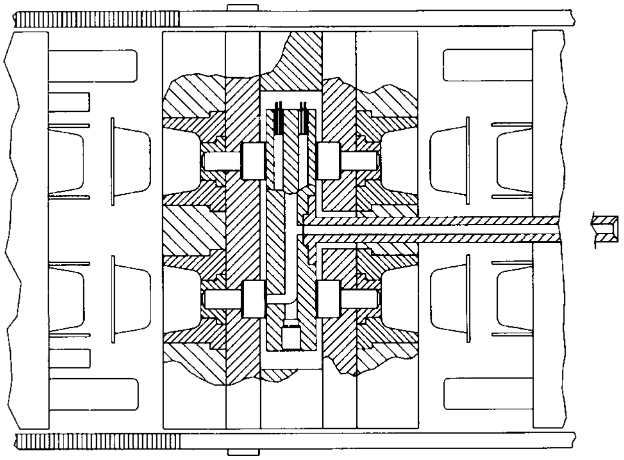


Figure 4.61. Schematic drawing of a stack mold.

4.4.6 Injection Mold Feed Systems

The feed system is the name given to the flow melt passage in the mold, between the nozzle of the injection molding machine and the mold cavities. This apparently utilitarian feature has a considerable effect on both the quality and economy of the molding process. The feed system must conduct the plastics melt to the cavity at the right temperature, must not impose an excessive pressure drop or shear input, and should not result in nonuniform conditions at the cavities of multi-impression molds. The feed system is an unwanted by-product of the molding process, so a further requirement is to keep the mass of the feed system at a minimum to reduce the amount of plastic material used.

This last consideration is a major point of difference between cold and hot runner systems. The cold runner feed system is maintained at the same temperature as the rest of the mold. In other words, it is cold with respect to the melt temperature. The cold runner solidifies along with the molding and is ejected with it as a waste product in every cycle. The hot runner system is maintained at melt

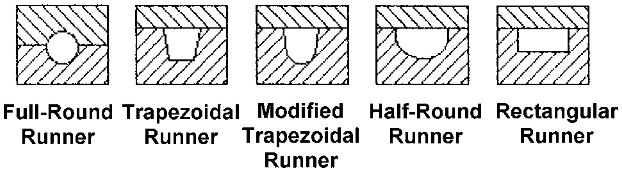


Figure 4.62. Common runner configurations.

temperature as a separate thermal system within the cool mold. Plastic material within the hot runner system remains as a melt throughout the cycle, and is eventually used on the next or subsequent cycles. Consequently, there is little or no feed system waste with a hot runner system. Effectively, a hot runner system moves the interface between the machine plasticizing system and the mold to a point at or near the cavities. In a cold runner system, the interface is at the outside surface of the mold, at a point between the machine nozzle and the sprue bush [62].

4.4.6.1 Cold Runners

Cold runner feed systems include three principal components: sprue, runner, and gate. The *sprue* is a tapered bore in line with the axis of the injection unit that conducts the melt to the parting line of the mold. The *runner* is a channel cut in a parting face of the mold to conduct melt from the sprue to a point very close to the cavity. The *gate* is a relatively small and short channel that connects the runner to the cavity. The gate is the entry point of the melt into the molding cavity [62].

Runners are produced in a variety of cross-sectional configurations (Fig. 4.62), but not all of them perform equally well. The best shape for the runner itself is a full-round section, cut in both halves of the mold. This is the most efficient form for melt flow without premature cooling. There are some instances when it is desirable to cut the runner only in one half of the mold, either to reduce the machining cost or where it is mechanically necessary over moving splits. In this case, the preferred runner sections are trapezoidal or modified trapezoidal. The half-round runner provides only a restricted flow channel combined with a large surface area for cooling and consequently is not recommended.

The concept of the hydraulic diameter (D_H) provides a quantitative means of ranking the flow resistance of the various runner configurations [63]. The hydraulic diameter is calculated from an expression chosen to give a full-round runner a value of $1D$, where D is the runner diameter, A = cross-sectional area, and P = perimeter:

$$D_H = 4A/P \tag{4.3}$$

The resulting values for equivalent hydraulic diameters (Fig. 4.63) clearly demonstrate the superiority of the full-round design for runners cut in both halves of the mold and the modified trapezoidal design for runners cut in one half of the mold.

Runner layouts should be designed to deliver the plastic melt at the same time and at the same temperature, pressure, and velocity to each cavity of a multicavity mold. Such a layout is known as a *balanced*

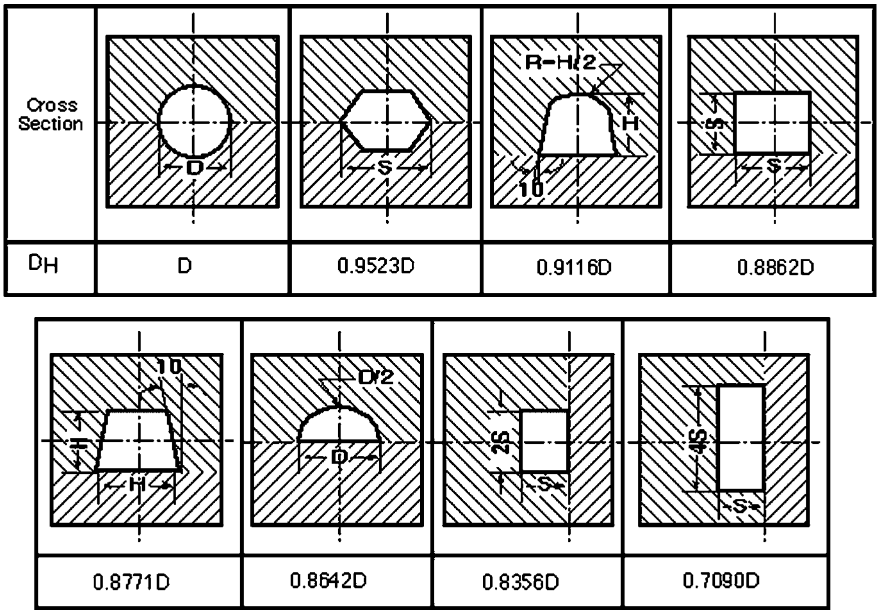


Figure 4.63. Equivalent hydraulic diameters for common runner configurations.

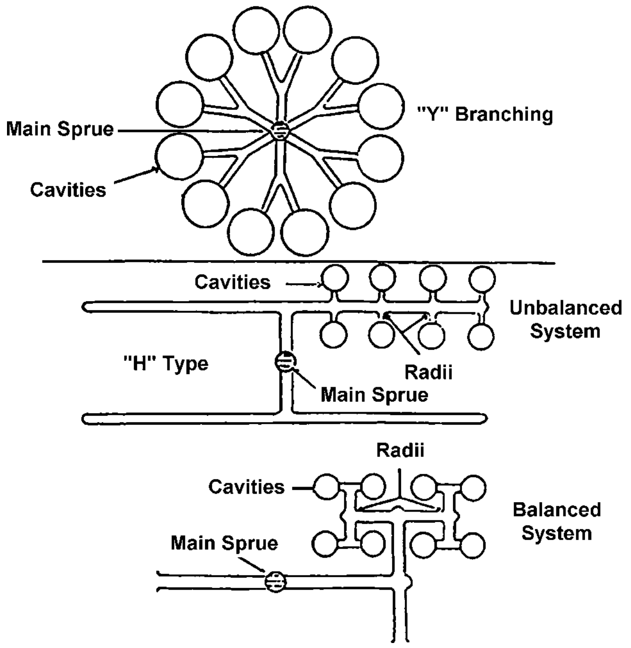


Figure 4.64. Balanced and unbalanced runner layouts.

runner (Fig. 4.64). A balanced runner will usually consume more material than an unbalanced type, but this disadvantage is outweighed by the improvement in the uniformity and quality of the moldings. Balance in a multi-cavity mold with dissimilar cavities (known as a family mold) can be achieved by careful variation of runner diameter in order to produce equal pressure drops in each flow path. Such balancing can only be achieved efficiently by the use of computer flow simulations, and this method really should now be the norm for injection mold design.

If flow simulation software is used, runner dimensions will be calculated precisely and can then optionally be adjusted to a standard cutter size.

4.4.6.2 Sprues

The sprue is often the thickest part in an injection molding shot and in extreme cases may influence the cycle time. Since the sprue is a waste part, this should not be allowed to happen. The reason that it sometimes does is that there is little control over the dimensions of the sprue. The length is fixed by the thickness of the fixed mold half while the diameter is largely a function of the machine nozzle bore and the necessary release taper. Sometimes the sprue can serve a useful function as a gripping point for an automated shot handling system, but the answer in most cases is to eliminate the cold sprue (Fig. 4.65) by means of a heated sprue bush (Fig. 4.66) that serves as a limited hot runner device. In this case, the material in the bush remains as a melt while the cold runner system is injected through a vestigial sprue. Elimination of the sprue typically saves a few grams of material waste per cycle.

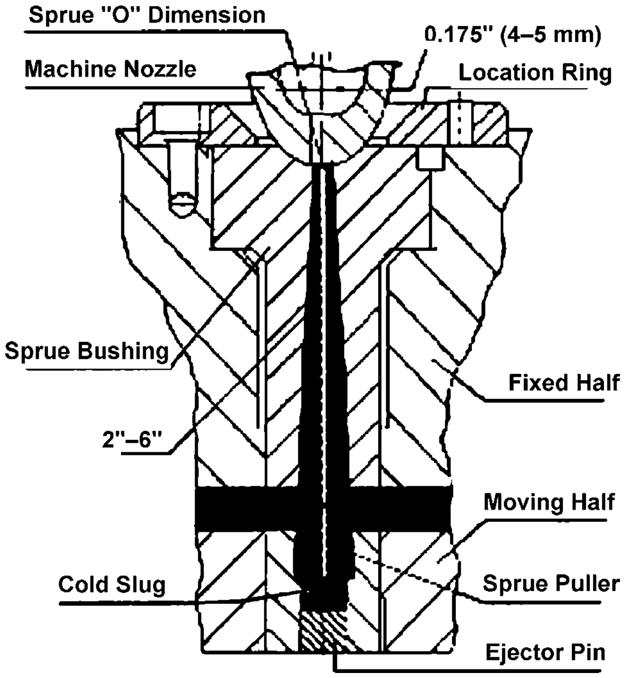


Figure 4.65. Typical cold sprue design.

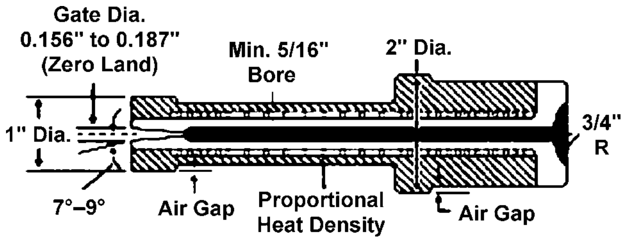


Figure 4.66. Example of heated sprue bushing.

4.4.6.3 Gates

The gate is the region of the feed system between the runner and the cavity. It is the entry point by which the plastics melt enters the cavity and is an important element of the mold. Its position and dimensions have a considerable influence on the finished molding. The position of the gate or gates directly influences flow paths in the cavity, and so has a major bearing on issues such as filling pressure, weld line quality, and gas traps. Gate positions must be judged individually for each molding case. An experienced practitioner can usually assess the best gate position for relatively simple part geometry but for complex parts, computer-aided flow analysis is preferred for gate positioning. Gate positions should be chosen with these general recommendations in mind:

- Gate near a thick section to ensure that it can be packed out
- Position the gate where the gate scar or witness mark will not be cosmetically objectionable
- Position the gate where it can be easily removed with cutting tools
- Position the gate for flow symmetry in symmetrical parts
- Gate to minimize gas traps and weld lines
- Gate so that unbalanced flow does not take place around cores
- Do not place the gate at a point where high stresses or high packing could cause problems
- Position the gate so that flow impinges on a mold surface rather than jets into a void
- Position the gate to minimize shrinkage differentials.

The gate is usually small in relation both to the molding and the upstream feed system. There are two principal reasons for this. The gate acts as a thermal valve that seals the filled mold cavity from the feed system. When the gate freezes, no more flow can take place. A very heavy gate would be slow to freeze and would possibly allow compressed melt to flow back out of the cavity and into the feed system, so one aim of gate design is to find a size that will remain open during the injection packing phase and freeze off immediately thereafter. The other reason for a small gate is so that the feed system can be easily removed from the molding, leaving little trace of its presence.

Flow conditions in the gate are extremely severe. The melt is accelerated to a high velocity and is subjected to a high shear rate. This is the main reason for keeping gates short. The gate length is often referred to as the *land length.* If the gate length is very short, there will be a weak section in the mold between the runner and cavity, and there will be insufficient clearance to use cutters for gate removal. During the passage of the melt through the gate, frictional heating is likely to occur and indeed is sometimes exploited in the design of feed systems for heat-sensitive materials. Here the strategy is to keep barrel temperatures low and generate additional heat at the last moment in the feed system.

Many different gate types (Fig. 4.67) have evolved to deal with a variety of molding needs. Some of these are associated with a particular geometry. For example, diaphragm and ring gates are usually employed

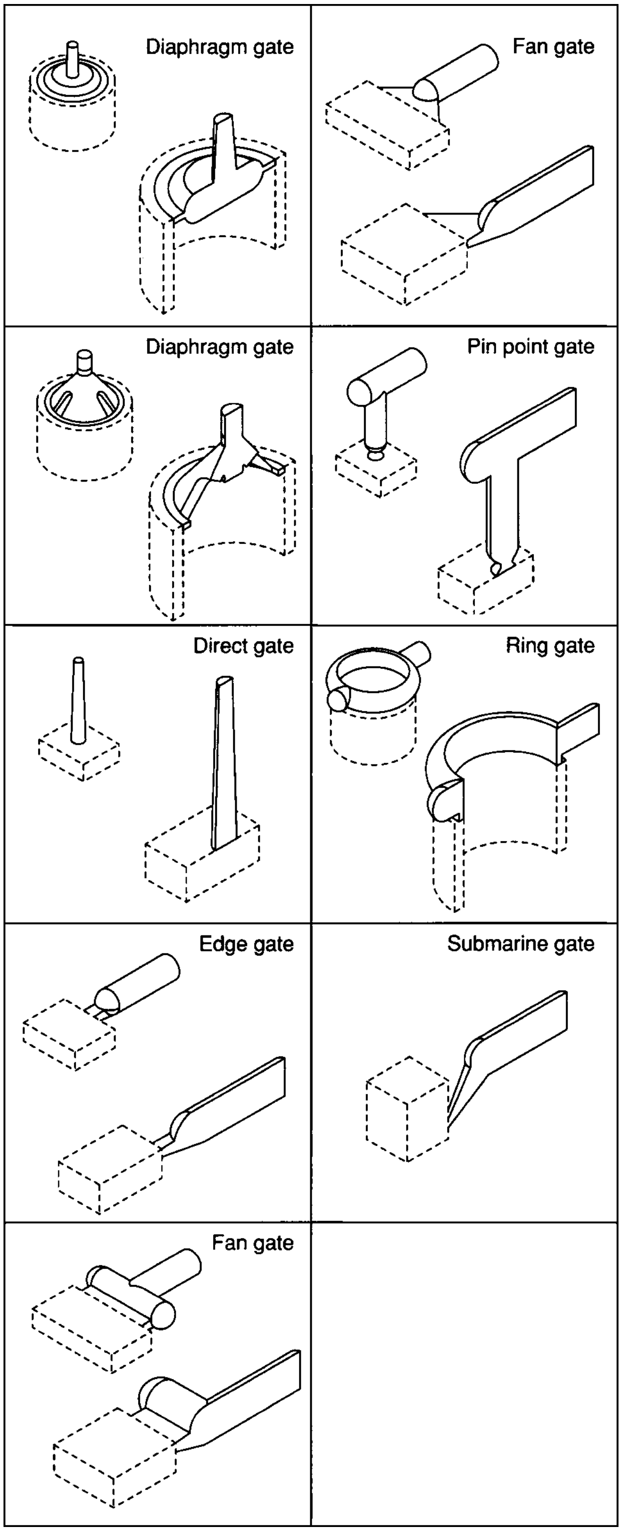


Figure 4.67. Examples of various gate types.

for parts with a cylindrical form. The pinpoint gate is normally used in three-plate molding. The most common gate type is the edge gate. The edge gate is usually square or rectangular in cross section and is cut in just one parting face of the mold. Circular section gates are also used but must be cut equally in both parting faces. Semicircular section gates are not recommended. Gate dimensions depend on product geometry and are frequently adjusted by trial and error during the testing of a new mold. The only practical way to do this is to start with a small gate and gradually enlarge it.

Simple large area parts in single-cavity molds may be gated by running the sprue directly into the cavity. This is known as *sprue-gating* or *direct sprue-gating*. The gate must be removed in a subsequent machining operation that leaves a witness mark. The sprue gate is perhaps the least sophisticated way of dealing with this type of molding. Fan gates are preferred for thin-walled parts of a relatively large area. The flash gate, a variant of the fan gate, is used for thin-walled parts that would be difficult to fill from individual gates at any point. The flash gate is very wide and shallow so that a large flow area is combined with a short freeze time. Ring and diaphragm gates are similar in concept to the flash gate. They are normally used to obtain cylindrical parts free of weld lines and core shift caused by unbalanced flow.

The submarine gate, also known as the tunnel gate, is cut into the one half of the mold rather than on a parting face. This constitutes an undercut, which is freed on ejection by the runner and gate flexing. The advantage of the submarine gate is that the feed system is automatically separated from the mold by the act of ejection that shears the gate off. The winkle or cashew gate is a variant in which the gate is machined in a curved form and is suitable only for flexible grades. A further gate type known as the tab gate is used to prevent jetting into an open cavity or when some defect is expected close to the gate. The tab is a small extension on the molding, which is fed at right angles to its axis by an edge gate; the tab is later removed from the finished part.

4.4.6.4 Hot Runners

Hot runner systems maintain the feed channels in a permanently molten state and eliminate the waste associated with a solidified cold feed system. Another advantage is that the pressure drop through the feed system is less than that of a comparable cold runner arrangement [61]. The principal disadvantage is the need to maintain two very different temperature regimes within the mold. This results in difficult problems of temperature control and differential expansion. The cost of a hot runner mold is also much greater than that of the cold runner equivalent. However, the important point is not the cost of the mold but that of the molding, and here hot runner molds have the advantage. Unless order quantities are low or frequent color changes are required, there are grounds to prefer the hot runner mold. Processors are still often deterred by control and engineering fears associated with hot runners, but there has been great progress in this area, and very sophisticated and reliable designs are now available as stock components. Most manufacturers of hot runner components now offer completely engineered systems that free the molder and mold builder from design responsibility. Traditionally, cold runner molds have been the norm and hot runners the exception but progress has been such that the project concept really should now start from the opposite premise.

The heart of a hot runner system (Fig. 4.68) is the manifold. This is a distribution block containing flow channels maintained at melt temperature. The channels distribute the melt from the single entry point at the sprue to multiple outlets at nozzles that feed individual cavities in a multicavity mold or serve as multiple gates in a single large cavity. The latter case is one of the most important applications of hot runners; multiple gates allow the flow lengths in a large part to be brought within easily manageable proportions. The same strategy also limits the necessary clamp force.

Contact between the hot manifold and the remainder of the cool mold must be kept to a minimum to prevent heat flow. This is normally achieved

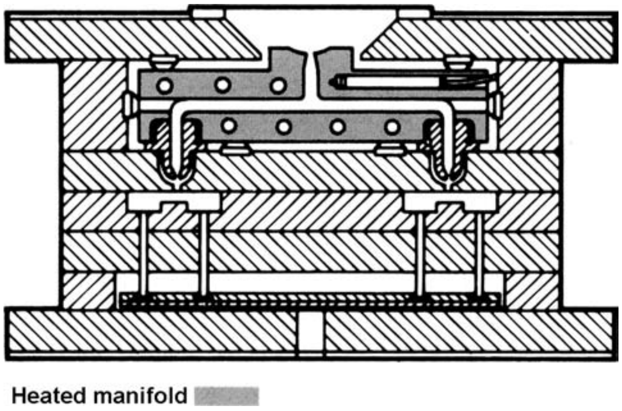


Figure 4.68. Schematic of hot runner mold.

by the use of air gaps that also allow for expansion, but care must be taken in the design to ensure that the mechanical strength of the mold remains adequate to deal with molding and clamping forces. The heat transfer problem is reduced with internally heated hot runners but the disadvantage is the relative inefficiency of the annular flow channel. These channels have higher pressure drops than unobstructed channels and are also prone to "slow flow" areas where material may stagnate and decompose.

A primitive variant of the hot runner is known as an insulated runner. This employs an unheated manifold with very large runners of 20–35 mm diameter, and relies on the poor thermal conductivity of plastics to ensure that a flow channel in the center of the large runner always remains molten. The insulated runner mold is not capable of precise and consistent control and is now rarely seen.

The connection between the hot runner manifold and the cavity is made by means of a hot nozzle that may operate in conjunction with a surrounding bushing. A wide variety of nozzle types allow for many gating options (Figs 4.69 and 4.70), with or without witness marks. Hot runner nozzles may be provided with shut-off valves for precise control of flow. Figure 4.71 shows the velocity profile in internally and externally heated hot runners. In recent years, great progress has been made in the design of hot runner nozzles for small and closely spaced cavities. These designs allow one nozzle to feed a number of cavities, and also permit gating options that are almost undetectable on the finished part.

Flow channels should be streamlined to prevent slow or stagnant flow. Corners should be radiused by contoured end plugs. Manifold support pads should have minimal surface contact and should be furnished in materials of relatively low thermal conductivity such as stainless steel or titanium. Precise temperature control is necessary for consistent results. The temperature of the manifold block should be uniform throughout. Each nozzle should be provided with individual closed-loop control.

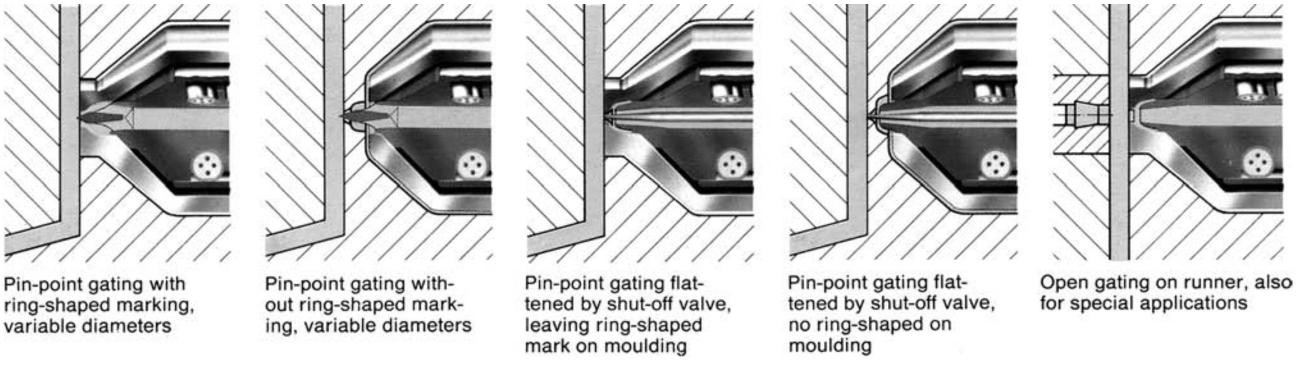
4.4.7 Injection Mold Features

4.4.7.1 Materials

Injection molds are subject to rigorous requirements that have a direct bearing on the materials of construction. Mold materials must withstand high injection pressures and clamp forces. They must be good thermal conductors, easy to machine, and be capable of reproducing fine detail and taking a high polish. They must be resistant to corrosion, abrasion, and wear. Specific materials required for construction of molds and other parts of injection molding machines for TPE processing is discussed individually for each group.

4.4.7.2 Cooling

It is a fundamental requirement of the injection mold to extract heat from the molding. With each cycle, the mold acts as a heat exchanger to cool the injected material from melt temperature to at least ejection temperature. The efficiency with which this is done has a direct bearing on the speed of production. Heat is removed from the injection mold by circulating a fluid coolant through channels cut through the mold plates and particularly through the cavities and cores (Fig. 4.72). The coolant is usually water but may be an oil if the mold is to be cooled at temperatures near or above the boiling point of water. Such a mold appears hot in relation to the ambient temperature, but it is still cold compared to the plastic melt. If the mold is to be chilled at low temperatures, it is usual to circulate a mixture of water and ethylene glycol. Occasionally the


Pin-point gating with ring-shaped marking, variable diameters

Pin-point gating without ring-shaped marking, variable diameters

Pin-point gating flattened by shut-off valve, leaving ring-shaped mark on moulding

Pin-point gating flattened by shut-off valve, no ring-shaped on moulding

Open gating on runner, also for special applications

Figure 4.69. Some types of direct hot runner gates.

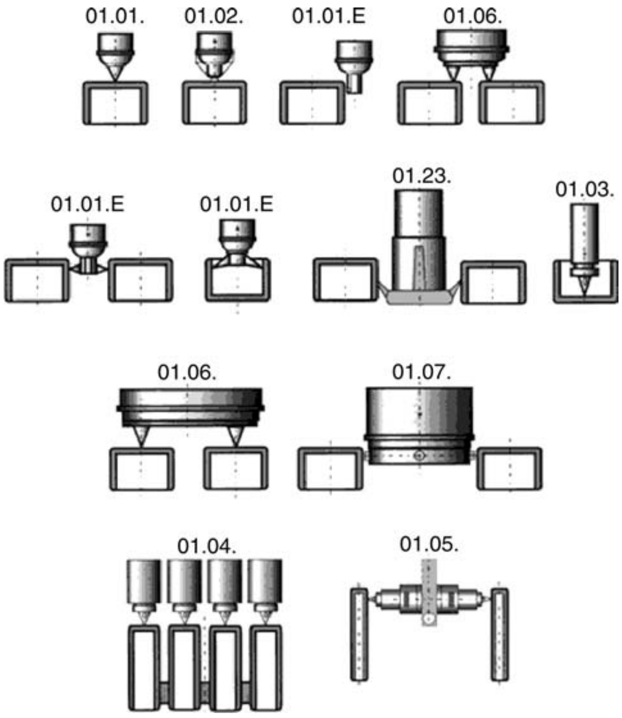


Figure 4.70. Advanced hot runner gates.

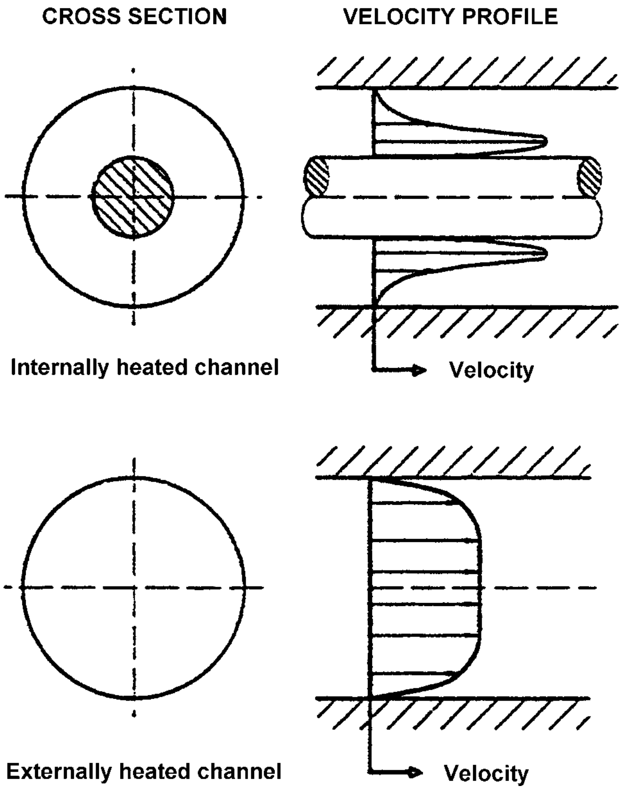


Figure 4.71. Velocity profiles in hot runners.

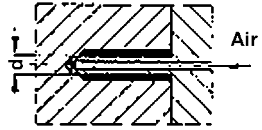
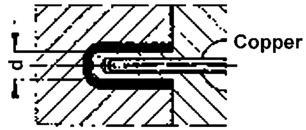
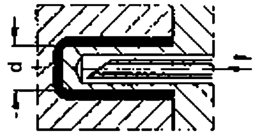
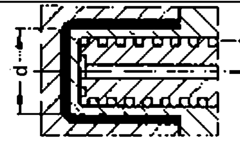
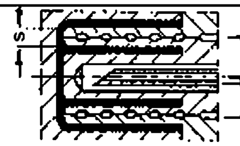
Core Diameter Core width d (mm)	Description	Design
≥ 3	Heat elimination by air with open mold	
≥ 5	Copper or thermally conductive pipe to conduct heat to the heating/cooling medium	
≥ 8	Long slender heating/cooling channel (with spiral)	
≥ 40	Spiral heating/cooling channel Pipe core	
Pipe core s ≥ 4	Heating/cooling for pipe core with a double flighted spiral	

Figure 4.72. Cooling arrangements for cores of various sizes.

coolant may be air, but this is an inefficient means of heat transfer and should be regarded as a last resort.

Cooling channels represent a real difficulty in mold design. Core and cavity inserts, ejector pins, fasteners, and other essential mechanical features all act as constraints on the positioning of cooling channels, and all seem to take precedence over cooling. However, uniform and efficient cooling is crucial to the quality and economy of the molding, so channel positioning must take a high priority in mold design.

Cooling channel design is inevitably a compromise between what is thermally ideal, what is physically possible, and what is structurally sound (Fig. 4.73). The thermal ideal would be flood cooling over the entire area of the molding, but the pressurized mold cavity would be unsupported, and mechanical details like ejectors could not be accommodated. Support could be provided by interrupting the flood-cooling chamber with supporting ribs, but the mold construction is complicated by the need to fabricate and seal the cooling chamber. The reasonable and practical compromise provides the cooling channels in the form of easily machined

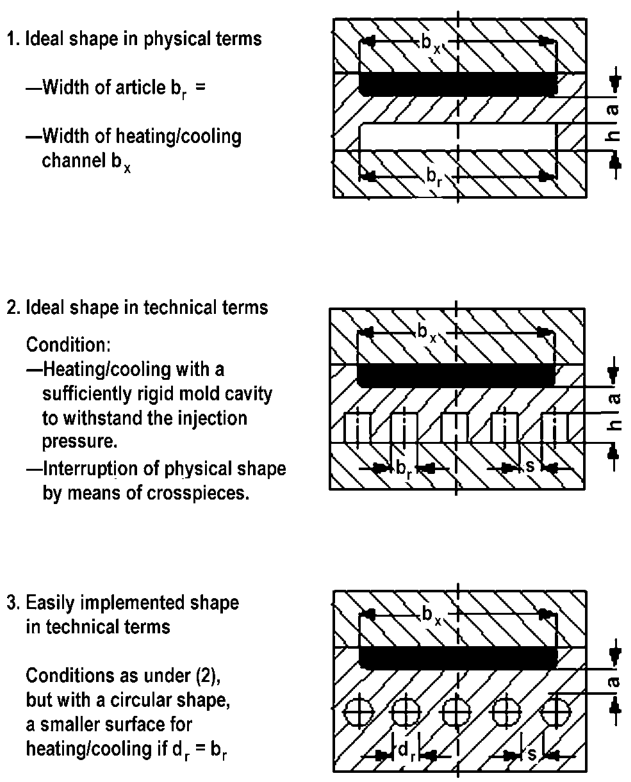
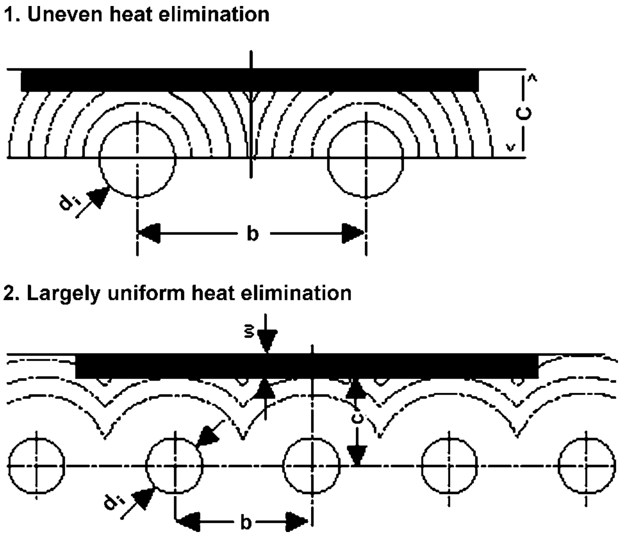


Figure 4.73. Cooling channel considerations.


1. Uneven heat elimination

2. Largely uniform heat elimination

Figure 4.74. Good and bad channel layouts.

through-bores that may be linked either inside or outside the mold to form a complete cooling circuit.

The correct placement of the channels is important. If they are too widely spaced, the result is a wide temperature fluctuation over the cavity or core surface (Fig. 4.74). If the channels are too closely spaced or too close to the cavity surface, the mold becomes structurally weak.

Another important consideration in cooling channel design is to ensure that the coolant circulates in turbulent rather than laminar (streamline) flow. The coefficient of heat transfer of the cooling system is drastically reduced in laminar flow.

For a channel of circular cross-section, turbulent flow occurs when the Reynolds number is greater than 2,300. The coefficient of heat transfer of the cooling system continues to increase as turbulence increases, so the design limit of the Reynolds number for cooling channels should be at least 5,000 and preferably 10,000. If the volume flow rate of the coolant remains constant, then the Reynolds number can be increased by reducing the size of the channel. This runs counter to the natural impulse to imagine that a larger channel must always result in better cooling. It is harder to achieve turbulent flow with oils or antifreeze solutions because of their greater viscosities compared with water. The significance of wall temperature is second to the wall thickness in its impact on cooling time [63].

Wall temperature differences could cause warping of the part. Thermoplastic molds are cooled with water and oil if higher temperatures are required because water tempering equipment is limited to 140°C (285°F).

4.4.7.3 Venting

When an injection mold fills, the incoming high-velocity melt stream is resisted by, and must displace, the air in the feed system and cavities. Molders often rely on incidental air gaps between the parting faces and between the assembled parts of the core and cavity to provide a leakage path for air, but this is no substitute for properly engineered venting, which should be designed into all molds. Provided the vent is machined to the correct depth, the injected material will not flash through the air gap. More than one vent may be used; if necessary up to 60% of the peripheral dimension can be vented. The width of individual vents should not exceed 6 mm (0.25 in.).

Venting can also be used to prevent or minimize gas traps. A gas trap occurs when the flow of injected plastics melt surrounds and isolates an area in the cavity, so trapping air, which is rapidly compressed and heated. Burned or charred material is often associated with gas traps. The best remedy is to redesign flow to do away with the gas trap but, if this is not possible, venting will help provided the vent is positioned in the correct spot. Most gas traps cannot be vented through the parting faces of the mold. Instead, the vent is machined in inserted pins or plugs. Such vents are prone to blocking unless one of the parts is in motion. For this reason, an ejector pin is often used for venting. An alternative method is to use an insert of porous steel.

4.4.7.4 Ejection

Ejection is the name given both to the process of removing the molding from the mold and to the means by which it is done. Ejectors inevitably leave witness marks on the molding, and this alone may determine the disposition of the part in the mold. Once that basic choice has been made, there is usually not much further freedom to position ejectors in cosmetically acceptable positions. The choices are much constrained by other features in the mold and the need to put ejectors where they are most needed to overcome the resistance of the molded part.

Ejection may be by means of pins or a stripper plate, or a combination of both. The stripper plate acts on the entire peripheral wall thickness of the part and so distributes the ejection force. This is the preferred method for thin-walled parts, but the method is difficult to apply to anything other than a circular periphery. A variant on this theme is the stripper bar which works on part of the periphery. Most ejection is performed by pins, usually cylindrical in form. Rectangular pins may be used in constricted areas; these are often referred to as blade ejectors. Hollow ejector pins known as sleeve ejectors are commonly used to push the molding off small core pins. Ejection of deep-drawn or thin-walled parts is often assisted by an air valve that breaks the vacuum between the molding and the mold core.

4.4.8 Materials of Construction

Products of the degradation of molten TPEs are in general not corrosive, thus it is not necessary to construct the parts of the machine that come in contact with molten polymers from corrosion-resistant metals, which are significantly more expensive than lower grades of steel. However, there are cases where it is necessary to use corrosion-resistant metals (see chapters describing the individual TPEs). Corrosion of process surfaces can result in the contamination of the finished product and deterioration of its physical properties. Details in the Table 4.16 show a list of the metals and suppliers recommended for the construction of various parts of the injection molding machine.

For injection molding machines used for the processing of thermoplastics producing corrosive decomposition products, materials like Xaloy 309 and Bernex C240 can be used for construction of barrels and Hastelloy C-276 for the screw, adapter, and nozzles. The corrosion rate of the mold surface will be lower than that of the other parts of the machine because its temperature will be lower than the melting point of the polymer. For short production runs, unplated molds of hardened tool steel, or high quality or chrome and nickel plating of the injection mold cavities normally provides sufficient protection. For longer runs, more corrosion-resistant materials of construction may be required.

4.4.9 Dimensional Stability of Parts

Close tolerances can be achieved provided that operating variables of the process are tightly controlled. Mold design is, however, the other critical factor in obtaining high precision molded parts. As tolerances become smaller, cost of manufacturing

Table 4.16. Some Corrosion-Resistant Metal Alloys and Their Suppliers

Metal	Supplier	Parts
Hastelloy C	Stellite Division, Cabot corporation, Nokomo, Indiana, USA	Screw, adapter, and nozzle
Hastelloy C-276	Stellite Division, Cabot corporation, Nokomo, Indiana, USA	Screw, adapter, and nozzle
Duranickel	International Nickel Co., Huntington, West Virginia, USA	Screw, adapter, and nozzle
Monel	Sales@espi-metals.com	Screw, adapter, and nozzle
Xaloy 309	Xaloy, Inc., New Brunswick, New Jersey, USA	Barrel and barrel lining
Brux	Brookes (Oldbury), Ltd, Oldbury, Warely, Worcestershire, UK	Barrel and barrel lining
Reiloy	Reiloy Metal GmbH, Köln, Germany	Barrel and barrel lining
Bernex C240	Berna AG, Olten, Switzerland	Barrel and barrel lining

Source: Reference [55].

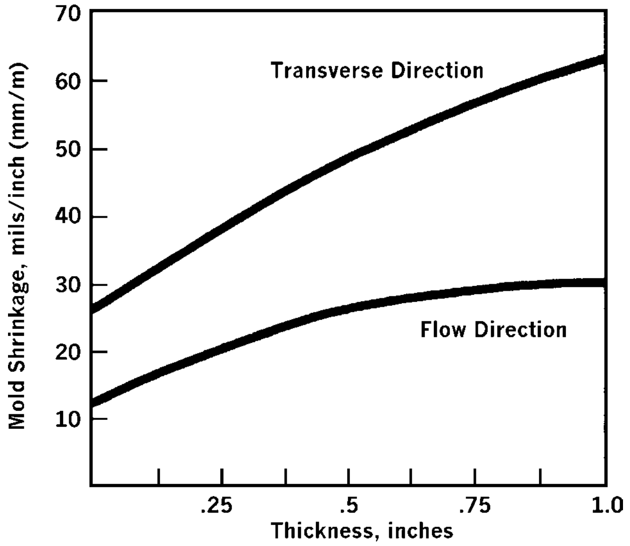
and complexity of the process grow. Almost every variable in the molding process affects the part dimensions. Shrinkage during the molding process is a critical factor in determining the final dimensions of the part.

Shrinkage increases with part thickness (Table 4.17) and mold temperature because in both cases cooling rate decreases. Consequently, crystallinity increases and internal stresses decrease. A number of plastics exhibit direction-dependent shrinkage (Figs 4.75 and 4.76). The least amount of shrinkage takes place in the direction of flow due to the highest degree of orientation in this direction. The rule-of-thumb that is useful to the design of molds is that the straighter the path, the lower the shrinkage. Table 4.18 shows the effect of various parameters on shrinkage of injection-molded parts. Annealing a molded part, that is, heating and holding it above its performance temperature, can prevent further shrinkage during its use.

Table 4.17. Shrinkage as a Function of Thickness

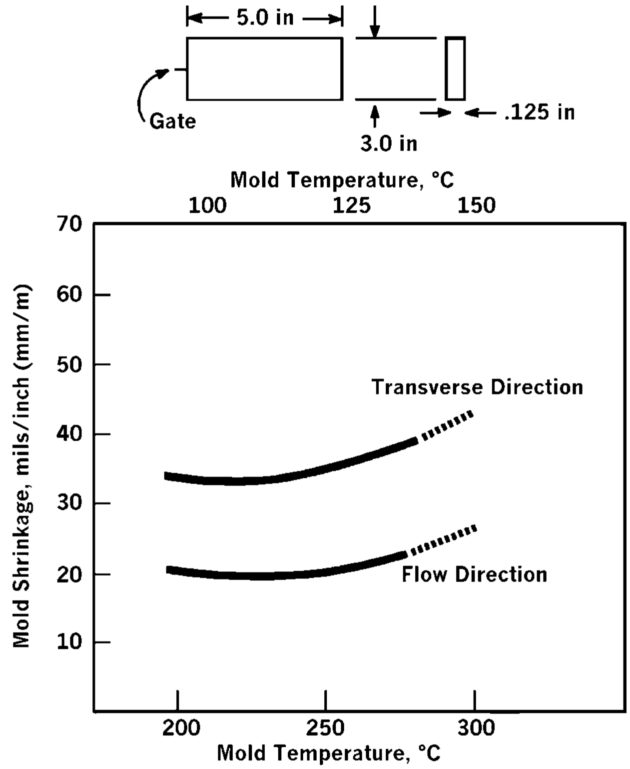
Part Thickness (mm)	Shrinkage	
	mm/m	%
3.2	35–40	3.5–4.0
6	40–45	4.0–4.5
12.7	45–50	4.5–5.0
19.1	50–60	5.0–6.0

Source: Reference [55].



Mold Temperature = 200°F/93°C
Melt Temperature = 625°F/330°C
Injection Pressure = 10,000 psi/70 MPa

Figure 4.75. Example of shrinkage vs thickness in flow and cross directions.



Part Thickness 0.125 in/3.2 mm
Melt Temperature 625–650°F/330–345°C
Injection Pressure 7,000–10,000 psi/50–70 MPa

Figure 4.76. Example of shrinkage vs mold temperature in flow and cross directions.

Table 4.18. Effect of Various Parameters on Shrinkage

Increase Shrinkage	Decrease Shrinkage
	Increased injection pressure
Increased Stock Temperature	
	Filler addition
Increased Mold Temperature	
Increased Part Thickness	
	Increased polymer orientation
	Straight melt flow during molding

Source: Reference [55].

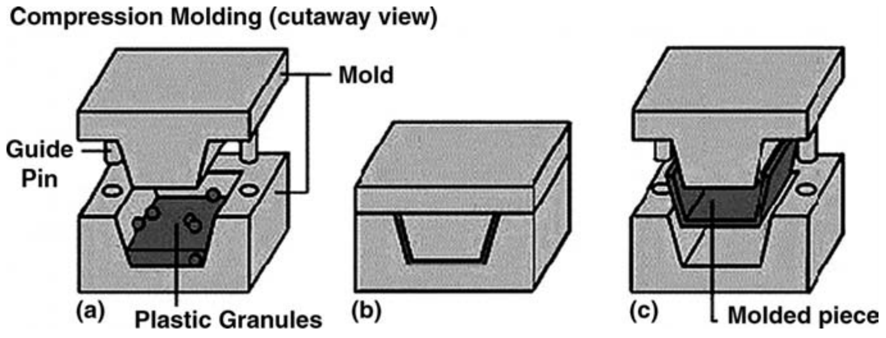


Figure 4.77. Schematic drawing of the stages of the compression molding process.

4.5 Compression Molding

Compression molding was among the first methods to be used to form plastics (Fig. 4.77). It involves four steps:

- Pre-formed blanks, powders, or pellets are placed in the bottom section of a heated mold or die
- The other half of the mold is lowered and pressure is applied
- The material softens under heat and pressure, flowing to fill the mold. Excess material is squeezed from the mold. If it is a thermoset plastic, cross-linking occurs in the mold. In thermoplastic molding, the part is hardened under pressure by cooling the mold
- The mold is opened and the part is removed.

As pointed out above, for thermoplastics, the mold is cooled before removal so the part will not lose its shape. Thermosets may be ejected while they are hot and after curing is complete. This process is slow, but the material moves only a short distance to the mold and does not flow through gates or runners like in injection molding. Only one part is made from each mold.

In the simplest form of compression molding, a molding powder (or pellets, which are also sometimes called molding powder) is heated and, at the same time, compressed into a specific shape. In the case of a thermoset material, the melting must be rapid since a network starts to form immediately and it is essential for the melt to fill the mold completely before solidification progresses to the point where flow stops. Commercial molding machines use high pressure and temperature to shorten the cycle time for each molding. The molded article is pushed out of the cavity by the action of ejector pins that operate automatically when the mold is opened. A schematic diagram of a complete compression molding press, the mold, and other process components can be seen in Fig. 4.78; a typical mold set is shown in Fig. 4.79.

In some cases, pushing the resin into the mold before it has liquefied may cause undue stresses on other parts. For example, metal inserts to be molded into a plastic electrical connector may be bent out of position. This problem is solved by transfer molding, in which the resin is liquefied in one chamber and then transferred to the mold cavity. When flat plates are used as the mold, sheets of various materials can be molded together to form a laminated sheet. In plywood, layers of wood are both adhered to one another and impregnated by a thermoset such as urea-formaldehyde, which forms a network on heating.

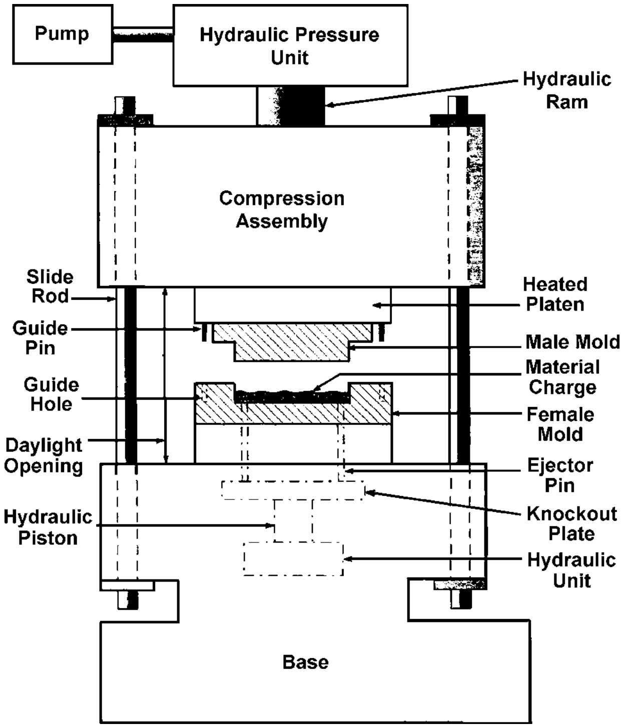


Figure 4.78. Schematic drawing of a compression molding press and its components.

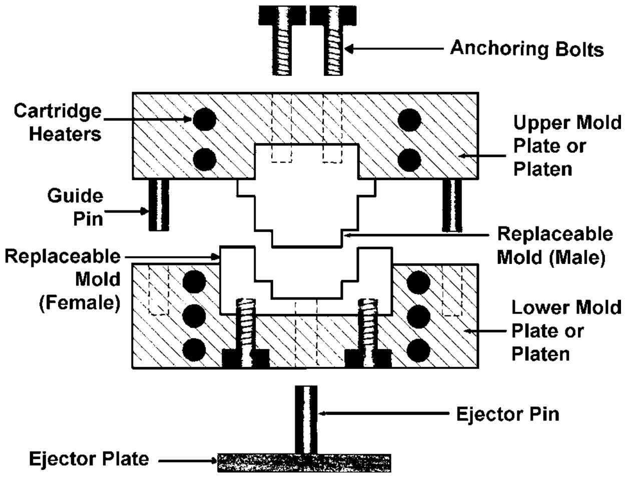


Figure 4.79. A typical compression mold set.

4.5.1 Types of Compression Molds

Compression molds for thermoplastics are equipped with cooling and heating cores to allow melting and hardening the resin. Electricity or steam and cold water are usually the heating and cooling medium of the mold.

There are three types of compression molds: hand molds, semiautomatic, and fully automatic. Hand molds are limited to prototypes, small size parts, and short runs. Semiautomatic molds are self-contained and securely installed in a conventional mold press. The operational sequence has to be carried out manually. Fully automatic compression molds are specially designed and constructed to fit a completely automatic compression press. Manual intervention in the operation is reduced to the loading of material hoppers and part removal from the press.

There are five standard designs for the cavities and the closure of compression molds as described below.

(1) *Flash type*. This is the oldest design of compression molds (Fig. 4.80) most suitable for manufacturing hollow parts. This type of mold may be used in the production of large parts, although part quality may be poor both from dimensional and aesthetics standpoints. This mold is overfilled slightly, forcing the excess plastic (flash) into the gap between the male and female mold halves. An insufficient charge of resin results in a part that is too small.

(2) *Fully positive*. Also called a direct positive mold (Fig. 4.81), this is solely used for large deep draw parts where maximum density must be obtained. These molds are limited to single cavity production requiring the weighing of each material charge to assure the depth (or the height) and the density of the finished part.

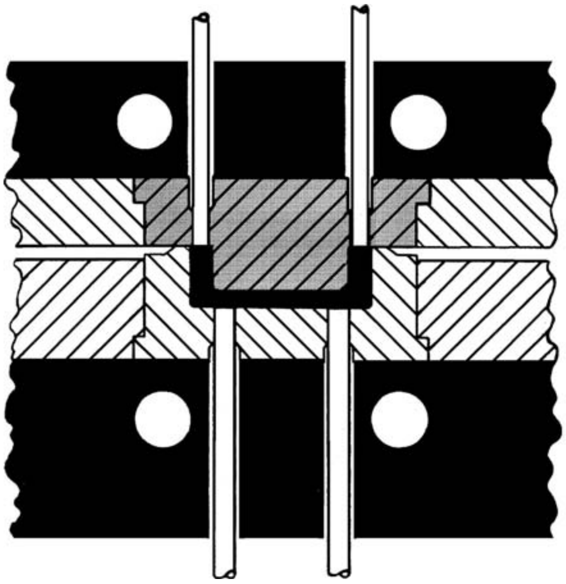


Figure 4.80. Flash mold design.

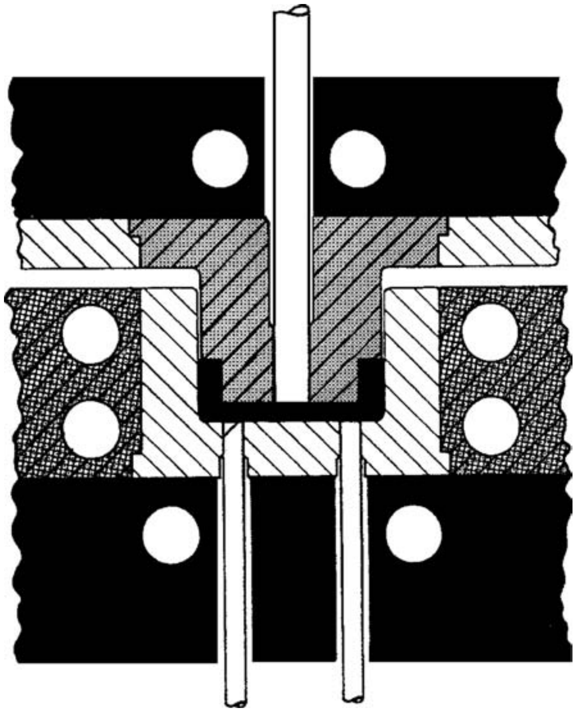


Figure 4.81. Direct positive mold design.

(3) *Landed positive*. Multi-cavity molds may take advantage of this design (Fig. 4.82). Escapements are installed on the force to allow development of maximum density with cavity-to-cavity height uniformity.

(4) *Semi-positive horizontal flash*. This is the most suitable design for automatic molds and is most common in the industry (Fig. 4.83).

(5) *Semi-positive vertical flash*. This design (Fig. 4.84) is helpful in cases where a visual flash line scar may be present on the molded parts. The cost of this design is considerable because of the required proper fit between force and cavity.

The positive type mold closure has a long shearing surface between the male and female segments of the mold. This surface is formed when the mold segments are in close proximity to each other. The gap between the male and female segments is maintained closely, thus no flash is formed. The amount of material charged into the mold is carefully controlled because excess material would prevent mold closure. Insufficient charge results in a short shot, that is, an incomplete part will form.

In semi-positive type closure, a horizontal land causes a gap to form between the plunger and the cavity. This gap is significantly larger than the gap in positive closure. Any excess material moves along the horizontal land and further up the vertical land, facilitating flash removal.

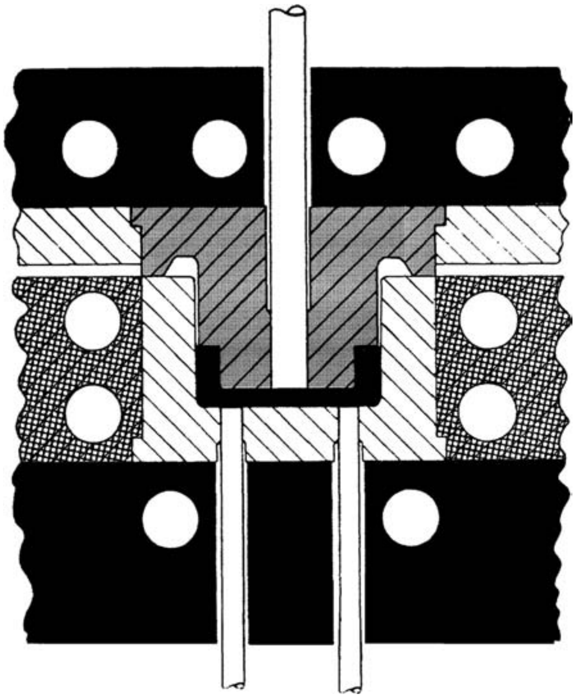


Figure 4.82. Landed positive mold design.

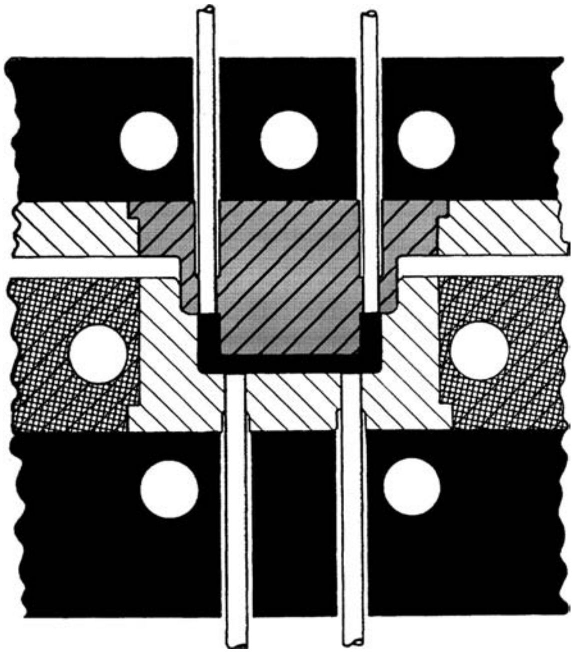


Figure 4.83. Semipositive horizontal flash mold design.

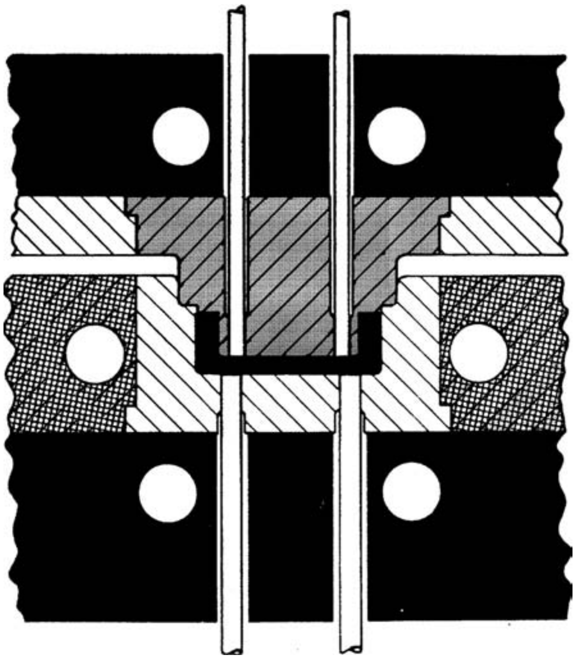


Figure 4.84. Semipositive vertical flash mold design.

The basic molding requirement calls for a mold that will compress the plastic into the desired shape and hold it under pressure and heat until the molding cycle has been completed. The operation must be done in the simplest manner and for the least cost, which requires that the mold be designed so that the resin and insert could be introduced easily and the part ejected. A good source to study the procedure for designing compression molds is *Plastics Mold Engineering Handbook* [64].

4.5.2 The Compression Molding Press

A compression molding press is usually a rugged piece of equipment that provides sufficient force to compress the material. The force necessary to mold a part must be smaller than the press capacity. The force required depends on the nature of the plastic and part geometry. Dependence on the nature of the material being compressed complicates the task of mathematical modeling of this process. There are complex approximate expressions that relate the force required to the geometry of the part and material properties.

Equation 4.4 [55] represents a practical approximation between the force and the part size. In this relationship, the required compression force (F) equals the cavity pressure (P_A) multiplied by the projected area (A) of the mold up to a depth (part thickness) of d_e. An additional force is needed when the part thickness (d_p) exceeds this minimum depth. The value of d_e depends on the material and p is the additional pressure factor; both are determined experimentally.

$$F = (A)[P_A + p(d_p - d_e)] \tag{4.4}$$

Most parts of common plastics that are less than 3 cm thick require 10–55 MPa (1,450–7,980 psi) pressure for consolidation. Parts that are over 3 cm (1.2 in.) (d_e) thick must be given 1–1.33 MPa/cm additional pressure (p).

A number of different types of presses are commonplace for compression molding. They include manual, semiautomatic, automatic, automatic rotary presses.

The conventional manual and semiautomatic press is vertical and closes upward, downward, or bidirectionally. The pressure medium is hydraulic fluid or air; clamp force is applied by hydraulic ramps or toggle clamps. The source of fluid can be separate or integrated in the press. Table 4.19 shows the force capacity (tonnage) of different press sizes.

Table 4.19. Manual and Semiautomatic Press Sizes

Press Size	Press Force (metric tons)
Small (Hand or Bench)	4.5–22.7
Production	45.5–455
Very Large	Up to 2,727

Source: Reference [55].

Automatic presses are self-contained and the cycles are computer controlled. Typically these presses are vertical and they are available from 22.7 to 273 tons. Other features such as the material loading mechanism and unloading trays are added to fully automate the operation of these presses. The tool cost is higher for automatic molds than manual or semiautomatic molds.

Automatic rotary presses are suitable for producing small parts that have a shallow draw with a smaller diameter than 7.6 cm (3 in.) [65]. This process should be considered whenever high production rates are required, so long as the part design would allow its use.

4.5.3 Compression Molding of Thermoplastics

The general procedure for compression molding is applicable to the molding of thermoplastics except that cooling the mold under pressure hardens the article. The length of the heating and cooling cycles is determined experimentally. Thermoplastic compounds cannot be pressed into a preformed charge. In contrast, a thermosetting compound undergoes a chemical reaction (cross-linking) during the hardening of the part.

Thermoplastic elastomers generally have high melting points, thus they need to be heated to an elevated temperature during compression molding. Heating and cooling make for long cycles and great power consumption in conventionally heated compression molds. Small molds are preferable to larger ones. Separate platen presses are used where one is a hot press that is electrically heated and the other is a cold press that is water cooled. The article is shaped in the hot press under pressure. The mold is then transferred, as rapidly as possible, to the cold press to chill the article under pressure. The article is removed after it has been cooled down to a sufficiently low temperature. To ease the removal of the part from the mold, its surfaces can be covered with aluminum foil that has been sprayed with a mold release agent.

The length of cycle time depends on the mass of the part and the properties of the polymer. The hot press is usually preheated to decrease the overall cycle time. Pressure is gradually increased during the heating cycle. Thicker parts require significantly longer cycles (many hours) to melt and fuse the resin and eliminate bubbles and voids.

4.6 Transfer Molding

Transfer molding was originally developed for fabricating parts from thermosetting polymers. It is a combination of injection and compression molding processes in which the polymer is melted in a pot, transferred into a mold, and compressed into the designated shape. Transfer molding differs from compression molding in that the plastic is heated in separate chamber but compressing is carried out in a conventional compression press. Cooling hardens thermoplastics as opposed to thermosetting resins that are hardened by cross-linking reaction. The mold design is modified to accommodate the melting pot or the heated mold.

4.6.1 Background

In general, transfer molding offers advantages for manufacturing certain parts.

(1) Parts requiring side draw core pins that must be removed prior to discharging the part from the mold
(2) Intricate parts that require inserts
(3) Complicated parts where tolerances are very close in three dimensions
(4) Small molded parts that assemble together
(5) Parts with low finishing cost (little flash is produced by this process).

For example, valves and fittings can be lined by the transfer molding process. The valve body or the fitting, along with mandrels and flange plates, direct and confine the flow of the molten resin and serve as the mold. The valve and fitting are preheated to above the melting point of the thermoplastic material before the melt is entered into the cavity. The source of the melt may be an extruder, an injection molding machine, or a melt pot. The molten resin is transferred into the cavity under pressure and held under compression for a length of time. At the end of the cycle, the resin is cooled under pressure before the mandrel assembly is removed. In the last step, the lined part undergoes minor finishing such as de-burring and trimming.

This method of molding requires the transfer of molten polymer from a well or a pot under pressure through runners and gates into the mold. Cavities are located inside a closed heated mold as shown in Figs 4.85 and 4.86. The charge is often preheated before it enters the pot. Preheating reduces pressure requirement for the transfer operation and shortens the mold cycle. The three variations of this technique include transfer in compression mold, plunger molding, and screw transfer molding.

Transfer molding is a versatile process capable of producing parts such as pump bodies, impellers, plug valve sleeves, and encapsulated butterfly valve discs. Generally, transfer molding can be divided into four areas: mold, melt, melt transfer, and cooling and disassembly; each is discussed in this section.

4.6.2 Transfer-In Compression Molding

In this technique (Fig. 4.85), a hydraulic ram is used and the plunger for the pot is fastened to the upper platen of the press. This arrangement allows pressure to be developed with the help of the hydraulic ram. The minimum differential between the area of the pot and the mold cavity should be +10% for successful melt transfer. This prevents the opening of the mold cavity and the formation of flash.

The productivity of this method exceeds that of compression molding even though the pot is usually manually operated. The pressure applied aids in filling the mold cavity rapidly, resulting in parts with good dimensional control and uniform density.

A three-plate mold is used with the plunger or ram positioned at the top plate (Fig. 4.87). The orientation of any elongated filler such as fibers is parallel to the flow because the molten plastic enters the mold at a single point (gate). By the same token, shrinkage in the flow direction and perpendicular direction is likely to be different and hard to predict, depending on the gate position and part design.

At the end of the cycle, when the mold is opened, the remaining polymer solidifies into a disk shape (cull). It is removed as a single piece along with the sprue. The part is removed by lifting the middle section of the mold followed by ejection pin action. In the transfer molding method, it is desirable to keep the sprue and the cull attached, contrary to injection molding.

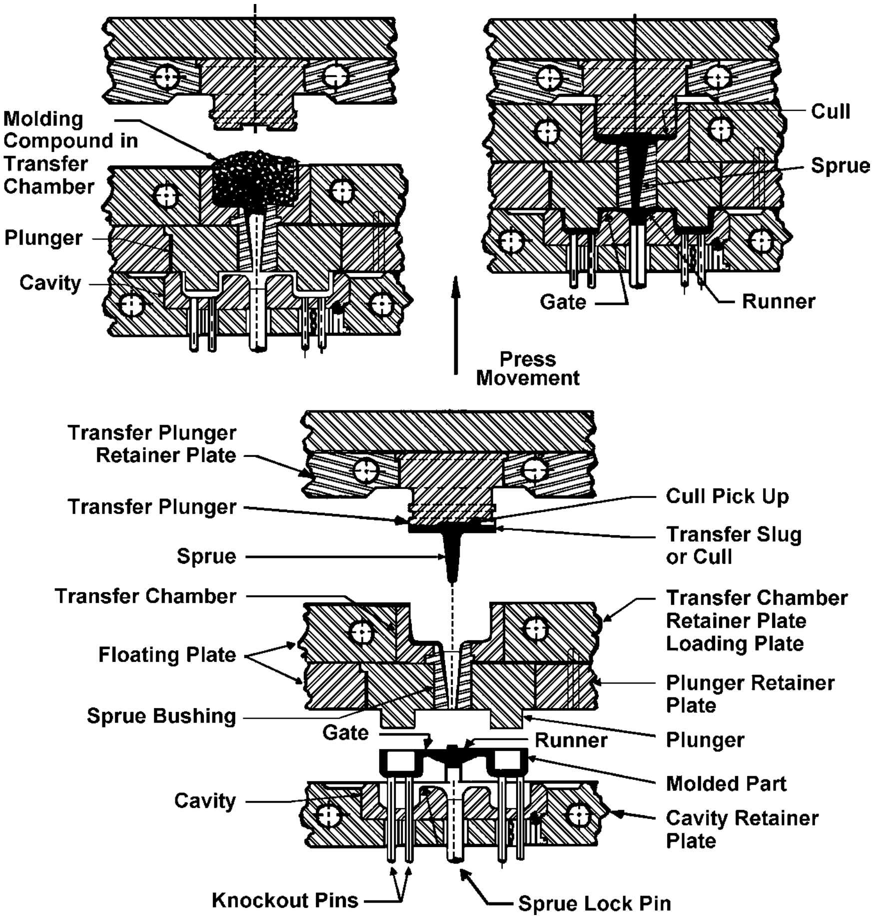


Figure 4.85. Schematic drawing of a pot-type transfer mold.

4.6.3 Plunger Molding

In the plunger molding (also called auxiliary ram transfer) process, an auxiliary ram exerts pressure on the molten plastic for transfer to the mold cavity (Fig. 4.88). The pressure forces the preheated material through runners into the closed two-plate mold cavity. This process is mostly conducted in semiautomatic closed presses.

The basic steps of plunger molding are similar to those of pot molding. After the plunger has been withdrawn and the mold is opened, the molded part can be removed in one piece with the runners and the cull attached. The length of the total plunger molding is shorter than pot molding because the removal of the sprue, runners, and the cull do not require a separate operation. The mold temperature, pressure, and dwell must experimentally be determined for each part and resin type.

4.6.4 Screw Transfer Molding

In this process, the plastic is heated and melted in a screw and then dropped into a pot of an inverted plunger mold (Fig. 4.89). The molten polymer is transferred to the mold by the same procedure as shown in Fig. 4.86. The screw transfer method and the sequence of the operational steps are depicted in Figs 4.89a and b. Screw transfer molding is an excellent process for full automation.

Screw transfer presses are capable of preparing shots from 50 to 2,500 g. Certain requirements must be met to control the heating of the resin adequately. The compression ratio (ratio of the shallowest to the deepest depth of flight) of a thermoplastic screw is much larger than that of a thermosetting resin. The length to diameter ratio is also considerably larger for thermoplastics. The mechanism of operation of the screw is similar to that of injection molding (see Section 4.4).

4.6.5 Types of Transfer Molds

There are three popular designs of transfer molds: loose-plate, integral, and auxiliary molds. The loose-type molds can be classified into manual and semiautomatic types based on the manner of mounting and mold operation.

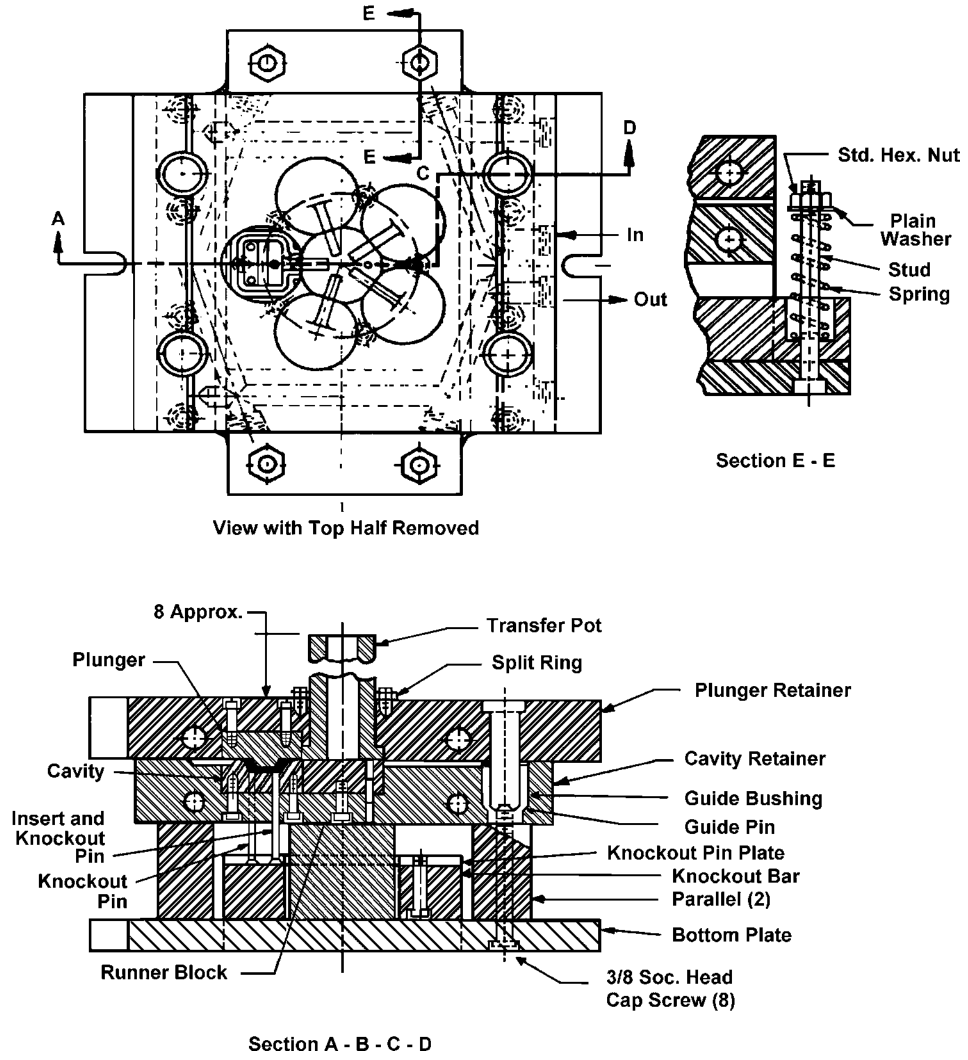


Figure 4.86. Design of a plunger-type transfer mold.

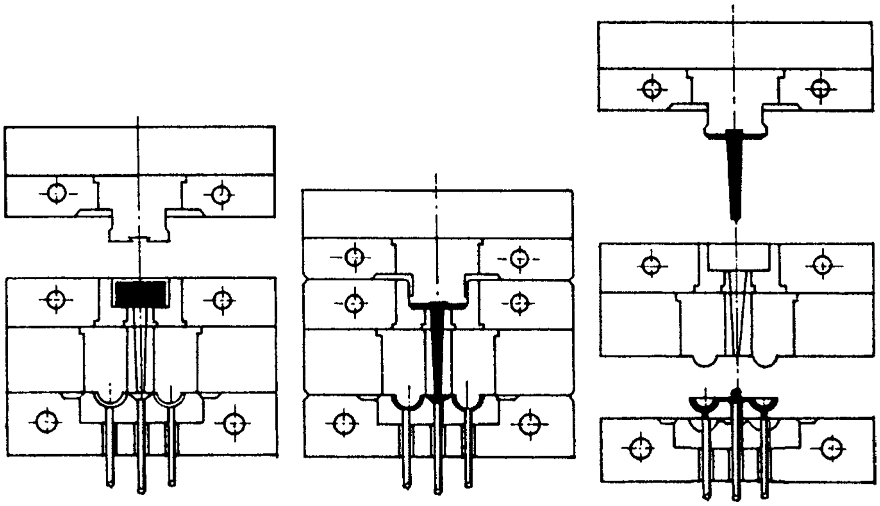


Figure 4.87. An illustration of the cycle transfer molding.

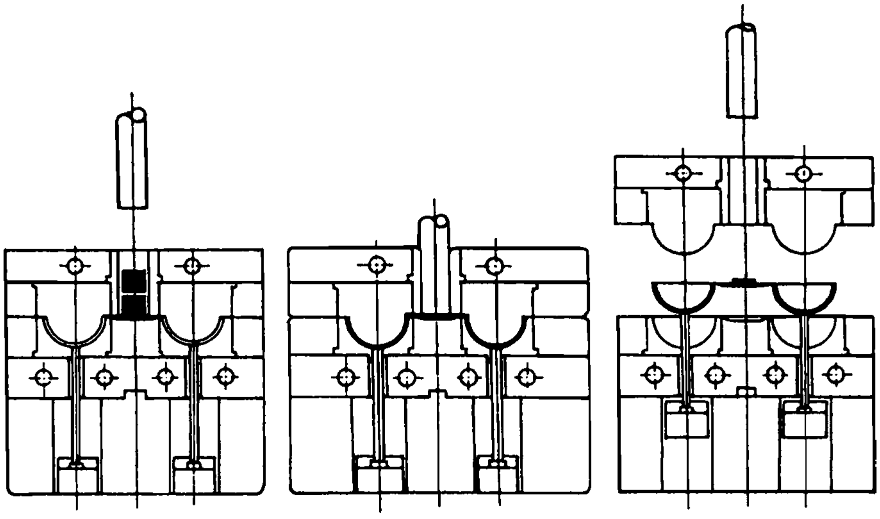


Figure 4.88. Schematic drawing of the plunger molding process.

Figure 4.90 illustrates one of the simpler manual transfer molds, which is particularly helpful when the molded piece contains a group of fragile inserts that traverse across the part. The mold is comprised of a plunger, a loose plate with bored through holes in its perimeter, and the cavity. The chamber above the loose plate forms the pot.

Figure 4.91 illustrates a semiautomatic floating plate (loose-plate) mold. The floating plate is a permanent component of the press. It has an opening at its center that will accommodate different size pots and plungers that are needed to fabricate different parts. The floating plate moves either by hydraulic or pneumatic force or by bolts/latches that are built into the mold. An important advantage of these molds is their low cost.

An integral mold comes equipped with its own pot and plunger (Fig. 4.92) and can be designed for manual or semiautomatic operation. The self-containment feature increases the efficiency of the mold because the design of the material transfer pot can be optimized with respect to specific cavity. The pot could be located above or below the mold. The molten plastic may flow through a sprue-runner-gate to enter the mold or the sprue can be placed inside the cavity, as is the case in the mold shown in Fig. 4.92.

Auxiliary-ram molds (Fig. 4.93) are "integral" in that the plunger action takes place using a separate double-acting cylinder that is installed on the press head. The cylinder/plunger system may be mounted on the bottom press platen within the ram, or on the tie rods or side column of the press. These methods of mounting and the corresponding molds are referred to as top-ram, bottom-ram, or side-ram. Auxiliary-ram molds provide the highest productivity and lowest mold cost. Material losses in the runners, sprue, and cull are minimized.

It is hard to compare the general benefits and shortcomings of the auxiliary-ram methods because of the strong impact of the design and the method of operation. The top-ram design is difficult to operate (load resin and eject part) due to space limitations. The bottom-ram type is easier to load because the transfer well is readily accessible when the mold is open. The molding cycle tends to be longer because the mold has to be completely closed prior to actuation of the plunger. The side-ram is less popular and is primarily used when the part design requires its ejection at the parting line.

4.6.6 Transfer Molding of TPEs

Generally, these polymers have relatively high melting points and high melt viscosity, and low critical shear rate, which renders it suitable for the slower processing rates of transfer molding techniques.

4.6.6.1 Mold Design

To minimize pressure and heat losses, the runners should be round and as short as possible. Another preferred choice is trapezoid runners that are easy to machine and provide the same amount of resistance to flow as round runners. They should blend smoothly into the gates, without abrupt cross-sectional changes. The runner's length should be reduced and its diameter increased when the thickness of the molded part increases. A runner

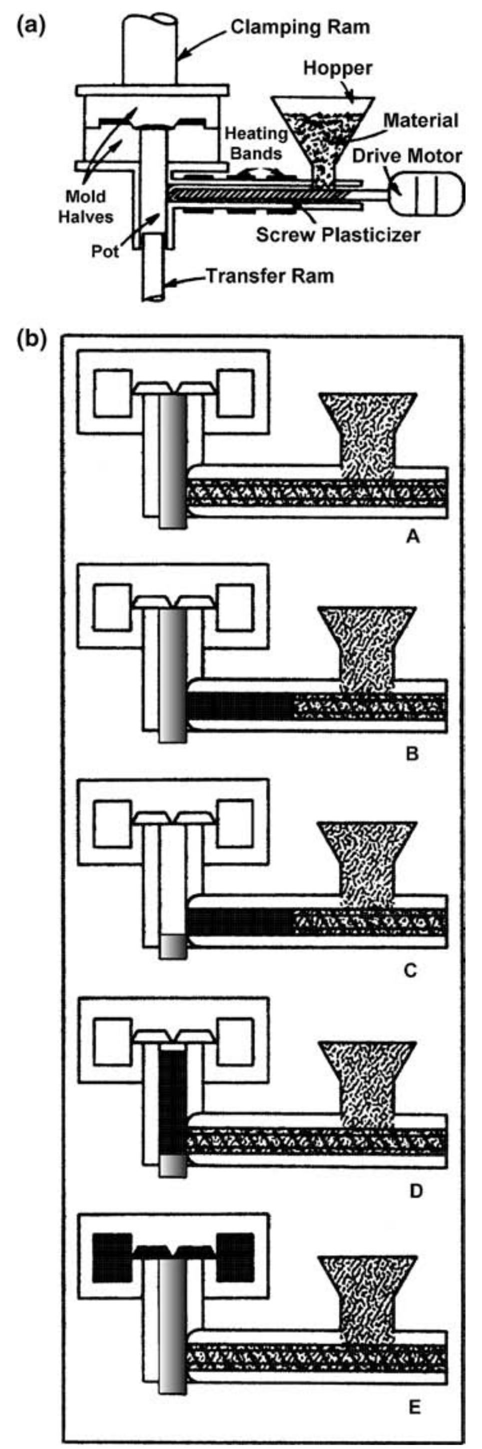


Figure 4.89. Schematic drawing of the screw transfer process: (a) sequence of the screw transfer process; (b) sequence of the screw transfer process; A—Melting of resin in the screw; B—material builds up at the end of the screw and drives the screw backward; C—after the shot is prepared, the ram lowers to open the transfer pot; D—the screw moves forward to press the melt into the pot; E—transfer ram advances through a bottom-transfer molding to fill the mold.

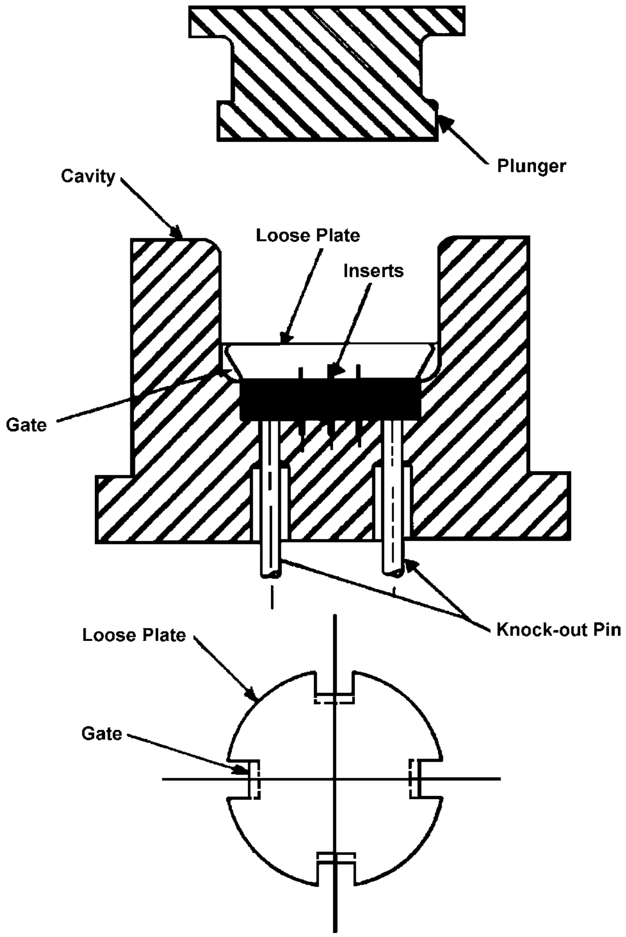
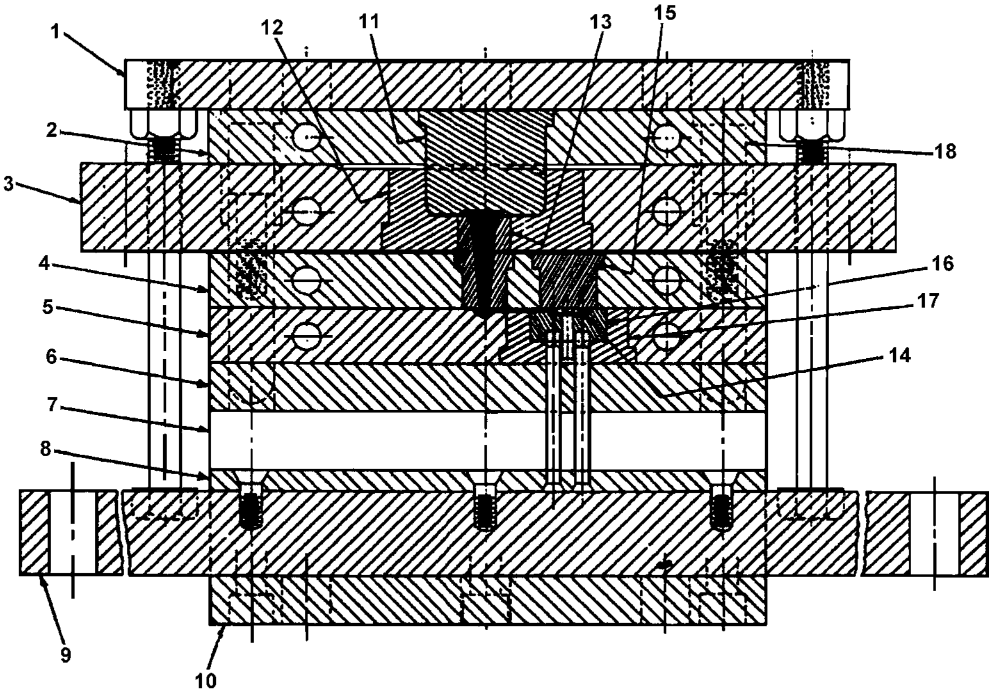


Figure 4.90. Design of manual loose-plate transfer mold.

diameter of at least 6 mm is required for a 10 mm thick part. Thicker parts require runners that are 50–100% larger in diameter than the thickness of the part. As in injection molding, pressure drop and material loss are determined by the length of the runners. In multi-cavity molds, balanced or lateral runner layout can be selected (see Section 4.5 for more explanation). A balanced runner provides an equal flow path between the sprue and all cavities. This means that the resin that reaches every cavity undergoes the same pressure drop and residence time.

All corners and edges must be generously rounded (minimum radius 2 mm or 0.08 in.) to avoid stress concentration in the molded liner. Fitting liners that contain sharp corners may fail at these locations in chemical service after multiple temperature cycling. Unrounded liners may fail because of stress concentration that occurs by the hindrance of resin flow during the transfer operation and subsequent shrinkage during the cool-down.



1. Top Plate
2. Upper Force Plate
3. Floating Platen
4. Force Plate
5. Cavity Plate
6. Backing-up Plate
7. Parallel
8. Pin Plate
9. Knock-out Bar
10. Bottom Plate
11. Upper Force
12. Loading Chamber
13. Sprue Plug
14. Molded Article
15. Force
16. Cavity
17. Chase
18. Guide Pin

Figure 4.91. Design of semiautomatic floating-plate mold.

Shearing of the molten plastic should be minimized to keep the stress concentration low. This is accomplished by designing the gate thickness equal to the wall thickness of the liner at the gate. Demolding becomes difficult when the gates are very small. Molten polymer may degrade mechanically due to abrupt changes of flow direction or cross-sectional changes in the gate areas. Diaphragm gates are preferred whenever possible, otherwise rectangular tab or fan type gates that are well flared in the mold cavity should be chosen.

In general, gates should be located at spots in the part that do not experience high impact or stress. Noncritical areas along the weld line are acceptable positions for the gates. The location of the gate should be such that minimal or no finishing is required and close to or at the thickest section of the part to reduce sink marks. Gate location should be at the center of a rotosymmetric part and, in all cases, consistent with the position of the vent.

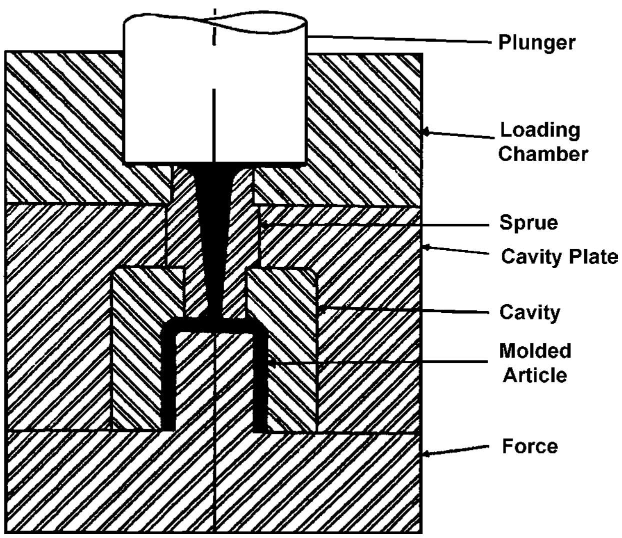
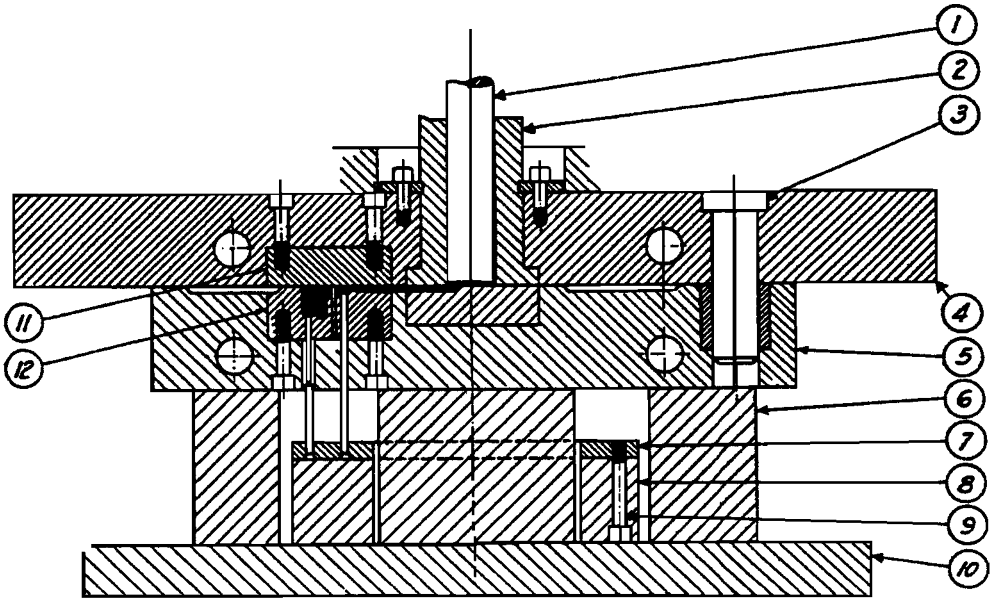


Figure 4.92. Design of integral transfer mold.

Improper venting of the mold can damage the part. Venting the mold prevents corrosion damage to the mold, allows complete filling of the mold, and the production of parts with high strength weld lines. Adiabatic compression of the molten resin in the mold can raise the temperature significantly to about 800°C (1,470°F) [66], which would rapidly degrade any thermoplastic.



1. Plunger
2. Loading Chamber
3. Guide Pin
4. Force Plate
5. Cavity Plate
6. Parallel
7. Pin Plate
8. Knock-out Bar
9. Pin-plate Screw
10. Bottom Plate
11. Force
12. Cavity

Figure 4.93. Design of auxiliary-ram mold.

4.6.6.2 Operation of the Mold

The operations of mold and melt removal from the oven and melt transfer should be conducted as rapidly as possible to prevent premature cooling of the melt. Thermoplastic elastomers have fairly high viscosity and require relatively long transfer time. To avoid premature cooling and freezing prior to the completion of transfer, mold temperature should be maintained at above the melting temperature of the polymer.

After the melt transfer has taken place and the mold has been filled, a hold-up time under pressure is required. This time allows shrinkage to take place while the resin is being cooled. The hold-up time allows stress relief in areas where shearing may have taken place. Cooling proceeds under pressure until the gate has been frozen, beyond which point no further pressure need to be applied until demolding occurs. Figure 4.94 illustrates an example of a transfer molding cycle for a typical thermoplastic.

4.6.6.3 Transfer Molding Process Variables

The important variables of transfer molding are the polymer type, melt temperature, pot hold time,

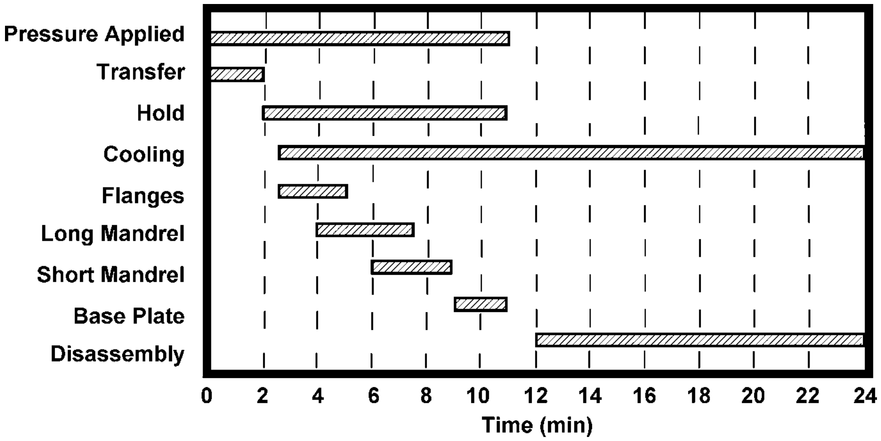


Figure 4.94. A typical transfer molding cycle.

transfer pressure, transfer rate, hold-up time in the filled mold, and the mold cooling. These variables are briefly reviewed in this section.

Viscosity of the molten polymer has a great influence on the transfer rate into the cavity. Temperature changes can alter polymer viscosity as long as it has sufficient thermal stability in the given temperature range. Cleanliness of the melt can affect the quality of the part and thermal stability of the molten resin.

The choice of temperature is significant because a small increase can have a substantial effect on reducing melt viscosity. Temperature uniformity of the molten resin is a common requirement regardless of the type of resin or part design. Screw plastification is more effective than the melt pot method due to the static nature of the latter and poor thermal conductivity of TPEs. Melt pots require significantly longer heat up time for the polymer to reach transfer temperature. There will always be a temperature gradient between the melt near the wall and the cooler material at the center of the pot.

After the molten polymer has been stored in the pot and reached the required temperature, it is transferred into the mold cavity under positive pressure. The pressure and rate of transfer are the significant variables of the process. Maximum flow rate (transfer rate) can be increased by enlarging the gate or increasing the temperature, which helps raise critical shear rate. In transfer molding, pressure is used as the independent control variable because most presses are not equipped with speed controllers for the hydraulic piston. The general range of transfer pressures at which most thermoplastics approach critical shear rates is 15–25 MPa (2,185–3,625 psi). Filling the mold in the "super shear" mode results in adverse effects on the properties of the molded part.

Pressures above 15 MPa (2,185 psi) help fill the mold before its components such as the mandrel and casings begin to cool down. Above 25 MPa (3,625 psi) melt pressure, the mold part may crack at the gate. The equipment should allow control of transfer rate and transfer pressure. Once the filling is nearly complete (90–95%), the transfer pressure should be lowered to half to two thirds of its initial value to avoid stress concentration in the gate area. The pressure profile has to maximize hold pressure for packing without crack formation at the gate [67].

Cooling of the filled mold is accomplished by ambient or fluid coolant such as compressed air and should take place slowly at a controlled rate. Low thermal conductivity of thermoplastics does not permit rapid cooling. The mold cooling should be begin at positions farthest from the gate and proceed slowly. A frozen front forms that moves towards the gate during cooling [66]. This approach allows addition of molten resin to the mold to compensate for the volumetric shrinkage, thus eliminating sink marks and shrinkage voids. Premature gate freezing or pressure release leads to void formation.

4.7 Blow Molding

Although blow molding of plastics dates from about 1880, rapid developments in machinery and technology only began in the late 1930s, virtually contemporaneously with the introduction of polyethylene. Blow molding is a relatively low-pressure process, using only 1% or less of the pressure levels employed in injection molding. This requires a low melt viscosity, produced by high shear rates and temperatures.

4.7.1 Blow Molding Processes

Blow molding is a process for converting thermoplastics into hollow objects. Like injection molding, the process is discontinuous or batch-wise in nature, involving a sequence of operations that culminates in the production of a molding. This sequence or cycle is repeated automatically or semiautomatically to produce a stream of molded parts.

The blow molded parts are formed in a mold that defines the external shape only. As the name implies, the inner shape is defined by fluid pressure, normally compressed air. In this respect, blow molding differs radically from many molding processes where both inner and outer forms are determined by mold members. The major advantage is that the inner form is virtually free of constraints because there is no core to extract. The main drawback is that the inner form is only indirectly defined by the mold, so high precision and independent internal features are impossible. This has a bearing on wall thickness, which can never attain the consistency and accuracy of a full-mold process such as injection molding.

Blow molding is now a highly developed process with many variant forms (Fig. 4.95). At its most basic, the process involves melt processing a thermoplastic into a tube that is generally referred to as a *parison*. While still in a heated ductile plastic state, the parison is clamped between the halves of a cooled mold, so that the open top and bottom ends of the parison are trapped, compressed, and sealed by the

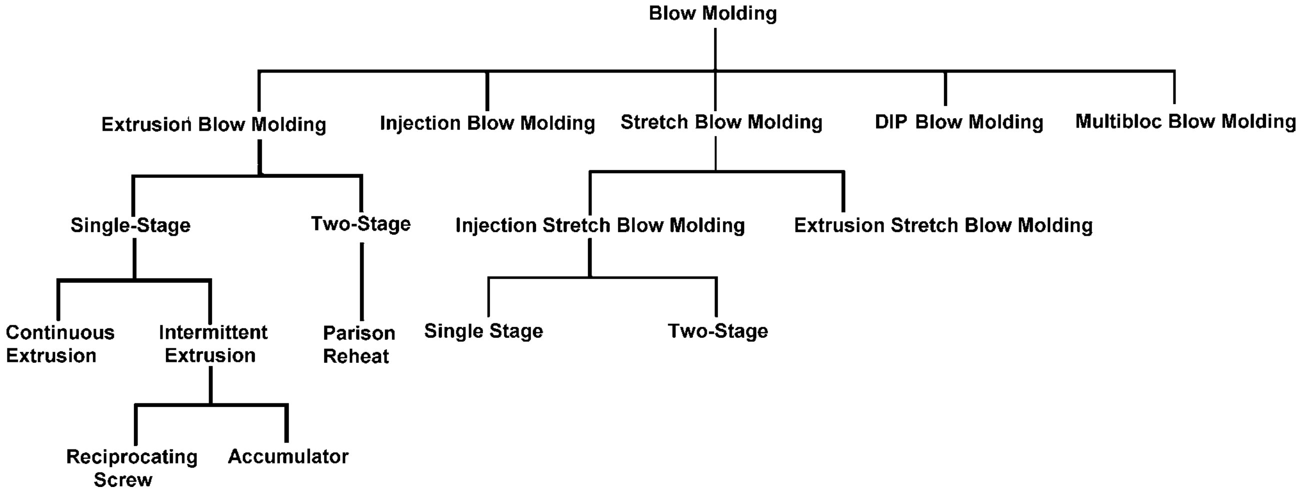


Figure 4.95. Blow molding processes.

mold faces. A blowing tube is also trapped in one of the parison ends, creating a channel through which air pressure is introduced within the sealed parison. Air pressure causes the parison to expand like a balloon, so that it takes the form of the mold cavities. Contact with the cooled mold chills the thermoplastic to its solid state, so the form is retained after the mold is opened and the part removed.

The many variations of the blow molding process are discussed later in this chapter, with an emphasis on those most important for processing thermoplastics. Two features, the extruder and parison head, are common to many blow molding processes and will be discussed separately.

4.7.1.1 The Extruder

Most blow molding processes begin with an extruded tube or parison. The extruder is of the single-screw type and follows the general principles described in Section 4.3.2 for an extruder for thermoplastics. The screw should have a length/diameter ratio of 24:1 to 30:1 or more. Screws at the high end of this range are preferable. The compression ratio should be about 3.5:1. A grooved barrel inlet improves extruder efficiency when working with thermoplastics. Melt temperatures depend on the type and grade of PP and, in particular, on the melt flow index.

4.7.1.2 The Parison Head

The *parison head*, sometimes called the *die head* or simply the *die*, is a specialized form of tubular extrusion die. Its function is to deliver a straight parison in the correct diameter, length, wall thickness, and at the correct temperature for blow molding. Prior to being clamped in the mold, the parison is suspended unsupported in free air. To avoid undue deformation, it is necessary to extrude the parison vertically downwards. The blow molder extruder is almost always arranged in a horizontal attitude, so the first task for the parison head is to turn the melt flow stream through a right angle. This is difficult to achieve in a way that meets the essential requirement for a constant flow rate at every point in the annular die gap. A second and related requirement is that the parison should carry as little evidence as possible of the weld line formed when the melt stream from the extruder flows around the torpedo. Many parison head designs have been evolved to deal with these problems. The example shown is known as the cardoid type (Fig. 4.96) [68]. Head design has benefited from computer analysis of the internal flow channels, which has removed much of the trial and error and given a greater assurance of success.

A further problem is one shared with pipe and tube extrusion dies. This is the difficulty of ensuring that the torpedo and mandrel remain coaxial with the die without dividing the melt stream with mechanical supports. The example shown in Fig. 4.96 uses no support in the melt stream, relying instead on an accurate seating between the torpedo and the housing. The parts need to be relatively massive for this design to be sufficiently rigid. Smaller torpedoes will need support in the melt stream and here the challenge is to minimize the formation of weld lines in the parison. Such supports include spider legs, staggered spider legs, breaker plates, screen tubes, and spiral mandrels. The problem is a difficult one

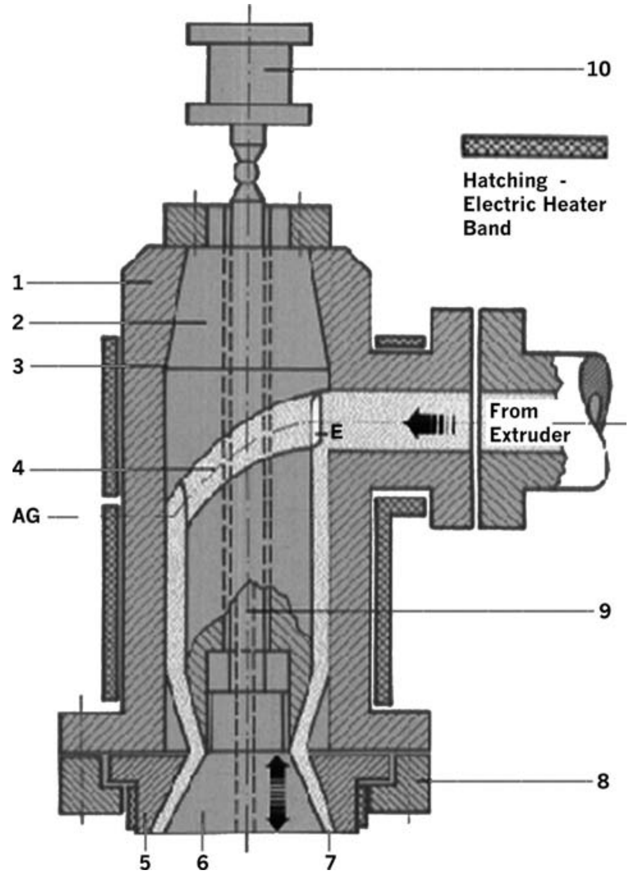


Figure 4.96. Typical parison head.

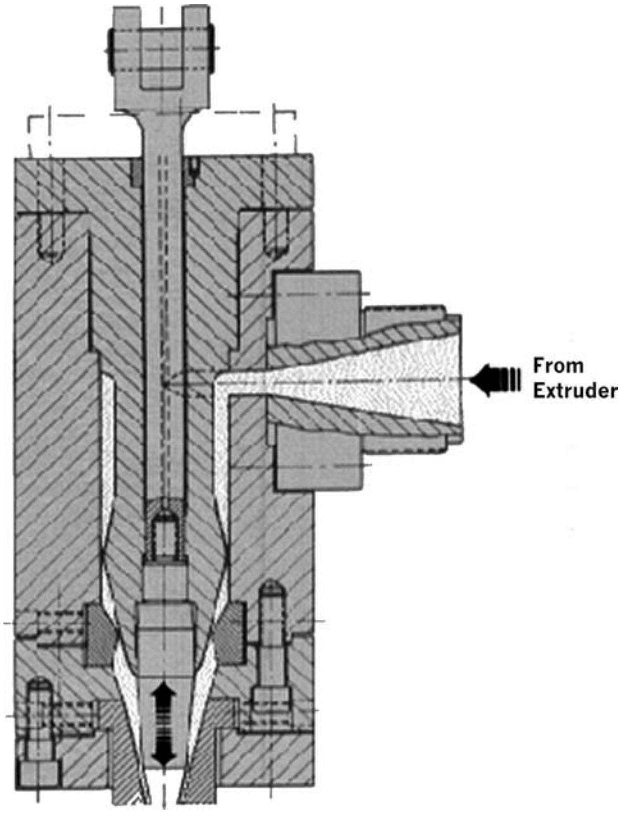


Figure 4.97. Principle of parison wall thickness control by axial movement of the mandrel.

and, in the worst case, the weld lines show up as local variations in the parison wall thickness.

The basic parison is a tube, which, in principle at least, has a constant wall thickness at all points around its circumference and along its length. In practice, circumferential thickness may vary as a result of weld lines, or if the mandrel is not truly coaxial with the die. Thickness along the parison length may vary due to tensile thinning caused by the weight of the dependent parison. However, the ideal parison with a constant wall thickness is not necessarily the optimum for blow molding. Even simple molded shapes encompass considerable variations in profile. For example, the body of a bottle is much greater in diameter than the neck. For some containers, there may be several significant variations along the axis, and the effect is usually pronounced in technical blow moldings. If such articles are blow molded from a parison of constant wall thickness, then the finished molding will be thinner where the parison has to expand the most and thicker where it has expanded the least. In most cases, the ideal is a finished product with a constant wall thickness at all points. To approach this ideal, a parison is needed in which the wall thickness varies along the length so that it is thickest where it must expand the most. This is achieved by parison programming or profiling.

The usual way to do this is by moving the mandrel in an axial direction relative to the die (Fig. 4.97) [68]. If both the die and the mandrel are provided with conical outlet features, this movement will increase or decrease the annular die gap between the two. The mandrel movements are controlled by a servo system acting on a pre-programmed thickness profile. The system may include a feedback loop to adjust parison profiling in response to screw speed variations in the extruder.

The concept is difficult to apply to the conical melt flow passage in variable die heads, but it can be taken to mean those zones in which melt passage thickness is substantially the same as the die outlet gap.

4.7.2 Extrusion Blow Molding

In extrusion blow molding, an extruder feeding a parison head is used to produce a parison as a

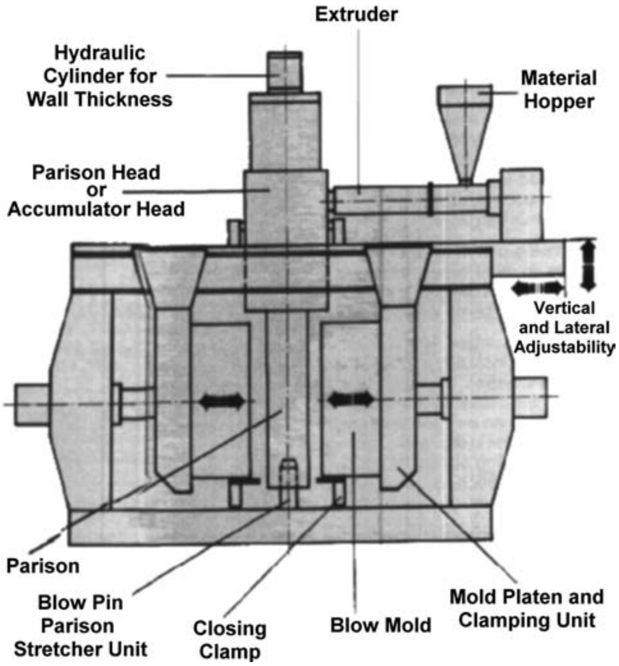


Figure 4.98. Typical extrusion blow molding machine.

precursor or preform for the molding process. The configuration of individual machines may vary greatly but some essential elements can be distinguished (Fig. 4.98) [68]. The extruder and parison head are arranged to extrude a parison vertically between the two halves of a blow mold. The mold halves are clamped to platens that are linked to a mold closing and clamping device. A blow pin is provided to inject air under pressure into the parison. Because blow molding is conducted at relatively low pressures, the construction of the machine and mold can be much lighter than is required for injection molding. Consequently, machines, and particularly molds, are much cheaper than those used in injection molding. Machine production rates can be increased by using multiple molds or multi-cavity molds with multiple parisons.

These general principles apply to a number of distinct extrusion blow molding processes which are described in the following sections of this chapter.

Single-stage extrusion blow molding produces a blown article in a single integrated process cycle. Blow molding immediately follows parison extrusion and relies on the melt condition of the parison for the deformation and flow necessary to take up the shape of the mold. There is no reheating of the parison before molding. The principal variants are the continuous extrusion and the intermittent extrusion processes. Extrusion in this distinguishing sense applies to extrusion of the parison rather than the operation of the extruder.

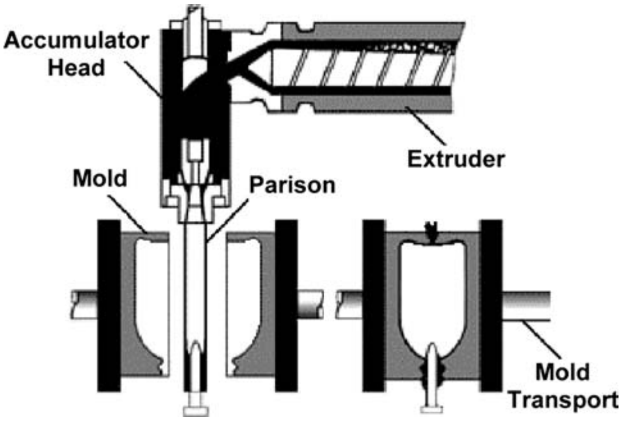


Figure 4.99. Basic extrusion blow molding process.

The *continuous extrusion* blow molding process is the most widely used for working with thermoplastics. In this process, the parison is extruded continuously from the parison head, between the open mold halves (Fig. 4.99) [69]. When the required length of parison has been produced, the mold is closed, trapping the parison, which is severed by a hot knife. Land or pinch-off areas on the mold compress and seal the upper and lower ends of the parison to make an elastic air-tight object. Compressed air is introduced through the blow pin into the interior of the sealed parison, which expands to take up the shape of the mold cavities. The cooled mold chills the blown object, which can then be ejected when the mold opens.

The blowing air can be introduced in a variety of ways. In the simplest case, the parison is extruded downwards so that the open end slips over a blow pin. Alternatively, the blow pin can be introduced from above the mold after the parison is severed, or blow needles can be built into the mold, where they pierce the parison as the mold closes.

Relative movement between the parison head and mold is necessary so that parison extrusion can proceed continuously while the mold is closed. This is achieved in many different ways. The mold may be lowered, moved aside laterally, or swung aside on an accurate path. Alternatively, the extruder may be moved while the mold remains stationary. Often, two molds are used in a shuttle arrangement, so that one is open for parison extrusion while the other is performing the blowing cycle. One method of mold movement results in very high production rates. In such machines, generally known as *wheel* *machines*, a number of molds are mounted on a rotary table. Movement of the table carries the closed mold away and presents a new open mold to the die head, allowing extrusion to continue.

Except for special cases such as the shuttle and wheel machines, the extrusion rate of the parison must be synchronized with the blow cycle for a single mold. This may involve a relatively slow extrusion rate, running the risk of thinning the parison as it stretches under its own weight. For this reason, continuous extrusion blow molding is best suited to thermoplastics with a high melt viscosity or high melt strength or to short or thin-wall parisons.

In *intermittent extrusion* blow molding, the parison is extruded from the parison head discontinuously. When a parison of the required length has been produced, extrusion is interrupted until the next parison is required for the subsequent blowing cycle. This makes it unnecessary to have relative movement between the die and mold. The process is generally used to make larger blow moldings like drums or automotive fuel tanks. These articles require large and heavy parisons which, when extruded normally, sag and thin down under their own weight. Intermittent rapid extrusion reduces this tendency, and it is achieved either by reciprocating screw or accumulator means.

Intermittent extrusion blow molding is best suited to long or heavy parisons and to thermoplastics with a low melt viscosity or low melt strength.

Reciprocating screw intermittent extrusion blow molding machines use an extruder unit in which the screw is capable of axial as well as rotational movement. The function is virtually identical to that of the injection unit on an injection molding machine, except that the blow molding unit functions at a lower melt pressure and flow rate. The parison is prepared in two steps:

- In the melt preparation phase, the screw rotates heating and melting the material, which is conveyed along the screw flights to the forward end of the screw. The extruder die block is closed by a valve, so the accumulating melt forces the still-rotating screw back against a controlled resistance until sufficient melt has accumulated to make the next parison. At this point, screw rotation stops
- In the parison extrusion phase, the extruder die block valve is opened and the screw performs the action of a ram by moving forward in the axial direction without rotating. This forces the accumulated melt at the forward end of the screw through the parison head, where it is extruded at a relatively high flow rate. In practice, the flow rate is limited by the onset of shear phenomena such as sharkskin and melt fracture.

Intermittent accumulator extrusion blow molding machines use a normal axially-fixed continuously operating extruder to prepare the melt. The accumulator is a heated reservoir where the melt is temporarily stored in the intervals between parison extrusion. The parison is extruded by a ram acting on the stored melt. This means that the melt volume in the accumulator fluctuates in a cyclic manner. It is substantially empty immediately after the parison is extruded, then it gradually increases during the blowing phase, reaching a maximum immediately before extrusion. Accumulators introduce a number of problems. They increase the heat history of the melt, and they involve valves and complex flow paths that offer flow resistance and may also lead to difficulties with cleaning and even degradation. Accumulators should be designed on the FIFO principle; the first material in must be the first out.

Blow molding accumulators take one of two forms. The separate accumulator is a heated chamber, which is an integral part of the blow molding machine. The capacity of such a chamber can be very large and can, if necessary, be served by several extruders. The other type of accumulator is built into the parison head (Fig. 4.100). This takes the form of an annular ram that surrounds the mandrel and torpedo. The construction of the parison head becomes quite complicated and there is the potential for melt leakage and degradation between the moving parts, so design and engineering must meet high standards. The shot volume available from an accumulator parison head is limited by practical considerations of head size and construction.

Two-stage extrusion blow molding treats the parison as a true preform by separating the functions of parison preparation and blow molding. Parisons are produced by conventional tube extrusion methods. The tube is cooled and cut into parison lengths that are stored before being reheated and blow-molded in the normal way. The reheating process can be selective, leading to a degree of control over the wall thickness in the blown article. The reheating process also tends to relax stress in the parison, resulting in a stronger product. However, the process has a number of disadvantages. The polymer heat

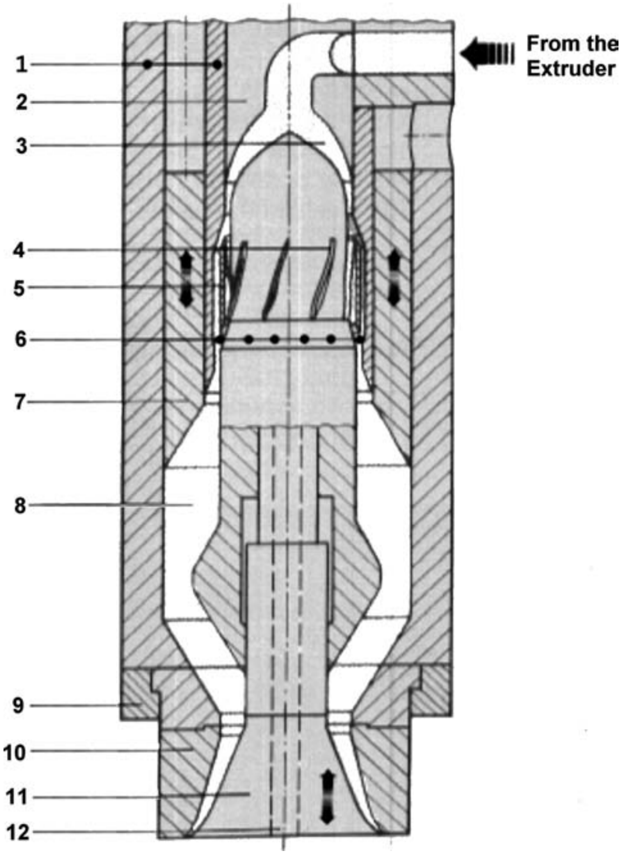


Figure 4.100. Example of accumulator parison head.

history is increased by the use of two heating cycles, energy use is increased, and costs arise from the storage and handling of parisons. The process is not suited to high production speeds and is little used.

4.7.3 Injection Blow Molding

The injection blow molding process uses injection molding rather than extrusion to produce the precursor; it is generally known as a *preform* rather than a parison. The injection blow molding machine has an integral injection unit and a multi-impression mold assembly in which the mold cores are mounted on a rotary table. The cores double as blowing pins and index in 120° steps between injection, blowing, and ejection stations (Fig. 4.101) [70]. Station one is the preform injection mold where the preform is formed over the core pin. The preform has a hemispherical closed end. The other end is an open bore, formed by the core pin. External details, such as the thread and neck flange for a screw-top container, are directly produced by injection molding. While the preform is still hot and plastic, the injection mold is opened and the preforms, still on the core pins, are rotated to station two, the blowing station. Here the preforms are enclosed within the blow mold, and the molding is produced by introducing blowing air through the core pins. The blow mold is then opened, and the finished articles, still on the core pins, are rotated to an ejection station where they are stripped off. The machine has three sets of core pins, so that the three stages take place simultaneously.

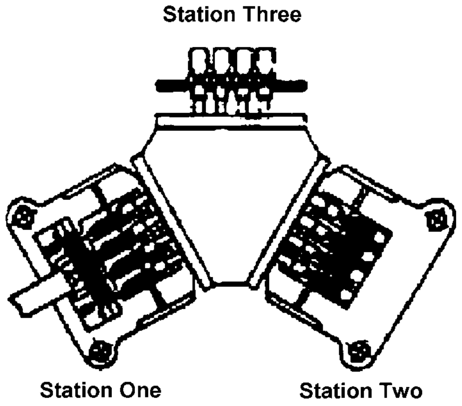


Figure 4.101. Injection blow molding stations.

The injection blow molding process has a number of advantages. The preform can be injection molded in a profiled shape that corresponds to the requirements of the blow mold form. The neck form is molded in its entirety at the injection stage, resulting in a quality and precision that is superior to a blow-molded neck. There is no pinch-off scrap to be removed and recycled and no bottom seam. There are some drawbacks too. The process is difficult to use with high melt viscosity materials. Integral handles, view stripes, and multi-wall constructions are all impractical.

4.7.4 Stretch Blow Molding

Stretch blow molding processes are designed to produce biaxial orientation in the blown article. Conventional blow molding imparts a degree of circumferential orientation, caused by the expansion of the parison into the mold cavity, but there is little or no axial expansion and, correspondingly, no axial orientation. Stretch blow molding provides for axial orientation by stretching the preform axially before or during blowing. This is normally accomplished by means of a stretch rod that is advanced axially inside the preform at a controlled rate. The disadvantages are that the process is more critical and complicated than conventional blow molding, and the capital cost of equipment is high.

Stretch blow processes cannot produce containers with integral handles. Stretch blow molding may be performed by injection or extrusion means.

Injection stretch blow molding processes use hollow preforms produced by injection molding. The preform is short and thick-walled relative to the finished blown article. The neck profile complete with screw thread is entirely formed by injection molding and is not modified by the blowing process. The other end of the preform is closed and typically dome shaped.

The design and precision of the preform has a critical influence on the degree of orientation and quality of the blown article. The actual wall thickness and any profiling will depend, of course, on the shape and size of the blown container. Like other preform processes, the finished blown article is free of seams, flash, and pinch-off scrap, and is characterized by precise neck dimensions. The injection molded preform may be converted to a blow molding either by the single-stage or the two-stage process.

In the *single-stage* injection stretch blow molding process, the preform injection molding step is integrated with the stretch blow machinery. The machines are generally arranged for rotary operation, so that the preforms pass directly from the injection molding station to a thermal conditioning station and thence to a stretch blow molding station (Fig. 4.102) [71].

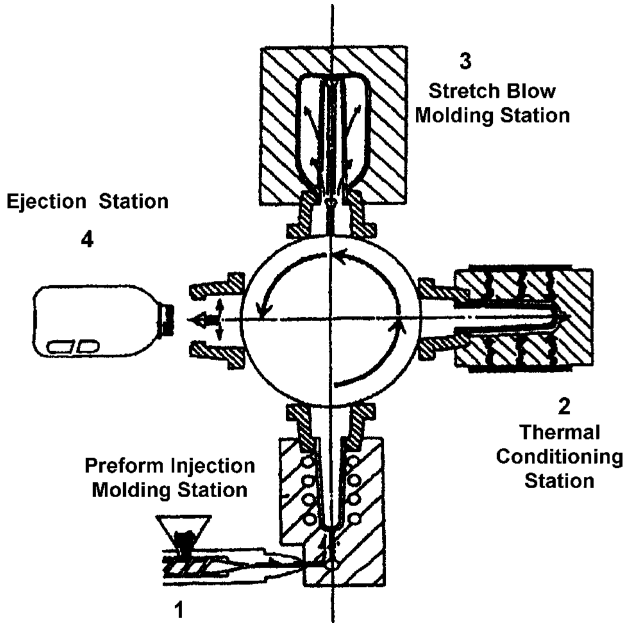


Figure 4.102. Single-stage injection stretch blow process.

The thermally conditioned preform is transferred to a blow mold and stretched and oriented axially by an internal stretch rod, either immediately prior to, or simultaneously with the blowing operation that provides radial stretch and orientation.

The *two-stage or reheat injection stretch blow molding* process completely separates the preform injection molding operation from the blow molding operation. Indeed, the two operations may be carried out in different locations by different manufacturers, with a substantial time interval between them. On the other hand, the process involves two heating operations, resulting in a greater energy use and increased heat history in the polymer. Another disadvantage is the need to store and handle preforms.

Before being blown, the preforms must be reheated from room temperature, then thermally conditioned and stretch blown in a manner similar to the single-stage process. The two-stage or reheat stretch blow machine is usually arranged for rotary high speed continuous operation.

Extrusion stretch blow molding is a two-stage process using two mold/mandrel sets—one for preblow and the other for final blow. An extruded parison is first pinched off and blown conventionally in a relatively small preblow mold to produce a closed-end preform. The preform is then transferred to the final blow mold where an extending stretch rod within the blowing mandrel bears on the closed preform end to stretch it axially. The stretched preform is then blown to impart circumferential stretch. Standard blow molding machines can be converted for extrusion stretch blow molding.

4.7.5 Dip Blow Molding

The dip blow molding process bears some resemblance to injection blow molding in that it is a single-stage process performed with a preform on a core/blow pin (Fig. 4.103) [68]. The difference is in the way the preform is made. The process uses an accumulator cylinder, which is fed by an extruder. The cylinder has an injection ram at one end while the other is a free fit over the blow pin. The blow pin is plunged into the melt so that a neck mold on the pin seals the end of the accumulator cylinder. The injection ram is advanced to fill the neck mold; then the blow pin is withdrawn at a controlled rate so that it is coated with a melt layer extruded through the annular gap between the pin and the accumulator cylinder. The thickness of the coating can be varied or profiled to an extent by varying the speed of the blow pin and the pressure on the injection ram.

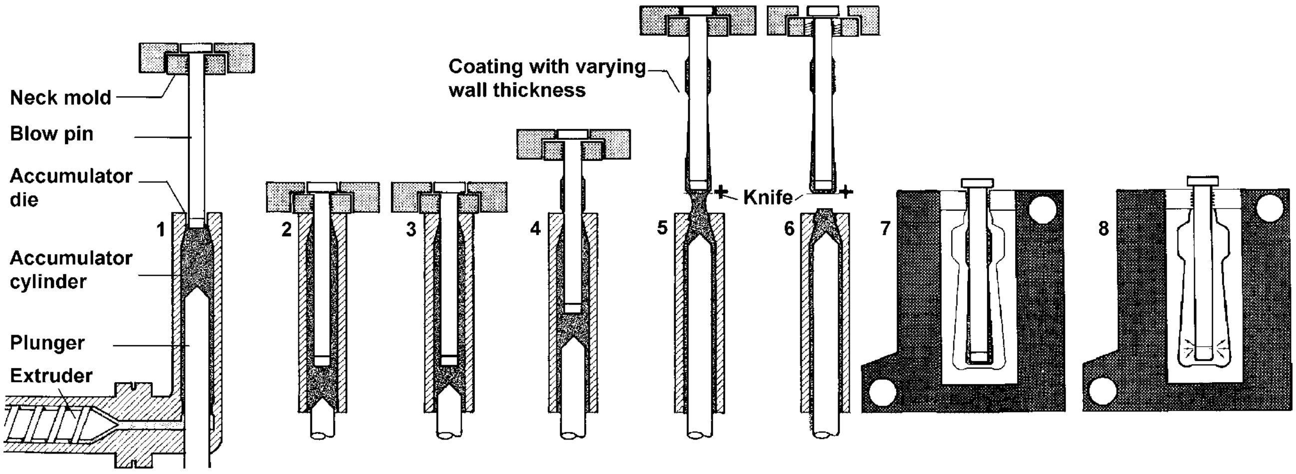


Figure 4.103. Stages in the dip blow molding process. 1—Accumulator filled; 2—Blow pin inserted; 3—Neck mold filled; 4—Blow pin partially withdrawn; 5—Blow pin fully withdrawn at variable speed; 6—Preform trimmed; 7—Preform clamped in mold; 8—Preform blow molded.

After trimming, the preform is blow molded in the same manner used for injection blow molding.

4.7.6 Multiblock Blow Molding

The multiblock process is used for high volume blow molding of very small containers such as pharmaceutical vials. A multi-cavity mold is used with an extruded parison whose circumference approaches twice the total width of the closely spaced cavities. Before the mold closes, the parison is stretched and semi-flattened laterally so that it extends across the full width of the cavities (Fig. 4.104) [68]. The process is usually combined with blow/fill/seal techniques.

4.7.7 Coextrusion Blow Molding Techniques

Just as in the production of film, coextrusion is now an essential technique in the production of high performance blow molded containers. The parison is coextruded with a number of different layers, each of which contributes an important property to the finished package.

Coextruded blow moldings commonly include from two to six layers, although more can be accommodated if necessary. The construction usually includes one or more barrier layers. These are polymers with a particular resistance to the transmission of water vapor or gases such as oxygen or carbon dioxide. Examples are polyamides, polyvinylidene chloride (PVDC), and ethylene vinyl alcohol (EVOH). Their presence greatly enhances the performance of the blow molding as a package for foodstuffs and other critical products.

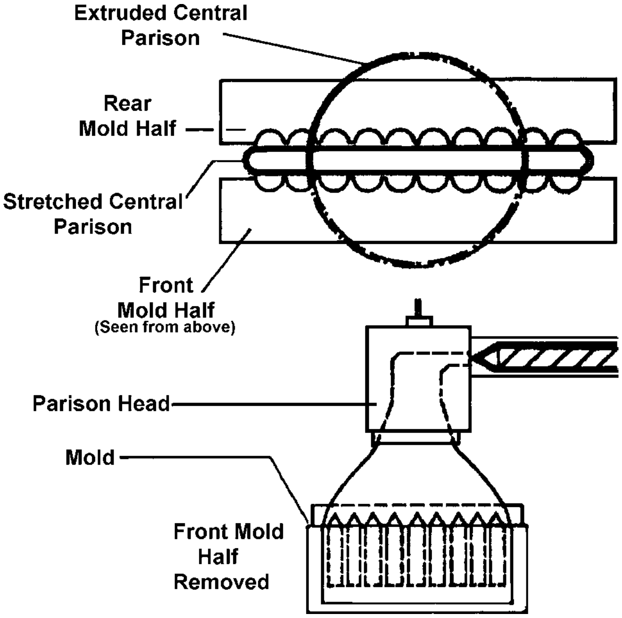


Figure 4.104. Multiblock blow molding process.

4.7.8 Sequential Extrusion

Sequential extrusion blow molding is a special multi-material technique (Fig. 4.105) [68] used for the production of technical articles. The different materials are chosen typically to contribute complementary mechanical properties and are present in distinct sequential zones in the finished part. Normally two materials are used but three or more are possible. The die head is served by separate external ram accumulators for each material. These are operated sequentially, typically in *A–B–A* sequence,

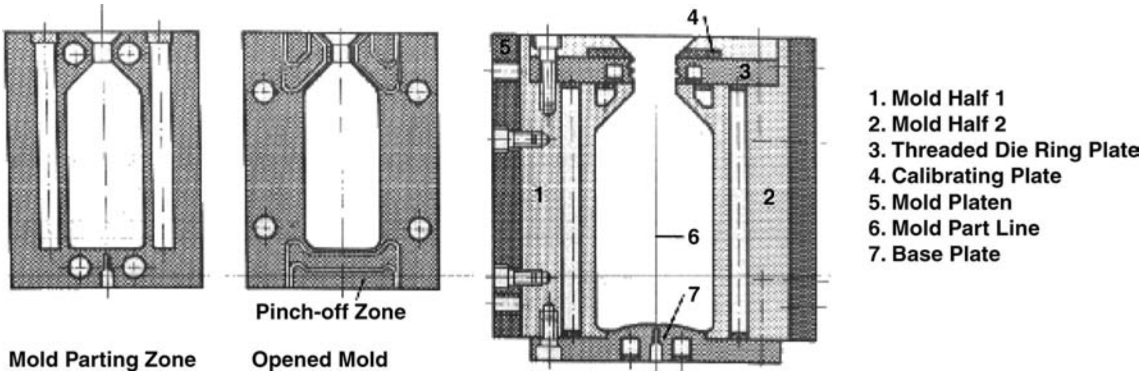


Figure 4.105. Principal features of an extrusion blow molding mold [1].

to produce a parison with three distinct material zones in axial succession. The parison is subsequently blow molded by normal techniques.

Because blow molding is performed on a cylindrical parison, the process is not well suited to the production of technical articles with complex forms that deviate substantially from the parison axis. Such forms can be produced by conventional blow molding, but only by using a large parison that, in its flattened form, blankets the complex mold cavity. The penalty for this is the formation of an excessive amount of pinch-off scrap.

Recent developments in parison handling equipment and in blow mold design now make it possible to manipulate a relatively small parison into the complex mold cavity. The result is a blow molding largely free of flash and scrap and offering considerable process savings. There are many such techniques, some of them proprietary property, and they are collectively known as *3D blow molding* (Fig. 4.106) [72].

4.7.9 Molds for Blow Molding

Essentially, the blow mold consists of two halves, each containing cavities which, when the mold is closed, define the exterior shape of the blow molding. Because the process produces a hollow article, there are no cores to define the inner shape. The blow molding process is carried out at relatively low pressures, so blow molds can be more lightly engineered than injection molds and are correspondingly cheaper and quicker to manufacture. Single-cavity molds are used when working with a single parison. When multiple parisons are in use, a number of single-cavity molds may be mounted on the machine platen, or the requirement may be met by a multiple-cavity mold. Mold details will vary considerably according to the geometry of the product and the blow molding process in use.

4.7.9.1 Basic Features

The mold consists of two halves that meet on a plane known as the *parting line*. The plane is chosen so that neither cavity half presents an undercut in the direction of mold opening. For articles of asymmetrical cross-section, the parting line is placed in the direction of the greater dimension. The two mold halves are aligned by guide pillars and bushings to ensure that there is no mismatch between the cavities. The parison passes across the mold in the axis of the cavity and is pinched and compressed between the faces of the closing mold at the neck and base regions of the cavity. These are known as the *pinch-off zones*. The base and neck regions of the mold are typically formed by separate inserted mold blocks. The mold includes channels for the circulation of cooling water.

4.7.9.2 Pinch-Off Zone

The pinch-off zone performs two functions. It must weld the parison to make a closed vessel that will contain blowing air, and it must leave pinched-off waste material in a condition to be removed easily from the blown article. To accomplish this, the pinch-off zone has a three-stage profile, consisting of pinch-off edge, pressing area, and flash chamber (Fig. 4.107) [68]. The pinch-off edge is flush with the mold parting line and forms part of the cavity periphery. The edge should be as narrow as possible depending on the material of construction. Steel (corrosion resistant metals for corrosive melts) edges can be from 0.3 to 1.5 mm (0.012 to 0.06 in.) wide; for softer materials the dimensions should be

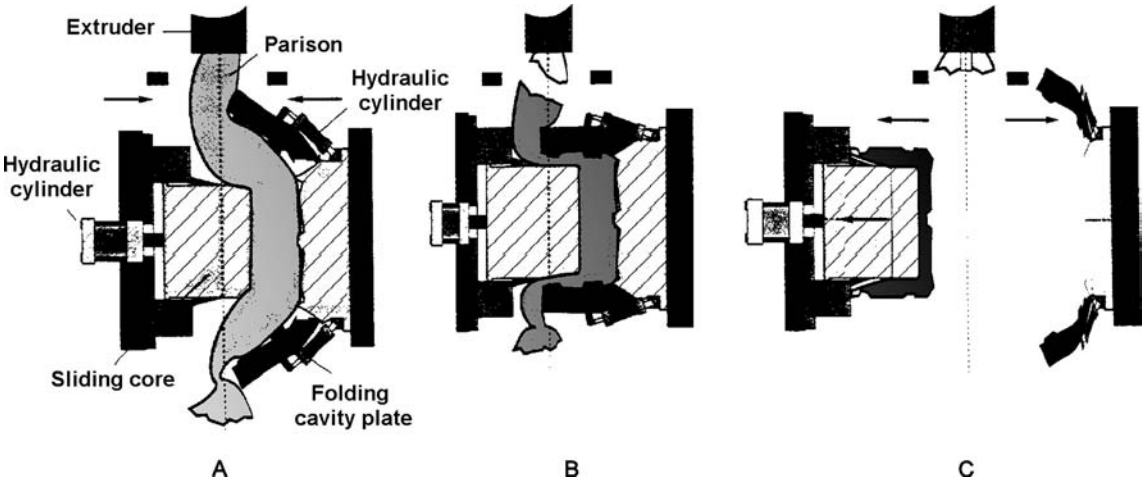


Figure 4.106. *Placo Process* for 3D blow molding. A—The mold begins to close on pre-pinched parison; B—mold fully closed with core forward and sidewalls hinged in; C—mold open and core retracted.

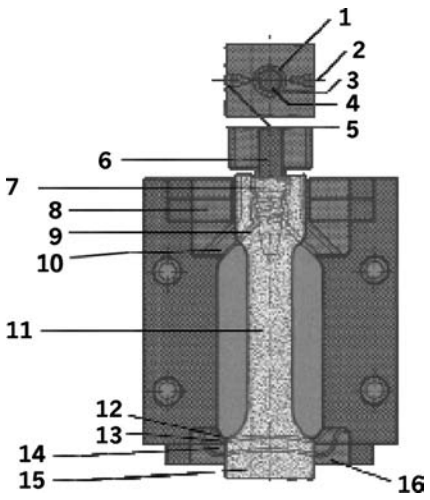


Figure 4.107. Pinch-off zones.

0.8 to 2.5 mm (0.032 to 0.10 in). The pressing area is recessed into the mold parting face by an amount depending on the parison thickness. Its function is to displace melt into the weld area to ensure a strong weld that is substantially equal in thickness to the blown wall thickness at the same point on the parison axis. The pressing area depth is typically determined by trial and error and is often given a ribbed surface to improve cooling of the waste material by increasing the area available for heat transfer. The flash chamber is recessed to a greater depth than the pressing area, typically to about the thickness of the parison. If it is made too deep, heat transfer will suffer and the parison scrap will cool too slowly. Its function is to limit the extent of the pressing area and so limit the force opposing mold closing. The steps between the different levels should be strengthened by angling the riser face by 30°–45° to the parting face.

4.7.9.3 Blowing and Calibrating Devices

The *blow pin* is the means by which blowing air is inserted into the parison through what will become a hole in the finished blow molding. In the case of a bottle (Fig. 4.108) [68], the blow pin is inserted through the neck before or after mold closing. The blow pin body has the secondary function of calibrating the bore of the bottle neck. If the blow pin is plunged into the neck after mold closing, it is possible to produce a flash-free bottle mouth. After the mold opens, the finished bottle is stripped off by retracting the blow pin through a stripper plate. The blowing pin contains channels for the circulation of blowing air and cooling water.

Many blow molded articles do not have an integral aperture that can accept a blow pin. In such cases, blowing air can be supplied through a blow needle that punctures the parison wall after the mold closes (Fig. 4.109) [68]. The needle can be advanced and retracted by means of an air or hydraulic cylinder and is located at a point close to a pinch-off edge. The parison is gripped by the mold at this point and so is unable to deflect away from the advancing needle point. The blow needle leaves a small witness hole, which can be sealed by a secondary operation.

4.7.9.4 Venting and Surface Finish

When a parison is blown, a large volume of air must be displaced from the mold cavity in a

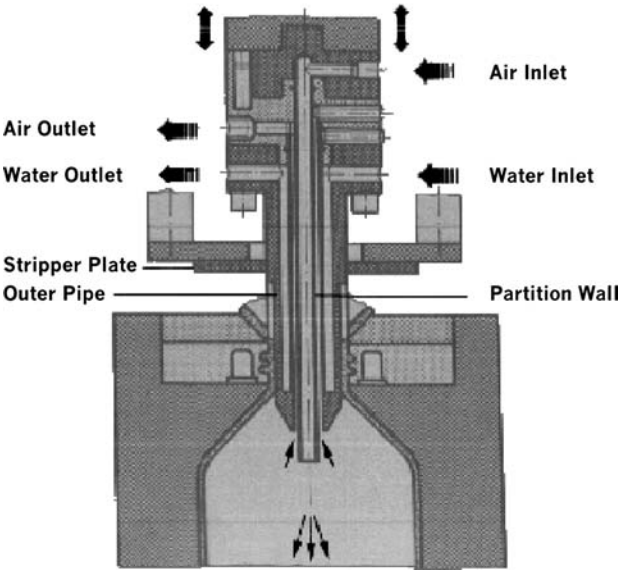


Figure 4.108. Example of calibrating blow pin.

short time. Because blowing is carried out at relatively low pressure, it is essential to provide venting to allow this air to escape without resistance. Unless a gloss finish is required on the molding, it is common practice to sandblast the cavity to a fine matte finish. This helps air to escape as the expanding parison touches the cavity face but it is not sufficient in itself. Vent slots may be cut at appropriate points into the mold parting face to a depth of 0.05–0.15 mm (0.002–0.006 in.), and venting can also be provided within the mold cavity by means of inserts provided with vent slots, porous sintered plugs, or by holes with a diameter not greater than 0.2 mm (0.08 in.). Such holes are machined only to a shallow depth and are relieved by a much larger bore machined from the back of the mold.

4.7.9.5 Cooling

Efficient mold cooling is essential for economical blow molding. Typically, up to 80% of a blow molding cycle is devoted to cooling. Molds are constructed as far as possible from high thermal conductivity alloys, and water cooling channels are placed as close as possible to the surface of cavities and pinch-off zones. Because blow molding is a relatively low-pressure process, the channels can be quite close to the surface and quite closely spaced before mold strength is compromised. The actual dimensions will depend on the material of construction but as a guide, channels may approach within 10 mm of the cavity and center spacing should not be less than twice the channel diameter. If the mold body is cast, the cooling channels can be fabricated in copper pipe to closely follow the cavity contours before being cast in place. If the mold is machined, channels will be produced by drilling and milling, and it is not usually possible to follow the cavity contours so closely. An alternative in cast molds is a large flood chamber. However, efficient water cooling requires turbulent flow and this may not be attained in a flood chamber or in large coolant channels. Many small channels are better than a few large ones. The cooling circuits will normally be zoned so that different areas of the mold can be independently controlled.

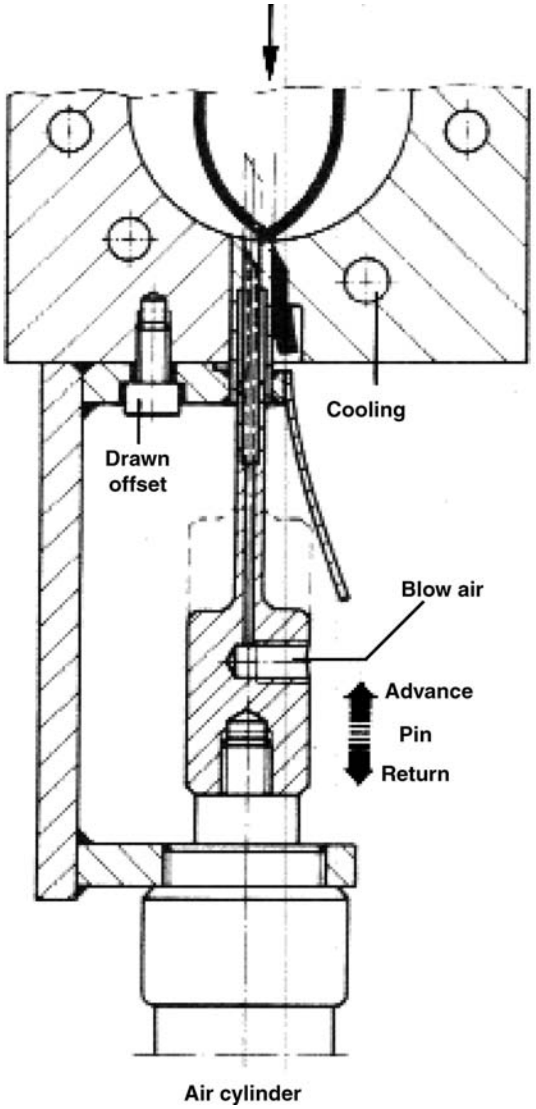


Figure 4.109. Example of blow needle.

4.7.10 Examples of Blow Molded Parts

A majority of blow molded parts have a multilayer construction to combine the properties of other plastics in a composite structure. The most common technique for producing multilayer sheet/film is coextrusion.

Coextrusion blow molding technology was employed [73] to produce corrugated tubing, pipe, and hose for applications that require flexibility and close tolerances such as in automotive industry. Composites of two or more layers formed the walls of these articles to take advantage of different materials. Tubing made by this technique has a high degree of flexibility, resistance to hydrolysis and bursting, and stability with respect to linear extension. For instance, in gasoline filler necks, it is important that the corrugated tubing have areas of great stretching stability and areas with reduced stretching stability, such as provided by this technology.

Monolayer hoses or pipes of two or more layers of polymers, which were compatible with each other or which required an interim tie layer, have been fabricated in many sizes, designs, and from many thermoplastics.

4.8 Rotational Molding

Rotational molding (also called *rotomolding* or *rotational casting*) is a process for manufacturing seamless hollow plastic parts for a variety of applications ranging from liquid storage tanks to containers of various shapes. Consumer products such as furniture, playground equipment, and toys are made by this technique. Rotational molding produces dolls, doll parts, sit-in and sit-on toys, and various sizes of heavy-wall balls.

The past decade has seen a large growth in the applications of rotational molding and lining technology. Along with this growth, interest has increased in understanding the complex technical aspects of this technique. Rotational lining is employed when the objective is to coat the interior of a metallic part, instead of manufacturing a plastic part.

Rotational molding (Fig. 4.110) involves the external heating of a thin-walled hollow metal mold containing a polymer powder. Heating occurs while the mold is rotated multiaxially. The powder melts and coats, or sinters, onto the interior wall of the cavity. The mold is then cooled which allows the part to solidify and crystallize in the case of thermoplastics. Finally, the part is removed and the mold is charged to repeat the cycle.

The rule-of-thumb for selecting rotational molding technology is part quantities of less than 25,000 per year and sizes larger than 200 l (530 gal). In the case of TPEs, smaller parts are also produced by this technology. It allows the production of parts with intricate geometry without imparting significant residual stresses or orientation to the part. These are the advantages of this process over blow molding in addition to its ability to fabricate larger parts. Rotomolding requires significantly smaller capital investment than injection and blow molding processes, thanks to its low-pressure requirement. Parts made by rotational molding often cost more than those manufactured by more conventional processes because of its relatively long cycle time.

Certain TPEs can be fabricated into hollow objects by rotomolding. They are, however, hard to mold due to their relatively high melting point and melt viscosity and usually only specific grades can be used for that. The TPEs reported to be processed by rotomolding include copolyester elastomers (COPE), olefinic thermoplastic elastomers (TPO), thermoplastic urethane (TPU), styrene-butadiene-styrene block copolymers (S-B-S), and styrene-ethylene-butylene-styrene block copolymers (S-EB-S).

4.8.1 Background

The modern day concept of rotational molding originated in the early 1900s. Today's technology resembles the *slush* molding process for fabricating hollow articles from polyvinyl chloride (PVC) plastisols in the late 1940s. Due to the absence of other suitable plastics, applications for rotational molding technology did not expand. Then polyethylene became available, which allowed the application of this technique in making parts for end uses where PVC was not economical. Large tank molding became a reality with the advent of modified and cross-linkable polyethylene in the 1970s.

Starting in the mid-1970s, more polymers became available including linear low density polyethylene, polyamides, PP, and polycarbonate. Almost 90% of the solid polymer consumed by rotational molding worldwide comprises of polyethylene [74]. The most suitable form of a plastic for rotational molding is powder or liquid form. This technique permits uniform wall thickness and higher thickness than blow molding. Undercuts, inserts, and ribs can be easily achieved in rotomolding. Thick corners are

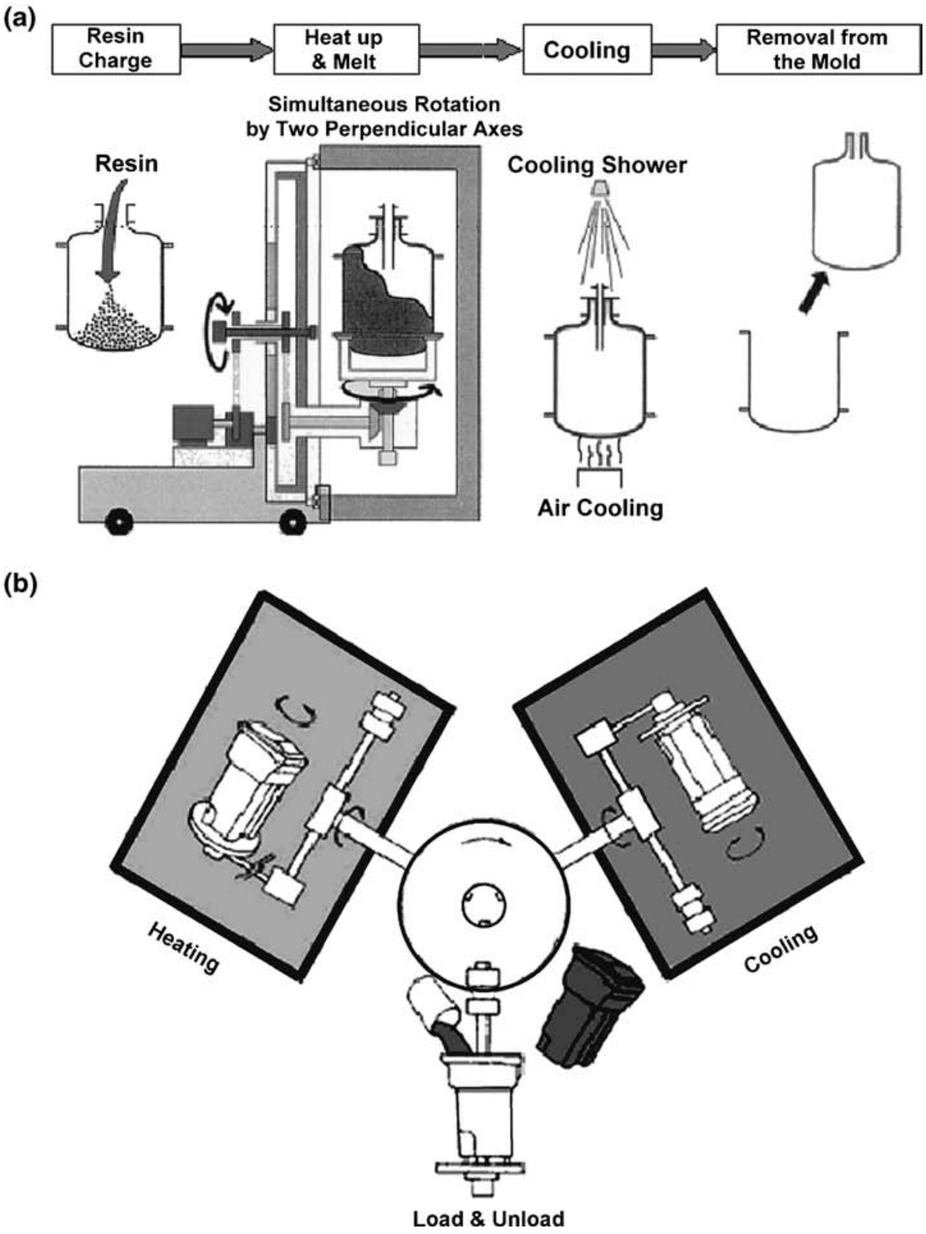


Figure 4.110. Schematic diagram of rotational molding process. (Courtesy Hanser Publishers).

obtainable by this technique compared to other hollow molding methods.

4.8.2 Basic Process Technology

Rotational molding is used to produce a broad array of seamless hollow plastic products. Except for permanent adhesion to the cavity wall, processing considerations in rotolining are otherwise identical to those in rotomolding. In this process, a premeasured amount of a plastic powder, granules, or liquid is charged inside a mold cavity. The mold is closed and heated in an oven while being rotated multiaxially (usually two axes). Figure 4.111 depicts a biaxial rotomolding machine. The major axis is the centerline of the arm of the mold. The minor axis rotates the mold perpendicular to the major axis. Typically, the minor axis revolves four times to every one time of the major axis. The basic steps of mold charging, heating, cooling, and part removal are shown in Fig. 4.111. In an alternative design, the molds undergo a "rock and roll" motion, rotating 360° around one axis and rocking about a perpendicular axis. In a majority of cases, the mold is heated by forced hot air. Open flame burners, as well as infrared, conductive, inductive, and dielectric heating techniques, have also been reported. The wall of the mold is usually heated to a temperature above the melting point of the polymer.

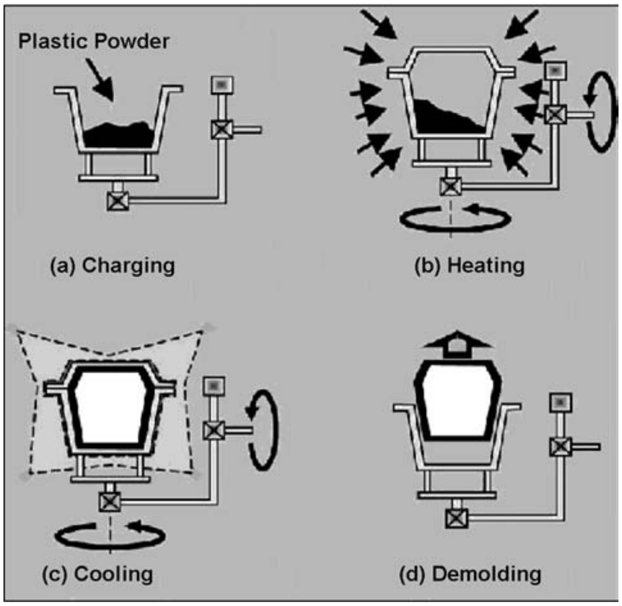


Figure 4.111. Biaxial rotomolding machine.

Heat transfer, from the hot air in the cavity and from the wall of the mold to the powder, melts the polymer which sticks to the hot cavity (Fig. 4.112). It results in the formation of an even coating on the interior wall of the cavity. The mold is cooled while it is rotated to retain the uniform wall thickness. Finally, after the polymer has solidified, the rigid part is removed from the mold. Volatile material formed during the heating period is removed from a vent port. The rotation rate, temperature, heating rate, and cooling rate are controlled throughout the process.

General advantages and limitations of the rotational molding process have been listed in Tables 4.20 and 4.21, respectively.

The rotomolding process is differentiated from *spin-casting* or *centrifugal casting* by its relatively low rotation speed that is usually in the range of 1–20 rpm. Rotation speeds range up to 40 rpm on the minor axis and 12 rpm on the major axis. These speeds are slow enough to prevent development of significant centrifugal forces.

The essential feature of centrifugal casting is the introduction of molten metal or plastic into a mold that is rotated during solidification of the casting. The centrifugal force shapes and feeds the molten material with great detail as the force of gravity drives the molten matter into the designed crevices and details of the shape. Centrifugal casting improves the homogeneity and accuracy in special circumstances. The process imposes limitations on the shape of castings, and is normally restricted to the production of cylindrical shapes.

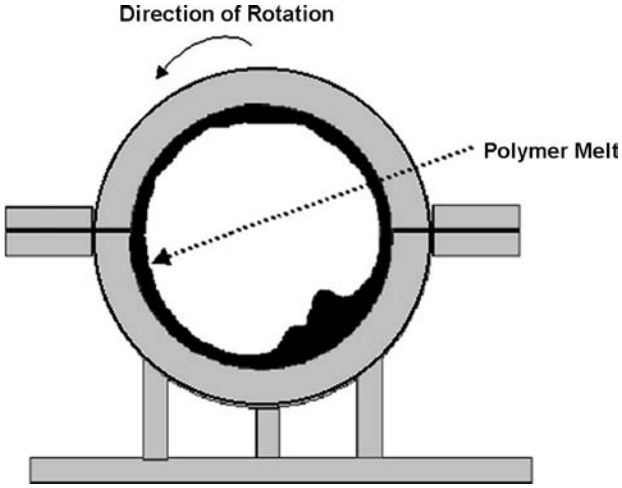


Figure 4.112. Schematic of adhesion of polymer melt to the mold wall and part formation.

The rotational molding process takes place in two stages. During the first stage the polymer melts, sinters, and densifies, while in the second stage the melt flows on the walls of the mold and fills all channels, undercuts, and other cavities in the geometry of the mold under shear stresses developed during the rotation. The main force acting on the polymer is gravity because, due to the low rotation speed, the centrifugal forces are negligible. The absence of significant shear requires high molding temperatures to reduce the viscosity of the polymer and expedite its mold filling action.

This method is ideally suited to the casting of spherical shapes, but the outer shape may be modified with the use of special techniques. Normally, metal molds are used and plastic is poured into the rotating mold that may spin about a horizontal, inclined, or vertical axis. The centrifugal force improves both homogeneity and accuracy.

Rotational molding of plastic foams (e.g., polyethylene) has become increasingly important due to its ability to obtain thicker walls with less weight increase, sound dampening, thermal insulation, and high stiffness. So far, rotomolding of TPE foams has been less commonplace than the foams of other thermoplastics. Foaming technology is discussed in Section 4.9.

4.8.3 Rotational Molding Equipment

The equipment for rotomolding is typically characterized by: (1) the weight of the maximum load that

Table 4.20. Benefits of Rotomolding Process

	Benefits
1	A hollow part can be made in one piece with no weld lines or joints
2	Simultaneous molding of different shaped parts
3	The molded part is essentially stress-free
4	The molds are relatively inexpensive
5	The lead time for the manufacture of mold is relatively short
6	Wall thickness can be quite uniform compared to blow molding or twin sheet forming
7	Wall thickness distribution can be altered without modifying the mold
8	Inserts are relatively easy to mold-in
9	Short production runs can be economically viable
10	It is possible to make multilayer, including foamed, parts
11	Low scrap rate
12	Low initial capital investment

Source: Reference [55].

Table 4.21. Limitations of Rotomolding Process

	Limitations
1	The manufacturing cycles are long
2	The choice of molding materials is relatively limited
3	Material costs are fairly high due to the need of special additive packages; moreover the material has to be ground to a fine powder
4	Some geometrical features, such as solid ribs, are difficult to mold
5	Sharp thickness variations cannot be easily accommodated; gradual transitions work best
6	Tight tolerances are hard to maintain
7	Wall thickness variation averages about ±10%
8	Molds must be designed using the proper shrinkage rate of the resin

Source: Reference [55].

can be supported by the arms, including the weight of the mold and the resin charge; and (2) by the diameter of the sphere of rotation by the mold. Rotomolding machines are capable of producing small objects like ping pong balls and large objects with a capacity of 4.5 metric tons weight and over 5.5 m (216 in.) mold swing that can fabricate large tanks (85,000 l or 22,500 gal).

Mold heating is usually done by hot air. The air can be heated by any means such as natural gas, oil, or electric sources. Some systems are heated by open flame, which is attractive for its lower tooling cost. Cooling is initially achieved by ambient or forced air, usually followed by water spray to achieve uniform cooling. An enclosed cooling chamber can be used optionally.

4.8.3.1 Batch Systems

This is the simplest and least costly form of the equipment but it requires the most labor. The mold is rolled into the oven for rotation and heating. Then it is moved out at the end of the cycle and another mold takes its place. The completed mold is transferred into the cooling station and, finally, the part is removed.

4.8.3.2 Carousel Machines

The most commonplace type of rotomolder is the *carousel* machine (Fig. 4.113) that has three stations or positions. It has a loading/unloading station, heating station (usually an oven), and cooling station. Cooling usually takes place in an enclosed compartment. The mechanism, as the name indicates, resembles that of a carousel. One or more spindles are connected at one end to a turret or central hub, and to one or more molds at the other end.

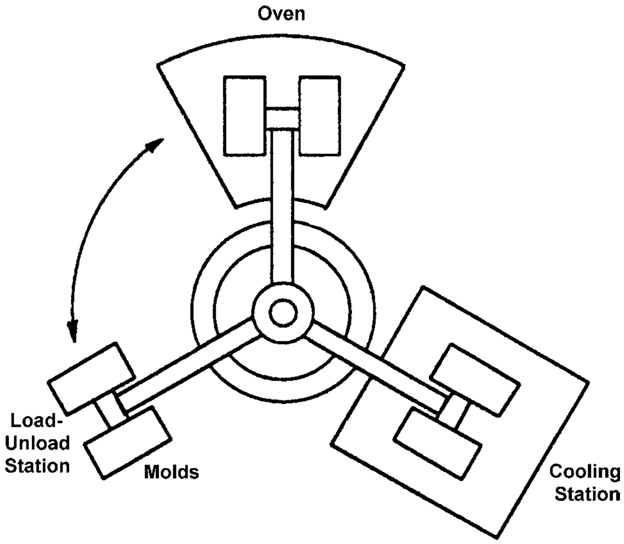


Figure 4.113. Schematic diagram of a carousel rotomolder.

A typical carousel can rotate a full circle freely. The spindles, or arms, are motorized and their motions are controlled independently of the central hub or the oven temperature and dwell time. Individual arms are simultaneously undergoing different phases. One arm is in the loading/unloading station, the second arm is rotating in the oven, and the third arm is in the cooling station. At the end of each cycle, the turret rotates 120° to move each mold to the next cycle. This means that no arm is idle at any time. Some units have more than three arms to increase productivity. More than one arm/mold can be in the oven with a multiple arm machine.

4.8.3.3 Shuttle Machines

Larger products, such as big containers, are fabricated in the *shuttle* rotomolder (Fig. 4.114) that generally operates in a straight line with the oven and the cooling stations at opposite ends. A movable mold cartridge holds the mold and the motors that drive its biaxial motions. The cartridge is mounted on a rail track that allows it to be rolled in and out of the oven. At the conclusion of the heating cycle, the mold is transferred into the cooling chamber. Another mold can be rolled into the oven to start the next heating cycle. By positioning the loading/unloading station between the cooling and heating stations on parallel tracks, transfer of molds occurs smoothly.

4.8.3.4 Clamshell Machines

The *clamshell* rotomolder is the third type of machine (Fig. 4.115). In this design, there is one arm, and the three stations are combined. Heating and cooling both occur in the same enclosure.

4.8.4 Equipment and Process Design

A number of factors should be taken into account in the design of a rotomolding process, regardless of the type of the rotational molding equipment. A list of the items to be considered is provided in Table 4.22.

Additional design information about the process can be found in a publication by the Association of Rotational Molders (ARM) titled, "Introductory Guide to Designing Rotationally Molded Plastic Parts." A number of often-overlooked considerations in designing a rotomolding process are listed in Table 4.23.

4.8.4.1 Molds

Molds for convection heating are relatively inexpensive; however, the cost is dependent on the type of plastics to be fabricated, processing temperatures, and the size, shape, and desired quality of the molded part. Multiple cavities are designed in the mold except for very large parts. The molds in this process are shell-like and are made from two, three, or more pieces for complex parts. The mold halves are retained together at the parting line by means of bolts or clamps. The mold is always equipped with a vent tube to equalize the internal pressure of the mold with the external environment. The location of the vent tube depends on the part design, although the fill port of the tank is often a good place to locate the vent.

Molds undergo a great deal of thermal stress because of cycling from room temperature to in excess of 400°C (752°F) for TPEs. The selection of the metal should take into account not only temperature, but also the corrosive nature of the degradation products of certain TPEs. The most common molds in the processing of the majority of thermoplastics,

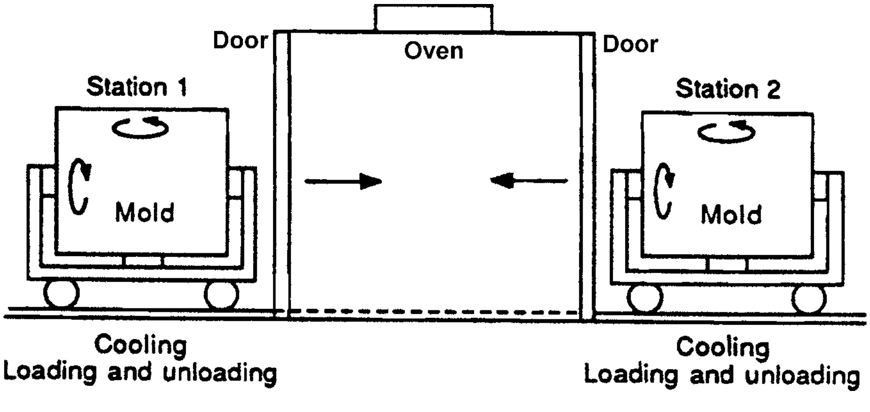


Figure 4.114. Schematic diagram of a shuttle rotomolder.

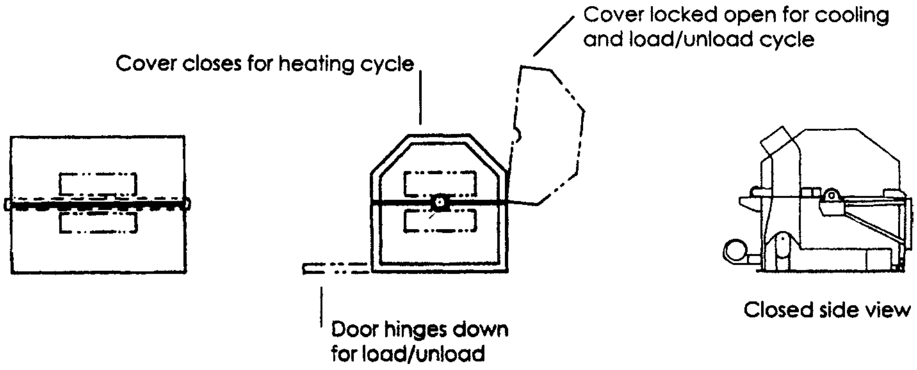


Figure 4.115. Schematic diagram of a clamshell rotomolder.

Table 4.22. Design Consideration for Rotomolding

Design Considerations	
1	Heat transfer of the mold and plastic materials
2	Parting line locations
3	Part size
4	Molding machine size
5	Mold weight and material on the arm
6	Shot size
7	Vent location
8	Fill ports
9	Mold clamping mechanism
10	Mold mounting mechanism
11	Construction material of the mold
12	The number of parts that the mold can make
13	Tooling construction
14	Color matching

Source: Reference [55].

Table 4.23. Guidelines for Rotomolding Process and Equipment Design

Guidelines	
1	Place the high stress away from parting lines
2	Design for very high coefficients of thermal expansion
3	Avoid designing flat surfaces and straight lines
4	Alter the deep pocket areas for better heat flow and thicker walls
5	Design in very high tolerances, larger than ARM recommendation
6	Put in a drop box to contain excess powder that may not fit in the cavity
7	Keep the component mount loads below 0.7 MPa (102 psi)
8	Keep inserts away from the sidewalls to allow proper material fill
9	For parts requiring good esthetics, keep parting lines above the normal level of eyesight

Source: Reference [55].

for example, PE are cast aluminum. Rapid heat transfer and low cost are their major advantages. Cast aluminum is sometimes porous and molds made from it can be easily damaged. This material is not suitable for most TPEs, due to the high temperature requirements of these polymeric materials.

Machined metal molds, especially aluminum, are used for applications that require extreme precision. Machined molds yield parts that are free of voids and surface porosity. Their use is limited to special cases due to the high cost of material and fabrication of these molds.

Sheet metal can be used to produce prototype and production molds. They are often used when a single cavity mold is required to produce large cavities. Sheet metal molds are frequently fabricated in-house by custom molders. The various pieces of the mold are welded together. Their advantages include lightweight and uniform thin walls. Electroformed or vapor-formed nickel is suitable for molding corrosive resins. These molds are unique in their capability to replicate fine surface details. Special construction material requirements related to the corrosive nature of degradation products of certain TPEs have been discussed in Section 4.4.8.

It is very important to consider the polymer that is going to be molded in rotomolding. Some materials are sufficiently flexible to allow some undercuts in the mold and still be easily removed. Other polymers shrink and still others require a light draft angle (1° or 2°) to allow release of the part.

The shrinkage rate of the polymer must be known in order to design tooling that is capable of producing parts that meet the specifications. Large flat surfaces are the most difficult to mold rotationally. Proper mold release techniques and internal air pressurization during cooling can minimize deformation of the flat surfaces. It would be best to design some type of stiffening into the flat sections. Contoured ribs or embossing are two examples of such designs. It is advantageous to design a convex mold to counter the tendency of flat plastic surfaces to cave inward. If aesthetics of the part permit, it would be helpful to put in "kiss-offs" which require a hollow insert on each half of the cavity (see Fig. 4.116) to form a support from one wall to another. The net effect is an increase in the modulus of the section containing the kiss-off areas, resulting is substantial stiffening. The recommended depth of the corrugations is four times the thickness of the part.

Mounting one mold on the arm is fairly straightforward. Multiple molds require careful design for mounting on a single spider. Improper mounting can result in an abnormally high rate of wear and tear on the mold and excessive flash formation on the part.

One of the most difficult maintenance issues in rotational molding is the parting line deterioration and flashing. There are steps to reduce this problem. Parting lines on sharp corners, along knife-edges or vertical lines should be avoided. Whenever possible, multiple pieces of the mold should be designed to use a slide or a hinge system to guide the opening and closing of the mold pieces. This design reduces the damage to the parting line and eases the operation of the mold.

A variety of clamps and quick release devices are available for holding the mold together but the best parting line is the pin-and-bushing type. It produces the cleanest parting line, but quick release clamps are appropriate when a clean parting line is not required. Some examples of parting lines are given in Fig. 4.117. Stepped and fabricated parting lines are less common than tongue and groove and pin and bushing types.

Rotational molding creates some unusual effects that are not encountered in other molding techniques. For example, outside corners of the part are thicker (Fig. 4.118) than the general thickness of the part because the resin powder accumulates in the corners of the mold. On the other hand, inside corners are thinner because the powder tends to fall away from the mold in these areas. The recommended corner radii (Fig. 4.118) help the uniformity of the part thickness. Altering the rotation speeds around the major and minor axis (discussed later in this chapter) can control wall thickness variations.

4.8.4.2 Mold Surface Preparation

The mold surface must be clean and free of chemicals and debris for a successful rotational molding and lining. A complete procedure includes multiple steps described here but the exact method depends on the type of resin, machine type, and the part. After a cycle or a production campaign has been completed, the inside surface of the mold must be degreased, followed by shot (grit) blasting. Afterwards, the mold is baked in a vacuum oven or under an inert gas such as nitrogen. This sequence removes the leftover resin, degradation products, and moisture from the mold.

4.8.5 Operation of Rotomolding Processes

In a typical rotomolding operation, the mold is charged with a determined amount of polymer powder, the mold pieces (halves) are assembled together, and the mold is put in an oven and rotated biaxially. The resin melts during the heating cycle, fuses, adheres to the wall of the mold, and forms the part. The mold is transferred into a cooling chamber where it is cooled down with air and/or water. At the conclusion of the cooling cycle, the mold is taken out and the finished part is removed.

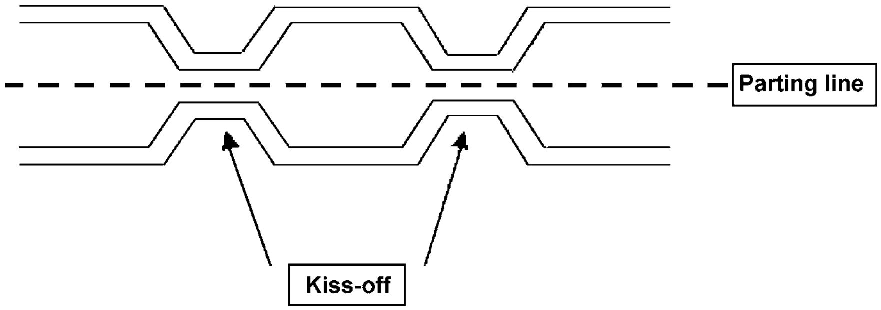


Figure 4.116. Cross-section showing two kiss-off areas.

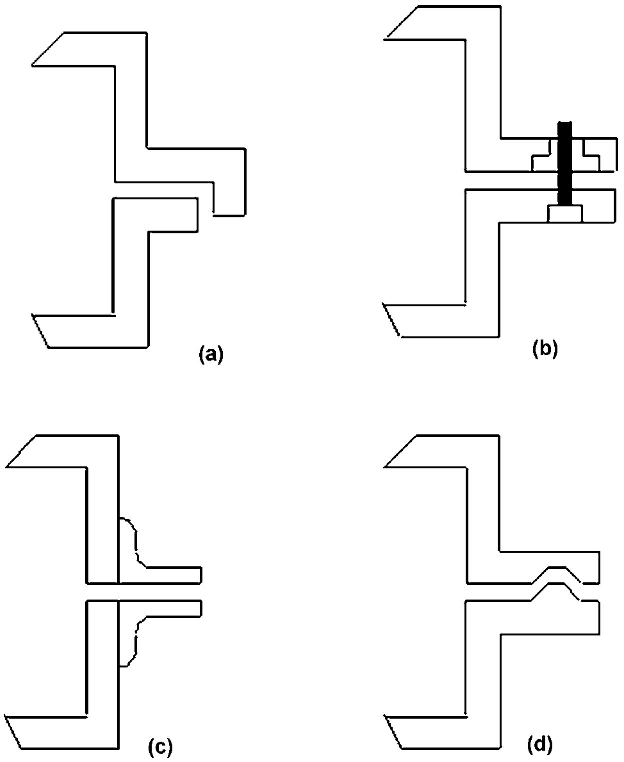


Figure 4.117. Examples of parting lines: (a) Stepped; (b) pin and bushing; (c) fabricated; (d) tongue and groove.

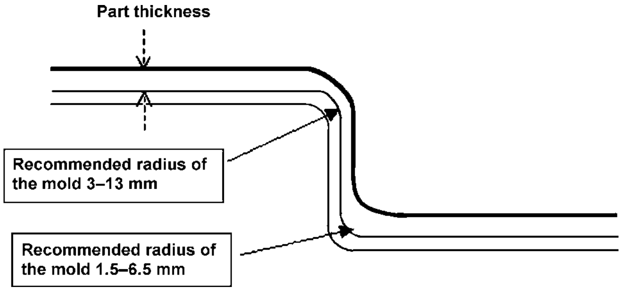


Figure 4.118. Part thickness and recommended radii in the corners of the mold.

The particle size of the resin is very important in the rotomolding process. Although an average particle size of 0.5 mm (0.02 in.) is an industry standard, smaller or larger particle sizes can also be processed.

Wall thickness can be decreased or increased by adjusting the amount of charge and the cycle time. Reducing the heat that is supplied to certain areas of the mold reduces the thickness of the part at those points. Areas that should be thinner can be shielded by insulation to reduce the build-up of molten resin. Conversely, extra heat is directed at the areas where more thickness is required. The distance between adjacent walls should be at least four times the wall thickness of the part to prevent bridging of the resin [75].

Surface texture can be controlled on the outside surface of the part because the molds are female. Rotationally molded parts generally have a good appearance on the outer surface without sink marks. Matte finish and grains can be readily obtained on the exterior part surface. A glossy finish is difficult to obtain and significantly increases the cost of the mold. Comparable parts with much smoother finish (gloss) can be obtained by injection molding.

The inside surface of the part is in contact with air. Cycle time and mold temperatures both affect the finish of the inside surface. Insufficient heat and cycle time leave some of the resin particles unmelted and result in a rough finish on both surfaces of the part. Excessive heat and cycle time causes discoloration of the part.

In practice, most molds are designed with little or no draft angle. They must be treated with a release agent. After each molding, the mold should be cleaned with a solvent and an abrasive.

4.8.5.1 Oven Dwell Time

The oven dwell time is the length of time that the mold containing the resin spends in the oven, known as the *oven residence cycle*. The time elapsed in the oven can be divided into two parts: *build-up time* and *fusion time*. The mold heats up and reaches the melt temperature of the resin during the build-up time. The part is formed on the wall of the mold during the fusion time.

4.8.5.1.1 Build-Up Time

A number of variables influence the length of the build-up time. They are listed in Table 4.24 in descending order of significance. The most significant factor is the nature of the heat transfer medium. It has a significant effect on the efficiency of heat transfer to the plastic material, thus on the length of the molding cycle.

Air is the dominant heat transfer medium for rotomolding. It is also the simplest choice from a safety and handling standpoint. Hot liquids, such as oils, could be sprayed on the mold while it is being rotated but hazards and operational problems have precluded their use. Liquid heat transfer medium can be used in jacketed molds, which results in improved heat transfer. The increase in the cost

Table 4.24. Variables Influencing the Buildup Time

Variable	Importance
Heat Transfer Medium: Convection or Conduction	**Most**
Oven Temperature	↓
Melt Temperature of the Resin	
Velocity of the Heating Medium Over the Mold Surface	
Wall Thickness of the Mold	
Surface-to-Volume Ratio of the Mold	
Heat Transfer Coefficient of the Mold Material	
Oven Recovery Time	**Least**

Source: Reference [55].

of fabricating jacketed molds makes it difficult to justify their inclusion in commercial operations unless they are required. For example, PA 6 parts are rotomolded in jacketed molds to avoid oxidation of the polymer.

4.8.5.1.2 Fusion Time

Fusion time is dependent on a number of parameters that are similar to those influencing the buildup time, but not all the same variables in the same order. They have been listed in Table 4.25 in the order of importance. The first two variables have a drastic influence on the fusion time. It is directly proportional to the wall thickness of the part, which is specified by its intended application. This means that, at a given temperature, to double the wall thickness of the part, the fusion time must also be doubled. Oven temperature has a large impact on the cycle time. Increasing the mold temperature by 100°C (180°F) can increase the fusion rate by as much as 25%.

The fusion time is the key factor in the determination of the total dwell time in the oven. A number of measures can be taken to reduce/minimize the length of time. They include thermal stabilization of the polymer to allow higher mold temperatures, reduction of the wall thickness of the mold, and improvements in the heat transfer to the mold by design improvement such as multiple zone temperature control. Another strategy is to vary the air temperature during the cycle, which can be designed to obtain a high quality molding. Cycle time may also be somewhat reduced.

Table 4.25. Variables Influencing the Fusion Time

Variable	Importance
Wall Thickness of the Part	**Most**
Oven Temperature	↓
Velocity of the Heating Medium Over the Mold Surface	
Surface-to-Volume Ratio of the Mold	
Particle Size of the Resin	
Heat Capacity of the Unit Area of the Mold	
Melt Temperature of the Resin	
Heat of Fusion of the Resin	**Least**

Source: Reference [55].

Thermal degradation, manifested by discoloration, bubbles, or surface roughness should be taken into account when deciding to increase the mold temperature to shorten the molding cycle. A loss in physical properties of the part accompanies these visible changes and would occur even if there is no perceptible color or appearance change.

Another consideration in raising the mold temperature is the longevity of the mold itself. It has been demonstrated [76] that operating the mold at extreme temperatures, even in the absence of thermal degradation of the plastic, affect the mold life and maintenance costs detrimentally. The balance of cycle time reduction and cost increase is unfavorable, especially for resins that require high temperatures.

One trick to lengthen the fusion time is to delay cooling after the mold has been taken out of the oven. The large thermal capacity of the mold stores a great deal of heat that will continue heating the resin for some time. The advantage of this approach is to shorten the oven cycle and increase throughput.

As the particle size of the molding powder is increased, a longer fusion time is required to obtain a surface smoothness equivalent to that of a smaller particle size powder. The likely cause of less efficient heating is the reduced contact surface area between the wall of the mold and the powder.

Melt temperature of the resin and the ratio of the mold surface to its volume are usually fixed by the part geometry and the requirements of the application. They cannot be changed during the cycle to influence the molding performance or the length of the cycle.

Air (heat transfer fluid) velocity is set at a value recommended by the oven manufacturer. This value is based on experimentation to maximize the heat transfer (flow is fairly turbulent) to the mold.

4.8.5.2 Cooling Cycle

Molds can be cooled externally by air or water and sometimes internally by pumping a cold fluid into the mold to directly cool the molded part. An effective way is to spray water on the mold to cool it down. The rate of water spray can be controlled so that it would be compatible with the use of oven inertia to complete the fusion of the resin. The cooling rate determines the extent of recrystallization of the molten polymer. Slow cooling of semi-crystalline polymers increases the crystallinity of the molded part and reduces its tendency to warp. Rapid cooling (quenching) of the part increases its amorphous content, resulting in an enhancement of the impact strength and flex fatigue of the part. Table 4.26 shows the impact of the cooling rate on a number of physical and mechanical properties of a part. A drawback to quenching is the thermal shock of the mold increasing required maintenance and shortening its life.

Internal cooling with air or water is also effective but more complicated than the external method. Water requires a special system that vents out the steam produced during the cooling. Water drops can leave marks on the molten resin which are called "pock marks" and are considered quality defects. The most common technique is air cooling, in which air is forced into and out of the mold. In addition to cooling, air pressure counteracts the shrinkage effect. The part tends to separate from the mold after it shrinks. Air holds the part against the mold, which can be an advantage to heat transfer when the mold is being cooled both externally and internally. The normal range of air pressure is 10–20 kPa (1.45–2.90 psi). Care must be exercised, as internal pressurization can damage molds, which are not designed to withstand internal pressures.

Table 4.26. Effect of Mold Cooling Rate on the Part Properties

Properties	Cooling Rate
	Fast → Slow
Crystal Size	Increases
Elongation	Decreases
Tensile Strength	Increases
Flexural Modulus	Increases
Flexural Strength	Increases
Flex Fatigue Life	Decreases

Source: Reference [55].

4.8.5.3 Venting

A vacuum forms during the cooling cycle of the rotomolding process. Cooling of the trapped air can create a fairly high vacuum causing quality problems in the part. Distortion of the part, particularly the flat section, is the most frequently encountered problem. The second problem is at the parting line, which, if not maintained carefully, can result in small bubble formations in the part. Moisture and air are drawn into the parting line and end up forming bubbles or holes through the wall of the part.

The simplest cure for the vacuum formation is to design a vent line that connects the inside space of the cavity with the atmosphere. A simple vent line is a tube made of inert material such as polytetrafluoroethylene (PTFE) that is inserted in a hole in the mold. Care must be taken to place the tube sufficiently deep into the mold to prevent its obstruction by the resin. Loose fiberglass batting should be stuffed in the line to prevent outside moisture from entering the mold. The batting also prevents the powdered plastic from spilling through the vent tube. Other stuffing materials can be used as long as they are not combustible. The size and location of the vent line is also important to the prevention of moisture back-flow.

4.8.5.4 Part Stripping

Parts are often removed while they are still warm. Cooling rates are uneven at different locations of the mold, leaving residual stresses in the part. There are also stresses that result from the weight of the part. These forces cause the part to distort after removal. The part is placed in a device that holds its geometry until the part has cooled and becomes stiff. The alternative approach is to increase the cooling rate and/or the length of the cooling cycle. The choice depends on the economics of the specific molding process.

Release agents are sometimes applied to the surface of the mold to facilitate demolding. These agents could have an adverse effect on the quality of the part surface [77]. Voids and bubbles are eliminated from the bulk of the polymer melt under the driving force of surface tension to minimize the available free surface. Bubbles are more stable at the interface of the part and the mold because of a reduced surface area where the mold release agents are present. The difficulty of eliminating the bubbles could result in the survival of some of them. Consequently, these surface agents can impart poor surface formation in the part.

4.8.5.5 Rotation Rate and Ratio

The axes in rotational molding have different lengths. The speed of rotation of the mold and the ratio of the two axes are very important variables of the rotational molding process. *Rotation ratio* is the ratio of the speed of the mold around the two axes according to Eq. (4.5). Speed is a function of the flow properties of the polymer and the ratio is related to the shape of the part. Shorter cycles and thinner part walls amplify the sensitivity of these two variables [76].

$$\text{Rotation ratio} = R_1/R_2 - R_1, \qquad (4.5)$$

where R_1 = is the rotation speed of the major axis (rpm) and R_2 = is the rotation speed of the minor axis (rpm).

Rotational molding does not occur due to centrifugal forces and, indeed, development of these forces is detrimental to the proper formation of the part. A large variation in the wall thickness is an indication of the development of centrifugal force development. The forces that develop because of high rotation speeds cause the molten resin to flow into the areas where the forces are concentrated contrary to even distribution on the wall of the cavity. Care must be exercised if high speeds are required in rotomolding. Large molds may damage the machinery at high speeds.

Melt flow and the rheological properties of the resin are the determining factors in setting the rotation speed. A high viscosity resin forms a uniform coating on the wall of the cavity at low rotation speeds. The slow rotation speed lengthens the molding cycle, thus requiring a lower temperature to avoid degrading the polymer. The longer cycle allows sufficient passes of the powder over the molten coating on the cavity surface to result in complete consumption of the polymer powder.

The rotation ratio of the two axes depends on the shape of the molding. Symmetric parts can be molded at a ratio of 4:1; examples include spheres, cubes, and regularly shaped articles. Table 4.27 shows rotation ratios for a few different shapes. Irregular objects require ratios ranging from 2:1 to 8:1. It is impractical to calculate the rotation ratio of a new part. A starting value can be estimated based on the shape of the part. The optimal ratio is then determined by trial and error and evaluation of the part made at a given value of the ratio.

4.8.6 Rotolining Process

So far, the discussion has focused on rotational molding to produce hollow parts. Rotation lining or rotolining (also rotocasting) allows the application of a seamless plastic lining to the interior surfaces of a metal part. Rotolining is ideally suited to lining the internal surfaces of complex-design parts such as pumps, valves, pipes, fittings, and vessels.

Table 4.27. Typical Rotation Ratios for Various Shapes

Shapes	Rotation Ratio	Rotation Speed of Major Axis (rpm)[a]
Horizontally Mounted Oblong Articles and Straight Tubes	8:1	8
Cubes, Balls, Odd Shapes, and Rectangular Boxes	4:1	8
Rectangular Shapes with More Than Two or Thin Sides When Run at a Ratio 4:1	2:1	8
Flat Rectangles Such As Gas Tanks	1:3	4 6 9.5
Pipe Angles and Curved Air Ducts	1:4	5
Vertically Mounted Cylinders	1:5	4

Notes:
[a] Speed around the minor axis can be calculated from Eq. (4.5) by substituting for the rotation speed and ratio.
Source: Reference [55].

Rotolining differs from rotomolding in that the metal component forms the internal cavity and, after the completion of the process, the lining is an integrated component of it. On the other hand, the products of rotomolding are free standing or are later inserted in another structure.

Rotolining has a number of advantages over the other methods of coating and lining. It allows a much thicker lining than electrostatic or dispersion coating techniques. Rotolining yields a more uniform thickness coating than the spray-on method. It is automated, compared to spray and electrostatic procedures, which are both manually applied.

Rotolining is limited to the interior surfaces while other methods, such as sheet lining, can also coat the exterior surface of a part. In the sheet lining process, the sheet is bonded to glass cloth fabric, which is then attached to the vessel (in general, any part) wall by an adhesive. Afterwards, the seams are welded and sealed using strips of the same, or another compatible, polymer. Sheet lining is suitable for large tanks that are beyond the size limitation of rotolining. It is not easy to line complex-geometry parts while in rotolining any geometry can be coated without difficulty. Sheet lining is also very operator sensitive and requires full access to all surfaces.

An important issue is the adhesion of the liner to the cavity wall. Shrinkage of the resin during the cooling period pulls the liner away from the wall, undesirable in rotolining but a positive phenomenon for rotomolding. Different strategies have been reported to obtain good adhesion. Both formulation and design approaches have been implemented to achieve this objective.

4.8.7 Melting of Polymer and Part Formation

In rotational molding, the particles of resin soften, stick to the mold surface, then adhere to other resin particles during which voids must be eliminated as a continuous layer of molten polymer is formed. It is widely accepted that sintering is the mechanism of void elimination as opposed to melt flow which occurs in extrusion or injection molding. Sintering of polymer particles is defined as densification of polymer particles by coalescence. During coalescence (Fig. 4.119), adjacent polymer particles combine under the driving force of surface tension. The first model for viscous sintering of two particles was developed by Frenkel [78] and improved upon by Kuczynski [79]. More recent studies have argued the inadequacy of Frenkel's and Kuczynski's models because of the exclusion of the role of melt viscosity and viscoelasticity in sintering [80]. The validity of Frenkel's model has been assessed for a number of polymers. Based on experiments with ultrahigh molecular weight polymers, it has been suggested that other factors, in addition to surface tension and melt viscosity, should be included [81].

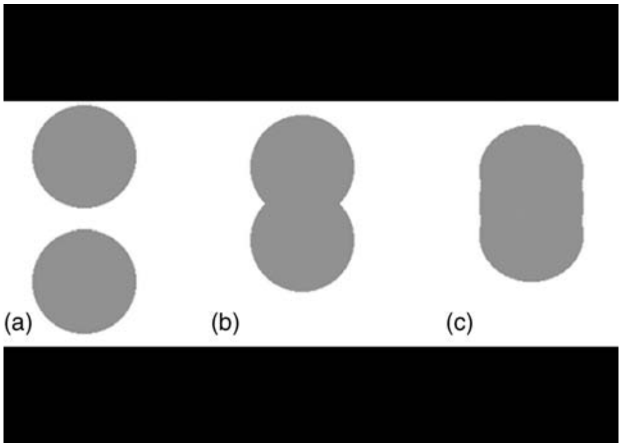


Figure 4.119. Schematic diagram of coalescence sequence of two adjacent polymer particles. a—Two adjacent particles. b—Particles form a neck. c—Coalescence has been completed.

Experimental studies have demonstrated that, in addition to viscous flow's [82–85] dominant role in sintering, viscoelasticity of the polymer [85–87] should be considered in polymer sintering and in rotational molding [88] Bellehumeur and Vlachopoulos [89] have derived one such model where Frenkel's approach has been modified [90] to include viscoelastic effects. The proposed model predicts that the sintering rate decreases as the relaxation time of a polymer increases, and it becomes independent of relaxation time when particle size or viscosity become very large.

Fundamental research in rotomolding has been aimed at estimating and reducing the length of the molding cycle, optimizing the mechanical properties of the part, and assessing the moldability of different polymers. Heat transfer in rotational molding has been studied to develop models for process and part property optimization. Rao and Throne [91] were first to model the rotomolding heat transfer. A number of other researchers have attempted to improve this model. Crawford and Nugent [92] have developed a numerical simulation of the process. Gogos et al. [93] proposed a solution for the heat transfer that used a lumped parameter for the heating cycle. This model is fairly simple and its predictions agree with the experimental data.

Table 4.28. Rotational Molding Troubleshooting Guideline for Most Thermoplastics

Part Problem	Possible Causes
Poor Part Release from the Mold	Insufficient draft angle
	Roughness on the mold surface
	Resin decomposition
	Insufficient application of release agent
	Undercuts are trapped
Rough Part Surface	Resin degradation
	Presence of foreign particles on the mold surface
Warping	Vacuum developed inside the part due to poor venting
	Part has pulled away from the mold surface because of cooling quickly
Nonuniform Wall Thickness	Incorrect mold rotation because of equipment problem or wrong rotation ratio
	Variation in the thickness of the mold wall resulting in uneven heat transfer, thus melting and fusion rate of resin
	Variation in the heat transfer to the mold
Poor Mechanical Properties	Cooling too slowly leads to excessive crystallinity
	Resin fusion is incomplete
	Poor filler dispersion in the polymer
Incomplete Resin Sintering	Short heating cycle
	Low mold temperature
	Slow heat transfer due to excessive wall thickness of the mold
Bridging of the Resin in the Mold	Poor resin powder flow
	Slow rotation rate
	Radii of the undercuts, ribs, and other recesses are too small
	Air trapped in the recesses, consider venting in these locations

Source: Reference [55].

A commercial numerical simulation of the rotomolding heat transfer [94] is available but it is restricted to simple geometries and does not allow the prediction of part porosity.

Heat transfer takes place through the outside surface of the mold in rotomolding during both heating and cooling cycles. Researchers have analyzed the effects of internal heating and cooling [95] to improve the heat transfer and shorten the molding cycle. The model predicted significant shortening of the cycle, which was corroborated by experimental data. Introduction of internal cooling increased the uniformity of the part structure and reduced warping.

4.8.8 Troubleshooting

Rotomolding is affected by a number of variables that are difficult to control and hard to scale when the size and design of the part change. It is important to follow a set of troubleshooting guidelines to take corrective action when the part is defective. Table 4.28 provides a list of typical problems and suggested corrective actions.

4.8.9 Conclusion

Rotational molding is a complex process and involves numerous related variables and details that must be set correctly to produce quality parts repeatedly. The details concern the design of the part, the choice of the plastic, the design and fabrication of the mold and, finally, the actual rotational molding process. The end use requirements usually provide guidance for specifying the construction material and the design and dimensions of the part. On the other hand, any design must be practical and economical. The cost of mold construction and the operating process are strongly influenced by the design of the part. Thermoplastic elastomers pose additional restraints on the process and part design due to their high melting temperature and viscosity.

A reader who would like to engage in rotomolding must consult other references that have addressed the subject in a thorough and in-depth manner. Complete coverage of this technology can easily occupy a separate volume that is beyond the scope of this book. This task has been most ably accomplished by a number of authors and experts. Some particularly helpful resources can be found in references [74, 96–99].

4.9 Foaming of Thermoplastics

4.9.1 Introduction

Polymeric foams or *cellular* or *expanded* polymers have played an important role in everyday life. Because of their special characteristics, they became attractive for many industrial and household applications.

The most important attributes of polymeric foams are light weight and good thermal insulation property. Other advantages are relatively high strength per unit weight and lower dielectric constant when compared to solid polymers. General attributes and drawbacks of polymeric foams are in Table 4.29.

The first commercial foam was rubber sponge, a polymeric material with open cells (see below) introduced in 1910 [100] but the oldest foam is wood that is a natural occurring foam of cellulose.

4.9.2 Background

Foam cells are bubbles that have been frozen in size and shape after solidification of molten polymer. Such a material can contain two types of cells; *closed cells* and *open cells*. In the *closed* cell foam each cell is an independent closed entity. The cells resemble small glass bubbles that have been dispersed in the polymer. The walls of a closed cell have no holes in them. The cell will contain gas in them if the polymer is impermeable to the gas used for the formation of the cellular structure. The cells in the *open* cell foam are interconnected, thus unable to hold gas. Liquids and gases can move through the open cell structures, like through common sponges.

Table 4.29. Advantages and Disadvantages of Polymeric Foams in Comparison to Solid Polymers

Advantages	Disadvantages
Light weight	Variable density
Good thermal insulation property	Loss of certain mechanical properties
High strength per unit weight	
Ease of molding	
Impact strength	
Lower dielectric constant	

Source: Reference [55].

Polymeric foams are also classified according to their mechanical properties. If the walls of the cell are stiff under stress and relatively inflexible, the foam is called *rigid*. If, on the other hand, the cells collapse under stress, the foam is called *flexible*. Both open cell and closed cell structures can form rigid and flexible foams.

Densities of polymeric foams range from about 1.6 to 960 kg/m^3 (0.1 to 60 lb/ft^3). Their mechanical properties are usually proportional to their densities. Low density polymeric foams (~30 kg/m^3) are used in applications such as furniture or automotive seating; high density foams are required for structural, load-bearing applications. Mechanical properties of conventional polymeric foams are lower than in solid parts due to a lower material content; however microcellular foams with a pore or cell size 1 to 10 μm provide good mechanical properties in addition to weight reduction.

Polyethylene, PP, and polystyrene are most common thermoplastic foams, although other base polymers, such as ethylene vinyl acetate (EVA), melt-processable fluoropolymers, and TPEs can be converted into cellular materials.

4.9.3 Foaming Technology

Many resins can be foamed by a variety of processes. Each method of foam manufacturing involves the following steps

- cell initiation
- cell growth
- cell stabilization.

There are three general methods of producing foams from thermoplastics: mechanical, chemical, and physical.

Initiation or *nucleation* is the formation of cells in the thermoplastic, which are small discontinuities in the melt continuum. The expansion condition of the foam allows the growth of the nuclei. The governing drive force for the growth of each cell is the difference between the pressure inside and the pressure outside that cell as shown by Eq. 4.6 [101]. The surface tension of the melt (γ) and the cell radius (r) are the two factors determining the pressure difference (ΔP):

$$P = 2\gamma/r \tag{4.6}$$

The surface tension of the melt is a function of many factors including the type of the polymer, temperature, pressure, and the additives present. The pressure outside the cell is the pressure that the melt is under, and the pressure inside the cell is the pressure that is exerted by the blowing/foaming agent. A gas or a solid can be used to initiate foaming.

Cell *growth* is a very complex process because the properties of the melt change during the cell growth phase. Several quantitative models have been established that completely describe the cell growth [102]. The viscosity change affects the cell growth rate and polymer flow. The pressure drop in the blowing agent is inversely proportional to the radius (see Eq. 4.6) in contrast to volume. It is important to note that the pressure is higher in small cells than in larger cells, leading to intercell gas diffusion or to breaking of the cell walls.

Thermodynamically speaking, generation and growth of cells in a polymeric melt is destabilizing. A fluid tends to minimize its free energy by reducing its surface area. The cell formation significantly increases the surface area of the polymer melt. The unstable foam at the end of growth phase requires *stabilization* to retain the cells in the foamed state. These stabilization methods have traditionally been used to classify the foaming technique as either *physical* or *chemical*. Also, a limited use of *mechanical* foaming is made in the industrial practice.

4.9.3.1 Mechanical Foaming

This technique is similar to whipping cream during which air is mixed in with the bulk of the melt. Mixing simply entrains air into the molten plastic where air becomes the foaming gas. An example of an application of this method is foaming of vinyl plastisols for producing thick vinyl flooring. Otherwise, the application of mechanical foaming for thermoplastics is limited [103].

4.9.3.2 Chemical Foaming

In this method, chemistry controls the foam formation process [104]. This may be the rate of formation of polymer, that is, the conversion of viscous fluid to a cross-linked (three-dimensional structure) or expanding a partially cross-linked polymeric melt (e.g., polyolefin foams) or expanding a thermoplastic melt with subsequent cooling. Chemistry also controls the rate of activation of the blowing agent, which is either by a drop in solubility in the monomer solution as the reaction proceeds, or by thermal decomposition. Blowing agents are used to decrease the density of the polymer, typically by 40–60% with loading levels of 0.5–20.5% by weight on the amount of polymer. The characteristics of the blowing agent determine the amount of gas generated, the rate of gas generation, the foaming pressure, and the net amount of gas retained in the cells. Chemical blowing agents can be classified as organic and inorganic and their decomposition may be endothermic or exothermic. They often require activators, such as alcohols, glycols, antioxidants, and metal salts, which lower their decomposition temperature.

Inorganic blowing agents include sodium bicarbonate, sodium borohydrate, polycarbonic acid, and citric acid. These evolve primarily carbon dioxide upon thermal decomposition. Sodium bicarbonate is the most widely used blowing agent from this group. It decomposes over a broad range of temperatures, namely from 100°C to 140°C (212°F to 240°F) and yields 267 ml/g of gas. Polycarbonic acid decomposes at about 160°C (287°F) and yields about 100 ml/g of gas.

Organic blowing agents evolve gas over a specific narrow temperature range. They produce a gas mixture composed mainly of nitrogen. Examples of organic blowing agents are in Table 4.30.

Chemical blowing agents are available as dry powders, liquid dispersions, and pellet concentrates.

4.9.3.3 Physical Foaming

In the physical foaming technique, a blowing (foaming) agent added to the thermoplastic volatilizes and/or expands during the melting. This agent can be either a liquid or a gas. A *nucleating agent* may have to be used to promote the cell nucleation and/or control the cell size and the number of cells formed. The chemical structure and composition of the polymer define the conditions of the foaming process. The key variables are temperature, type of foaming agent, and the cooling rate of the expanded structure in order to stabilize it dimensionally. The nature of the foaming agent and its concentration in the polymer determine the rate of gas evolution, gas pressure, gas retention in the cells, and heat absorption/release due to the degradation/activation of the blowing agent [104]. Physical blowing agents are compressed gases or volatile liquids. Compressed gasses, usually

Table 4.30. Examples of Organic Chemical Blowing Agents (CBAs)

Commercial Name	Chemical Name	Decomposition Temperature °C (°F)	Gas Yield (ml/g)
OBSH	4,4′-oxybis(benzene sulfonyl hydrazide)	157–160 (315–320)	125
ABFA	Azodicarbonamide	204–213 (400–415)	220
TSSC	p-toluenesulfonyl semicarbazide	228–236 (442–456)	140
5-phenyltetrazole	5-phenyl-1H-tetrazole	240–250 (460–480)	190
THT	Trihydrazinotriazine	250–275 (480–527)	225

nitrogen, are injected under high pressure into the polymer melt; as the pressure is relieved, the gas becomes less soluble in the polymer melt and expands to form the cells. Nitrogen is inert, nonflammable, and can be used at any processing temperature. It produces coarser foams than nitrogen produced from organic chemical blowing agents. The use of nucleating agents can be added for a finer cell structure. Other gases besides nitrogen used as physical blowing agents (PBAs) include hydrogen, helium, air, mixture of helium and air, and CO_2.

Liquid PBAs are volatile and change from liquids to gaseous state when heated to polymer processing temperatures. Some of them are aliphatic hydrocarbons that can present safety hazard due to their flammability. Others, short chain chlorinated and fluorinated hydrocarbons (CFCs) have been phased out from most formulations due to their role in reduction of stratospheric ozone and replaced by hydrogen containing CFCs (HCFCs).

Examples of PBAs are in Table 4.31 and the ozone depletion potential (ODP) for selected PBAs is in Table 4.32.

4.9.4 Foam Manufacturing Processes

A variety of processes are used to produce foamed parts. The process used has to accommodate the three key stages of initiation, growth, and stabilization (see Section 4.9.3). These processes are classified by the manner of achieving pressure differences between outside and inside the foam cell. If the external pressure is lowered, the process is called *decompression* foaming. The process in which the internal cell pressure grows is called *expandable* foaming. Other methods of creating a cellular

Table 4.31. Examples of Physical Blowing Agents (PBAs)

Name	Chemical Formula	Boiling Point (°C)	Flammable
n-Pentane	C_5H_{12}	36.1	Yes
Methyl chloride	CH_3Cl	−24.2	Yes
CFC-11	$CFCl_3$	23.8	No
CFC-12	CF_2Cl_2	−29.8	No
CFC-113	$CFCl_2CF_2Cl$	47.6	No
CFC-114	CF_2ClCF_2Cl	3.6	No
HCFC-22	CHF_2Cl	−40.8	No
HCFC-142b	CF_2ClCH_3	−9.2	Yes
HCFC-152a	CHF_2CH_3	−24.7	Yes
HCFC-123	$CHCl_2CF_3$	27.1	No
HCFC-123a	$CHFClCF_2Cl$	28.2	No
HFC-124	$CHFClCF_3$	−12	No
HFC-134a	CH_2FCF_3	−26.5	No
HFC-143a	CH_2FCF_3	−46.7	Yes
Carbon dioxide	CO_2	−78.5	No

Table 4.32. Ozone Depletion Potential[a] of Selected PBAs

Blowing Agent	Boiling Point (°C)	Ozone Depletion Potential
CFC-11	23.8	1.0
CFC-12	−29.8	0.9
HCFC-142b	−9.6	0.066
HCFC-22	−40.8	0.05
HFC-134a	−26.4	0
HFC-152a	−24.7	0
Carbon dioxide	−78.5	0

Notes:

[a] Ozone depletion potential (ODP) is defined as a number that refers to the amount of ozone depletion caused by substance. It is the ratio of the impact on ozone compared to the impact of a similar mass of CFC-11.

Source: Environmental Protection Agency (www.epa.gov).

structure are sintering the resin particles in the presence of a gas or a solid (e.g., glass hollow beads) in the molten polymer. Decompression and expandable foaming can be stabilized by both chemical and physical methods.

Common melt-processing methods, such as extrusion, injection molding, compression molding, blow molding [105–107] and rotomolding [108] are used to produce foamed articles.

Foam extrusion is a widely used process, consisting of the following steps:

1. Extrusion
2. Mixing
3. Cooling
4. Expansion
5. Aging.

The process is illustrated by a block diagram (Fig. 4.120).

Commercially these process steps can be executed on single-screw extruders having a long screw, twin-screw extruders, and on tandem-extruder lines. Such lines consist of a *primary extruder* that melts the polymer and mixes the melt with solid additives and liquid blowing agent. The second, *cooling extruder* cools the mixture to the optimum temperature (Fig. 4.121) and can also be design to act both as a mixer for the blowing agent and as cooler (Fig. 4.122) [109]. A foam extrusion line is shown in Fig. 4.123.

Other foam extrusion processes include *accumulating extrusion* and *flash extrusion* and are described in reference [109].

4.10 Thermoforming

4.10.1 Process Basics

Thermoforming is a process for converting thermoplastics into shell forms, using sheet material as

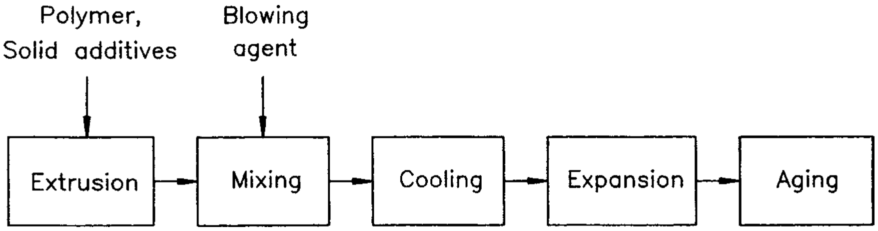


Figure 4.120. Flow diagram of foam extrusion process (Courtesy Hanser Publishers).

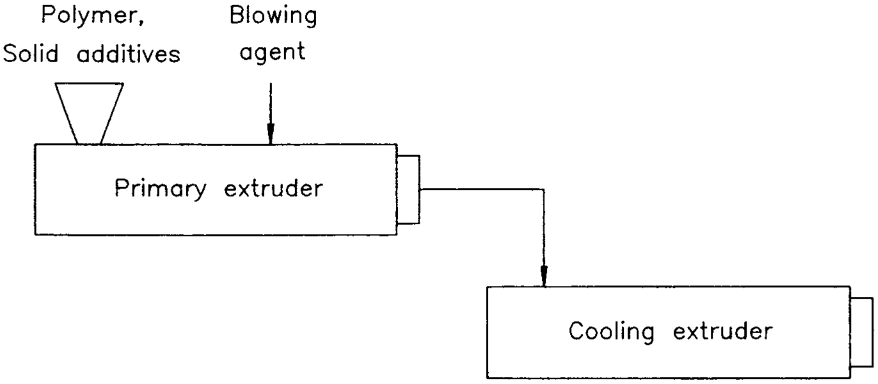


Figure 4.121. Schematic diagram of a tandem extruder for foam (Courtesy Hanser Publishers).

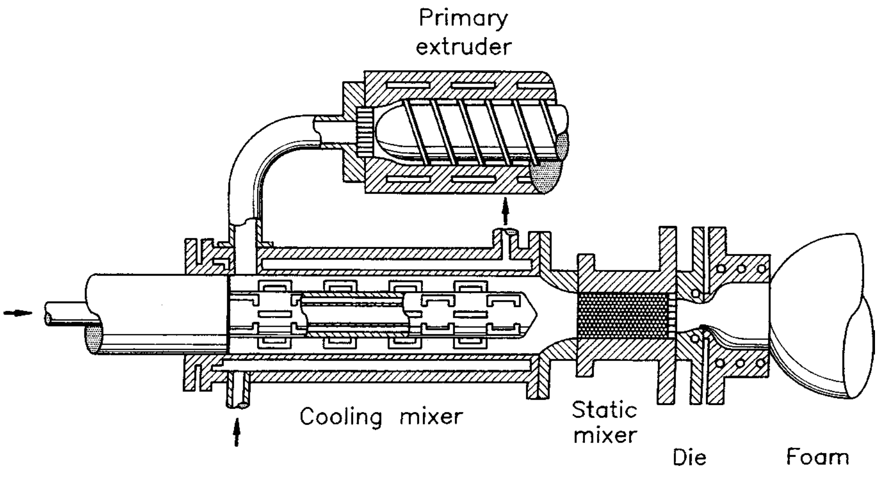


Figure 4.122. Tandem with the second extruder as mixer and cooler (Courtesy Hanser Publishers).

a preform. At its most basic, thermoforming is performed by clamping a heated thermoplastic sheet over a mold cavity and drawing a vacuum in the cavity. This causes atmospheric air pressure to press and plastically deform the sheet into the mold cavity, where it is cooled to retain the formed shape. This is known as vacuum forming, a term that is less comprehensive than thermoforming, although the two are often erroneously treated as interchangeable and synonymous. In practice, the key factors in thermoforming all have two to three optional forms (see Table 4.33). For example, the forming force can be supplied by vacuum, by positive air pressure, or by power press. These options can be assembled in many different permutations to create a very wide variety of thermoforming processes. In this chapter, the principal processes (Table 4.34) and the main factors are discussed.

Figure 4.123. Foam extrusion line (Courtesy Battenfeld Gloucester Engineering Company).

4.10.2 Process Factors

The principal factors in thermoforming are the forming force, mold type, method of prestretching the sheet, the material input form, and the process

Table 4.33. Principal Options Available in the Thermoforming Process

Process Factor	Options
Forming Force	Vacuum Positive air pressure Power press
Mold Type	Female Male Matched male/female
Sheet Prestretch	Vacuum Positive air pressure (billow) Mechanical plug
Material Input	Extruder (in-line, hot forming) Reel (reheat, cold forming) Cut sheet (reheat, cold forming)
Process Phase	Solid phase Melt phase
Heating Mode	One side of sheet Both sides of sheet (sandwich)
Heating Means	Radiation: rod, ceramic, quartz, or infrared heaters Convection: hot roller, contact panel, or hot oil bath

Source: Maier, C., and Calafut, T., *Polypropylene*, William Andrew Publishing, 1998, p. 223.

Table 4.34. Principal Thermoforming Process

Process	Forming Force	Mold Type	Sheet Prestretch
Basic Vacuum	Vacuum	Female	None
Basic Pressure	Positive air pressure	Female	None
Drape	Vacuum	Male	None
Snap Back	Vacuum	Male	Vacuum
Billow	Vacuum	Male	Positive air pressure
Plug Assist	Vacuum	Female	Mechanical plug
Billow Plug Assist	Vacuum	Female	Positive air pressure and mechanical plug
Air Slip	Vacuum	Male	Positive air pressure
Air Slip Plug Assist	Vacuum	Male	Positive air pressure and mechanical plug
Matched Mold	Power press	Matched male/female	None
Twin Sheet	Positive air pressure	Matched male/female	None

Source: Maier, C., and Calafut, T., *Polypropylene*, William Andrew Publishing, 1998, p. 224.

phase condition. These factors have a critical influence on the appearance, quality, and performance of the thermoformed part.

4.10.2.1 Forming Force

Thermoforming is essentially a low pressure process, in which the forming force is generated by vacuum, or positive air pressure, or by a combination of both. However in a matched mold (or matched die) thermoforming the force is supplied by a power press and may be much greater.

In *vacuum forming* (Fig. 4.124), the heated sheet forms part of the closed cell together with the mold. When the air in this cell is evacuated, the atmospheric pressure forces the sheet into contact with the mold. The force so generated clearly cannot exceed atmospheric pressure and in practice is rather less because of the difficulty of creating perfect vacuum in the mold/sheet cell. A vacuum of 85–90% of theoretical maximum is more likely and this will generate a forming force no greater than 90 kPa (13 psi).

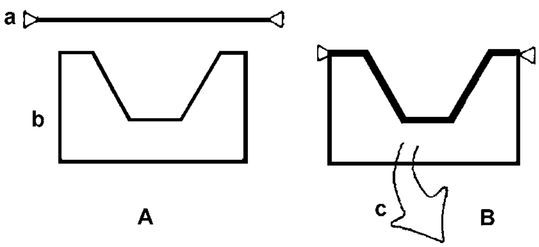


Figure 4.124. Vacuum forming: A—Preheated sheet prior to forming; B—Formed sheet into female mold; a—Preheated, clamped sheet; b—Female mold with vacuum holes; c—Vacuum.

Pressure forming (Fig. 4.125) overcomes the force limitations of vacuum forming by applying air under pressure on the nonmold side of the sheet instead of vacuum on the mold side. Typical air pressures used in this method are in the range 550–710 kPa (80–100 psi) and this pressure may be sufficient for many applications.

The pressure in *matched mold (die) forming* (Fig. 4.126) is supplied by a power press, as mentioned earlier, and the force used in this method is usually in the range from 1.5 to 4 MPa (218 to 580 psi).

Examples of typical production thermoforming equipment are in Figs 4.127 and 4.128.

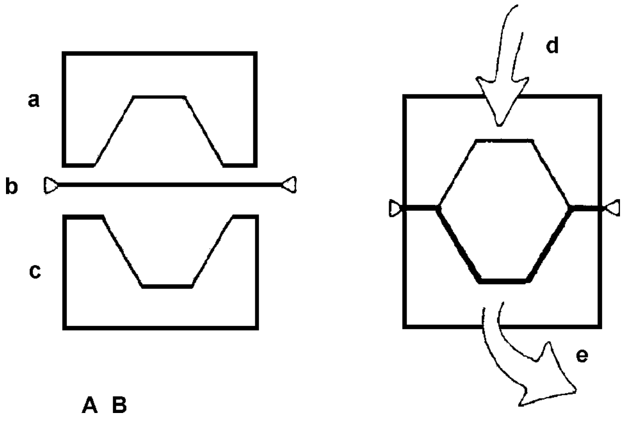


Figure 4.125. Pressure forming: A—Preheated sheet prior to forming; B—Formed sheet into female mold; a—Pressure box; b—Preheated, clamped sheet; c—Female mold with vacuum/vent holes; d—Applied air pressure; e—Venting of vacuum.

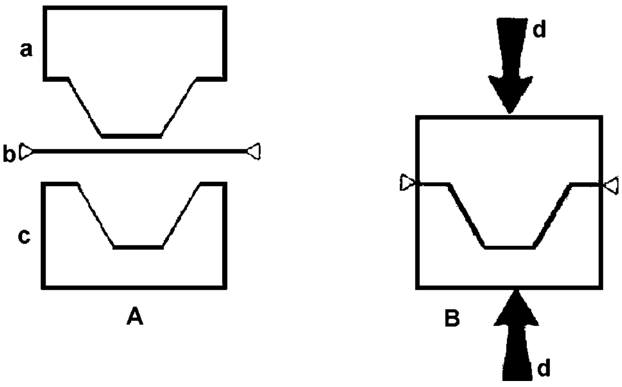


Figure 4.126. Matched mold (die) forming: A— Preheated sheet for forming; B—Sheet formed by simultaneous motion of two mold halves; a—Male mold half; b—Preheated, clamped sheet; c—Female mold half; d—Applied force.

4.10.2.2 Mold Type

Thermoforming is a shell process in an open mold that defines only one surface of the product. Definition of the second surface is indirect and imprecise. Thermoforming molds are classified as male and female and matched.

The *female mold* consists of a recessed cavity or cavities formed in a mold block. This is the most common mold form because it is easy to clamp the heated sheet across the unobstructed mold face.

The *male mold* consists of a form or punch projecting from a mold block. The punch interferes with the plane of the sheet preform so sheet clamping must take place outside the mold.

The third mold type used in thermoforming is the *matched mold.* This is a closed mold consisting of two halves, each defining one surface of the finished article. The matched mold is similar in concept to a compression mold but the cavity geometries remain limited to shapes attainable by the sheet preform.

4.10.2.3 Sheet Prestretch

It is often advantageous to prestretch the heated sheet immediately prior to forming it in the mold. There are two principal reasons for that. First, particularly when simple vacuum forming is combined with solid phase forming the available force might be insufficient to stretch and form the sheet efficiently. A second reason is that some shapes, for example, cup or box forms of relatively high aspect ratio, give rise to excessive variations in wall thickness when formed without prestretch.

Selective prestretching, necessary for more complex shapes is achieved by means of specially shaped

Figure 4.127. Direct extrusion thermoforming line (Courtesy Brown Machine).

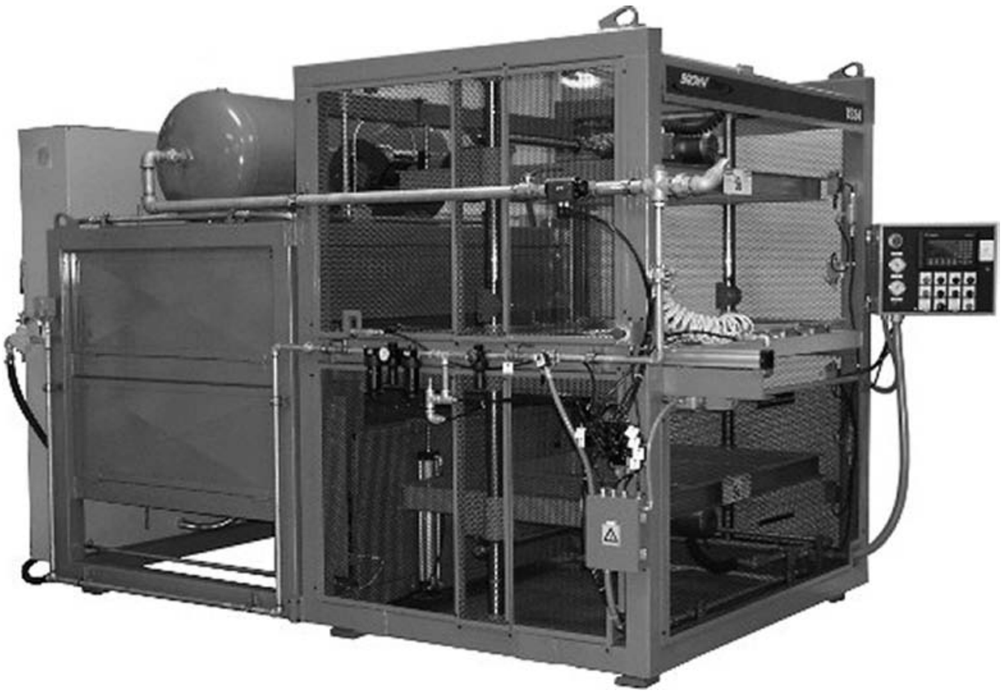


Figure 4.128. Cut sheet equipment for heavy gauge industrial products (Courtesy Brown Machine).

plugs, which are mechanically advanced into the heated sheet to produce local stretching in a way calculated to counteract the thinning tendency imposed by the mold geometry. This method is generally referred to as *plug assist*.

4.10.2.4 Material Input

The raw material for thermoforming is a thermoplastic material in sheet form. The sheet is mainly produced by extrusion and can either pass directly into extruder to the thermoformer or can pass through an intermediate storage. After being stored, the material must be completely reheated before forming.

4.10.2.5 Process Phase

If a semi-crystalline material is thermoformed, it can be processed either below or above its crystalline melting point. When forming is done below the crystalline melting point, it is known as *solid phase forming*; *melt phase forming* is done at temperatures above the crystalline melting point.

The two techniques result in products with rather different characteristics (see Table 4.35). Melt phase forming requires less force and so generates lower residual stress in the finished part. Another advantage of this technique is that the part has a reduced tendency to distort or to revert to the original sheet form. Modern solid phase thermoforming can produce high quality products, particularly when carried out with multilayer coextruded film and sheet [110].

Table 4.35. Comparison of Product Characteristics between Solid Phase and Melt Phase Forming

Property	Solid Phase Forming	Melt Phase Forming
Wall Thickness Distribution		More even
Residual Stress		Lower
Optical Properties	Clearer	
Mechanical Properties	Stronger	
Heat Resistance		Greater

Source: Maier, C., and Calafut, T., *Polypropylene*, William Andrew Publishing, 1998, p. 228.

4.10.2.6 Heating

The heating process is of critical importance in thermoforming, both economically and technically. Heating accounts for some 80% of the total energy demand for thermoforming. Heating of the sheet can be performed by radiation, convection, or conduction. When radiation or conduction is used, there is the option to apply heat to either one or both surfaces. In the case of convection, both sides of the sheet will be heated. Given the difficulty of heating the sheet core uniformly, it is preferable to heat both surfaces of the sheet. The upper limit of sheet thickness for effective single-sided heating is about 1 mm (0.040 in.) [111].

Infrared radiant heating is now the most widely used means of sheet heating for *reel-fed* or *in-line* thermoforming machines. The heaters are normally arranged in a heating tunnel in a series of independently controlled zones that gradually increase the sheet temperature first to stress relaxation temperature (typically about 120°C or 248°F), then to the forming temperature.

The arrangement for *cut-sheet* machines is different. It is usual to preheat the sheets by convection in static ovens, followed by final heating of both surfaces in a radiant sandwich heater operating near the mold. Other methods, used less frequently, are heated rolls, or heated flat contact plates, or immersion baths filled with heat transfer liquid.

4.11 Calendering

Calendering is a process originally developed for shaping rubber compounds into sheets and films and for applying rubber compounds onto different types of fabric. The equipment, called *calender*, is a heavy duty machine equipped with three or more chrome-plated steel rolls, which revolve in opposite directions. The rolls for conventional rubber processing are heated by steam or circulated water, and have gears that allow them to operate at variable speeds. Over the years, calenders have developed into a useful machinery for some thermoplastic materials, most notably PVC to produce films and sheets. Calenders for thermoplastics have typically four rolls that are heated with circulating oil, or other heating liquids, or electrically since higher processing temperatures are required than for conventional rubber compounds. During operation, the melt is mostly fed between the rolls by means of an extruder or directly from a continuous mixer. Several TPEs, namely TPV [112], melt-processable rubber (MPR) [113], TPU [114], and TPO [115, 116] are reported as being processed by calendering.

The advantages of a calender over an extruder are:

- Higher output than extruder
- Easier access and possibility for rapid material changes
- Possibility to produce embossed films and sheets
- Possibility to produce laminates.

Drawbacks are the high initial cost, the large size of the calender and additional equipment, and high operating cost (mainly energy consumption).

Different roll arrangements of four-roll calenders are in Fig. 4.129.

4.12 Secondary Manufacturing Processes

4.12.1 Film and Sheet Orientation

Polymer sheets and films made by the usual techniques, such as extrusion, casting, and calendering

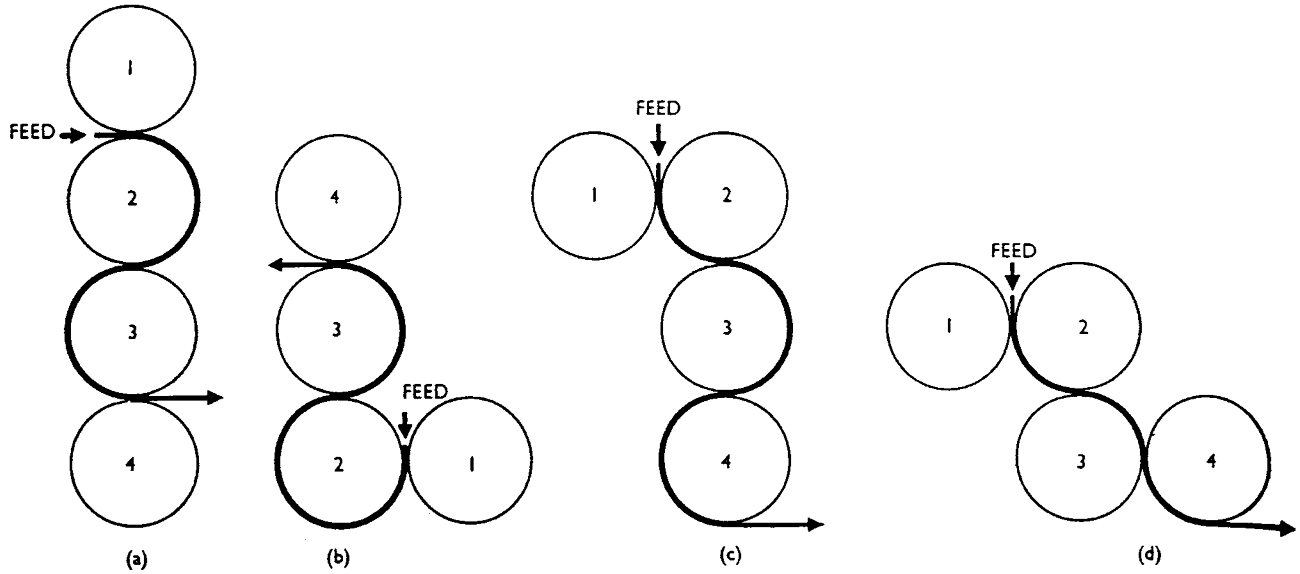


Figure 4.129. Different roll arrangement in four-roll calenders: (a) I (Four in line); (b) L; (b) Inverted L; (c) Z.

can be oriented by drawing. Certain amount of orientation occurs already during the processing; particularly in extrusion and calendering since the processed melt is stretched in the direction of flow and in blown film process, the stretching is along the circumference of the bubble. In these cases, the amount of orientation is relatively small because of competing molecular processes. While melt drawing tends to straighten out the polymer molecules and align them in the direction of the force applied, there is always a countering force within the molecule to return it to its natural coiled state. How fast this relaxation occurs depends on the viscosity of the melt, but it is generally fast enough so that very little permanent molecular alignment can be achieved by drawing a polymer melt.

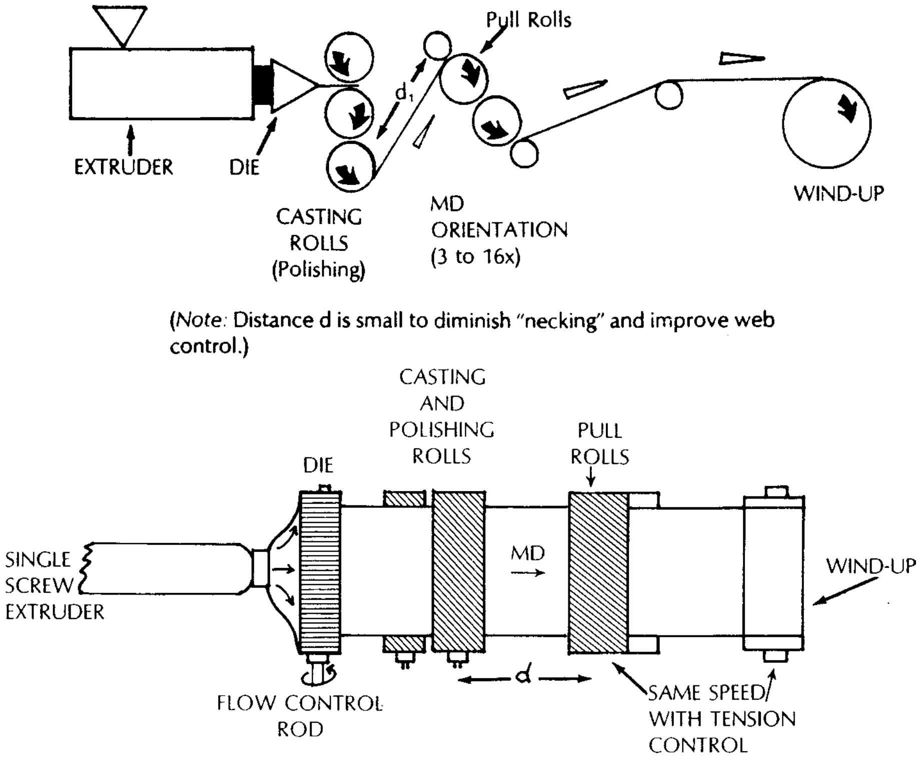
Orientation of amorphous polymers or polymers with low degree of crystallinity, the process is relatively simple. Such material is heated up above its glass transition temperature to bring it into the viscoelastic region. Then it is cooled to the proper temperature and stretched at the appropriate rate. If desired, it is then annealed at carefully controlled conditions to reduce thermal shrinkage. The annealing process is omitted if thermal shrinkage is desired (see below).

A crystalline polymer has to be first heated up above its crystalline melting temperature (T_m) to destroy crystallinity and then quenched rapidly to a temperature below its crystalline melting temperature to minimize crystallinity and preserve the amorphous condition. In the next step, it is reheated and oriented by stretching at a temperature somewhat above T_g but below T_m. Then it is annealed (if desired) or quenched rapidly to freeze in the shrink energy. For this step, it is constrained from shrinkage during the heating [117].

When a film is drawn in only one direction, the molecular chains and/or crystallites align themselves in that direction. The film then exhibits great strength and stiffness in that direction but the strength in the other direction is low. Although there are some applications where orientation in one direction is sufficient, in most cases orientation in two perpendicular directions, *biaxial orientation*, is required.

4.12.1.1 Machine Direction Orientation

Machine direction orientation (MDO) is accomplished by drawing the film or sheet between rolls rotating at different speeds, with the second set of rolls running faster than the first set (see Fig. 4.130). The first set of rolls stabilizes the sheet surface temperature and allows time for inner sheet temperature balance. The nip controls simultaneous rolling and stretching at optimum



(*Note*: Distance d is small to diminish "necking" and improve web control.)

Figure 4.130. Schematic diagram of machine direction orientation (Courtesy Taylor & Francis).

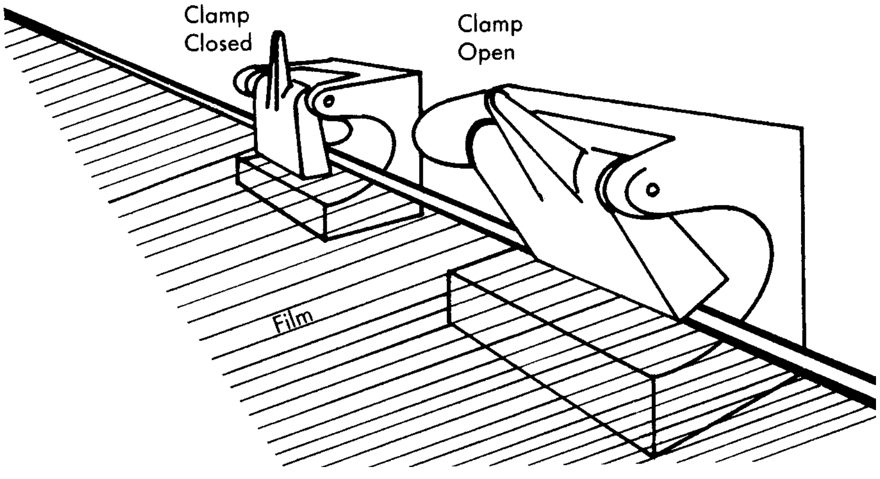


Figure 4.131. Tenter clips (schematic diagram).

orientation temperature. The final two rolls are used for heat setting and/or cooling the uniaxially stretched polymeric sheet. The stretching of the web is typically 3–16 times of the original length. Very often MDO is the first step in biaxial orientation, and is followed by *transverse direction orientation* (TDO).

4.12.1.2 Transverse Direction Orientation

Transverse direction orientation is stretched on a *tenter frame*; a machine consisting of two continuous chains like two racetracks mounted side by side [118]. Clamps (see Fig. 4.131) are mounted on top of each link and these grip each edge of the film. The film, then, is carried along as the chain is driven forward. The two chains move gradually apart, and as they do, they draw the film in the transverse direction between them. The chain rides on well-lubricated sliding surfaces or ball bearings at speeds up to 1,000 feet/min [118]. At the end of the stretching section, the clamps release the film and the chain turns around a wheel and is returned to the beginning of the stretching section where it reverses direction again. The clamps that ride on the chain must be able to grip the film securely as the film enters the stretching section, hold it against the stretching force applied to the film, and then release the film as it leaves the stretching section.

The tenter frame is enclosed in an oven that is usually heated with hot air. The temperature for TDO is generally higher than that for MDO, since during the MDO some crystallization has been induced that increases the resistance to stretching. Typically, the oven is often separated into two zones, each of them being heated to different temperature (Fig. 4.132). The usual stretch ratio in a tenter frame is 3:1 to 8:1.

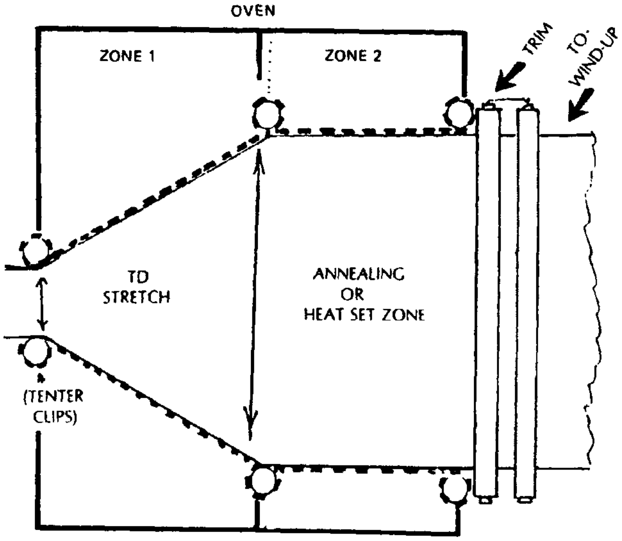


Figure 4.132. Schematic diagram of a tenter frame (Courtesy Taylor & Francis).

4.12.1.3 Biaxial Orientation

Biaxial orientation is a process whereby a plastic film or sheet is stretched in such a way that the polymeric chains are oriented parallel to the plane of the film. Biaxially oriented films exhibit exceptional clarity, very high tensile properties, improved flexibility and toughness, improved barrier properties, and can be relatively easily made shrinkable.

The widely used *two-step biaxial orientation* process is the combination of the MDO and TDO as mentioned in Section 4.12.1.1. The system consists of an extruder, MDO equipment (two or more sets of rolls running at different speeds) and of a tenter frame for the MDO. An example (biaxial orientation of polystyrene) is shown in Fig. 4.133). *One-step biaxial orientation* eliminates the

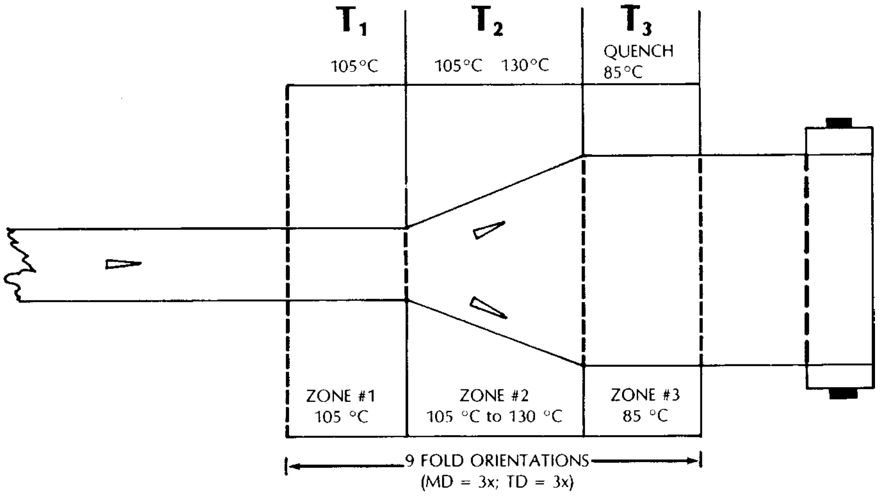


Figure 4.133. Schematic diagram of two-step biaxial orientation of polystyrene.

MDO stretching part and uses a tenter frame with accelerating clips. The process is mechanically rather complicated and it is difficult to adjust the balance between the two stretch directions, so it is used less frequently [119].

Bubble process, also called blown process or *tubular process* uses a tubular die to extrude a relatively thick-walled tube in a vertical direction, either upward or downward. Downward extrusion (Fig. 4.134) allows the tube to be quenched rapidly in a water bath after which it is collapsed as a layflat for passage over nip and idler rollers. The film passes through a reheating tunnel where it is raised to a temperature above the softening point but below the melting point. The heated tube is then inflated by internal air pressure that forms a bubble in which the film is stretched in all directions. Some machine-direction stretch may take place in the ovens upstream of the bubble; the haul-off rate can be adjusted if necessary to secure an orientation balance. An air ring similar to that used in other blown film processes provides bubble cooling. Subsequent calibration and bubble collapsing operations are also similar. The stretch ratio in the bubble process can vary from 3:1 up to 12:1 [120].

At this point, the film retains shape memory. If it is reheated, it will shrink and revert to dimensions approaching its pre-stretch shape. If a shrink film is required, the layflat is edge-trimmed, separated, and reeled as two webs at this stage. Non-shrink film is produced by subjecting the layflat to a further heat treatment in which it is annealed or heat set under tension in an oven. The annealing temperature is set slightly higher than the stretching temperature.

In general, films oriented by the bubble process have more balanced properties in the machine and transverse directions than tentered films as shown on the example of oriented PP films (Table 4.36).

4.12.1.4 Heat Shrinkable Films and Tubing

This class of oriented films exhibits high shrinkage (25% or more) at relatively low temperatures

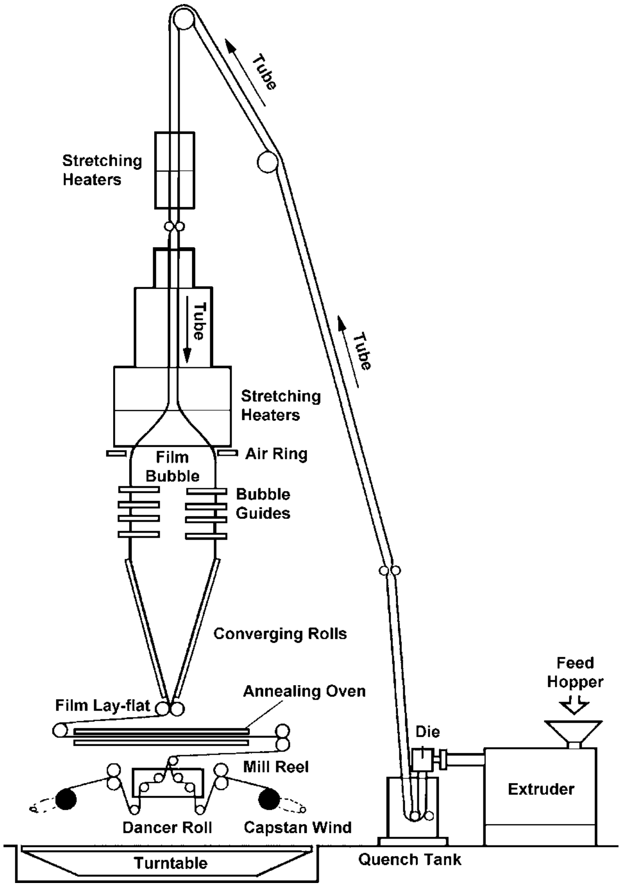


Figure 4.134. Bubble process for biaxially oriented film.

Table 4.36. Properties of Oriented Polypropylene

Property	Bubble Process	Tenter Process
Thickness (mil)	0.60	0.75
Tensile strength (psi)		
MD	26,000	17,000
TD	26,000	42,000
Elongation (%)		
MD	40–50	120
TD	40–55	50
Shrinkage (%), 1 hr at 124°C		
MD	8	3.5
TD	15	3.5

Source: Reference [117].

(less than 100°C, or 212°F in most cases). Generally, polymeric systems with reduced crystallinity are employed. Since it is rather difficult to produce a film with balanced shrinking properties by the two-step flat orientation (MDO plus TDO), the tubular process is the one most often used in shrinkable films and tubing [121].

For good shrinking properties, some polymer systems must be modified either by copolymerization or cross-linking (frequently by electron beam irradiation). The properties of shrinkable films depend largely on the polymer system used. Tensile strength, for example, ranges from 9,500 psi (62 MPa) for low density polyethylene (LDPE) to 26,000 psi (179 MPa) for PP. Also, the temperature range over which significant shrinkage occurs varies from 65°C to 120°C (150°F to 248°F) for polyethylene to 120°C to 165°C (248°F to 329°F) for PP [122, 133].

4.12.2 Welding

Welding is a method of joining parts without sacrificing the load-bearing capacity of the part. There is a variety of welding techniques for thermoplastic polymers that allow formation of strong joints, even approaching the strength of the parent material itself. All welding methods are not applicable to all thermoplastics, including TPEs. In general, applicability of a specific welding method is related to the rheology of the polymer. High melt viscosity makes welding difficult and reduces the number of applicable methods. Some of the most common methods include heated tool (hot plate), hot gas, ultrasonic, vibration, spin, and infrared welding techniques.

4.12.2.1 Heated Tool Welding

In heated tool (hot plate) welding, a heated platen is used to melt the joining surfaces of two thermoplastic surfaces. After the interfaces of the plastic parts have melted, the heated platen is removed, and the plastic parts are held together under low pressure to form a permanent and hermetic seal (see Fig. 4.135). A hot plate is used for flat joining surfaces; for curved or irregular joining surfaces, complex tools that allow the hot surfaces to match the contours of the joint interface are required. The platens can be coated by a PTFE coating, tape, or film to inhibit melt sticking [124–126].

4.12.2.2 Hot Gas Welding

In *hot gas (hot air) welding* [125–129] a heated gas is used to heat thermoplastic parts and a filler rod. The rod and the parts then soften and fuse, forming a high-strength bond upon cooling. Hot gas welding is commonly used for fabrication and repair of thermoplastic components and for lap welding of thin sheets or membranes. The bond strengths achieved by this method can be as high as 90% of the bulk material. Gases that can be used are air, nitrogen, carbon dioxide, and oxygen,

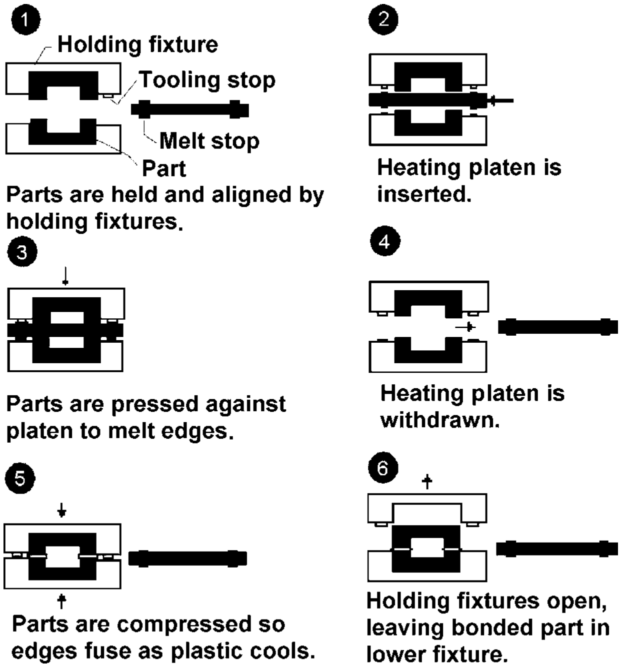


Figure 4.135. The hot tool welding process.

with air being the most common. The gas is heated to the melting temperature of the thermoplastic and is applied to the part and the thermoplastic rod through a nozzle or a tip (see Fig. 4.136). The filler rod is almost always composed of the same material as the part and is positioned at the joint. Hot gas welding methods may be manual or automatic, the manual method being used mostly for short seams. Gas temperatures usually range from 200° C to 600°C (390°F to 1110°F) depending on the melting temperature of the plastic material. Joint surfaces must be cleaned to assure a good bond. The cleaning can be done by mild soap, detergent, or a solvent (e.g., methyl ethyl ketone). A good bond has a fine bead on both sides (see Fig. 4.137).

4.12.2.3 Ultrasonic Welding

Ultrasonic welding [130–132], the most widely used welding method for thermoplastics, uses ultrasonic energy at high frequencies (20–40 kHz) to produce low amplitude (1–25 μm) mechanical vibrations. The vibrations generate heat at the joint interface of the parts being welded, resulting in melting the thermoplastic materials and weld formation after cooling. Ultrasonic welding is the fastest known welding technique with weld times of less than one second. Ultrasonic welding is used for both soft and rigid thermoplastics and for thermoplastic composites.

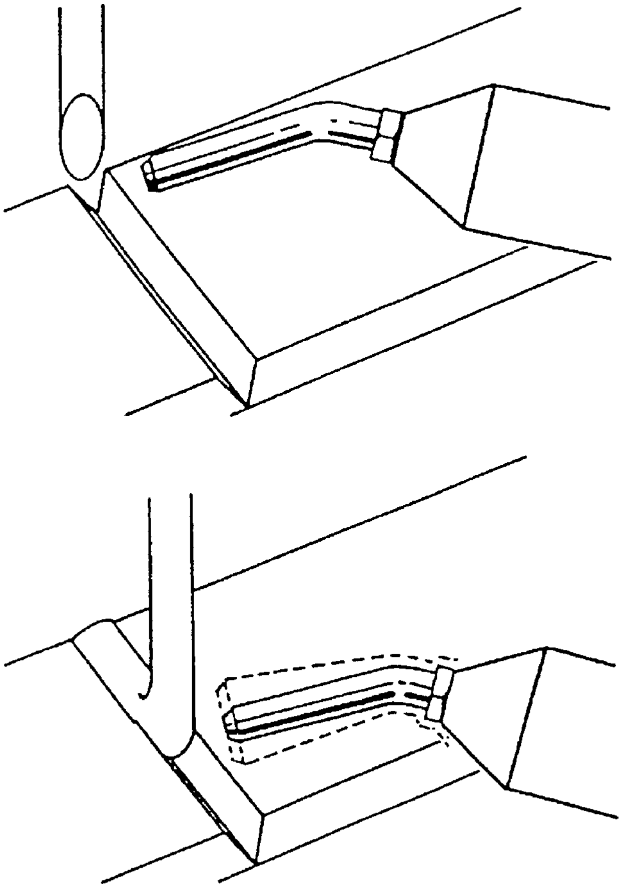
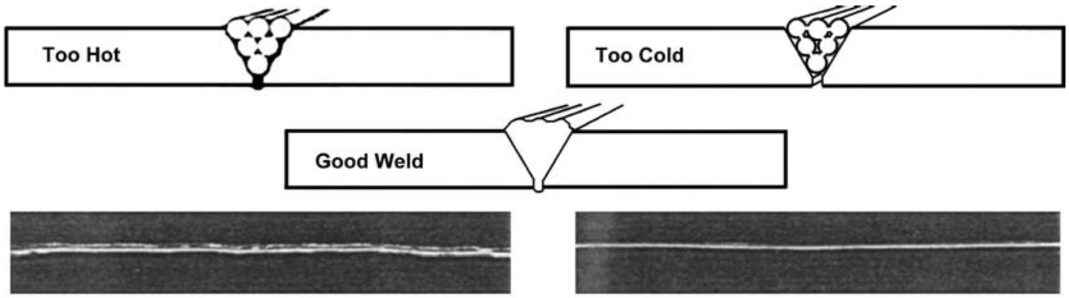


Figure 4.136. Manual hot gas welding.

Components necessary for ultrasonic welding are a generator or power supply, a converter or transducer, booster, and a horn or sonotrode (see Fig. 4.138). The generator converts low voltage electricity at 50–60 Hz and 120–240 V to high-frequency (20–40 kHz) and high voltage (13 kV) electrical energy. The electric current enters the converter, which contains piezoelectric ceramic crystals that expand and contract when excited by electrical energy. The electrical energy is converted into mechanical energy, and the converter expands and contracts at the frequency of the crystals [130–132]. The booster increases or decreases the amplitude of the mechanical vibrations of the converter, depending on the amplitude desired for welding, and conveys the vibratory energy to the horn or sonotrode. The horn, made of titanium, steel, or aluminum, can further increase the amplitude of the mechanical vibrations. It contacts one of the parts during welding and transmits vibratory energy to the part. For optimal energy transmission, the end of the horn that contacts the part is designed to mate with the part of the geometry. Fixtures hold the parts in place and apply pressure during welding. Ultrasonic welding begins after parts have been loaded and a particular force (trigger force) or distance has been reached by the horn [130–132].

Ultrasonic vibrations, applied to the part under pressure generate sinusoidal standing waves throughout the parts being welded at frequencies usually 20–40 kHz (see above). In a viscoelastic material, such as a thermoplastic, this energy produced under sinusoidal strain is dissipated through intermolecular friction, resulting in heat buildup.

Semi-crystalline polymers are characterized by regions of ordered molecular structure. A high amount of heat is required to disrupt this ordered arrangement. The melting point is sharp and the re-solidification occurs rapidly as soon as the temperature drops slightly. The melt that flows out of the heated region solidifies rapidly. When in the solid state, semi-crystalline molecules are spring-like and absorb a large part of the ultrasonic vibrations instead of transmitting them to joint interface,



Weld too hot. Scorched area around irregular bead.

Weld too cool. Poor bonding.

Stretched weld. Wil break at thin stretched points.

Good weld. Has a fine bead on both sides of the weld.

Figure 4.137. Weld quality analysis by its appearance.

so larger amplitude is necessary to generate sufficient heat for welding [132, 133].

4.12.2.4 Spin Welding

Spin welding [134–136] is a frictional process, in which thermoplastic parts with rotationally symmetrical joining surfaces are rubbed together under pressure using unidirectional circular motion. The heat generated thereby melts the thermoplastic in the joining zone, forming a weld upon cooling. It is a fast, reliable process that requires only minimal, basic equipment but that can be completely automated. After the rotational speed stabilizes, pressure is applied axially, perpendicular to the joining surfaces (see Fig. 4.139). When melting begins, heat is generated through internal friction within the molten material. As the melt thickness increases under pressure, part of the molten material is squeezed out of the bond area into a flash bead around the interface.

The main process parameters for spin welding are the speed of rotation, weld or axial pressure, and weld time. Parameters used depend on the material and the diameter of the joint. In commercial machines, rotational speeds can range from 200 to 14,000 rpm. Weld times may range from a tenth of a second to 20 s; typical values are about 2.0 s,

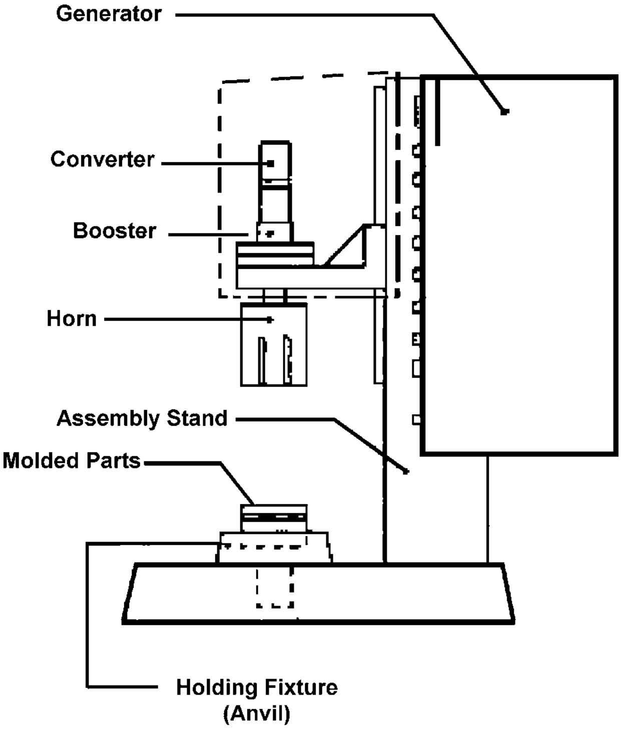


Figure 4.138. Components of an ultrasonic welder.

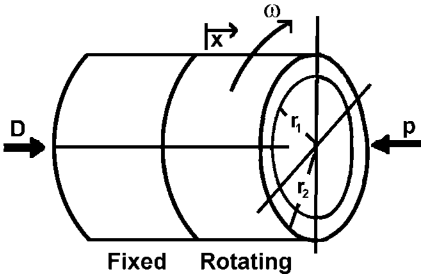


Figure 4.139. Spin welding. One part is fixed, while the other is Rotated using rotational motion w. Pressure is applied axially, along the *x*-direction. The tubes joined here have inside radius r_1 and outside radius r_2.

with an actual spin time of 0.5 s and a cooling time, when pressure is applied but spinning is stopped, of 0.2 to 0.5 s. Axial pressures range from about 1.0 to 7.0 MPa. The pressure must be high enough to force any contaminants or bubbles out of the joint, and the combination of speed and pressure must be controlled but high enough to cause melting at the interface as opposed to grinding.

4.12.2.5 Infrared Welding

In infrared welding, the joint surfaces of thermoplastic parts are heated to the melting temperature using infrared radiation, at wavelengths 1–15 μm. When melting begins, the parts are brought together under pressure, forming a weld upon cooling. Infrared welding is a non-contact welding method; the part surfaces are not in direct contact with the heat source but are at distances of up to about 20 mm (0.8 in.). Practically all known thermoplastics can be infrared welded, and the high temperatures that can be obtained at short heating times make this method especially suitable for temperature resistant materials. Infrared welding is similar to hot tool welding.

Rigid clamping devices hold parts and heaters in place, preventing distortion and misalignment during the welding process, and pneumatic actuators can be used to move heaters and parts as necessary during the welding. Hot tool welding equipment is commonly adapted for the use of infrared welding.

4.12.2.6 High Frequency Welding

High frequency welding, or radio-frequency (RF) welding, or dielectric welding, uses high frequency (13–100 MHz) electromagnetic energy to generate heat in *polar* materials, resulting in melting and weld formation after cooling. A high intensity radio signal is used to impart increased molecular motion in two similar or dissimilar polymers. This causes the materials to rise in temperature, increased polymer chain mobility, and melting. Ultimately, the polymer chains of the two materials penetrate their interface and become entangled, forming a weld. Radio frequency welding is frequently used in packaging and sealing applications and is particularly suitable for medical device industry because it uses no solvents or adhesives, which are possible sources of contamination [137].

The RF welding press has two platens—a movable one, and a fixed one, also called a *bed.* During the process, the press lowers the moveable platen and closes the electric circuit. The parts to be welded are placed in a set of metal die or electrodes, which are usually activated by a compressed air cylinder to apply a preset amount of pressure at the joint area. Radio frequency energy flows and the materials melt. The joint cools under pressure and after an appropriate time the press opens and releases the welded assembly.

Energy used in the RF welding process, typically 27 MHz is applied to the electrodes, and the resulting alternating current induces a rapidly reversing (several million times per second) electric field around the parts. Polar molecules tend to orient in the field direction, so that the positive (or negative) end of the dipole aligns to the negative (or positive) charges in the electric field, a process called *dipole polarization.* As the dipoles try to align with the rapidly reversing, high frequency electric field, their orientation becomes out-of-phase. The imperfect alignment causes internal molecular friction and results in the generation of heat. The electrical delay between changes in electric field direction and changes in dipole polarization are represented in Fig. 4.140. An oscillating electric field, *E* generates an oscillating current *I*, within the dielectric material. At high frequencies, the two curves are out-of-phase by the phase angle θ; the loss angle is defined as 90–θ, or δ. The amount of energy absorbed per cycle from the electric field is represented by the power factor and the dissipation factor; the power factor is defined as cos θ, and the dissipation factor or loss tangent is tan δ, a ratio of the current dissipated into heat to the current transmitted.

Radio-frequency equipment consists of three major components: a RF generator, a press, and a die or electrode. Generators commonly provide power ranging from 1 to 25 kW. Power requirements are determined by the welding area of the electrode and the thickness of the materials to be welded.

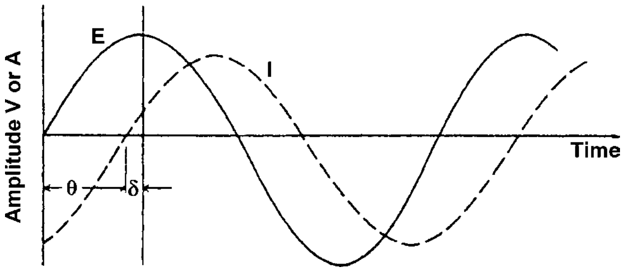


Figure 4.140. Electrical representation of dipole polarization resulting in heat generation due to imperfect alignment.

4.12.2.7 Vibration Welding

Vibration welding uses heat generated by friction at the interface of materials to produce melting in the interfacial area. The molten materials flow together under pressure and bond, forming weld upon cooling. Vibration welding can be accomplished in a short time (8–10 s cycle time) and is applicable to a variety of thermoplastic parts with planar or slightly curved surfaces. There are two types of vibration welding: *linear*, in which friction is generated by a linear back-and-forth motion and *orbital*, in which the upper part to be joined is vibrated using circular motion in all directions. Linear welding is most commonly used, but orbital vibration welding makes the welding of irregularly shaped plastic parts possible.

In linear vibration welding, the surfaces to be joined are rubbed together in an oscillating, linear motion under pressure applied at 90° angle to the vibration. Process parameters are the amplitude and frequency of this motion (weld amplitude and weld frequency), weld pressure, and weld time, all of which affect the strength of the resulting weld (Fig. 4.141).

Most industrial welding machines operate at weld frequencies of 120–240 Hz, although machines with higher frequencies are also available. The amplitude of the vibration produced by exciting a tuned spring-mass system, is usually less than 3 mm. Weld times range from 1 to 10 s (typically 1 to 3 s), with solidification times, after vibratory motion has ceased, usually of 0.5–1.0 s. Typical cycle times range from 6 to 15 s, resulting in 4–10 cycles/min [138, 139].

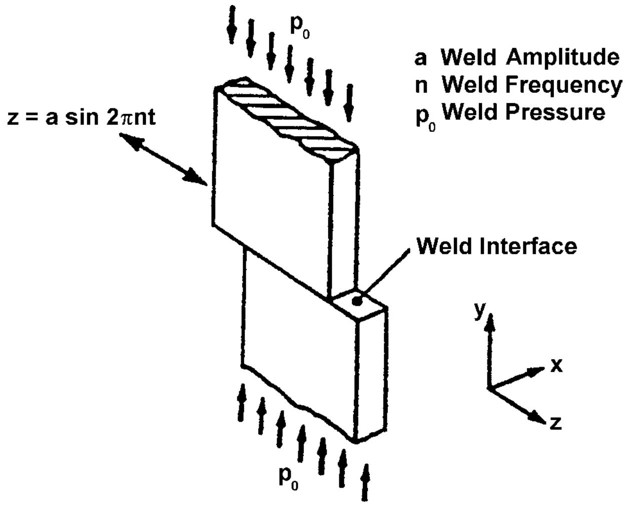


Figure 4.141. Linear vibration welding.

Weld pressure varies widely (0.5–20 MPa), although usually pressures at the lower end of this range are used. Welding time and pressure depend on the material being welded. Higher pressures decrease the welding time; however, higher strength of the welded parts is usually achieved at lower pressures due to greater melt layer thickness.

Most equipment used in vibration welding produces linear vibratory motion. Equipment is classified as low frequency (120–135 Hz) or high frequency (180–260 Hz) and can be variable frequency or fixed frequency. Most vibration welding systems are electrically driven and consist of three major components: a vibrator assembly suspended on springs, a power supply, and a hydraulic lifting table. A schematic of vibration welding machine is in Fig. 4.142 [139]. Tooling used in vibration welding equipment is simple, consisting of aluminum plates machined to the contour of the parts at the joint. For complex part geometries, slides and actuators can be incorporated using polyurethane poured nests.

4.12.2.8 Induction Welding

Induction welding uses induction heating from high RF alternating current to magnetically excite ferromagnetic particles embedded in a bonding agent (with a thermoplastic or adhesive matrix) placed at the joint interface of the two parts being welded. The heat released is used to melt and fuse thermoplastics, to heat hot-melt adhesives, or to provide rapid adhesive cures for thermosets. It is a reliable and rapid technique, ranging from fractions of a second for small parts to 30–60 s for parts with long (400 cm, or 160 in.) bond lines, and results in structural, hermetic, or high-pressure welds [140–142].

Inducting welding is a type of electromagnetic (EMA) welding, along with RF welding and microwave welding, which uses electromagnetic energy to heat materials. The three methods differ in the frequencies used for heating: 0.1 kHz to 10 MHz for induction welding, 13–100 MHz for RF welding and 2–10 GHz for microwave welding. Induction welding is frequently referred to as electromagnetic welding [137].

Heat in induction welding is generated from interaction of the magnetic field with the ferromagnetic material (stainless steel, iron) and from current induced in the metal. The high frequency alternating current moves through a copper coil, generating a rapidly reversing magnetic field. Ferromagnetic materials align with the magnetic field; alignment changes as magnetic field direction changes.

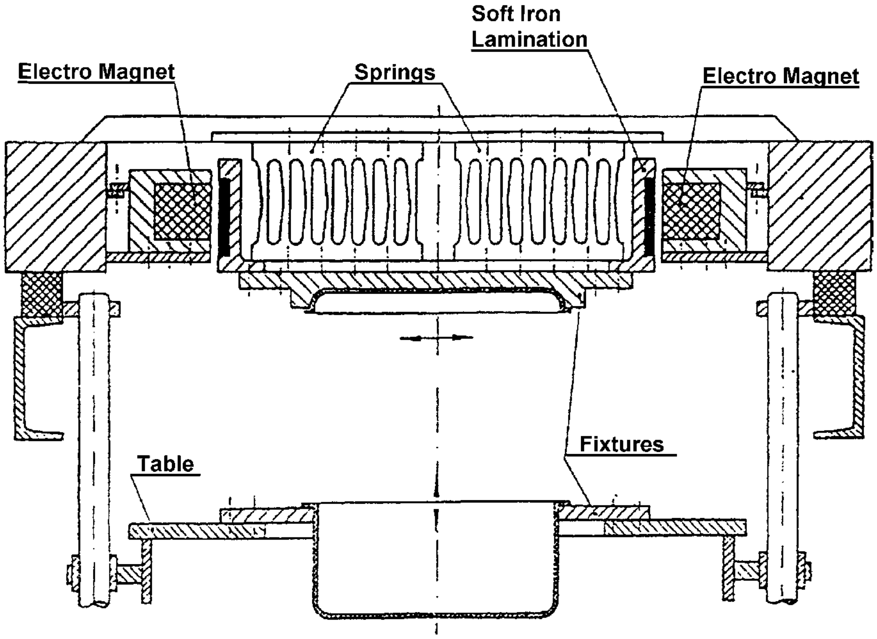


Figure 4.142. Schematic diagram of a vibration welding machine.

Atoms do not return to the initial alignment existing before the magnetic field changed direction but to slightly different alignment; some of the previous alignment is retained. This phenomena, referred to as *hysteresis*, results in heat losses within the metal, which are transferred to the plastic matrix through conduction. Alternating current also induces voltage within metallic ferromagnetic materials, resulting in internal currents, called *eddy currents*. Eddy currents dissipate as heat, which is also transferred to the thermoplastic matrix. With higher eddy currents, more current is required in the coil to maintain particular field strength [143].

High frequencies are achieved using an induction generator, which converts a 50–60 Hz supply to frequencies usually 1.8–10 MHz with power 1–5 kW, depending on the application. The magnetic field is formed by passing high frequency current through *work* or *induction coils*, water-cooled copper coils of different sizes and shapes.

In the induction welding of thermoplastic, the *bonding agent*, ferromagnetic particles embedded in a thermoplastic matrix, is placed in the joint before the welding (see Fig. 4.143). Slight pressure (0.1–0.3 MPa) is applied to the parts to be welded, and high frequency current is passed through the coil. Welding can be accomplished in 1–2 s for parts 6.4 mm (0.25 in.) or thicker.

Induction welding is less dependent than other welding methods on the properties of the materials being welded. It can be used to weld almost all thermoplastics, crystalline and amorphous.

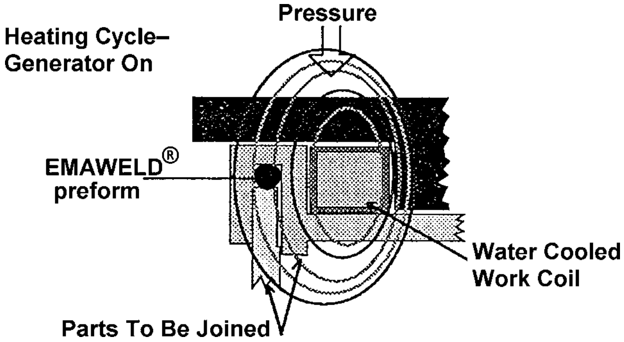


Figure 4.143. The induction welding process.

The equipment for induction welding consists of the induction generator, work or induction coils, and fixtures or nests. Placement nests hold work coils in place; one nest is generally fixed and the other movable. They are made of electrically nonconductive materials in order not to reduce the intensity of the magnetic field. Typical induction welder is shown in Fig. 4.144.

4.12.2.9 Microwave Welding

Microwave welding uses high frequency electromagnetic radiation to heat a susceptor material located at the joint interface; the generated heat melts thermoplastic materials, producing a weld upon cooling. The frequencies used for this method are 2–10 MHz, as pointed out earlier (see Section 4.12.2.8).

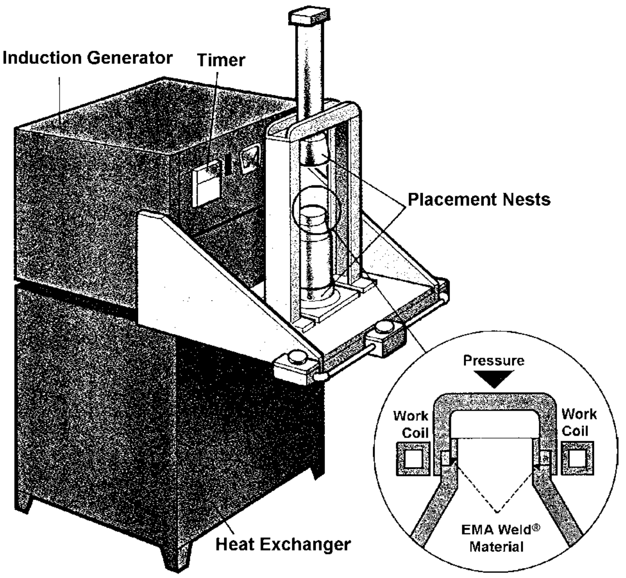


Figure 4.144. A typical induction welder.

The susceptor materials contain polar groups in their molecular structure or are electrically conductive. In an applied electric field, polar groups align in the field direction. In a microwave, the magnitude and direction of the field changes rapidly; polar molecules develop strong oscillations as they continually align with the field, generating heat through friction [144].

Equipment for microwave welding can be as simple as a conventional microwave oven. A more sophisticated, single mode microwave system is shown in Fig. 4.145. The microwave power source has a magnetron generating 3,000 W power at a frequency of 2,450 MHz. The welding is performed in the double-slotted applicator connected to the tuner. A dummy load connected to the applicator converts transmitted energy into heat; water is used for cooling. This system produces a traveling wave pattern used in adiabatic heating. Connection to a pressure device consisting of a solenoid valve, air cylinder, and relay provides pressure regulation during welding [137, 144, 145].

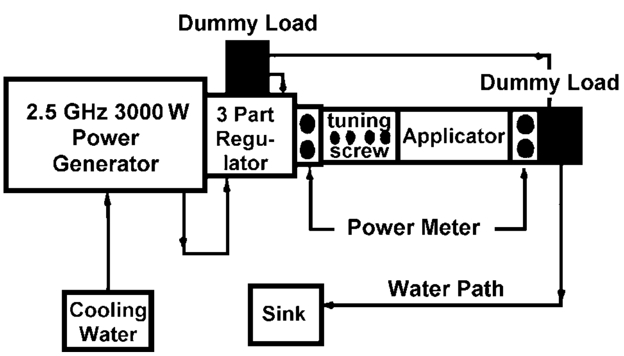


Figure 4.145. A single mode microwave system.

4.12.2.10 Other Welding Methods

Resistant welding, also called *resistance implant welding* is a method, in which current is applied to a conductive heating element or implant placed at the joint interface of the parts being welded. The implant is heated through Joule heating, and the surrounding plastic melts and flows together, forming a weld. Heating elements can be carbon fiber prepregs, woven carbon fabric, or stainless steel foil or mesh. Stainless steel heating elements can be used alone in welding thermoplastics. The heating element comprises the innermost portion of the weld stack (see Fig. 4.146) and is sandwiched between the parts to be joined, referred to as adherends. Insulators on the outermost ends of the weld stack complete the assembly. The weld stack can be autoclaved for consolidation [146–151].

Extrusion welding is a reliable technique developed from hot gas welding, in which thermoplastic filler identical to the welded material is extruded into a groove in the preheated weld area. The filler material fills the groove and forms a weld after

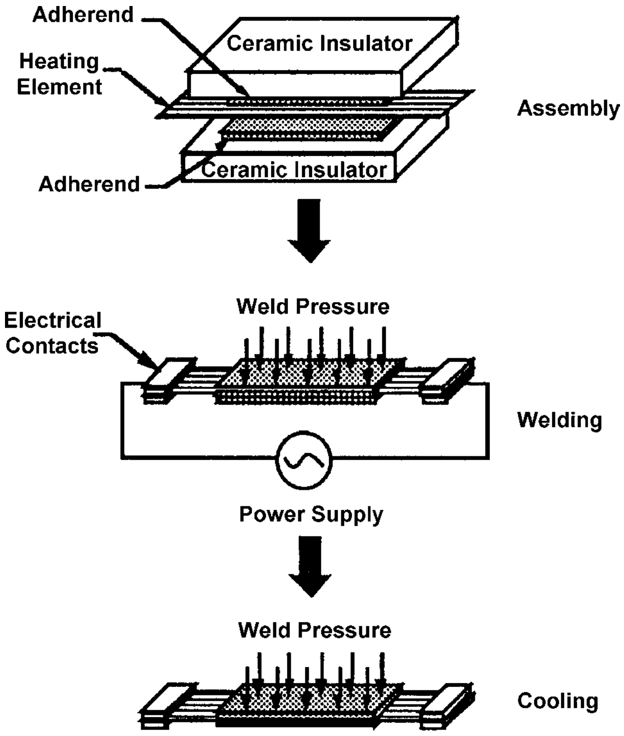


Figure 4.146. The resistance welding process.

cooling. Extrusion welding is usually performed manually, but it can be automated.

The extrusion welding for a *V-type seam* is in Fig. 4.147. Cleaned, ground, and scraped parts are positioned in a specific geometry, and the welding area is preheated by hot air from a nozzle that moves along the joint line just before the welding shoe. Both the hot air nozzle and the welding shoe are attached to the welding head, which moves along the joint line at a particular welding speed. Molten extruded thermoplastic material is applied under pressure by the welding shoe, filling the joint area [152, 153]. The process for a *lap seam* (Fig. 4.148) used for joining waterproofing membranes is similar, except that the joining pressure is applied to the flat membranes during welding [154].

Preheating of the joint surfaces, in order to form a surface melt layer, is essential for obtaining a good quality weld and is the most important determinant of the mechanical properties of the weld. Parameters that influence the preheating process include hot air temperature, welding velocity, geometry of the air nozzle, and the thickness of the parts being welded. Greater melt thickness produces a weld of greater strength.

Laser welding is a relatively new process, in which a high intensity laser beam is used to increase the temperature at the joint interface of thermoplastic materials to or above the melting temperature. The molten plastics cool down and solidify, forming a weld.

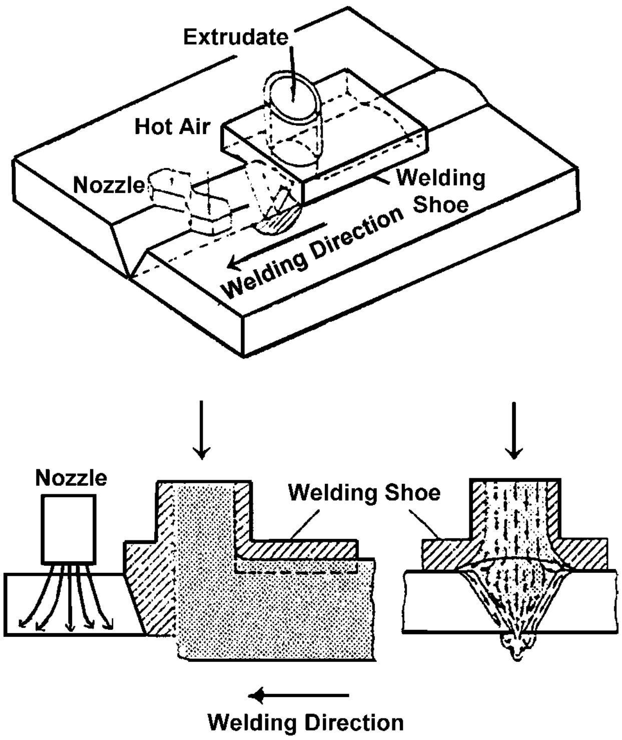


Figure 4.147. Extrusion welding, a V-type seam.

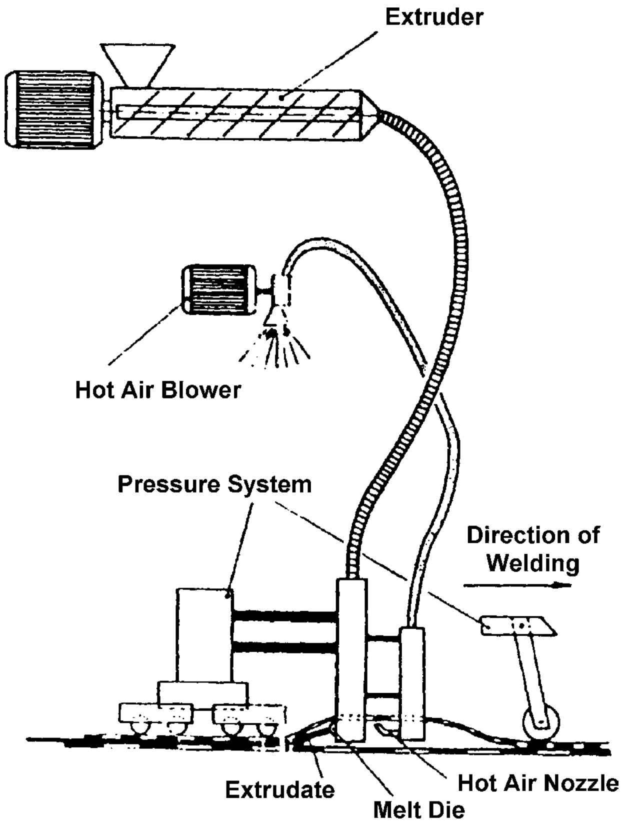


Figure 4.148. Extrusion welding lap seam.

Carbon dioxide and Nd-YAG (neodymium ions in a medium of yttrium aluminum garnet) lasers are predominantly used in industrial applications. Carbon dioxide lasers emit radiation at wavelength of 9.2–10.8 μm at range in power from 30 W to 40 kW. The laser beam is transmitted through the air, reflected from mirrors, and focuses using ZnSe lenses. In the Nd-YAG laser, flash lamps excite Nd^{+3} ions in a solid crystal rod, resulting in radiation with the strongest emission at a wavelength of 1.06 μm. The short-wavelength beam is transmitted through fiber optic beam delivery system, and power ranges from 30 W to 2 kW. Lasers can generate radiation continuously (continuous wave), or it can be emitted in short bursts of microsecond or millisecond duration (pulsed). Carbon dioxide lasers generally operate in a pulsed mode, while either pulsed or continuous wave modes can be used with Nd-YAG lasers [155, 156].

In laser welding, parts being joined are clamped onto a moving table. Pressure can be applied throughout the process or may only be applied after heating is terminated. In the presence of a shielding gas, the high-intensity laser beam travels at a high speed across the weld interface of the parts being joined. The beam causes heating that is localized near the joint interface that can rapidly result in melting, degradation, and vaporization of the polymer in the weld interface. Degraded material in the joint interface, which has a negative effect on joint strength, is pushed out of the weld due to external pressure, forming flash on top and bottom surfaces, and is vaporized due to the high-intensity beam. Molten material flows together at the joint interface and forms a weld after cooling is complete [157, 158].

Radiation reaching the joint surface can be reflected, transmitted, or absorbed. Reflected radiation hits the part surface and bounces off, while transmitted radiation travels through the part unaffected. Reflection from all plastics is low (5–10%). Laser radiation can be absorbed at the surface of the material or can penetrate to various depths depending on the wavelength of the incident beam and the amount and type of pigment, filler, or reinforcing additives in the plastic material. Absorption results in heat generation within the plastic. The laser welding process is depicted in Fig. 4.149. A detailed description of laser welding is in references [155–158].

4.12.3 Adhesive Bonding

The majority of thermoplastics can be bonded by adhesives. Some of them can be joined without any surface treatment; others require surface treatment to achieve a sufficient adhesion.

4.12.3.1 Principles of Adhesive Bonding

An adhesive is a substance capable of holding materials together by surface attachment. There are many types of adhesives available; they may be classified in several ways, for example by the mode of application, chemical composition, suitability for certain substrates, and cost.

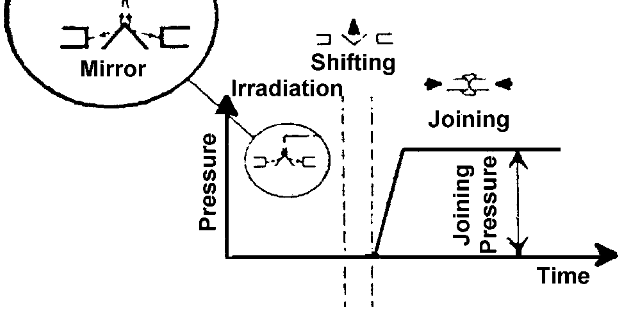


Figure 4.149. The laser welding process.

Essentially, an adhesive must be applied to the *substrate* (or *adherend*) in a fluid form to wet the surface completely and leave no voids, even if the surface is rough. To meet these requirements, it has to have a low viscosity at the time of application. In order to create a strong bond, the adhesive layer has to exhibit a high *cohesive strength*, that is, it has to set. This usually happens by the removal of the solvent or water, by solidification, crystallization, polymerization, and/or cross-linking.

Wetting of a surface and spreading of a liquid depends primarily on the nature of the surface of the substrate and on the *surface tension* of the liquid. The wettability of a solid surface depends on its *surface energy*, expressed by its *critical surface tension*. The critical surface tension indicates the maximum surface tension permissible in a liquid (i.e., adhesive) for a particular substrate. To assure spreading and wetting, the liquid adhesive should have a surface tension *no higher* than the critical surface of tension of the substrate (i.e., solid adherend). When the substrate is organic and not too polar, *solubility parameter* (δ) is a quantity useful in the selection of a suitable adhesive to it. The solubility parameter is defined [159] as:

$$\delta = (\Delta E/V)^{1/2} \tag{4.7}$$

where ΔE is the energy of vaporization and V is the molar volume. The term $\Delta E/V$ is referred to as *cohesive energy density*. The values of solubility parameter and critical surface tension are related [160]. Examples for selected polymers are in Table 4.37.

The degree of wetting and spreading is quantitatively expressed in terms of the *contact angle* [161]. Contact angle (θ) is the angle (in the liquid) between the air–liquid and liquid–solid interface (see Fig. 4.150), resulting as a mechanical equilibrium of a drop resting on a plane solid surface under the action of three surface tensions—γ_{LV} at the interface of the liquid and vapor phases, γ_{SL}, at the interface of the solid and the liquid, and γ_{SV} at the interface of solid and vapor – hence,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\theta \tag{4.8}$$

From this relation, the critical surface tension, γ_c is derived for an individual substrate by measuring contact angles of a homologous series of liquids with known surface tension values on it, and plotting

Table 4.37. Solubility Parameters and Critical Surface Tensions for Selected Polymers

Polymer	Solubility Parameter δ hildebrands	Critical Surface Tension, γ_c (dynes/cm)
Polytetrafluoroethylene	6.2	18.5
Silicone, polydimethyl	7.6	24
Butyl rubber	7.7	27
Polyethylene	7.9	31
Natural rubber	7.9–8.3	—
Polyisoprene, cis	7.9–8.3	31
Styrene-butadiene rubber	8.1–8.5	—
Polyisobutylene	8.0	—
Polybutadiene, cis	8.1–8.6	32
Polystyrene	9.1	32.8
Poly(methyl methacrylate)	9.3	39
Poly(vinyl chloride)	9.5–9.7	39
Poly(ethylene terephtalate)	10.7	43
Poly(vinylidene chloride)	12.2	40
Polyamide 6,6	13.6	43
Polyacrylonitrile	15.4	44

Source: From reference [177].

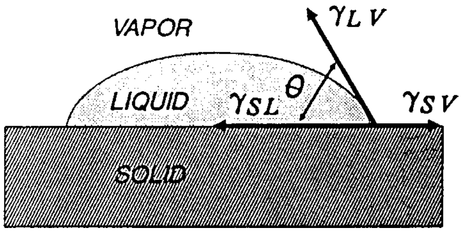


Figure 4.150. Contact angle of a sessile drop.

the results as shown in Fig. 4.151 (often referred to as the *Zisman plot*). Extrapolating to a zero contact angle (i.e., cos $\theta = 0$) and extending the intercept to the surface tension axis gives the critical surface tension of the solid surface [162].

If the contact angle is near zero degrees, the liquid spreads and wets the substrate completely. Larger values of the contact angle indicate a poorer wetting. An extreme case is when θ is 180°; then there is absolutely no wetting of the substrate. Detailed discussion of wetting and spreading of liquids on solids are in references [161, 162].

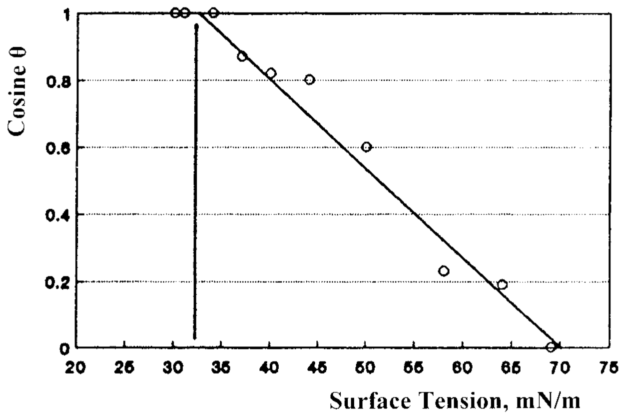


Figure 4.151. Determination of the critical surface tension.

4.12.3.2 Methods of Surface Treatment

The surfaces to be bonded, regardless of the bonding method or the type of adhesive, have to be clean. Often it is sufficient to wash them with solvents to remove contaminants such as oils, sometimes grinding the surface cleans it and the roughness improves the bonding by virtue of providing a greater surface area.

However, if the surface of the polymer to be bonded by adhesive has a too low surface energy, it has to be treated in order to increase the surface

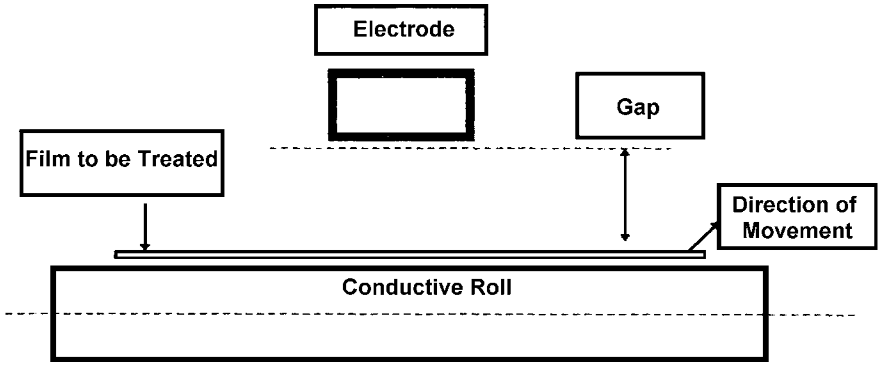


Figure 4.152. Conceptual schematic diagram of a film corona treatment system.

energy, which improves the wetting by the adhesive. The methods used for that most frequently are:

- Flame treatment
- Corona treatment
- Plasma treatment.

Flame treatment is a commercial process to render polyolefins and polyethylene terephtalate receptive to adhesives, coatings and printing inks. The polymer article (e.g., film) is passed over an oxidizing flame formed by an oxygen-rich (relative to stoichiometry) mixture of hydrocarbon gas. The gas flame contains excited fragments and species such as atomic oxygen (O), NO, OH, and others that can abstract hydrogen from the surface of the polymer, which is then replaced by oxygenated functional groups (mostly —C=O and —OH).

Corona discharge treatment takes place at atmospheric pressure in contrast to low temperature (cold) plasma (see below) that requires vacuum. Corona is a stream of charged particles such as electrons and ions that is accelerated by an electric field. It is generated when a space gap filled with air or other gas is subjected to a sufficiently high voltage to set up a chain reaction of high-velocity particle collisions with neutral molecules resulting in the generation of more ions. The treated surface has higher surface energy and can be therefore readily wetted. One of the widely used configurations (Fig. 4.152) uses corona discharge produced by high-frequency high-voltage alternating current [163]. The main parameters for the control of this treatment process include the voltage, width of the air gap, film/web speed, and the width of the electrodes. Most machines allow treatment on one side of the web (see Fig. 4.153) and require two passes for two-sided treatment.

Plasma (glow discharge) is produced by exciting a gas with electrical energy (Fig. 4.154). It is a collection of charged particles containing positive and negative ions [164]. Other types of fragments, such as free radicals, atoms and molecules, may also be present. Plasma is electrically conductive and is influenced by magnetic field. It is intensely reactive, which is the reason why it can modify surfaces of plastics [165, 166]. It can be used to treat parts to make their surfaces harder, rougher, more wettable, less wettable, and easier to adhere to. Plasma treatment can be carried out on a variety of plastic parts and even on powder additives like pigments and fillers.

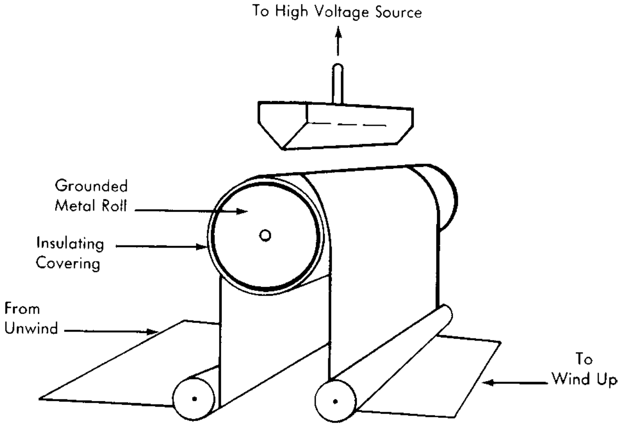


Figure 4.153. A typical single side corona treatment machine.

The plasma used for treating surfaces of materials is called *cold plasma*, which means its temperature is about room temperature. Cold plasma is created by introducing the desired gas into a vacuum chamber (Fig. 4.155), followed by radio frequency (13.56 MHz) or microwave (2,450 MHz) excitation of the gas [166]. As pointed out earlier, the energy dissociates the gas into electrons, ions, free radicals, and metastable products. Practically any gas may be used for plasma treatment but oxygen is the most common. The electrons and free radicals created in the plasma collide with the

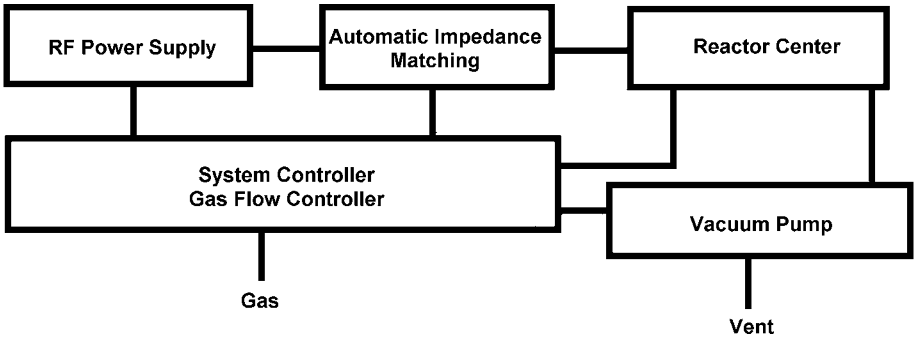


Figure 4.154. Schematic diagram of a plasma system.

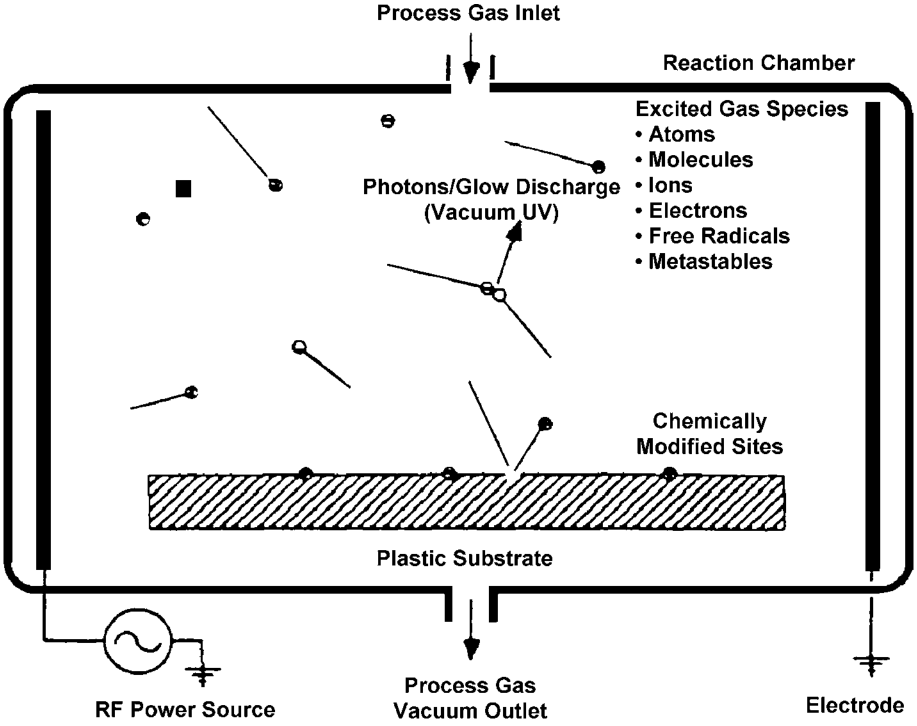


Figure 4.155. Schematic diagram of the surface modification of plastics in a gas plasma reactor.

polymer surface and rupture covalent bonds thus creating free radicals on the surface of the polymer.

Other methods of surface treatment include: *Etching and oxidation* using chromic acid and other strong oxidizing compounds, *thermal treatment*, which is done by a blast of hot air (~500°C or 932°F) [167, 168] and *surface grafting* that is performed by irradiating the substrate by electron beam in the presence of acrylic acid [169]. *Laser treatment* is done by XeCl, ArF, and KrF lasers and introduces oxygenated functional groups to the surface and removes surface contaminants [170].

Primers are reactive compounds that are applied to the substrate surface before the application of the adhesive. They form a chemical bridge between the substrate and adhesive through multifunctional groups that react preferentially with either adhesive or substrate [171].

Methods of surface treatment of materials for adhesive bonding are covered thoroughly in references [172, 173].

4.12.3.2.1 Evaluation of the Level of the Surface Treatment

There are several ways to test the level of any of the above treatments. One common method involves using solutions made from two chemical compounds that produce liquids ("dyne liquids") with surface tensions in the range 30–70 dynes/cm. The test consists of placing droplets of the various dyne liquids on the treated surface and observing the spreading of the drops in two seconds. Successive liquids with different surface tensions allow narrowing of the surface tension range of the web. This method is subjective but it provides a rapid means of assessment of the treatment level. There are also pens operating in a similar fashion as the dyne liquids. A more quantitative approach is the measurement of contact angle, which decreases with the increase of the treatment level [174].

4.12.3.3 Types of Polymeric Adhesives

As pointed out earlier, polymer-based adhesives can be classified in several different ways. They may be liquids of different viscosity, represented by *solvent-based adhesives*, *aqueous dispersions* or *emulsions,* and *latexes monomers*, or *oligomers*. In all cases the main component is an organic compound, such as a polymer (dispersions, emulsions, and latexes) or a monomer or oligomer that forms the adhesive film. Polymers used in adhesives are mainly thermoplastics or elastomers that often are combined with tackifying resins. Monomers and oligomers have to polymerize in order to form a strong enough film. In some cases all these adhesive substances may be cross-linked in order to further increase the cohesive strength, heat resistance, and chemical resistance of the bond.

Contact adhesives are mainly solvent-based or water-based adhesives most frequently containing elastomers combined with tackifiers and exhibit an aggressive tack. Once the components coated with contact adhesives are joined, the bond is strong and permanent.

Hot-melt adhesives are 100% nonvolatile materials, that is, containing no solvents, or water, or other volatile carriers. They are solid at room temperature, but fluid at elevated temperatures. Hot melt adhesives are applied in the molten state with special equipment, often as beads or stripes. After application, bonding and cooling, hot-melt adhesives return to the solid state and develop their ultimate strength.

Heat activated assembly adhesives are solution-based adhesives that are applied to the surfaces of two substrates and dried. Then, prior to assembly, the coated surfaces are heated to a sufficiently high temperature, and then pressed together.

Two-part adhesives consist of two components, kept packaged separately, which are mixed just prior to use. After these two components are mixed they start to react. As the reaction proceeds, the adhesive layer becomes stronger. The reaction is most widely a polymerization (polyaddition, polycondensation, etc.). The reaction may be completed in short times (minutes), but it may takes hours or days, depending on the system.

Moisture-cure adhesives are based on compounds that cure by the exposure to moisture. They are kept in impermeable packaging until they are applied onto the substrate. The reaction takes usually days to be completed since it depends on diffusion of moisture through the applied layer.

Anaerobic adhesives are single-component liquids that can be stored at ordinary temperatures in the presence of oxygen and then polymerize rapidly to solids on being confined between two surfaces that exclude air.

As for the chemical nature, there are many polymers used in adhesives. A detailed list is beyond the scope of this work, so only the most widely used polymers, monomers, and oligomers will be listed.

Elastomers are widely used in solvent-based, water-based (latexes), contact, pressure-sensitive and hot-melt adhesives. Elastomer-based adhesives may contain a wide variety of component materials, such as resins, tackifiers, fillers, plasticizers, antioxidants, curing agents, etc. Solvent-based adhesives are prepared by simply dissolving the rubber compound in a suitable volatile solvent. Elastomer-based hot melts are generally mixtures of the base elastomer and a tackifying resin and other ingredients that affect its melting and melt viscosity. No volatile ingredients are present in hot melts, as pointed out earlier. Latex-based elastomeric adhesives contain a variety of other materials, such as protective colloids, emulsifiers, surfactants, thickeners, and emulsion stabilizers.

The following elastomers are typically used in most commercial adhesives: Natural rubber, polyisoprene, styrene-butadiene rubber, polybutadiene rubber, acrylonitrile rubber, polychloroprene, acrylate rubber, polyurethane rubber, polysulfide rubber, silicone rubber, carboxylic elastomers, and copolymers of ethylene and vinyl acetate.

Thermoplastic elastomers such as S-B-S, styrene-isoprene-styrene block copolymer (S-I-S), and TPU are most widely used in hot-melt, pressure-sensitive, contact and heat activated adhesives alone or in blends with other elastomers and resins.

Epoxy resins are mostly employed in two-part adhesive systems with different curing time and with different bond characteristics.

Polyurethane- and isocyanate-based adhesives. Certain types of polyurethane adhesives are two-part systems, consisting of a polyol (often an oligomeric polyol) and of a polyisocyanate, which are kept separately and mixed only prior to use. The bond strength develops rather rapidly. Other polyurethane adhesive systems include TPUs used in hot-melts, polyurethane aqueous dispersions, powders, and films. Isocyanates alone are used as primers [175] or as cross-linking agents in certain elastomeric adhesives prepared with thoroughly dried inert solvents [175].

Silicones. Silicones can be used in two-part systems and also as single-package moisture curing adhesives and sealants.

Cyanoacrylates. Cyanoacrylate adhesives form a strong adhesive bond rapidly, typically in less than a minute. This is the result of an anionic polymerization initiated by weakly basic species, such as water or alcohol, at ambient temperatures [176].

Other polymers used for adhesives are: Ethylene-vinyl acetate copolymers, polyvinyl acetal, polyamides, polyimides, polybenzimidazoles, polybenzotriazoles, and others used for specialized applications.

The reader can find more on the subject in reference [177].

4.12.3.4 Application of Adhesives

Most of the adhesives are applied in liquid form. The commonly used methods of application are:

- Brushing
- Spraying
- Dipping
- Curtain coating
- Application by roll
- Application of a bead or stripe of a hot melt.

4.12.3.5 Formation of an Adhesive Bond

When an adhesive is applied as a solution in a volatile solvent or as an aqueous dispersion or emulsion, the solvent or water has to be evaporated. In most cases this happens over a relatively short time at ambient temperature. Sometimes the drying time can be reduced by applying hot air to the surface of the parts to be joined or by using infrared heaters.

The assembly of the joint has to take place while the adhesive layer has a sufficient tack. So each type of adhesive has a specific *open time*. Open time or *bonding range* is the maximum time two surfaces coated with an adhesive may be allowed to dry (or cool down if applied in molten state) before bonding and still have satisfactory adhesion. It depends on the specific application and can vary from less than one minute to more than 24 hr.

The adhesive joint can be formed by pressing the two adherends together. If the adhesive has a high tack (e.g., a contact adhesive), no additional pressure is required. Similarly, for the bond formed by hot melts a brief application of pressure is needed until the melt solidifies. In other cases pressure has to be applied for a certain period of time by placing the joint between platens of a press or into a specialized fixture that holds the joined parts together until the bond is sufficiently strong. The same applies to adhesive bonds that become stronger due to a chemical reaction. Occasionally heating of such joints is used to reduce the time for a sufficiently strong bond or to achieve considerably higher bond strength.

4.12.3.6 Measurement of the Bond Strength

There are many tests of measuring the strength of the bond between an adhesive and a substrate. They are used for five main purposes [178]:

(1) To check the quality of an adhesive to see if it falls within well-defined limits;
(2) To determine the effectiveness of the surface treatment;
(3) To gather data for the prediction of the performance of the adhesive joint;
(4) To select an adhesive from a group for a specific application;
(5) To evaluate the effect of aging on the performance of the joint.

The most common test configurations are:

- Tensile
- Shear
- Peel.

Shear tests are most commonly used tests for a quick assessment of adhesion between two rigid substrates. The simplest test configuration is the *lap shear test* using two principal forms of test pieces, the single lap joint (Fig. 4.156) [179], and the double lap joint (Fig. 4.157) [180]. The advantage of the lap joint is that it can be easily manufactured and quickly tested. After the test piece is ready for the test, it is pulled apart in the axis of

Figure 4.156. Single lap joint.

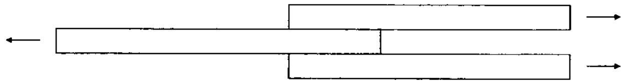


Figure 4.157. Double lap joint.

the bond and the failure load is then calculated. The test results are of restricted value in the design of adhesively bonded components, because of its complex stress distribution [181]. However, in spite of that, this test provides a rapid assessment of the shear stress of the adhesive and may serve as a good method of screening adhesives for a specific application.

The test piece for the adhesive *tensile test* can take several forms; one simple configuration consists of two cylinders (Fig. 4.158) that are bonded together at their ends. The joint is loaded to failure at right angles to the plane of the adhesive and the failure stress is determined by dividing the failure load by the loaded area [182]. The tensile test pieces are widely used for testing the strength of bonds of rubber and plastics to metals.

Peel tests are generally used for elastomeric adhesives. A typical version is the *T-peel test*, in which two strips of substrate bonded together face to face are peeled and the force required to pull them apart is recorded. The peeling can be done at a 90° angle, typically for two flexible substrates (Fig. 4.159) [183] or at a 180° angle for peeling of a flexible substrate from a rigid substrate (Fig. 4.160) [184].

Other adhesive tests, such as wedge test, cleavage strength test, impact strength test, and fatigue strength test [177] are designed for specific applications and service conditions.

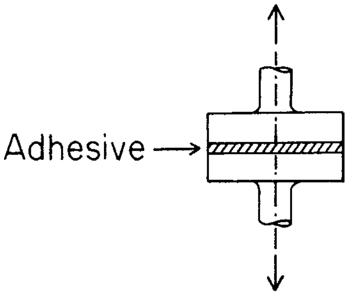


Figure 4.158. Adhesion tensile test piece.

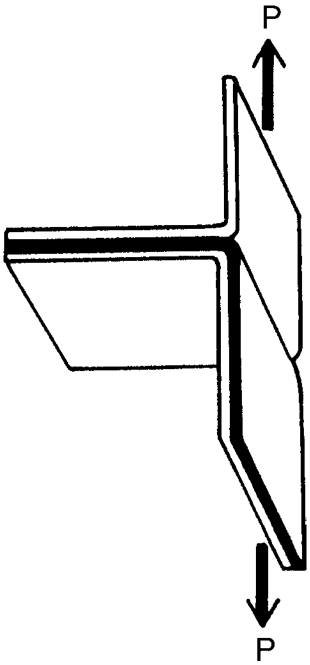


Figure 4.159. 90° peel test.

4.12.4 Mechanical Fastening

Mechanical fastening is a simple and versatile joining method. Mechanical fasteners are made from plastics, metals, or a combination of the two materials and can be periodically removed and replaced or reused when servicing of the part is necessary. Screws, nuts, and inserts can be made from plastics or metals; rivets are generally made from metals. Plastic fasteners are lightweight, corrosion resistant,

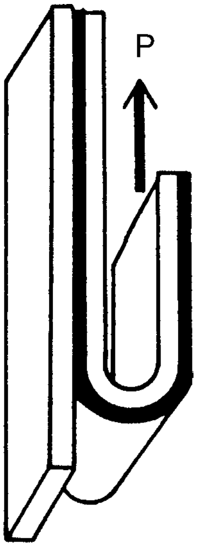


Figure 4.160. 180° peel test.

and impact resistant. They do not freeze on threads of screws and require no lubrication. Metal fasteners provide high strength and are not affected by exposure to extreme temperatures [185].

Screws, nuts, washers, pins, rivets, and snap-type fasteners are examples of non-integral attachments, in which the attachment feature is a separate part. Use of separate fasteners requires plastic materials that can withstand the strain of fastener insertion and the resulting high stress near the fasteners. Snap-fits are examples of integral attachments, attachment features that are molded directly into the part. Strong plastics that can withstand assembly strain, service load, and possible repeated use are required for non-integral attachments. Separate fasteners add to product cost due to increased assembly time and use of additional material, and can be difficult to handle and insert; as a result, use of integral attachment features is increasing [186–188].

Wider and more detailed discussion of the subject of joining plastics is in references [189–191].

4.12.5 Decorating

Plastics decorating involves the modification of a plastics surface, using a coating or impression, by the application of heat, pressure, or combination of both.

4.12.5.1 Appliqués

Appliqués are surface coverings applied using heat and pressure for a specific period of time; they maybe applied as decals, during molding, or by hot stamping, hot transfer, or water transfer [191].

4.12.5.2 Painting

Parts may be painted to provide color for color matching, a high gloss or matte finish, a wood grain, luminescent or metal flake appearance, a textured appearance, or coverage of surface imperfections. Paints and coatings can also provide enhanced performance properties such as improved chemical, abrasion or weathering resistance, and electrical conductivity. Painting requires clean surfaces, and the paint should be compatible with the substrate. Parts should have uniform walls, and molding should be stress free [191].

4.12.5.3 In-Mold Decorating

Parts can be decorated during molding by the placement of a predecorated carrier into the mold; the molten plastic then fuses with the film during processing. They must have good thermal stability due to the high temperatures encountered during the molding process. There should not be sharp edges, and complex surfaces may result in problems caused by air entrapment or stretching of the film.

4.12.5.4 Metallization

Plastic surfaces are metallized to give the material surface a metallic appearance and make its properties more similar to that of metal. Conductive paints composed of pigments and conductive particles (nickel, copper, silver, graphite) can be applied to the part with air atomizing or airless spray equipment.

Vacuum metallization (or Physical Vapor Deposition—PVD) is a process in which the metal used for the application to the surface of the plastic (very often aluminum, although other metals are also used) is heated in a vacuum chamber and to its vaporization point, which is lower than the melting point of the plastic material. The metal vapor then condenses on the cooler plastic surface. The parts to be metallized are held in an appropriate fixture that can rotate to expose all surfaces to be metallized. Several power sources are used for metal evaporation, such as resistance heating, induction evaporation, electron beam guns, or vacuum arc. Resistance heated tungsten filaments are most often used. Aluminum chips or staples are placed on the filaments or into a thermally heated boat or crucible.

Frequently the thin metal layer is coated by a transparent topcoat to improve its abrasion resistance and to protect it against environmental influences, such as humidity.

Flame and arc spraying are easy, low-cost metallization processes, where a hand-held or automated pistol is used to spray liquid metal onto a part. The metal layer produced is thick compared to other metallization techniques and the deposition rate is high. However, the coatings prepared by the these two methods are quite porous, coating adhesion is lower and the surface roughness is relatively high. In flame spraying, a metal powder or wire is heated and propelled onto the plastic surface by a stream of hot gases. Arc spraying is comparable to flame spraying, but in arc spraying a direct current (DC) electric arc is used. The arc is struck between two continuous consumable wire electrodes that form the spray material.

Sputtering is a process in which metal atoms are dislodged with inert gas plasma instead of heating the metal. In cathode sputtering, the metal is attached to the cathode, with the plastic acting as the cathode. An electron beam dislodges positively charged metal ions, which then condense on the plastic surface. Sputter coating has a better adhesion and is more resistant to abrasion than vapor deposition coatings, due to a higher kinetic energy of the deposited metal atoms. Also, sputter coatings can be easily applied over large surface areas with a uniform layer thickness.

Sputter coating can be done batch-wise or in line with the injection molding process. Examples are compact disks produced in-line with an injection molding machine with sputter coating cycles of less than 2 s.

Plating processes of plastic materials can be divided into electroless plating process without a galvanic electric current and electroplating, where electric current is used in a galvanic process. Plating in general yields better adhesion than vacuum metallization, but the process is less environmental friendly, less safe, and also expensive.

In *electroless plating* a metallic coating is deposited onto electrically nonconductive plastics. Nickel and copper are most frequently deposited this way. The surface of the part to be plated is first etched with a strong oxidizing solution. After etching, the part is immersed into a solution, and a metallic coating is formed in a chemical reaction between the reducing agent present in the solution and the metal ions.

Electrolytic plating is the deposition of a metal on a conductor using an electric current. A plastic surface must be first made conductive in order to be electrolytically plated. The process essentially comprises of three steps: activation or treatment of the surface of the plastic, sensitization, and coating. Stannous chloride is frequently used as sensitizer. Electric current is then used to deposit metals onto the prepared substrate from metal salt solutions. The anode is usually made from the same metal, and dissolves during the plating process, replenishing the plating bath.

Metallizing makes surface flaws more apparent and the physical characteristics of the resin may change. Clean surfaces are required; no mold release agents should be present, and precleaning processes should be checked for compatibility. Design considerations include [192]:

- Uniform wall sections
- Radiused sharp edges (0.5 mm or 0.020 in. minimum)
- Avoidance of deep vertical walls
- Gradual wall transitions
- Minimal amount of projections
- Avoidance of flat areas
- Hole depth of a diameter ratio less than 5 to 1
- Recesses less than 51 mm (2 in.) with greater than 5° draft
- Minimum wall thickness about 2 mm (0.080 in.)
- Maximum walls ranging to 4.8 mm (0.190 in.).

4.12.5.5 Printing

In printing, a mark or impression is made on a plastic surface. Printing processes include pad transfer, screen printing, laser printing, dyeing, and fill and wipe.

Pad transfer is used to print on flat and irregular surfaces. A metal plate with an etched pattern is covered with ink, and soft silicone rubber pad is pressed onto it. The pad picks up the ink pattern (in reverse) and is pressed against the part. The pad can wrap 180° around a small part (360° with specialized equipment), and coverage is excellent. Parts for pad transfer decorating should be designed with smooth and even transitions, and sharp edges should be avoided. The surface finish affects sharp line intersections, and thickness can be inconsistent in large print areas. The size of the printing area should be minimized [192].

In *screen printing*, a pattern is produced by selectively sealing holes in a fine mesh screen. The mesh is then placed on the part, and a squeegee is used to force ink through the open holes onto the part surface. Parts should be designed with smooth and even transitions, with all coverage areas in one plane, and points and projections should be avoided.

In *diffusion process* (wet or dry), dry solids are transferred below the surface of a plastic (to a depth of 0.025–0.100 mm or 0.001–0.004 in.) using heat or heat and pressure. Inks used in this process undergo sublimation—they change from a solid to a gas and back without passing through the liquid phase. In wet diffusion, pad transfer methods are used to transfer the inks from a solvent suspension, which evaporates after exposure to heat, to the plastic substrate. Dry diffusion is similar to hot stamping; designs are reverse printed on a carrier, then applied to the surface by heat and pressure over a period of time. Wet diffusion is more economical; however dry diffusion can transfer multiple colors in one operation [192]. Since dye inks are translucent, diffusion is appropriate only to parts that have planar or slightly curved surfaces, and the surface finish affects sharp line intersections. Wall sections should be thick enough to be stable during the heating process of dry diffusion.

Laser printing uses a CO_2 or YAG laser to produce marks on the surface. The laser beam vaporizes the plastic surface, changing the color. It is useful for placing permanent lettering (e.g., codes) on parts too small for conventional printing. Pulse power, rate, and marking speed control the depth of etching; the amount of contrast produced is important in determining the quality of the finish. Design considerations include gradual wall transitions, and a minimization of sink marks.

In *fill and wipe* processes, the part is etched, and the ink is used to fill the recesses. Excess ink is then wiped away. For sharp detail, the surrounding surface should be very smooth, and edges should be sharp. Adjacent surfaces should be polished. Thick, rather than thin borders should be used, and inside corners should be radiused. Recesses should be 0.38–0.76 mm (0.015–0.030 in.) deep; small character openings may not be filled in [192].

4.12.5.6 Other Decorating Processes

Textures and lettering can frequently be molded into the surface of the part, in order to hide surface imperfections and provide decoration at no additional cost. Additional draft is required to eject a part with textured sides. Surfaces with molded-in texture do not usually maintain optical clarity [192].

Another special process is *flocking*, in which the surface is coated with an adhesive and exposed to an electrostatic charge. Short textile fibers are then blown onto the surface and stand on end due to the charge. As in other processes, flocking requires clean surfaces, with a minimal amount of sink marks, wall transitions, and projections. Sharp corners should be broken to a minimum of 0.5 mm (0.020 in.) [193].

4.12.6 Cross-Linking

Typically, thermoplastic materials are not subjected to cross-linking. However, in some cases cross-linking is used to improve mechanical properties, to influence the flow of the material [194], to increase heat resistance, to reduce swelling in oils and solvents, and to eliminate dissolution of the polymer in oils and solvents. An example is the use in wire and cable insulation where cross-linking improves resistance to abrasion and cut-through as well as the heat resistance. Another application is in the production of foams, where partial cross-linking increases the melt strength of the polymer required for the proper behavior during the foam expansion. Cross-linking is also used for the manufacture of heat-shrinkable films and sheets. Although chemical methods of cross-linking of many thermoplastics are possible, irradiation by electron beam is the most widely used method in the industrial practice where relatively thin layers are handled in a continuous process and in large volumes. Two distinct advantages of cross-linking by electron beam are that the depth of penetration of the beam can be controlled by the accelerating voltage and the degree of cross-linking by the radiation dose [195]. In some cases, an addition of a radiation promoter (prorad) is required to improve the process efficiency. Many thermoplastics can be cross-linked by electron beam, but there are some, which are either degraded by electron beam or resistant to the effects of irradiation [194].

4.13 General Processing Technology of TPEs

The ability of TPEs to exhibit good flow properties upon heating and then solidifying upon cooling allows the manufacturers to use highly productive thermoplastic melt-processing equipment, such as injection molding, extrusion, and blow molding described in previous sections for the production of elastomeric articles. This represents a substantial savings when compared with multi-step fabrication of rubber articles from thermoset elastomers. Vulcanization (cross-linking) of thermoset elastomers alone requires long times (minutes to hours) and consumes a great deal of energy as opposed to short cycles (minutes or less) used in melt-processing techniques.

4.13.1 Compounding of TPEs

Traditional processing involves the use of a large number of ingredients, such as fillers, plasticizers, resins, curing agents, accelerators, activators etc., requires intensive mixing that consumes great mounts of energy, and is labor intensive. In general, TPEs may be used without additives, but in many cases they are blended with other polymers; they may be mixed with fillers, oils, and resins to achieve required processing characteristics and/or properties. In such cases the final compound may contain less than 50% of the original polymer [196]. Not only is the volume of the added ingredients, but also their distribution, important. In block copolymers, the added materials can accumulate in the soft phase or in the hard phase, in both phases or may form an entirely separate phase.

If the additive accumulates in the hard phase, it increases its relative volume and the material becomes harder. If the additive is a polymeric material, its glass transition temperature must be higher than that of the hard phase; otherwise it reduces the high temperature performance of the block copolymer.

If the additive accumulates in the elastomeric phase, it increases its relative volume and makes the material softer. It may change the glass transition temperature of the elastomeric phase, which may in turn affect some end use properties such as low temperature flexibility and tack.

If the additive forms a separate phase, it depends on its molecular weight. Low molecular weight additives, such as oils and resins are often compatible with both phases. Polymeric additives with sufficiently high molecular weight usually form a separate third phase, which is co-continuous with the block copolymer and affects the properties of the finished product.

If the additive goes into both phases, it will reduce the degree of phase separation and consequently weaken the product. For that reason such a situation should be avoided.

The choice of mixing equipment is determined by the overall volume of the compounds to be mixed and their assortment. In such cases, where a small number of very large volume compounds is mixed, large equipment, such as an internal mixer is suitable since it is capable of mixing large-size batches in short times. However, equipment of this type represents a large capital investment.

Other choices are single-screw extruders, twin-screw extruders, reciprocated single-screw extruders (e.g., Buss Kneader) and the selection depends mainly on the type and volumes of materials being mixed.

Twin-screw extruders used for TPE compounding have typically L/D ratios from 36:1 to 41:1, depending on the number of process tasks involved in the process [197]. Operating conditions are greatly dependent on the type of TPE being processed. For styrenic block copolymer (SBC), TPU, and COPE, the main compounding concern is to maintain the material integrity and obtain proper blending of components. Thermoplastic polyurethane in particular is sensitive to both moisture and shear. Thermoplastic polyurethane compounding process design is critical since "overwork" can lead to a catastrophic molecular weight reduction [197].

Thermoplastic vulcanizates are generally robust materials that can be processed under a wide range of temperatures and mixing speeds, however the challenge here is to obtain homogeneity in a system containing a cured rubber phase that does not accept color or other additive as well as the thermoplastic phase. Additional challenge in compounding of TPVs is keeping the balance between the cross-linking process and the mixing process. Mixing PP and the elastomer (most commonly ethylene propylene diene monomer (EPDM)) is not easy because the polymer viscosities are very different and because the viscosity changes during the cross-linking. The degree of cross-linking determines most of the mechanical properties and flow behavior during subsequent processing operations. The most common mixing procedure has two steps: EPDM and PP are premixed in an internal mixer and the dynamic vulcanization takes place in an extruder. However, a single-step of preparing a TPV in an extruder has been patented [198]. The single-step has the advantage of eliminating batch-to-batch variation, but the longer extruder needed for this process can limit the throughput [197].

Direct extrusion, in which the raw materials are compounded and then made directly into a sheet or profile, eliminates the pelletizing step and has been used in some cases, mainly for TPOs. The equipment used is a standard compounding extruder that has to be lengthened by approximately 8 L/D and the screw has to be modified [197].

4.13.2 Injection Molding

The injection molding process is adapted to TPEs rather readily. The various classes of TPEs will generally mold well. Historically the TPUs were the exception due to their high viscosity, but in recent years TPU grades that injection mold well have been commercialized. In order to process TPEs the key process variables, including melt temperature, melt viscosity, and shrink rate have to be set to accommodate the particular properties of any given class of TPE.

The TPVs represent a special case since the structure does not consist of a single polymer type.

Thermoplastic vulcanizates have a cross-linked rubber phase dispersed in a thermoplastic phase. This morphological structure makes them very shear dependent such that the viscosity is quite low at the high shear rates used during injection molding (1,000–100,000 s^{-1}). Then at very low shear (and when static) the viscosity is quite high giving the TPV melt a relatively high stiffness. The grades of TPVs commercially available also vary widely in their suitability for injection molding. Some are highly tailored to injection molding and work extremely well. These molding grade TPVs work better in thin and difficult to mold parts [199]. Typical injection molding parameters for commercial TPEs are in Table 4.38 and typical temperature settings in Table 4.39.

4.13.2.1 Overmolding

There are many reasons to use "soft-touch" materials over rigid parts for industrial and consumer goods. Rigid components, such as plastics and metals, provide the required strength, stiffness, and structural integrity and the soft materials applied over them provide improved esthetics, better tactile properties, enhance grip of products while absorbing vibrations transmitted to the hand. Products are more durable and comfortable to use. Typical overmolding applications are in automotive interiors, house wares, personal care items, appliances, hand tools, calculator and computer keys, sporting goods, and lawn care products.

Traditional joining techniques, such as snap-fit designs, mechanical fasteners, adhesion and welding techniques (ultrasonic and heat) are still being used. These usually involve labor-intensive secondary assembly steps, which increase costs and limit control over product integrity.

Processing techniques such as co-injection, two-shot molding, and insert molding have been used with increasing frequency since they offer significant cost and performance advantages.

Co-injection molding provides the greatest adhesion between the rigid substrate and the soft TPE compound, but it is difficult to control and expensive. In this method the substrate and the TPE are injected simultaneously and the TPE migrates into the proper position [200].

Two-shot molding uses a complex mold with several gates and activated slides. The rigid substrate is

Table 4.38. Typical Injection Molding Parameters for Commercial TPEs

TPE Class	Typical Melt Temperature (˚C)	Typical Injection Pressure (MPa)	Typical Shrinkage Rate (%)
SBC	190–200	1.0–5.5	0.3–0.5
TPO Blend	175–205	1.0–10.0	0.8–1.8
EPDM TPV	190–230	1.0–10.0	0.5–4.7
NBR TPV	190–230	1.0–10.0	1.0–2.2
MPR	199–255	1.0–5.5	1.1–1.9
TPU	175–205	1.0–7.0	0.5–2.5
COPE	180–260	2.0–10.0	0.5–1.6

Table 4.39. Typical Injection Molding Temperature Setting for Commercial TPEs

TPE	SBS	TPO	TPV	MPR	TPU	COPE
Zone	Temperature (˚C)	Temperature (˚C)	Temperature (˚C)	Temperature (˚C)	Temperature (˚C)	Temperature (˚C)
Feed/Rear Barrel	120–150	185–200	170–190	171–177	160–182	200–215
Center Barrel	170–182	190–210	170–190	171–177	177–199	205–235
Front Barrel	185–195	200–220	170–190	171–177	188–210	210–235
Nozzle	190–200	200–220	170–210	171–177	190–210	215–240
Melt	190–200	207–216	185–205	171–177	185–210	220–245
Mold	22–32	10–50	10–80	21–49	38–60	20–50

injected first, then the mold is indexed to another barrel, and the TPE compound is injected onto the rigid substrate.

Insert molding is a method, in which the TPE compound is injected and overmolded onto the rigid part that has been molded in a separate process. The TPE provides the formation of a joint through melt flow or through chemical bond.

Specific processing conditions for all applicable techniques described in this chapter are discussed in more detail in chapters covering individual TPEs.

4.14 Process Simulation

At the heart of every decision is an understanding of the relationship between the decision variables to the expected outcomes. Since such knowledge is so significant in product design and manufacturing process development, phenomenological simulation and numerical analysis is a continuous activity. The act of developing these simulations provides significant insight into the process physics, and the results are very useful for integrated product and process design.

The development of aerospace, automobile, and high-technology industries requires the development of advanced plastic processing technologies in order to manufacture parts with light weight, high strength, high precision, high efficiency and at low cost, with a short period and a friendly environment, and with intellectualization and digitization. There are key problems to be solved urgently in the research and development of advanced plastic processing technologies, and FEM numerical simulation in combination with physical modeling and theoretical analysis has been playing a more and more important role in this field.

There are several major resources for process simulation. *Moldflow* [201] is a software that simulates the injection-molding process, trying out any shape of mold that the designer can imagine. It displays color-coded pictures of the way molten plastic will flow into the mold and how the plastic will shrink or warp when it cools. This information can be used to design a mold, to add extra cooling channels into the mold if needed and to beef up plastic sections that might warp. The toolmaker uses the computer-generated design to make the mould.

Compuplast [202] specializes in offering the computer simulation tools for the analysis and design of almost any extrusion related process including sheet and film extrusion, cast film process, blown film extrusion, pipe and profile extrusion, wire and cable coating, and extrusion blow molding. Separate software packages are available for injection molding and thermoforming.

4.15 Product Development and Testing

Development of new products and processes as well as their improvement are important factors in growing any business based on manufacturing products. There are essentially two ways to develop ideas for new products and processes [203]:

- R&D can make technological forecasts of new developments in basic and applied research leading to new products and processes
- At the same time marketing and sales employ the tools of market research to identify unfulfilled needs in the marketplace or opportunities to compete with other products and/or applications.

The financial success of any new product is assured when there is demand for it in the marketplace and when it can be manufactured in a cost-effective manner. When a product is properly designed it has the following key features:

- Unique performance properties that demand a premium in the marketplace or at least provide a competitive alternative to existing materials and products
- Can be manufactured to a specified consistency and in a cost-effective manner
- Does not require alteration during and after production, which can increase the chance of inconsistency
- Performs to the expectations and claims of the manufacturer under the environmental conditions for which it was intended to be used.

It is fair to say that product design has a direct bearing on product quality. Poorly designed product that is made from inferior or improper material, and/or by improper process will not perform to the customer expectations and will ultimately fail in the marketplace.

There are many factors that contribute to the success and failures of product development programs, such as:

- R&D philosophy of the company
- Management support
- Technical aspects of synthesis and product testing.

Specific attributes that are typically used to evaluate a product based on polymers are:

- Physical and mechanical properties
- Processing (rheological properties)
- Chemical nature and aging
- Methods of quality control (probability and statistics).

Thus, it is extremely important to understand not only the principal methods of testing but also the regression and statistical approaches in planning the experiments and in evaluation of the test results.

In some organizations the development process is performed in a sequence, where specialists contribute to each phase of product development effort, passing it from one function to the next. Each functional group makes its major contribution to the product only once, and there is little dialogue between them.

In a completely different, parallel approach everyone responsible for any aspect of the development is brought in to formulate the development strategy. All participants continue to interact throughout the process. Typically, members of the technology department, marketing, production, and quality assurance work together. The parallel approach brings together a broad range of talent for trying things out, learning from each attempt, and then trying again. Through recycling and interactive approach, it enables more reliable products to be developed in a shorter time [203].

A typical product development project starts with the selection of the material to be used. It may be a polymer, blends of polymers, or a compound containing a variety of components. The initial series of candidate materials is evaluated as to their rheology, physical and mechanical properties, and sometimes for aging on the laboratory scale. If the project is rather involved, consisting of a large number of experiments, a systematic approach, such as design of experiments (DOE) [204] should be used. In the first step (screening stage) the independent and dependent variables within the relevant range are identified. In the next phase (limited response surface) the number of independent variables is reduced and major variables are defined. The next phase (response surface defined) will allow some interpolation and leads to the next phase that allows scale-up prediction [203]. This method is suited to both material and process development and optimization.

Once the best candidate material is found, it is evaluated on pilot equipment that in most cases is similar to that used in production. In this stage the experimental procedure involves process optimization resulting in optimum process parameters. The next stage is a scale-up from pilot to production equipment, usually for a short run. This may include mixing and processing into the final product. Often some adjustments are needed to achieve a smooth run. The first products are then frequently subjected to field testing. The type and duration of the field tests depend on the type of products and expected service conditions. The transition to full scale production occurs after a thorough analysis of the short run and the results of field tests. The initial production run requires a close monitoring and statistical analysis [204] to assure a uniform quality of products.

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5 Styrenic Block Copolymers

5.1 Introduction

Styrenic block copolymers (SBCs) are based on simple molecules of the type *A–B–A*, where *A* is polystyrene and *B* is an elastomeric segment. The most common structure of SBCs is that where the elastomeric segment is a polydiene, such as polybutadiene or polyisoprene. Using the nomenclature proposed in reference [1], they are poly(styrene-b-butadiene-b-styrene) or poly(styrene-b-isoprene-b-styrene). The more convenient and more widely used nomenclatures for these SBCs are S–B–S and S–I–S, S being styrene, B butadiene, and I isoprene. Materials with this structure form two separated phase systems, which are very different from the corresponding random copolymers. These two phases retain many of the properties of the respective homopolymers and the copolymer exhibits two glass transition temperatures (T_g) unlike random copolymers, which exhibit a single intermediate T_g [2, 3–7] (see Fig. 5.1). The consequence of which is that in SBCs at room temperature, the polystyrene is rigid and strong and the elastomeric phase is elastic and can be easily extended.

The structure representing a styrenic thermoplastic elastomer (TPE) is shown schematically in Fig. 5.2. The polystyrene phase, which is present as a minor part of the total volume consists of separate spherical regions (domains). These domains are attached to the ends of elastomeric chains and form in this way multifunctional junction points similar to cross-links in a conventionally vulcanized elastomer (vulcanizate). The difference is that these cross-links are of a physical nature that is in contrast to the chemical nature of cross-links in the vulcanizate and therefore considerably less stable. At ambient temperatures, this block copolymer behaves in many ways like vulcanized rubber. When it is heated, the polystyrene domains soften, the network becomes weaker, and eventually the material is capable of flowing, and when it is cooled again, its original elastomeric properties are regained as the polystyrene domains become rigid. S–B–S and S–I–S block copolymers can also be dissolved in such solvents, in which both respective homopolymers are soluble. After the solvents are evaporated the original properties are regained. Block copolymers, such as S–I–S–I– ···· and $(S–B)_x$ (where x represents a multifunctional junction point), can form similar continuous networks, provided the polystyrene blocks are the minor component. However, structures such as I–S–I, B–S–B, S–I, S–B are not capable of forming continuous networks because only one end of each polydiene chain is terminated by a polystyrene block and the resulting materials are weak with no resemblance to conventional vulcanized rubber [4]. Other block copolymers with alternating hard and soft segments, such as polycarbonate-polyether, poly(dimethyl siloxane)-poly(silphenylene siloxane), polycarbonate-polyether [8], and segmented polyurethanes [9, 10] form materials with useful properties. A list of known TPEs based on styrenic copolymers

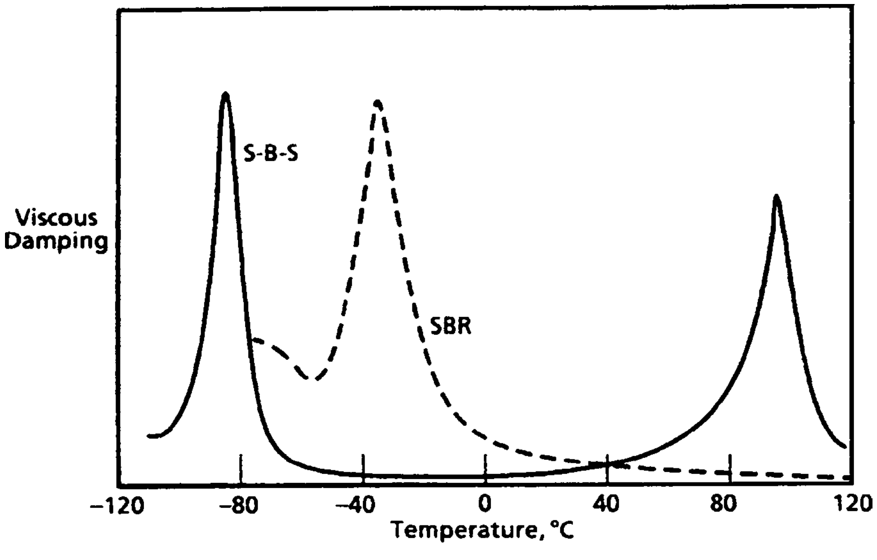


Figure 5.1. Glass transition temperatures of S–B–S and SBR (viscous damping) (Courtesy Hanser Publishers) [2].

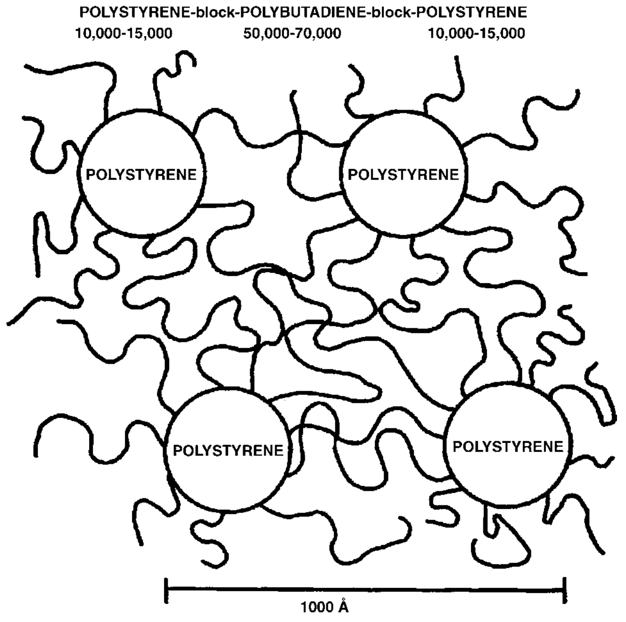


Figure 5.2. Schematic of a styrene–butadiene–styrene block copolymer.

is given in Table 5.1. It should be noted that commercially, the triblock and branched styrenic copolymers with polybutadiene (S–B–S), polyisoprene (S–I–S), ethylene/butylene (S–EB–S), ethylene/propylene (S–EP–S), polyisobutylene (S–IB–S), and ethylene/ethylene/propylene (S–EEP–S) center blocks have been commercially successful. The S–IB–S block copolymers are produced by carbocationic polymerization (see Section 5.3).

5.2 Polystyrene–Polydiene Block Copolymers

5.2.1 Synthesis of Polystyrene–Polydiene Block Copolymers

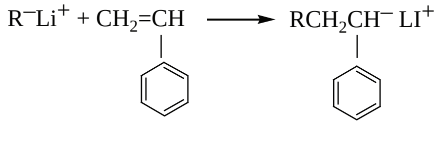
Block copolymers of the S–B–S and S–I–S type are made by anionic polymerization [11–14], which is applicable only to three common monomers — styrene (including substituted styrenes), butadiene, and isoprene. The solvents usually used are inert hydrocarbons, such as cyclohexane or toluene. Oxygen, water, or any other impurity must be completely eliminated to prevent undesirable reaction of the highly reactive propagating species. These measures assure a precise control of the molecular weight of the copolymer. This is in contrast to other block or graft copolymers, which have typically broad segmental or molecular weight distributions and broad distribution of a number of segments [15]. Organolithiums are preferred and also most frequently used initiators, although others can be used [12]. There are essentially three synthetic methods for the preparation of this type of SBCs:

(1) *Sequential,* in which the polymerization starts at one end of the molecule and continues to the other end.

(2) *Coupling*, in which polymerization starts at each end of the molecule and then the reactive chains are joined together by a coupling or linking agent.

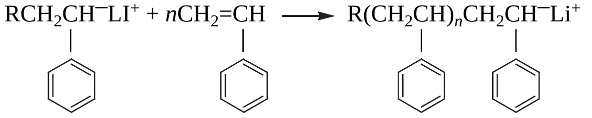
(3) *Multifunctional initiation*, in which the polymerization starts at the center of the molecule and continues to the ends, using initiators, which have more than one active group.

The preferred initiator for the sequential and coupling polymerization methods is sec-butyllithium because it initiates the polymerization very readily [13]. The initiation rate is high in comparison to the rate of subsequent polymerization. The initiator reacts with one molecule of styrene, thus:


$$R^-Li^+ + CH_2{=}CH \longrightarrow RCH_2CH^- Li^+$$

This is referred to as the *initiation reaction.*

In the next stage, the above species reacts with the styrene in the *propagation reaction*:


$$RCH_2CH^-Li^+ + nCH_2{=}CH \longrightarrow R(CH_2CH)_nCH_2CH^-Li^+$$

The new product is referred to as polystyrol lithium (the effects of the terminal sec-butyl radical are ignored) denoted as S^- Li^+. If a diene (in this case butadiene) is added, the S^- Li^+ can initiate further polymerization.

$$S^-Li^+ + nCH_2{=}CHCH{=}CH_2 \longrightarrow S(CH_2CH{=}CHCH_2)_{n-1}CH_2CH{=}CHCH_2^-Li^+$$

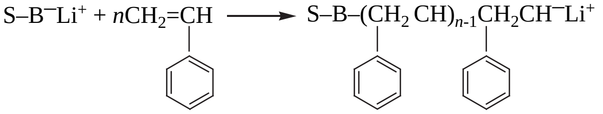
In the above example, the polymerization is shown to take place exclusively through the end, that is, 1,4 carbon atoms. In inert hydrocarbon (nonpolar) solvents at least 90% of the resulting polymer is in this arrangement. The remaining copolymer is polymerized through the 1,2 carbon atoms (with butadiene) or through 3,4 carbon atoms (with isoprene). For the above reaction, the

Table 5.1. Thermoplastic Elastomers Based on Styrenic Copolymers

Hard segment, *H*	Soft (elastomeric) segment, *E*	Structure
Polystyrene	Polybutadiene and polyisoprene	*T*, *B*
Polystyrene	Poly(ethylene/butylene) and poly(ethylene/propylene)	*T*
Polystyrene and substituted polystyrenes	Polyisobutylene	*T*, *B*
Poly(α-methylstyrene)	Polybutadiene and polyisoprene	*T*
Poly(α-methylstyrene)	Poly(propylene sulfide)	*T*
Polystyrene	Polydimethylsiloxane	*T*, *M*
Poly(α-methylstyrene)	Polydimethylsiloxane	*M*

Notes: *T* = Triblock, *H–E–H*, *B* = branched, $(H–E)_nX$, *M* = multiblock, *H–E–H–E–H–*···
Source: Reference [15].

product can be denoted as $\text{S–B}^-\text{Li}^+$. This species is also an initiator, so if more styrene monomer is added, it will polymerize onto the "living" end of the polymer chain:



$$\text{S–B}^-\text{Li}^+ + n\text{CH}_2\text{=CH(C}_6\text{H}_5) \longrightarrow \text{S–B–(CH}_2\text{CH(C}_6\text{H}_5))_{n-1}\text{CH}_2\text{CH(C}_6\text{H}_5)^-\text{Li}^+$$

When this reaction is completed, the product ($\text{S–B–S}^-\text{Li}^+$) can be made inactive by the addition of a protonating species such as an alcohol and this will also terminate the reaction, thus:

$$\text{S–B–S}^-\text{Li}^+ + \text{R–OH} \longrightarrow \text{S–B–SH} + \text{ROLi}$$

If *coupling* is the method of choice, the first three reactions above remain unchanged, but instead of the $\text{S–B–S}^-\text{Li}^+$ initiating further polymerization of styrene, it is reacted with a coupling agent:

$$2\text{S–B–S}^-\text{Li}^+ + \text{X–R–X} \longrightarrow$$
$$\text{S–B–R–B–S} + 2\text{LiX}$$

The example above shows the reaction of a difunctional coupling agent, but coupling agents of higher functionality (e.g., SiCl_4) will produce branched or star-shaped molecules $(\text{S–B})_n x$. If divinylbenzene is added at the end of the reaction, the products are highly branched, that is, the value of *n* is very large [16, 17].

In *multifunctional initiation*, a multifunctional initiator $\text{Li}^{+-}\text{R}^-\text{Li}^+$ is first reacted with the diene (here butadiene is used):

$$n\text{CH}_2\text{=CH–CH=CH}_2 + \text{Li}^{+-}\text{R}^-\text{Li}^+ \longrightarrow$$
$$\text{Li}^{+-}\text{B–R–}^-\text{Li}^+$$

The subsequent steps are similar to the corresponding steps in the sequential polymerization described earlier. When the reaction to produce $\text{Li}^{+-}\text{B–R–B}^-\text{Li}^+$ is completed, the styrene monomer is added and the result is the formation of a growing polymer with "living" chain ends, $\text{Li}^{+-}\text{S–B–R–B–S}^-\text{Li}^+$. The reaction is terminated by the addition of a protonating species (e.g., an alcohol) to give the block copolymer S–B–R–B–S.

Multifunctional initiation is used less frequently than the other method discussed earlier since the "living" ends tend to associate if the reaction is carried out in hydrocarbon solvents resulting in the formation of gel in the early stage. The use of other solvents, for example, ethers, changes the microstructure of the polydiene [18].

S–B–S and S–I–S block copolymers are precursors of SBCs with saturated elastomer center segments [19]. If S–B–S copolymers are used, they are polymerized in the presence of a structure modifier to give elastomer segments, which are a mixture of 1,4 and 1,2 isomers and these are subsequently hydrogenated to yield ethylene–butylene (EB) copolymers. Polyisoprene elastomer segments can be hydrogenated in a similar fashion into ethylene–propylene (EP) copolymers. The resultant block copolymers, S–EB–S and S–EP–S, are due to their saturation resistant to heat and oxidative degradation.

Styrene is the preferred monomer for almost all anionically polymerized block copolymers of this type, although substituted styrenes can also be used (see Section 5.2.4.1.4). Essentially, these copolymers have polystyrene end blocks.

5.2.2 Morphology of Polystyrene–Polydiene Block Copolymers

The structure of SBCs shown in Fig. 5.2 was postulated from their mechanical and rheological

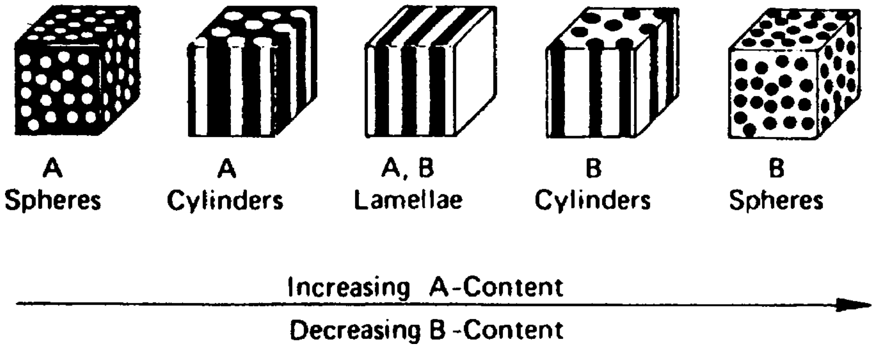


Figure 5.3. Changes in morphology of an A–B–A block copolymer as a function of composition.

behavior; there were no direct observations to support it [20]. At the same time, another postulate was made regarding the changes in phase arrangement with the relative proportions of the two segmental types [2]. The domains forming these copolymers are too small to be observed in visible light and this is why these copolymers are optically transparent. Only the development of staining techniques with osmium tetroxide allowed the morphologies to be established by electron microscopy [21]. A more detailed picture was proposed [22] that is illustrated by Fig. 5.3. As the proportion of styrene is increased, the morphology of the polystyrene changes from spheres to cylinders, both dispersed in the continuous elastomer phase. When the volume fractions of both components are about equal, the two form alternating lamellae. As the styrene content increases, a continuous polystyrene phase forms in which either cylinders or spheres of the elastomer are dispersed [20]. At lower styrene content, about 30%, a regular hexagonal array of polystyrene domains dispersed in the elastomer matrix can be obtained, especially if the sample is slowly cast from a solvent [23] (see Fig. 5.4).

The morphologies of films cast from solvent solutions depend on the nature of the solvent used. Good solvents for the polystyrene segments, such as toluene, favor the formation of a continuous polystyrene phase. When the solvent is evaporated, the film is relatively stiff and inelastic. On the other hand, good solvents for the elastomer segments, such as cyclohexane, favor the formation of a continuous elastomer phase with a dispersed polystyrene phase, yielding softer and elastic films [24, 25].

In general, these styrenic-diene block copolymers, particularly those with a continuous polystyrene phase, exhibit stress softening upon being stretched below their ultimate elongation and subsequently let retract and then restretched. It becomes softer during the second stretching than during the first one. This behavior akin to so-called Mullins effect in conventional vulcanized rubber reinforced by fillers (mainly carbon black) [26–28] appears to be the result of rupture of the continuous polystyrene phase during stretching to give discrete domains [28].

5.2.3 Critical Molecular Weight for Domain Formation

The condition for complete miscibility of two substances is that the Gibbs free energy of mixing (ΔG_m) be favorable, that is, negative. On the other hand, if ΔG_m is positive, phase separation will occur. In the case of block copolymers, a positive value of the free energy of mixing means that

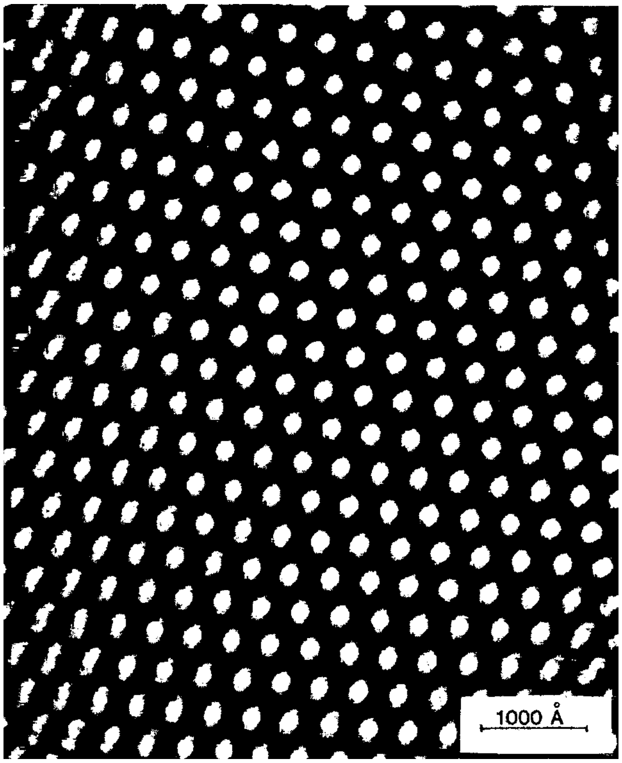


Figure 5.4. Electron micrograph of an $(S–I)_nX$ copolymer. The polyisoprene phase is stained black.

separate domains will be formed. The free energy of mixing can be expressed as follows:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{5.1}$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing, and T is the absolute temperature. For the styrene-diene block copolymers, the enthalpy of mixing is positive because there are no strongly interacting groups and it increases as the two polymers forming the segments become less alike. T and ΔS_m will always be positive and consequently the product $(-T\Delta S_m)$ will always be negative. This term will approach zero, however, as the molecular weights of the segments become large and/or as T decreases. Thus, the domain formation will be favored by the following conditions:

- High degree of structural difference between the segments
- High molecular weights of the segments
- Low temperature.

Based on this approach, the values of *critical molecular weights* and temperatures for domain formations have been developed and can be predicted quite well [29]. Findings reported from studies [30–32] are:

- An S–B–S block copolymer with end segments having molecular weights of 7,000 changes to a one-phase system at about 150°C.
- Similar block copolymers with end segment molecular weights of 10,000 and greater appear to be separated at temperatures up to 200°C.
- The critical molecular weight for domain formation in S–B–S block copolymers appears to be about 7,000.

5.2.4 Properties of Polystyrene–Polydiene Block Copolymers

5.2.4.1 Structure–Property Relationships

5.2.4.1.1 Effects of Molecular Weight

The *melt viscosities* of SBCs are considerably higher than those of homopolymers of similar molecular weight. The reason is the persistence of the two-phase domain structure in the melt and the extra energy required to disrupt it during flow.

The total molecular weight has little or no effect on the *modulus* of the material at ambient temperatures, if the styrene content is held constant. This phenomenon is attributed to the fact that the modulus of the elastomer phase is inversely proportional to the molecular weight between entanglements (M_e) in the elastomer chains [2] and the fact that this quantity is not affected by the total molecular weight (see Section 5.2.4.1.3).

5.2.4.1.2 Effect of Polystyrene Content

SBCs become harder and stiffer as the proportion of the hard styrene segments is increased. The stress–strain behavior of otherwise similar block copolymers with a wide range of polystyrene contents shows a family of stress–strain curves [2, 33, 34]. As the styrene content increases, the products change from soft, weak, rubbery materials to strong elastomers, then to leathery materials, and finally to hard, glassy thermoplastics [35].

5.2.4.1.3 Effect of the Elastomer Type

The nature of the elastomer segment affects many of the properties of these block copolymers. Both polybutadiene and polyisoprene have one double bond in the original monomer unit, which are prone to a chemical attack and limit the thermal and oxidative resistance of the S–I–S and S–B–S block copolymers. In contrast, poly(ethylene-butylene) is saturated and S–EB–S copolymers are much more stable than the former. The modulus of these block copolymers should be inversely proportional to the molecular weight between the entanglements (M_e). Some values of M_e for various polymers [36] are given below:

Polymer	M_e
Polyisoprene (natural rubber)	6,100
Polybutadiene	1,900
Poly(ethylene-propylene)	1,660

The M_e for poly(ethylene-butylene) can be assumed to be similar to that for poly(ethylene-propylene); thus, the S–I–S copolymers are softer than S–B–S and the S–EB–S copolymers are the hardest.

Since the elastomer segments of the above copolymers are nonpolar, they can be used for formulations containing hydrocarbon oils as plasticizers. Another consequence of that is that neither of them will resist too much to swelling in hydrocarbon oils and solvents.

5.2.4.1.4 Effect of the Hard Segment Type

The nature of the hard segment type determines the upper service temperature. If the styrene in SBCs is replaced by α-methyl styrene, the result is an increase in both the upper service temperature and the tensile strength [33, 34]. However, the polymerization of α-methyl styrene is relatively difficult, so block copolymers using it have not been commercialized [37].

5.2.4.2 Tensile Properties

Styrenic TPEs behave like thermoset (vulcanized) rubber at least at ambient temperature, which makes them useful for practical use. A study published already in 1966 [19] compared stress–strain behavior of an S–B–S to that of vulcanized natural rubber and vulcanized SBR. The tensile strength was found to be well in excess of 4,000 psi (28 MPa) and elongation at break over 800% (Fig. 5.5). These values (particularly tensile strength) measured on most block copolymers of this type are in this range and are much higher than those measured on vulcanized compounds based on SBR or polybutadiene, unless they contain reinforcing carbon black. For materials with constant polystyrene content, the tensile moduli and tensile strength values of both S–B–S [38] and S–I–S [39] do not depend on the molecular weight of the polymer, as long as the polystyrene molecular weight is high enough to form strong and phase-separated domains under the condition of the test. The theoretical aspects of this behavior as well as failure mechanisms for this type of copolymers and of their swelling behavior are in reference [40]. The exceptionally high elastic modulus is explained by trapped entanglements in the elastomer center segments acting as cross-links. Thus, the molecular weight between entanglements M_e is considered to be a critical parameter [40] useful for calculating both the elastic modulus [2] and the degree of swelling in solvents (see Section 5.2.4.5).

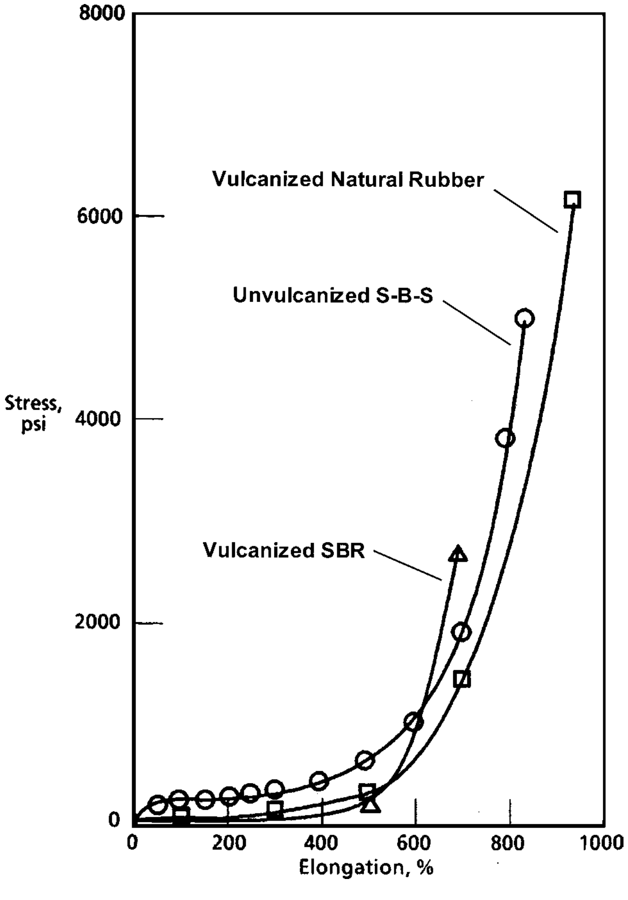


Figure 5.5. Stress–strain curves for different elastomers.

5.2.4.3 Viscous and Viscoelastic Properties

Under low shear conditions, the melt viscosities of S–B–S and S–I–S block copolymers are much higher than those of either polybutadienes [41], polyisoprene [42], or random copolymers of styrene and butadiene [43] of equivalent molecular weights. The comparison of viscosities of an S–B–S and a polybutadiene each with molecular weight of 75,000 is in Fig. 5.6. S–B–S and S–I–S block

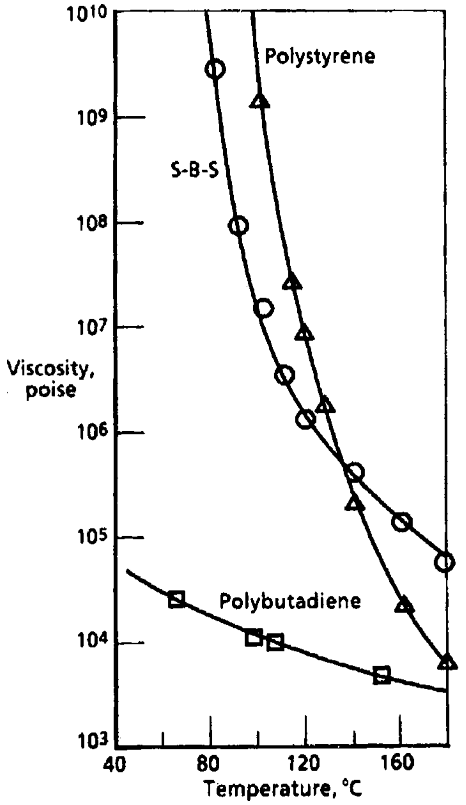


Figure 5.6. Viscosities of polymers at constant shear stress.

copolymers also exhibit non-Newtonian flow behavior in that their viscosities increase as the shear decreases and apparently approach infinite values at zero shear. This behavior has been found under both steady-state [37, 44] and dynamic conditions [45, 46] (see Fig. 5.7). This is attributed to the persistence of the two-phase structure in the melt, similar to that shown in Fig. 5.2. In such a structure, flow can only occur if the polystyrene segments at the ends of the elastomer chains are pulled out of their domains. Above a critical molecular weight (see Section 5.2.3), the polystyrene segments are phase separated at all temperatures of practical importance and so even if the polystyrene is above its T_g and therefore fluid, it requires an extra amount of energy to bring it into the elastomer phase. This energy is manifested as an increased viscosity. The viscosity increases with the degree of incompatibility between the end and center segments. This is particularly pronounced in S–EB–S block copolymers, which have very high and highly non-Newtonian viscosities because of their extreme segmental incompatibility [47].

Because these block copolymers exhibit two glass transition temperatures as mentioned previously, their dynamic mechanical behavior cannot be described as that of most polymers using the Williams Landel Flory (WLF) equation [48]. To do that this approach has to be modified. There are several modifications, such as calculating the shift factors at low temperatures using separate reference temperatures for polybutadiene and polystyrene [49]. At other temperatures they are calculated using a "sliding" T_g intermediate between the two [50]. In another method, an extra factor is added at higher temperatures to reflect the viscoelastic response of the polystyrene domains [51].

Viscoelastic behavior of block copolymers can be widely modified by using various resins to soften the polymer and to dilute the elastomer phase [52]. This has been of importance in their utilization in pressure sensitive adhesives [49].

5.2.4.4 Solution Properties

Dilute solutions of SBCs in relatively good solvents exhibit quite normal behavior. Because of the existence of the elastomer and polystyrene segments, the usual theoretical analysis is more complicated, since there are difficulties applying theories of molecular behavior that apply to theta solvents. The reason is that no solvent can simultaneously provide theta conditions for both the polystyrene and the elastomer segments [53]. A good approximation is possible by using intrinsic viscosity of dilute solutions, measured in a range of solvents. The maximum value of intrinsic viscosity was found when the solubility parameter of the solvent was about 8.6 $(\text{cal/cc})^{1/2}$ [54] (see Fig. 5.8). In more concentrated solutions, phase separation begins and ordered structures can be observed. Several studies were carried out to establish domain sizes, interdomain distances, and morphologies [55–59]. The conclusions point out that domain sizes depend on the polystyrene molecular weights and on the thermal histories of the solutions [60]. Trends observed in solution viscosity with changes in molecular structure (linear vs branched) and in molecular weight are in Fig. 5.9.

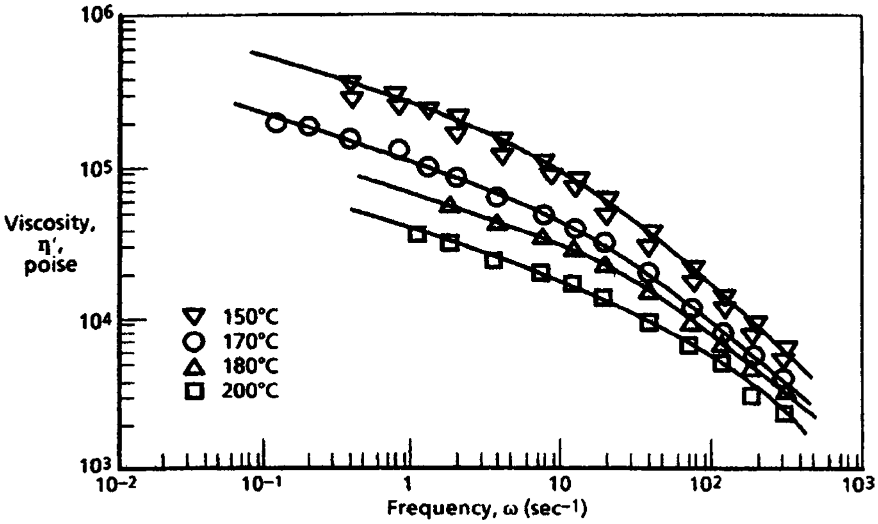


Figure 5.7. Dynamic viscosity of an S–B–S block copolymer at various temperatures.

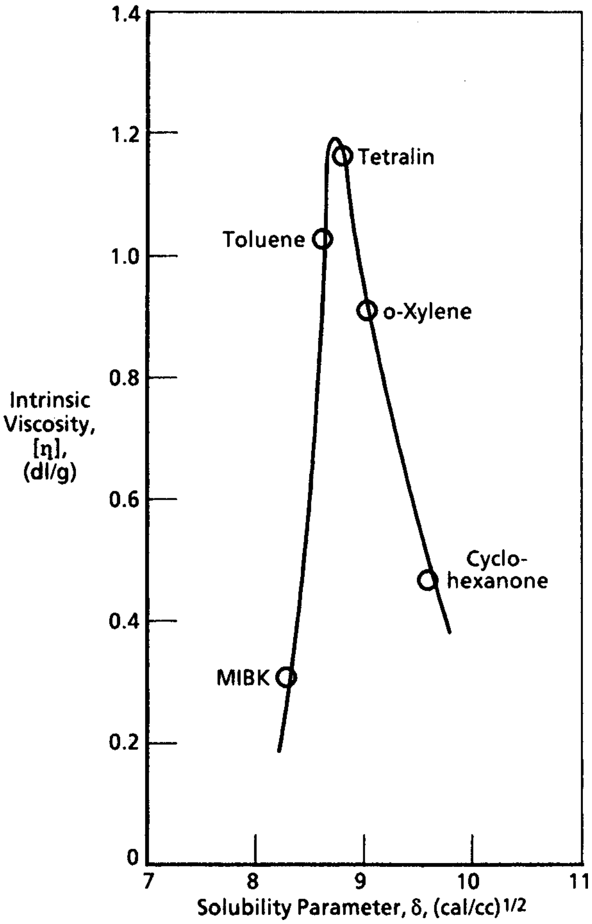


Figure 5.8. Effect of solvent solubility parameter on the intrinsic viscosity of an S–B–S block copolymer.

5.2.4.5 Swelling

Swelling in liquids is frequently used to estimate the molecular weight between effective cross-links in conventionally vulcanized elastomers. This molecular weight, M_c, is calculated from the *Flory–Rehner Equation* [61] (Eq. 5.2):

$$M_c = \rho_2 V_1(\phi_2^{1/3} - \phi_2/2)/\ln(1 - \phi_2) + \phi_2 + \chi_1\phi_2^2 \tag{5.2}$$

where M_c is the molecular weight between effective cross-links, ρ_2 is the density of the elastomer in the unswollen state, V_1 is the molar volume of the swelling agent, ϕ_2 is the volume fraction of the elastomer in the swollen state, and χ_1 is the Flory–Huggins solvent interaction parameter.

This equation can be applied to SBCs also if the swelling liquid is chosen so that it is very compatible with the rubber phase but does not affect the polystyrene domains [62]. This was applied to a series of S–I–S copolymers that were swollen in isooctane and the value of M_c was found to be about 10,000 [63]. If the M_c is identified with the M_e (molecular weight between entanglements), the value for polyisoprene, found in this study, is consistent with that obtained by other methods [64].

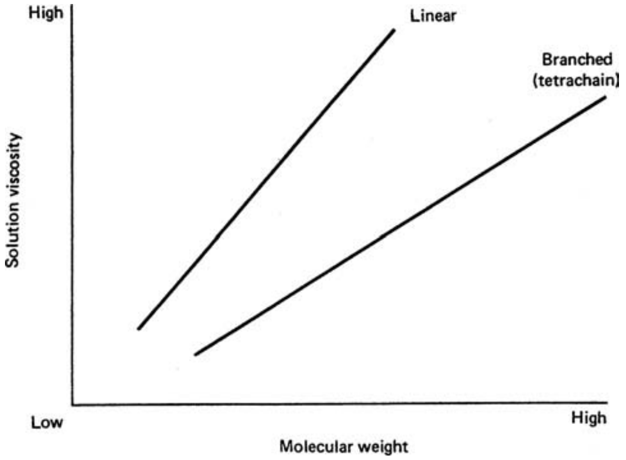


Figure 5.9. Molecular weight and structure effects.

5.2.5 Formulating Styrenic TPEs

Unlike most thermoplastics, styrenic TPEs are seldom used as pure materials. Like conventional thermosetting (vulcanizable) elastomers they can be formulated to meet the required processing behavior, and required mechanical and physical properties. They can be blended with other polymers, including conventional elastomers, and compounded with fillers, plasticizers (e.g., oils), processing aids, resins, colorants, and other compounding ingredients.

Formulations based on S–B–S and S–EB–S can be prepared in a large range of hardness values, from as soft as 5 Shore A to as hard as 55 Shore D. Large amounts of compounding ingredients can be added and in some cases the contents of the TPF is as little as 25% by weight [65]. This is an economic advantage because most of the compounding ingredients added in large volumes, such as fillers and oils, are very inexpensive. A list of typical compounding ingredients and their effects on the properties of the final compounds is in Table 5.2.

5.2.5.1 Formulating S–B–S Block Copolymers

Polystyrene is a valuable ingredient for S–B–S block copolymers since it improves processing and makes the materials stiffer.

Table 5.2. Compounding Styrenic Thermoplastic Elastomers

Property	Component					
	Oils	**Polystyrene**	**Polyethylene**	**Polypropylene**	**EVA**	**Fillers**
Hardness	Decreases	Increases	Increases	Increases	Increases slightly	Increases slightly
Processability	Improves	Improves	Variable	Variable	Variable	Variable
Ozone Resistance	No change	Increases slightly	Increases	Increases	Increases	No change
Cost	Decreases	Decreases	Decreases	Decreases	Decreases	Decreases
Other	Decreases UV resistance	—	Often gives satin finish	Improves high-temperature properties	—	Often improves surface appearance

Oils (or plasticizers) also improve processing but make the products softer. Naphtenic oils are preferred but oils with high contents of aromatics should be avoided since they soften (plasticize) the styrene domains. Oils may provide benefits in resistance to crack growth during flexing. Materials other than oils (e.g., resins, processing aids) may act as plasticizers, especially at elevated temperatures.

Crystalline hydrocarbon polymers (polyethylene or ethylene-vinyl acetate copolymers) improve solvent and ozone resistance.

Inert fillers, such as clay, whiting, precipitated calcium carbonate, and talc can be added in large volumes without adversely affecting the properties of the base polymer and reduce cost markedly. Reinforcing fillers like highly reinforcing carbon black, silica fillers, or hard clays are seldom used because they produce stiff "boardy" materials [66]. However, they offer certain benefits, such as increase in tear strength, abrasion resistance, and improved flex life [67].

5.2.5.2 Formulating S–EB–S Block Copolymers

Formulations based on these copolymers are prepared in a similar fashion as those made from S–B–S types. The important difference is that for these, *polypropylene* is the preferred polymeric additive. It improves the properties of the formulations in two different ways [66]:

(1) It improves processability, particularly when used in combination with processing oils. Paraffinic oils are preferred here because they are more compatible with the poly(ethylene-butylene) center segments than naphtenic oils. Here again highly aromatic oils should be avoided for the same reason as above.

(2) When the compounds are processed under high shear and then rapidly cooled (e.g., in injection molding or extrusion), the PP and the S–EB–S/oil mixture form two continuous phases. The PP phase has a relatively high crystalline melting point (approx. 165°C or 330°F) and is insoluble. Thus, this continuous polypropylene phase increases the solvent resistance and the upper service temperature significantly.

Blends with *silicone oils* are used in some medical applications [68]. Inert fillers are used in a similar way in S–EB–S types as with S–B–S block copolymers.

The central block, if consisting of diene elastomers, can be degraded by oxidation even during normal finishing operations and storage. For that reason these block copolymers require addition of an antidegradant. In most cases additional antidegradant may not be required when compounded. However, depending on their use, these polymers and their compounds may need to be protected against oxidative degradation and in some cases against UV degradation. As effective *antioxidants* hindered phenols combined with thiodipropionate synergists are used. Combinations of benzotriazoles with hindered amines are very good *UV stabilizers* [66]. Titanium dioxide and carbon black also provide good protection against UV radiation in materials that do not have to be clear. The polymer with saturated central block is inherently more stable and may not usually need any added protection.

When under stress, unsaturated block copolymers are susceptible to attack by ozone. The protection against ozone attack can be attained by the addition of small amounts of EPDM or ethylene-vinyl acetate copolymer. Chemical *antiozonants* include nickel dibutyl dithiocarbamate and dibutyl thiourea. Certain microcrystalline waxes also offer some ozone protection alone or in combination with a chemical antiozonant.

5.2.6 Compounding

5.2.6.1 Melt Mixing

Compounding of formulations from SBCs is done in standard mixing equipment. It is simple, the only condition that has to be met being that the equipment be heated to a temperature of at least 40°C (72°F) above the glass transition temperature of the polystyrene segment (this being 95°C or 203°F) or 20°C (36°F) above the melting point of the polymeric additive being added, whichever is greater. The glass transition and crystalline melting temperatures of the respective segments are shown in Table 5.3. A mastication on a cold roll mill, typical for certain conventional elastomers (e.g., natural rubber) is not required for styrenic TPEs, in fact, the resulting breakdown of the polymer (essentially reduction of molecular weight) is detrimental to the properties of the final product [66].

Unfilled and slightly filled compounds are mixed in a single-screw extruder fitted with a mixing screw. To get sufficient dispersion the screw should have the L/D ratio of 24:1. A twin-screw extruder is also suitable to prepare such compounds. Highly filled compounds are best mixed in an internal mixer (e.g., Banbury mixer), the output of which is fed into an extruder. In a typical mixing cycle, resins and fillers are added early, oils and other softeners are added somewhat later. If high amounts of oils are required, they are added in several increments to prevent slipping on the mixing rotors. Typical dump temperatures are in the range 280–320°F (128–160°C); the use of polypropylene may increase it to 350°F (177°C) or more. The mixing cycles vary in length with the type of formulation being mixed and are typically in the range 3–6 min.

The extruder used in the final stage of the compounding process is usually fitted with a pelletizer, which can be either strand cutting or an underwater face cutting system.

Table 5.3. Glass transition and crystalline melting temperatures[a]

Block Copolymer Type	Soft Rubbery Phase T_g (°C)	Hard Phase T_g or T_m (°C)
S–B–S	−90	95 (T_g)
S–I–S	−60	95 (T_g)
S–EB–S	−60	95 (T_g) 165 (T_m)[b]

Notes:

[a]Measured by DSC.

[b]In compounds containing polypropylene.

Source: *Handbook of Thermoplastic Elastomers*, 2nd edition (Walker B.M., and Rader, C.P., Eds.), Van Nostrand Reinhold, New York, 1988, p.28.

5.2.6.2 Dry Blending

Dry blends may be prepared by mechanically mixing ground or powdered elastomer with other ingredients at a temperature less than that required to flux [69]. In most formulations, added oil tends to bind an even coating of filler and other ingredients to the polymer particles, resulting in a homogeneous, free-flowing mixture. This mixture can be fed directly into the fabricating equipment capable of handling powder forms. Intensive mixers (e.g., Henschel type) or ribbon blenders are suitable for dry blending.

5.2.6.3 Solution Mixing

This method is useful for the preparation of solvent-based adhesives, sealants, and coatings. The polymers are soluble in a wide range of common, inexpensive solvents, dissolve relatively quickly, and display a fast solvent release. Since two phases are present, the solvents have to be selected so that both the hard polystyrene phase and the elastomeric segment are considered. Both have to be truly in solution. The dissolution of polystyrene domain temporarily destroys the network, which reforms after the solvent is subsequently released and the strength of the polymer or compound is restored. However, the morphology of the polymer deposited from different solvents may be different [70].

Good solvents for elastomeric block copolymers of styrene with diene center blocks (polybutadiene, polyisoprene) include cyclohexane, toluene, methyl ethyl ketone, diethyl ether, and styrene. Mixtures of solvents, for example, naphta-toluene, hexane-toluene, and hexane-toluene-ketone are often found practical [71].

Another useful processing method is based on the fact that block copolymers can absorb large amounts of mineral oil and still exhibit some useful properties. Ground polymer is mixed with oil and a fluid mixture is obtained that may be used in compression molding, injection molding, casting, and rotational molding. After heating, the mixture fuses into a solid, usual soft product [71].

5.2.7 Processing of Compounds from SBCs

As pointed out earlier, SBCs are seldom used in the pure form to fabricate the finished products. In most cases, they are used compounded, as described in previous sections. In general, processing, in the majority of cases, shaping of the compounded materials is done by standard techniques used for processing of melts, such as extrusion, injection molding, blowmolding, rotational molding, etc. Other techniques involve processing in the liquid form, that is, in solvent solutions, dispersions, etc. In general, there are specific grades of the polymers that are suitable for the given process, for example, extrusion grades, grades for injection molding, solution processing, etc. As a rule of thumb, compounds based on S–B–S copolymers are processed under conditions suitable for polystyrene, whereas those based on S–EB–S are processed under the conditions suitable for polypropylene [72].

5.2.7.1 Extrusion

Typical techniques used for melt-processable thermoplastics, such as extrusion of tubing, extruded, and cast film, blown film profiles, are applicable to SBCs and compounds prepared from them. Since these materials exhibit low die swell, relatively simple extrusion dies are used for the extrusion of rather complex shapes [73].

5.2.7.1.1 Extrusion of S–B–S Block Copolymers

Extruders for the processing of the S–B–S copolymers and their compounds should have the *L*/*D* ratio at least 20:1 with an optimum being 24:1. The recommended screw design features include low compression ratios and rather deep-flighted metering section. Both single stage and two-stage screws are suitable for these materials. Vented and particularly vacuum vented two-stage screws are effective in preventing the formation of bubbles in the extrudate. Screws with a mixing section (e.g., a Maddox head) or mixing pins often improve the dispersion of color concentrates and melt uniformity [74].

Extrusion melt temperatures should range from 300°F to 390°F (148 to 198°C) and should not exceed 400°F (205°C). The feed zone temperature should not be higher than 175°F (80°C). Increasing the zone temperatures along the extruder barrel from about 300°F (148°C) at the zone next to the feed zone, to about 390°F (198°C), at the die body produces best outputs.

Because of the unsaturation of the midblock of the S–B–S polymers, they tend to degrade if extruded at high temperatures and/or high shears. To prevent contamination on start-up by foreign materials or possible thermal degradation after prolonged shutdown, it is important to purge the extruder. Polystyrene is recommended for the purging [74].

Production rates for S–B–S-based compounds for a given extruder size depend almost linearly on the screw speeds. Typical output from a 3.5 in. (90 mm) extruder is 200 lb/hr (90 kg/hr) at 30 rpm and about 500 lb/hr (220 kg/hr) at 70 rpm.

5.2.7.1.2 Extrusion of S–EB–S Block Copolymers

The advantage of S–EB–S block copolymers over many engineering plastics and other TPEs is their excellent thermal stability, resistance to shear degradation, and fast setting melts [73]. Many of the practices used in the extrusion of S–B–S polymers and compounds apply also to S–EB–S polymers and compounds with some differences:

- Screws with *L*/*D* at least 24:1 are preferred
- Screws with compression ratios 2.5:1 to 3.5:1 and long, rather shallow metering zones
- Balanced screws (with equal number of flights in the feed, transition, and metering zones), of the design typically used for the extrusion of polyolefins.

Similar to S–B–S-based materials, both single stage and two-stage screws can be used for the extrusion of the S–EB–S compounds.

Extrusion conditions:

- Melt temperatures during extrusion: 375–450°F (190–230°C). Because of the resistance of the central block to elevated temperatures, temperatures up to 500°F (260°C) are permissible
- The feed zone temperature should not be higher than 175°F (80°C)
- Increasing the zone temperatures along the extruder barrel from about 375°F (190°C) at

the zone next to the feed zone, to about 455°F (235°C) may be tried initially and can be modified if necessary, depending on the polymer grade and extruder screw design.

5.2.7.1.3 Other Extrusion Techniques

Blown film extrusion is best done with polyolefin type of screws, described in Section 5.2.6.1.2. Melt temperatures should be in the range 325–375°F (160–190°C) for the S–B–S-based compounds and 400–475°F (205–245°C) for the S-EB-S compounds. Die gaps of 0.025–0.030 in. (0.635–0.762 mm) can be used with blowup ratio up to 2:1. Film 2 mil (0.05 mm) thick can be produced under these conditions [74].

In addition to the above, styrenic TPEs can be used for the following processes:

- Film casting
- Melt spinning
- Coextrusion
- Calendering.

Each of the above processes requires specific equipment and process conditions, depending on the requirements.

5.2.7.2 Injection Molding

SBCs are usually processed on *conventional reciprocating screw injection molding machines* since these machines provide required low operating temperatures and more uniform melt characteristics, desirable for these materials [74].

The screws used in the injection molding machines are *general purpose screws* with compression ratios 2:1 to 3:1; 60° tip angles and some mechanism to prevent backflow. These screws are typically used to process PVC and polyolefins. Twostage *vented screws* are useful to remove any surface moisture that might be present in the compounds [74].

Conventional *nozzles*, nozzles with reverse tapers or nozzles employing some means of positive shut-off are equally acceptable for the injection molding of the compounds based on S–B–S and S–EB–S.

Standard *sprues* with draft angles at least 3° are typical for this type of compounds. The low thermal shrinkage of the S–B–S-based compounds requires runners to be smooth [74].

Hot runner systems or *hot-weld cold runner systems* should be larger than the cold runner system to keep mold back pressure constant. Minimum temperature of the runner core through the unloading cycles should be approximately 350°F (177°C) for S–B–S compounds and 375°F (190°C) for the S–EB–S compounds.

Compounds from styrenic TPEs will mold well with conventional *gate* types. In general, the gate should be large enough to fill the mold without causing degradation by excessive heat generation. Thickness of the gate should be about 15–25% of the part thickness at the gate location.

Molds for S–B–S and S–EB–S compounds should be designed without abrupt changes in flow pattern, thus, corners and transition zones should have radius rather than being sharp. A good *venting* is necessary because these types of compounds are molded at fast injection rates. The typical vent size is ¼ in. × 0.0003 in. (6.35 mm × 0.00762 mm), although some might be larger. For *ejection* of the molded parts, *stripper plates* are most reliable. Another method is using air or air-assisted ejection. *Ejector pins* should be large enough to prevent damage to the molded part. Mold cooling is most commonly provided by circulating cooled water [74]. Mold temperature is typically 50–105°F (10–40°C) for S–B–S, and 95–150°F (35–65°C) [72, 74].

Shrinkage is specific to each grade and the composition of the compound. It ranges from about 0.0005 to 0.020 in./in. (0.5–2%). Shrinkage is usually greater in the direction of the flow in the mold. Compounds with higher contents of fillers exhibit lower shrinkage.

Typical operating conditions are [72, 74]:

Cylinder temperatures: For S–B–S the feed zone temperature should be 150–200°F (65–95°C), and 390°F (200°C) at the nozzle. For the S–EB–S compounds the temperature at the nozzle is 440°F (225°C) for average size parts, but can be as high as 500°F (260°C) for large parts.

Injection rate: moderate to fast (depending on grade and part size).

Injection pressure: typically 500–1,000 psi (3.4–6.89 MPa).

Screw speed: typically 25–75 rpm.

Back pressure: normally 50–100 psi (0.34–0.68 MPa)

Hold time: typically 2.5 s.

Clamp pressure: typically 1.0–2.5 tons/in.^{2} (0.25–0.75 tons/cm^2).

Clamp time (cooling time): 7–60 s, depending on grade and part thickness.

5.2.7.3 Blow Molding

Blow molding techniques of compounds from styrenic TPEs are similar to those established for polyethylene [75]. Although they have been successfully molded on various machines, those producing an intermittent fast drop parison are particularly well suited for use with these materials because this feature minimizes the parison sag.

Deep flighted low compression ratio *screws* are well suited because they allow a broader temperature range to be used without overheating and ultimately degrading the polymer.

Molds used for blow molding S–B–S and S–EB–S are of conventional design with typical land width and normal pinch-off configuration.

Typical operating conditions are [74]:

Melt temperatures: 300–390°F (150–200°C) for S–B–S and 375–475°F (190–245°C) for S–EB–S.

Blow ratio: 2.2–2.5:1 typical, but can be as high as 2.9:1.

Blowing pressures: 35–120 psi (0.24–0.83 MPa) depending on size and wall thickness of the molded part.

5.2.7.4 Thermoforming

Thermoforming of sheets extruded from S–B–S and S–EB–S is easily done by conventional methods using molds requiring relatively shallow drawdown with simple vacuum or drape-forming procedures. Deeper draws require the use of plug assist and/or billow forming.

Optimum *heating times* vary greatly, depending upon oven temperature, efficiency of the heating source, and thickness of the extruded sheet [74], and are typically 30–100 s. *Oven temperatures* also depend on sheet thickness, polymer grade amount of draw-down required, and may be in the range 400°F (205°C) to 500°F (260°C).

Thermoformed finished parts from styrenic TPEs have sharp and well-defined details and exhibit good impact resistance, flexibility, and elasticity.

5.2.7.5 Compression Molding

In compression molding, the styrenic TPE compound has to be placed in a hot mold and allowed to soften before applying pressure to initiate the flow into the cavity [76]. After the part is formed, in most cases, it is necessary to cool the mold to a temperature below the softening point before opening it to prevent a distortion of the part. Using a mold release agent or molding between sheets of foil helps in the easy removal of the article from the mold.

Because compression molding has a low productivity, it is used mainly for preparing test samples, prototypes, or unusual parts.

5.2.7.6 Bonding and Sealing

Because of the thermoplastic nature of the styrenic TPEs, articles made from them can be bonded and sealed by standard methods used for bonding and sealing of plastics. Such procedures include thermoplastic welding, sealing by heat, solvent, ultrasonic treatment, microwave, and adhesive bonding. For microwave procedures, additives that respond to microwave energy, such as carbon black, have to be added in sufficient amounts. Some of these methods can also be employed to produce laminates with plastics or metallic materials [77]. The styrenic TPEs remain elastomeric at the point of sealing or welding [75].

5.3 SBCs Synthesized by Carbocationic Polymerization

A fairly recent development in the synthesis of SBCs is the living carbocationic polymerization [78, 79], producing well-defined poly(styrene-b-isobutylene-b-styrene) (S–IB–S).

The differences from the anionically synthesized SBCs are [79]:

1. The polymerization system (i.e., cationic mechanism) that is somewhat more complex than the anionic system discussed in the previous section.
2. Only polyisobutylene can comprise the center (elastomeric) block.
3. Not only polystyrene, but also substituted styrenes or other polyaromatics can be used as the rigid blocks.

5.3.1 The Polymerization Process

The initiators used in this polymerization method have two or more functionalities and the general formula $(F{-}\mathrm{R})_n\ x$, where $F{-}R$ represents a hydrocarbon moiety with a functional group F, and x represents an n-functional junction point. The functional group F can be chlorine, hydroxyl, or methoxy group. Thus, the simplest case, where a

Table 5.4. Comparison of properties of S–IB–S (TS Polymer®, Kuraray) and S–EB–S (Kraton® G)

Property	S–IB–S	S–EB–S
Tensile strength (MPa)	6–17	28
Modulus at 300% elongation (MPa)	1–11	4.7
Elongation at break (%)	250–1100	500
Tear strength, die C (kN/m)	10–78	38
Compression set (70 h, R.T.) (%)	25–45	25
Melt flow at 190°C, 10 kg (g/10 min)	0.5–88	No flow
Hardness, Shore A2	23–87	76
Ozone resistance	Excellent	Excellent
Gehman low temperature stiffening (°C)		
T5	−45	−40
T10	−50	−48
Air permeability · 10^8 (m^2/Pa s)	11.4	171

Source: Reference [82].

linear triblock is produced, is *F–R–F*. As in anionic polymerization, the block copolymer is formed sequentially in two stages:

$$\text{Stage 1: } F\text{–}R\text{–}F + 2n(\mathrm{IB}) \longrightarrow {}^{+}(\mathrm{IB})_n\text{–R–}(\mathrm{IB})_n^{+}$$

The product ${}^{+}(\mathrm{IB})_n{}^{+}$ is a difunctional living polymer. It can initiate further polymerization. With the addition of styrene monomer, a styrene block copolymer S–IB–S is formed (see Stage 2 below):

$$\text{Stage 2: } (\mathrm{IB})_n^{+} + 2m(\mathrm{S}) \longrightarrow {}^{+}\mathrm{S}_m(\mathrm{IB})_n\mathrm{S}_m^{+}$$

The process is carried out at temperatures −80°C (−112°F) in a moderately polar solvent. $TiCl_4$ or BCl_3 are used as coinitiators [80].

5.3.2 Properties of S–IB–S Block Copolymers

As pointed out earlier, currently, only poisobutylene can form the elastomeric block. Because of its relatively inflexible chain and very high molecular weight between entanglements, the S–IB–S copolymers are softer than comparable block copolymers made from polyisoprene, polybutadiene, or poly (ethylene-butylene). Additional characteristics of isobutylene are its very low resilience [81], which is reflected in the S–IB–S block copolymers and its their very high mechanical damping leading to an ability of the S–IB–S block copolymers to absorb vibrations. Other interesting features of the S–IB–S block copolymers are:

- High thermal stability due to the full saturation of the IB block and the absence of tertiary carbon atom. This saturation eliminates the necessity of hydrogenation, used in the synthesis of saturated midblocks in S–B–S and S–I–S
- Low glass transition temperature (−70°C) of the IB block [82] contributes to good low-temperature properties of these materials
- Low gas permeability, again reflecting the low gas permeability of the IB block.

A comparison of commercial S–IB–S and S–EB–S block copolymers is in Table 5.4.

Stress–strain curves of SBCs with different elastomeric midblocks are in Fig. 5.10.

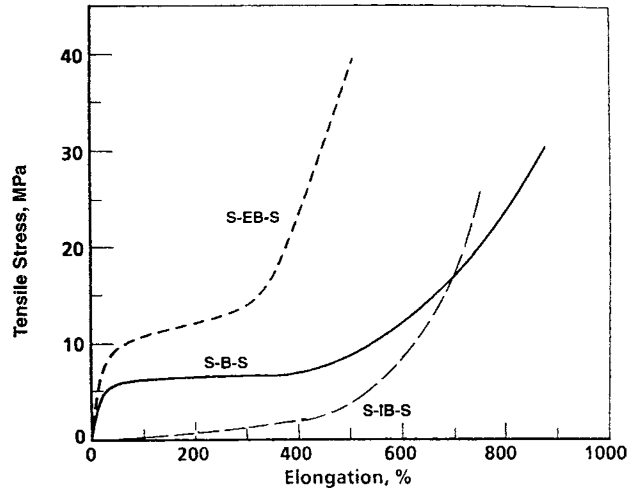


Figure 5.10. Stress–strain curves of styrenic block copolymers with different elastomeric midblocks.

Table 5.5. Glass Transition Temperatures of Some Glassy Homopolymer Segments Used in TPEs Synthesized by Cationic Polymerization

Glassy Segment	T_g (°C)	Comment
Polystyrene	100	Most widely used, great deal of experimental data
Poly(α-methyl styrene)	173	Low cost, high T_g but difficult to polymerize
Poly(p-methyl styrene)	108	–
Poly(p-tert-butyl styrene)	142	Low cost monomer
Poly(p-chloro styrene)	129	Flame resistant
Indene	170–220	Low cost monomer, high T_g

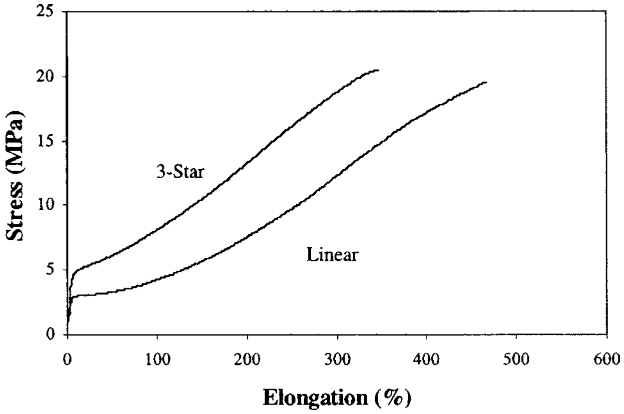


Figure 5.11. Comparison of stress–strain curves of linear and three-star S–IB–S copolymers 40%wt polystyrene; M_n (PIB) = 60,000 (linear) and 90,000 (three-arm star).

In contrast to anionically prepared SBCs the styrenic block can be made up from α-methyl styrene, para-methyl styrene, para-tertiary-butyl styrene, para-chloro styrene, and other monomers (see Table 5.5). The high T_g values of these substituted styrenes and others mean a higher upper service temperatures than the analog S–IB–S and S–EB–S block copolymers.

Cationic polymerization using multifunctional initiators opens the possibilities to synthesize a variety of SBCs, such as multiarm star block copolymers and arborescent block copolymers comprising a dendritic (tree-like) PIB core carrying multiple polystyrene outer blocks [82]. The multiarm star-block copolymers are alternatives to linear block copolymers because their superior combination of physical and processing properties, including high moduli combined with lower viscosities at similar molecular weights [83]. A comparison of stress–strain curves of a linear and a three-arm star S– IB–S copolymer is in Fig. 5.11.

S–IB–S triblock copolymers hold promise for a large number of commercial applications including hot melt adhesives, medical and biomedical applications [84–86], and vibration damping [87].

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6 Thermoplastic Elastomers Prepared by Dynamic Vulcanization

6.1 Introduction

Blends of elastomer with thermoplastics have become useful materials over the last two to three decades [1–3]. They have many properties of elastomers yet they can be processed as thermoplastics, that is, by usual melt processing methods [4] and do not need to be vulcanized (cross-linked) during fabrication into the final product. This difference in fabrication represents a substantial economic advantage over the vulcanized, thermoset rubber.

Ideally, in such blends the finely divided elastomer particles are dispersed in a relatively small amount of a thermoplastic matrix. These elastomeric particles have to be cross-linked to promote elasticity of the material [5]. This favorable morphology has to be unchanged during the fabrication of the material into parts and during their use. Because of these requirements for an ideal case, the usual methods of preparing elastomer-plastic blends by standard melt mixing, solution blending, or latex mixing are not sufficient [6].

A well-established and widely used method to prepare thermoplastic compositions comprising vulcanized elastomer particles in melt-processable matrix is called *dynamic vulcanization*. The elastomer is vulcanized during its melt-mixing with a suitable molten thermoplastic [7–10] The fact that these compositions are mostly prepared from standard, well-established elastomers and thermoplastics using well-established equipment is significant. Thus, initial investment costs for new materials, including high-volume polymerization units and processes, and other barriers such as environmental concerns can be avoided.

The thermoplastic elastomers prepared by dynamic vulcanization, frequently referred to as thermoplastic vulcanizates (TPVs) have properties equal to or in some cases better than those prepared by block copolymerization. One of them is, for example, the first commercially successful Santoprene® prepared by dynamic vulcanization of a blend of ethylene propylene diene monomer (EPDM) and polypropylene (PP) [9, 10]. The commercial products of this type were growing at a rate of about 60 products a year during the last half of the 1980s [11]. The commercialization of the technology was greatly aided by the discovery of preferred compositions based on Lewis acid-catalyzed methylol-phenolic vulcanization systems for the new thermoplastic elastomers [2].

The elastomer particles of the TPV material have to be small enough and fully vulcanized in order to attain optimum properties, which in comparison to block copolymers are, for example [5]:

- Lower permanent set
- Improved mechanical properties (tensile strength, elongation at break)
- Better fatigue resistance
- Lower swelling in fluids, such as hot oils
- Higher melt strength
- Improved utility at elevated temperatures
- Greater stability of phase morphology in the melt
- Greater melt strength
- More reliable processing characteristics in melt processing.

These enhanced properties are explained to be the result of many vulcanized elastomer particles physically interacting with one another forming a “network” during the fabrication of a finished part. Since this network consists of touching and loosely bound particles it is reversible and the material becomes melt processable again when subjected to sheer in reworking the melt or to grinding [13]. Comparison of different types of EPDM/PP blends is given in Table 6.1.

Although thermoplastic vulcanizate compositions can be made from a relatively large numbers of elastomers and thermoplastics, only limited number of their combinations is technologically useful. Early investigations concluded that when surface energies of the two major components are matched, when the molecular weight between the entanglements of the elastomer is low and when the plastic is at least 15% crystalline a useful thermoplastic elastomer would be obtained [13]. Another important finding

Table 6.1. Comparison of Unvulcanized and Highly Vulcanized EPDM/PP Blends

Property	Blend A[a]		Blend B[b]	
	Unvulcanized	Vulcanized	Unvulcanized	Vulcanized
Extractable Rubber (%)	33	1.4	—	—
Cross-Link Density (mol.cm^3)	0	1.6×10^{-4}	—	—
Hardness, Duro A	—	—	81	84
Tensile Strength, psi (MPa)	717	3526	583	1905
Elongation at Break (%)	190	530	412	725
Modulus at 100% Elongation, psi (MPa)	701	1160	412	725
Compression Set (%)	—	—	78	31
Tension Set (%)	—	—	52	14
Swelling in ASTM No. 3 oil (%)	—	—	162	52

Notes:
[a] Blend A (parts by weight): EPDM rubber, 60; polypropylene, 40.
[b] Blend B (parts by weight): EPDM rubber, 91.2; polypropylene, 54.4; extender oil, 36.4, carbon black, 36.4.
Source: Reference [1], p. 86.

was that very strong elastomeric compositions of EPDM and PP were obtained by dynamic vulcanization provided that peroxide curatives were avoided [9, 10]. If enough plastic phase is present in the molten state, then the compositions can be processed as thermoplastics. Plasticizers and extender oils can be used to expand the volume of the elastomer ("soft") phase. In the molten state, a suitable plasticizer can expand the volume of the plastic ("hard") phase. If the hard phase material is crystalline material, such as PP, then, upon cooling, the crystallization of the hard phase material can force the plasticizer out of the hard phase to the soft phase. In this case the plasticizer can be a processing aid at melt temperature, but a softener in the finished part.

In such cases, where the two components are not compatible, they can be compatibilized by the addition of a small amount of a compatibilizing agent (typically about 1%) before the dynamic vulcanization. The compatibilizing agent is a block copolymer, which contains segments similar to the two components to be made compatible. It acts as a macromolecular surfactant promoting the formation of small droplets of the elastomer. These become very small particles of vulcanized elastomer dispersed in the plastic matrix [14].

6.2 The Dynamic Vulcanization Process

The process of dynamic vulcanization used to produce TPVs has been used and patented since the early 1960s [7, 8, 15]. However, it has been developed and made practical by a group of scientists at Monsanto [16–28]. The well-established and commercially widely exploited "static" vulcanization used from the mid-1800s [29], involves heating a fully compounded rubber formulation, including a curing agent (usually sulfur, organic peroxide, or other) to temperatures from typically 140°C to 200°C (284°F to 392°F) for relatively long time (minutes to hours). This process produces a thermoset, elastic, tough, and durable material as a result of chemical cross-linking of the base elastomer (natural rubber (NR), SBR, Nitrile rubber (NBR), butyl rubber, EPDM). The *dynamic* vulcanization, on the other hand, involves in the first step the melt mixing of the elastomer and the plastic in an internal mixer (most commonly in a Banbury mixer) or in a twin-screw mixer. After sufficient mixing, in the second step, vulcanizing (curing, cross-linking) agents are added. During the continuation of the mixing process, the elastomeric component vulcanizes. The more rapid the rate of vulcanization is, the more rapid the mixing must be to ensure good processing properties of the composition. The progress of the vulcanization process can be followed by monitoring the mixing torque or the mixing energy requirement during the mixing. Once the curves for mixing torque or energy requirement reach maximum, mixing can be continued to improve the processability of the material. After discharge from the mixer the blend is further homogenized and usually chopped or pelletized.

Polyolefins, in particular PP and polyethylene are by far the most commonly used thermoplastics; however, others such as polyamides (PAs) [21, 23, 26], copolymers of styrene and acrylonitrile (SAN) [24], acrylonitrile-butadiene-styrene (ABS) [24], acrylates [24], polyesters [25], polycarbonates [24], and polystyrene [23, 24] can be used to prepare TPVs. The elastomer used may be a diene rubber, such as NR, styrene-butadiene rubber, polybutadiene, butyl rubber [17], EPDM [18], butadiene-acrylonitrile rubber [27], or chlorinated polyethylene [26].

During the mastication stage, the mixing must be continuous otherwise a thermoset material will result [30]. The temperature reached during the mixing must be sufficiently high to melt the thermoplastic resin and to have an effect on the cross-linking reaction in the next stage. A good dispersion is achieved if the viscosities of the rubber and molten resin are comparable.

The properties of a given composition were found to correlate with certain parameters of the elastomeric and thermoplastic components [24]. These are the differences between the wetting surface tensions ($\Delta\gamma$), of the rubber and plastic components, the fraction of crystallinity (W_c) of the plastic and the critical entanglement spacing (N_c) of the rubber macromolecules. Both tensile strength and elongation at break have been found to increase with decreasing $\Delta\gamma$ and N_c and with increasing W_c.

The vulcanization of the rubber phase of a TPV results in numerous improvements of properties. Thermoplastic vulcanizates are considerably less soluble in ordinary solvents for rubber; they only swell in them. A clear evidence of TPV is a level of rubber extractibles of 3% or less with cyclohexane at room temperature. Additional definitive evidence is a rubber cross-link density greater than approximately 7×10^{-5} moles/cm^3, as measured by equilibrium solvent swelling [9].

The hardness values of the composite material can vary in a wide range from 50 Shore A to 60 Shore D. The softer materials are obtained by the addition of plasticizers, the harder ones by the incorporation of large amounts of the thermoplastic resin.

6.3 Properties of Blends Prepared by Dynamic Vulcanization

6.3.1 TPVs Based on Polyolefins

6.3.1.1 TPVs from EPDM–Polyolefin Blends

Technologically, the most widely used compositions are based on dynamically vulcanized EPDM blended with a polyolefin resin. Below is an example for such a composition [31]:

EPDM	100 parts by weight (pbw)
Polyolefin resin	*X*
Zinc oxide	5
Stearic acid	1
Sulfur	*Y*
TMTD	*Y*/2
MBTS	*Y*/4

where X is the amount of a polyolefin (polyethylene or PP), typically 66.7 parts by weight (pbw) and Y is a variable amount of sulfur, typically in the range 0.5–2.0 pbw.

The dynamic vulcanizate based on the blend of EPDM and PP displays a disperse morphology. This morphology is known to be independent of the elastomer-thermoplastic ratio or the molecular weights of the constituent polymers [32]. The particles of vulcanized EPDM are distributed uniformly throughout the PP matrix (see Fig. 6.1). Cross-link density is an important factor in improving mechanical properties. Its effect on tensile strength and tension set (plastic deformation under tensile stress) is illustrated by Fig. 6.2. The size of vulcanized EPDM particles has an important effect on tensile strength and elongation at break. As the average particle diameter decreases, both these properties increase (see Fig. 6.3). This behavior is paralleled by a number of other properties [33].

6.3.1.2 TPVs from Diene Rubbers and Polyolefins

Thermoplastic elastomers based on blends of polyolefins with diene rubbers, such as, butadiene

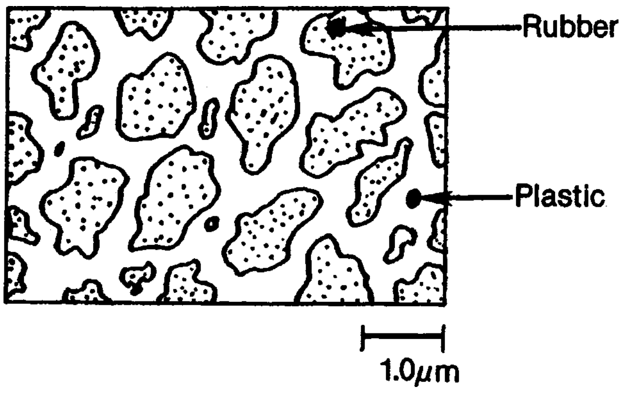

Figure 6.1. Morphology of thermoplastic vulcanizate.

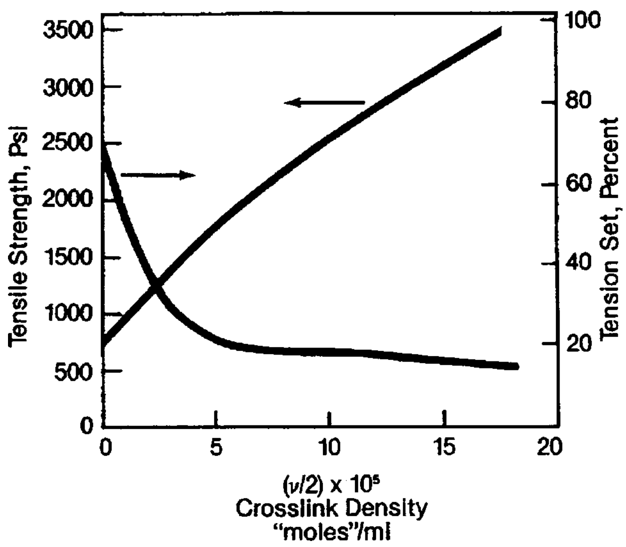

Figure 6.2. Effect of cross-link density on tensile strength and tensile set of a TPV.

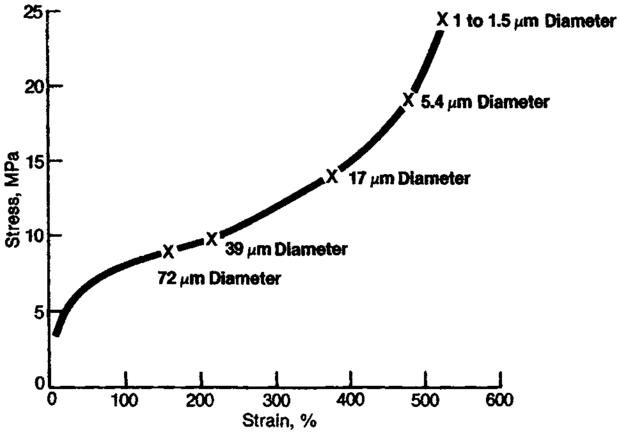

Figure 6.3. Effect of vulcanized rubber particle size on mechanical properties (x denotes failure).

rubber (BR), NR, NBR, SBR, etc., have fairly good initial tensile properties, and their thermal stability is somewhat better than that of standard thermoset rubber materials [16, 34, 35]. Compositions based on partially vulcanized NR [36] and on fully vulcanized NR with PP [37] exhibit, unlike thermoset NR, very good resistance to cracking induced by ozone (Table 6.2). They also have a fairly good retention of tensile properties in hot air at 100°C (212°F) for up to one month (Table 6.3). The brittle point temperature increases as the proportion of NR decreases.

6.3.1.3 TPVs from Butyl and Halobutyl Rubber and PP Resins

Butyl and halobutyl rubbers exhibit very low gas and moisture permeability. This is why they have been used for many years in tire innertubes, tire innerliners, medical applications, and sporting goods. Thermoplastic vulcanizates prepared from butyl and halobutyl rubbers combined with PP exhibit air and water vapor permeability values that are much lower than those for EPDM/PP TPVs and almost as low for conventional thermoset butyl rubber materials (see Table 6.4). Triblends of the type rubber-rubber-PP with one of the elastomers dynamically vulcanized offer some advantages over two-component systems [38].

6.3.1.4 TPVs from Butadiene-Acrylonitrile Rubber and Polyamides

Thermoplastic elastomers based on blends of butadiene-acrylonitrile rubber (NBR) and PAs can be prepared by melt blending of the components in an internal mixer. The temperatures used for the mixing depend on the melting temperature range of the PA used.

The commercial nitrile-butadiene elastomers are available in two types, namely *self-curing,* that is, curing (cross-linking) at elevated mixing temperatures in the absence of curatives) and those *resistant to self-curing*. The difference is based on the behavior of the NBR elastomers during mixing at 225°C (437°F). At that temperature, the self-curing types generally crumble typically after 1–8 min, whereas the other types can be mixed for 20 min or longer without crumbling.

The preparation of PA/NBR blends is complicated by the response of the NBRs during mixing and is rather difficult when blending self-curing NBRs with PAs having high melting points. The effect of adding curative is minimized since the properties of the composition are improved by the cross-linking of the elastomer, which occurs just from mixing. The addition of curatives has a greater effect with the NBR that does not self-cure but the best properties are obtained from the self-curing nitrile elastomer.

The addition of dimethylol-phenolic compound improves the properties of PA/NBR blends substantially [39]. High strength blends are obtained even when the gel content of the NBR is as low as 50%. The addition of m-phenylenebismaleimide, another curative, induces a considerable gel formation in the elastomer phase. The improved product properties are associated with the gelation of the elastomeric phase [39]. The effect of curatives is shown in Table 6.5.

Table 6.2. Mechanical Properties of Different NR/PP-based TPVs

Property	ASTM	Composition			
Hardness, Durometer	D2240	60A	70A	90A	50D
Tensile Strength (MPa)	D412	5.0	7.6	11.4	20.8
Modulus at 100% Elongation (MPa)	D412	2.1	3.7	6.5	10.5
Elongation at Break (%)	D412	300	380	400	620
Tension Set (%)	D412	10	16	35	50
Tear Strength (kN/m)	D624	22	29	65	98
Compression set (22 h)	D395				
23°C (%)	Method B	24	26	32	45
100°C (%)		30	32	38	63
Brittle Point (°C)	D746	−50	−50	−45	−35
Ozone Resistance at 40°C (100 ppm of O_3)[a]	D746	10	10	10	10
Specific Gravity	D297	1.04	1.04	1.02	0.99

Note:

[a] Ozone rating of 10 indicates no cracks after specified time.

Source: Reference [5], p. 165.

The number of possible products from the dynamically cured combination of NBR and PAs is very large because of the multitude of grades of both components available. The nitrile elastomers can have different acrylonitrile content, different viscosity, can be self-curing or not. The PAs may have different melting points and different polarities. Moreover, there are varied effects of curing systems on the final properties of the compositions. The properties of the base compositions can further be altered by the incorporation of fillers and/or plasticizers.

Table 6.3. Hot Air Aging of NR/PP-based TPVs

TPV Hardness Durometer	Property	Aging Time (Days at 100°C)			
		1	7	15	30
60A	Tensile strength, % retention	99	91	80	40
	Modulus at 100% elongation, % retention	104	65	80	68
	Elongation at break, % retention	98	110	126	85
70A	Tensile strength, % retention	100	87	76	43
	Modulus at 100% elongation, % retention	100	90	86	80
	Elongation at break, % retention	98	110	113	56
90A	Tensile strength, % retention	103	91	86	66
	Modulus at 100% elongation, % retention	107	103	104	99
	Elongation at break, % retention	92	93	93	60
50D	Tensile strength, % retention	101	95	80	66
	Modulus at 100% elongation, % retention	108	109	102	103
	Elongation at break, % retention	93	93	91	70

Source: Reference [5], p. 165.

Table 6.4. Comparison of Air Permeability of Butyl/PP, EPDM/PP TPVs with the Permeability of Thermoset Butyl Rubber

Composition	Relative Air Permeability
Butyl/PP TPV	1.45
EPDM/PP TPV	4.44
Thermoset butyl (innerliner)	1.00

Note: Method—ASTM D1434 at 35°C, sample thickness: 0.76 mm.
Source: Reference [5], p. 166.

Studies with different NBR grades revealed that there is no simple relationship between the strength of the composition and the characteristics of the elastomeric component. However, the self-curing grades of NBR give the highest values of tensile strength. Another observation was that the effect of curative addition is much more pronounced in NBR grades that are not self-curing [40].

The content of acrylonitrile has a similar effect on oil resistance as in the standard vulcanizates of NBR, namely the resistance increases with the increasing content of acrylonitrile. There was no difference found between the self-curing and the self-curing-resistant NBR grades.

The NBR/PA ratio has a major effect on mechanical properties. An increase in the proportion of the elastomer leads to the reduction of stiffness and strength and the reduction of permanent set. On the other hand, the extensibility is increased somewhat. If the proportion of the NBR is more than 50% compositions with tension set values lower than 50% are obtained. However, high proportions of the elastomer can produce compositions with poor processing characteristics [41].

The addition of plasticizers is chosen for the improvement of processing and for the softening of the compositions. The most common effect besides softening of the material is a decrease of tensile strength. Ultimate elongation can be either increased or decreased, depending on the type of plasticizer used. This is due to different effects of a given plasticizer on the crystallinity of the PA phase. In some cases the reduction of viscosity of the PA phase may promote the formation of more perfect crystals after crystallization from the melt; in others the plasticizer only softens the PA component [42, 43].

The effect of *fillers* depends on the type and amount added. In general, the filler accumulates in the elastomer phase and causes both its stiffening and an increase of its volume. These effects are opposite and largely cancel each other. Small amounts of clay reduce extensibility and Young's modulus but have little effect on hardness, stiffness, and strength [44]. The processing of a composition is adversely affected since the addition of a filler reduces its thermoplasticity. This can be rectified by the addition of a suitable plasticizer. Plasticizers improve thermoplasticity and increase extensibility. Because of large choice of both PAs and NBR grades, there is a large variety of TPVs with a

Table 6.5. Properties of Cured NBR/PA Blends with Different Types of Curatives[a]

Curative Type	Tensile Strength (MPa)	Modulus at 100% Strain (MPa)	Elongation at Break (%)	Tension set (%)	Durometer D Hardness	True Stress at Break (MPa)
None (control)	3.1	2.5	290	72	17	12.3
Accelerated Sulfur[b]	8.3	7.4	160	15	35	21.7
Activated Bismaleimide[c]	8.5	3.7	310	51	28	34.9
Peroxide[d]	7.9	6.1	220	31	32	25.3

Notes:
[a] Blends consist of 40 parts of PA 6/6-6/6-10 terpolymer (melting point 160°C) and 60 parts of Chemigum N365 (non-self-curing NBR with 39% acrylonitrile).
[b] The system contains 5 phr of ZnO, 0.5 phr of stearic acid, 2 phr of tetramethylthiuram disulfide, 1 phr of morpholinothiobenzothiazole, and 0.2 phr of sulfur (phr=parts per hundred parts of rubber).
[c] Activated bismaleimide is 3 phr of *m*-phenylenebismaleimide and 0.75 phr of 2,2-bisbenzothiazolyl disulfide.
[d] The curing system consists of 0.5 phr of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (90% active), Lupersol® L-101.
Source: Reference [5], p. 169.

relatively high strength, excellent resistance to hot oil with a wide range of hardness values.

6.3.1.5 TPVs Based on Polyacrylate Rubber and Polyamides

Dynamically vulcanized elastomeric compositions based on polyacrylate rubber (ACM) and PA represent a class of TPVs withstanding a long-term exposure to air and oil at high temperatures (up to 150°C or 302°F) [45–48]. The ratio of ACM to PA determines the properties of the resulting product, such as hardness, tensile modulus, and elongation at break, strength, melting range, and other. Thus a multitude of grades of these TPVs consisting of different ratios of ACM and PA is possible. Currently, two grades with different hardnesses are commercialized [49].

6.4 Processing and Fabrication of TPVs

Thermoplastic vulcanizates as all other thermoplastic elastomers essentially use processing and fabrication techniques common to thermoplastics.

In general, the processing of a thermoplastic material is a function of its melt rheology, of the processing temperature and of the shear rate. An additional factor, particularly in extrusion, is the strength of the molten material under the strain applied to it during processing, that is, its resistance to the melt fracture. Melt fracture can cause poor surface of the extrudate and often completely defective, useless parts.

6.4.1 Rheology

Rheology (flow properties) of a polymeric material is critical for its processing behavior. Thermoplastic vulcanizates exhibit a highly non-Newtonian rheology, that is, their melt viscosity varies greatly with shear rate, much more so than most polymeric systems [50]. At high shear rates the viscosity-shear rate profiles of the TPV materials are similar to those of a thermoplastic resin. However, at low shear rates, the viscosity of the TPV material is very high and in blends containing high proportions of elastomer, the viscosity of the material can approach infinity when the shear rate approaches zero, presumably due to the cured elastomer particle-particle interference [51]. The comparison of the melt rheology of an elastomer-plastic composition with the melt rheology of plastic is in Fig. 6.4.

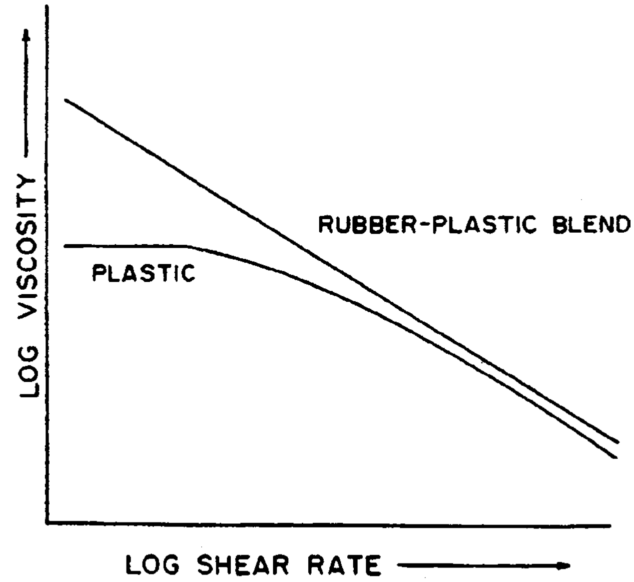

Figure 6.4. Relationship between viscosity and the shear rate for a plastic and its blend with an elastomeric material.

Under the conditions of melt extrusion, the molten material undergoes a rapid flow in the die. Then, as the material exits the die, the rate of deformation drops to zero and, since the viscosity is approaching infinity, there is no noticeable die swell taking place.

The effect of temperature on the viscosity in contrast to the effect of shear rate is rather modest. The temperature dependence of the viscosity of an EPDM/PP TPV with high levels of elastomer is shown in Fig. 6.5. For compositions based on other types of thermoplastics, the viscosity may show more temperature sensitivity [51]. Both Figs 6.4 and 6.5 indicate that, when processing these types of elastomer-plastics blends by extrusion or injection molding, shear rates should be kept high enough to facilitate an adequate flow.

The high melt viscosity of such blends may be of advantage when they are processed [51]. It can provide high melt integrity also called "green strength," which is necessary for parts produced by extrusion or blow molding to retain their shapes. The low die swell resulting from a high viscosity is also beneficial in calendering of sheets and films.

6.4.2 Extrusion

Extrusion is widely used to fabricate a large variety of products from TPVs. Simple extrusion is used for tubing, sheets, and complex profiles. Coextrusion is also used for products made from different hardnesses, different properties, colors, etc.

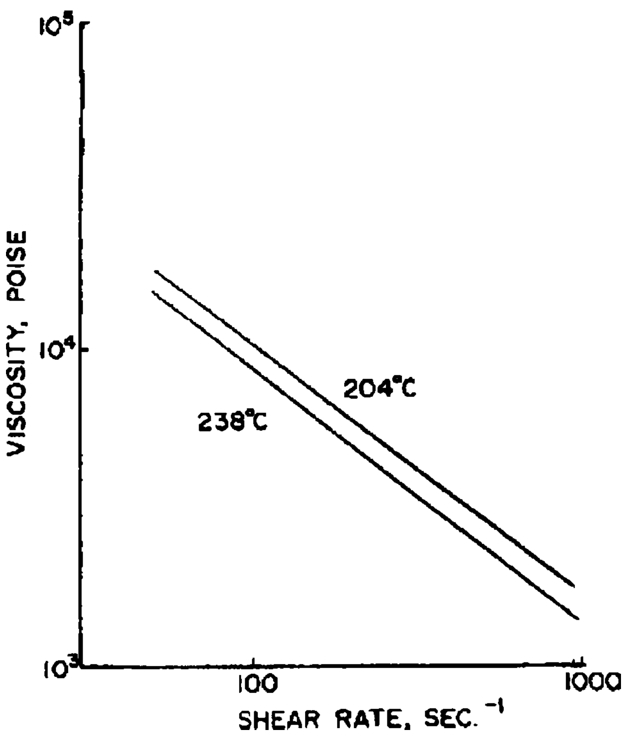

Figure 6.5. Effect of temperature on the viscosity-shear rate for a typical TPV (EPDM-PP).

Wire and cable jacketing, hose jacketing, and other similar assemblies are produced by the cross-head extrusion.

Extruders commonly used for thermoplastics, typically with L/D ratio of 24:1 or greater to assure sufficient homogeneity are suitable for the extrusion of TPVs of the EPDM/PP type. The most widely used feed screw design is polyethylene type metering screw with a square pitch (57.3° helix angle). The recommended feed screw compression ratio should be between 2.0:1 and 4.0:1 with 2.5:1 up to 3.0:1 being the optimum [52]. Other screw designs, such as flighted barrier, Maddox mixing, pin mixing can be used but without screw cooling [53].

During start-up the temperature should be maintained at 205°C (401°F). The melt temperature in the extruder should be between 190°C and 230°C (374°F and 446°F), although temperatures up to 250°C (482°F) can be approached without degrading the material [53].

The die-swell, important for the dimensional control of the extrudate increases with the shear rate, with the hardness of the composition and with the decreasing extrusion temperature.

Other important aspects of the extrusion of the TPVs are the drying of the material, typically for 2–3 hr at 65 ton 75°C (149–167°F) in a desiccant dryer and a thorough purge with either polyethylene or PP after the extrusion of the TPV material is finished.

6.4.3 Injection Molding

Fast injection rates (under high pressures) in injection molding give very low viscosities of the material as a result of the high sensitivity of its viscosity to shear rate. Consequently, the low viscosity facilitates a rapid and complete mold filling. As the mold is filled, the melt viscosity increases greatly due to the shear rate being reduced to zero. The increased viscosity, which may approach infinity, enables a more rapid removal of the part from the mold. The overall effect is a shorter injection molding cycle [51]. The low to moderate dependence of viscosity on temperature of such compositions provides a broad temperature window for processing. Examples of injection molding and extrusion conditions of an EPDM/PP TPV composition are in Tables 6.6 and 6.7, respectively.

Injection molding of the dynamically cured TPVs has been successfully done in reciprocating screw injection molding machines. The cycle times are considerably shorter than those used for thermoset rubber materials, and the scrap accumulated in the sprues and runners can be recycled instead of being discarded. The use of hot runners represent additional improvement since it can eliminate scrap and the need for its recycling [54]. The injection molding cycle should take advantage of the unusual rheological properties of the TPV materials as pointed out above. A high injection pressure should be used to fill the mold cavity as rapidly as possible taking advantage of the high shear sensitivity of the material and low viscosity at the shear rates commonly used in injection molding, being typically higher than 500 s^{-1}. The high viscosity at low shear rates allows rapid and easy ejection of the partially cooled part with a solidified skin and molten interior without permanent distortion. The mold shrinkage is minimized by adequate packing in the mold and by high melt temperature. Typical shrinkage of injection-molded parts is 1.5–2.5%. Mold release agents are not needed or recommended [53]. The equipment should be cleaned before and after the run either by purging with PP or PE or by mechanical cleaning.

6.4.4 Compression Molding

Compression molding of TPVs is used mainly for the preparation of standard laboratory test

Table 6.6. Conditions for Injection Molding of EPDM/PP-Based TPVs.

Rear-Zone Barrel Temperature, °C (°F)	180–220 (356–428)
Center-Zone Barrel Temperature, °C (°F)	205–220 (401–428)
Nozzle Temperature, °C (°F)	205–220 (401–228)
Melt Temperature, °C (°F)	20–65 (68–149)
Injection Pressure, MPa (psi)	35–140 (5,100–203,560)
Hold Pressure, MPa (psi)	30–110 (4,200–15,400)
Back Pressure, MPa (psi)	0.7–3.5 (100–500)
Screw Speed (rpm)	25–75
Injection Speed	Moderate to fast
Injection Time (s)	5–25
Hold Time (s)	15–75
Total Cycle Time (s)	20–100

Source: Reference [5], p. 188.

specimens from pellets or preformed slabs, with the latter being preferred. The material is first preheated at 190–215°C (374–419°F) for 40 min to melt completely. The melt is then molded in a compression mold at 165–190°C (329–374°F) and 200–400 psi pressure. Demolding can be done at temperatures below 120°C (248°F). As in injection molding, no mold release agent is needed. In general, compression molding is not used for production of molded parts because it is not economically competitive to the speed and efficiency of injection molding.

6.4.5 Blow Molding

Hollow articles from TPVs can be readily made by blow molding. It is a more efficient method than injection molding where a solid core has to be used and subsequently removed. In blow molding just compressed air has the function of the core. Both extrusion and injection blow molding are used for the manufacture of hollow parts from TPVs. The preferred method of extrusion blow molding is continuous extrusion, intermittent parison drop, although other methods are practical and possible. The extrusion system should have a multizoned single screw with the L/D ratio of 24:1 [55].

6.4.6 Thermoforming

Thermoforming, another method used typically for thermoplastics and not applicable to thermoset rubber materials is easily applied to TPVs. It lends itself to the processing of harder grades of TPVs (hardness Shore A 73 and above [56]) by converting a sheet of rubber by simultaneous application of heat and pressure (either positive or vacuum) into a desired shape. Because of the high melt strength of the TPVs they exhibit uniform and predictable sag during heating similar to ABS.

Table 6.7. Conditions for the Extrusion of EPDM/PP-Based TPV

Rear-Zone Barrel Temperature, °C (°F)	175–210 (347–410)
Center-Zone Barrel Temperature, °C (°F)	175–210 (347–410)
Front-Zone Temperature, °C (°F)	190–220 (374–428)
Adapter Temperature, °C (°F)	200–225 (392–437)
Die Temperature, °C (°F)	205–225 (401–437)
Melt Temperature, °C (°F)	205–235 (401–455)
Screw Speed (rpm)	10–150

Source: Reference [5], p. 188.

The sheet temperature, which is the principal variable in thermoforming depends on the hardness of the material and varies from 174°C (345°F) for hardness Durometer 73A to 210°C (410°F) for Durometer 50D. Depth of draw ratios 3:1 is typical for TPVs and the draw rate should be slower than that commonly used for ABS [56].

6.4.7 Calendering

Calendering is suitable for the manufacture of sheets from TPVs in the range of gauges from 0.010 to 0.05 in. (0.25 to 1.25 mm). The material has to be melted with required melt temperature being 190°C (378°F) in an internal mixer (Banbury) or a mixing extruder and delivered to the calender. The setting of calender roll temperatures depends on the hardness of the TPV material and examples of calendering conditions for different TPV materials are in Table 6.8.

6.4.8 Extrusion Foaming

Extruded foamed articles (sheets, tubing, and profiles) from TPVs are produced in two specific gravity ranges, namely *high density* (specific gravity 0.7–0.9) and *low density* (specific gravity 0.2–0.7). These foamed articles have a thin solid skin and uniformly foamed interior.

The *high-density* extrusion is done by using a chemical blowing agent (e.g., azodicarbon-amide)

Table 6.8. Conditions for Calendering EPDM/PP-Based TPV on a Four-Roll Calender

Temperature Setting	Hardness, Shore		
	73A	87A	50D
Melt, °C	193 ± 5	193 ± 5	193 ± 5
°F	380 ± 10	380 ± 10	380 ± 10
Drop Mill, °C	182 ± 5	182 ± 5	182 ± 5
°F	360 ± 10	360 ± 10	360 ± 10
Calender Roll 1, °C	179 ± 5	179 ± 5	171 ± 5
°F	355 ± 10	355 ± 10	340 ± 10
Calender Roll 2, °C	182 ± 5	182 ± 5	171 ± 5
°F	360 ± 10	360 ± 10	345 ± 10
Calender Roll 3, °C	185 ± 5	185 ± 5	177 ± 5
°F	365 ± 10	365 ± 10	350 ± 10
Calender Roll 4, °C	188 ± 5	188 ± 5	179 ± 5
°F	370 ± 10	370 ± 10	355 ± 10

Note: Mixed 2 min in Banbury mixer.
Source: Reference [1], p. 125.

in amounts typically being 0.50–0.75% by weight. The blowing agent is mixed into the material just prior to extrusion. A single screw extruder (with a screw *L*/*D* of 24:1 or greater and compression ratio 3:1) is recommended. Examples of temperature settings are in Table 6.9.

The *low-density* extrusion foaming uses either two tandem extruders each with the *L*/*D* ratio of 24:1 or a single screw extruder with a minimum *L*/*D* of 32:1. A physical blowing agent, an environmentally safe liquid such as a hydrochlorofluorocarbon (HCFC), hydrofluorocarbon (HFC) of pentane is metered directly into the injection port of the primary extruder.

6.4.9 Bonding of TPVs

Bonding of TPVs to itself or other materials is required in many manufacturing operations. Bonding to itself is easily accomplished by a simple heat welding. Heat welding without any adhesive can be accomplished if the other substrate is compatible with the EPDM-based TPV, such as PP, polyethylene, or ethylene vinyl acetate. In such a simple welding, both materials have to be heated to 165°C (329°F), the melting point of TPV. The surfaces to be bonded can be heated by a contact with hot metal surface (230–300°C or 446–572°F), hot air (210–260°C or 410–500°F), by ultrasonic welding, or by linear vibration heating. Heat welding will generate bonds with typically 50–80% of the strength of the two materials. This method gives best results in bonding a TPV to itself or another TPV.

Table 6.9. Temperature Settings for the Extrusion of High-Density Foam from EPDM/PP TPV (Specific Gravity of Foam: 0.7–0.9)

Feed Throat	No Heating
Feed Zone, °C	182 ± 5
°F	360 ± 10
Transition Zone, °C	177 ± 5
°F	350 ± 10
Metering Zone, °C	166 ± 5
°F	330 ± 10
Front Zone, °C	154 ± 5
°F	310 ± 10
Golead/Gate, °C	182 ± 5
°F	360 ± 10
Die, °C	177 ± 5
°F	350 ± 10
Melt, °C	182 ± 5
°F	360 ± 10

Source: Reference [1], p. 127.

Bonding to dissimilar materials, such as metals, textile, other thermoplastics, or elastomers requires often the use of a specific adhesive system compatible with both materials to be bonded. The most widely used methods are coextrusion, cross-head extrusion, and insert injection molding. Some surfaces require the application of a primer to attain a sufficiently strong bond. In cases where solid TPV is bonded to another solid, such as metal, thermoplastic, or vulcanized rubber a suitable adhesive has to be found. The common practice is such that the adhesive is applied to both surfaces that are then joined under pressure at either ambient or elevated temperature.

Surface of TPV products can be hot stamped or printed on by inks or by applying a variety of colored paints by spraying or brushing.

The above sections regarding processing and fabrication provide only a general guidance and it should be noted that processing conditions have to be adjusted according to the compositions being processed, equipment, and/or mold designs used.

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7 Polyolefin-Based Thermoplastic Elastomers

7.1 Introduction

Polyolefin thermoplastic elastomers are defined as materials combining polyolefin semi-crystalline thermoplastic and amorphous elastomeric components. They exhibit rubber-like characteristics and can be processed as melts by common thermoplastic processing equipment. There are several distinct types of polyolefin-based thermoplastic elastomers (TPEs), which include [1]:

- Blends (mechanical mixtures), referred to as TPOs
- Dynamically vulcanized blends of ethylene-propylene random copolymer (EPM) or ethylene propylene diene monomer (EPDM) with an olefin (TPVs)
- Random block copolymers, for example, ethylene α-olefin copolymers
- Block copolymers, for example, hydrogenated polybutadiene-isoprene-butadiene block copolymer
- Stereoblock polymers, for example, stereoblock polypropylene
- Graft copolymers, for example, polyisobutylene-*g*-polystyrene.

Most of the polyolefin TPEs depend on crystallization of polymer chains to produce the elastomeric characteristics. In the *random block copolymers* that are similar in structure to thermoplastic polyurethanes (TPUs), ethylene sequences long enough to crystallize at the operating temperature form the physical cross-links for the amorphous elastic chain segments. In *stereoblock copolymers* changes in intrachain tacticity provide crystalline and amorphous sequences. *Graft copolymers* contain polyolefin chains that form glassy or crystalline phase that are grafted onto a polyolefin rubbery backbone and provide physical cross-links for the system. In most block and graft copolymers the elasticity is accomplished by having rubbery chains connected by reversible, physical cross-links. The elastic network is formed by the combination of physical cross-links and trapped entanglements among the rubbery chains and is very similar to that of chemically cross-linked rubber and the retractive force is entropic in nature [2].

The difference between the *mechanical blends* (TPOs) and *dynamically vulcanized blends* (TPVs) is that the former are co-continuous phase systems (both elastomeric and crystalline polyolefin phase) and in the latter the elastomeric phase is cross-linked and discontinuous. The polyolefin phase in a TPV is continuous and surrounds the cross-linked elastomeric phase. The dynamically vulcanized blends are subject of a separate chapter (Chapter 6).

7.2 Thermoplastic Polyolefin Blends

Polyolefin blends TPEs (TPOs) are based primarily on ethylene-propylene random copolymer (EPM) and isotactic polypropylene (iPP) and represent an important family of engineering materials [3]. The simple blends are prepared by mixing the hard polymer and the elastomer together on high-shear compounding equipment, such as internal mixer (e.g., Banbury) or continuous mixer (e.g., single- or twin-screw extruders). The condition for an elastomeric material is a three-dimensional, co-continuous structure with the continuous hard phase providing the strength and the continuous soft phase providing the flexibility. Because neither phase is cross-linked, both can flow, thus being a true thermoplastic elastomer. A two-dimensional representation of a hard polymer/elastomer blend is in Fig. 7.1. The viscosities of the two polymers must be matched at the temperature and shear rates of the mixing. The shear rate should be in the range 100–1,000 s^{-1} with the lower end of this

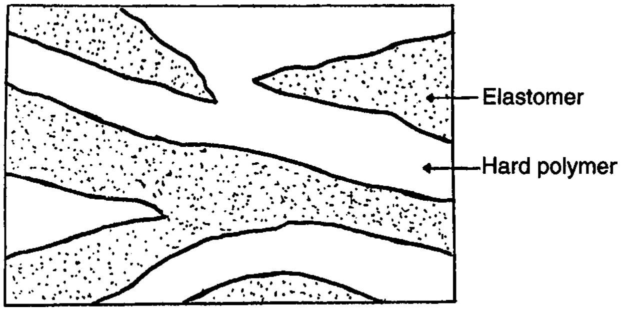

Figure 7.1. Morphology of Hard Polymer/Elastomer blends (Courtesy Hanser Publishers) [3].

range being typical for the rubber mixing equipment and the upper end being typical for plastics processing equipment, such as twin-screw extruders [4]. The optimum viscosity match also depends on the proportion of the two components (A and B) and the proportion of these components in the mixture (see Fig. 7.2). The other important factor is the compatibility of the two components, which is often expressed by the difference between their solubility parameters [5]. If the volumes of the two components are about equal, then for ideal mixing, their viscosities should also be about equal. If the volumes are not equal, then the component with the larger volume should also have the higher viscosity [5].

In the simplest blends of EPM and iPP, an intensive mixing results in two continuous phases. By adjusting the viscosity ratios, both phases can be kept continuous over a considerable range of volume fraction in this blend (e.g., 80/20 to 20/80) [6].

Thermoplastic elastomer blends based on polypropylene are very significant commercially because polypropylene is low in cost and has a low density. Its crystalline structure and relatively high crystalline melting point ($T_m = 145–165°C$, depending on grade) give it resistance to oil, solvents, and elevated temperatures. Elastomers of EPDM and EPM types are a logical choice for the elastomeric phase because of their thermal stability, low cost, flexibility at low temperatures, and structural similarity to polypropylene. This similarity also means a good compatibility in blending [5]. Since EPM is even less expensive to produce than EPDM, it eventually became the material used almost exclusively for the blends. The extra diene co-monomer used in EPDM is several times more expensive than either ethylene or propylene and is required only if the elastomer is to be vulcanized. On the other hand, the double bonds provide wider choice in raw material selection and affect the green strength of the elastomer by changing the number of branch points in the rubber molecule [6]. Isotactic polypropylene (homopolymers or copolymer with a small amount of ethylene) is the preferred polymer for the hard domain.

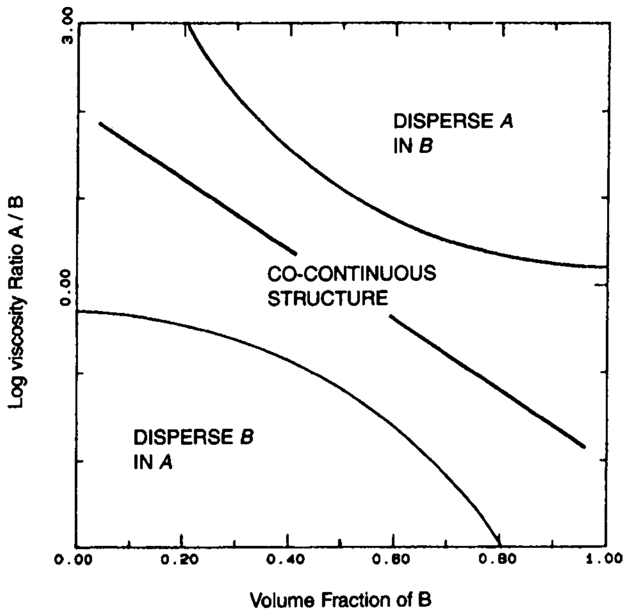

Figure 7.2. Relationship between the ratio of the viscosities of two components (A and B) and their proportion in the mixture.

Advances in Ziegler-Natta and metallocene catalysis allowed the copolymerization of an elastomeric soft component in a shell or skin of crystalline polypropylene. Such products are referred to as *reactor thermoplastic polyolefins* (RTPO) [7].

7.2.1 Compounding of TPOs

In addition to rubber and polyolefin, a large variety of other ingredients are used in compounding of a TPO formulation. These may include fillers, reinforcing agents, plasticizers, lubricants, processing aids, flow modifiers, antioxidants, heat stabilizers, UV absorbers, colorants, flame retardants, etc.

In general, most of the additives are contained in the rubber phase at room temperature. A study has found that even in a TPO formulation that contained 20% by weight carbon black, virtually none of the black was in the polypropylene phase [8]. At processing temperatures, some additives may move into the polyolefin phase. Smaller molecules that are soluble in a polyolefin are free to move to that phase once the polyolefin has melted. For example hydrocarbon oils partition between the phases greatly lowering the viscosity of the melt. Upon solidification the oil returns to the rubber phase and gives the desired result of softening and extending the rubber [9].

Other additives are used for specific properties. For example, carbon blacks are added to achieve electrical semiconductivity with a typical amount of 30% in the formulation. Mineral fillers are added to increase damping and reduce cost. Most of the compounding ingredients are used in a similar fashion as in thermoset (EPDM) formulations or in thermoplastic polyolefins with comparable effects. In some cases the additives tend to migrate easier to the surface as they would in the individual

(EPDM or polyolefin) formulation. This can be prevented by careful compounding.

Commercial TPO compounds are delivered as fully compounded materials and additional compounding is in general not successful and may be, in fact, dangerous to personnel or equipment. Therefore, it is advisable to consult the supplier about any compound modification [10].

7.3 Morphology

The morphology of a TPO compound is complex. The distribution, size, and shape of both the rubber and polyolefin phases are determinants of the properties of the compound. The polyolefin phase is almost always continuous. The rubber phase may be either continuous or discrete, depending on the amount of rubber relative to the amount of the polyolefin (most frequently polypropylene) the type of rubber, the mixing procedure, and other ingredients. In most formulations, the rubber phase will be continuous if that phase is between 45% and 48% of the total volume. In this range both polypropylene and rubber phases are continuous. At either extreme of this range, the viscosity of the rubber relative to that of the polypropylene is the main factor in deciding whether the rubber or the polypropylene phase is continuous (see previous sections). Other factors are the physical form of the varied additives, their compatibility with either phase, etc. [10].

7.4 Properties of TPOs

7.4.1 Mechanical Properties of TPOs

Products made of TPOs cover a wide range of properties that essentially bridge the gap between soft rubber and engineering plastics. They can be formulated to combine strength and toughness with properties and feel from soft traditional rubber to stiff products with high impact strength. These products are available in the hardness range from 60 Shore A to 70 Shore D.

Their flexural modulus can range from 1,000 to 250,000 psi (6.9 to 1,725 MPa). The specific combination of properties such as hardness, flexural modulus, tensile strength, tear resistance, impact strength, and so on will vary with a specific grade of TPO.

7.4.1.1 Stress–Strain Properties

The stress–strain properties of a highly elastic amorphous EPDM [11] and various polyolefin resins are shown in Table 7.1. Blends containing high amounts of EPDM (70 or more) are quite rubbery with elongation at break values 150% or more and elongation set at break 30% or less. In contrast, when pure high molecular weight polyolefin resins are extended, they undergo a yield at low elongation followed by a typical drawing mechanism, and there is little recovery after drawing [12]. When a semi-crystalline EPDM is used in similar

Table 7.1. Properties of EPDM-Polyolefin Blends

Blend[a]							
EPDM,[b] Parts	80	70	60	80	60	80	60
Polypropylene,[c] Parts	20	30	40	—	—	—	—
Low-Density Polyethylene,[d] Parts	—	—	—	20	40	—	—
High-Density Polyethylene,[e] Parts	—	—	—	—	—	20	40
Physical Properties							
Tensile Strength, MPa	8.3	10.5	13.9	5.8	8.0	8.5	10.2
Elongation at Break, %	220	150	80	290	190	210	130
Elongation Set at Break, %	28	30	30	35	30	25	33

Notes:
[a] Banbury mixer, approx. 7 min mixing time, maximum temperature about 200°C (392°F).
[b] Amorphous, high molecular weight ethylene-pripylene-dicyclopentadiene (~5wt%) terpolymer.
[c] Density 0.903, MFI 4.0 at 230°C.
[d] Density 0.919, MFI 2.0 at 190°C.
[e] Density 0.956, MFI 0.3 at 190°C.
Source: Reference [12].

Table 7.2. Properties of Semi-Crystalline EPDM-Polyolefin Blends

Blend[a]				
EPDM, Parts	80	80	80	80
EPDM Crystallinity, wt%	12.9	2.7	12.9	2.7
LDPE,[b] Parts	20	20	—	—
HDPE,[c] Parts	—	—	20	20
Physical Properties				
Tensile Strength, MPa	15	5.4	14.5	7.6
Elongation at Break, %	730	940	720	880

Notes:
[a] Mill mixed at 150°C (302°F).
[b] Density 095.
[c] Density 0.92.
Source: Reference [13].

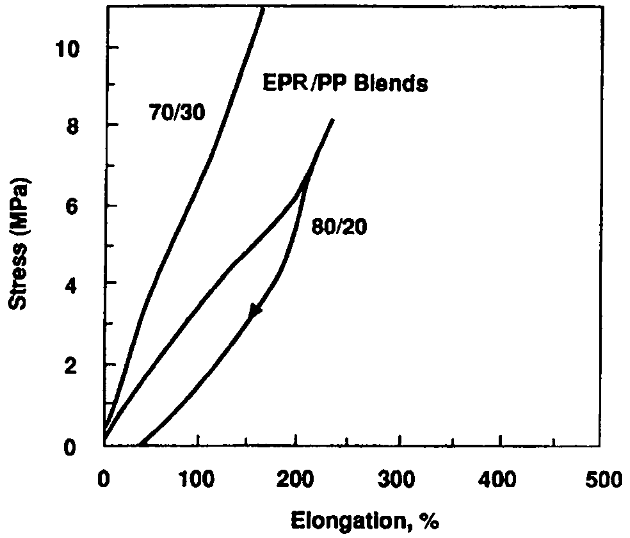

Figure 7.3. Stress–strain properties of blends of ethylene-propylene random copolymer and isotactic polypropylene. Return from 200% elongation is shown.

blends the results show a considerable improvement in properties, especially in elongation at break. It appears that in addition to the crystallinity in the unstrained state, the increase in crystallinity during extension has an appreciable effect on the stress–strain properties of the blend (see Table 7.2) [13]. The stress–strain curves for two unfilled blends of amorphous ethylene-propylene random copolymer and isotactic polypropylene are shown in Fig. 7.3.

7.4.2 Service Temperatures

The upper limit of use temperature is determined by several factors. A part from TPO may be exposed to the elevated temperature for only a brief period of time. An example would be when a painted part goes through a baking oven. On the other hand, long-term exposure, that is, weeks, months, or years of continuous use will be evaluated differently.

The melting point of the hard domain polymer(s) of a TPO is of importance for short-term exposures. In most cases the melting point of PP is a limiting factor. Polypropylene homopolymers melt at about 160°C (320°F) and most TPOs made from it will retain useful properties up to 140°C (284°F).

For long-term exposures the aging resistance of the material is of equal importance as the melting temperature of the hard domain. The oxidative stability can be assured by the addition of antioxidants and antidegradants. The most effectively stabilized TPO products will withstand operating temperatures up to 125°C (257°F) [14].

As to the performance at low temperatures, softer grades often have a low-temperature brittle point less than −80°C (−112°F). Figure 7.4 illustrates the change in stiffness of a TPO with 80 Shore A hardness as the temperature is reduced.

7.4.3 Weathering

Most TPOs are made from polymers that do not contain unsaturation in their backbone. Therefore they are not susceptible to ozone attack and retain their original physical properties when exposed to sunlight and weather [15]. However, they should not be assumed to be light-fast during an outdoor exposure. Polymers themselves do not change, but certain compounding ingredients may cause discoloration [16]. Therefore, special stabilizers have to

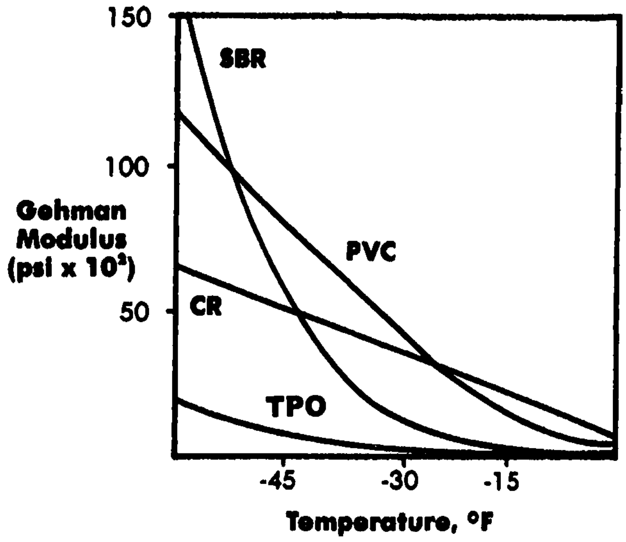

Figure 7.4. Low temperature Gehman stiffness (Courtesy Springer).

be added to prevent discoloration during outdoor exposure.

7.4.4 Chemical Resistance

The resistance of olefinic TPEs to solvents and fluids varies with the grades. All TPO products are unaffected by water or aqueous solutions of chemicals and resist acids and bases. Hydrocarbon solvents tend to swell and soften TPO products. This effect is much more pronounced for softer grades. The chemical resistance of general purpose TPO is shown in Table 7.3.

7.4.5 Adhesion

The chemically inert, low energy surface of TPOs makes bonding them to other materials difficult. Only limited number of adhesives is available for the low energy untreated polyolefin surface and it is always necessary to ensure that the bond has an adequate strength and durability for the intended application. In many cases mechanical interlock or interference fits are the most reliable methods. Some hot melt and anaerobic adhesives give good results [17].

7.4.6 Electrical Properties

By their chemical nature, most TPO compounds are good electrical insulating materials. They have good dielectric strength and do not absorb moisture. Typical electrical properties for a filled grade of TPO are in Table 7.4.

Table 7.3. Typical Chemical Resistance Properties of TPO

Chemical	Resistance
Acetone	Good
ASTM Oil No. 1	Fair
ASTM Oil No. 3	Fair
ASTM Fuel B	Poor
Bromine, Anhydrous	Fair
Butyl acetate	Good
Butyl alcohol	Good
Butter	Fair
Sodium hypochlorite, Aqueous	Good
Chromic acid	Good
Detergents	Good
Ethyl acetate	Fair
Ethyl alcohol	Good
Ethylene glycol	Good
Formaldehyde	Good
Formic acid	Good
Furfural	Good
n-Hexane	Poor
Hydrochloric acid	Good
Hydrogen peroxide, Aqueous	Good
Isooctane	Poor
JP Jet Fuel	Poor
Methyl alcohol	Good
Methyl methacrylate	Fair
Skydrol® 500B	Fair
Sodium carbonate	Good
Sodium hydroxide	Good
Sulfuric acid, Diluted	Good
Tetrahydrofuran	Poor
Toluene	Poor
Water	Good

Source: Handbook of Thermoplastic Elastomers, 2nd Edition (Walker, B.M., and Rader, C.P., Eds.), Van Nostrand Reinhold Co., New York, 1988, p.57.

7.5 Processing of TPOs

These blends may be processed on the standard equipment for thermoplastics. Products from TPO can be made by injection molding, extrusion, vacuum

Table 7.4. Typical Electrical Properties of TPO

Property	Test Procedure	Test Result
Dielectric Strength (V/mil)	ASTM D 149	500
Volume Resistivity (23°C and 50% RH) (ohm-cm)	ASTM D 257	1.6×10^{16}
Arc Resistance s	ASTM D 495	114
Dielectric Constant at	ASTM D 150	
60 Hz		2.4
1 kHz		2.39
1 MHz		2.37

Note: Tested on a molded plaque 0.080 in. (2.0 mm thick).

Source: Handbook of Thermoplastic Elastomers, 2nd Edition (Walker, B.M., and Rader, C.P., Eds.), Van Nostrand Reinhold Co., New York, 1988, p.58.

forming, injection blow molding, and extrusion blow molding. Because of the versatility of the compounding the materials can be prepared to the specific equipment, process, and process conditions.

In general, TPOs do not require any special handling and since they are not hygroscopic, they do not have to be dried prior to processing. If for some reason the TPO compound has to be dried (e.g., supplier's recommendation or the use of hygroscopic fillers), usually drying for 1–2 hr at 80–95°C (176–203°F) should be sufficient.

7.5.1 Injection Molding

7.5.1.1 Equipment and Process Conditions

These mechanical mixtures can be processed on either reciprocating screw or plunger injection molding machines, although the reciprocating screw machine is preferred since it produces a more uniform melt, which translates directly into the part quality. Recommended screw compression ratio is 2.5:1 to 3.5:1 [18]. Since standard TPO materials are not corrosive the screw may be made from standard hard durable steel. Only if halogen-based flame retardants are used, corrosion resistant alloys may be considered for the equipment. The process conditions for injection molding are in Table 7.5. Purging of the equipment is done by polypropylene.

7.5.1.2 Mold Design

The draft angles and taper for the molds used for TPOs should be generous, particularly for softer grades [19]. Draft angles should be at least 3° to facilitate the part ejection. Knock-out pins and pusher plates should be large enough to prevent marking of softer parts. Thick ribs should be avoided since they may cause sink marks in the surface opposite the rib. In general, gates should be made larger than those for other thermoplastic materials and should be designed to avoid high-shear areas that may cause overheating of the compound. Their diameter should be chosen according to the wall thickness of the part [19].

7.5.2 Extrusion

Extrusion is used for the production of profiles, tubing, sheets, hose, for coating of wires, and jacketing of cables.

7.5.2.1 Equipment and Process Conditions

The length of the barrel of an extruder used for TPO should be at least 20 times longer than its inside diameter with the optimum ratio being 24:1 to 30:1 [19]. The recommended screw compression ratio is 2.7–3.5:1 but not higher than 3.5:1 and its configuration ⅓, ⅓, ⅓. A single stage screw is sufficient for the extrusion of TPO compounds [20]. Typical process conditions are in Table 7.6. As in injection molding polypropylene is used for purging the equipment.

Tooling and dies for the TPO extrusion should be designed as streamlined as possible. The die should be designed with a minimum land of 0.125 in (3 mm) and smooth transition and heated with a separate control. Wire coating or jacketing dies can be either the tubing or pressure type design with lead-in angles 22–35°. Standard flexible-lip, coat-hanger-type extrusion dies are suitable for the extrusion of TPO sheets. Die lips should have at least 1 in. (25 mm) band length and should be set for a 30–50% draw-down with thinner sheets requiring less draw-down [21].

Table 7.5. General Injection Molding Parameters for TPO

Machine Parameter	Typical Value
Clamp Pressure	3–5 tons (41.3–68.9 MPa) per square inch projected part area
Nozzle Length	As short as possible
Barrel Temperature Profile (Nominal)	
Nozzle	420˚F (215˚C)
Front	420˚F (215˚C)
Center	410˚F (210˚C)
Rear	400˚F (204˚C)
Mold Temperature Range	
Cavity	85–125˚F (29–52˚C)
Core	75˚F (24˚C)
Hot Runner, Manifold, and Tips Temperature	420˚F (215˚C)
Injection Pressures	
High	500–1,500 psi (34–103 bar)
Low	350–1,000 psi (24–70 bar)
Back Pressure Range	50–300 psi (3.5–20.0 bar)
Cushion	0.25–0.50 in. (6.35–12.7 mm)
Melt Decompression	Minimize to eliminate nozzle drool
Injection Speed	Medium to fast, typical range 0.4–3.2 in./s (10–80 mm/s)
Screw Speed	Medium, typical range 50–100 rpm

Sources: 1. *Injection Molding, Processing and Troubleshooting*, Solvay Engineered Polymers, Auburn Hills, MI. 2. Reference [18].

Table 7.6. General Extrusion Parameters for TPO

Parameter	Temperature Range, ˚F (˚C)
Barrel Temperature	
Rear Zone	350–370 (177–188)
Center Zone	370–390 (188–199)
Front Zone	390–410 (199–210)
Clamp Temperature	380–400 (193–204)
Adapter Temperature	380–400 (193–204)
Screen Changer Temperature	390–410 (199–210)
Die Temperature	380–410 (193–210)
Melt Temperature	370–400 (188–204)

Source: *TPO Profile Extrusion Guide*, Solvay Engineered Polymers, Auburn Hills, MI.

7.5.3 Other Processing Methods

Calendering can be used to fabricate sheet and film with gauges ranging from 5 to 50 mil (0.127–1.27 mm). A four-roll calender is best suitable for this process. Typical roll temperatures are:

- Top rolls: 350˚F (177˚C)
- Center roll: 300˚F (149˚C)
- Bottom roll: 275˚F (135˚C)

A minimum stock temperature of 350˚F (177˚C) is needed to provide a uniform melt and a smooth sheet. The calendered sheet can be embossed using conventional methods [22].

Thermoforming has become an important manufacturing method for large automotive parts with the development of TPO grades with higher melt strength [23, 24] and know how. Recommended conditions

Table 7.7. Recommended Conditions for Thermoforming TPO

Parameter	Condition
Sheet Temperature	320–360°F (160–182°C)
Tool Temperature	170–190°F (77–88°C)
Part Removal Temperature	140–170°F (60–77°C)
Minimum Vacuum	25 in Hg (635 mmHg)
Drying Temperature	120–180°F (49–82°C)[a]

Note: [a]Normally drying is not necessary; however, drying at the above conditions for 1–4 hr may lead to a better surface and optimum sheet performance.

Source: *Troubleshooter's Guide to Thermoforming TPO Materials*, Solvay Engineering Polymers, Auburn Hills, MI.

for thermoforming are in Table 7.7. *Negative thermoforming*, that is, drawing a heated sheet into a cavity, is used to produce TPO skins for automotive instrument panels. The result is improved appearance [25].

Blow molding is used for interior and underhood air ducting. A high melt strength TPO grade is required for this manufacturing method [26].

Slush cast molding, a method used mainly for plasticized PVC, has been adapted for powdered TPO material replacing PVC in interior automotive parts. Powder TPO prepared by cryogenic pulverization, remains ductile longer than PVC (twice as long) remains ductile at lower temperatures compared to PVC and does not contribute to fogging. Compared to TPU that is also used in this application, it is considerably less expensive [27, 28].

Foamed TPOs can be prepared rather easily because of their favorable viscosity characteristics. Several methods can be used, depending on application. Foaming is done either by using chemical blowing agent [29–31], by physical blowing agent, for example, CO_2 or by supercritical gas [32]. The parts can be manufactured by injection molding, compression molding, or extrusion. Typical foamed TPO has a density 700 kg/m^3.

7.6 Painting of TPOs

The largest volume of parts made from TPOs is used in automotive applications. Therefore they have to be made paintable with automotive finish to match or accent the painted finish of the other body panels. As pointed out in Section 7.4.5, TPOs being polyolefin-based have surfaces that do not react readily with most paints. To achieve an adequate adhesion of paint, the TPO surface has to be modified to obtain a reactive surface by creating polar groups on it. This can be accomplished by the following surface pretreatments [33, 34]:

- Corona discharge
- Plasma treatment
- Flame treatment
- Chemical treatment (chromic acid or potassium permanganate)
- Application of adhesion promoter primer.

Chlorinated polyolefins (CPOs) dissolved in aromatic solvents have been in use for a long time as adhesion promoters [34]. Recently, other promoter primers have been used, such as nonchlorinated adhesion promoter primer systems and waterborne adhesion promoter primer systems [34].

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8 Thermoplastic Elastomers Based on Halogen-Containing Polyolefins

8.1 Introduction

The presence of halogen atoms in elastomeric macromolecules lends them some very advantageous properties, such as chemical resistance, flame retardancy, low swelling in hydrocarbon solvents and oils. Thermosetting elastomers containing halogens, such as polychloroprene, chlorinated polyethylene, fluoroelastomers, chlorobutyl rubber, bromobutyl rubber have been used commercially for decades. However, halogen-containing thermoplastic elastomers are relatively new and some of them are currently still in development.

The first halogen containing polymer that exhibits rubber-like properties and still maintaining thermoplasticity is plasticized polyvinyl chloride (PVC). Plasticizers used for this purpose are both low molecular weight liquids and high molecular weight solids [1–5]. However, true thermoplastic elastomers are blends of PVC with cross-linked or elastomeric polymers. The first such material is a blend of PVC with acrylonitrile-butadiene rubber (ASTM designation NBR), prepared mainly as proprietary blends by flexible PVC fabricators. Polyvinyl chloride is also compatible with other elastomers, such as copolyester elastomers and with thermoplastic polyurethanes (TPUs) and such blends are thermoplastic elastomers with unique properties. Another halogen containing TPE is Alcryn®, developed by the DuPont Company. It is a melt-processible rubber (MPR) introduced in the late 1980s as fully compounded pelletized product for direct fabrication. It can be processed by equipment typical for the processing of thermoplastics, such as injection molding machines, extruders, calenders, etc.

8.2 Blends of PVC with Nitrile Rubber (NBR)

Before 1970, PVC was added to copolymers of acrylonitrile and 1,3-butadiene (NBR or nitrile rubber) to improve ozone and solvent resistance of its vulcanizates. Later, NBR grades, already available in the bale form, were developed and commercialized in powder form to be used specifically in the PVC processing industry. By the mid-1980s more grades, including food grades and grades with improved processing have been made available.

Thermoplastic blends of PVC and NBR are produced when PVC is the predominant polymer. Typically, they also contain liquid PVC plasticizers for PVC, such as, for example, phtalates or adipates, fillers, stabilizers etc. These blends bridge the gap between conventional liquid plasticized PVC (PVC pastes) and conventional NBR cured rubber. Properly formulated PVC-nitrile rubber blends are rubber-like in appearance and feel. They are flexible at low temperatures and have a good tear strength, low compression set, good abrasion resistance, and exhibit minimum swelling or extraction when immersed in oils or solvents [6].

The important compounding variables affecting the processing behavior and final properties are:

- PVC/NBR ratio
- Acrylonitrile (ACN) content in the NBR
- Mooney viscosity of the NBR
- Molecular weight of the PVC
- Type and amount of liquid plasticizers
- Type of stabilizer(s) used
- Type and amount of filler(s) added.

In general, NBR elastomers used for such blends should have 30–40% of ACN to obtain single-phase homogeneous blends with the optimum content being 40% [7]. The single-phase material exhibits a single value of glass transition temperature (T_g) as measured by differential thermal analysis [8] intermediate between the T_g values of the two polymers. The absence of two phases was established by electron photomicroscopy [9]. Some studies reported two T_g values [10] and micro-domains rich in one or the other of the components [11], which indicates that the morphological behavior of these blends is rather complex. The NBR used may be either without cross-links or containing various amounts of cross-links. The blends with NBR, which does not contain cross-links, have low viscosity, thus requiring relatively low energy to process. This provides a wider processing margin before thermal degradation of PVC occurs. The lower viscosity blends are suitable for injection molding. The blends with partially cross-linked NBR provide the lowest die swell making them suitable particularly for extrusion or calendering. Products containing an increased cross-link density exhibit a lower compression set.

8.2.1 Melt Compounding and Processing

As pointed out earlier, NBR used for blends with PVC is in the form of a free-flowing powder to be suitable for the handling and mixing common in the PVC technology. These powders consist of particles with average size of about 0.5 mm (0.02 in.) and contain about 10% of a partitioning agent, which may be PVC, calcium carbonate, or silica [12]. The NBR powder is usually added to the dry blending cycle after the PVC has absorbed all of the liquid plasticizers (so-called dry point). The temperature of the PVC blend to which the NBR powder is added should not be higher than 40°C (104°F) to avoid rubber agglomeration [13]. The mixing can be done in conventional mixing equipment for thermoplastics, such as low intensity or high intensity mixers, single-screw and twin-screw extruders, continuous mixers, and kneaders. The finished blends can be further melt compounded into pellets before processing or used directly to produce the finished products. In recent years, fully compounded commercial PVC-NBR blends have been marketed as alternatives to flexible vinyl, mid-performance elastomers and to "in-house" prepared PVC/NBR blends.

8.2.2 Physical and Mechanical Properties

Physical properties of the PVC-NBR blends are similar to those of mid-performance thermoset rubber materials. The stress–strain curves for three different compounds [14] are shown in Fig. 8.1. It is obvious that with increasing cross-linking of NBR and viscosity the stiffness of the compound increases slightly and the elongation decreases. Other physical and mechanical properties are in Table 8.1. It can be seen that the compression set at low and high temperatures is slightly improved with increasing cross-linking. Other properties are not affected significantly.

Physical properties of a typical PVC/NBR blend and two typical thermoset rubber materials were compared at temperatures up to 121°C (250°F). At room temperature, the tensile strength of the blend was comparable to that of thermoset rubber but was considerably lower at higher temperatures [9]. The relatively high tensile strength of the blend, containing slightly cross-linked NBR can be attributed to the cross-links in the elastomer combined with the strong hydrogen bonding between PVC and the NBR. As the temperature increases, the hydrogen bonding becomes gradually weaker and eventually the tensile strength depends only on the partially cross-linked NBR. Thus the values cannot match those of a fully cross-linked elastomer.

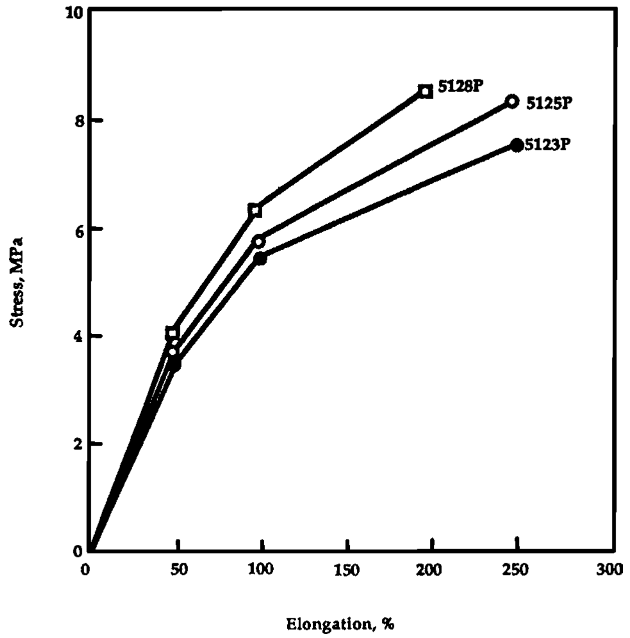

Figure 8.1. Stress–strain curves for PVC/NBR rubber compounds (Courtesy Springer) (see Table 8.1.) [14].

Liquid low molecular weight plasticizers are used to improve the flexibility of PVC/NBR blends at low temperatures. Adipate and triglycol ester-type plasticizers are more effective than phtalate ester types in maintaining both their low-temperature flexibility and resistance to swelling in certain liquids, such as ASTM Reference Fuel B.

8.2.3 Other Properties

The blends of PVC/NBR exhibit a fair resistance to swelling in ASTM Reference Fuel B. The degree of swelling is reduced slightly as the degree of cross-linking of the NBR component increases. The compounds containing dioctyl phtalate (DOP) harden excessively during swelling in ASTM No. 1

Table 8.1. Flexible PVC Compounds Based on Powdered Nitrile Rubber (NBR)

Grade	5123P	5125P	5128P
NBR Rubber Properties			
Acrylonitrile Content (%)	33	33	33
Money Viscosity, ML-4	30	55	80
Pre-Cross-Linking	None	Medium	High
Shore A Hardness			
Instantaneous	68	68	69
15 s Delay	64	64	63
Taber Abrasion Resistance			
H-18 Wheel, 1,000 g load, 2,000 rev (g loss)	0.657	0.644	0.713
Tear Strength, ASTM D 624, Die C (kN/m)	38.5	42	40.3
Brittle Point, ASTM D746 (°C)	−36	−37	−36
Compression Set, ASTM D 395 B (22 hr, 25% Compression)			
23°C (%)	23	20	19
100°C (%)	71	70	65

Source: Reference [14].

Oil and exhibit low volume swelling at the same time. This is attributed to the extraction of the DOP during the immersion [14]. In such a case the use of a polymeric plasticizer that resists extraction by the swelling media alleviates the problem, however at a somewhat higher formulation cost.

Since the nitrile rubber contains double bonds, it is susceptible to oxidation. To prevent that, antioxidants must be added to the compound if a long-term resistance to aging is required. A compound without an antioxidant becomes brittle and shows a considerable loss of elongation and considerable hardening when aged in oven at 113°C (235°F) for 1 week [15]. The addition of an antioxidant brings about less reduction in elongation but the compound will still harden when it contains a liquid plasticizer(s). The hardening is the result of the loss of the plasticizer due to its volatility. The use of a nonvolatile polymeric plasticizer will minimize the hardening as pointed out in the previous paragraph. The PVC/NBR compounds are not sufficiently resistant to UV radiation so if they are intended for a long-term outdoor exposure, an addition of an adequate UV protection package is required. This will contain pigmentation (titanium dioxide, zinc oxide, or carbon black), or UV absorbers, or a combination of both.

8.3 Blends of PVC with Other Elastomers

8.3.1 Blends of PVC with Copolyester Elastomers

Copolyester elastomers (COPEs), random block copolymers consisting of crystallizable tetramethylene terephtalate (4GT) hard segments and amorphous elastomeric polytetramethylene ether glycol (PTMEG-T) soft segments, described in Chapter 12 are compatible with plasticized PVC. Their blends yield materials that combine the elastomeric properties of the copolyester elastomers with the excellent processing characteristics of plasticized PVC [16]. The COPEs used for these blends are usually low-melting grades, which typically contain about 33% 4GT and melt below 180°C (356°F).

Addition of COPEs to plasticized PVC formulation improves its low-temperature flexibility and impact resistance, abrasion and tear resistance, and resistance to oils and fuels [17]. As little as 25% of COPE improves these properties, but also increases hardness and torsion modulus at room temperature [18]. A compound containing equal amounts of PVC and COPE exhibits properties that are significantly better than those typical for conventionally plasticized PVC. The blend has a superior low-temperature flexibility, heat aging resistance, abrasion resistance, and greater elongation at break both before and after oil immersion. Additionally, it exhibits good electrical properties (dielectric strength, volume resistivity), good resistance to water, chemicals, and cut growth. Because of that, it is used in wire and cable applications, such as cable jacket compound [17]. Compounds for outdoor applications have to be protected against effects of ultraviolet radiation. A typical protective package contains a UV absorber (e.g., a benzotriazole), a light stabilizer (e.g., a hindered amine), a hindered phenol antioxidant at 0.1–0.2 phr (parts per hundred parts of rubber) and a small amount of rutile TiO_2. If color is not an issue, small amount of carbon black (typically 2.5 phr) provides an effective UV screen [17].

The PVC component of the blend is prepared by mixing suspension grade PVC with plasticizer(s), stabilizer(s), etc., in a standard fashion using high-intensity mixer or a heated ribbon blender. The COPE can be mixed into plasticized PVC powder blend before the melt compounding, or the PVC and COPE can be metered independently to the melt compounding equipment, such as Banbury mixer, kneader, single-screw or twin-screw mixing extruder. Maximum melt temperature should be less than 190°C (374°F) to prevent degradation of PVC. The product is dried to less than 0.10% moisture and packaged in moisture-barrier packaging [19].

The blends of PVC/COPE are processed by standard equipment used for thermoplastics, such as injection molding presses and extruders. Since COPEs tend to degrade at processing temperatures, it is absolutely necessary that the compound be dry. The melt temperature must not exceed 190°C (374°F) and ideally should be kept in the 160–170°C (320–338°F) range and the heat history has to be kept at the minimum to prevent degradation of the PVC component [19].

8.3.2 Blends of PVC with Thermoplastic Polyurethane Elastomers

Thermoplastic polyurethane elastomers (TPUs) (see Chapter 9 for detailed description) are multi-block copolymers consisting of sequences of amorphous or low melting soft segments and rigid, hard segments, which have crystalline melting point above room temperature. Many TPUs are compatible with PVC and their blends exhibit only one major glass transition whose position on the temperature scale is raised with increasing levels of PVC [20].

The melt compounding and subsequent processing of the PVC/TPU blends is very similar to that of PVC/COPE blends discussed in the previous section. Because of the heat sensitivity of PVC only the softest TPU grades, that is, those with hardness values of Shore A of 80 can be melt mixed with it safely. The PVC/TPU blends are also sensitive to moisture during processing, so it is necessary to dry them to less than 0.03% moisture content to maintain optimum properties [21].

For the protection of the PVC/TPU compounds against UV radiation during outdoor exposure either benzotriazole UV absorber for neutral or color compounds at amounts up to 2% loading or carbon black up to 5% loading for black formulations is recommended. Antioxidants, such as hindered phenols or organosulfur types will extend the life of the products in outdoor exposures [21].

Blends of PVC with TPUs combine the toughness of the TPU with the stiffness and high modulus of the PVC. It is possible to obtain a wide range of hardness values by blending PVC with different hardness grades of TPU and by adding varied amounts of plasticizers to the PVC resin. The blend of PVC/TPU in the ratio of 70:30 by weight is equivalent to a commercial plasticized PVC compound in all respects yet displays a higher abrasion resistance and low-temperature flexibility.

The oil resistance of PVC/TPU blends is also improved over the plasticized PVC compounds. The immersion of such material in ASTM No. 3 Oil for 7 days at ambient temperature has a negligible effect on the volume swell and causes no decrease in tear strength. The flexural performance improves with the increasing content of TPU: a compound containing 30% of TPU is markedly better than a commercial plasticized PVC material of the same hardness in both flex life and the cut growth resistance after oil immersion and the trend continues with increasing proportion of TPU [21]. There appears to be an optimum TPU content of 40% for oil resistance and an optimum of 50% for the other properties [22].

8.4 Melt-Processible Rubber

This family of materials is described as "alloys of proprietary ethylene interpolymers and chlorinated polymers, in which the ethylene component has been partially cross-linked *in-situ*" [23]. They are comprised of a blend of molecularly miscible polymers having a single T_g (see Fig. 8.2). These polymers can be used for compounds, containing usually different additives, such as carbon black, clay, plasticizers and stabilizers, which give them desired processing characteristics and end-use properties.

8.4.1 Physical and Mechanical Properties

Unlike two-phase materials, such as most other TPEs (e.g., styrene-butadiene-styrene (S-B-S) and dynamically vulcanized TPVs), these are *single-phase*, primarily amorphous polymeric systems, soft and flexible with a good recovery. Their stress–strain curves are essentially identical to those of typical cross-linked thermoset elastomeric systems (see Fig. 8.3). Because of these inherent factors of rubbery character they are defined as *melt-processible rubber* (MPR) in contrast to the two-phase systems, referred to as *thermoplastic elastomers* (TPEs) and *thermoplastic vulcanizates* (TPVs).

When comparing MPR to TPV, vulcanized NBR and vulcanized polychloroprene (ASTM designation CR) at hardness approximately 70A durometer, it can be clearly seen that MPR has the initial slope of the stress–strain curve almost identical to those of NBR and CR. Since the initial slope is the measure of stiffness of the material, the much higher slope of the TPV indicates that the material is much stiffer than the others at the same durometer hardness. The tensile stress of TPV at 25% elongation is about three times higher than that of the other materials at the same point. In addition to being stiffer, TPV displays a plastic behavior by yielding at about 35% elongation, while MPR, NBR, and CR remain elastic well beyond 100% elongation. Hysteresis curves comparing MPR with TPV with equal hardness (Fig. 8.4) also indicate that MPR is more resilient having much lower hysteresis than TPV. Thus, based on above observations and field experience, MPR is considered to be a true rubber [24].

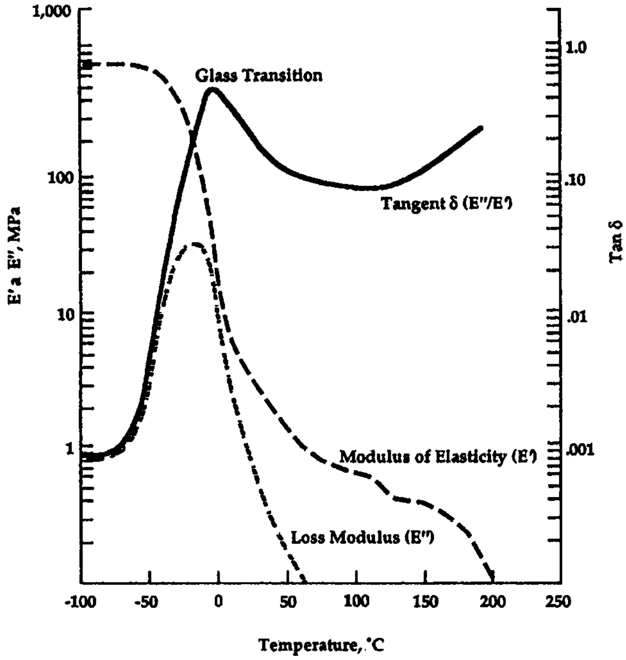

Figure 8.2. Glass transition of a 70 Shore A MPR from a Rheovibron data (Courtesy Springer) [23].

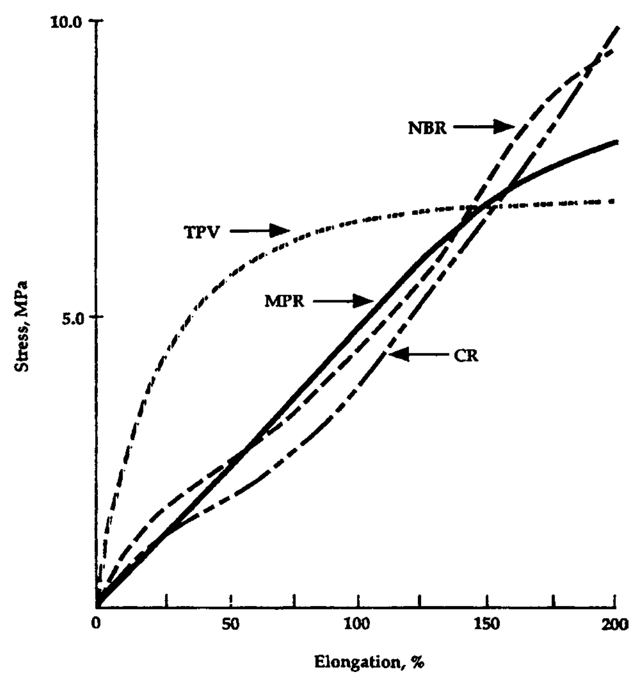

Figure 8.3. Stress–strain curves of different 70 Shore A hardness materials.

MPR is also compared to other polymeric materials in Table 8.2. Based on stiffness (initial slope of the stress–strain curve), yield strain (the percent elongation at which the material exhibits plastic yielding), and ultimate tensile strength, MPR is clearly the most rubber-like material of this group.

Like other thermoplastic elastomers, the melt-processible rubber is inferior to thermoset rubber materials in high temperature compression set and creep (see Table 8.3). As for the estimated service temperature in terms of retention of mechanical properties and heat aging without embrittlement MPR has a somewhat lower performance, when compared to TPV and copolyester [25] with 120°C vs 135°C and 150°C for TPV and copolyester respectively.

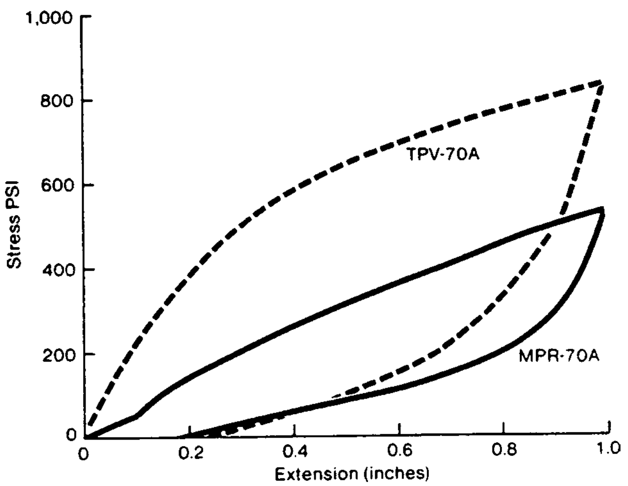

Figure 8.4. Hysteresis curves: comparison of MPR and TPV.

The coefficient of friction of MPR is another attractive property of MPR. For example a compound with a hardness of 70 Shore A has a friction coefficient well over 1.0, comparable to that of most thermoset rubber materials (ranging between 0.4 to over 1.0) (see Table 8.4). This is almost twice that of similar TPVs and styrenic TPEs [26].

8.4.2 Chemical Resistance

Melt-processible rubber has broad fluid resistance for a thermoplastic elastomer. In general, the harder grades swell slightly less than the softer ones, but the differences are small. It exhibits a high resistance to oil, higher than vulcanized polychloroprene (CR) or chlorosulfonated polyethylene (CSM) and comparable to NBR with medium content (33%) of acrylonitrile. It resists petroleum-based oils, greases, fuels, and solvents more than TPV; it exhibits less than half of the volume swelling after a 7-day immersion in hydrocarbon oil at 100°C. Under these conditions, styrenic block copolymer (SBC) would practically dissolve. Melt-processible rubber is also resistant to most mineral acids, bases, to ethylene glycol and other automotive fluids (except proprietary hydraulic fluid Skydrol 500), to silicone grease (unlike TPV), to lithium grease, to insecticides and agricultural sprays, to mineral and vegetable oils, and to fuels (gasoline, diesel, and kerosene). It holds up in ASTM Reference Fuels A and B, has fair resistance to unleaded gasoline and gasohol, but is moderately to severely attacked by ASTM Reference Fuels C and D. It resists alcohols, amines, and paraffinic hydrocarbons; however, it has poor resistance to aromatic hydrocarbons and is severely attacked by ketones, esters, and chlorinated solvents [27].

8.4.3 Weather and Flame Resistance

Melt-processible rubber has a saturated polymeric backbone and therefore it is not attacked by ozone and resists effects of sunlight, UV radiation, and other effects of weather much better then other TPEs (SBC, TPV, TPU, and COPE) as well as many thermoset rubber materials. Black grades of MPR remain unchanged over long-term outdoor exposure without any antidegradants. However, light-color grades need the addition of light stabilizers, such as hindered amine light stabilizers (HALS) and benzotriazole if an enhanced protection against the effects of weather is required.

Table 8.2. Tensile Properties of MPR Compared to Other Materials

Material	Stiffness[a] (MPa)	Yield Strain[b] (%)	Tensile Strength[c] (MPa)
CR Vulcanizate, 70 Shore A	10	>100	10
MPR, 70 Shore A	10	>100	10
TPV, 70 Shore A	40	35	12
Copolyester, 55 Shore D	200	10	35
Nylon	1200	3	80

Notes:
[a] Initial slope of the stress–strain curve.
[b] Elongation (%) at which the material exhibits plastic yielding.
[c] Stress at break.
Source: Reference [25].

Table 8.3. Compression Set and Creep of MPR Compared to Other Elastomers

Elastomer	Compression Set[a] (%)	Creep in Compression[b] (%)	Creep in Tension[c] (%)	Stress Relaxation[d] (%)
MPR 1	78	31	—	21
MPR2	—	—	40	—
EPDM Rubber	79	18	—	25
COPE	91	9	—	19
S-EB-S	—	—	90	—
NBR	46	18	30	15
TPV	68	50	170	30
TPU	100	26	—	30

Notes:
[a] 25% compression, constant strain, 1,000 hr at 212°F.
[b] 25% compression, constant load, 1,000 hr at RT.
[c] 10% elongation, constant load, 1,000 hr at RT.
[d] 15% compression, 1,000 hr at RT.
Source: Reference [24].

Because most grades contain 9–20% by weight of chlorine, they are flame resistant even as sold, several of them even having UL-94 HB (horizontal burning) rating [28]. For the higher flame resistance rating, UL-94 V-0, (vertical burning) a flame retardant such as antimony trioxide must be added.

8.4.4 Electrical Properties

Melt-processible rubber grades are suitable for low voltage applications (≥600 V) only [29] but their major benefit is the ability to dissipate static charge already as sold. Some comparable data are in Table 8.5 [30]. This feature can be further enhanced by the addition of conductive fillers to obtain semi-conductive materials.

8.4.5 Grades of MPR

Because of its many true properties of rubber MPR is unique in that it can be processed in both plastic and certain modified rubber equipment. Since its market introduction in 1986 a multitude of products with specific processing behavior, physical and mechanical properties (mainly hardness), and colors have been available. Complete listing is in reference [31] and Appendix 5.

Extrusion/Calendering Grades produce relatively viscous melts as shown in Fig. 8.5 and are well suited for extrusion, extrusion blow molding, and calendering. Since all grades of MPR are compatible with chlorinated plastics they form completely fused extrudate when coextruded with rigid or semi-rigid

Table 8.4. Coefficient of Friction of Different Elastomeric Materials

Material	Dry			Wet		
	Steel	Glass	Lucite®	Steel	Glass	Lucite®
EPDM Rubber	3.1	3.5	3.9	2.2	1.0	2.2
CR (Polychloroprene)	2.2	1.4	3.8	1.3	1.3	1.0
MPR, 60 Shore A	2.6	2.6	1.8	1.4	0.4	1.5
MPR, 70 Shore A	2.3	2.8	2.7	1.2	0.5	1.5
TPV, 70 Shore A	0.9	0.8	1.2	0.7	0.6	0.8
S-EB-S (Kraton® G)	0.9	1.3	2.2	0.8	0.9	1.0

Note:
ASTM D 1894.
Source: Reference [26].

Table 8.5. Antistatic Properties of Different Materials

Material	Static level (kV)
Rigid PVC	10.0
Typical Commercial Carpet	3.5
Flexible PVC (Shore A 70)	2.8
Carpet for Computer Rooms	2.0
MPR (Alcryn® 30 65NC)	1.0
Alcryn® 2070NC/Flexible PVC (50/50)	1.0
Alcryn® 2070NC	0.7

Note: Test Method 134-1986 (Association of Textile Chemists and Colorists).

Source: Alcryn®, *Tech Notes*, Static (October 1997), Advanced Polymer Alloys, Wilmington, DE.

PVC. In these hard/soft composite profiles MPR provides the flexible rubbery seal on a rigid PVC support.

Injection Molding Grades have enhanced melt flow when compared to the extrusion/calendering grades, low mold shrinkage, and significantly superior dimensional stability. Certain grades with enhanced adhesion properties are designed for overmolding applications. They will bond to rigid plastics such as polycarbonate, acrylonytrile-butadiene styrene (ABS), styrene and acrylonitride (SAN) and acrylate-styrene-acrylonitrile (ASA), polycarbonate/ABS alloys, COPE, TPU, and PVC.

8.4.6 Blends with Other Polymers

MPR is compatible in all proportions with PVC and certain types of COPEs and TPUs. Each of these polymers was found to add a specific benefit [32]:

- PVC lowers cost and improves tear resistance
- COPE improves compression set, tear resistance, and low temperature properties
- TPU improves toughness, abrasion, and oil resistance.

Mixtures of these components yield property combinations not available in any single component of the mixture, for example, the property enhancement of flexible PVC by the addition of MPR and COPE. One improvement is a greater resistance of plasticizer extraction by dry cleaning solvent (perchloroethylene); another one is an improvement of the resistance to stiffening animal and vegetable fats, which often occurs in food processing applications. These improvements are achieved without sacrificing the good resistance to detergents, which is also required in such environments. Flexural resistance, the key mechanical property, is improved by a factor of five.

Various acrylic processing aids, used alone or in combination with each other increase the melt flow of high-viscosity MPRs, in some cases up to 100-fold. Some of them do not significantly change the key physical properties while others increase hardness and stiffness along with the melt flow [33].

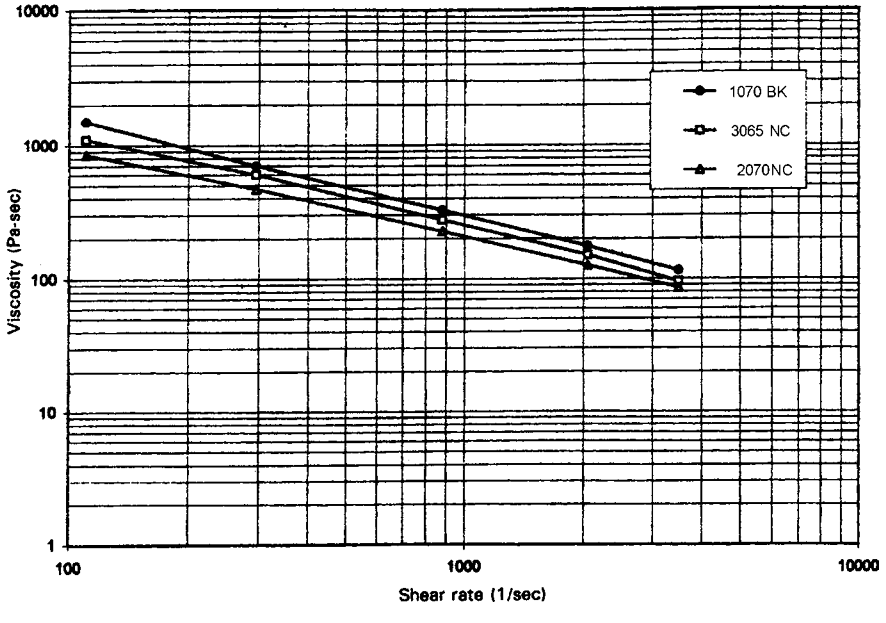

Figure 8.5. Viscosity at 190°C as a function of shear rate for three extrusion/calendering grades of MPR.

8.4.7 Processing

The rheology of MPR differs from that of conventional thermoplastic materials because of its partially cross-linked structure. Since MPR is essentially amorphous, there is no significant drop in viscosity to the hard-segment glass transition temperature or crystalline melt point. The melt flow can be only induced by application of a shearing force in combination with elevated temperature. The viscosity is very high and is more sensitive to shear rate than to temperature. *Pseudoplastic flow* (shear thinning) (see Fig. 8.6) is the main mechanism by which different shapes are produced from MPR. The shear thinning effect is clearly evident on the viscosities of four different grades of MPR at 340°F (171°C) (see Fig. 8.7).

8.4.7.1 Injection Molding

During injection, high shear must be maintained to keep the melt viscosity low through the use of rapid first stage injection rates (1–3 in.^{3}/s) and small diameter nozzles, runner system, and gates. Such rapid fills (0.5–2 s) require generous mold venting to avoid burning and facilitate complete mold fill. MPR does not exhibit discontinuous volume change due to crystallization upon cooling. Molded parts rapidly develop strength in the mold and therefore can be demolded relatively hot. The combination of rapid injection and demolding hot mean short overall molding cycles and very high productivity.

Melt-processible rubber can be processed on reciprocating screw machines. General purpose, gradual transition screws with compression ratios 2.5:1 to 3.5:1 and with *L*/*D* ratios >20:1 are usually suitable for molding MPR [34]. Flow passages through the machine have to be carefully streamlined to eliminate melt stagnation and subsequent degradation.

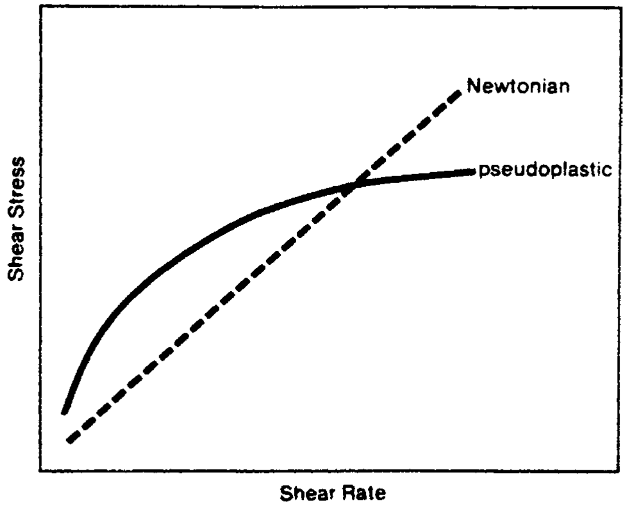

Figure 8.6. Flow curves for Newtonian and pseudoplastic materials.

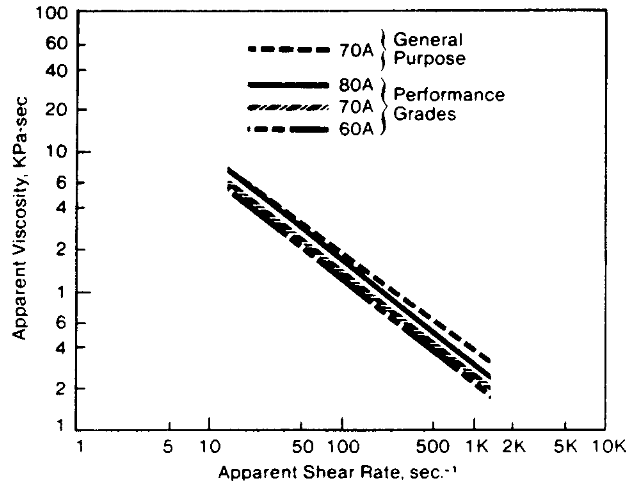

Figure 8.7. Viscosity vs. shear rate at 171°C (340°F).

Melt-processible rubber degrades if overheated to temperatures 400°F (204°C) or higher or if held at processing temperatures for more than 30 min. The onset of degradation is around 385°F (196°C) and during the degradation gaseous products, including HCl evolve. Therefore, the use of corrosion resistant materials for the screw, the barrel liners, and nickel-plated steel for molds are recommended for maximizing the equipment life.

The rheology of MPR makes it suited to the high shear of injection molding. A combination of barrel heat and shear is necessary to attain a properly fluxed, uniform melt. The melt temperature measured at the nozzle should be maintained between 340°F and 375°F (171°C and 191°C). Typical temperature settings are in Table 8.6 and operating conditions in Table 8.7 [34].

If the machine is shut down for more than 1 hour and the temperature is above 350°F (177°C) purging with low viscosity, low density polyethylene is recommended.

8.4.7.2 Extrusion

As pointed out in the previous section, the polymer is brought to the melt stage more by shear than by heat. Heat generated by the shearing of the melt has to be removed to avoid degradation of the material. Therefore it is necessary to provide an

Table 8.6. Temperature Settings for Injection Molding of MPR (Reciprocating Screw Injection Molding Machine)

Barrel, °F (°C)	
Rear	340–350 (171–177)
Front	340–350 (171–177)
Nozzle, °F (°C)	340–350 (171–177)
Mold, °F (°C)	70–120 (21–49)

Source: Reference [34].

Table 8.7. Operating Conditions for Injection Molding of MPR (Molding Stages), Reciprocating Screw Machine

Injection Speed (fill rate)	1–3 cu.in./s (16–49 ml/s)
Injection Pressure	700–1200 psi (4.83–8.27 MPa)
Injection Time (first stage boost)	0.5–2 s
Second Stage Pressure	300–800 psi (2.07–5.52 MPa)
Second Stage Time	3–10 s
Cooling Time	2–20 sec
Screw Speed	50–100 rpm
Back Pressure	30–80 psi (0.2–0.6 MPa)
Shot Size	Control to fill mold

Source: Reference [34].

efficient cooling to avoid overheating the melt. On the other hand, the temperature profile has to be designed so as to give maximum pressure at the die and to assure an equal flow rate across all sections.

Melt-processible rubber can be extruded on extruders commonly used for the processing of PVC or polyolefins, with typical L/D ratios between 20:1 to 24:1 (with 24:1 preferred) and compression ratios between 2.5:1 and 3.5:1. For most extrusions, a simple three-zone screw, having a transition (compression) zone at least one third of the screw length is recommended [35]. As in extrusion, machine parts coming in contact with the melt should be corrosion resistant. Efficient cooling to remove the shear heat is essential for high productivity and to prevent degradation. Some general extruder configurations with examples of typical temperature guidelines are in Table 8.8 [35].

Overhead and tangential-type feed throats used usually with single-screw extruders can be used with MPR. Water cooling of the throat is recommended to prevent excessive heating of the resin as it is entering the screw and to serve as protection of the drive bearings. Hopper drying is not usually necessary for MPR [35]. Melt temperature depends on the grade used and should be 180 ± 10°C (356 ± 18°F) for general purpose grades and 185 ± 5°C (365 ± 9°F) for injection molding grades [35].

8.4.7.3 Extrusion Blow Molding

Having sufficiently high melt strength, MPR can be fabricated into hollow articles by extrusion blow molding. Continuous extrusion, accumulator head, and reciprocating screw systems can be used with proper residence times and temperature control [36]. For the extrusion of MPR, continuous extrusion systems are preferred; second choice is the accumulator head system and third choice is the ram-accumulator system. Essentially, the same guidelines, such as basic screw design, avoiding polymer degradation and the use of corrosion resistant machine parts discussed earlier apply.

The melt temperature measured at the parison die or at the exit to the accumulator head should be in the range 160–185°C (320–365°F). Barrel temperatures are set so that the feed zone is set to a higher

Table 8.8. Temperature Profile for the Extrusion of General Purpose MPR Grades

Length/Diameter	Compression Ratio	Type of Profile	Feed	Transition/Meter	Adapter/Die
Long	High	Increasing	300°F (150°C)	320–340°F (160–171°C)	325°F (163°C)
		Flat	325°F (163°C)	325°F (163°C)	325°F (163°C)
Short	Low	Reverse	350°F (177°C)	340–320°F (171–160°C)	325°F (163°C)

Note: Temperature should be increased 18–27°F (10–15°C) for extrusion injection molding grades.
Source: Reference [35].

temperature than the extruder head). Moderate pressures, that is, between 200 and 700 kPa gauge (30–100 psig) are typical and depend on the part size and parison wall thickness [36].

8.4.7.4 Calendering

Unsupported sheets, coated substrates, such as fabrics can be produced on three- or four-roll calenders commonly used for calendering plastics. The calender roll temperatures for calendering MPR need to be controlled in the range between 160°C and 185°C (320°F and 365°F). The stock is usually fluxed in batch or continuous mixers or a hot roll mill and then fed into the calender as a metered strip or a "pig" from a roll mill. It must be well fluxed and maintained at temperatures between 165°C and 185°C (320°C and 365°F). The top rolls of the calender should be set to the same temperature in the range 160–185°C and the temperature of the lower rolls should be high enough to maintain tracking but low enough to prevent sticking to the rolls (as low as 140°C or 285°F). Embossing is easily accomplished by using an embossing roll while the stock is still warm. Uneven speed between adjacent rolls prevents the formation of blisters in the calendered sheet. A small uniform bank must be maintained at the roll nip. A small, pencil-thin bank between the second and third rolls will prevent blisters or blemishes in the sheet. The usual speeds between adjacent rolls are frequently uneven with speed ratio 1.05:1 to prevent blisters.

In most cases the MPR stock has enough internal lubrication to be released from the calender rolls. Only under extreme conditions, such as very thin gauges, high calendering speeds and high roll temperatures, it may be necessary to add internal lubricant (such as oxidized polyethylene waxes) to avoid sticking of the stock to the rolls. The internal lubricants have to be incorporated during the pellet fluxing process [37].

8.4.7.5 Compression Molding

Compression molding is a less efficient way to produce molding parts but is useful for preparing test plaques, prototypes, and unusual parts. The *single press* method is rather cumbersome because it requires that the mold with the part requires cooling down to about 120°F (50°C) before the part can be removed from the mold. *Two-press* method (one heated, one cold) is more efficient, because the hot mold is transferred into the second press for cooling down to the demolding temperature [38].

The compression mold procedure consists of the following steps:

1. Heating the press and the empty mold to 350°F (177°C).
2. Loading the mold with a sufficient amount of milled preform to ensure complete fill and some flash (excess stock).
3. Dropping platen until it touches the preform and heating the filled mold for 1–2 min or 5 min for thicker parts.
4. Closing the press and bringing it to full pressure and holding for at least one minute; then cool at full pressure to about 120°F (50°C) before releasing pressure.
5. Removing from press and demolding parts.

Note: With two presses, the mold is moved from the hot to the cold press, the pressure is raised quickly to maximum and then held until cooled to 120°F (50°C). Then the part is demolded (see Step 5 above).

8.4.7.6 Bonding and Welding

Although MPRs can be joined to itself or other materials by friction or snap fit or mechanical fasteners, other methods of assembly may give better joints often at a lower cost. Various *adhesive systems* provide satisfactory bonds to thermoset rubber materials, metals, plastics, textiles, leather, wood, etc. The disadvantages of adhesive bonding include handling hazards and difficulties, material costs, environmental considerations (the use of solvents or toxic substances), and processing speed. *Direct overmolding* is used where possible, because it is rather simple and fast and provides very good bonds to a very large number of substrates. It is feasible only if the part is made in large series because a mold, often very costly, is required. In many other instances, *welding* is used as it is simple, fast, and reliable and in most cases gives excellent bonds. The welding methods applicable to MPR include ultrasonic welding, external heating by hot plate or gas, radio frequency, and electromagnetic induction [39].

8.4.7.6.1 Bonding MPR to Itself

Bonding at *room temperature*, requires an adhesive. There are two classes of adhesives; one includes adhesives commonly used for rigid and flexible PVC (e.g., Hercules Plastic Pipe Cement or Waxman Plumbcraft Cement). The second class includes urethane adhesives, such as Lord 7540 A/B (Lord Corporation, Erie, PA). This system is a two-part adhesive and requires that the joints be first coated by a primer (e.g., Chemlock® 480).

Adhesive bonding at *elevated temperatures* is used mainly for laminations. For that purpose, specialty adhesives such as a combination of Chemlock® 480 with Chemlock® Curative 44 (Lord Corporation, Erie, PA) are used. Best results are obtained at laminating temperatures above 200°F (93°C) and pressures at least 100 psi (690 kPa) with dwell time minimum 10 min.

Melt bonding techniques are very common in bonding MPR to itself because of its thermoplastic nature. Butt welding on hot knife is done mainly for extruded shapes at temperatures in the range from 500°F to 600°F (260°C to 315°C). Heating the surfaces to be joined with a hot gun is another method to obtain good bonds but requires precise technique.

Ultrasonic welding has been successful in sections up to 40 mils (1 mm) thick. *Dielectric (RF) welding* is accomplished at a frequency of 27.17 MHz [38].

8.4.7.6.2 Bonding MPR to Other Materials

Bonding to *thermoset rubber* is accomplished in a similar way as bonding to itself, namely by using, for example, the combination of Chemlock® 480 primer and Lord® 7540 adhesive for room temperature bonding and Chemlock® 480 and Chemlock® Curative 44, for example, for bonding at temperatures above 200°F (93°C) as described in the previous section.

Bonding to *metals* requires that the metal surface be prepared by making it rough (blasting with sand, grit, etc., or by chemical etching). In the next step, primer and bonding adhesive are applied to the surface to the metal. The bonding can be accomplished at room temperature by a proper adhesive system (see previous section) or by using the pretreated metal as an insert, placing it into a mold and injecting MPR (melt temperature 340–360°F, or 170–180°C) to fabricate the part.

Bonding of MPR to other materials, such as different plastics, textile, wood, and leather requires specific adhesive systems and the applicable procedures are covered in detail in [38].

8.5 Thermoplastic Fluorocarbon Elastomer

There is one commercial product, which is essentially a thermoplastic fluorocarbon elastomer. Its structure is that of a block copolymer with hard segment consisting of a fluororesin and a soft segment formed by a fluoroelastomers (see Fig. 8.8).

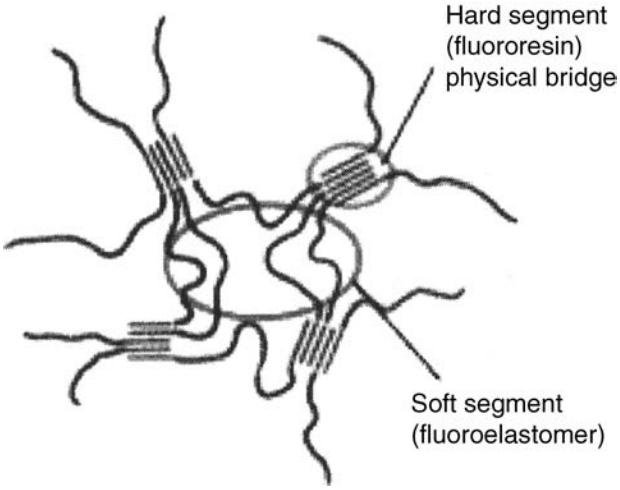

Figure 8.8. Schematic drawing of the structure of a thermoplastic fluorocarbon elastomer (Courtesy Daikin (www.daikin.com)).

Table 8.9. Typical Properties of Thermoplastic Fluorocarbon Elastomer

Property	Value
Specific Gravity	1.88
Hardness, JIS A	67–73
Melting Point, °C (°F)	220 (428)
Pyrolysis Initiation Temperature, °C (°F)	380 (716)
Tensile Strength, MPa (psi)	17 (2,470)
Elongation at Break, %	600
Tear Strength, kN/m (pli)	29 (154)
Rebound Resilience (%)	10
Coefficient of Friction	0.6
Taber Abrasion (Wheel CS-17, 1,000 g), mg/1,000 cycles	2
Low Temperature Torsion Test, Gehman T50, °C	−9
Compression Set (24 hr at 50°C (122°F)), %	11
Volume Resistivity, ohm-cm	5×10^{13}
Dielectric Breakdown Strength (kV/mm)	14
Dielectric Constant (23°C, 10^3 Hz)	6.6

Source: Reference [40].

Currently, there are two grades on the market that claim good transparency, low extractables, and an excellent chemical resistance. Typical properties are listed in Table 8.9.

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9 Thermoplastic Polyurethane Elastomers

9.1 Introduction

Polyurethanes represent a large segment of polymers used in high-performance materials, such as films, coatings, adhesives, fibers, and elastomers. They are formed by a simple polyaddition reaction, but since many different compounds can be utilized to produce polyurethanes, there is a large number of possible final products. This also opens up the possibility of producing materials with tailormade properties.

Thermoplastic polyurethane elastomers (TPUs) were the first homogeneous elastomeric materials that could be processed by methods commonly used for the processing of thermoplastics. Their growth contributes to the overall rapid growth of thermoplastic elastomers [8].

The credit for the discovery of polyurethanes belongs to the group led by Otto Bayer at the I.G. Farbenindustrie in Germany (now known as Bayer A.G.). The original work concentrated on the duplication or improvement of synthetic polyamide fibers [1]. The first patent issued to this group was in 1937 [2]. Subsequent patents covering elastomeric properties of polyurethanes were issued to DuPont [3] and ICI [4]. The first polyurethane elastomer dubbed "I-Rubber" had very poor properties [1]. Additional development work led to products that had considerably improved properties. The commercial products developed during that period were Vulkollan® (Bayer), Chemigum SL® (Goodyear Tire and Rubber Co.), and Adiprene® (DuPont) [5, 6]. The early polyurethane elastomers consisted of three basic components [1]:

- a polyester or polyether high-molecular diol
- a chain extender (water, low-molecular weight diol)
- a bulky diisocyanate, such as naphthalene-1,5-diisocyanate (NDI).

These polyurethane elastomers were not true thermoplastics, because their melting temperatures were higher than the decomposition temperature of the urethane linkages [1]. Major breakthrough was achieved when NDI in the above systems was replaced by diphenylmethane-4, 4-diisocyanate (MDI). The first records of true TPUs are from 1958 [7]. Today, it is well established that the elastomeric properties of TPUs are the result of a *multiblock structure of phase-separated systems* [1].

The *hard segment* is formed by the addition of the chain extender, such as butadiene diol to the isocyanate (in most cases MDI). The *soft segment* consists of the flexible polyether or polyester chains that connect the two hard segments (see Fig. 9.1).

The two segments are incompatible at room temperature, which results in microphase separation. The driving force for the separation is to a degree the development of crystallinity in the hard segments. Additional factors are the difference in melting points and polarity of the two segments. The hard segments have a much higher melting point and polarity than the much less polar and low-melting soft segments.

When the material is heated above the melting temperature of the hard segments, the polymer becomes a homogeneous viscous melt that can be processed by usual methods used for plastics, such as extrusion, injection molding, and blow molding. Cooling of the melt results again in phase separation due to the recovery of hard and soft segments and the polymer develops its elastic properties.

The soft segments form an elastomeric matrix responsible for most part for the elastic properties of TPUs, and the hard segments act as multifunctional tie points, functioning as both cross-links and reinforcing fillers. These cross-links can be removed by heat or by the use of solvents. The TPU network can be recovered by cooling, as mentioned earlier, or by the evaporation of the solvent. In order to obtain thermoplasticity, the average functionalities of the starting materials should be close to 2.00, that is, each prepolymer and monomer

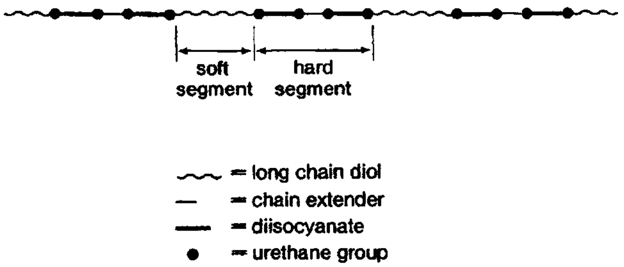


Figure 9.1. Schematic representation of TPU composed from diisocyanate, long chain diol, and chain extender.

unit should have two terminal groups. This ensures the formation of high-molecular weight linear chains with no or only few branch points [9–11].

9.2 Synthesis of TPUs

The basic reaction of the polyurethane chemistry is that between an isocyanate and a compound containing a hydroxyl:

$$\underset{\text{Isocyanate}}{R\text{–}N{=}C{=}O} + \underset{\text{Alcohol}}{R'\text{–}OH} \rightleftharpoons \underset{\text{Ester of a carbamic acid}}{R\text{–}NH\text{–}CO\text{–}OR'}$$

The resulting compound is an ester of a carbamic acid. The trivial name *urethane*, which is used for the compound ethyl carbamate, gave the polyurethane chemistry its name; polyisocyanates and polyols form polyurethanes [12]. There are many other possible reactions of the isocyanate group, the most common are those with compounds containing groups with active hydrogen, such as $-NH_2$, $-NH-$, $-COOH$, and $-CONH_2$, and of course, with water.

The reactions that are of importance for the preparation of thermoplastic polyurethanes are those between diisocyanates and a variety of compounds containing terminal hydroxyl groups, such as diols. Clearly, isocyanates and diols form linear polyurethanes.

In general, TPUs are prepared from long-chain polyols with the average molecular weight in the range of 600 to 4,000, chain extenders with molecular weights in the range 61–400, and a polyisocyanate. The choice of the components of the reaction mixture and their ratio determines the properties of the final product, which may range from soft and flexible to hard, high-modulus material.

9.2.1 Raw Materials for TPUs

9.2.1.1 Raw Materials for Soft Segments

The soft segments of a TPU are long and flexible and control the low-temperature properties, the resistance to solvents, and the resistance to weather. The main raw materials for soft segments are hydroxyl-terminated polyesters and polyethers. Generally, more polyesters than polyethers are used for the polyol component [13]. Typical examples of polyesters are adipates, polycaprolactones, and aliphatic polycarbonates [14]. Typical examples of polyethers used on a large scale are poly(oxypropylene) diols and the poly (oxytetramethylene) diols. Mixtures of polyethers and polyesters are sometimes used and yield a very useful combination of properties at an attractive cost [15, 16]. General trends in properties produced by the commonly used polyols are shown in Table 9.1.

9.2.1.2 Raw Materials for Hard Segments

As pointed out earlier, the raw materials used for hard segments are isocyanates and chain extenders.

Table 9.1. Important Polyols[a] and Corresponding TPUs[b]

Polyol Nomenclature	Polyols		Elastomers	
	T_e (°C)	T_m (°C)	T_e (°C)	Hydrolytic Stability
Poly(ethylene adipate) glycol	−46	52	−25	Fair
Poly(butylene-1,4 adipate) glycol	−71	56	−40	Good
Poly(ethylene butylene-1,4 adipate) glycol	−60	17	−30	Fair/good
Poly(hexamethylene-2,2 dimethylpropylene adipate) glycol	−57	27	−30	Good
Polycaprolactone glycol	−72	59	−40	Good
Poly(diethylene glycol adipate) glycol	−53	/	−30	Poor
Poly(hexadiol-1,6 carbonate) diol	−62	49	−30	Very good
Poly(oxytetramethylene) glycol	−100	32	−80	Very good

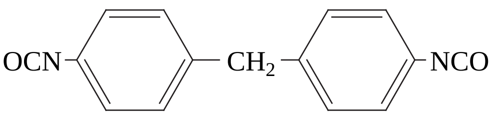
Notes:

[a] Molecular weight 2,000.

[b] Hardness approx. 85 Shore A.

T_e: Lower end of glass transition range.

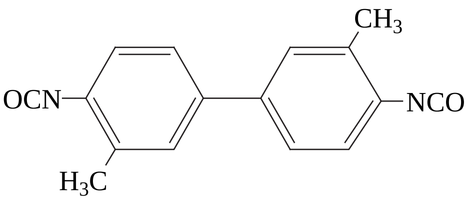
From the commercially available polyisocyanates, only a very few are being used for the manufacture of thermoplastic polyurethanes [17]. The most widely used is MDI:



Other isocyanates used for TPUs are hexamethylene diisocyanate (HDI):

$$OCN-(CH_2)_6-NCO$$

and 3,3′-Dimethyl-4,4′-biphenyl diisocyanate (TODI) [18]:



The most widely used chain extenders are linear low-molecular weight diols, such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and hydroquinone bis(2-hydroxyethyl) ether, and these are the most suitable for TPUs.

9.2.1.3 Other Raw Materials

Other materials used widely in the thermoplastic polyurethanes are as follows:

- *Mold release agents* are useful for fast and economical cycle times. These are either derivatives of fatty acids, or silicones, or certain fluoroplastics. They are added in amounts 0.1–0.2% by weight.
- *Antidegradants*, such as aromatic carbodiimides, are added to polyester-based TPUs to reduce their hydrolytic degradation in amounts typically 1–2% by weight. Sterically hindered phenols and certain amines reduce the degradation by heat and oxidation.
- *UV absorbers*, such as benzophenones or benzotriazols combined with sterically hindered amines (HALS) stabilize the TPU materials against discoloration by ultraviolet (UV) light [19].
- *Mineral fillers,* such as calcium carbonate, talc, and silica fillers, are added for better release in molding and in film production. They often act as nucleating agents (to promote crystallization) or produce a rough surface.
- *Reinforcing fillers* (mica, glass fibers, organic fibers) are used to reinforce TPU materials.
- *Lubricants,* such as graphite, molybdenum sulfide, polytetrafluoroethylene (PTFE) micropowders, or silicone oil, are used to reduce the coefficient of friction.
- *Plasticizers* are used to produce soft grades of thermoplastic polyurethanes and are added in amounts up to 30% by weight [20].

The isocyanate-to-hydroxyl ratio is critical to the molecular weight control of the TPU products. The initial molecular weights of the products decrease with the increase or decrease of NCO/OH ratios from the equivalence point, that is, where NCO/OH = 1 (see Fig. 9.2). However, the molecular weights of the products synthesized above the equivalence point ultimately will increase because of the reaction of excess isocyanate with moisture, urethane, and urea groups, to give urea, allophanate, and biuret, respectively.

The reaction components are mixed and heated to temperatures above 80°C (176°F). To achieve optimum results, the ratio of isocyanate groups to the sum of the groups reacting with them should be close to 1.0. If this ratio is lower than 0.96, polymers with insufficiently low molecular weight are obtained, and if it is higher than 1.1, cross-linking

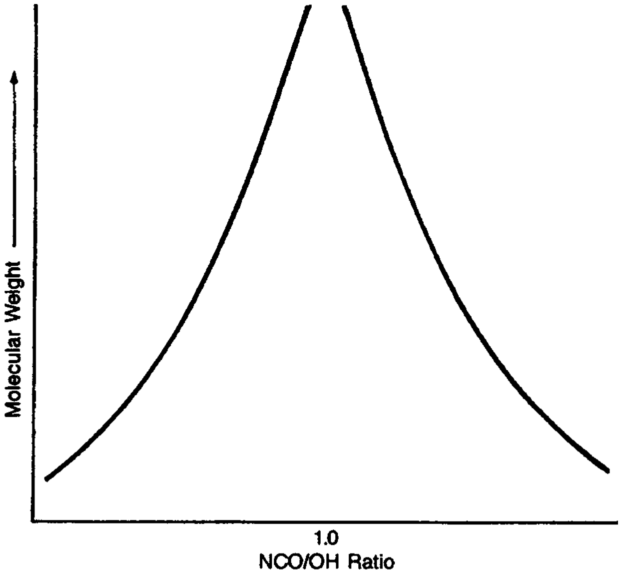


Figure 9.2. The relationship of the initial molecular weight of TPU and the NCO/OH ratio (Courtesy Hanser Publishers).

and other reactions occur (see above), which yield products that are difficult to process by thermoplastic processing methods. An average molecular weight (M_n) of 40,000 is sufficient for the development of satisfactory properties and this can be achieved if the ratio of the reacting groups is 0.98 and higher.

There are several ways to carry out the reaction. In the *one-shot method,* all the reactants are mixed together. In the *prepolymer method*, the isocyanate is first reacted with the polyol. This produces a prepolymer that is then reacted with the chain extender. The polymer can be produced in a batch process [21] or continuously in a mixing chamber or a reaction extruder [22–24].

For large-scale industrial production, two methods are commonly used, namely the *belt process* and the *reaction extruder process*. In the belt process all ingredients are mixed together and poured onto a belt. The product solidifies on the surface of the belt forming a slab. The slab is then converted into granules. The granules may be used as such but they are often fed into an extruder and extruded into pellets that are more uniform in size. In the reaction extruder process, the reaction is almost complete at the end of the extruder and the product is immediately extruded into pellets.

The heat history during the production of TPUs is very important because the phase separation of the soft and hard segments is temperature-dependent. Another factor is shear conditions during the build-up of the molecular weight. In the belt process, the reacting melt does not experience any shear after leaving the mixing chamber, whereas during reactive extrusion the melt is subjected to a significant shearing stress all the time. Typically, TPUs produced by reactive extrusion show a less pronounced phase separation resulting in lower crystallinity [25].

Since the phase separation determines essentially the properties of the TPU, it is possible that even when starting from the same reaction mixture, the physical properties of the resulting polymers will be very different [26–33].

9.3 Morphology

The morphology of the multiphase system is an important factor in determining the final properties of the polymer. In general, desired properties of a material can be obtained by controlled variation of the morphology. For that reason, a very good knowledge of the morphology is essential for the understanding of structure–property relationship. In the case of urethane block copolymers this became a formidable challenge because of complications due to physical phenomena such as crystallization, phase mixing, hydrogen bonding in both segments, and dependence of properties on thermal history. In general, a higher degree of phase separation is expected for a copolymer system where one component is crystallizable. In polyurethanes, both the soft and hard phases may be amorphous or partially crystalline [34].

The chemical composition and the molecular weight of the long-chain diols have a major effect onthe extent of phase separation of the TPU. Because of stronger hydrogen bonding, the phase mixing of a polyester-based TPU is generally greater than that of a polyether-based TPU. The phase separation is determined by the molecular weight of the long-chain diols; the higher their molecular weight, the better the phase separation will be [35].

9.3.1 Morphology of Hard Segments

Extensive studies were performed to elucidate the nature of the hard-segment domains, using wide-angle X-ray scattering [36], small-angle X-ray scattering (SAXS) [37–42] and X-ray diffraction [43, 44]. Hard segments formed by the reaction of linear glycols and polyisocyanate (MDI) would be expected to be crystalline. However, under normal conditions, crystallinity appears to be inhibited [36]. The ordered state of the hard segments has been referred to as *paracrystalline* [37] and a suitable heat treatment was reported to transform the structure from paracrystalline to crystalline [38]. Relatively high temperatures and long annealing times (190°C, 12 hr) are reportedly required to produce a significant hard-segment crystallinity [45].

9.4 Thermal Transitions

Thermal transitions, such as melting, glass transitions, and phase segregation have been studied by several investigators. A study analyzed the thermal response of a TPU based on a polyesterdiol, butanediol (BDO), and MDI with respect to engineering properties using differential scanning calorimetry (DSC) [46]. With increasing hard segment content, the glass transition is broadened and shifted toward higher temperatures. The observed glass transition shift may be explained by an increasing amount of hard segments that are "dissolved" in the soft matrix. It was postulated that a concentration gradient of hard segments exists near the phase interface.

The kinetics of phase separation has been studied and reported in [47, 48]. Polyester TPUs were quickly heated and then rapidly quenched to room temperature. Changes in phase separation were monitored by SAXS and DSC as a function of time. It was shown that it took as much as several days to regain equilibrium as a result of kinetic and viscous effects.

Interphase mixing phenomena, as studied by thermal analysis and SAXS have been explained in terms of the hydrogen-bonding ability of soft segments [49–51]. Other, more involved studies on specific systems employing DSC [52, 53], thermomechanical studies, DSC, X-ray scattering, and infrared analysis [53–57] were performed to elucidate their structural organization and thermal transitions. A similar study is described in [58].

In general, it can be concluded that the glass transition temperature of the soft segments is a sensitive measure of the degree of phase separation. As the hardness of the TPU is increased by the increasing proportion of hard segments, the extent of phase mixing also increases resulting in a decrease of low temperature flexibility. This can be offset by incorporating soft segments with a higher molecular weight or by the use of preextended polyols [59].

9.5 Properties

As pointed out earlier, TPUs were the first polymeric materials to combine both rubber elasticity and thermoplastic characteristics. The proportion of hard segments (formed by the diisocyanate and the short chain diol) is the factor determining the majority of properties of the resulting material, such as hardness, modulus, tear strength, and upper use temperature. The proportion of soft segments determines the elastic and low-temperature properties. Typically, the molar ratios polyol:chain extender:diisocyanate range from 1:0.5:1.5 for soft grades (Shore A hardness about 60) up to 1:20:21 for harder grades (Shore D values higher than 70) without the use of plasticizers or reinforcing agents. With Young moduli values ranging from 5 to 2,000 MPa [60, 61], TPUs are virtually bridging the gap between elastomers and plastics (see Fig. 9.3). The stiffness of a given TPUs can further be increased by inorganic and organic fillers, especially glass fibers [62]. The exceptional flexibility of the chemistry used in the synthesis of TPUs accounts for the numerous products available commercially.

9.5.1 Mechanical Properties

Thermoplastic polyurethane elastomers exhibit high tensile strength and ultimate elongation (see Fig. 9.4). Additional valuable attributes are an exceptional resistance to tear propagation

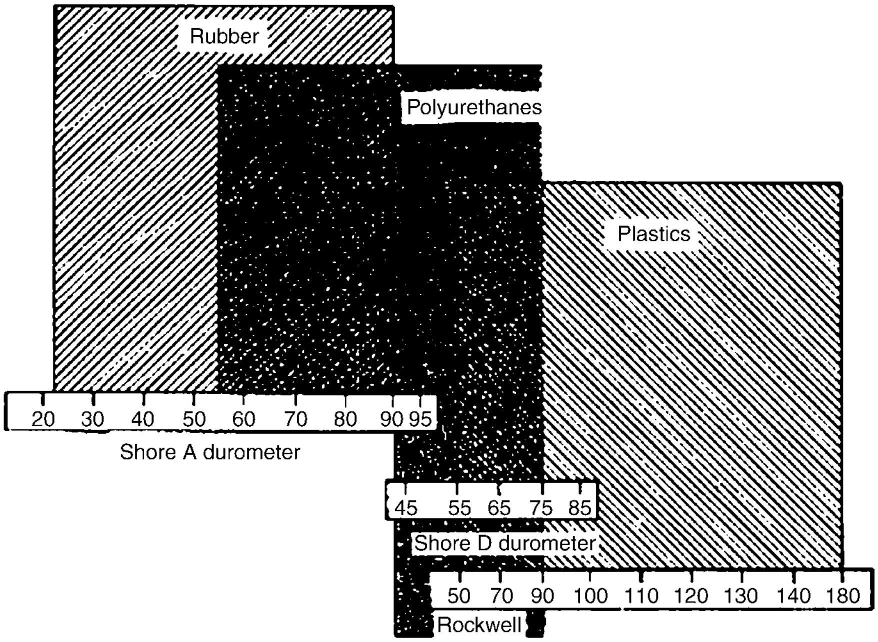


Figure 9.3. TPUs bridging the gap between elastomers and plastics.

and abrasion. The properties are dependent on temperature (see Figs 9.5a and 9.5b) and on hardness (compare Figs 9.5 and 9.6). Most commercial TPUs are ester based and the mechanical properties of these grades are superior to those of TPUs made from the more expensive poly(oxytetramethylene) diol. These polyether-based materials are well suited for situations where high resistance against hydrolysis or microbial deterioration and/or improved low-temperature flexibility is required [63]. Poly(oxypropylene) diols are used mainly in mixture with polyester glycols and such hybrid products are a good compromise, having properties and cost between those of ether- and ester-based TPUs. Further advantages are often gained when preparing ether–ester TPUs by a special synthesis procedure [64].

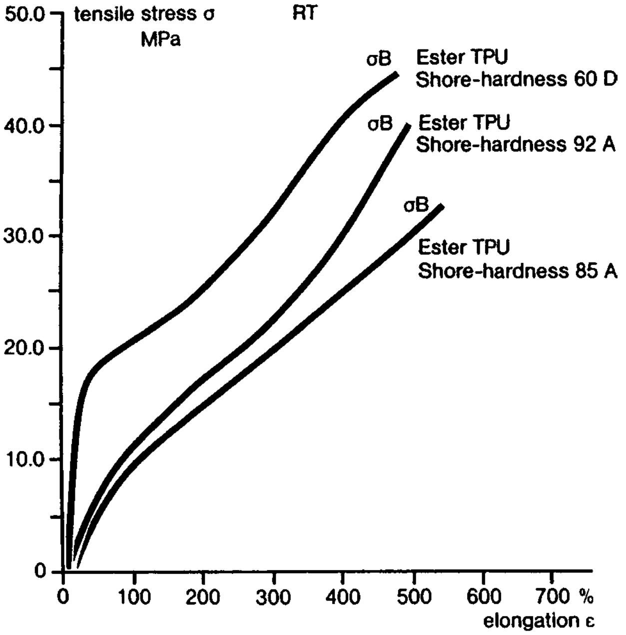


Figure 9.4. Stress–strain curves of three TPUs with different hardness values.

The properties of TPUs are strongly affected by domain morphology, as pointed out earlier. Phase mixing takes place during the heat processing or treatment of the TPU, while phase separation occurs upon rapid cooling. Several studies showed that the mechanical properties of TPUs are strongly related to the time-dependent formation of domain morphology [65–68]. Therefore, in order to obtain optimum properties, postcuring is recommended after thermal formation. Postcuring conditions vary with the type of TPU material. Often it is sufficient to store it at ambient temperature for 2–3 weeks. If it is necessary to attain ultimate physical properties on TPU parts immediately after fabrication, a postcure

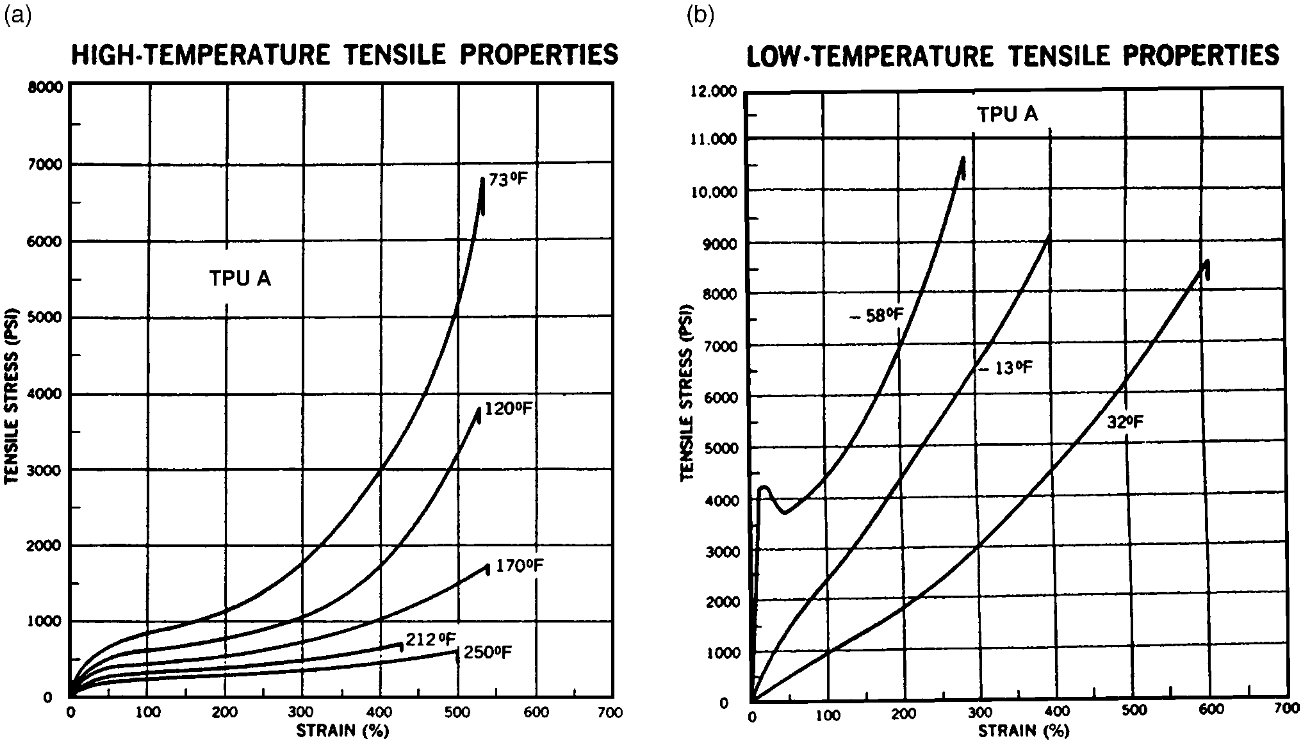


Figure 9.5. (a) Effect of high temperatures on the stress-strain curve of TPU A (hardness 85 Shore A). (b) Effect of low temperature on the stress–strain curve of TPU A (hardness 85 Shore A).

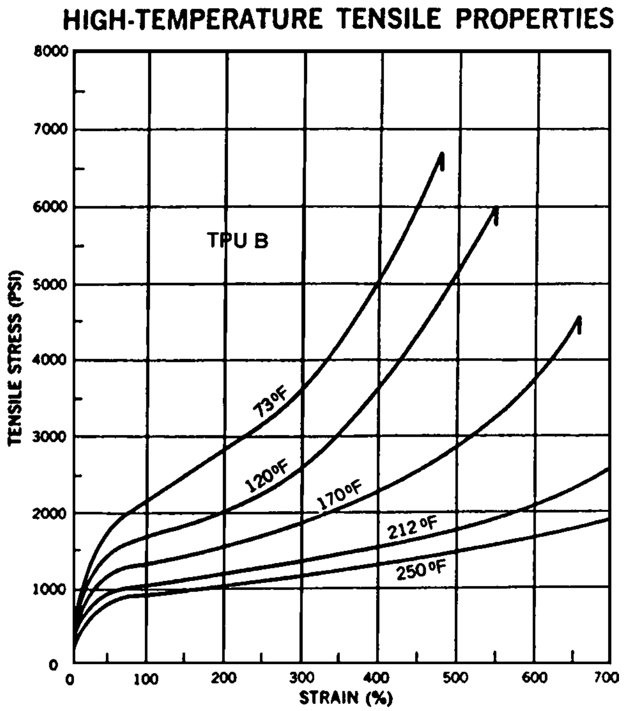


Figure 9.6. Effect of high temperature on the stress–strain curve of a TPU B (hardness 55 Shore D).

in a circulating hot air oven for 8–16 hr at 230°F (110°C) is usually sufficient [69]. Since postcuring is time-consuming and means additional work, most production parts are not subjected to a postcuring cycle. Postcuring is used mainly in cases where improvement of compression set is desired [70].

9.5.1.1 Stress–Strain Properties

Thermoplastic polyurethane elastomers offer high tensile strength and elongation. Depending on their chemical structures and hardness, tensile strength values of TPUs range typically from 25 to 75 MPa (3,600 to 10,000 psi) (see Fig. 9.4). The stress–strain curve of TPU is generally believed to be affected by the hard segment to soft segment ratio, soft segment length, hard segment crystallinity, and susceptibility of the hard segment to reorientation and alignment. Because this reorientation is time dependent, the stress–strain curve is affected by the extension rate [71]. Temperature also affects the stress–strain curve of TPUs as pointed out earlier (see Figs 9.5 and 9.6). This is explained by the finding that the moduli at fixed strain decrease with increasing temperature [71].

9.5.1.2 Compression Set

The compression set is an elastic recovery behavior under a specific loading or a specific deflection at various times and temperatures. The usual method is ASTM D 395, Method B that includes 22-hr loading at a constant deflection of 25%. Typical values for TPUs measured at room temperature range from 10% to 50% depending on the polymer and conditioning cycle [72]. When measured under a 25% deflection at 70°C (158°F) for 22 hours, the values are typically in the range of 60–80% without postcuring and 25–50% with postcuring. Slightly crosslinked TPUs give lower compression set values [73].

9.5.1.3 Hardness

Hardness of a material is its ability to resist deformation, indentation, or scratching. Shore A and Shore D tests (ASTM D2240 or ISO 868) are most commonly used to measure the hardness of TPUs. The softer materials are measured by Shore A, the harder ones by Shore D. Because of their block copolymer nature, TPU with hardness values between Shore 70 A and about Shore 80 D can be obtained by varying the ratios of hard segment to soft segment. The hardness, along with modulus, load-bearing capacity (compressive stress), tear strength, and specific gravity of a TPU normally increases with increasing hard segment content.

9.5.1.4 Stiffness

The stiffness is expressed by the flexural modulus, which is determined during the initial bending of a test specimen. It is obtained from test according to ASTM D 790. Although hardness of a TPU is related to its flexibility, it is not directly indicative of its stiffness.

9.5.1.5 Dynamic Properties

Thermoplastic polyurethane elastomers have higher mechanical damping than most elastomeric materials [74]. The mechanical loss factor, tan δ, the ratio of loss modulus and storage modulus (G''/G'), and its dependence on temperature are shown in Fig. 9.7 for two TPUs with different hardnesses. It is lower in the softer grades at room temperature. The temperature rise is also lower at equivalent deformation. Figure 9.7 also depicts the temperature dependence of the storage (shear) modulus (G').

Since TPU is a poor thermal conductor, the heat resulting from dynamic loading is dissipated slowly. The heat build-up is a function of both frequency and force applied. Therefore, parts, such as solid wheels or rollers made from TPU should not

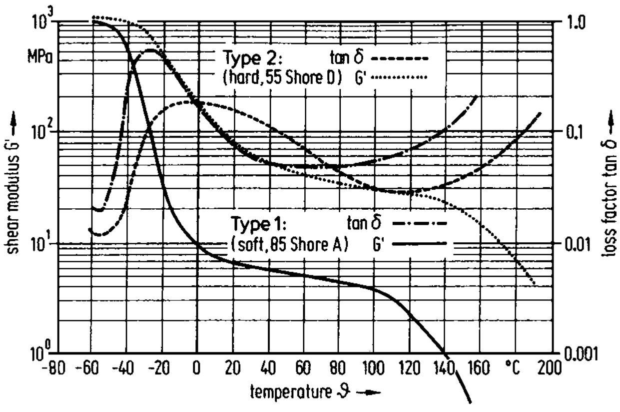


Figure 9.7. Mechanical loss factor (tan δ) and storage (shear) moduli vs. temperature for TPUs of different hardnesses (Courtesy Hanser Publishers).

run at high speeds or be overloaded. The choice of a suitable TPU for dynamic application depends on modulus. The higher the stiffness, the lower is the deformation under comparable load.

9.5.2 Thermal Properties

Thermoplastic urethanes can be used from −40°C to 80°C (−40°F to 176°F) for long-term use and up to 120°C (248°F) for short-term exposure. In some cases even higher temperatures can be tolerated [75].

The following factors contribute to higher service temperature [76]:

- proportion of hard segments
- type and amount of chain extender
- type of diisocyanate.

The harder the product (more isocyanate and chain extender), the higher the service temperature.

Mechanical properties, including stiffness and elasticity, also depend on temperature, and hardness shows similar dependence on temperature.

Most of the changes described above occur due to the change in morphology (e.g., melting of the hard segments) and are related to the thermoplastic nature of the TPU materials. This process is reversible.

The other process taking place at higher temperatures is chemical degradation, a destructive change in chemical structure. The thermal stability of a TPU is strongly dependent on the structures of the isocyanates and chain extenders used for its synthesis [77, 78]. The majority of TPUs decompose slowly at 150–200°C (302–398°F) and at a measurable rate at 200–250°C (398–482°F) [69]. Several studies indicate that the thermal decomposition of ether-based TPUs is predominantly an oxidative process. The ester-based TPUs normally exhibit considerably better thermal and oxidative stability than the ether-based ones [79].

Other thermal properties, such as thermal conductivity, specific heat, heat of fusion, and coefficient of linear expansion (in U.S. units) are shown in Table 9.2.

9.5.3 Hydrolytic Stability

Thermoplastic polyurethane elastomers contain ester (and/or ether) urethane linkages, some degree of hydrolysis will inevitably occur. From published data [80], the hydrolytic stability of TPUs based on three different long-chain diols is shown as follows:

Polyether > Polycaprolactone > Polyester

Although the urethane linkage can be hydrolyzed, the cleavage of ester linkage is the primary route for hydrolytic degradation of the ester-based TPUs [80]. Acids present in the TPUs tend to catalyze the cleavage of carboxylic esters. This can be prevented by the addition of carbodiimides that act as acid scavengers [80, 81]. The hydrolysis of urethane linkages is the major way of the decomposition of ether-based TPUs. It is believed to cause chain cleavage that leads to the reduction of average molecular weight. When the molecular weight is reduced to a critical value, cracks will develop on the surface of the material [82]. With increasing

Table 9.2. Typical Thermal Properties of TPUs

Property	Test	Unit	Value
Thermal Conductivity	ASTM D2214 Cenco-Fitch	BTU/ (ft^2) (hr) (°F/in)	1.5–2.5
Specific Heat (at 212 °F)	DTA	BTU/ (lb) (°F)	0.40–0.45
Heat of Fusion	DTA	BTU/ (lb)	1.8–6.6
Coefficient of Linear Thermal Expansion	ASTM D696	10^{-5} / °F	6.5–9.5

Source: Reference [80], p. 233; [92].

hardness the materials become more resistant to hydrolysis because of the hydrophobic nature of the hard segments.

9.5.4 Chemical Resistance

In general, TPUs are resistant to pure mineral oils, diesel oils, and greases. However, some additives in these media may adversely affect the resistance of the TPU material. TPU generally resist well to gasoline and other petroleum fuels if they do not contain alcohol. Such fuels containing alcohols and aromatics cause a reversible swelling of the TPU material. The extent of such swelling is proportional to the content of such ingredients [83].

Nonpolar solvents, such as hexane or heptane, have practically no effect on TPUs. On the other hand, chlorinated hydrocarbons and aromatic hydrocarbons cause a very severe swelling [84]. The degree of swelling depends on the structure of the TPU; soft TPU swell more than hard ones. The ether types of TPU swell more than the polyester types.

Polar solvents, including dimethylformamide, tetrahydrofuran, N-methyl pyrrolidone, dimethylacetamide, and dimethylsilfoxide are considered good solvents for TPUs [85]. Soft linear polyurethanes can be dissolved in the mixtures of methyl ethyl ketone and acetone and applied as adhesives. Harder linear polyurethanes are dissolved and applied as coatings on textile, leather, and other substrates [86].

Thermoplastic polyurethane elastomers are sensitive to acids and bases and are attacked even by diluted acids and bases at room temperature. At higher temperatures they cannot withstand concentrated acids and alkali [86]. However, the effect of solutions of weak acids or bases (pH 5.5–8) can be considered similar to that of water [82].

9.5.5 Abrasion Resistance

Thermoplastic polyurethane elastomers exhibit an excellent resistance to abrasive wear. However, the abrasion of a lubricated TPU is considerably affected by the surface heat buildup during the test, which is believed to be related to the coefficient of friction, stress loading and contact areas. The abrasive wear of a lubricated wear is generally lower than that from an unlubricated specimen, probably because of a decreased heat build-up from friction [73]. A comparison of abrasion resistance (abrasion weight losses) of TPU to several other polymers is found in Table 9.3.

Table 9.3. Abrasion Resistance of Different Polymers

Material	Weight Loss (mg)
TPU	0.4–3.2
Ionomer	12
Nylon 6/10	16
Nylon 6/6	58
Impact Resistant PVC	89
Nylon 6	104
Natural Rubber Tread Formulation	146
SBR Premium Tread Formulation	177
SBR Tread Formulation	181
High Impact Polystyrene	545

Note: ASTM C501, CS-17 Wheel, 100 g load, 5,000 revolutions.
Source: Reference [92].

9.5.6 Ultraviolet Stability

Thermoplastic polyurethane elastomers based on aromatic isocyanates exhibit loss of mechanical properties and discoloration (yellowing) upon exposure to sunlight [87]. The discoloration is explained by the photooxidation of the aromatic diurethane bridges [79]. TPUs based on aliphatic diisocyanates, such as HDI or H12-MDI, do not show this discoloration [73]. The UV stability can be improved by the addition of UV stabilizers [88, 89]. Compositions containing carbon black also exhibit improved UV stability [90].

9.5.7 Electrical Properties

Because of the hydrophilic nature of TPUs, they are not used in applications where consistently high insulating resistance is required [91]. However, due to their flexibility and excellent abrasion resistance, they are being frequently used as protective coverings in cable applications. Typical electrical properties are shown in Table 9.4.

9.6 Processing of TPUs

The ease of processing is one of the major advantages of TPUs. They can be processed by the usual melt-processing methods, such as extrusion, injection molding, and calendering. Since some of the compositions can be dissolved in solvents, they can

Table 9.4. Typical Electrical Properties of TPUs

Property	Test	Unit/Condition	Value
Volume Resistivity	ASTM D257	10^{12} Ω-cm	2–50
Surface Resistivity	ASTM D257	10^{12} Ω	3–120
Dielectric Constant	ASTM D150	@ 60 Hz	5–7
		@ 10^3 Hz	5–7
		@ 10^6 Hz	4–5
Dissipation Factor	ASTM D150	@ 60 Hz	0.015–0.050
		@ 10^3 Hz	0.020–0.050
		@ 10^6 Hz	0.050–0.100
Loss Factor	ASTM D150	@ 60 Hz	0.12–0.22
		@ 10^3 Hz	0.12–0.16
		@ 10^6 Hz	0.22–0.33
Capacitance	ASTM D150	μμF @ 60 Hz	65–70
		μμF @ 10^3 Hz	61–69
		μμF @ 10^6 Hz	52–57
Arc Resistance		s	0.122
Dielectric Strength	ASTM D149	V/mil, short time	300–500

Sources: References [80], p. 233; [92].

be processed by the solution fabrication. Not all the grades can be used universally, each method requires specific grades with appropriate morphology and melt viscosity.

9.6.1 Rheology of TPUs

Under processing conditions, TPU melts have much higher viscosities than those of low-molecular weight fluids. The melts exhibit non-Newtonian flow behavior or pseudoplasticity, that is, the melt viscosities depend not only on temperature and pressure, but also on the rate of deformation (see Fig. 9.8). The response of melt viscosity to temperature, which is important in processing, is shown for different grades of TPU in Fig. 9.9. Increasing the melt temperature by 10°C typically results in an increase of the melt volume ratio (MVR) by a factor of 2–4 [83].

9.6.2 Drying

Thermoplastic polyurethanes absorb moisture rapidly upon exposure to atmospheric air. The moisture pickup and equilibrium level are humidity dependent (see Fig. 9.10). Since the optimum moisture content of the material to be processed is less than 0.05%, it has to be dried. Excessive moisture content in the material being processed results in molding and extrusion difficulties. In extrusion process bubbles, poor surfaces, wave forms, surging, and degradation are observed. In injection molding, defects due to excessive moisture are blisters, splay marks, bubbles, porous (foamy) melt, nozzle drool, and poor physical properties of the finished parts. One possible drying procedure is on trays in an oven by circulating air heated to 80–100°C (176–212°F) [83] for several hours. In such a case, pellets of the TPU should be spread 1 inch deep maximum. A better method is using desiccant hopper driers (Fig. 9.11) capable of providing hot air with a dew point of –18°C (0°F) maximum. In this drying equipment, softer grades of TPUs are dried typically at temperatures 82°C (180°F), harder grades at 104°C (220°F) with residence times 1–3 hours [92]. Prolonged drying should be avoided to prevent material discoloration [93].

9.6.3 Injection Molding

The primary function of injection molding is to shape polymeric materials into desired articles. It is a discontinuous process, divided into plasticating, injection, and ejection stages. TPUs can be molded on both-in-line reciprocating screw-type or ram-type

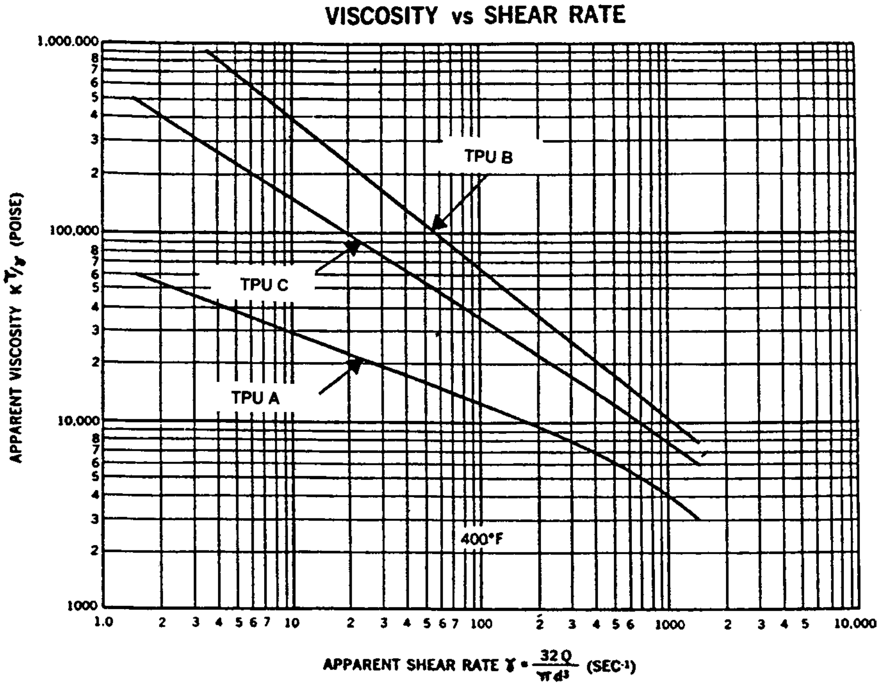


Figure 9.8. Melt viscosity vs. shear rate of different grades of TPU.
TPU B (55 Shore D)
TPU C (91 Shore A)
TPU A (85 Shore A)

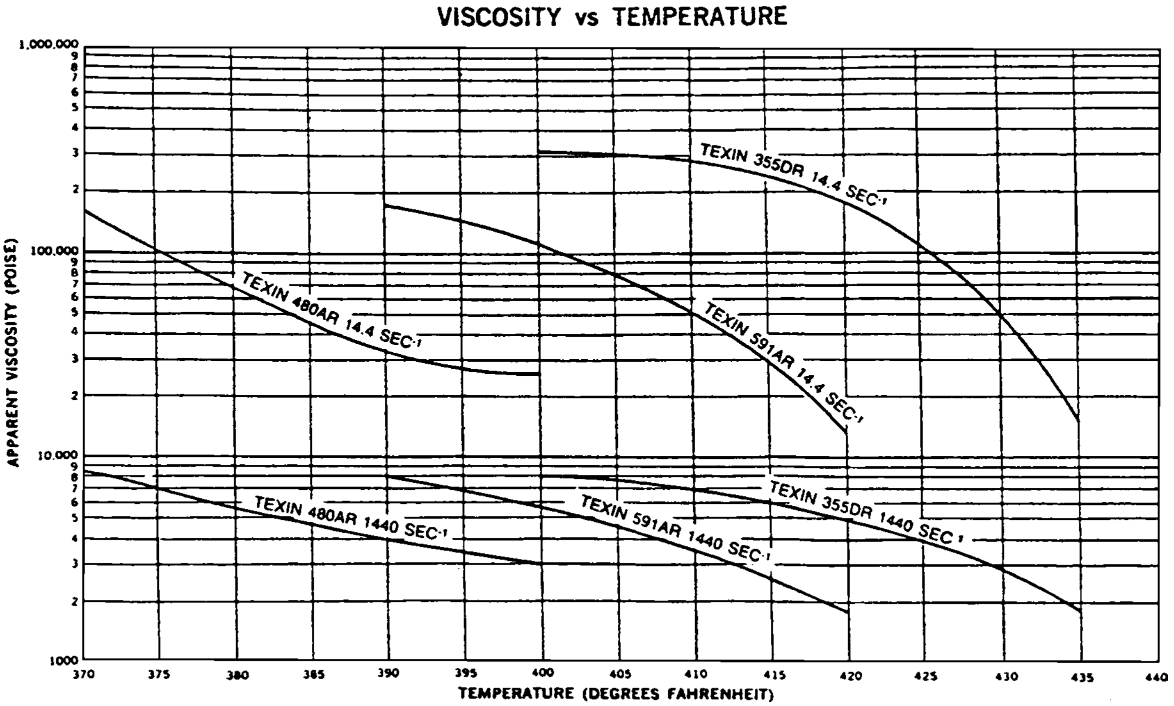


Figure 9.9. Melt viscosity vs. temperature of different grades of TPU.
Texin 355 DR (55 Shore D) (TPU B)
Texin 591 AR (91 Shore A) (TPU C)
Texin 480 AR (85 Shore A) (TPU A)

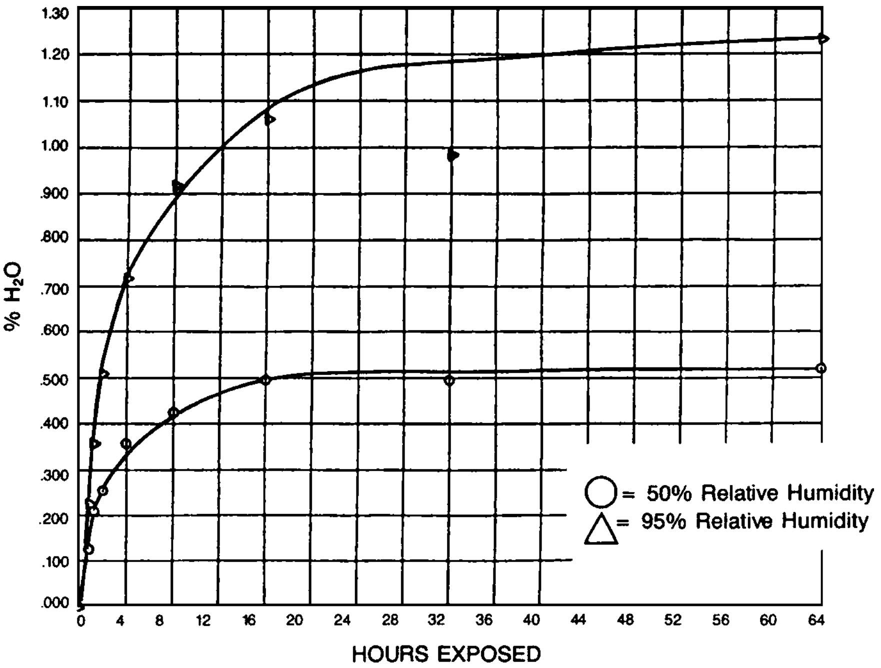


Figure 9.10. The moisture pickup rate in dependence on relative humidity for an 85 Shore A TPU.

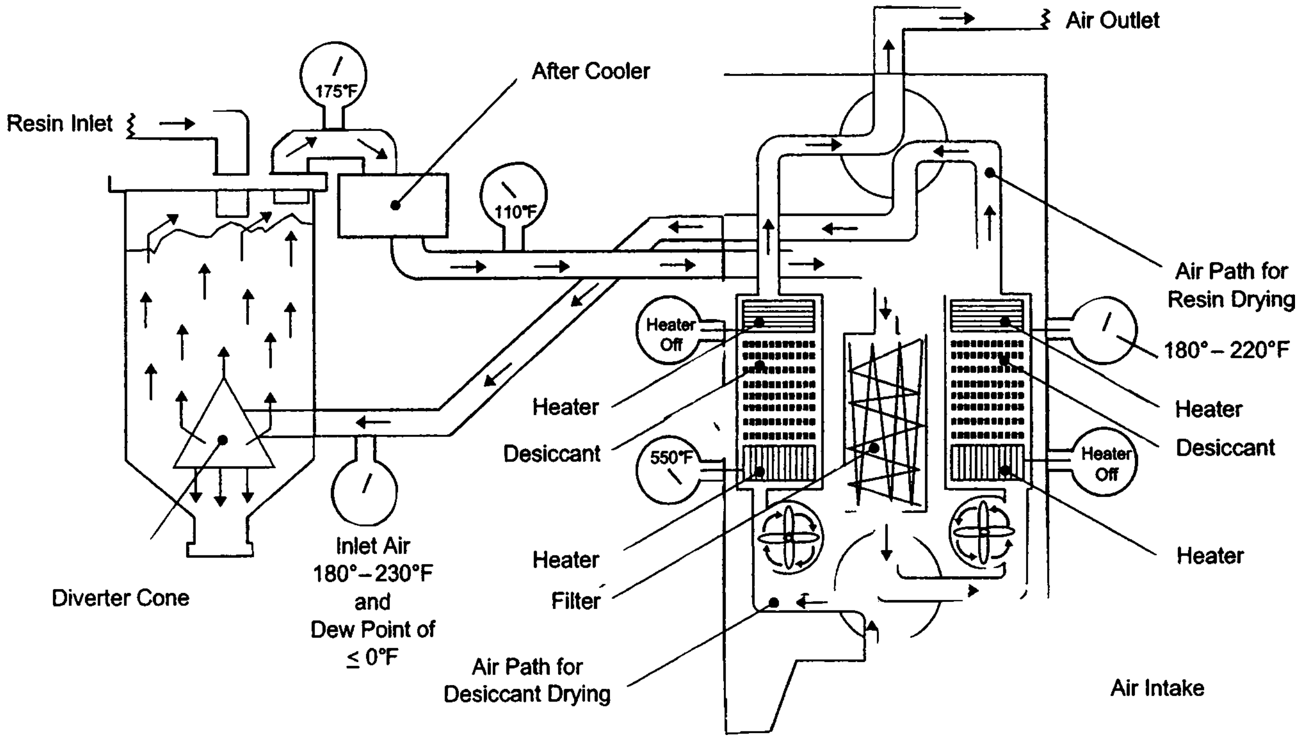


Figure 9.11. Schematic of a desiccant dehumidifying hopper dryer system (Courtesy Bayer MaterialScience).

machines. The in-line reciprocating screw machine is preferred because it provides a more homogeneous melt with more uniform temperature. Moreover, it permits processing at lower temperatures, which is generally an advantage.

A machine suitable for the injection molding of TPUs should have temperature control capabilities up to 475°F (246°C) and deliver an injection force up to 15,000 psi (105 MPa). The mold clamp force needed for most TPUs is 3–5 tons/in.^{2} or 0.5–0.8

metric ton/cm^2 of the projected area of the part. A nonreturn valve is recommended to ensure that the maximum pressure is developed. A free-flowing nozzle with a reverse taper is most often recommended. A sliding check-ring made from hardened steel, preferably nitrided to retard wear should be installed near the screw tip area to prevent backflow and maintain maximum pressure.

A general purpose screw with a length-to-diameter ratio *L*/*D* of at least 20:1 with a compression ratio 2.0:1 to 3.0:1 is preferred, although 2.5:1 compression ratio is satisfactory for most applications (see Fig. 9.12). Nylon-type (rapid-transition screws) are not recommended because they cause excessive build-up of melt temperature and very likely will cause its degradation. A chrome-plated screw is advantageous for an easy cleaning. The barrel liner should be made from a bimetallic abrasion resistant alloy, such as Xaloy™ [94].

A general purpose, free-flowing nozzle with a reverse taper at the nozzle exit has been found to be suitable for the processing of TPUs. The nozzle should be as short as possible. It is essential that the nozzle and sprue bushing mate properly and its orifice should be slightly smaller (about 20%) than the sprue bushing orifice. A separate temperature control for the nozzle is preferred.

Uniform molding cycles are essential to maintaining optimum processing conditions and producing the highest quality parts. This can be accomplished by the installation of state-of-the-art closed-loop systems that can ensure both the precise injection stroke and the switchover point that are critical for molding quality parts. This control equipment can adjust hold pressure in increments to minimize sinks and voids. In addition, it can maintain melt pressure in the mold cavity uniformly from shot to shot despite variations in the operating conditions of the machine.

When using screw-type machines, utilization of 40–80% of the barrel capacity is desirable. If the shot weights are smaller than 40%, there is a chance that the material can degrade due to its small weight and excessive heat build-up in the melt.

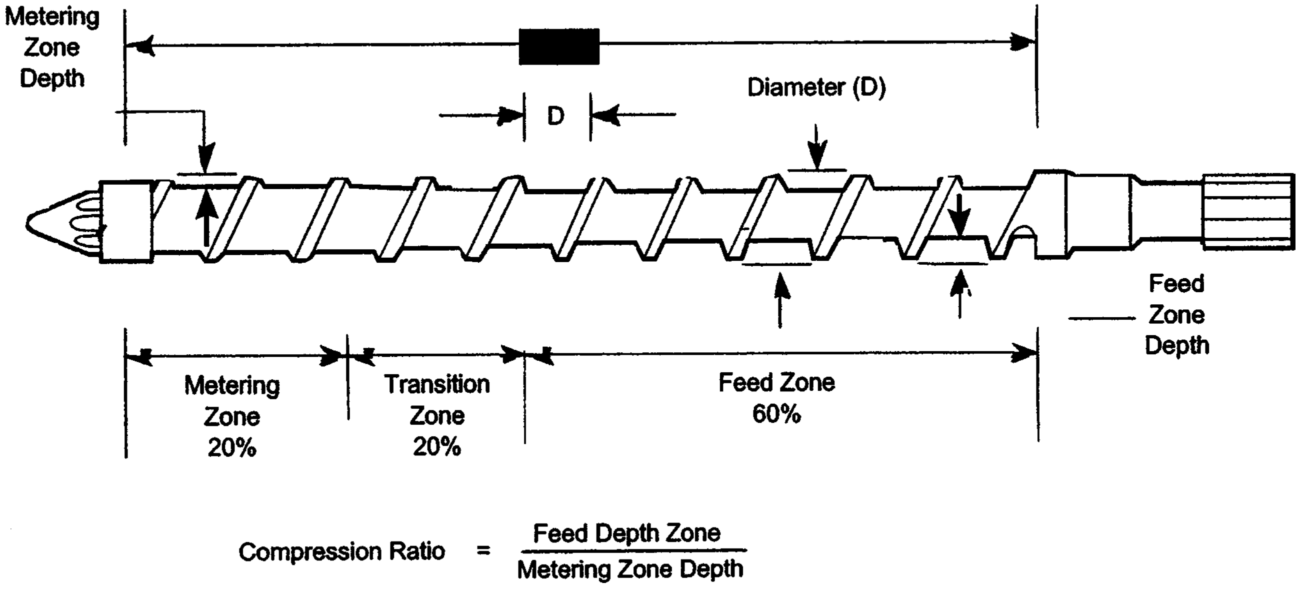
9.6.3.1 Operating Conditions

Operating parameters of temperature, time, and pressure affect the properties of the finished part to high degree. A homogeneous and off-white to beige color melt should be obtained with the proper processing conditions.

Barrel temperatures vary with different grades of TPUs (different hardness), with part design, ratio of shot volume to barrel volume, and cycle time. Typical temperature profile ranges from 350°F to 450°F (177°F to 232°C).

Injection pressure in the range 6,000–15,000 psi (41–103 MPa) is adequate for most parts made from TPUs. Low injection molding pressures may not fill the mold completely with the material. Too much pressure may cause the material to overfill the mold and create flash.

Hold pressure. Typically, hold pressure is about 60–80% of the injection pressure.



$$\text{Compression Ratio} = \frac{\text{Feed Depth Zone}}{\text{Metering Zone Depth}}$$

Figure 9.12. Injection molding screw for TPU.

Injection cushion (resin feed). Best results are obtained when the cushion does not exceed 0.125 in. (3.175 mm). Too much cushion can lead to overpacking of the part [94].

Screw backpressure below 200 psi (1.4 MPa) is needed for sufficient homogenization.

Screw speed. Since low shear is generally required for processing TPUs, screw speeds of 20–80 rpm are typical, with 20–40 rpm being preferred [95].

Injection speed. It is of advantage to fill the mold as fast as possible to minimize the appearance of weld lines, improve weld-line strength, improve surface appearance, and lower the injection pressure. Thicker section parts require a slower injection speed; thinner ones require a faster injection rate. Overall injection time depends on the machine and the part geometry.

Mold temperature. The optimum mold temperature varies with the thickness of the part and hardness of the TPU being processed. Thicker parts require a lower temperature to effectively cool the resin within a reasonable cycle time. Softer resins require lower mold temperature than harder ones. The range is typically 50–150°F (10–66°C). Proper mold temperature ensures a proper release of parts.

Cycle time. The optimum cycle to produce quality parts includes a fast fill, a hold time just long enough for the gates to freeze, and cooling time long enough so that the part ejectors do not penetrate the part. Cooling time is the major part of the total molding cycle.

9.6.3.2 Insert Molding

Thermoplastic polyurethane elastomers can be combined with a variety of materials that are molded inside the resin as an insert. The design of the insert can be straight, smooth wall, but can also have knurls, splines, reverse tapers, or undercuts.

9.6.3.2.1 Metal Inserts

Inserts of steel, aluminum, brass, zinc, and other metals can be molded into TPUs. In a majority of cases sufficient bond strength can be obtained by simply degreasing the insert, applying an adhesive to their surfaces, and heating them to 220–250°F (104–121°C) before placing them into the mold. Very often polyurethane-based adhesives work well [94].

9.6.3.2.2 Nonmetalic Inserts/Overmolding

Thermoplastic polyurethane elastomers can also be joined to many nonmetallic parts, including other thermoplastics in the mold, thus obtaining molded parts with both flexible and rigid components. Usually, the rigid substrate (molded part) is molded first and placed after a short time (usually less than 3 hr to assure a proper bonding) to an injection mold and the flexible component is injected onto it [94]. The factors for a good bond are as follows:

- chemical affinity (adhesion)
- mechanical anchoring potential of the substrate material
- processing order.

Bonding of TPUs to different materials is illustrated in Table 9.5.

9.6.3.3 The Use of Regrind

Sprues, runners, and scrapped parts from TPU can be ground and reused. Although up to 100% regrind has been used successfully [96], the maximum amount of 20% may be used with virgin material, depending on the end-use requirements of the molded parts. The regrind must be clean, dried at 180–230°F (82–110°C) for 1–3 hr [94] and thoroughly blended with virgin resin prior to drying and processing. The use of regrind should be avoided where material properties equivalent to virgin resin are required, including color, impact strength, and load-bearing performance.

9.6.4 Extrusion

9.6.4.1 Screw Design

Thermoplastic polyurethane elastomers can be extruded on all modern conventional, single screw extruders. The screws for the extrusion of TPU should have an L/D ratio at least 24:1 with a compression ratio at least 3:1. The transition zone should be long and gradual, the metering zone long (up to 50% of the entire screw length). The metering zone should be rather shallow in order to sufficiently homogenize the melt temperature. The material recommended for screws is SAE 4140 steel or a similar material with flights either flame hardened or made from Stellite™ (Cabot Corporation) alloy. The screw surface should be chrome plated for optimum resin flow. A removable tip is desirable to allow the later addition of a mixing segment for improved processing of custom materials.

Table 9.5. Bonding of Different Injection Molded Materials

Substrate	Material Injection Molded to Substrate	Adhesion
ABS	TPU	Good
PC	TPU	Good
PC/ABS Blend	TPU	Good
Rigid PVC	TPU	Good
Rigid TPU	TPU	Good
PBT	TPU	Inadequate
PA	TPU	Inadequate
TPU	ABS	Good
TPU	PC	Good
TPU	PC/ABS Blend	Good
Flexible TPU	Rigid TPU	Good
TPU	PBT	Better, depending on type
TPU	PA	Better, depending on type
PE	TPU	Nil
PP	TPU	Nil
TPU	PE	Nil
TPU	PP	Nil

Source: Reference [94].

9.6.4.2 Die Design

Because of their relatively high elastic recovery, TPU resins exhibit a significant die swell. The extrudate should be cooled as soon as it exits the die, either by immersion in water or by refrigerated cooling air, to preserve the extrudate shape [97].

9.6.4.3 Extrusion Temperature Profiles

The temperature during extrusion depends on the size of the extruder, the throughput, and the grade of the material processed, and may vary between 350°F and 450°F (175°C to 230°C). The temperature profile used for TPU usually increases from the feed zone to the compression zone and then gradually drops off at the metering zone.

It is recommended that a water-cooled throat section be used to minimize any tendency of the material to bridge in the hopper feeder [97, 98].

9.6.4.4 Extrusion Methods Used

Thermoplastic polyurethane elastomers are versatile materials and can be used for the following extrusion methods:

- extruded sheet and film
- cast film
- blown film
- tubing
- profiles
- crosshead extrusion (wires or other substrates).

9.6.4.5 PostExtrusion Conditioning

Most extruded products from TPUs are used in service without any particular treatment, because they attain their ultimate properties shortly after normal fabrication [98]. However, if lower compression set, lower creep and tensile decay are required a postextrusion conditioning will enhance these properties. Usually, the property improvement is attained after 2–3 weeks storage at ambient air. To achieve ultimate mechanical properties immediately after fabrication, the products are annealed at 230°F (110°C) for 4–16 hr in a circulating air oven.

9.6.5 Calendering

Continuous sheet, film, and coating of varied flat substrates can be readily done on a multiroll calender. Special lubricated TPU grades with processing temperature range between 280°F and 330°F (140°C and 165°C) are required for this process. The molten material can be delivered to the calender from an extruder or from a heated roll mill [99].

9.6.6 Blowmolding

At the time of writing this book there were only two reports on blowmolding of TPU: a process of blowmolding TPU over and through holes in aluminum or steel inserts [100] and a process of making bellows from TPU [101].

9.6.7 Thermoforming

TPUs alone are not processed by thermoforming but sheets prepared by coextrusion with other polymers or lamination, for example, onto ABS, are. TPU provide abrasion resistance, soft feel, and improved weather resistance [102].

9.7 Blends of TPU with Other Polymers

Thermoplastic polyurethane elastomers are miscible with certain other polymer [103–105], but they are not compatible with polyolefins. When preparing blends with compatible polymers, temperatures above 280°C (536°F) should be avoided. TPU can be used as a modifier if used as a minor component, for example, for improving impact resistance of high-modulus plastics [106]. Another use is as nonmigrating, nonvolatile plasticizer of PVC [107] and for improvement of adhesion of less polar thermoplastic elastomers (TPEs) to ABS [108].

Other examples of blends of TPUs with other polymers:

- TPU/polycarbonate: good processing properties and an interesting profile of mechanical data in the modulus range around 1,000 MPa [109].
- TPU/ABS: These two materials show miscibility over the complete range. Increasing the ABS content results in a higher modulus and reduced abrasion resistance and tear strength. Due to the low cost of styrenics, such blends may offer economic advantage [110–112].
- Many other blends with different styrene copolymers are reported in [113–115].
- Small amounts of ABS (less than 20%) are used as low temperature impact modifier for high-modulus TPUs or as phase compatibilizer for hard polyester-based grades [116–118], in applications such as ski boots. Other polymers, such as acrylics, copolyamides, and ionomers, can be used as processing aids [119–121].

Mixing of different grades of TPUs is a common practice. Blends of grades of different hardness provide materials with intermediate properties or with improved processing. Blends of materials with different melt viscosities are reported to give better demolding properties in blow molding operations [122].

9.8 Bonding and Welding

9.8.1 Heat Welding and Sealing

Because of their thermoplastic nature, TPUs can be readily joined by welding. There are several methods to do so. The simplest one is *heat* or *hot plate welding*. In this method, a heated platen usually coated with PTFE, contacts two plastic parts until the joint area melts. The parts are then pressed together under slight pressure until the bond is set.

Bar sealing involves holding films between a double-heater element for a short period time at a given temperature and pressure, depending on the polymer used and film thickness.

Other welding methods are [123, 124]:

- *Hot air or nitrogen welding* (the gas stream should be heated to 290–330°C (554–626°F); a round cord of TPU can be used as a weld-filling material)
- *Heated mirror welding* (suitable for welding of profiles at the front. The mirrors are heated to temperatures 270–320°C (518–608°F)
- *Heating tool and thermal impulse welding* is used mainly for thin wall articles, such as films
- *High frequency welding* is suitable for flat parts with wall thickness up to 2 mm (0.08 in.)
- *Friction welding* can be done on parts that are rotationally symmetrical. They have to have sufficient torsional stiffness and resistance to pressure
- *Ultrasonic welding* is a method using high frequency vibration (typically 20–40 kHz) to melt mating surfaces.

9.8.2 Solvent and Adhesive Bonding

A TPU can be bonded to itself using solvents as N-vinyl pyrrolidone or dimethylformamide as long as the surface is small. Two-component reactive polyurethane adhesives are suitable to bond TPUs to themselves and other polar plastic materials, metals, woods and leather, and other substrates [125]. Epoxy resins can also be used in most cases.

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10 Thermoplastic Elastomers Based on Polyamides

10.1 Introduction

The polyamide elastomers, polyesteramides (PEAs), polyetheresteramides (PEEAs), polycarbonate-esteramides (PCEAs), and polyether-*block*-amides (PE-*b*-As) belong to the group of segmented block copolymers. The hard segments are based mainly on aliphatic polyamides and the soft segments are based on aliphatic polyethers and/or polyesters. Both segments are linked by ester or amide groups. As in other segmented block copolymers, the chemical structure and composition of both types of segments determine the mechanical and thermal properties. The soft segments, which are normally above their glass transition temperature, contribute to the flexibility and extensibility of the elastomers. The glassy or semi-crystalline hard segment domains act as physical cross-links reducing the chain slippage and viscous flow of the copolymer [1].

10.2 Synthesis

These block copolymers are classified according to the polyamide in the hard segment and the composition of the soft segment. The hard segments of currently available commercial products are based on aliphatic and semi-aromatic amides. The thermoplastic elastomers (TPEs) with hard segments based on aliphatic amides and soft segments based on polyethers, developed originally by Atochem are referred to as PE-*b*-As. It should be noted that the conventional nomenclature indicates that these are diblocks, but in reality they are segmented block copolymers. The elastomers, developed originally by Dow Chemical, contain segments based on semi-aromatic amides and soft segments based on aliphatic polyesters, aliphatic polyethers, or aliphatic polycarbonates. They are designated PEAs, PEEAs, and PCEAs [1].

There are essentially two synthetic routes to prepare the elastomers. The PE-*b*-A copolymers are made by the esterification reaction between carboxylic acid-terminated aliphatic amide blocks and hydroxyl-terminated polyether diols (Scheme I). The polymer forming reaction of the PEA, PEEA, and PCEA copolymers is the reaction between an aromatic isocyanate and an aliphatic carboxylic acid to form the amide moiety (Scheme II) [2]. The carboxylic acid-terminated polyester or polyether diols form the soft segments. Thus, the amide-based hard segments are formed at the same time as the polymer.

Scheme I

Synthesis of PE-*b*-A:

HOOC-polyamide-COOH + HO-polyether-OH →
[polyamide-ester-polyether-ester]

Scheme II

a. Synthesis of PEA or PCEA:
OCN-Ar-NCO + HOOC-R-COOH + HOOC-polyester-COOH →
[[poly-Ar-amide]polyester]

b. Synthesis of PEEA:
OCN-Ar-NCO + HOOC-R-COOH + HOOC-ester-polyether-ester-COOH →
[[poly-Ar-amide]-ester-polyether-ester].

Because the semi-aromatic amide does *not* undergo the ester–amide interchange reaction either under the reaction conditions or during subsequent processing, an ester-based soft segment can be employed. However, when aliphatic amide is used, the ester–amide interchange reaction would randomize the blocks, and the polymer would lose the properties associated with segmented block copolymers [1].

The soft segments generally used in PEEA elastomers are based on commonly available polyoxyalkylene glycols such as polyoxyethylene glycol, polyoxypropylene glycol, and polyoxytetramethylene glycol. Polyester polyols such as hexamethylene adipate glycol or tetramethylene azelate glycol are also used to make PEA elastomers. PCEA, a special subset of PEA elastomers, use soft segments based on aliphatic polycarbonate glycols such as hexamethylene carbonate glycol to impart improved property balances [3].

10.2.1 Synthesis of PEAs, PEEAs, and PCEAs

The polymerization leading to PEAs, PEEAs, and PCEAs is usually carried out homogeneously in a polar solvent (i.e., not reactive with isocyanates at elevated temperatures—typically 200–280°C) by controlled addition of the isocyanate to a solution of the other co-monomers. The polymer is recovered by precipitation or by solvent removal under vacuum [3].

These elastomers can also be prepared by a one-step or two-step reactive extrusion process [4, 5].

The amide content of the elastomer and the crystallinity of the hard segment domains can be changed by varying the amounts and type of dicarboxylic acid chain extenders in the formulation and/or by changing the molecular weight of the polyester, polyether, or polycarbonate soft segments. The most commonly used hard segment extenders are adipic (C-6) and/or azelaic (C-9) acids [3]. The value of the melting point (T_m) of the hard segment relative to the T_m of the analogous homopolymers generally reflects the extent of crystallinity in the hard domains. By varying the content of the hard amide segment and the molecular weights of the hard and soft segments, the products can be made in the range of hardnesses from Shore 80A to Shore 70D. The type of amide used and the type of the soft segment can be chosen to further fine-tune the performance characteristics of the products [3]. The elastomers produced by this method are transparent, with a pale brown color, and are soluble in dimethylformamide (DMF), dimethylacetamide (DMAC) and N-methylpyrollidone (NMP). Examples of different elastomers of this type are in Table 10.1.

10.2.2 Synthesis of PE-*b*-As

The PE-*b*-A elastomers are prepared by the melt polycondensation of the dicarboxylic acid amide block and the polyoxyalkylene glycol at elevated temperatures (200–300°C or 392–572°F) and under high vacuum (less than 2 mmHg) for 2 or more hours. The use of suitable catalysts increases the rate of the esterification and the molecular weight of the product [6, 7]. The reaction can be carried out batchwise or as a continuous process [8].

The products range from nearly transparent to opaque white materials, depending on the amide content in the polymer [9]. The amide segments in PE-*b*-A elastomers have molecular weights in the range of 800–5,000. The ether soft segments have molecular weights ranging from 400 to 3,000 and they make up 5–50% by weight of the product. Softer, more elastic products can be made by using amide and ether segments with molecular weights in the ranges 500–2,000 and 1,000–3,000, respectively. In that case the content of soft segments is 60–80% by weight [10]. The polymer chain may contain different types of polyamides (PA 6, PA 12, PA 11, PA 66, etc.) and all kinds of polyethers or copolyether glycols derived from tetrahydrofuran (THF), and from propylene or ethylene oxide [11]. The hard and soft segments are linked by ester bonds. Typical hardness values range from Shore 25D to 70D. Examples of different PE-*b*-A elastomers and their properties are in Table 10.2.

10.2.3 Synthesis of Other Thermoplastic Polyamide Elastomers

Hüls process. The copolymers are produced from lactam 12, dodecanedioic acid, and poly

Table 10.1. Glass Transition Temperatures and Melting Points of Different Polyamide TPEs

Polymer	Hardness Shore	Hard Segment Extender	Amide (%)	T_g (soft) (°C)	T_m (hard) (°C)
PEA-1	88A	Adipic	25	−40	270
PEA-2	94A	Azelaic	35	−28	230
PEA-3	94A	Adipic	33	−34	275
PEA-4	55D	Azelaic/adipic	37	−33	236
PEA-5	60D	Azelaic/adipic	39	−33	238
PEA-6	70D	Azelaic/adipic	42	−34	240
PEEA-1	92A	Azelaic/adipic	31	−50	251
PEEA-2	92A	Azelaic	31	−40	264
PEEA-3	90A	Adipic	31	−40	290
PCEA-1	88A	Azelaic	35	−40	230
PCEA-2	92A	Adipic	35	−38	252
PCEA-3	92A	Azelaic	35	−30	230

Notes: PEA: polyesteramide; PEEA: polyetheresteramide; PCEA: polycarbonate-esteramide.
Source: Reference [3].

Table 10.2. Example of PE-*b*-A Elastomers and Their Physical and Mechanical Properties

Polymer	Hardness Shore	T_m (°C)	Tensile Strength MPa (psi)	Elongation at Break (%)	Flexural Modulus, MPa (psi)
PE-*b*-A-1	25D	148	34.1 (4,944)	640	14.5 (2,102)
PE-*b*-A-2	35D	152	38.6 (5,597)	580	19.3 (27.98)
PE-*b*-A-3	40D	168	39.3 (5,698)	390	89.7 (13,006)
PE-*b*-A-4	55D	168	50.3 (7,293)	430	20.0 (2,900)
PE-*b*-A-5	63D	172	55.9 (8,105)	300	339 (49,155)
PE-*b*-A-6	70D	174	57.2 (8,294)	380	460 (66,700)

Source: Reference [9].

(tetramethylene oxide) (PTMO) in one step at temperatures >250°C in order to convert the lactam into the corresponding amino acid. The resulting copolymers have a statistical distribution of hard and soft segments over the length of the chain [12].

EMS process. The hard segments of the copolymers are also based on lactam 12. There are no ester linkages; the bonds between the hard and soft segments are amides. The polyetheramide is formed directly [11].

Ube process. One-step [13] and two-step [14, 15] processes were patented. The product has the general formula:

$$\mathrm{HO}-\left[\mathrm{CO{-}Polyamide{-}CO{-}NH{-}Polyether{-}NH}\right]_x-\mathrm{H}$$

Hard segment Soft segment

The special feature of the product is that a dimer acid (derived from a fatty acid) is incorporated in the polyamide chain, linking two amino acid units and acting as a chain limiter [11].

10.3 Morphology

The domain structure of the polyamide elastomers can be established by differential scanning calorimetry (DSC). Figure 10.1 shows the DSC thermograms for typical PEA and PEEA and Fig. 10.2 for three different types of PE-*b*-A elastomers. Such multiple endotherms for the T_m are commonly observed on semi-crystalline polymers and are the result of different degrees of crystalline order present in the hard segment domains. The relative size of these domains would change when the polymer is annealed.

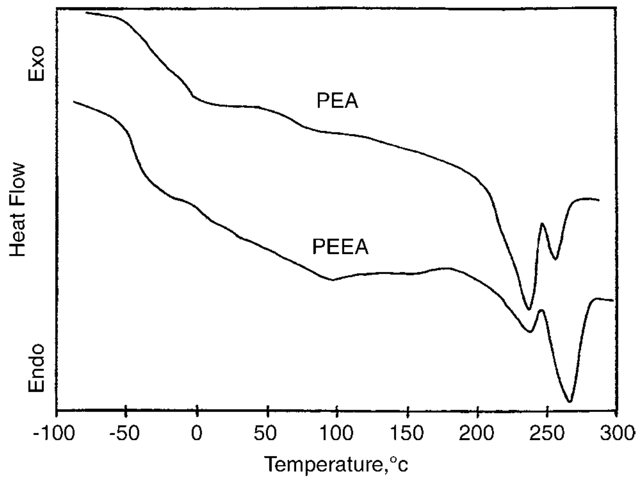

Figure 10.1. Typical DSC chart of PEA and PEEA elastomers. Heating rate: 20°C/min.

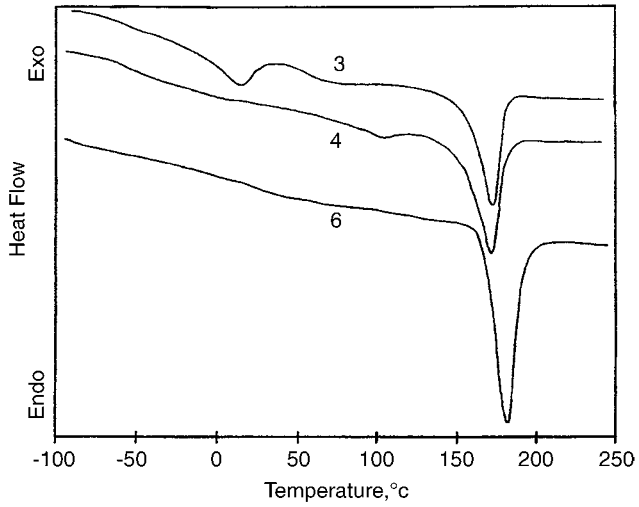

Figure 10.2. Typical DSC chart of PE-*b*-A elastomers. Heating rate 20°C/min. 2 = PE-*b*-A-2; 4 = PE-*b*-A-4; 6 = PE-*b*-A-6 (refer to Table 10.2 for specifics).

Table 10.1 contains results from measurements of T_g and T_m for several PEA, PEEA, and PCEA elastomers formulations. If the copolymers were completely phase-separated into soft and hard domains, the hard segments would have values of T_m from 50°C to 100°C higher and the soft segments would have values of T_g considerably lower. Thus, the values of T_m for the hard segments and T_g for the soft segments would approach those for the respective pure polymers. In real systems, these values change also with the copolymer composition. For example, the T_g of the soft segment of PEA-2 is 28°C above that of pure soft segment and the T_m of the hard segment is 95°C lower than that of the analogous high-molecular weight polyamide. These shifts in the values of T_m and T_g are characteristic of a segmented elastomer in which the phases are partially mixed [16]. The data in Table 10.1 also illustrate the effect the chemical composition can have on the phase separation and indicate that the phase separation affects the hardness of the resulting copolymer somewhat. For example, the polyether-based PEEA-2, which has the same hard segment content and hard segment length as PEA-2, is more phase separated as indicated by the T_g and T_m shifts. The chemical composition of the hard segment, which affects the amount of crystallinity, also affects the phase separation of the elastomer. Thus, PEEA-2 is several points softer in durometer hardness.

10.4 Structure–Property Relationships

In general, certain physical properties of thermoplastic segmented block copolymers are dependent on such factors as the chemical composition of the hard and soft segments and also their respective lengths and weight ratios. Of those, the chemical composition of the hard and soft segments and the hard segment composition have the most pronounced effect.

In polyamide TPEs, the effects of the hard segments are generally associated with the degree of crystallinity of the amide hard segments and the crystalline melting point of these crystallites. This ultimately determines the service temperature of the elastomers. Highly crystalline hard segments also tend to lead to a higher degree of phase separation, which produces softer materials. Another effect of that is an increased chemical resistance of the copolymer, since its solubility and effects of solvents on it are greatly reduced with increasing degree of crystallinity.

The chemical composition of the soft segment, which is often the major component by weight in these copolymers, affects their thermal oxidative stability. For example, polyether-based elastomers are generally more susceptible to oxidative chain scission than those based on polyesters [17]. On the other hand, many of the elastomers with polyether-based soft segments are more hydrophobic than the esters and more resistant to hydrolysis. The molecular weight of the segment can affect the degree of compatibility (short chains cause forced compatibility), which in turn affects the degree of phase separation, resulting in the changes in hardness mentioned previously [18, 19]. The chemical structure has the main influence on the T_g of the soft segment. The degree of phase mixing affects the degrees of freedom of the soft segment chains, which also affects the T_g. Thus several factors define the lower limits of the "leathery" region in the performance range of the elastomer. The ratio of hard to soft segments, or the proportion of the amide content has effect on the physical properties as the polymer gradually changes from a soft polyether or polyester to a hard polyamide. The major correlations between structure and properties of the polyamide TPEs are shown in Table 10.3.

10.5 Physical and Mechanical Properties

10.5.1 Tensile Properties

Typical stress–strain behavior of several formulations of polyamide TPEs is depicted in Fig. 10.3. The initial moduli of these elastomers, which depend on the amine content, are much higher than those of many other TPEs in the same hardness range. The reason for that is the higher load-bearing capacity of the crystalline portion of the amide segment domains. The deformation of the hard segments in the low-strain region is mostly reversible. However, at higher strains disruption or reorganization of the crystalline lamellae occurs and the stress–strain curves level out as the chain slippage relieves some of the stress [20]. This change is irreversible and results in the observed tensile set. Finally, the load is borne by the soft segments, which become oriented and crystallize as shown by DSC studies [21]. This increases the strength of the elastomer gradually until a catastrophic failure occurs at break [22, 23]. PEA does not exhibit tensile yield even at the

Table 10.3. Correlation Between the Structure and Properties of Polyamide TPEs

Property	Hard Segment Composition	Soft Segment Composition	Amide Content
Hardness	X	0	X
Degree of Phase Separation	X	X	X
Crystalline Melting Point	X	0	0
Low Temperature Properties	0	X	X
Tensile Properties	X	0	X
Hydrolytic Stability	0	X	X
Chemical Resistance	X	X	X
Thermal Oxidative Stability	0	X	X

Notes: X: Definite correlation; 0: no correlation.

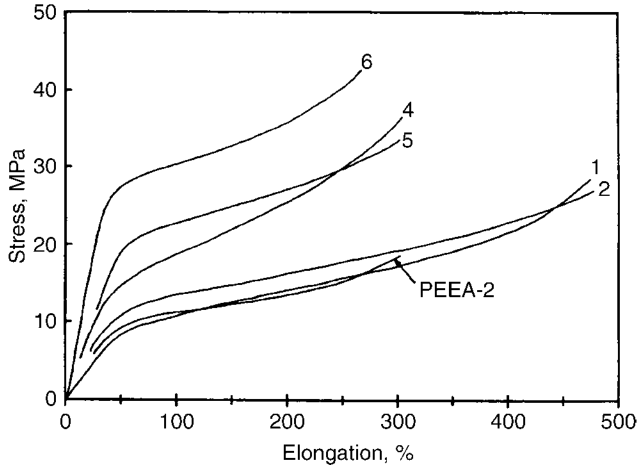

Figure 10.3. Stress-strain curve (ASTM D 412) at RT, typical for PEA (PEA-1, PEA-2, PEA-3, PEA-4, PEA-5, PEA-6) and PEEA (PEEA-2) elastomers (refer to Table 10.1 for specifics).

hardness as high as 70 Shore D, and therefore it has a lower permanent set than some of the other crystalline TPEs. This is an indication of the integrity of the crystalline amide hard segment domains on a microscopic scale.

The tensile properties of PEA and PEEA materials improve after being annealed above the T_g of the amide hard segment. In addition to the relief of molded-in stresses, annealing also promotes the reorganization of the short-range ordered amide segments in the hard segment domains into larger and more perfect crystallites. The net result is often higher modulus values, higher tensile strength values, and better elongations, as shown in Table 10.4.

10.5.2 Properties at Elevated Temperatures

Polyesteramide- and polyetheresteramide-based TPEs exhibit higher resistance to elevated temperatures than any other commercial TPEs. The high temperature performance of these segmented elastomers is closely dependent on the hard segment crystallinity and its melting point. They retain useful tensile properties under conditions where most other TPEs could not even be tested [24]. This applies also to the lower hardness materials where high temperature performance is most difficult to achieve in a thermoplastic elastomer, which is significant (see Table 10.5).

Polyesteramide and polyetheresteramide elastomers are also highly resistant to long-term dry heat aging, even at 150°C even without any added heat stabilizers. Some of the room temperature tensile properties improved after aging for 5 days at 150°C (see Table 10.6). This is due to annealing effect rather than to an oxidative cross-linking since the samples were still soluble. Similar studies at 175°C revealed that PEA elastomers lost only very little in tensile properties, while PEEA were affected much more. The explanation is the inherent oxidative instability of the ether linkage [25]. With the addition of stabilizers the thermal stability of the PEEA elastomers is greatly improved [26].

In humid aging the tensile properties of PEA elastomers are reduced due to susceptibility of the ester group to hydrolysis and subsequent reduction of molecular weight. This problem can be alleviated by the use of a sacrificial stabilizer (such as polymeric carbodiimides-based additive). The problem is reduced as the hardness of the elastomers increases

Table 10.4. Examples of Tensile Properties of PEA, PEEA, and PCEA (ASTM D 412)

Polymer	Modulus, MPa (psi) at			Tensile Strength, MPa (psi)	Elongation at Break (%)	Tensile Set (%)
	50% Elongation	100% Elongation	300% Elongation			
PEA-1	8.5 (1,232)	10.8 (1,566)	18.2 (2,639)	28.1 (4,074)	470	—
PEA-1A[a]	8.7 (1,261)	12.0 (1,740)	21.0 (3,045)	31.0 (4,495)	495	—
PEA-2	11.3 (1,638)	13.2 (1,914)	19.2 (2,784)	26.2 (3,799)	470	50
PEA-2A[b]	12.6 (1,827)	16.4 (2,378)	28.8 (4,176)	31 (4,495)	370	40
PEA-4	14.7 (2,132)	18.9 (2,740)	—	36.0 (5,220)	295	34
PEA-6	27.0 (3,915)	30.1 (4,364)	—	42.2 (6,119)	265	92
PEEA-2	9.2 (1,334)	11.5 (1,668)	18.4 (2,668)	18.6 (2,697)	300	16
PEEA-2A[b]	9.6 (1,392)	12.6 (1,827)	16.7 (2,422)	18.8 (2,726)	410	50
PCEA-2	10.2 (1,479)	13.5 (1,958)	18.8 (2,726)	20.5 (2,972)	390	—
PCEA-3	15.8 (2,291)	16.5 (2,392)	—	21.9 (3,176)	270	—

Notes: Refer to Table 10.1 for more details about the above polymers.

[a] Sample annealed at 175°C for 4 hr.

[b] Sample annealed at 200°C for 3 hr.

Source: Reference [21].

Table 10.5. Examples of Tensile Properties of PEA at Elevated Temperatures (ASTM D 412, D 3196)

Polymer	Test Temperature (°C)	Modulus, MPa (psi) at			Tensile Strength, MPa (psi)	Elongation at Break (%)
		50% Elongation	100% Elongation	300% Elongation		
PEA-1	RT	8.7 (1,262)	12.0 (1,740)	21 (3,045)	31 (4,495)	495
	150	6.5 (942)	8.9 (1,290)	13.3 (1,928)	14.8 (2,146)	340
PEA-2	RT	11.3 (1,638)	13.2 (1,914)	19.2 (2,784)	26.2 (3,799)	470
	100	7.4 (1,073)	9.7 (1,406)	9.7 (1,406)	14.6 (2,117)	480
	150	5.5 (798)	5.9 (855)	6.3 (914)	7.7 (1,116)	320
PEA-4	RT	14.7 (2,132)	18.9 (2,740)	—	36.0 (5,220)	295
	100	5.8 (841)	8.1 (1,174)	15.8 (2,291)	20.6 (2,987)	390
	150	3.7 (536)	5.1 (740)	9.1 (1,320)	9.6 (1,392)	310
PEA-6	RT	27.0 (3,915)	30.1 (4,364)	—	42.2 (6,119)	265
	100	9.0 (1,305)	9.0 (1,305)	14.3 (2,074)	26.9 (3,900)	490
	150	6.1 (884)	6.1 (884)	9.4 (1,363)	16.2 (2,349)	540

Notes: 1. Refer to Table 10.1 for more details about the above polymers.
2. All samples were annealed for 3 hr at 200°C except PEA-1, which was annealed for 4 hr at 175°C.

Source: Reference [24].

since amount of ester component is reduced. The PEEA elastomers are much less sensitive to moisture because the ether linkage does not hydrolyze. The carbonate-ester-based PCEA elastomers exhibit even higher moisture resistance because of the greater resistance of the carbonate ester to hydrolysis.

The PE-*b*-A elastomers that also have ether-based soft segments, have good resistance to

Table 10.6. Dry Heat Aging of PEA, PEEA, and PCEA

Sample	Modulus at 100% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Aging 120 hr at 150°C			
PEA-1			
Original	10.8	28.1	470
Aged	8.9	26.3	430
% Retention	82	93	91
PEA-2			
Original	13.2	26.2	470
Aged	16.0	29.7	390
% Retention	121	113	83
PEEA-2			
Original	11.5	18.6	300
Aged	14.6	18.0	260
% Retention	127	97	87
Aging 120 hr at 175°C			
PEA-1			
Original	10.8	28.1	470
Aged	5.8	19.1	320
% Retention	54	68	68
PEA-2			
Original	13.2	26.2	470
Aged	15.9	26.9	300
% Retention	120	103	64
PCEA-2			
Original	16.5	21.9	270
Aged	18.6	23.0	250
% Retention	113	105	93

Notes: 1. Refer to Table 10.1 for details about the polymers above.
2. Samples were annealed at 200°C for 3 hr. No stabilizers were added.
Source: Reference [25].

hydrozlysis during water immersion at 100°C. Their performance can be further improved by reducing the carboxylic acid end group content of the polymer [27].

10.5.3 Tear Strength

Tear strength (ASTM D 624, Die C) of softer grades (PEA-2) is typically 150 kN/m (856 lb/in.) at room temperature and 50 kN/m (285 lb/in.) at 150°C for softer grades and somewhat higher for harder grades, for example, PEA-4 [28]. Values of tear strength for several PEA and PE-*b*-A elastomers are in Table 10.7.

10.5.4 Abrasion Resistance

Abrasion resistance (Taber abrasion test, ASTM D-1044) of polyesteramide-based TPEs is comparable to that of thermoplastic polyurethanes and to that of copolyetheresters of similar hardness under the same conditions. Results using different abrasive wheels are in Table 10.8 [29].

Table 10.7. Tear Strength of PEA and PE-*b*-A Elastomers (ASTM D 624, Die C)

Sample	Tear Strength kN/m (lb/in.)	
	RT	150°C
PEA-2	151 (862)	51 (291)
PEA-4	169 (965)	58 (331)
PE-*b*-A-1	38.5 (220)	
PE-*b*-A-2	45.5 (260)	
PE-*b*-A-3	70.0 (400)	
PE-*b*-A-4	114 (1,090)	
PE-*b*-A-5	149 (651)	
PE-*b*-A-6	158 (902)	

Source: Reference [29].

Table 10.8. Abrasion Resistance of PEA and PE-*b*-A Elastomers (ASTM D 1044, Taber Abrasion)

Polymer	Weight Loss (mg/1,000 revolutions)		
	CS-17 Wheel	H-18 Wheel	H-22 Wheel
PEA-2	4	89	60
PE-*b*-A-1	46	94	
PE-*b*-A-2	25	81	
PE-*b*-A-3	14	70	
PE-*b*-A-4	11	65	
PE-*b*-A-5	12	46	

Notes: PE-*b*-A from Arkema technical literature. PE-*b*-A samples injection molded, aged 14 days at 23°C and 50% humidity.

10.5.5 Compression Set

When measured under constant load conditions (ASTM D 395, Method A), polyamide elastomers exhibit very low compression set because of their high-modulus and load-bearing capacity. Test results from measurements with constant compression (ASTM D 395, Method B) indicate that the high initial modulus is somewhat detrimental because of the very high stress level generated (see Table 10.9) [29].

10.5.6 Flex Properties

The flex resistance of a TPE depends in general on the T_g of soft segments and its distance from the test temperature. The polymer becomes leathery as the T_g is approached. Copolymers with a greater phase separation usually have lower T_g values and often exhibit a better performance in flex fatigue tests. For example, PEA-1 with the $T_g = -40°C$ has a considerably better flex performance than PEA-2 ($T_g = -28°C$) (see Table 10.10).

Table 10.9. Compression Set of PEA and PE-*b*-A Elastomers (ASTM D 395, Methods A and B)

Polymer	Compression set (%)		
	Temperature (°C)	Method A	Method B
PEA-1	RT	—	36
PEA-1	100	—	79
PEA-2	RT	2	40
PE-*b*-A-1	70	62	—
PE-*b*-A-2	70	54	—
PE-*b*-A-3	70	21	—
PE-*b*-A-4	70	10	—
PE-*b*-A-5	70	6	—
PE-*b*-A-6	70	6	—

Table 10.10. Ross Flex Growth Test (ASTM D 1052) for PEA

Sample		Test temperature	
		−25°C	−35°C
PEA-1	Cycles[a]	1,050,000	1,011,000
	% Cut growth	0	0
PEA-2	Cycles	26,800	12,300
	% Cut growth	800	1,000[b]

Notes:
[a]Test stopped at 1 million cycles.
[b]Sample failed.

10.6 Chemical and Solvent Resistance

As in all segmented block elastomers, the nature of the hard segment has a large effect on chemical and solvent resistance. The semi-crystalline amide hard segments of the PEA have low solubility in many solvents. Thus, the material has an excellent resistance to oil, fuels, and grease. It is also resistant to phosphate-based hydraulic fluids but tends to swell in toluene. With the increased proportion of hard segments the chemical and solvent resistance also increases (see Table 10.11) [29].

Table 10.11. Chemical Resistance of PEA (ASTM D 543, Immersed for 7 days at RT)

Polymer	Change	ASTM No. 3 Oil	Brake Fluid	Skydrol 500	Toluene	Lithium Grease
PEA-2	Volume (%)	+1.5	+29	+31	+41	+0.5
	Weight (%)	+1.3	+27	+29	+31	+0.8
	Hardness (points)	+2	+6	−9	−5	+3
PEA-4	Volume (%)	+0.7	+16	+21	+35	+0.3
	Weight (%)	+0.6	+14	+20	+27	+0.3
	Hardness (points)	+6	−8	−15	−13	−3
PEA-5	Volume (%)	—	+17	+12	—	—
	Weight (%)	—	+15	+11	—	—
	Hardness (points)	—	−20	−8	—	—

Note: Samples were annealed at 200°C for 3 hr.

Table 10.12. Examples of Electrical Properties of PEA and PE-*b*-A Elastomers

Property	Test Method	PEA[a]	PE-*b*-A
Volume Resistivity (Ω cm)	ASTM D257	8.13×10^{10}	2.10×10^{11} to 6×10^{12}
Surface Resistivity (Ω)	ASTM D 257	3×10^{12}	4×10^{10} to 5×10^{10}
Dielectric Constant at 60 Hz	ASTM D 150	10.3	6.0 to 12.8[b]
Dissipation Factor at 60 Hz	ASTM D 150	0.092	0.02 to 0.17[b]

Notes:
[a] 22°C and 50% relative humidity.
[b] Depending on grade.
Source: References [32, 33].

10.7 Electrical Properties

Polyamide elastomers are suitable for low voltage applications and for jacketing, where their mechanical toughness, oil, solvent and chemical resistance can be utilized. The electrical properties of individual types vary with their composition. Examples for PEA and PE-*b*-A are in Table 10.12.

10.8 Other Properties

10.8.1 Weatherability

PEA exhibits a very good outdoor and indoor resistance to ultraviolet (UV) radiation even without stabilizers. Since the original color of PEA is yellow brown, there is no discernible discoloration after 2,500 hr of exposure [25]. Other polyamide elastomers require the addition of UV stabilizers [30, 31].

10.8.2 Adhesion

The adhesive properties of PEA were measured on lap shear specimens prepared from wire-brushed, unprimed aluminum sheets and thin PEA films by compression molding. Lap shear strength values ranging from 7.6 to 9.2 MPa (1,100–1,300 psi) were obtained at room temperature [32].

10.9 Compounding

Polyamide elastomers can be compounded with other polymers and/or ingredients to alter or enhance their properties such as toughness, flexibility, tack, resistance to oxidation and ozone, flame resistance, and cost [33].

Blends with other polymers are done in the melt stage mostly in a compounding extruder. Polymers compatible with the polyamide block are likely to produce hard material, while those compatible with the soft polyether or polyester segment are likely to produce a soft, tacky, flexible composition. Other possibilities are using polyamide elastomers as impact modifiers for engineering thermoplastics, such as PET, PBT, PPO, PPS, or increasing the hardness and flexural modulus of the polyamide

TPE by the addition of small amounts of polyamide or PBT.

Stabilizers are added in sufficient amounts by the manufacturers to assure stability during the manufacture of the polymer and during its storage. However, additional stabilizers may be required if the material would tend to deteriorate during service due to thermal oxidation, ozone attack, UV radiation, or hydrolytic degeneration. TPEs with polyether soft blocks may be susceptible to thermal and UV radiation. Combinations of phenolic antioxidants and/or dithiocarbamates with dilauryl thiodipropionate effectively increase oxidative stability. Additional stabilizers, such as benzothiazoles, will increase resistance to UV radiation and prevent discoloration [34].

Fillers such as carbon black, glass fibers, or mineral fillers will affect processing behavior and/or physical and mechanical properties.

Pigments, dyes, and color concentrates are used to obtain desired colors or color shades. For polymers with high processing temperatures, special high temperature pigments or dyes are usually required.

Other additives include the following:

- processing aids or lubricants that improve the processing behavior, flow, decrease viscosity, decrease tackiness and improve surface gloss of the finished product
- antistatic or antiblocking agents
- flame retardants for flame-resistant compositions
- blowing agents to produce foams
- fungicides.

10.10 Processing

Polyamide TPEs have been processed by injection molding, extrusion, blow molding, thermoforming, and rotational molding. In general, they can be processed in a relatively wide range of temperatures and provide a wide processing window and good melt strength.

10.10.1 Rheology

The viscosity–shear rate correlation is shown in Fig. 10.4. Because the processing conditions are generally related to the melting points of the polymers, the shear rate must be considered during zone temperature adjustment for the given screw design or equipment.

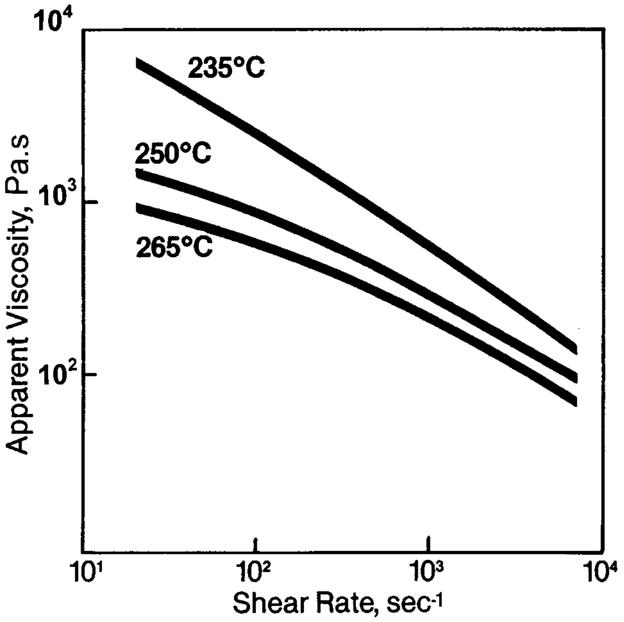

Figure 10.4. Apparent viscosity vs. shear rate for a PEA elastomer (Courtesy Springer) (refer to Table 10.1 for specifics).

10.10.2 Drying

Polyamide TPEs must be completely dried prior to any melt processing, using the standard equipment for polyamides. Typical drying conditions for PEA are 4–6 hr at 100–110°C (212–230°F) with air of –30 to –40°C dew point in the dehumidifying hopper dryer and then stored under dry conditions at 15–30°C (59–86°F). The material should have less than 0.02% moisture [35]. The typical drying curve for a PEA elastomer is in Fig. 10.5.

Polyether-*block*-amide must be completely dry at the moment of use (less than 0.20% of moisture) using the normal techniques for polyamides. Recommended drying procedure is 4 hours at 80°C (176°F) or 6 hours at 70°C (158°F). The granules of PE-*b*-A are packed in sealed bags with moisture content ≤ 0.15% and are ready to use. The bags should be brought to the processing plant at least 24 hr prior to use, to prevent condensation of the ambient moisture. If the bags remain open for more than one hour, the material has to be oven dried to the maximum moisture content of 0.20%.

10.10.3 Injection Molding

General conditions for the injection molding of PEA and PE-*b*-A are in Tables 10.13 and 10.14, respectively. Since the polymers are available in many grades, specifics about processing conditions,

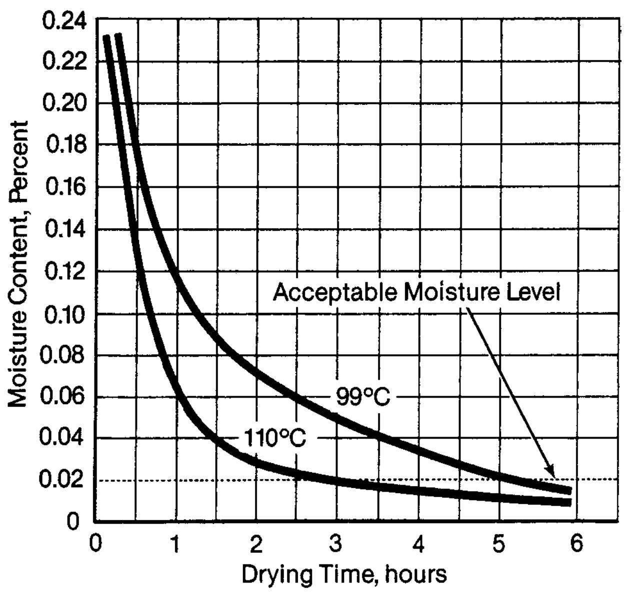

Figure 10.5. Typical drying curve for a PEA elastomer.

Table 10.13. General Conditions for Injection Molding of PEA Elastomers

Zone	Temperature	
	°F	°C
Feed	450	232
Transition	475	246
Metering	475	246
Nozzle	460	237
Melt	475	237
Mold	170	77
Pressure	psi	MPa
Injection	1,200	8.3
Back Pressure	100	0.7
Screw Speed (rpm) 80–100		
Cycle Time (s)		
Injection	10	
Hold	5	
Cooling	20	

Source: Reference [37].

screw configurations, mold designs, and safety precautions should be obtained from the resin manufacturers.

Shrinkage on molded parts varies significantly and depends on the material, on the thickness and shape of the molded part, and on molding conditions. For PEA, the reported mold shrinkage is 1.5% parallel to the flow and the perpendicular shrinkage, 1.0% [36]. Average shrinkage for PE-*b*-A is reported to be 0.5–1.0% [37] and for PA copolymers based on PA 12 is 0.7–1.0% [38]. Similar to many other TPEs, polyamide TPEs can be used for overmolding. Compatibility with other thermoplastics as applies to overmolding and to a degree to coextrusion is shown in Table 10.15.

Table 10.14. Recommended Temperatures for Injection Molding of PE-*b*-A

Grade	Melt Temperature, °C (°F)	Mold Temperature, °C (°F)
PE-*b*-A-1	180–200 (356–392)	20–40 (68–104)
PE-*b*-A-2	200–240 (392–464)	20–40 (68–104)
PE-*b*-A-3	200–240 (392–464)	20–40 (68–104)
PE-*b*-A-4	240–280 (464–536)	20–40 (68–104)
PE-*b*-A-5	240–280 (464–536)	20–40 (68–104)

Sources: References [37, 39].

10.10.4 Extrusion

Polyamide TPEs can be extruded and coextruded into a variety of products, including cast or blown films (down to 10 μm or 0.0004 in.), sheets, tubings and profiles, and wire and cable jacketing. General conditions for extrusion of PEA and PE-*b*-A are shown in Tables 10.16 and 10.17, respectively.

10.10.5 Other Processing Methods

In addition to injection molding and extrusion, polyamide TPEs can be processed by blow molding, rotational molding, and thermoforming [40]. Each of these methods requires a specific grade.

10.11 Bonding and Welding [38]

10.11.1 Bonding

Adhesive bonding is possible by using single component cyanoacrylate or acrylic adhesive or two-component polyurethane or epoxy adhesives. In most cases, some surface treatment of the bonded parts, such as corona, low-pressure plasma, or flame treatment, are needed. In some cases a primer is applied prior to the application of the adhesive.

Table 10.15. Compatibility of Selected PE-*b*-A Grades in Coextrusion and Overmolding

Insert, Resin, Minor Component	Overmolding, Coextruding, or Alloy Component Resin				
	PE-*b*-A-1	PE-*b*-A-2	PE-*b*-A-3	PE-*b*-A-4	PE-*b*-A-5
PE-*b*-A-1	G	G	G	G	G
PE-*b*-A-2	G	G	G	G	G
PE-*b*-A-3	G	G	G	G	G
PE-*b*-A-4	F	G	G	G	G
PE-*b*-A-5	F	F	G	G	G
Polyamide 11 and 12	F	F	G	G	G
Polyamide 6	P	P	P	P	P
Polycarbonate	G	G	G	G	G
Plasticized PVC	G	G	G	G	G
Rigid PVC	G	G	G	G	G
Polyurethane	G	G	G	F	F
EVA (28% VA)	G	G	G	G	G
Carboxylated NBR	G	G	G	G	G

Source: Pebax® Processing Publication 2624E/0.1.97.

Table 10.16. General Conditions for Extrusion of PEA Elastomers

Zone	Temperature	
	˚F	˚C
Rear	450	232
Middle	470	243
Front	480	249
Die	480	249
Melt	480	249
Screw speed (rpm)	50	—

Source: Reference [37].

Table 10.17. Recommended Temperatures for the Extrusion of PE-*b*-A

PE-*b*-A Grade	Recommended Temperature Range, ˚C (˚F)
PE-*b*-A-1	170–210 (338–410)
PE-*b*-A-2	190–220 (374–428)
PE-*b*-A-3	210–230 (410–446)
PE-*b*-A-4	210–230 (410–446)
PE-*b*-A-5	210–240 (410–464)

Source: Pebax® Processing Publication 2624E/01.97, Arkema.

10.11.2 Welding

Polyamide TPEs can be welded by using any of the following methods:

- heated tool welding
- high-frequency and heat impulse welding
- ultrasonic welding
- spin welding
- laser welding
- vibration welding.

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11 Thermoplastic Polyether Ester Elastomers

11.1 Introduction

Thermoplastic polyester elastomers (copolyesters, COPEs) are multi-block copolymers, which can be represented by a generalized formula $(\text{–A–B–})_n$ [1]. They are essentially copolyether esters with alternating, random-length sequences of either long-chain or short-chain oxyalkalene glycols connected by ester linkages [2]. Structurally, they are related to polyurethanes (Chapter 9) and polyamide elastomers (Chapter 10) in that they also contain repeating high-melting blocks that are capable of crystallization (hard segments) and amorphous blocks with a relatively low glass transition temperature (soft segments). Typically, the hard segments are composed of multiple short chain ester units such as tetramethylene terephtalate units and the soft segments are derived from aliphatic polyether and polyester glycols [2]. At useful service temperatures these materials resist deformation because of the presence of a network of microcrystallites formed by partial crystallization of hard segments. These microcrystallites function as physical cross-links. At processing temperatures the crystallites melt and form a viscous melt that can be shaped by usual melt-processing methods. After cooling the hard segments recrystalize and keep their shape. The ratio of hard to soft segments determines the characteristics of the product. Thus, the products range from soft elastomers to hard elastoplastics [2].

An example of the composition of such copolymer is [3]:

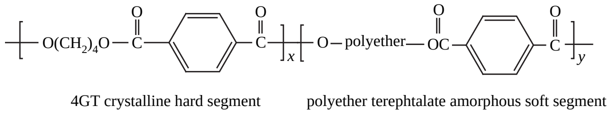
$$\text{— } [4GT]_x\ [BT]_y\ [4GBT]_z \text{ —}$$

where 4G is butylene glycol, B is poly(tetramethylene ether glycol), and T is dimethyl terephtalate.

Copolyesters were commercialized in the early 1970s by DuPont under the trade name Hytrel® and by Toyobo under the trade name Pelprene®. Within the following decade several other U.S. manufacturers developed their own versions of copolyester elastomers; GAF Corporation (Gaflex®), Eastman Chemical Products (Ecdel®), General Electric Company (Lomod®). They have been often referred to as *engineering thermoplastic elastomers* because of their high flexural modulus and other characteristics (see below) [4].

11.2 Synthesis

These multiblock thermoplastic elastomers are synthesized, for example, from dimethyl terephtalate, poly(tetramethylene ether glycol), and tetramethylene glycol via a transesterification reaction in the melt using titanium catalysts [5]. During the final stage of polymerization, excess short-chain diol is removed by distillation. Other monomers are also used [6] to produce a family of materials having a multi-block structure. An example of a COPE structure is given below [7]. A detailed review of synthetic methods is in [8].



The stoichiometry favors the formation of long sequences of tetramethylene terephtalate (4GT) units in block copolymers consisting of crystallizable 4GT hard segments and amorphous elastomeric poly(alkylene ether terephtalate) soft segments [7].

11.3 Morphology

The morphology of copolyether esters based on poly(tetramethylene terephtalate) (4GT) and poly (tetramethylene oxide) terephtalate (PTMOT) is rather complex. They have a two-phase morphology consisting of a pure crystalline 4GT phase surrounded by a single co-continuous amorphous phase. The amorphous phase contains uncrystallized hard segments and soft segments. The soft segments alone are composed of PTMOT. The phase separation occurs by crystallization of the 4GT hard segments and a thermally reversible three-dimensional network is formed resembling conventionally cross-linked elastomers. There are several models based on different methods of characterization of the morphology. These are reviewed in detail in [9]. A model of the microstructure and chain conformation is in Fig. 11.1. The DSC thermogram of a copolyester containing 58% of 4GT and 42% of PTMOT is in Fig. 11.2.

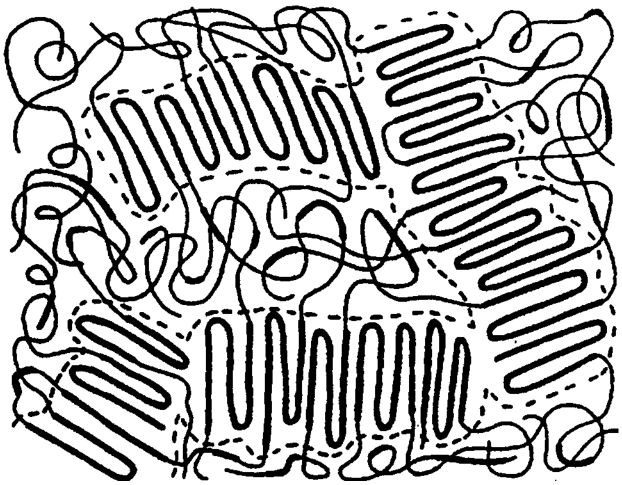


Figure 11.1. Model of microstructure of chain conformation in the polyester-polyether block copolymer materials.

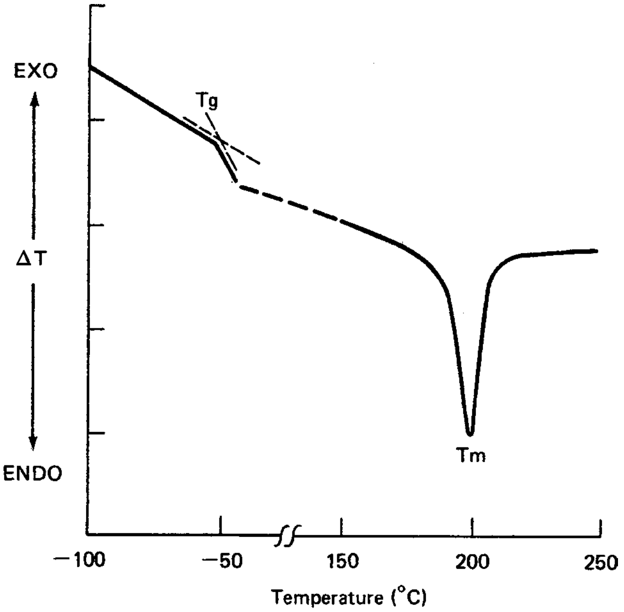


Figure 11.2. Differential scanning calorimetry thermogram for a COPE with 58 wt.% of 4GT (hardness Shore D 55). T_g (amorphous) is at –50°C, while the crystalline melt temperature, T_m is at 200°C.

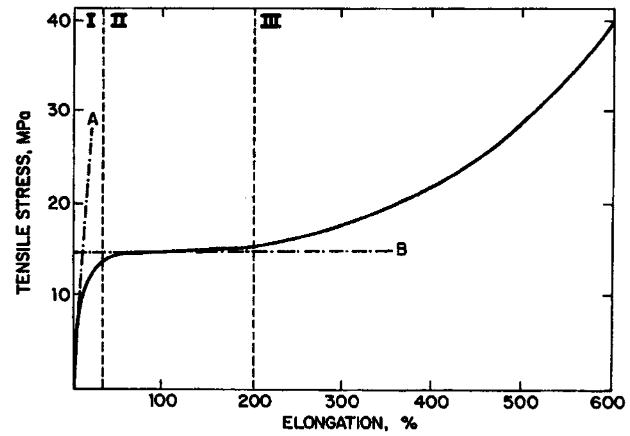


Figure 11.3. Stress–strain curve for polyester with 58 wt.% of 4GT (A) slope = Young's modulus (B) is yield stress.

11.4 Properties of Commercial COPEs

11.4.1 Stress–Strain Properties

These materials are elastic, but their recoverable elasticity is limited to low strains. When strained beyond the proportional limit, the materials undergo ductile yielding to ultimate elongations as high as 500%. The region where these resins act as springs is at low strains. The "useful elastic" region appears to be 7% for stiffer grades and 25% for more flexible grades [10]. A typical stress–strain curve for a medium hardness COPE at low strain rate is in Fig. 11.3. While the quantitative aspect of the curve depends on the hard segment of the copolymer, its shape reflects its morphology. The high initial (Young's) modulus (Region I) is due to pseudoelastic deformation. At greater elongation, in the Region II, a drawing process takes place, in which the original crystalline structure is reorganized. The process continues up to about 300% elongation and results in irreversible disruption of the crystalline matrix, which is indicated by a considerable permanent set observed on specimens stressed to these intermediate levels. At elongations higher than 300% only very limited increases in orientation occur and the stress is transmitted primarily by the rubbery phase until the specimen breaks (Region III) [11]. Elastic load bearing capacity (spring characteristics) of copolyester elastomers is compared to other materials in Fig. 11.4. They are a decade higher than engineering thermoplastics and a decade lower than rubber in useful elasticity. This stress–strain behavior shows that the COPEs are not engineering thermoplastics or rubber materials. They combine the strength of the engineering thermoplastics with some of the elasticity of rubber and are therefore described best as engineering thermoplastic elastomers as mentioned earlier [10]. The tensile stress for several grades of COPE at low strain is in Fig. 11.5.

11.4.2 Dynamic Properties

Copolyester thermoplastic elastomers exhibit exceptional dynamic performance. Operating within

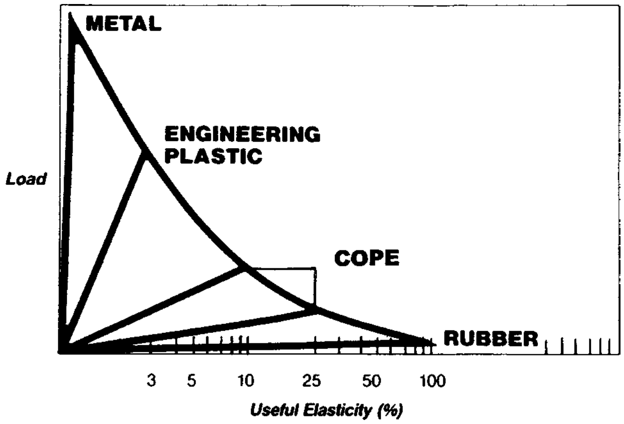


Figure 11.4. Elastic load-bearing capacity of several materials.

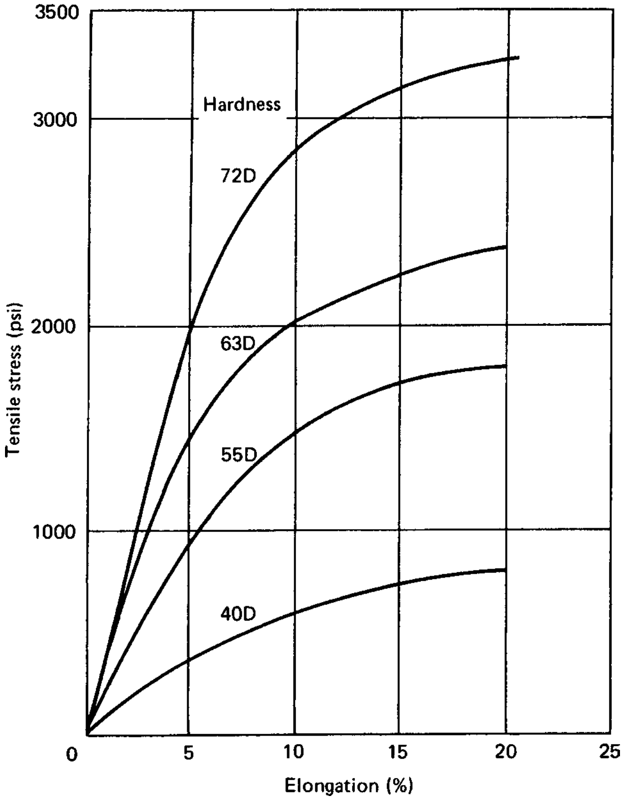


Figure 11.5. The tensile strength of COPE at low strain (strain rate: 1 in/min or 25.4 mm/min).

their elastic range, they are very resistant to creep and withstand high loads for long periods of time without noticeable stress relaxation. In addition, their dynamic response is excellent: they can be subjected to repeated cycles of tension and compression without any significant loss of mechanical strength. Parts functioning at low strain levels usually exhibit a complete recovery and continue to do so in cyclic applications with little heat buildup. Copolyester elastomers also exhibit excellent fatigue resistance as demonstrated by results from Goodrich Flexometer Test (Table 11.1). The sample temperature rises rather quickly because of hysteresis, and remains fairly constant for the rest of the test. Fatigue limits (defined as the limiting stress value that will yield a very large number of cycles before failure) for three different grades of COPEs are in Table 11.2. All these exceptional dynamic properties make them suitable for applications requiring long-term spring properties and long flex life [12].

Table 11.1. Temperature rise from hysteresis

COPE Grade, Shore D Hardness	Sample Temperature After 20 min	
	°C	°F
40	48	118
55	66	151

Note: Goodrich Flexometer, ASTM D 623, 2.54 mm (0.1 in. stroke), 1.0 MPa (145 psi) static load, 23°C (73°F)
Source: Reference [13].

Table 11.2. Fatigue Limits for General Purpose COPE Grades

COPE Grade, Hardness Shore D	Fatigue Limit	
	MPa	psi
40	5.2	750
55	6.9	1,000
72	11.0	1,600

Note: Samples tested to 2.5 million cycles without failure.
Source: Reference [13].

11.4.3 Cut Growth Resistance

Resistance to cut growth during flexing, as measured by Ross Flex Test is outstanding, mainly because of the high resilience and low heat buildup of these materials (see above). Table 11.3 shows the comparison of flex life of several COPE materials and thermoplastic polyurethanes.

11.4.4 Impact Resistance

COPEs exhibit outstanding impact resistance. For example, the more flexible grades with flexural modulus values below 300 MPa (43,000 psi) do not break when tested by conventional notched Izod tests. For such materials a drop-weight test is a better

Table 11.3. Flex Fatigue of COPE in Comparison to TPUs in Ross Flex Test

Material	Hardness Shore ASTM D 2240	Ross Flex (ASTM D 1025), kilocycles to 5× Cut Growth	
		23°C (73°F)	–40°C (–40°F)
COPE	40D (92A)	>300[a]	>12[b]
TPU-ESTER	80A	30	Immediate
TPU-ESTER	91A	>300[a]	Immediate
TPU-Ether	90A	144	Immediate
COPE	55D	>300[a]	>12[c]
TPU-ESTER	55D	84	Immediate
COPE	63D	280	Immediate

Notes: Pierced specimens.

[a] No change in the length of the pierced area after 300,000 cycles.

[b] Test terminated after 3×cut growth.

[c] Test terminated after 4×cut growth.

Properties were measured on injection-molded test specimens.

Source: *Handbook of Thermoplastics Elastomers*, Chapter 4 (Walker, B.M., Ed.), Van Nostrand Reinhold, New York, 1979, p. 119.

measure of impact resistance than Izod test since it simulates a more typical impact during use. Grades with flexural modulus 300 MPa or higher exhibit some notch sensitivity and may exhibit brittle impact failure at very low temperatures [13].

11.4.5 Responses to Changes of Temperature

Flexural modulus and other mechanical properties generally follow the pattern of increasing stiffness with decreasing temperature. Copolyester elastomers are generally superior to polyester thermoplastic polyurethanes in that they retain flexibility better at low temperatures, and display smaller changes in properties with temperature. The COPEs with the lowest moduli exhibit brittle points below –70°C (–94°F) and are suitable for cryogenic applications [14].

At elevated temperatures copolyester elastomers exhibit some softening and property loss as most thermoplastics. The mid- to high-modulus materials offer the best high-temperature performance and retain useful mechanical properties to temperatures as high as 180°C (356°F). At the temperature of 148°C (300°F) they retain about 50% of their room temperature properties [15]. Stress–strain curves at elevated temperatures for a COPE with hardness Shore D 55 are in Fig. 11.6.

11.4.6 Abrasion Resistance

Abrasion resistance is a complex function of tear strength, coefficient of friction, resilience, heat dissipation, and other properties and comparative values depend on the type of test. In general, COPEs are superior in abrasion resistance to many flexible materials including PVC and some rigid plastics [15]. If high mechanical strength is required in abrasive environment, copolyester elastomers will outperform polyurethanes and rubber. If scuff resistance is important, polyurethanes and rubber will often give

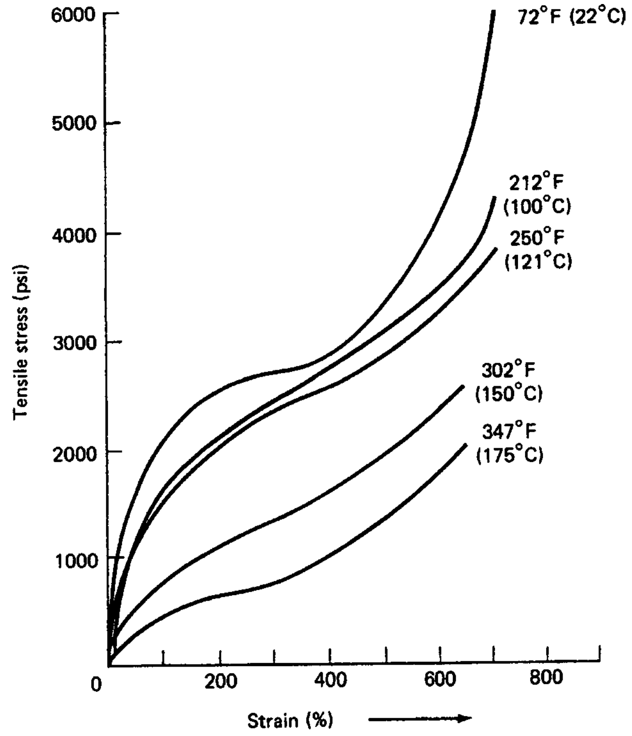


Figure 11.6. High temperature tensile properties of a COPE with hardness Shore D 55 (Courtesy Springer) [15].

better resistance than COPEs [15]. A comparison of abrasion test results from typical copolyester elastomers and thermoplastic polyurethanes (TPUs) are in Table 11.4.

11.4.7 Electrical Properties

Typically, COPEs are used in electrical applications for voltages 600 V and less. They are attractive for applications where their good dielectric properties, high mechanical strength, creep resistance, spring properties, high impact strength, abrasion resistance, wide range of service temperatures, and resistance to chemicals and solvents are required [16]. Typical electrical properties are listed in Table 11.5.

11.4.8 Chemical Resistance

Chemical resistance varies greatly with the composition of the copolymer, that is, the ratio of hard and soft segments. Hydrocarbon resistance depends on the resin stiffness; stiffer grades offer the best performance. Many COPEs are suitable for service in hot oil, grease, fuels, and hydraulic fluids.

Resistance to polar fluids, including water, acids, bases, amines, and glycols is also dependent on the composition of the copolymer, on pH, and temperature. Most copolyester elastomers are attacked by polar fluids at temperatures above 70°C (158°F).

Copolyester elastomers are essentially resistant to the same classes of chemicals and fluids as

Table 11.4. Comparison of Abrasion Tests from COPE and Polyurethanes of Comparable Hardness

Material	Hardness Shore (ASTM D 1044)	Abrasion Resistance		
		Taber Abrasion (ASTM D 1044) mg/1,000 rev		NBS Index (ASTM D 1630) %
		CS-17 Wheel	H-18 Wheel	
COPE	40D (92A)	3	100	800
TPU-ETHER	90A	6	No data	395
COPE	55D	5	64	3,540
TPU-ESTER	55D	2	80	1,200
COPE	63D	8	160	2,300
COPE	72D	13	66	4,900

Note: Properties were measured on injection-molded test specimens.

Source: *Handbook of Thermoplastic Elastomers,* Chapter 4 (Walker, B.M., Ed.), Van Nostrand Reinhold, New York, 1979.

Table 11.5. Electrical Properties at Room Temperature and 50% Relative Humidity

Property	ASTM Method	COPE Grade, Hardness Shore D			
		40	55	63	72
Volume Resistivity (Ω.cm)	D 257	8.2×10^{10}	1.2×10^{11}	9.7×10^{11}	1.8×10^{12}
Dielectric Strength, kV/mm (V/mil)	D 149	16.1 (410)	17.3 (440)	16.1 (410)	18.1 (450)
Dielectric Constant	D 150				
0.1 kHz		5.2	4.5	4.4	4.0
1 kHz		4.6	4.2	3.7	3.5
1,000 kHz		4.6	4.2	3.7	3.5
Dissipation Factor	D 150				
0.1 kHz		0.005	0.006	0.018	0.016
1 kHz		0.008	0.009	0.02	0.019
1,000 kHz		0.06	0.04	0.04	0.03

Hytrel® Design Guide—Module V, Publication H-81098 (00.2), DuPont Engineering Polymers, Wilmington, DE.

both polyester- and polyether-based polyurethanes [17]. Fluid resistance of three different copolyester elastomers is shown in Table 11.6.

11.4.9 Other Properties

Resistance to permeation. Copolyester elastomers are rather permeable to polar molecules such as water, but are resistant to penetration by nonpolar hydrocarbon and refrigerant gases.

Resistance to ionizing radiation. In contrast to many elastomers, which tend to embrittle when exposed to ionizing radiation (electron beam or gamma rays) due to cross-linking or soften due to main chain scission, copolyester elastomers resist to radiation doses up to 150 kGy (150 kJ/kg).

Table 11.6. Resistance to Fluids

Fluid	COPE1	COPE2
Oils	B	A
Aliphatic Hydrocarbons	B	A
Gasoline	C	A
Alcohols	B	B
Ketones	B/C	B
Ethylene Glycol	—	A
Fluorinated Hydrocarbons	—	A
Weak Acids	B	A
Strong Acids	A	B/C
Bases	A	A/B
Phenols	—	C
Salt Solutions	A	A
Organic Acids and Oxidants	C	B/C

Note: A = excellent; B = good to moderate; C = poor.
Source: Reference [17].

Flame resistance. Without modification, copolyester elastomers are rated HB by the UL flame resistance test. Compounded grades containing proper flame retardants will meet UL 94-VO [18].

Weathering resistance. Copolyester elastomers are not resistant to exposure to sunlight for extended periods of time and require an addition of chemical UV absorbers, such as substituted benzotriazoles, or carbon blacks (if color is not an issue), or titanium dioxide (for white or colored compounds). Properly protected COPEs retain their properties after 10 years of exposure to Florida climate [18].

Thermal properties. Typical melt temperatures of COPEs range from 170°C to 248°C (340°F to 480°F). As a rule, stiffer grades have higher melting points and their melting and crystallization temperatures are closer together than the more flexible grades. Typical melting behavior of several commercial grades of copolyester elastomers are in Table 11.7. Copolyester elastomers without antidegradants rapidly degrade in air at elevated temperatures, with a reduction of polymer intrinsic viscosity [19]. However, properly formulated compositions containing a stabilizer package (e.g., hindered phenolic antioxidant and secondary amine antidegradant) are thermally very stable and do not change significantly after prolonged periods at elevated temperatures, for example, up to one hour at processing temperatures. The slight change in melt flow rate indicates a high thermal stability of the resin (see Fig. 11.7).

Table 11.7. Melting Characteristics of Several General Purpose Grades of COPE

COPE Grade, Hardness Shore D	Melt Temperature, Peak of Endotherm, °C (°F)	Melt Complete, Extrapolated End Point, °C (°F)	Crystallization Temperature, Peak of Exotherm, °C (°F)	Glass Transition Temperature, T_g °C (°F)	Heat of Fusion, H_f J/g
35	156 (313)	180 (356)	107 (225)	–40 (–40)	8
40	170 (338)	190 (374)	120 (248)	–37 (–35)	17
47	208 (406)	225 (437)	170 (338)	–45 (–49)	27
55	215 (419)	230 (446)	173 (343)	–35 (31)	33

Note: Differential Scanning Calorimetry (ASTM D 1238).
Source: Hytrel®, Product Information, Publication E-84283-1 (11/93), and Injection Molding, Publication H-81091 (00.1), DuPont Engineering Polymers, Wilmington, DE.

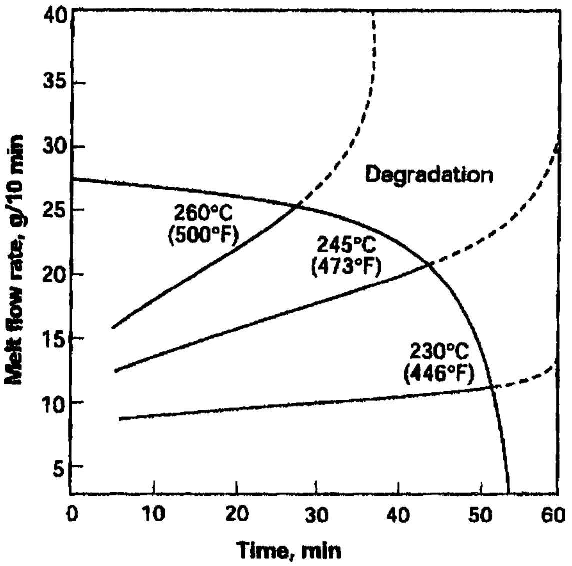


Figure 11.7. Thermal stability of a general-purpose resin at processing temperatures (moisture content <0.1%).

11.5 COPE Blends

Because of the low melt viscosity and melt stability COPEs can be blended with other COPE grades or with entirely different polymers. In general, the blending accomplishes the following [20]:

- Improving impact resistance at low temperature
- Providing elastomeric character
- Compatibilizing the mixture.

There are many possibilities and only few can be mentioned here.

11.5.1 Blends of Different Grades of COPE

An example is blending of a 4GT homopolymer with substantial amounts of soft and medium hardness copolyester elastomers (4GT/PTMOT) to attain higher yield strength at room temperature and greater flexibility and better impact resistance at low temperatures [21, 22]. A blend of this sort often contains an added chain extension agent such as carbodiimides or a multifunctional epoxide [20].

11.5.2 Blends with Other Polymers

Blends of polyester resin-polycarbonate with a copolyether ester are often further modified to include rubbery impact modifier of the general class of rubbery polymers grafted with vinyl monomers (e.g., methacrylates and acrylates) [23].

Other blends are immiscible mixtures of copolyester elastomer with dissimilar polymers such as polypropylene [24] or polyacetal [25] with the objective to improve processing and to toughen the base polymer.

Another example is a dynamically vulcanized blend of an elastomer and a COPE, in which the COPE is forming the continuous phase with the cross-linked elastomer being the disperse phase. The objective is to obtain a more elastic molding compound [20].

Blends of COPE with plasticized poly(vinyl chloride) (PVC) have improved mechanical properties such as modulus, elongation at break, tear strength, hardness, tensile strength, dynamic modulus, and impact strength [26, 27], low temperature flexibility and low temperature flex life [28] as the COPE content is increased. At concentrations of 75% of COPE, particles of the COPE are dispersed in the continuous phase. AT 85% COPE the phases are co-continuous without phase inversion. There are two crystalline phases, 4GT and PVC, but only a single glass transition [29].

11.6 Processing

11.6.1 General

Copolyester elastomers can be processed by injection molding, compression and transfer molding, blow molding, and rotational molding [30] on standard thermoplastic processing equipment using mostly conventional techniques. They can be readily extruded and calendered [31–33]. The polymers have relatively low viscosity, good melt stability, and harden rapidly from the molten state. The excellent melt stability allows the addition of regrind to the virgin polymer in amounts up to 50% [30].

Processing conditions are generally based on melting temperatures of the polymers, which are typically related to their morphology, that is, hardness (see Table 11.7). The melt temperature at the die of the machines for most melt-processing techniques should always be equal to or greater than the temperature at which the polymer is completely melted.

For good results and to attain best ultimate properties, it is essential that the polymers and compounds prepared from them be dry for processing. Most of the copolyester elastomer manufacturers dry them to less than 0.1% moisture content and supply them in moisture-proof containers. Then the materials can be used directly from sealed containers without drying. However, if the material, which is hygroscopic, is exposed to ambient atmosphere for more than one hour it may absorb enough moisture from the air (see Fig. 11.8) to cause degradation during processing. When drying COPE, dehumidified air ovens are recommended. Typically, drying takes 2–3 hr in a dehumidified oven at 100°C (212°F) or overnight at 70°C (158°F). Drying ovens without dehumidifiers may be used but will require 4–6 hr or more, depending on quantity being dried and the humidity in the environment [34]. Prolonged drying (more than 12 hr) is not recommended. If regrind is used, it also has to be dried prior to the use.

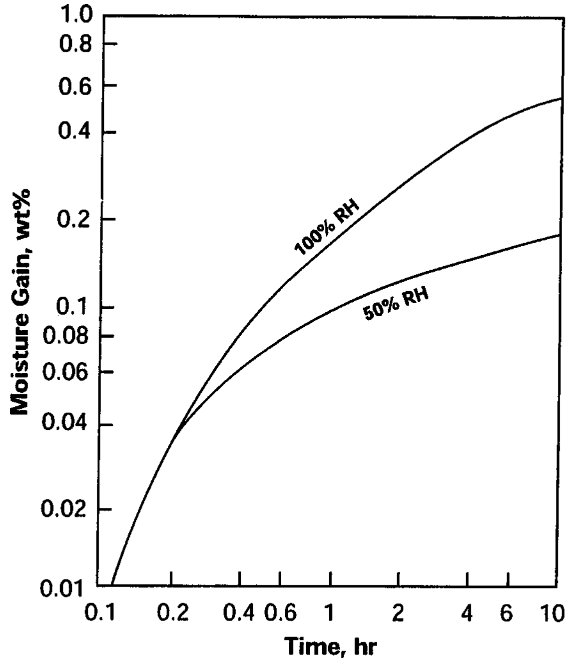


Figure 11.8. Moisture absorption (ASTM D 570) at ambient temperature for COPE with hardness Shore D 55.

11.6.2 Melt Rheology

The apparent melt viscosity of COPEs decreases much less with the increase in shear rate than that of most other polymers [35]. Over the range of shear rates common for calendering, extrusion, and injection molding (10–7,000 s^{-1}) the melt viscosity drops from 1,000 to 300 Pa.s, while a typical polyurethane of a similar hardness will drop from 7,000 to 300 Pa.s over the same range. Because of their low viscosity at low shear rate, COPEs are suitable for low-shear processes, such as calendering, rotational molding, melt casting, and impregnation of porous substrates [36]. The viscosity can be readily controlled by adjusting the process temperature. The resin manufacturers offer a variety of products with rheological properties matching the process. Dependence of viscosity on shear rate is in Fig. 11.9 and on temperature in Fig. 11.10.

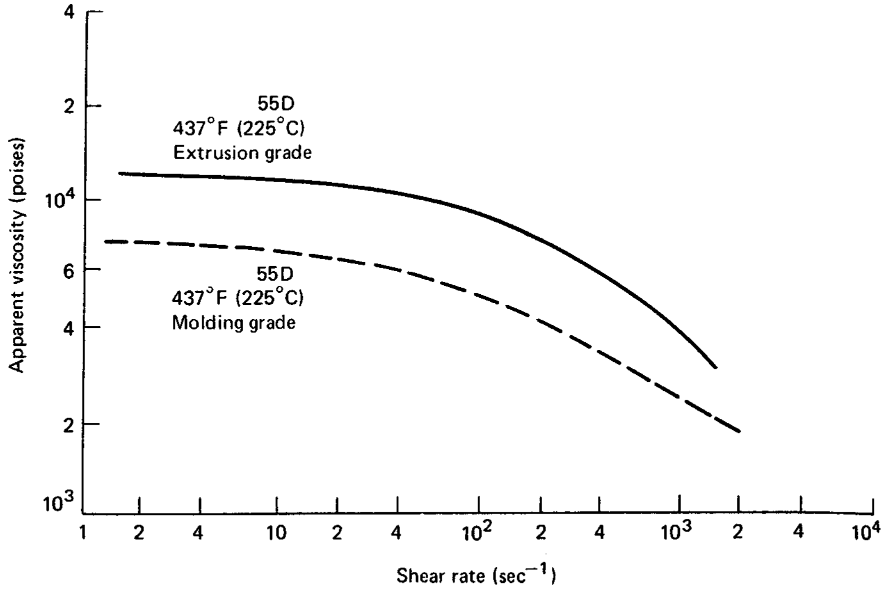


Figure 11.9. Apparent viscosity vs. shear rate for an extrusion grade COPE.

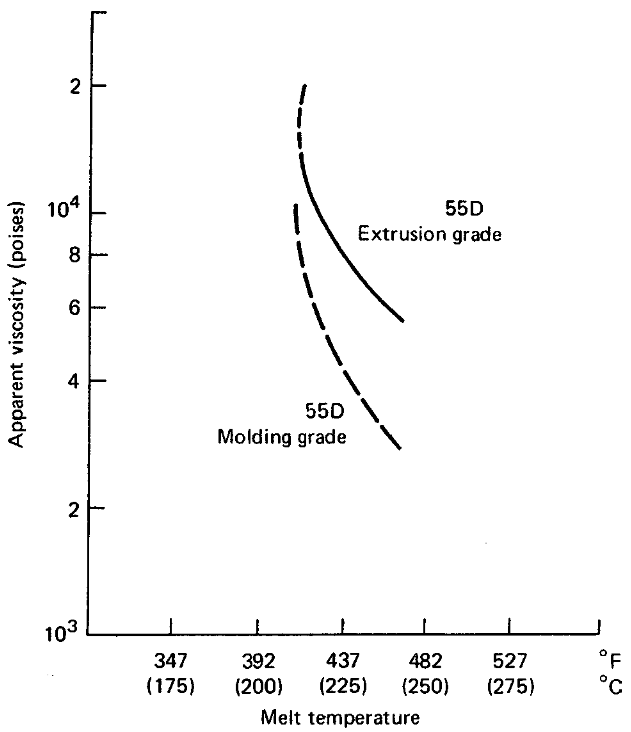


Figure 11.10. Viscosity vs. temperature for extrusion and molding grades of COPE (shear rate: 139 sec^{-1}).

11.6.3 Injection Molding

Copolyester thermoplastic elastomers can be processed on standard injection molding machines. Even when the standard grades of COPE degrade, no corrosive products are formed and therefore the equipment does not need to be made from corrosion resistant materials.

11.6.3.1 Screw Design

General purpose screws with a gradual transition zone are recommended. To avoid excessive shearing of the polymer or bridging of the pellets, the screw compression ratio should not exceed 3:1 to 3.5:1. The metering zone should be relatively deep, about 2.5–3.0 mm (0.100–0.120 in.) for a 60 mm (2.36 in.) diameter screw. The recommended screw L/D ratio should be at least 20:1 to assure good melt uniformity and good mixing.

11.6.3.2 Clamping Force

Most well-built molds can be adequately clamped if the machine has a clamping force of 48–69 MPa (3.5–5.0 tons/in.^{2}) based on projected area, since injection pressures are seldom over 100 MPa (14 kpsi) and fill rates are moderate [37].

11.6.3.3 Molding Conditions

Molding conditions can be varied over a broad range of temperatures since COPEs have excellent melt stability and low melt viscosity as mentioned previously. Higher melt temperatures can be used for thin-walled parts to aid filling the mold, while thicker parts can be molded with melt temperatures close to the polymer melt points.

Injection pressures are usually in the range of 6,000–14,000 psi (40–95 MPa). In general, shrinkage is reduced by the increase of injection pressure, which compresses elastomeric materials. The lower the hardness of COPE being molded, the greater effect a higher molding pressure has on controlling mold shrinkage (see Section 11.6.3.5). Excessive pressure can result in overpacking and sticking of the part in the mold cavity [37].

Mold filling rates vary with the thickness of the part and its geometry. Thin wall moldings (thinner than 0.125 in. or 3 mm) should be filled rapidly before the melt viscosity becomes too high. Thicker parts (wall thickness of 0.25 in. or 6 mm) need much slower filling rates.

Molding cycle time is depending on part size and the temperatures of the melt and of the mold cavity. Typical range of cycle times is 0.5–3 min. Molding cycles can be adjusted to reduce shrinkage. Optimum screw forward time can be found by successively increasing time until the weight of the part no longer increases, indicating that the gate has frozen. At this condition the shrinkage (see Section 11.6.3.5) will be at its minimum [38].

Details regarding injection molding of general-purpose grades are in the following tables: Table 11.8 (Recommended optimum melt temperatures), Table 11.9 (Setup conditions), Table 11.10 (Typical operation conditions).

11.6.3.4 Molds

Molds for most grades of COPEs can be made from standard materials used for the majority of thermoplastics since most of the COPE grades have no corrosive action on the alloys used for molds and cavities. An exception is when molding flame-retardant compounds containing halogens at high temperatures or employing long residence times. Textured and mat finished cavity surfaces minimize the effects of flow lines or marks or scratches on the part. Highly polished, plated surfaces may cause difficulty in ejecting the soft grades of COPE below Shore hardness 47D [37]. Details pertaining to mold design (gates, sprue system, runner system, venting, part ejection etc.) are in covered thoroughly in reference [37].

Table 11.8. Recommended Optimum Melt Temperatures for General Purpose Grades of COPE

COPE Grade, Shore D Hardness	Recommended Optimum Melt Temperature, ˚C (˚F)
40	200 (390)
55	230 (445)
63	240 (465)
72	245 (475)
82	250 (480)

Source: Hytrel® Injection Molding, Publication H-81091 (00.1), DuPont Engineering Polymers, Wilmington, DE.

11.6.3.5 Shrinkage

As in all thermoplastics, the shrinkage of injection molded COPE parts depends on many factors, such as:

- COPE grade
- Part geometry and thickness
- Molding conditions (injection pressure, SFT, mold temperature, etc.)
- Mold design, runner and sprue systems, gate size.

Shrinkage is measured on a standard test specimen at room temperature and 50% relative humidity 24 hr after molding according to ASTM D 955. It increases significantly after molding, but tends to reach maximum after 24 hr [37].

Nominal values of shrinkage for different grades obtained at standard conditions are in Table 11.11.

Most grades of COPE exhibit nominal mold shrinkage from 0.5% to 3% with thick-walled

Table 11.9. Injection Molding Setup Conditions for General Purpose Grades of COPE

COPE Grade, Shore D Hardness	Melt (Stock) Temperature Range, ˚C (˚F)	Typical Cylinder Temperature, ˚C (˚F)			
		Nozzle	Front	Center	Rear
40	190–220 (325–425)	190 (375)	205 (400)	205 (400)	180–205 (355–400)
55	220–250 (430–480)	220 (430)	235 (455)	235 (455)	205–235 (400–455)
63	235–260 (455–500)	235 (455)	245 (475)	245 (275)	220–245 (430–475)
72	240–260 (465–500)	240 (465)	245 (475)	245 (475)	220–245 (430–475)
82	240–260 (465–500)	240 (465)	245 (475)	245 (475)	220–245 (430–475)

Source: Hytrel® Injection Molding, Publication H-81091 (00.1), DuPont Engineering Polymers, Wilmington, DE.

Table 11.10. Typical Operating Conditions for Injection Molding of COPEs

Screw Rotation Speed	100 rpm is adequate in most cases; higher for compounds with additives
Screw Forward Time (SFT)	SFT depends strongly on the grade, is shorter for harder grades: Shore D 72–82: 4–5 s/mm (101–127 s/in.) Shore D 44–63: 5–6 s/mm (127–152 s/in.) Shore D 35–40: 7–8 s/mm (178–203 s/in.)
Injection Speed	Varies with part thickness and geometry
Injection Pressure	To be set to the minimum pressure required for filling the cavity
Holding Pressure	For grades above Shore D 55 the holding pressure can be set equal to the injection pressure; for softer grades (below Shore D 47), it should be set to follow a decreasing pressure profile
Back Pressure	0.34–0.55 MPa (50–80 psi) can be used to improve mixing

Source: Hytrel® Injection Molding, Publication H-81091 (00.1), DuPont Engineering Polymers, Wilmington, DE.

Table 11.11. Nominal Values of Shrinkage for General-Purpose COPE (ASTM D 955)[a]

COPE Grade (Shore D Hardness)	Recommended Temperature, °C (°F)[b]	Shrinkage (%)
35	190 (375)	0.5
40	200 (390)	0.8
47	240 (465)	1.4
55	240 (265)	1.6

[a]Measured on standard test specimens in flow direction, 3.2 mm (0.125 in.) thick molded at 70 MPa (10,150 psi) at optimum SFT and recommended melt temperatures shown[b].

parts showing higher shrinkage, while thinner parts exhibit low shrinkage with an exception of very thin parts. The actual shrinkage can be calculated from the nominal value by considering factors such as actual mold temperature, actual injection pressure, and actual thickness [37].

Post-molding shrinkage is measured after annealing parts at 120°C (248°F) for 4 hr. The absolute value of post-molding shrinkage even for stiffer and highly crystalline grades is small, typically less than 0.1%.

11.6.3.6 Overmolding (Insert Molding)

In this process a thermoplastic material is molded directly onto a second thermoplastic material (the insert). Copolyester thermoplastic elastomers mold best over other grades of COPE but can be used to mold over polybutylene terephthalate (PBT), polycarbonate, and acrylonitrile-butadiene-styrene (ABS) with good adhesion between the two materials [37].

For optimum results, the insert should have relatively low melting point (such as 190°C or 374°F or less), and preferably wide melting range for slower crystallization. To achieve a good bond, the material used as the overmold should be injected at a temperature 30°C (54°F) higher than the usual melt temperature used for its injection molding. That way the higher melting overmold material melts the surface of the insert and establishes a good bond. If this method of overmolding is not possible, the part can be designed by incorporating a mechanical bond (molded-in mechanical locking device) or by using some flash or projection, which can melt together to form a bond. The insert can be also mechanically abraded to form a rough surface or even coated with an adhesive to establish a good bond.

11.6.4 Extrusion

Best results in the extrusion of COPEs are obtained by using single-screw machines. Twin-screw extruders tend to generate excessive heat due to high shearing forces and are therefore not recommended. Since the melts of most COPEs are not corrosive to metals, the screws and barrels do not need to be made of corrosion resistant alloys. The screws should have hardened (nitrided) surfaces for good wear resistance, however. Extruder barrels used for common plastics, such as PVC, polyolefins of plasticized polyamides with length to diameter (*L*/*D*) ratios 24:1 or more will also be suitable for the extrusion of COPEs. The resin manufacturers recommend that the barrel be equipped with at least four heat control zones, and the temperature of each zone controlled by a separate thermocouple and proportional control instrument [39].

11.6.4.1 Screw Design

Simple three-zone screws having approximately equal length feed, transition (compression), and metering zones are sufficient for the extrusion of most COPE materials. The *L*/*D* ratio should be minimum 24:1 for good uniformity of extrudate (i.e., minimum variations in temperature and pressure). Compression ratios should be between 2.5 and 3.5:1, as determined by the depth of the feed zone channel divided by the depth of the metering zone channel.

Complex screw designs, especially high-shear mixing devices are not suitable because they cause excessive local heat buildup. However, certain deigns, such as barrier screws have been used successfully in critical extrusion applications (e.g., high-speed tubing extrusion) [39].

11.6.4.2 Processing Conditions

As in other melt processing of COPE, the resins have to be dried to the maximum moisture content of 0.1%. For details see Section 11.6.1.

The melt viscosity of the COPE extrudate depends significantly on its temperature as pointed out earlier (see Section 11.6.2). The melt temperatures slightly above the nominal melting point

(5–15°C or 10–30°F) give the highest viscosity and therefore the easiest handling in most extrusion techniques. Typical processing parameters for the extrusion of general-purpose copolyester thermoplastic elastomers are in Table 11.12.

11.6.4.2.1 Extrusion Techniques

The following extrusion techniques are used commonly to process COPEs:

Profiles of different size and complexity (smooth, ribbed, U-channels) can be extruded successfully using free extrusion. For more complex profiles vacuum calibration may be necessary.

Tubing is frequently produced by free extrusion, as long as its OD is 6 mm (0.25 in.) or less. Larger diameters are produced by the differential pressure sizing method, also called "vacuum calibration of tubing."

Monofilaments are prepared from medium viscosity extrusion grades by free extrusion. The melt temperatures of typically 15–20°C (30–40°F) above the nominal melting temperature should be used. The draw-down ratio, as measured by the die diameter relative to the monofilament diameter leaving the first water quench batch, should be between 4:1 and 10:1.

Cover extrusion is a method to cover different types of products, such as hoses, ropes, cables, and wires, using cross-head dies. The cross-head dies may be arranged with a pressure (packing) die or a tubing (sleeving) die [39].

Cast film process. In this technique molten COPE is extruded through a slit die onto a polished metal roll (referred to as "chill roll"), which quenches the melt. Cast films from COPE are as thin as 0.013 mm (0.0005 in.). To avoid sticking, the quench temperature should not exceed 50°C (122°F) for soft grades (Shore D 35–40), 80°C (176°F) for harder grades (Shore D 47–63) and 100°C (212°F) for Shore D 72 and harder grades.

The same technique is used for the production of *sheeting* with thickness ranging from 0.25 to 0.5 mm (0.010 to 0.020 in.). Sheeting of greater thickness is made on a three-roll finisher that is in the film casting line. The roll temperatures should be controlled individually. Typical roll temperatures are [39]:

Grades with hardness Shore D 35 and 40
15–30°C (59–86°F)
Grades with hardness Shore D 47–82
40–70°C (104–158°F).

The temperature of the upper roll is limited to the temperature at which the sheet sticks to it and is normally kept as low as possible [39].

Fabric coating is done either on a sheeting line or on an extrusion coating line. On the sheeting line the fabric is introduced above the extruded melt, between the top and middle rolls. In the extrusion coating line the melt is extruded through a slit die onto the fabric or other substrate in the nip between the chill and pressure roll.

Blown film from COPE is produced on a standard film blowing equipment. Because of the high strength of COPEs they can be extruded into films 250 μm (0.010 in.) thick with blow-up ratios of up 3:1. Softer grades (hardness Shore D 35 and 40) can be blown into films up to about 150 m (0.006 in.), at blow-up ratios up to approximately 2.8:1. In some cases antiblocking agents may be required to prevent blocking of the films (i.e., sticking to itself) or to the rolls in the extrusion line [39].

Table 11.12. Typical Processing Parameters for Extrusion of General-Purpose Grades of COPE

Processing Parameter	COPE Grade, Shore D Hardness		
	40	55 and 63	72
Barrel Temperature, °C (°F)			
Zone 1	155–165 (311–329)	195–210 (383–410)	205–210 (401–410)
Zone 2	170–180 (338–356)	210–225 (383–437)	210–215 (410–419)
Zone 3	170–180 (338–356)	210–225 (383–437)	215–225 (419–437)
Adapter and Neck, °C (°F)	170–180 (338–356)	210–225 (383–437)	215–225 (419–437)
Die, °C (°F)	170–180 (338–356)	210–230 (383–446)	215–230 (419–446)
Melt, °C (°F)	170–180 (338–356)	210–230 (383–446)	225–235 (437–455)

Source: *Handbook of Thermoplastic Elastomers* (Walker, B.M., Ed.), Van Nostrand Reinhold, New York City, 1979.

Coextrusion is common in combining COPEs with other polymers in hoses, tubing, profiles, sheeting, and film. Copolyester thermoplastic elastomers are compatible in coextrusion with most rigid and flexible PVC, melt-processable rubber (MPR), thermoplastic polyester resins, PBT and polyethylene terephthalate (PET). For coextrusion with incompatible resins a suitable intermediate "tie" layer is used to provide bond between the extruded layers.

Foam extrusion. Foamed profiles from COPE can be produced by extruding compositions containing a chemical blowing agent (e.g., azodicarbonamide). Typical specific gravity of foamed (cellular) products is in the range 0.6–0.8 [40].

11.6.5 Blow Molding

Because of the high melt strength typical for COPEs, these materials are well suited for blow molding. Resin manufacturers offer products designated specifically for this process. The blow molding machines used to produce hollow parts from COPEs are:

- Continuous extrusion machines
- Accumulator head machines.

The techniques used include conventional blow molding, coextrusion blow molding (simultaneous extrusion of two or more compatible layers through the parison wall) and sequential three-dimensional blow molding. The sequential blow molding is a development of coextrusion blow molding where the layers are "switched on and off" in a programmed way. This allows production of parts, which combine sections made from two or more resins, for example hard, rigid sections in one material and soft flexible bellows in a different material [41]. While sequential mold blowing technique is used for the manufacture of specific parts, the majority of parts from COPE are still processed by conventional techniques using continuous extrusion and accumulator head machines.

Screw design recommended for COPE blow molding is: three-zone screw L/D ratio minimum 24:1 with compression ratio between 2.7 and 3.5:1 (as measured by depth of feed zone divided by the depth of metering zone), nitrided (wear resistant) steel surface. Flight lands can be hard surfaced with an alloy (e.g., Stellite). Hard chrome plating of the other surfaces of the screw is also recommended [40].

Barrel design. Smooth, cylinder design, made from Xaloy 100/101 or 800 types (or equivalent) for improved wear.

Mold design. Production molds are made mainly from steel (machined or cast), beryllium copper (machined or cast), and aluminum (machined or cast). Other materials such as Kirksite (low melting metal alloy), filled epoxies, and cast polyurethanes are used mainly for prototypes or short production runs. Double dam type of pinch-off design is frequently used for COPE blow molding materials.

11.6.5.1 Processing Conditions

As in all melt processing the resins used in blow molding have to be dry with the maximum moisture content of 0.02% [40]. Resin that was exposed to air for an hour or longer and regrind have to be dried, typically 2–3 hr at 100–120°C (212–248°F) in a desiccant (dehumidifying) dryer.

Setup conditions for and typical processing conditions for blow molding grades of COPE are in Tables 11.13 and 11.14, respectively.

11.6.6 Melt Casting

Melt casting is a process combining elements of both extrusion and injection molding (details see in Chapter 4). Copolyester thermoplastic elastomers

Table 11.13. Setup Conditions for Blow Molding

COPE Grade, Shore D Hardness	Process Melt Temperature Range, °C (mid-point)	Mold Temperature (°C)	Mold Clamping Force N/cm Pinch Length
45	210–225 (215)	10–50	800–1,200
47	210–225 (215)	10–50	800–1,200
50	210–225 (215)	10–50	800–1,200
55	215–225 (220)	10–50	800–1,200
65	230–240 (235)	10–20	800–1,200

Source: Blow Moulding Processing Manual, Publication L-11866 (04.99), DuPont Engineering Polymers, Geneva, Switzerland.

Table 11.14. Processing Conditions for Blow Molding of COPE Resins (Blow Molding Grade, Hardness Shore D 47)

Process Parameter	Typical Range
Barrel Temperatures (˚C)	
Rear	220–240
Center	220–250
Front	220–250
Nozzle	220–250
Melt Temperature (˚C)	225–250
Parison Hold Temperature (˚C)	95–170
Core Rod Temperature (˚C)	150–190
Screw Speed (rpm)	80–120
Parison Molding Cycle (s)	
Injection	0.5–4.0
Hold	1–10
Blow Air Pressure (bar)	5–15
Blow Molding Cycle (s)	
Blow	4–10
Exhaust	3–5
Total Cycle Time (s) (Based on 3-Station Operation Making 3 Parts per Cycle)	10–15

Source: Blow Moulding Processing Manual, Publication L-11866 (04.99), DuPont Engineering Polymers, Geneva, Switzerland.

are suitable for this processing method because of their relatively low melt viscosity.

11.6.7 Rotational Molding

Hollow parts such as balls, boxes and small pneumatic tubeless tires are made by rotational molding from 35-mesh powders of COPE resins. The parts have void-free surfaces and uniform thickness.

For example, pneumatic tires with dimensions 12 × 4 in. weighing approximately one pound (0.45 kg) are produced in aluminum molds with wall thickness of 8.5 in [41]. Typical rotational speed of major axis is 6 rpm and that of minor axis 2 rpm and typical oven temperature is approximately 700 ˚F (370 ˚C). Typical oven time is 5.5 minutes which is short enough to prevent thermal degradation of the resin. Release agent is often used for this type of part since it provides lubrication for the polymer as it melts and permits air to escape during the melt flow across the surface of the mold [41].

11.6.8 Welding and Bonding

11.6.8.1 Welding

Copolyester films can be *welded by heat* relatively easily, with soft grades being easier to weld. Harder grades need to be wiped by a mixture of methylene chloride and dimethyl formamide in the ratio 1:2 [42]. The same solvent mixture is suitable for *solvent welding* of some copolyester grades.

Ultrasonic welding of all but the softer grades is difficult because of the polarity of the material [42]. *Laser welding* is especially well-suited for assembly of sensitive parts, electronic components, automotive parts, medical containers and devices, packaging materials, for example, and works best for transparent or slightly opaque materials that are still sufficiently transparent to laser light [43]. Other welding methods used are vibration and hot plate welding. Hot air and high frequency (HF) welding methods are mostly suitable for films and sheets [44].

11.6.8.2 Bonding and Adhesion

Bonding to metal is done commonly during injection molding, compression molding or melt casting operations using suitable metal preparation (degreasing, grit blasting) and application of primer systems. Copolyester thermoplastic elastomers can be bonded to tool steel, stainless steel, aluminum, and brass [42, 44].

Bonding to fabrics such as polyesters and polyamides can be accomplished by treating the substrates by isocyanates or isocyanate prepolymers [42].

Bonding of COPEs to *other thermoplastics* can be accomplished either by the use of a suitable adhesive (compatible by both materials) or by overmolding [44].

11.6.9 Finishing

Copolyester elastomers can be *coated* by a variety of coatings or *painted* usually without any special adhesion promoters provided no silicone-containing mold release agents were used in producing the part or no oil or other contamination is on its surface. An important consideration that the flexibility of the coating or paint matches the characteristics (stiffness) of the COPE material used [45].

Metallization of COPE is best accomplished by using the vacuum metallization procedure. Harder grades of COPE are better choice for metallization due to the low flexibility of the metal film [45].

Printing on copolyester elastomers can be done using standard equipment without difficulty. Both conventional and laser printing methods may be used [45].

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12 Ionomeric Thermoplastic Elastomers

12.1 Introduction

Exploratory work done predominantly after the Second World War led to discovery of a variety of copolymers of ethylene with other monomers, such as vinyl acetate [1], vinyl chloride [2], vinylidene chloride [3], vinylidene fluoride [4], carbon monoxide [5], sulfur dioxide [6], and many others [7]. It was recognized that most of these co-monomers brought about an increase in elasticity of ethylene.

Copolymers of ethylene and methacrylic acid prepared by a careful control of polymerization conditions exhibited excellent adhesion to aluminum foil [8]. This copolymer became commercial under the trade name Surlyn® in 1961. Because of the ionic nature of this and other similar copolymers, they are referred to as *ionomers*. These include a variety of copolymers of ethylene, butadiene, and other monomers.

In general, ionic polymers (ionomers) have a hydrocarbon backbone containing pendant acid groups. These are then neutralized partially or fully to form salts. If the salts content is very high (e.g., every monomer unit has a pendant salt group), the products are referred to as polyelectrolytes and are generally soluble in water. Another group with a much lower number of ionic pendant groups (up to about 10 mol%) exhibits high extensibility and low permanent set, that is, the characteristics of elastomers [9]. Such elastomers exhibit properties of vulcanized rubber yet can be processed as thermoplastics. They have all the advantages of thermoplastic elastomers, that is, they can be processed by a variety of methods (extrusion, blow molding, thermoforming, injection molding), can be heat welded, and their scrap can be recycled. They require little compounding and their properties can be easily set by changing the ratio of components. However, they also have a number of disadvantages typical for many thermoplastic elastomers (TPEs), such as softening and melting with increasing temperature, showing creep on extended use. In addition, unlike many thermoplastic elastomers, they deteriorate in the presence of water [9]. Selected commercial products are listed in Table 12.1 and an example of an ionomer based on ethylene and methacrylic acid is shown on the bottom of this page.

12.2 Synthesis

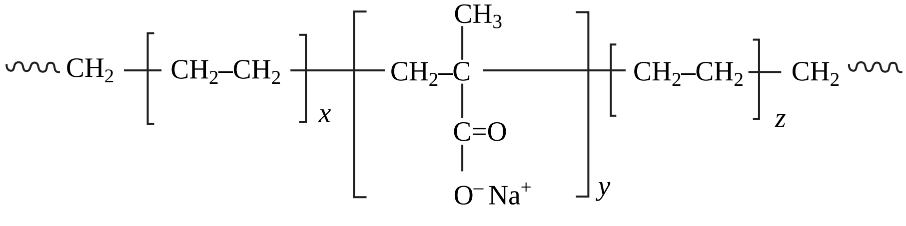
Ionomers are typically prepared by copolymerization of functionalized monomer with an olefinic unsaturated monomer or by direct functionalization of a preformed polymer. For example, carboxyl-containing ionomers are obtained by direct copolymerization of acrylic or methacrylic acid with ethylene, styrene, and similar co-monomers by free radical copolymerization. The product is generally available in the form of a free acid that can be neutralized to the degree desired with metal hydroxides, acetates or similar salts, or diamines [10].

The second route to ionomers involves modification of a preformed polymer. An example is sulfonation of EPDM with a content of sulfonic acid groups in proportion to the amount of sulfonating agent [11]. These reactions are conducted in solution permitting direct neutralization of the acid functionality to the desired level. The neutralized polymer is isolated by conventional techniques, such as coagulation in a nonsolvent or by solvent flashing.

An alternative technique of modification of preformed polymer is a reaction conducted on polymer melt, usually in extruder [12], using the same sulfonating agents typically used in solution.

12.3 Morphology

Experimental and theoretical evidence indicates that salt groups in ionomers exist in two different



$$\sim CH_2 - \left[CH_2{-}CH_2 \right]_x - \left[CH_2{-}\underset{\underset{O^- Na^+}{|}}{\overset{\overset{CH_3}{|}}{C}}(C{=}O) \right]_y - \left[CH_2{-}CH_2 \right]_z - CH_2 \sim$$

Table 12.1. Commercial Ionomers

Copolymer System	Trade Name	Manufacturer	Characteristics
Ethylene-methacrylic acid	Surlyn®	DuPont	Modified thermoplastic
Ethylene-acrylic acid	Iotek®	Exxon	Modified thermoplastic
Butadiene-acrylic acid	Hycar®	Goodrich	High green strength elastomer
Perfluorosulfonate ionomers	Nafion®	DuPont	High chemical resistance

environments, termed *multiplets* and *clusters*. The multiplets are considered to consist of small numbers of ion dipoles (perhaps up to six or eight) associated together to form higher multipoles, namely, quadrupoles, hexapoles, octapoles, and so on. These multiplets are dispersed in the hydrocarbon matrix and are not phase separated from it. Thus, in addition to acting as ionic cross-links, they affect such properties of the matrix as the glass transition temperature, water sensitivity, and so on. The clusters are considered to be small (< 5 nm), microphase-separated regions rich in ion pairs but also containing considerable quantities of hydrocarbon. They possess at least some of the properties of a separate phase, including relaxation behavior associated with a glass transition temperature, and have a minimal effect on the properties of the hydrocarbon matrix. The proportion of salt groups that reside in either of the two environments in a particular ionomer is determined by the nature of the backbone, the total concentration of salt groups, and their chemical nature. The details of the local structure of the clusters are not known and neither is the mechanism by which the clusters interact with low-molecular weight polar impurities such as water [13].

12.4 Properties and Processing

The typical properties of ionomers are attributed either to ionic aggregation or to cluster formation (see previous section), or the interaction of polar groups with ionic aggregates. Changes in physical properties caused by ionic aggregation in elastomeric systems or in polymeric melts are most readily detected. A high green strength resulting from that is typical for most ionomer-based systems. The ionic aggregation is also causing an increased melt viscosity. In polyethylene-based metal carboxylate ionomers, the high melt viscosity is well suited to heat sealing and also provides good extrusion characteristics. On the other hand, this increased melt viscosity is not favorable for injection molding [14], although most of the commercial ionomers can be injection molded [15]. Other attributes typical for them include the following:

- toughness
- outstanding abrasion resistance
- oil resistance.

An interaction of various polar agents with the ionic groups and resulting property changes are unique to ionomer systems [14]. An interaction of metal stearates with sulfonated EPDM introduces softening of the material. Plasticization of this kind is required for good processability to thermoplastic elastomers based on this technology. It was found that a crystalline additive, such as zinc stearate, can strongly affect material properties, in addition to being a highly effective preferential plasticizer for the ionic aggregates [15].

The high tensile strength of ionomeric TPEs compared to base polymers is attributed to their ability to relieve local stresses by an ion exchange mechanism. In general, they exhibit low permanent set even at considerable levels of stress relaxation and creep. The creep and stress relaxation behaviors are explained by the exchange mechanisms between time-dependent cross-links. However, the creep recovery indicates that some of the cross-linked sites are very stable. These sites are expected to be relatively large aggregates of clusters of ionic groups and to be stable even at high temperatures [16].

The sulfonated TPE is usually compounded with mineral fillers, antioxidants, process oils, and/or polyolefins (PP or PE) using conventional mixing equipment for elastomers. Typical compounding ingredients for ionomeric TPEs are in Table 12.2. The formulations typically vary in hardness from soft (Shore A 45) to hard semiplastic compositions with hardness values in Shore D scale. Table 12.3 lists property ranges of materials made from ionomeric TPEs. An example of a practical formula is in Table 12.4 [17].

Processing conditions are similar to those for flexible PVC [14], although the temperatures are set somewhat higher.

Table 12.2. Typical Compounding Ingredients for Ionomeric Thermoplastic Elastomers

Ingredient	Range (phr)	Examples
Ionolyzer	5–35	Zinc stearate, zinc acetate, stearamide
Plasticizer	25–200	Paraffinic oil, naphtenic oil
Filler	25–250	Carbon black, silica, clay, calcium carbonate, metal oxides
Other polymers	10–125	Polyethylene, polypropylene
Processing aid	2–10	Waxes, lubricants
Antioxidant(s)	0.2–2.0	Diphenylamine derivative, hindered phenol compound

Source: Reference [17].

Table 12.3. Typical Property Range of Ionomeric Thermoplastic Elastomers

Property	Range
Hardness, Shore A	45–90
100% Modulus, MPa (psi)	1.2–6.9 (174–1,000)
Tensile Strength, MPa (psi)	3.4–17.2 (500–2,480)
Elongation at Break (%)	350–900
Trouser Tear, kN/m (lb/in) (ASTM D 1938)	8–55 (45–315)
Specific Gravity	0.95–1.95
Compression Set (%)	30–35
Brittle Point, °C (°F)	−57 to −46 (−71 to −51)
Processing Temperature, °C (°F)	93–260 (199–500)

Source: References [17, 19].

Typical extrusion conditions are as follows [18]:

Barrel temperature, °C (°F)	
Rear	160 (320)
Front	180 (356)
Die	350 (662)
Melt temperature, °C (°F)	160–168 (320–335)

Table 12.4. Example of a Formula for Sheeting Made from Sulfonated EPDM

Ingredient	Description	phr
Sulfonated EPDM[a]	Base polymer	100
Zinc stearate	Ionolyzer	25
Parafinic Oil (Sunpar 2280)	Plasticizer	75
N110 Carbon Black	Reinforcing filler	60
N550 Carbon Black	Semireinforcing filler	30
Marlex 6060	High density polyethylene	15
Naugard 445	Modified diphenylamine antioxidant	1

Note:
[a] Containing 25 meq of sulfonation per 100 g of rubber.
Source: Reference [17].

Most of the ionomeric thermoplastic elastomers can be processed by injection molding. For that process a combination of high shear and high temperature is required [18].

Other processes applicable to ionomeric thermoplastic elastomers are blow molding, thermoforming, and heat welding.

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13 Other Thermoplastic Elastomers

13.1 Elastomeric Star Block Copolymers

Star-branched, radial, or multi-arm star copolymers are copolymers consisting of a core and arms held together by, or emanating from, the core (Fig. 13.1). Besides the chemical nature of the constituents, the properties of star copolymers mainly depend on two structural factors, namely, on the molecular weight of the arms and the number of arms. Certain properties of the star copolymers, such as intrinsic viscosity and shear sensitivity, depend only on the molecular weight of the arms, not on the total molecular weight of the polymer, and are independent of the number of arms above a certain number of arms [1, 2]. The core of a star copolymer is usually viewed as a volumeless and weightless point, since its volume and weight are negligible in comparison to the volume and weight of the entire star. A core can be a single linking agent, complex microgel, or a multifunctional initiator residue. The first report on the synthesis of nonlinear copolymers with controlled structures having extent of cross-linking without gelation was by Flory and coworkers [3]. The resulting copolymers having four or eight arms were prepared from ε-caprolactam and tetra- or octacarboxylic acids as multifunctional reactants, respectively. Fetters and coworkers [4, 5] prepared star copolymers with polybutadiene arms using tri- and tetrachlorosilane as linking agents. Rempp and coworkers [6–10] synthesized polystyrene arms by living anionic polymerization techniques and subsequently added divinylbenzene as the linking agent to the living charges.

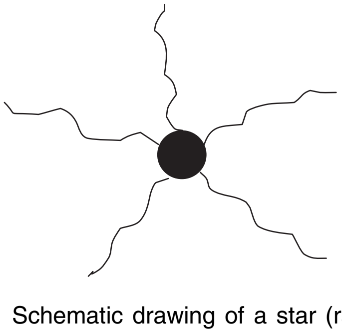

Figure 13.1. Schematic drawing of a star (radial) blocks copolymer.

13.1.1 General Methods for the Synthesis of Star Copolymers

There are two major synthetic routes to star copolymers, namely, *arm-first* method and *core-first* method. Besides these two major methods, several other methods have been reported in the literature.

Arm-first method starts with the preparation of tailormade "prearms." These prearms may be synthesized from a wide variety of monomers by living cationic [11–15], living anionic [4, 5, 16, 17], and by group transfer [18–24] polymerizations. Prearms can be linked by di- or multifunctional linking agents.

Star copolymers with arms, consisting of polystyrene (PSt) [25, 26], polydiene (polyisoprene (PIP) and polybutadiene (PBD)) [27–29], poly(methyl methacrylate) (PMMA) [30, 31], poly(vinylpyridine) (PVP) [32], and polystyrene-*block*-polydiene (PSt-*b*-PIP and PSt-*b*-PBD) [33–36] have been synthesized by living anionic polymerization. In most cases divinylbenzene (DVB) has been used as the linking agent [32–37].

The advantage of the arm-first method with the use of difunctional polymers is the ease of producing fairly high degrees of branching (i.e., number of arms) and well-defined arms structures directly from precisely designed prearms. The major drawbacks of this method are the difficulty to form terminal arm functionalities on the arms, difficulty in achieving complete linking, ill-defined cores, and loss of control over the number of arms [38].

The preparation of star copolymers using multifunctional linking agents in cationic polymerization methods is described in [39–46]. In contrast to anionic systems, in cationic polymerization methods the living polymer chain ends are electrophilic; thus, the linking agents must be nucleophilic.

A more detailed review of methods and monomers for both anionic and cationic systems used is in references [38] and [47].

In the core-first method, a multifunctional initiator containing a known number of initiating sites is prepared first. Then the star copolymer is formed by initiation from the initiating sites by living polymerization. The residue of the multifunctional initiator becomes the core. The Scheme 3 illustrates the process.

This method has been used for the synthesis of star copolymers by anionic [48–50], cationic, group transfer, radical, and condensation polymerizations [51]. Multifunctional initiators were found to be more efficient in cationic polymerizations than in anionic polymerizations, for the preparation of stars [52].

The advantage of the core-first method is that the preparation of a star copolymer with a functional group at the polymeric arm end and the preparation of block star from the living chain end can be readily carried out. The maximum number of arms can be controlled when a well-defined core, that is, multifunctional initiator, is used. In addition, the star formation takes a shorter time than the arm-first method, since it is not diffusion controlled. The drawback of this method is its high dependence on initiating efficiency to obtain the target product with the correct number of arms and the loss of control over the precise molecular weight of the arms or the block composition [53].

Additional methods of preparation of star copolymers have been reported. Ito and coworkers synthesized star copolymers of poly(ethylene oxide) using homopolymerizable macromonomers [54].

13.1.2 Physical Properties of Star Block Copolymers

Star block copolymers prepared by anionic methods have been shown to exhibit superior mechanical properties and lower melt viscosities than linear triblock copolymers with the same molecular weight [17]. The star copolymers with low-molecular weight arms exhibited low viscosities and were easily processed [17].

Dynamic viscosity studies performed on the above star block copolymers established that their melt viscosities were largely independent of the extent of branching [55–58]. Leblanc [58] observed that star block copolymers with four PSt-*b*-PBD arms exhibit lower activation energy of flow than that of linear triblock counterparts with comparable block composition. He assumed that an "aggregate flow" with low activation energy takes place. These results indicate that processing of star block thermoplastic elastomers (TPEs) should be easier than that of linear triblock copolymers.

Table 13.1. Stress–Strain Behavior of Different Styrenic Block Copolymers

Block Copolymer	Tensile Strength (MPa)	Elongation at Break (%)
S–I–S, linear	33.4	1,030
$(SI)_3$-Si (3-arm star)	36.8	970
$(SI)_4$-Si (4-arm star)	37.3	1010
$(SI)_6$-DVB (6-arm star)	38.3	940
$(SI)_9$-DVB (9-arm star)	42.2	1050
S–B–S, linear	29.4	1050
$(SB)_{15}$-DVB (15-arm star)	41.2	730

Notes: Films cast from benzene/heptane 9/1 (v/v). S—polystyrene; I—polyisoprene; B—polybutadiene. Si—silicon tetrafluoride linking agent. DVB—divinyl benzene linking agent.
Source: From reference [23].

Mechanical properties of TPEs are, like those of thermoset rubber materials, characterized by tensile tests. Star block copolymers prepared by anionic polymerization, that is, star PSt-*b*-PBD and PSt-*b*-PIP, exhibit tensile properties, which are superior to those of corresponding linear triblock copolymers [17] (see Table 13.1). Polyisobutylene (PIB)-based TPEs, including linear triblock copolymers, are reported to exhibit excellent tensile properties [48]. High tensile strengths (up to 26 MPa) have been reported to form various PIB-based star block copolymers with arm numbers greater than three, prepared by living cationic polymerization techniques [13, 20, 59, 60].

Star block copolymers with PSt-*b*-PIP arms exhibit better adhesive properties than their linear counterparts [61].

13.2 TPEs Based on Interpenetrating Networks

Generally, an interpenetrating polymer network (IPN) is defined as a combination of two polymers in network form, at least one of which is synthesized and/or cross-linked in the immediate presence of the other. A *thermoplastic IPN* contains physical cross-links in both polymers, rather than covalent cross-links [62]. To be of a practical utility, such a material has to behave as a thermoset at lower temperatures and must be able to flow as a thermoplastic at higher temperatures.

The physical cross-links that can be present in these networks can be introduced by block copolymers, partially crystalline or ionomeric structures. A thermoplastic IPN can be composed of networks of the same kind or of two completely different ones.

Another important feature is dual phase continuity, sometimes referred to as "co-continuous phases." The domains can be shaped as long cylinders, various interlocking structures, alternating lamellae, and so on [62].

In the IPNs containing covalent cross-links, the domain sizes are frequently governed by the cross-link density and are typically of the order of 0.05–0.3 μm. Since many of the thermoplastic IPNs are prepared by blending (see below), the domains are almost always somewhat coarser [62].

13.2.1 Synthesis of Thermoplastic IPNs

In general, thermoplastic IPNs are prepared by shearing or mixing either of the two polymers, or by polymerization of one or both of the polymers, or by the ionization of an ionomer component. At any rate, the final product has some kind of dual phase continuity [62].

An example is a thermoplastic IPN prepared from S–EB–S and polyamides, polyesters, or polycarbonates [63–65] with the addition of polypropylene. The S–EB–S is a triblock copolymer with hydrogenated polybutadiene center block and polystyrene end blocks and is a well-known commercial TPE. The other polymer added to the S–EB–S copolymer in reported studies is usually semi-crystalline. An example of such a blend is shown in Table 13.2. The final products exhibited dual phase continuity [66] and the authors claim that all three polymer phases (i.e., S–EB–S, the added semi-crystalline polymer and the polypropylene) are separate. The polypropylene makes up the interface between the other two polymers serving as a binder for them. The material is unusual by exhibiting a nearly constant modulus in the leathery range from the glass transition temperature of the center block (i.e., EB) near −60°C up to the melting temperature of the semi-crystalline component, which is typically 200°C or somewhat higher. This behavior was found advantageous by automotive design engineers and the material was used for the insulation of spark plug wires.

Another possible combination is that of a triblock copolymer with an ionomer. The ionic groups in ionomers cluster together and form a physically bonded network [62]. The experiments performed to synthesize this type of copolymers employ two distinct methods [67, 68]:

Table 13.2. Example of a Composition for a Co-Continuous Interlocking Network Phases

Component	Composition (parts by weight)
S–EB–S[a]	100
Poly(butylene terephtalate)	100
Extending oil (paraffinic)	100
Polypropylene	10
HALS antioxidant	0.2
Non-staining antioxidant (e.g., LTDP)	0.5
Titanium dioxide	5

Note:
[a] Molecular weight distribution 25,000–100,000–25,000.
Source: From reference [64].

- The *chemically blended* thermoplastic IPNs are prepared, for example, by dissolving S–EB–S in the mix of styrene monomer, methacrylic acid, and isoprene in the volume ratio 90/10/1. Then 0.4% of benzoin is added for subsequent photopolymerization.
- The *mechanically blended* thermoplastic IPN is prepared in such a way that the styrenic monomer mix is photopolymerized separately and then melt blended with the S–EB–S triblock copolymer in an internal mixer.

Both types of IPNs are neutralized by aqueous 10% solutions of either sodium hydroxide or cesium hydroxide in an internal mixer (as above).

13.2.2 Properties and Processing of Thermoplastic IPNs

The rheological and mechanical data are analyzed in reference [69]. It was concluded that on neutralization the triblock copolymer component, being the less viscous, assumes greater phase co-continuity. On the other hand, the mechanical data suggest that the phase inversion process remains somewhat incomplete, probably because of the relatively equal melt viscosities of the two polymers.

Recent research in this area has concentrated on decross-linking and/or depolymerization [70] with the objective of creating thermoset polymeric materials that can flow at some later time by means of chemical reactions. Such materials are referred to as reworkable thermosets and show potential in electronics and biomaterials.

13.3 TPE Based on Polyacrylates

One of the widely used and well-defined TPEs are triblock and radial-block copolymers of styrene and diene (butadiene, isoprene) based on the spontaneous and thermoreversible cross-linking in strong relation to the phase morphology [71]. However, the upper service temperature (UST) of a typical S–B–S block copolymer is limited to 60–70°C as a result of the partial miscibility of the styrene and butadiene blocks which decrease the glass transition temperature of polystyrene by about 20°C at $M_n = 1.5 \times 10^4$ [72]. A substantial research work has been performed to alleviate this shortcoming by developing novel block copolymers. One approach is to prepare triblock copolymers containing at least one poly(alkyl methacrylate) constitutive block. Depending on the substitute, the T_g of this family of polymers can be extended over a large temperature range, for example, from −60°C for poly(2-ethylhexyl acrylate) up to 130°C for highly syndiotactic poly(methyl methacrylate), sPMMA. Thus, this sPMMA is an attractive substitute for PSt in the effort to increase the UST of a S–B–S block copolymer. Moreover, poly (alkyl acrylates) with low glass transition temperature have better heat and oxygen resistance than polydienes and are therefore a suitable replacement for them in the central block of the triblock copolymer [73].

13.3.1 Synthesis of Triblock Copolymers Based on Methyl Methacrylate and Butadiene

Triblock copolymers with the combination of poly (methacrylate) and polybutadiene blocks (M–B–M) are prepared by sequential anionic polymerization but require several modifications to produce the desired rubbery *cis*-1,4 polybutadiene structure and a highly sPMMA block with a high T_g [74, 75]. These include the use of difunctional initiators and a seeding technique proposed in reference [76]. Detailed discussion of the synthesis is in reference [75].

13.3.2 Properties of M–B–M Triblock Copolymers

The substitution of sPMMA for PSt in the traditional S–B–S TPEs results in the increase of UST by approximately 40°C without sacrificing the elastic properties of the final product. The ultimate mechanical properties of the two types of triblock copolymers of the same molecular weight (125,000), composition (64% of polybutadiene), and polybutadiene microstructure (45% of 1,2 units) are comparable. The values obtained from M–B–M triblock copolymers at 90°C (ultimate tensile strength = 14.3 MPa and elongation at break = 1,240%) are similar to those from S–B–S at 50°C (13 MPa and 1,200%, respectively) [77].

13.3.3 Synthesis of Poly(MMA-tBA-MMA) Elastomers

Although there are several possible routes for the preparation of fully acrylic triblock copolymers the simplest method appears to be a two-stage process using difunctional anionic initiators. The most favorable situation is the initiation of MMA by living poly (*t*-BA) anions. Poly(MMA-*b*-*t*BA-*b*-MMA) can readily be converted into triblocks containing a central polyacrylate block of a low T_g. Transalcoholysis of poly(tert-butyl acrylate) P*t*BA by long-chain alcohols can be carried out selectively and quantitatively in the presence of PMMA by acid catalysis. Direct polymerization of this type of polymers is not possible because the anionic polymerization of primary and secondary alkyl acrylates cannot be controlled [78].

Using a similar technique, star-shaped copolymers of the type poly(MMA-*b*-alkylacrylate)$_n x$ or poly(St-*b*-alkylacrylate)$_n x$ have been synthesized by the "arm-first" method that consists of initiating the polymerization of a small amount of a bis-unsaturated monomer by the living diblock precursor (see Section 13.2.1.1) [79].

13.3.4 Synthesis of Poly(MMA-b-Alkylacrylate -b-MMA)

The synthesis of fully acrylic TPEs by anionic polymerization has the major disadvantage of requiring the preliminary synthesis of a precursor triblock followed by its chemical modification into the desired polymer. Therefore, experiments were carried out to prepare them by sequential controlled radical polymerization [80, 81]. Triblocks containing 17–28 mol% of MMA, with central poly(*n*-BuA) block of $M_n = 105{,}000$ and $M_w/M_n = 1.20$ have been synthesized [82]. It was found that whenever radical process is used the PMMA outer block is less syndiotactic than the counterpart synthesized by anionic polymerization (57% vs 79%) [82].

13.3.5 Mechanical Properties of Fully Acrylic Triblock and Branched Block Copolymers

A series of fully acrylic triblock and branched block copolymers were prepared by transalcoholysis of common poly(MMA-*b*-*t*BA-*b*-MMA) precursors by ethanol, n-propanol, n-butanol, and isooctyl alcohol. The resulting copolymers were then compared in stress–strain behavior to traditional S–I–S copolymer with comparable composition and molecular weights of the blocks. The well-defined and extended rubbery plateau typical for the S–I–S TPE was no longer evident in fully acrylic series [82]. The star-shaped copolymers behaved in the same way [79]. The ultimate mechanical properties (tensile strength and elongation at break) were found to be about half of those typical for S–B–S type TPE. A detailed discussion of polyacrylate-based TPEs and corresponding issues involving their synthesis and properties are in chapter 17 of *Thermoplastic Elastomers*, 3rd edition (Holden, G., Kricheldorf, H.R., and Quirk, R.P., Eds.), Hanser Publishers, Munich, 2004.

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14 Thermoplastic Elastomers Based on Recycled Rubber and Plastics

14.1 Introduction

It is possible to produce thermoplastic elastomers (TPEs) based on ground rubber waste from tires, waste ethylene propylene diene monomer (EPDM) rubber, acrylonitrile rubber (NBR), recycled rubber latex waste, and waste plastics. A multitude of studies were made with the goal to prepare thermoplastic materials with more or less elastic properties from blends of elastomers to replace part of the elastomer, or the plastic, or both [1].

Partial devulcanization of thermoset rubber materials results in the loss of physical properties [2]; however, the physical properties of TPEs remain unchanged after repeated recycling [3].

Ground rubber waste from tires could be blended with polyolefins in the presence of functional polymers acting as compatibilizers. However, the result was an impact-resistant plastic rather than a TPE because of the dominance of the plastic phase in the composition and because in most of them the elongation at break was less than 50% [4–8]. Fresh natural rubber (NR) was found to compatibilize compositions based on ground tire rubber waste filled polypropylene [9].

Blends of ground rubber tire waste with polypropylene with the addition of small amounts of ethylene-vinylacetate copolymer (EVA) are melt-processable elastomers and have been patented [10]. Waste rubber powder was incorporated into styrene–butadiene–styrene (SBS) block copolymer. Improved tear strength, tension set (at 300% elongation and compression set) of such blends over unfilled SBS block copolymer was observed [11]. Materials ranging from impact-resistant thermoplastics to TPEs were prepared from blends of recycled rubber with TPEs that have been compatibility treated. The properties of the resulting material depend on the ratio of the components in the blend or on changing the components themselves, and the process as well as the materials are the subject of a patent. Both natural and synthetic rubbers were used for that purpose and the thermoplastic component included mainly polyolefins [12].

Another reported method of preparing TPEs is based on ultrasonically devulcanized ground rubber tire scrap combined with polypropylene [13]. Materials based on recycled rubber with polypropylene alone were found to have elongation at break only 40% and therefore cannot be classified as TPEs [14].

14.2 EPDM Scrap

Dynamically vulcanized blends of EPDM, ground tire scrap and of high density polyethylene (HDPE) modified by acrylic acid yield true TPEs with values of elongation at break up to 380% and tensile strengths well over 7 MPa [15–17].

Thermoplastic elastomer compositions containing ground EPDM are based on blends of EPDM and PP in the ratio 70:30. About 45% of the EPDM rubber can be replaced by the ground scrap without adversely affecting the processing behavior and mechanical properties of the original material. The elongation at break is reported to be above 200% and the tension set at 100% elongation less than 25%. The blends can be reprocessed and the properties after reprocessing are within acceptable limits [18].

14.3 Butadiene-acrylonitrile Rubber (NBR) Scrap

Thermoplastic elastomers based on NBR scrap were prepared by adding the ground NBR scrap to a thermoplastic elastomeric composition consisting of a blend of NBR and styrene-co-acrylonitrile (SAN) in the ratio 70:30. It is reported that about 45 to 50% of the NBR can be replaced by the ground NBR scrap. The resulting material has the values of elongation at break well above 200% and tension set at 100% elongation 20–26% and can be recycled without an adverse effect on its mechanical properties [19].

14.4 Recycled Rubber

Another rather comprehensive study found that TPEs can be prepared from the blends of NR and

PP by replacing up to half of the NR by reclaimed rubber without adversely affecting the mechanical properties of the blend [20]. Others prepared thermoplastic elastomeric by mixing reclaimed rubber and scrap plastics. A 50:50 rubber to plastic ratio was found to be the optimum for processability, elongation at break, and permanent set [21]. A sulfur-based curing system was found to be better than a peroxide system for the dynamic vulcanization used in this process. Another work in this category was based on blending reclaimed rubber with polyethylene (LDPE and HDPE) [22].

14.5 Waste Latex

Waste latex products blended with polypropylene yield TPEs [23]. A typical composition is 60% latex rubber and 40% polypropylene. The properties of such blends are reported to be comparable to those of NR/PP blends and exhibit values of elongation at break in the range 200–300%. Dynamic vulcanization of the elastomeric phase increases the tensile strength and the addition of the reclaimed latex changes the brittle failure of the polypropylene to a ductile one.

14.6 Waste Plastics

Several studies attempted to prepare useful products by blending different scrap plastics with elastomers. Blending pulverized polypropylene from recycled computer cases with EPDM pellets and subsequent dynamic vulcanization in a twin extruder yields useful TPEs. Optimum elastomeric properties were reported for blends containing 40–45% EPDM by weight [24]. The preparation of TPEs from scrap polyesters is covered by a Firestone German Patent [25]. Combination of scrap plastics and scrap elastomers yields construction materials, noise protection walls, and traffic signs [26].

Another patented process for the preparation of TPEs from mixed scrap of thermoplastics (HDPE, LDPE, and PP) is blending it with 20–50% parts of NR and/or NBR and 40 parts of reinforcing fillers and by heating it to approximately 200°C (392°F) with the addition of vulcanizing agents [27].

Novel TPEs are based on blends of scrapped computer cases (containing mainly acrylonitrile butadiene styrene (ABS)) with NBR [28]. The products with rubber to plastics ratios of 60/40 to 80/20 exhibit thermoplastic elastomeric behavior. The dynamic vulcanization is beneficial mainly for blends with higher rubber content. These compositions are recyclable.

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15 Applications of Thermoplastic Elastomers

15.1 Introduction

Since the commercial introduction of thermoplastic elastomers (TPEs) in the late 1960s, about 50 manufacturers of different sizes have entered the field [1]. Thermoplastic polyurethanes (TPUs) were the first TPEs used in the United States and their main applications were automotive exterior parts (bumpers) and shoe soles. Styrenic block copolymers gained rapidly market shares from TPUs in footwear and also established themselves in adhesives and sealants [2]. Olefinics (TPOs) replaced TPUs in automotive sight shields and filler panels and were accepted in wire and cable industry and in hose [3]. By 1983, worldwide TPE demand had reached 421,000 metric tons; its share in the United States was 148,000 tons, 199,800 tons in Western Europe, and 73,900 tons in Japan [3, 4]. During the 1980s there was a rapid growth of use of TPEs in automotive, footwear, wire and cable industries, and adhesives. By the end of 1980s they captured nearly 18% of the U.S. market for medical goods [5]. Total current worldwide annual market demand as pointed out in Section 1.2.6 is about 2,300,000 metric tons and growing at a rate of approximately 6% per year.

The TPE market in general, and in the United States in particular, is gradually attaining commodity status, affecting a slew of changes in terms of price and profit margin. Current prices of the base (not compounded) TPEs at moderately large volumes (300,000–500,000 pounds annually) are typically in the $1.50–2.50 per pound range for most grades but may be considerably higher for specialty grades. Given the current raw material situation, the prices will probably grow continuously. Compounded materials are in general less expensive since in most cases the added components used in the compound, such as fillers and/or plasticizers (oils) are less expensive than the base polymer used. Another factor entering the cost picture is the volume cost that frequently favors polymers with low density. In fact, what is very important is the performance/price ratio. This ratio often enters the decision process as to what material to use for a given application. A very simplified chart (Fig. 15.1) attempts to show qualitatively the price and performance ranges for the most widely used TPEs.

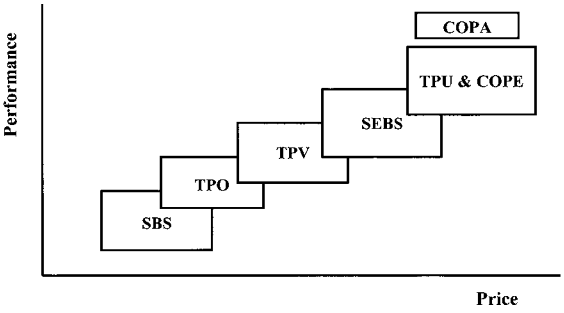

Figure 15.1. Approximate ranges of performance vs cost for commercial TPEs (not to scale).

The ability of TPEs to exhibit good flow properties upon heating and then solidifying upon cooling allows the manufacturers to use highly productive thermoplastic processing equipment, such as injection molding, extrusion, and blow molding for the production of elastomeric articles. This eliminates the complicated and costly intensive mixing and vulcanization steps typical for conventional rubber technology. This means reduced labor expenses and increased output. Moreover, the scrap can be reground and reused in virgin materials.

Since there are numerous types of TPEs, they cover a wide range of applications, from replacement of conventional vulcanized rubber to special adhesives and sealants. Some of the TPEs in contrast to conventional rubber are very pure and are therefore suitable for medical applications and for articles that come in contact with food. The only case where TPEs have weakness is their service temperature, which depends on their melting point. This can be mitigated by cross-linking, but this reduces the possibility of their recycling. The following sections discuss specific applications of individual types of TPEs.

15.2 Applications for Styrenic TPEs

The balance between properties and processability typical for styrenic TPEs leads to focusing on unique applications in addition to the replacement of general-purpose rubber. Styrenic block copolymers are rarely used as neat polymers and can be readily mixed with other polymers, oil, and fillers, which allow versatile tuning of product properties. In most cases the compounded material contains less than 50% of the block copolymer [6].

Formulated styrenic TPEs have several major applications:

(1) Replacement for vulcanized rubber;
(2) Adhesives, sealants and coatings;
(3) Polymer blends;
(4) Bitumen modification;
(5) Viscosity index improvers for lubricating oils;
(6) Modifiers for thermosets.

The 2002 U.S. styrenic block copolymer demand reported in 2003 [7] was estimated at 647 million pounds, with 30% being in adhesives and sealants, 22% in asphalt modification, 13% in polymer modification, 13% in roofing, 4% in fibers, 3% in consumer products, 3% in footwear, and 12% in other applications.

15.2.1 SBCs as Replacement of Vulcanized Rubber

Styrenic block copolymers used for these applications are mainly styrene-butadiene-styrene block copolymers (S–B–S) and styrene-(ethylene-butylene)-styrene block copolymers (S–EB–S) types compounded to the desired specifications. The compounding ingredients used for that purpose are polystyrene (PS), polypropylene, polyethylene, ethylene-vinyl acetate, oils, and miscellaneous fillers (see Section 5.2.5).

Typical applications of compounded styrenic block copolymers are shoe soling, milk tubing, sound deadening materials, grips, wire and cable insulations, flexible automotive parts [8], automotive parts, sporting goods, parts for construction, as well as molded and extruded industrial goods. Specialized compounds based on S–B–S and S–EB–S are processed into blown or extrusion cast films including heat shrinkable films [9]. Such films are very soft and flexible, exhibit low hysteresis, and low permanent set. Because of their purity they can be used in contact with skin and with certain foods.

Solutions of blends of S–EB–S and oils can replace natural rubber latex in the manufacture of dipped articles such as surgeon's gloves, condoms, etc. [10]. The finished products do not cause allergic reactions as do those made from natural latex and have a much higher resistance to oxygen and ozone due to the saturated center block in the copolymer.

Styrene block copolymers can be compounded to produce materials that enhance grip, feel, and appearance in applications such as certain automotive parts (Figs 15.2–15.6), tools (Figs 15.7–15.10), electrical insulation (Fig. 15.11), and molded technical parts, such as plugs (Fig. 15.12), knobs (Fig. 15.13), in personal hygiene (Fig. 15.14), consumer goods (Figs 15.15–15.19), toys, packaging, and others.

Figure 15.2. Automotive parts (Courtesy PolyOne Corporation).

Figure 15.3. Door handle seal (Courtesy Vi-Chem Corporation).

Figure 15.4. Auto floor mat (Courtesy PolyOne Corporation).

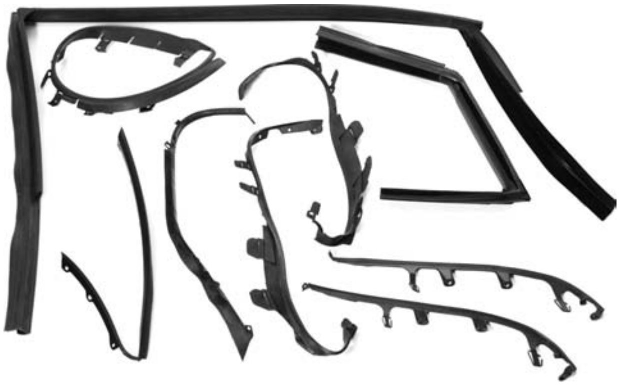

Figure 15.5. Seals (Courtesy Vi-Chem Corporation).

Figure 15.6. Parts interior collage (Courtesy Vi-Chem Corporation).

Figure 15.7. Hand grinder (Courtesy Kraiburg TPE Corporation).

Figure 15.8. Rake handle (Courtesy Vi-Chem Corporation).

Figure 15.9. Head lamp (Courtesy Kraiburg TPE Corporation).

15.2.2 SBCs in Adhesives, Sealants, and Coatings

The use of SBCs in adhesives and sealants is the major segment of their applications (see Section 15.2). A large amount of SBCs is used in hot-melt adhesives, although some adhesives are produced by dissolving them in solvents, taking advantage of their low solution viscosity. The end products

Figure 15.10. Self-inking stamp (Courtesy Kraiburg TPE Corporation).

Figure 15.11. Power cords (Courtesy Teknor Apex Company).

Figure 15.12. Plugs (Courtesy Vi-Chem Corporation).

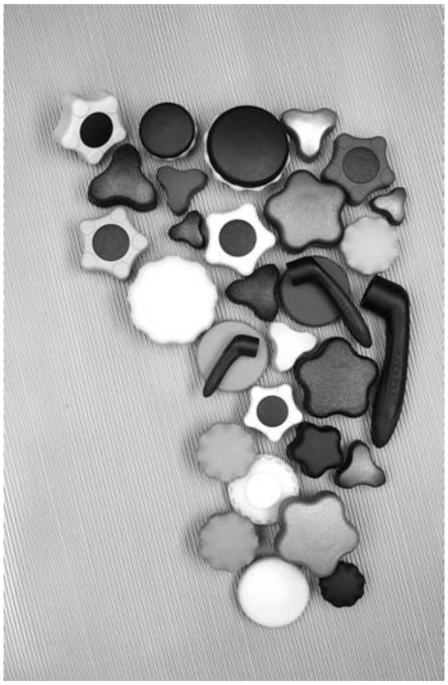

Figure 15.13. Knobs (Courtesy RTP Company).

Figure 15.14. Toothbrush handles (Courtesy PolyOne Corporation).

are tapes, labels, adhesive fasteners etc. Different types of SBCs are used in different adhesive applications [11]:

Styrene-isoprene-styrene block copolymers (S–I–S) and (S–B–S) types having unsaturated elastomeric midblock can be formulated to provide good pressure sensitive adhesives (PSAs). Because

Figure 15.15. Soft shoe inserts (Courtesy Teknor Apex Company).

Figure 15.16. Tongue exerciser (Courtesy Kraiburg TPE Corporation).

Figure 15.17. iPod (Courtesy GLS Corporation).

Figure 15.18. Cooler (Courtesy GLS Corporation).

Figure 15.19. CD Case (Courtesy GLS Corporation).

of the unsaturation, the addition of stabilizers is required. Possible applications are pressure sensitive tapes and labels, contact adhesives, hot-melt adhesive adhesives, construction adhesives and mastics. Styrene-(ethylene-butylene)-styrene (S–EB–S) and styrene-(ethylene-propylene)-styrene block copolymers (S–EP–S) have saturated midblock, exhibit high resistance to degradation by heat, ozone, and ultra violet (UV) light, and have high tensile strength. These SBC types can be processed at higher temperatures than the others. Possible applications are hot-melt adhesives with long pot life, sealants, and coatings exposed to UV.

Styrene-(ethylene-butylene)-styrene *copolymers grafted with maleic anhydride* have saturated mid-blocks, good adhesion to polar substrates and can be cross-linked via condensation reactions. These types can act as compatibilizers in multipolymer formulations. Main adhesive application is in structural adhesives, sealants, and PSAs.

Polyisoprene-based star block copolymers and *S–EB–S block copolymers with high proportion of 1, 2 isomer* have been developed. These elastomers can be cross-linked when applied to the tape [12]. This process gives the adhesive improved solvent resistance, which is important for applications in masking tapes [13].

15.2.2.1 Solution Behavior of SBCs

15.2.2.1.1 Solvents for SBCs

The domains and the elastomer blocks can be dissolved in suitable solvents to give solutions of SBCs. The removal of the solvents causes the domains to become hard and glass-like again, and the polymer again acts like a conventional vulcanized rubber. The polymers can be dissolved in many single solvents, such as toluene, and in many solvent blends, such as hexane/methyl ethyl ketone (MEK). In contrast to the usual plastics and rubbers, which have only a single phase, SBCs have two phases. In order to form a true solution, the solvent system must be capable of dissolving both of these phases. Dissolving the PS end-blocks unlocks the network, permitting separation of the solvated rubber blocks. Since SBCs are relatively low in molecular weight, they produce solutions with lower viscosity or with higher solids content relative to solutions of other rubber polymers.

Many inexpensive hydrocarbon solvents and some nonhydrocarbon solvents will dissolve both phases. If blends of solvents are used, an even wider variety of solvent systems may be considered. Viscosity, as well as other properties, can be adjusted by the choice of solvent or solvent blend, in accordance with properties desired in the final product.

In selecting solvents for SBCs, the solubility parameter (δ) is a useful tool, particularly when working with hydrocarbon solvents. A hydrocarbon polymer will usually dissolve in those hydrocarbon solvents with solubility parameters close to that of the polymer itself. In general, the higher the molecular weight of the polymer, the closer the solubility parameters must be matched. The relationships involved in the solubility parameter concept are less definite with oxygenated and halogenated compounds, where polar and hydrogen bonding forces become increasingly important. Even in these cases, however, solubility parameters can aid in correlating and predicting solubilities. Viscosity of an S–EB–S grade in various solvent systems is in Table 15.1.

Dilute solutions tend to be Newtonian in nature. As concentration increases, solvated domains begin to form in solution just as in the final product. Thus, more viscous solutions become non-Newtonian, particularly when compounded with higher molecular weight polymers [14].

15.2.2.1.2 Effect of the Addition of Resins and Oils

When blended with SBCs, resins improve adhesion, peel strength, shear strength, and reduce solution viscosity. They also help to compatibilize other additives with the block copolymers. High softening point resins which associate with the PS end-blocks increase tensile strength and hardness at a given concentration. An initial yield point in the stress–strain response often results when this type of resin is used.

Table 15.1. Viscosity of S–EB–S in Various Solvent Systems (20% Solids)

Solvent(s)	Solvent Ratio (wt/wt)	Viscosity, cP
Heptane	100	Gel
Heptane/Acetone	80/20	350
	60/40	Insoluble
Heptane/PCBTF[a]	80/20	850
	60/40	530
	40/60	655
	20/80	2170
PCBTF	100	Gel
Heptane/tBAc[b]	80/20	580
	60/40	310
	40/60	550
	20/80	Gel
tBAc	100	Insoluble

Notes:

[a] p-chlorobenzotrifluoride.

[b] Tertiary butyl acetate.

Source: Kraton® Brochure K0388 bBRa0U, Kraton Polymers LLC, Houston, TX, June 2003.

Liquid or low softening point resins, which associate with the midblock, can be used to soften the final product, to lower tensile strength, and to increase elongation. Oils have a similar effect.

Since four different elastomeric midblocks are typically used in SBCs, the added midblock associating resins and oils must be chosen to be compatible with the particular rubber used in each polymer. Examples of compatibility of a variety of resins and plasticizers with the various midblock elastomers and with the PS end-blocks are shown in Table 15.2.

Resins that associate with both phases usually give plasticized products of lower strength, while those that associate with neither phase may result in inhomogeneous and sometimes brittle products.

15.2.2.2 Examples of Applications

15.2.2.2.1 Pressure Sensitive Adhesives

Pressure sensitive adhesives are the major end use for SBCs. The adhesive compounds are applied frequently as hot-melts, although solvent application is also used taking advantage of the low viscosity of their solutions (see Section 15.2.2.1). The tack formulations are based on the combination of the polymers with tackifying resins and/or oils (see Section 15.2.2.1). The resins soften the elastomeric phase, which allows the adhesive conform to the substrate in the bonding (slow stage). They also adjust the glass transition temperature of the elastomeric phase, which causes the stiffening of the adhesive layer and resisting the removal of the adhesive from the substrate (fast stage). Hot-melt PSAs are mostly based on softer grades of SBCs, such as S–I–S, while solvent based adhesives are frequently prepared from S–B–S and S–EB–S block copolymers using suitable solvents.

Table 15.2. Compatibility of Various Resins and Plasticizers with SBC Segments

Additive	Compatible with Segments
Synthetic Polyterpenes (Polymerized C5 Resins)	Polyisoprene
Hydrogenated Rosin Esters	Polybutadiene
Saturated Hydrocarbon Resins	Poly(ethylene-butylene)
Aromatic Resins	Polystyrene
Paraffinic Oils	Poly(ethylene-butylene)
Naphtenic Oils	Polyisoprene, polybutadiene
Low Molecular Weight Polybutenes	Poly(ethylene-butylene)

Source: Reference [1].

15.2.2.2.2 Sealants

Sealants are either hot-melts or solvent based and prepared mainly from S–EB–S block copolymers. Diblock polymers are often used in sealants because they reduce the viscosity of the hot-melt product or allow the formulation of a solvent-based sealant to be made with higher solids content. Other components of a sealant formulation are resins, oils (plasticizers) and fillers, unless a clear sealant is required. Styrenic block copolymers-based hot-melt sealants are used in many manufacturing processes, sometimes applied by robotics [15] and can be processed also as foamed products and as formed-in-place gaskets. Solvent-based sealants are mostly used in construction industry [15].

15.2.2.2.3 Coatings

Protective coatings are formulated in a similar manner as adhesives but in many cases they contain large amounts of fillers and UV protective additives (UV stabilizers and titanium dioxide). Such coatings are used on roofs and other outdoor surfaces. Other applications are strippable temporary coatings and in chemical milling of metals [15].

15.2.2.2.4 Oil Gels

Oil gels are primarily blends of oil and gelling agents. The oil comprises the majority of the blend and can be naphthenic or paraffinic processing oil, a mineral oil, a synthetic product such as a polybutene, or a silicone. Gelling agents include waxes, fumed silica, fatty acid soaps, and SBCs. The gelling agent content is usually less than 10%. Products, which range from strong elastomers to weak gels and even greases, can be formulated. Oil gels can be used for sealants, lubricating greases, strippable coatings, corrosion protection, binders, etc. [16].

An example is a blend of S–EB–S (typically 5% by weight), a large amount of mineral oil (90%), and the remainder of wax (5%) are used as cable-filling compounds for “bundled” telephone cables [17, 18]. Their function is to prevent water intrusion and wicking. A potential application of such gels is in toys, hand exercising grips, soft pads, etc. [19].

15.2.2.2.5 Viscosity Index Improvers

Styrene-(ethylene-propylene) (S-EP) diblocks and certain star block copolymers [19, 20] are used in small amounts in motor oils. The typical amount of changing SAE 10 weight oil into multigrade oil (10/30 or 10/40) is 0.7–2.0 wt%. At low temperatures the SBC molecules are compact and cannot crystallize in oil, thus allowing an easy starting of the engine. At high temperatures, the SBC molecules expand in the oil thus maintaining its viscosity and maintaining thick enough lubricating film on bearings and other parts of the engine and reducing wear [21].

15.2.3 Blends of SBC with Other Polymers

Styrenic block copolymers are compatible with a large number of polymers. Many blends of SBCs with other polymers yield materials with improved properties when compared to the original polymers and this applies to both thermoplastics and thermosets. The improved properties are impact resistance, tear strength, stress crack resistance, low temperature flexibility, and elongation. Some effects are shown in Table 5.2 (Section 5.2.5). Examples of such blends and their properties are discussed below.

15.2.3.1 Blends of SBCs and PS

The most widely used application is improving impact resistance and crack resistance of clear PS for cups, food containers, and films. Others are further increase of impact resistance of impact resistant PS, creating a super-impact PS, and restoring impact resistance of PS after flame retardants were added to it [21].

15.2.3.2 Blends of SBCs and Polyolefins

The addition of SBCs improves low-temperature impact resistance of *polypropylene*. Blends of SBC and *polyethylene* are used mainly in blown and cast films (Fig. 15.20). The resulting film has improved tear strength and impact resistance [21]. Blends of SBCs, particularly of S–EB–S and olefins (polypropylene and polyethylene) are used in a variety of applications, including "soft touch" and ultrasoft materials. Examples of applications of blends of SBCs with polyolefins are illustrated by Figs 15.21–15.23.

Other useful blends of SBCs are with engineering thermoplastics such as polyphenylene oxide [22] and polycarbonate [23] and as impact modifiers in polyamides and polyesters [24].

Figure 15.20. Films (Courtesy PolyOne Corporation).

15.2.3.3 Blends of SBCs with Thermosets

Special types of PS-elastomer block copolymers were developed for the use in sheet molding compounds (SMCs). Sheet molding compounds are thermosetting compounds that contain unsaturated polyesters, styrene monomer, chopped fiberglass, and fillers and are used for rigid parts in automobile exteriors. The addition of the special type of SBCs is used to control shrinkage during cure. The final products have improved surface appearance and better impact resistance [25, 26].

Figure 15.21. Grips on pens (Courtesy Teknor Apex Company).

Figure 15.22. Super soft clear gel (Courtesy Teknor Apex Company).

Figure 15.23. Swim fins (Courtesy Teknor Apex Company).

15.2.4 Modified Asphalt

The modification of asphalt is one of the fastest growing applications for PS block copolymers. Styrene block copolymers are added at amounts less than 20% of the total weight and in some cases even as little as 3%.

Styrene block copolymers absorb the "oily components" from the bitumen increasing their volume to as much as 10 times the polymers volume. The network formed by the styrene domains is inflated but can remain intact throughout the binder giving it elastic properties over a much wider temperature range. This reduces the viscous behavior at high temperature and the brittle behavior at low temperature [27].

Modified asphalt is used for road pavements [28], for chip seals (used to hold the aggregate together when road is resurfaced), slurry seals, and road crack sealants. Other applications are flat rolled roofing, shingles, pressure sensitive modified asphalt membranes, hot mopped asphalt, and other waterproofing applications [29, 30].

15.3 Applications of Thermoplastic Vulcanizates (TPVs) and ETPVs

15.3.1 Introduction

Introduced commercially in 1981, the TPVs had found annual worldwide aggregate applications in excess of 20 million pounds (9,000 metric tons), by the mid-1980s, with more than one thousand different commercial uses [31]. The current estimated consumption (2004) is 162,000 metric tons with projections to 2014 to be 332,000 metric tons [32].

15.3.2 Comparison of TPVs and Thermoset Rubber Materials

Direct comparison of performance and costs of main grades of TPVs and thermoset elastomers have properties somewhere in the range of EPDM, CR (polychloroprene), and CSM (chlorosulfonated polyethylene-Hypalon®) [33]. Another comparison [34], which charts various thermoset and TPE materials according to their service performance in hot air and the swelling in IRM 903 (ASTM #3 Oil) at this temperature positions the EPDM/EPM-based TPVs between CR, EPDM, and CSM and NBR-based TPVs near nitrile and epichlorohydrin rubber materials. Thus the former is a logical candidate for applications requiring a broad spectrum of properties of special purpose elastomers (CR, EPDM, CSM) and the latter for applications requiring an oil resistance comparable to that of NBR [33]. DuPont™ ETPV withstands temperatures up to 160°C (320°F), retains flexibility down to −40°C (−40°F) and resists oil, grease and chemicals, which makes it suitable for a variety of automotive applications.

15.3.3 Commercial Applications of TPVs

Because of the wide spectrum of properties of TPVs, they found applications in many areas such as

- Automotive
- Hose, tube, and sheet
- Mechanical rubber goods and consumer goods
- Architectural and construction
- Electrical and electronic
- Medical and food contact.

15.3.3.1 Automotive Applications

The automotive industry was the first to utilize the performance/cost advantages of TPVs, since these materials are well suited to the specific needs and trends of that industry. Significantly more than half of the rubber materials used in an automobile is found in non-tire uses [31].

The most important factors determining the automotive applications are:

- Steadily increasing under-the-hood temperatures
- Continuing emphasis on safety and reliability
- Quality and cost of rubber articles
- Ease of installation of the rubber parts into the vehicle subassembly.

The currently used components manufactured by melt-processing techniques, such as injection molding, blow molding, simple and crosshead extrusion are, for example [31, 35]:

- Convoluted boots protecting rack and pinion steering gear assemblies
- Drive shaft boot (Fig. 15.24)
- Window seals
- Hose coverings
- Air inlet duct covers (Fig. 15.25)
- Vibration dampeners
- Gaskets and seals (Fig. 15.26)
- Ignition cable coverings
- Body plugs
- Steering column collar (Fig. 15.27).

Figure 15.24. Drive shaft boot (Courtesy Zeon Chemicals LP).

Figure 15.25. Clean air intake duct (Courtesy Zeon Chemicals LP).

DuPont™ ETPV has been used in automotive ducts (Fig. 15.28), brake hoses (Fig. 15.29), spark plug boots (Fig. 15.30), seals, body plugs, and others.

15.3.3.2 Hose, Tubing, and Sheet

The main advantage of this group of products is that they can be manufactured by simple melt-processing methods such as extrusion and calendering and no vulcanization is required after the processing.

The widest application of TPV sheeting is a roofing membrane that can be easily seamed on site by heat sealing. Other extruded or calendered sheets are used for die-cut seals and gaskets.

Figure 15.26. Dust seal (Courtesy Zeon Chemicals LP).

Figure 15.27. Automotive steering column collar (Courtesy Solvay Engineered Polymers Inc.).

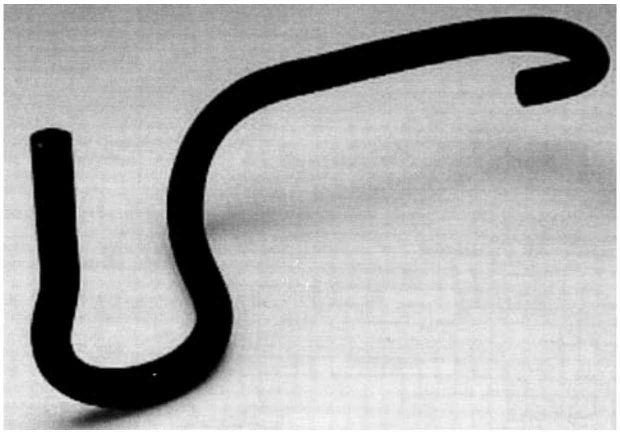

Figure 15.28. ETPV automotive fuel vent tube (Courtesy DuPont).

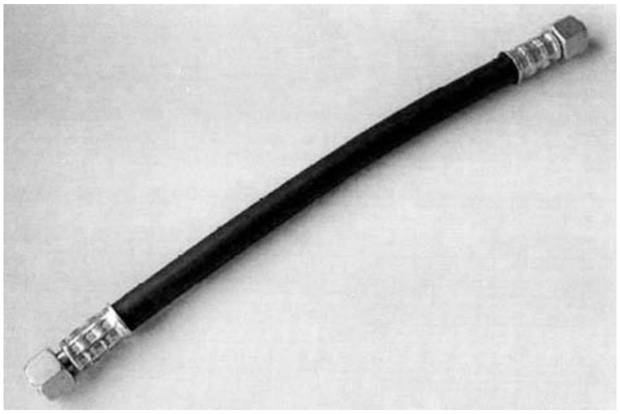

Figure 15.29. ETPV automotive brake hose (Courtesy DuPont).

Figure 15.30. Spark plug and ignition coil boots (Courtesy DuPont).

Extruded tubing from TPV can be used as inner-liner or jacket of hose, or both for hose reinforced by textile or metal mesh. In hose applications the TPEs can be combined with compatible thermoplastics, such as polypropylene, polyethylene. Typical examples are: hydraulic (wire braid) hose, agricultural spray, plant air–water, and mining hose, and industrial tubing [35]. Tubing extruded from stiffer grades can be used as a hose without reinforcement for less demanding applications.

15.3.3.3 Mechanical Rubber Goods and Consumer Goods

This very large group of products comprises the multitude of applications such as parts of industrial equipment, household appliances, recreational and sporting goods, tools, and other; these are manufactured mainly by injection molding, blow molding, and extrusion. Examples are seals, gaskets, valve seats, bushings, grommets, appliance feet, caster wheels injection molded over thermoplastic core, torque couplings, vibration isolators, suction cups, caps, rollers, extruded profiles, bumpers, housings, convoluted bellows, housings, shields, toys, ski pole grips, and soft-feel tool grips, foamed profiles and sheets. Examples of such applications are in Figs 15.31–15.38.

15.3.3.4 Architectural and Construction

Thermoplastic vulcanizates are widely used in expansion joints, roofing, flooring, weather seals around doors, windows and other exterior openings in large commercial buildings, such as shopping centers, warehouses, office buildings, high-rise apartments, and hotels. Specific examples are soft extruded window glazing material and metal-reinforced weather stripping. Applications requiring fire resistance can employ special TPV grades formulated with reliable flame retardants [36].

15.3.3.5 Electrical and Electronics

Electrical properties of TPVs [37] indicate that TPVs can be used as primary insulator, jacketing material, or both. Wire and cable insulations are most widely fabricated by crosshead extrusion over a metal conductor or over its dielectric insulation. Electrical connectors, plugs, and insulators for electrical and electronic assemblies are mainly produced by injection molding, often with metal inserts [36]. Other applications are in computer hardware,

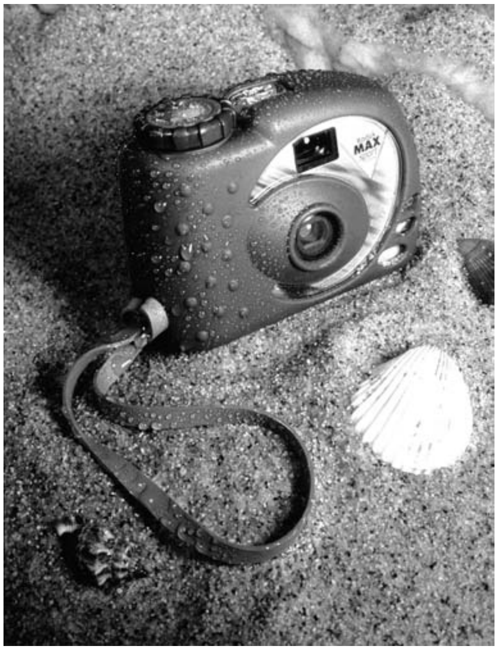

Figure 15.31. Camera (Courtesy GLS Corporation).

Figure 15.32. Sippy Cup (Courtesy GLS Corporation).

Figure 15.33. Hand drill (Courtesy GLS Corporation).

Figure 15.34. Bicycle grip (Courtesy Teknor Apex Company).

Figure 15.35. Grip on iron (Courtesy Teknor Apex Company).

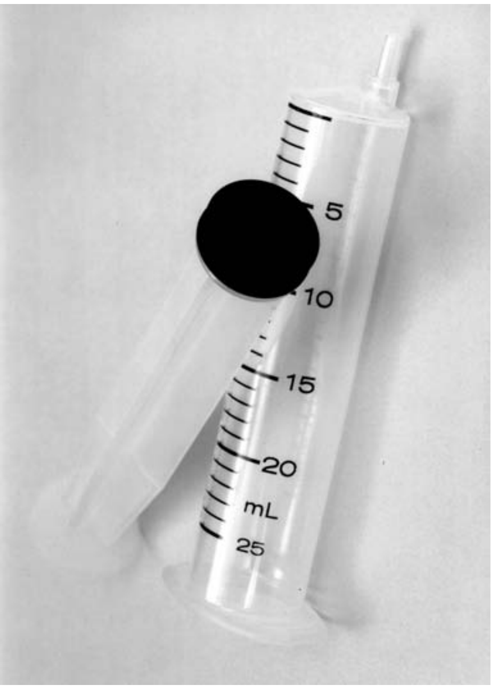

Figure 15.36. Syringe seal (Courtesy Teknor Apex Company).

telephones, electronic appliances, and office equipment. An example of electrical application is a conductive cap (Fig. 15.39).

15.3.3.6 Medical and Food Contact

Thermoplastic vulcanizates based on EPDM are suitable for use in direct contact with foods, beverages, pharmaceuticals, and living tissues. These applications employ grades approved by U.S. Food and Drug Administration. Medical applications include drug vial stoppers, syringe plunger tips, aerosol valve seals, medical tubing, liquid dispenser pump diaphragms, and nursing bed sheets.

Figure 15.37. Grips on screwdrivers (Courtesy Teknor Apex Company).

Figure 15.38. Soft touch applications (Courtesy Teknor Apex Company).

Figure 15.39. Conductive TPE cap (Courtesy RTP Company).

15.4 Applications of Thermoplastic Polyolefin Elastomers (TPOs)

Polyethylene-poly(α-olefin) block copolymers have rather complex morphology; the distribution, size, and shape of both soft and hard phases determine the properties of the copolymer. The polypropylene phase is almost always continuous and the rubber phase may be either continuous or discrete, depending on the amount of rubber in the compound relative to polypropylene [38].

The copolymers are very flexible at low temperatures; however their upper service temperature is rather low, suggesting that the polyethylene segments are rather short. The lower service temperature can be near −80°C (−112°F) the upper service temperature up to 140°C (284°F) for short-term exposure, and 105°C (221°F) for long-term exposure. They have some resistance to oils and solvents [39]. Commercial TPO materials are available in the hardness ranging from 65 Shore A to 70 Shore D.

Thermoplastic polyolefinics are supplied as pelletized compounds developed for specific applications and processing methods. They are processed mainly by injection molding, extrusion, injection blow molding, and vacuum forming, and as blown film [40].

Thermoplastic polyolefinics products are used in a variety of applications with major market areas being

- Automotive
- Wire and cable
- Mechanical goods.

15.4.1 Automotive

Automotive applications are their largest market. Thermoplastic polyolefinics are used in many soft, durable exterior parts to replace sheet metal, giving parts that are not easily damaged by minor collisions, including bumper covers, bumper end caps, body side cladding, body side molding, air dams, fairing pieces, fender liners, rocker panel covers, rub strips, scuff plates, sight shields, stone deflectors, wheel well moldings, grills, and valance panels. Parts in the engine compartment include heating air ducts, conduits, grommets, hood seals, and firewall pads. In the interior, the applications include air bag covers, instrument panels, knee bolsters, glove box doors, door panels, door inserts, and soft skins laminated to polyolefin foam for interior trim. Examples of automotive applications are in Figs 15.40–15.44.

15.4.2 Wire and Cable

Wire and cable applications include flexible cords, battery booster cables, appliance wires, low voltage wire, control cables, hook-up wire, submersible pump cable, and cable jackets. Excellent electrical properties, ozone resistance, and water resistance are the main attributes in these applications [40]. Wire and cable products include both standard and flame retardant grades.

15.4.3 Mechanical Goods

The mechanical goods market is very diverse and many applications include small molded parts where TPO compounds replace vulcanized rubber. For example, they replace butyl rubber in molded parts for electrical applications, CR in bumpers, seals, and electrical plugs. Other parts include gaskets, pump impellers, molded feet, and wheels. The

Figure 15.40. Automotive bumper fascia and grille surround (Courtesy Solvay Engineered Polymers Inc.).

Figure 15.41. Mold-in-color metallic exterior wheel opening trim (Courtesy Solvay Engineered Polymers Inc.).

Figure 15.42. Automotive instrument panel-upper (Courtesy Solvay Engineered Polymers Inc.).

Figure 15.43. Automotive interior, roof pillar cover (Courtesy Solvay Engineered Polymers Inc.).

advantages of TPO in all these applications is that production and postconsumer scrap can be recycled and that production cycles for TPO parts are much shorter. Examples are in Figs 15.45 and 15.46.

Extruded products in the mechanical goods field, where TPO is used are sheets, films (extruded and blown), weather strips, profiles, tubing, hose, etc.

Figure 15.44. Thermoformed all terrain vehicle deck (Courtesy Solvay Engineered Polymers Inc.).

Figure 15.45. Clean room scanner (Courtesy RTP Company).

Figure 15.46. Electric probes (Courtesy RTP Company).

15.4.4 Other Applications

Other applications include transmission belts, specialty conveyor belts, housewares, toys, recreational and sporting goods, luggage handles, shoe

Figure 15.47. Bicycle hub (Courtesy RTP Company).

soles, drum covers, garden hose, spatulas, sealants, tapes, and hot-melt adhesives. Examples are in Figs 15.47 and 15.48.

15.5 Applications of Melt-Processible Rubber (MPR)

Single-phase MPR introduced in 1985 [41] produces parts that have the appearance and feel and perform like those made from vulcanized rubber. At the same time, it offers an unusual combination of resistance to heat, oil and chemicals, and weathering. Depending on grade, the brittleness temperatures range typically from −87°C (−124°F) and the upper continuous service temperature is typically 120°C (248°F) [42]. Another valuable attribute of MPR is a high coefficient of friction; well over 1.0, which is almost double of that of other TPEs such as styrenics and TPVs of similar hardness [42]. Since most commercial MPR grades contain from 9% to 20% of chlorine, they are flame-resistant enough to pass UL-94 HB (horizontal burning) rating as sold and with the addition of a suitable flame retardant they can attain the UL-94 V-0 (vertical burning) rating [42].

As supplied, MPR grades are static-charge dissipative and can be made semi-conductive by compounding them with conductive fillers. These properties made them suitable for applications where static discharge could lead to explosions of dust or solvent vapors (conveyor belts or conveyor hose) or to damage of electronic components.

Figure 15.48. Cutting board (Courtesy Vi-Chem Corporation).

Melt-processible rubber can be processed in plastic and certain modified rubber processing equipment and has been used in a variety of applications, including flexible tubing, molded parts, seals, gaskets, weatherstripping, reinforced hose, wire and cable jacketing, and coated fabrics.

Principal market segments for MPR are extruded and molded goods, and sheeting. The most widely used processes are extrusion, injection molding, blow molding, and compression molding [41, 42].

15.5.1 Industrial Hose

Melt-processible rubber is suitable for the use in tube and cover for general purpose, weather resistant, oil resistant, chemically resistant hose, and hose with static dissipative or semi-conductive properties (see above).

15.5.2 Automotive

The outstanding weathering resistance of these materials, coupled with durable outstanding elastic properties makes them the primary choice for automotive glass seals. Other automotive components made from MPRs are fuse holders, interior trim, knobs, grips, steering wheels, outer belt strip moldings [43], fuel lines, boots, bellows, dust covers, etc. Examples of automotive applications are in Figs 15.49 and 15.50.

15.5.3 Wire and Cable

In general, MPR is used mostly for some low-voltage (≤600 V) applications, where toughness, environmental endurance, and rubbery quality are required. Typical applications are flexible cord applications, welding cable with excellent spark burn-through resistance and as jacketing in higher-voltage construction to provide durable protection to primary insulation.

15.5.4 Elastomeric Sheeting

Sheeting from MPR can be fabricated either by sheet extrusion or by calendering. Calendered sheets, unsupported or fabric reinforced can be easily produced in a single pass without blisters or defects. If desired, the sheets can be embossed by embossing rolls while the stock is still warm [43]. Typical application of sheeting is as roofing membranes, pit and pond liners.

15.5.5 Molded Goods

In this market, MPR is being used for molded parts in industrial, automotive original equipment manufacturer (OEM) equipment, automotive aftermarket, appliances, and oil field outlets. The parts are predominantly produced by injection molding and blow molding and may include articles with metal inserts or parts prepared by bonding rubber to metal by specialized adhesives. Of particular importance are "soft touch" molded articles, used as grips of tools, grips, push buttons, and parts of instruments and hand-held devices as well as handles and other flexible parts of household appliances. Many of these are made by overmolding of rigid components by a soft-touch MPR materials. In some cases an entire device is encased in MPR protective layer for comfortable use and protection from workplace hazards such as drops and fluid spills [44]. Examples are in Figs 15.51–15.53.

Figure 15.49. Wind lace (Courtesy Advanced Polymer Alloys).

Figure 15.50. Hummer latch (Courtesy Advanced Polymer Alloys).

15.5.6 Fabric Coating

In fabric coating, MPR has replaced vulcanized rubber in some applications, where the unusual hand and drape of MPR-coated fabric are of interest. An example of this application is as inner and outer coating on fabric used to make huge inflatable pillow-tanks for environmental protection. Such tanks are stored on the decks of oil tankers and can be deployed in case of emergency to transfer the oil from the tanker and be launched into the sea. The capacity of such pillow tank can be as much as 20,000 cubic meters (706,300 cf) [44]. Other application in this area is to modify PVC compounds to reduce sheen and add to drape and hand [41].

Figure 15.51. Buck knife handle (Courtesy Advanced Polymer Alloys).

Figure 15.52. Drill handle (Courtesy Advanced Polymer Alloys).

15.5.7 Other Applications

Many articles from MPR find applications in the consumer market, including toys. Since the commercial grades are clear or translucent and light in color, they can be easily colored by the addition of a variety of inorganic and organic pigments and color concentrates and it is possible to obtain bright colors as well as variety of special effects, such as metallic, pearlescent, thermochromic, etc.

Figure 15.53. Stream light (Courtesy Advanced Polymer Alloys).

Other applications are architectural window and door seals, home and commercial irrigation systems, agricultural equipment, variety of seals, telephone and calculator keypads, grips on cameras and more. Architectural applications of MPR are in Figs 15.54 and 15.55.

15.6 Applications of PVC Blends

15.6.1 PVC–Nitrile Rubber (NBR) Blends

Poly(vinyl chloride) and NBR have been blended in different ratios for many years. In blends, where the predominant component is PVC, NBR acts as a true plasticizer and the resulting blends are more rubbery than PVC plasticized with liquid plasticizers (e.g., dioctyl phthalate) but not very elastomeric. In general, NBR with the acrylonitrile contents of 40% is needed to obtain a single phase blend [45]. The NBR can be non-cross-linked or pre-cross-linked to different degree. The former yields blends with lower viscosity suitable mainly for injection molding. Pre-cross-linked NBR provides a material with a resistance to compression set and other elastomeric characteristics to be considered a true TPE. It also increases melt viscosity of the blend so that it is more suitable for extrusion and calendering.

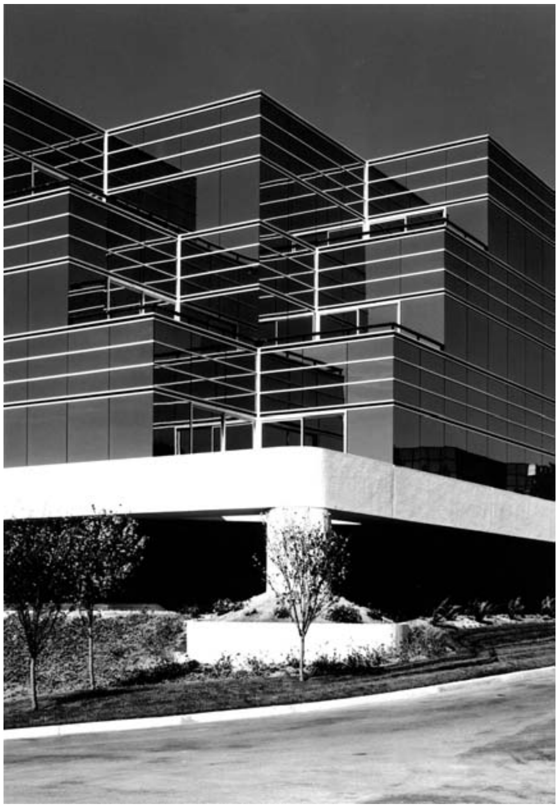

Figure 15.54. Building with MPR curtain wall seals (Courtesy Advanced Polymer Alloys).

Figure 15.55. Architectural extrusions (Courtesy Advanced Polymer Alloys).

When properly formulated, PVC–NBR blends exhibit an excellent resistance to chemicals and to swelling in oils, and a very good abrasion resistance. They can be welded by heat, radio frequency, or ultrasonic methods or bonded by adhesives. Depending on the melt viscosity (see above), they can be processed by injection molding, extrusion, calendering, or extrusion blow molding. Typical articles made from these blends are seals and gaskets, hose tubing and cover, cable jackets, boots and soling, grommets and plugs, and bellows and sleeves.

15.6.2 PVC–Copolyester Elastomer (COPE) Blends

Although plasticized (flexible) PVC (FPVC) and COPEs are compatible in wide range of ratios, only such blends where FPVC is used to increase flexibility of COPE are practical, the reason being the high cost of COPE in comparison to FPVC. For the reason of preventing decomposition of PVC during processing only low melting COPEs with about 33% 4GT and melting temperature below 180°C (356°F) are being used.

Typical applications of PVC–COPE blends are as a lower cost alternative to TPUs in hose tubing and cover. Other uses are automotive primary wiring that is more heat resistant than PVC wiring, protective jackets for retractile cords for telephones and domestic electrical appliances that have better memory characteristics than FPVC. Another lower cost alternative to TPU is in sport shoe soling.

15.6.3 PVC–TPU Blends

Most of the TPUs are very compatible with PVC and such blends exhibit only one major glass transition, whose position on the temperature scale is raised with increasing levels of PVC [46]. As it is the case with PVC–COPE blends, most widely used blends are those where PVC is added to TPU to maintain desirable properties of TPU while reducing cost [47].

The main applications of blends of PVC–TPU are in shoe soles and heels. Their main attributes are good wear resistance, good flexibility, good compression set, oil resistance, and reasonable cost. Essentially the materials have better performance than pure PVC but lower cost than pure TPU.

15.7 Application of TPUs

15.7.1 Introduction

Thermoplastic polyurethane elastomers are multiblock copolymers with alternating hard and soft segments. The hard segments (predominantly crystalline) are polyurethanes or polyureas. The soft, elastomeric segments are amorphous and are based on polyesters or polyethers. Each of these types of TPUs has specific attributes (see Section 9.5) that make them useful in a great variety of applications. The ester-based TPUs have excellent tensile strength, load-bearing capacity, and resistance to abrasion, ozone, oxygen, fuel, oils, and solvents. The ether-based TPUs provide excellent low temperature properties and resistance to hydrolysis, and to microbial attack. Thermoplastic polyurathanes with special properties can be obtained by reinforcement or polymer blending.

Depending on the structure and additives used in specific compounds, TPUs have the following distinctive properties:

- Abrasion resistance
- Clarity
- Cut resistance
- Flexibility
- Heat sealability
- Load bearing capacity
- Low-temperature flexibility
- Non-marking
- Oil resistance
- Toughness
- Vibration damping.

15.7.2 Commercial Applications

In some applications TPUs are replacing vulcanized rubber [48], although in majority of cases they are used because of their unique combination of properties. The specific areas, where TPUs are widely used include automotive, hose and tubing, wire and cable, wheels and casters, film and sheet, adhesives, sealants and coatings, and general purpose articles.

15.7.2.1 Automotive

Typical TPU articles in automotive applications are: gaskets, seals, bushings, bellows, steering gear parts, fuel line hose, timing belts, shock absorbers (Fig. 15.56), bumpers, fender extensions, membranes of hydro-pneumatic suspension system, hatchback strap, side shields, filler panel, fender and quarter panel extension, windshield and close-out lace, valance panel, instrument panel, interior trim, skins of instrument panels (Fig. 15.57), automotive center consoles (Figs 15.58 and 15.59), gear knobs (Fig. 15.60), car keys (Fig. 15.61) gears and assembly line equipment.

15.7.2.2 Hose and Tubing

Examples of the TPU hose and tubing are irrigation hose, garden hose, fire hose, hydraulic hose, sewer hose, fuel line hose for snowmobiles and small gasoline engines, pneumatic tubing for robotics, surfboard lashes and cords, medical tubing.

15.7.2.3 Wire and Cable

Wire and cable applications include seismographic cable, audio wire, camera cable, computer cable, head-set cable, marine cable, welder cable, air gun control cable, communication wire, towing leader, abrasion resistant cable jacketing, plugs (Fig. 15.62), etc.

Figure 15.56. Elastic element for shock absorber (Courtesy Bayer MaterialScience LLC).

Figure 15.57. Skins of instrument panels (Courtesy Martin Thomas International).

Figure 15.58. Auto tamber door (Courtesy Bayer MaterialScience LLC).

15.7.2.4 Wheels and Casters

Examples for these applications are wheels and casters for shopping carts, food service carts, and hospital carts, wheels for inline skates and skateboards, and others.

Figure 15.59. Gear shifting handle (Courtesy RTP Company).

Figure 15.60. Gear shift knobs (Courtesy Bayer MaterialScience LLC).

Figure 15.61. Car key (Courtesy Bayer MaterialScience LLC).

Figure 15.62. Electrical plugs (Courtesy Bayer MaterialScience LLC).

15.7.2.5 Film and Sheet

Thermoplastic polyurethane films and sheets are produced by flat film extrusion, blown film extrusion, or calendering in gauges from approximately 20 µm up to several mm typically using materials with hardness between 60 and 95 Shore A. The films can be laminated to PU foams and textiles and show high puncture resistance [49]. Special grades based on poly(ethylene glycol) soft segments with high water vapor transmission are used for breathable films in the textile industry [50].

15.7.2.6 Adhesives, Sealants, and Coatings

The number of applications of TPUs in adhesives, sealants, and coatings is smaller than rubber replacement and other uses. In adhesive technology, they are applied mostly as hot-melts [51], although some grades can be applied from solutions in polar solvents, such as MEK of dimethyl formamide. The hot-melts are useful in footwear for attaching soles to the uppers, and in coextrusions, where they are used as tie layers between dissimilar polymers [52]. Thermoplastic polyurethane-based coatings are used mainly for coating fabrics used for inflatable boats (Fig. 15.63), collapsible canoes, life rafts, life jackets, and oil barriers [53]. Coating of individual yarns increases greatly the tenacity of the yarn and protects it again soiling. Special yarns coated with transparent TPU are woven into decorative textiles used in car seats, armchairs, and office chairs [53]. Other applications are shoe lacquers, inks, magnetic tape binders, luggage, gel seats, and artificial chamois products [54]. An example of an application of clear TPU protective coating on fabric is in Fig. 15.64.

Figure 15.63. Inflatable raft from TPU-coated fabric (Courtesy Merquinsa).

15.7.2.7 Mechanical Goods, Consumer, and Sporting Goods

Thermoplastic polyurethanes are used in drive belts, gaskets and seals (Fig. 15.65), industrial hose and tubing, tire chains, shoe soles and heels, grommets and spring sleeves, bushings and dust caps for supporting joints, wire and cable jackets, overmolded parts with a soft grip, such as handles

Figure 15.64. Automotive seat from fabric treated with clear TPU coating (Courtesy Bayer MaterialScience).

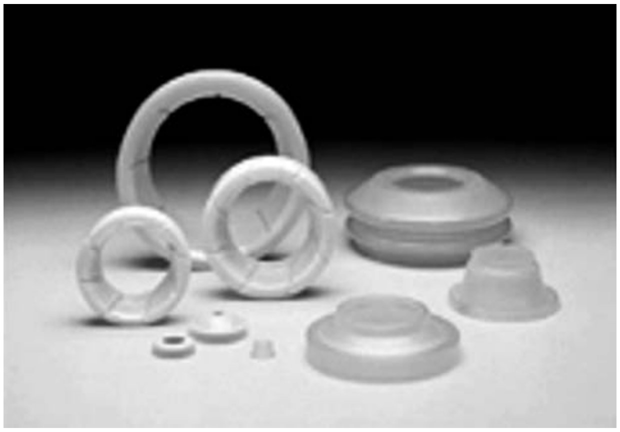

Figure 15.65. TPU seals (Courtesy Bayer MaterialScience LLC).

of machines, tools, appliances and furniture [53], sporting goods (frames of ski goggles, ropes for surfboards, parts of ski bindings, studs for sport shoes, and shells of inline skates, golf ball covers), soccer ball covers (Fig. 15.66), tennis racquet components (Fig. 15.67). Grades with hardness greater than 55 Shore D are used in shells for ski boots, utilizing their exceptional scratch resistance, low temperature impact resistance, and low relative sensitivity of stiffness to temperature. Animal identification tags (short-term and long-term tags) are rather unique application for TPU, using grades with 90–95 Shore A hardness based on polyether or polycarbonate soft segments [55] (Fig. 15.68). An example of a TPU lap station is in Fig. 15.69.

Figure 15.66. TPU soccer ball (Courtesy Bayer MaterialScience LLC).

Figure 15.67. Tennis racquet components (Courtesy RTP Company).

15.7.2.8 Medical Applications

Thermoplastic polyurethanes are compatible with human blood and tissue and therefore can be used in medical devices, such as catheters and tubing [53, 55]. Materials based on methylene diphenyl diisocyanate (MDI) cannot be in contact

Figure 15.68. Animal tags (Courtesy Merquinsa).

Figure 15.69. Lapstation (Courtesy GLS Corporation).

with human tissue for more than 28 days, however TPUs based on aliphatic diisocyanates can be used for longer exposures, even as body implants [55].

15.7.2.9 Blends with Other Polymers

Blends of TPU with many thermoplastic and elastomers are relatively easy to prepare. The only polymers that show little or no compatibility are non-polar polymers, such as polyolefins [56]. The most widely used blends of TPUs are those with plasticized PVC (see Section 15.6.3) that have good flex life, oil resistance, abrasion resistance, and low-temperature flexibility and are being used in special footwear [57].

15.8 Application of Thermoplastic Polyether Ester Elastomers

15.8.1 General Properties and Processing

Thermoplastic polyether ester elastomers comprise of alternating hard and soft segments, where the hard segments are crystalline polyester, poly(butylene terephtalate) and the soft (elastomeric) segments are almost always copolymers of terephtalic acid with poly(oxytetramethylene glycol). They are tough materials exhibiting high tear strength, high flex-cut resistance, abrasion resistance, creep resistance, high oil and solvent resistance, and low compression set. At low strains they have a low hysteresis, behaving almost like a perfect spring [58]. Thermoplastic polyether ester elastomers are resistant to hot oils, and this makes them competitive with chemical resistant and specialty elastomeric materials based on NBR, epichlorohydrin, and polyacrylate. Commercial grades are available in the range of Shore D hardness values from 30D to 82D. Special grades contain UV stabilizers, heat stabilizers, flame retardants, or hydrolysis resistant additives.

They can be processed easily by conventional thermoplastic processes like injection molding, blow molding, calendering, rotational molding, extrusion, and meltcasting.

15.8.2 Commercial Applications

In commercial applications, COPEs can replace a variety of conventional materials, such as metal, cast polyurethanes, leather, and rubber. Within their elastic design range, COPEs offer 2–15 times the strength of vulcanized rubber. Because of that, it is common to redesign rubber parts for one-half to one-sixth the original part thickness and weight. Non-reinforced COPEs also can replace composites of rubber with metal, fibers, and fabric.

15.8.2.1 Automotive Applications

Automotive applications include constant velocity drive joint (CVJ) boots (Fig. 15.70), spoilers, air dams, side moldings, fascia, grills, hinges and locks [59, 60], protective boots in suspension joints, primary pump for automotive fuel lines [61]. In these applications, if needed, the parts are easily painted or sputter chrome coated because of their excellent molded surface and heat resistance.

15.8.2.2 Electrical/Electronic Applications

Electrical/electronic applications include thin wire insulations, retractable coiled cables (Fig. 15.71),

Figure 15.70. CVJ Boot (Courtesy DuPont).

Figure 15.71. Retractable coiled electric cable (Courtesy DuPont).

hermetically sealed units, switches and connectors, panel insulator covers [59, 60, 62]. In fiber optics technology, COPEs are used as the primary coating, secondary coating, buffer tube, and jacket taking advantage of their combination of their mechanical strength and environmental resistance [62, 63].

15.8.2.3 Extruded and Molded Mechanical Goods

Typical applications for COPEs in this field are specialty hose tube (Fig. 15.72), hydraulic hose and cover with service temperatures −65°F to +250°F (−54°C to +121°C) and 275°F (135°C) for intermittent use [60], pneumatic tires (without reinforcement) with a high load-bearing capacity (made by rotational casting). Other products are flexible couplings, backup rings for hydraulic piston devices, gears power drive belts, toothed belts for office equipment, pipe clamps, tracks for recreational, farm and military vehicles, railroad draft gear, liner of butterfly valves, power tool handles, heel cushioning system of running shoes, wrist protector for snowboard riders [61], and many molded articles with high wear resistance, very good flexibility and impact resistance [62, 63]. Examples of such applications are in Figs 15.73–15.76.

Figure 15.72. PVC tubing with COPE lining (Courtesy New Age® Industries Inc.).

15.8.2.4 Other Applications

An important application of COPEs is in *medical devices*, where compatibility of the resins with human blood and tissue, their chemical purity and inherent resistance to radiation used for sterilization are key advantages [64–66]. An example for a medical application is an IV bag shown in Fig. 15.77.

Higher hardness polyethylene oxide (PEO)-based polyether esters exhibit a high water vapor transmission rate and are for that reason used in *waterproof, breathable films* that are laminated with fabrics and used in the manufacture of outer garments, such as jackets, pants [67], gloves, tents, footwear [68] and single-use surgical gowns [61]. Another application of breathable COPE films is in carpet underlay. The film is laminated to the surface of the carpet foam cushion. Such laminate allows easy cleanup of spills by blocking the penetration of the spilled liquids and minimizes the undercarpet moisture buildup by allowing its escape through the film [61].

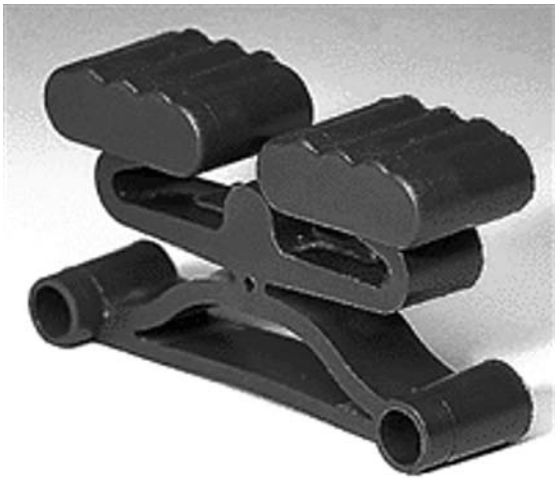

Figure 15.73. Spring bed slats (Courtesy DuPont).

Figure 15.74. Power tool handle (Courtesy DuPont).

Figure 15.75. Telescoping trekking pole (Courtesy DuPont).

15.9 Applications of Polyamide TPEs

15.9.1 Introduction

Polyamide TPEs consist of alternating hard and soft segments joined by amide linkages. The hard, crystalline segments are polyamides and the soft, elastomeric segments are polyethers or polyesters. Depending on the type of building blocks used, the products have different properties. They may be as soft as 65 Shore A and as hard as 70 Shore D. The upper service temperature depends on the choice of polyamide segment and can be as high as 200°C (392°F). Resistance to oils and solvents of these materials is good.

These TPEs can be compounded with various resins or additives to alter or enhance their basic properties. Compounding can be used to adjust cost, toughness, flexibility, tack, and resistance to

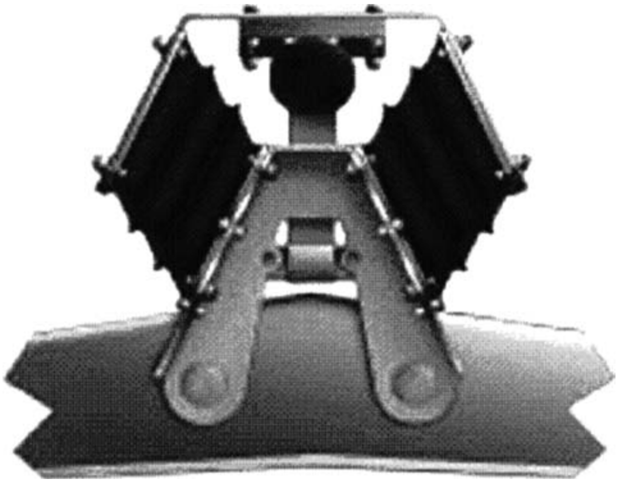

Figure 15.76. Auxiliary spring (Courtesy DuPont).

Figure 15.77. I.V. bag (Courtesy Eastman Chemical Company).

oxidation and effects of ozone, flame resistance, and other properties. They also can be blended with other polymers in the melt stage to form alloys of unique properties. Resins that are compatible with the polyamide block tend to produce hard materials with no tack, while the addition of resins compatible with the soft ether or ester segments will produce soft, flexible tacky compounds.

Polyamide elastomers can be processed by usual melt-processing techniques, such as injection molding, extrusion, blow molding, rotational molding, and thermoforming. To obtain optimal properties the resins have to be dried to have moisture content less than 0.02% before processing and it is recommended that the feed hopper be purged with dry nitrogen to maintain the low moisture level [69].

15.9.2 Commercial Applications

Because of their high service temperatures, good thermal aging, and chemical resistance, polyamide elastomers can fill the gap between TPUs and silicone-based polymers. This definitely makes them primary candidates for automotive under-the-hood applications and for high-temperature insulations of wires and cables [69]. Their high impact strength, tear resistance, abrasion resistance, low temperature resistance, and resistance to flex fatigue open a great variety of applications in hose and tubing, seals and gaskets, bellows and other molded technical goods, for sporting goods and others.

15.9.2.1 Automotive

Typical uses of polyamide TPEs in automobiles are under-the-hood parts, such as fuel systems, hydraulic and pneumatic systems, various functional parts, seals, gaskets, bellows and protective boots (Fig. 15.78), windshield washer tubings, airbag doors, and shock-absorber parts [70], timing belts (Fig. 15.79), automobile exterior and interior parts [71].

15.9.2.2 Sporting Goods

The attributes of polyamide elastomers useful for this market are low weight, excellent mechanical properties, particularly resistance to flexural fatigue, flexibility over a wide range of temperatures, very good UV stability, ozone resistance, easy coloring, and good processing. Products in this category are shells of ski boots (Figs 15.80 and 15.81), soles of athletic shoes (Fig. 15.82), soles with studs (Fig. 15.83), protective and decorative layers of skis [71] and snowboards (Figs 15.84 and 15.85), decorative films for tennis racquets (Fig. 15.86), ski goggles (Fig. 15.87), swimming goggles (Fig. 15.88) footballs, and basketballs [72].

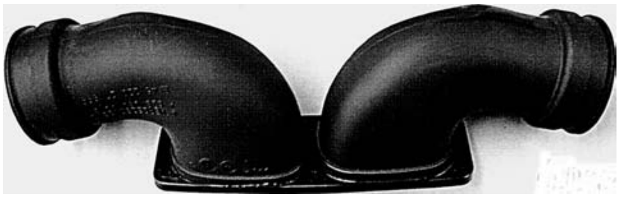

Figure 15.78. Air duct (Courtesy Kraiburg TPE Corporation).

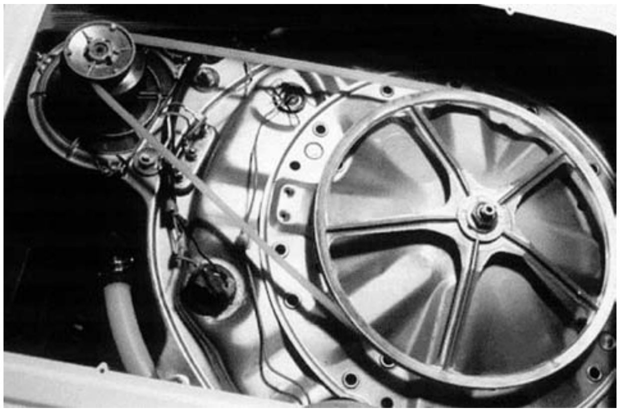

Figure 15.79. Automotive timing belt (Courtesy Arkema Inc.).

Figure 15.80. Shell of alpine boots (Courtesy Degussa AG).

Figure 15.81. Shell of telemark ski boot (Source: DPA).

Figure 15.82. Sole of athletic shoes (Courtesy Arkema Inc.).

15.9.2.3 Wire and Cable

Polyamide elastomers are used in wire and cable industry, particularly for high-temperature insulations, abrasion resistant cable jackets, and for nonkinking wires.

15.9.2.4 Technical Goods

Hose and tubing (Fig. 15.89), seals and gaskets, conveyor belts, rollers, silent gears (Fig. 15.90),

Figure 15.83. Sole of soccer shoes (Courtesy Degussa AG).

Figure 15.84. Protective and decorative layers for snowboards (Courtesy Degussa AG).

Figure 15.85. Molding of a snowboard (Courtesy Degussa AG).

Figure 15.86. Decorative films for tennis racquets (Courtesy Degussa AG).

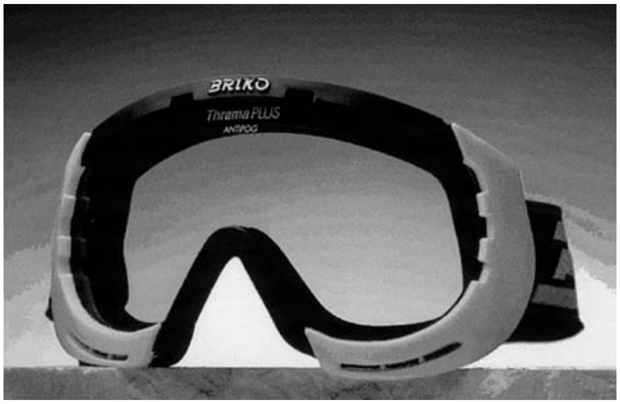

Figure 15.87. Ski goggles (Courtesy Arkema Inc.).

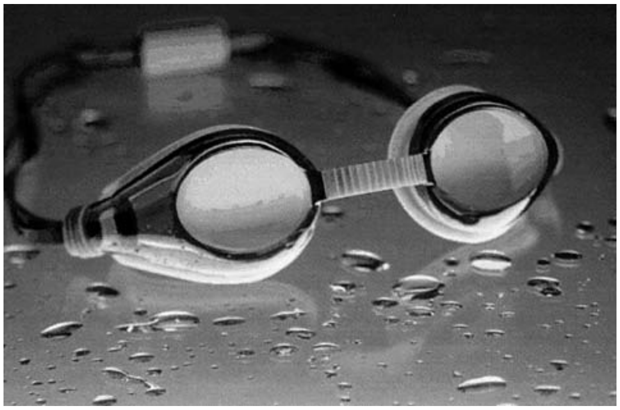

Figure 15.88. Swimming goggles (Courtesy Arkema Inc.).

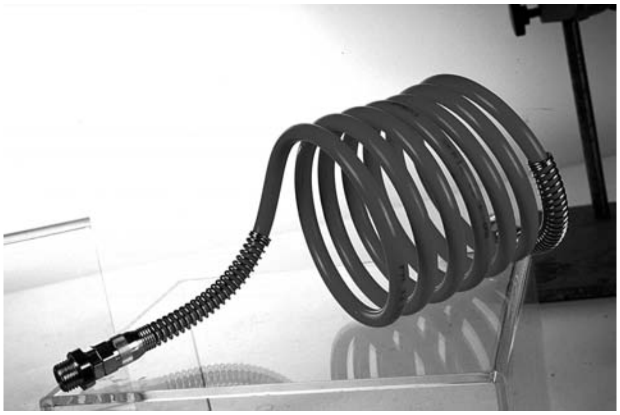

Figure 15.89. Paint spray hose (Courtesy Degussa AG).

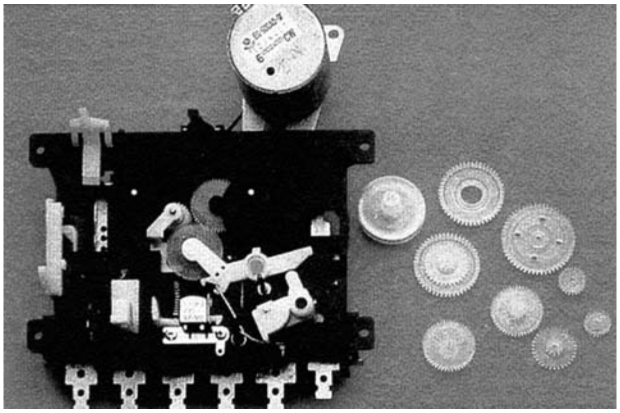

Figure 15.90. Silent gears (Courtesy Arkema Inc.).

powder coated parts, waterproof membranes [70], bellows and boots for different types of equipment [72, 73], flexible couplings, tire chains, wheels, and semi-conductive films used in packaging applications for electromagnetic interference/radio frequency (EMI/RF) shielding [73] are typical applications in this category.

15.9.2.5 Medical Applications

Medical applications include catheters, tubing (Fig. 15.91) and breathable membranes, surgical garments, surgical sheeting, baby diapers, adult incontinence articles [72], and dental floss (Fig. 15.92).

15.9.2.6 Other Applications

Specialty grades of polyamide TPEs are used in decorative and protective films for consumer goods [71], protective gloves (Fig. 15.93), keyboard covers (Fig. 15.94), food packaging (Fig. 15.95), and processing aid for extrusion of TPUs [71].

Figure 15.91. Oxygen mask and tubing (Courtesy Nycoa).

Figure 15.92. Dental floss (Courtesy Arkema Inc.).

Figure 15.93. Protective gloves (Courtesy Arkema Inc.).

Figure 15.94. Keyboard cover (Courtesy Arkema Inc.).

15.10 Applications of Ionomeric TPEs

15.10.1 Introduction

Ionomeric elastomers have been developed in late 1950s and introduced in the early 1960s [74], but their full potential has not been yet realized [75]. The ionomeric aggregation or formation of clusters (large ionic aggregates), or the interaction of the polar groups have major effects on the physical, mechanical, and rheological properties of the polymers. General characteristics, of ionomer-based systems are enhanced green strength, and high melt viscosity. The high melt viscosity is useful for heat sealing and in extrusion; however, it may be a limitation in injection molding. Other desirable properties are toughness, outstanding abrasion resistance, and oil resistance. The TPEs in this category are based on carboxylated and sulfonated polymers.

Figure 15.95. Film pouch for cooking noodles (Courtesy Arkema Inc.).

For practical applications, the base polymers are compounded with mineral fillers, plasticizers (mostly process oils), antioxidants, and polyolefins (polyethylene or polypropylene) using conventional rubber mixing equipment. The finished compositions range typically from relatively soft (hardness 70 Shore A) to very hard, semi-plastic materials (hardness greater than 50 Shore D) [74, 75]. The processing conditions for this class of TPEs are similar to those used for flexible PVC [75]. Blends of ionomeric TPEs with other polymers, such as sulfonated EPDM with polypropylene, sulfonated butyl rubber with polypropylene, high-density polypropylene, and SBC, maleated high-density polyethylene with maleated EPDM, and other similar blends usually exhibit synergistic effects on mechanical properties. These are attributed to the formation of interpenetrating networks and/or ionic interaction between the components [76].

15.10.2 Commercial Applications

15.10.2.1 Adhesives

One of the fast growing applications of ionomeric TPEs is adhesive technology. Ionic ethylene vinylacetate copolymers are used in various hot-melt and solvent adhesive systems [75]. Carboxyl and sulfonate-containing polymers are used for water-based PSAs often combined with emulsified tackifiers (aliphatic petroleum resins) to facilitate bond formation on contact [74].

15.10.2.2 Other Applications

Sulfonated EPDM is used in shoe soles, garden hose, and calendered sheets, heat-sealable sheeting (e.g., roofing membrane) [76]. Other applications of ionomeric TPEs include packaging films for processed meats and medical packaging, skin packaging for electronic and hardware items, foil and paper coatings of multiwall bags, golf ball covers, roller skate wheels, bowling-pin coating, etc. [76], coatings to encapsulate diverse materials (e.g., fertilizers or oxidizing chemicals to assure controlled release [77]. Elastomeric ionomers when added at 5–10% level to asphalt greatly improves the performance of asphalt in roofing applications. Relatively low levels of sulfonated EPDM to various thermoplastics, such as polyamide or polypropylene oxide improve their impact resistance [75]. Recently developed products [74, 78, 79] are suitable for kitchenware, trim for small appliances and office furniture as well for automotive interiors (e.g., shifter knobs) and automotive bumpers and fascias [78]. Potential future applications include foams, elastic fibers with high strength, polymer modifiers, coatings, and more [75].

15.11 Applications of Other TPEs

15.11.1 Applications of Star Block Copolymers

Star block copolymers prepared by anionic methods have been shown to exhibit superior mechanical properties and lower melt viscosities than linear triblock copolymers with the same molecular weight. The star copolymers with low molecular weight arms exhibited low viscosities and were easily processed (see Section 13.1.2).

Because of their unique properties, star block copolymers are widely used in specialty applications. Due to their unusual viscosity behavior, they find use as viscosity modifiers, viscosity index improvers, dispersants, and pour point depressants [80–85] and in adhesives and sealants [86–88]. Star polymers with functional terminal groups are efficient cross-linking agents. For example, star polymethacrylates are reported as reinforcing agents for polyurethanes [89–91]. Since polyisobutylene (PIB) star block copolymers exhibit a superior strength [92] and improved processing properties compared to their linear counterparts, it is quite possible that they might in the future replace some linear triblock TPEs in certain applications.

15.11.2 Applications of Thermoplastic Interpenetration Networks

Thermoplastic interpenetrating networks (IPNs) are mostly leathery at the temperatures at which they are used. They exhibit a high flexibility, but are not soft and rubbery as many TPEs discussed in other chapters. The value of certain IPNs exhibit nearly constant modulus in the leathery range from T_g of the center block, –60°C up to the melt of the semi-crystalline component (typically 200°C or slightly higher [93]). They are suitable materials

Figure 15.96. Overmolded grips (Courtesy Teknor Apex Company).

Figure 15.97. Grip on electrical carving knife (Courtesy Teknor Apex Company).

Figure 15.98. Mouth guard (Courtesy RTP Company).

Figure 15.99. Intermec Handheld (Courtesy RTP Company).

for automobile bumpers, under-the-hood wiring in automobiles, etc. [94].

15.11.3 Applications of Special Blends and Proprietary Compounds

Some companies develop specialized compounds based on standard TPEs, their blends or blends with other polymers or use proprietary processes for their preparation. Such materials have often unique properties, such as exceptional softness, unique feel, high resistance to wear, resistance to high temperatures, clarity etc. Examples of such applications are in Figs 15.96–15.99.

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16 Recycling of Thermoplastic Elastomers

16.1 Introduction

In general, recycling of thermoplastic materials, whether from production or from postconsumer collection, can be directed at four modes of reuse of resources:

- use as generic plastic
- use of mixed plastic
- regeneration of raw materials
- use in energy recovery.

Recycling to generic plastic is essentially the typical secondary recycling. It begins with collection of postconsumer items, such as used bottles, cleaning, shredding into granular form or converting into pellets by melting, melt filtration, and subsequent pelletization. Granules and pellets are most frequently added in required proportion to virgin resins. It should be noted that most thermoplastics cannot be remelted indefinitely without adverse effects on the polymer, such as loss of mechanical properties, discoloration, and possibly partial cross-linking. For that reason, the use of 100% recycled material is seldom practiced.

Recycling to mixed plastic involves mixing of often incompatible plastics into commingled plastic structures [1]. Such materials are mostly used for the manufacture of plastic lumber.

Regeneration of raw materials typically involves depolymerization. For example, condensation polymers, such as PET or polyamides, can be depolymerized via reversible synthesis reactions to initial diacids and diols, or diamines. Typical reactions used here are alcoholysis, hydrolysis, and glycolysis. For example, methanolysis of PET recreates dimethyl terephthalate and ethylene glycol. Depolymerization of condensation polymers can be nearly stoichometric and the recovered raw materials are used mainly to produce new virgin polymer, although they can be used for other syntheses.

Energy recovery uses several methods. One of them is simple incineration of the collected scrap and the combustion heat is used to heating or to producing electrical energy. Other methods employed are thermolysis (pyrolysis and gasification), hydrogenation, and liquefaction. The resulting products are then used as fuel (gases) or as refinery feedstock (liquids) [2].

16.2 Recycling Methods for Thermoplastic Elastomers (TPEs)

Since TPEs behave essentially as conventional thermoplastics, they can be recycled using the same methods. Many TPEs tolerate multiple recycling [3]. The Society of Automotive Engineers (SAE) has classified commercial TPEs generically to enable their segregation into mutually compatible categories for recycle purposes [4]. In this scheme, TPEs are categorized in the same manner as that used for rigid thermoplastics such as polypropylene and polystyrene (PSt).

Thermoplastic vulcanizates (TPV) are widely used in automotive applications (weather stripping, rack and pinion steering gear bellows, constant velocity joint boots, air bag door covers, body plugs, interior skins, etc.) and in appliances (disk drive seals, dishwasher sump boot, door seals, compressor mounts). The used articles as well as production scrap are simply ground in a granulator and the granulate is added in relatively high proportions to the virgin material. The TPV granulate is compatible with granulate prepared from thermoplastic olefins (TPO). In fact it was found that the addition of TPV granulate improves the properties of the TPO material [5]. Many automotive manufacturers have started extensive car dismantling programs and are working together with polymer manufacturers to recycle and reuse material, often in “closed loop” systems, where the material goes back into the original product [6].

Other recycling routes for used TPE components are not significantly different from the route for other elastomers, such as incineration with energy recovery. The main benefit of TPEs in this context is that they contain relatively little sulfur, with consequent beneficial effects on incinerator flue gas composition.

While components made from TPEs can in theory be recycled like other thermoplastics, they still suffer from the disadvantage that they are not pure TPE but have inserts or are composites or blends of materials used in overmolded parts. In the case of the largest class of TPE, styrenic block copolymers, up to one-third of the total production is used in inherently nonrecyclable applications, such as oil modifiers, adhesives, or bitumen modification [7].

Recent development that allows recycling of materials from overmolded and coextruded parts is the use of *magnetic separation*. Magnetic separation is a well-established technique used for high-volume separation in mining, aggregate, and other industries. It is also widely used to remove metal contaminants from plastics and rubber. In order to be applied for the separation of polymeric materials from mixtures, for example, TPE from polypropylene or other rigid plastic, it is required that a magnetic additive be mixed into the TPE material. The amount of this additive is typically 1%. It has been established that the additive does not have adverse effect on either the physical properties of the material or on the overmolding adhesion. In the recycling process, the granulated scrap is placed onto a belt conveyor and the particles of the resin with the magnetic additive are separated at the end of the belt by a roll with imbedded powerful rare-earth magnets. The particles attracted to the roll are collected in a hopper after they fall away from it. A mechanical barrier or "splitter" helps separate the two particle streams [8].

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17 Recent Developments and Trends

17.1 Current State

Thermoplastic elastomers (TPEs), introduced commercially only in the 1960s, have developed within the last four decades from being a technological curiosity due to their combination of elastic behavior and thermoplastic processing into a formidable array of materials. Their current worldwide annual consumption is over 2 million metric tons and they grow at an overall rate of over 6% per year. This growth is almost a double of the growth rate for thermoset (vulcanized) rubber [1].

Although TPEs cannot match the high elasticity of some conventional fully cured elastomers, such as natural rubber (NR) or polybutadiene rubber, and their resistance against softening with increasing temperature, they offer a large number of other benefits, such as simpler processing, purity, and attractive appearance.

The major current commercial applications of TPEs are, as shown in preceding chapters, automotive, industrial and consumer products, medical, construction, adhesives, coatings, and polymer modifications.

17.2 Drivers for the Growth of TPEs

The simplified processing with fewer manufacturing steps, virtual elimination of scrap, considerably shorter cycles, lower energy consumption, and lower volume costs (due to low density of most TPEs) are clearly the strongest drivers for the growth of TPEs.

Legislative and environmental pressures force the manufacturers and users to reduce scrap and provide conditions for recycling. This is evident particularly in the field of vehicles, where the trend is essentially to a complete recycling. In fact, automobile manufacturers design the vehicles often with this in mind.

The issues around PVC alone and the use of plasticizers in PVC, raised strongly in some European countries, open the opportunities for TPEs to replace PVC in certain applications.

The use of "soft-touch" TPEs alone or in combination with rigid substrates using overmolding of coextrusion represents a multitude of entirely new applications characterized by comfort, functionality, ergonomics, and often just plain attractive appearance. Many of the TPEs are light colored or even water white and clear and can easily be colored into a great variety of colors.

The purity and inertness of some of the polymers alone make them suitable for many medical applications and applications where they come in contact with food and drugs.

The efforts to match resilience and resistance to permanent deformation (set) at ambient and elevated temperatures are still important and strong drivers in the technical programs.

17.3 Trends in Technical Development

Many developmental programs still have the goal of providing materials that have properties equal to thermoset elastomers, as pointed out earlier. Other goals are improved processing (increased melt strength and improved melt flow) and increasing use of fabrication methods other then the usual injection molding and extrusion, namely, blow molding, rotomolding, and thermoforming. As for desired properties, increased softness, greater transparency, improved adhesion, and compatibility with a variety of other polymers and substrates are the subject of many active research and development projects.

Modifications of established polymers, compounding methods to attain desired processing behavior and performance, including reduced fogging and flame resistance at lowest possible cost, are high on the list.

17.3.1 Trends in Development and Uses of Individual TPEs

In *styrenic TPEs* the developments include modifications to the polymer structure, such as incorporation of styrene into styrene–ethylene–butylene–styrene (SEBS) mid-blocks, which can also be subjected to dynamic cross-linking. The increased cross-link density leads to increased moduli and resistance to heat and oil. Hydrogenation of side groups in styrene–butadiene–styrene (SBS) resins increases thermal resistance and in addition improves processability and low-temperature properties of the resulting polymer [2]. Other recently reported developments in styrenic block copolymers (SBC) technology are as follows [3]:

- Enhanced rubber segment SEBS polymers have been developed in the past few years. These materials have higher melt flow index, lower hardness, and a better compatibility with polypropylene
- Higher molecular weight functionalized SEBS with maleic anhydride having improved compression set even at elevated temperatures and a better overmold adhesion
- Oil extended sequential SBS that has a better color and processing stability than conventional oil extended SBS. Polymers from these series can be oil extended to very soft hardness values
- Multiarm 75% styrene content polymer that in comparison with traditional high-styrene content polymer has much lower flexural modulus. It is particularly suited for extruded sheet and film, with very little orientation, excellent toughness, and transparency.

Hydrogenated styrene block copolymers having hard blocks cross-linkable with peroxide/coagent, electron beam, or ultraviolet (UV) light irradiation. The resulting materials have higher temperature resistance, lower compression set at ambient and elevated temperatures, and better oil resistance [4].

TPV developments include compositions with greater resistance to elevated temperatures, resistance to swelling in oils and other fluids, improved flame retardancy, lower emissions, and lower gas permeability. The use of different diene co-monomer in EPDM produces higher degree of cross-linking, resulting in considerably lower compression and tension set values. The new peroxide-cured TPVs have a lighter color, low moisture uptake, and improved chemical resistance [5]. Engineering thermoplastic vulcanizates (ETPV) were introduced by DuPont recently. They contain a cross-linked, high-performance acrylate rubber phase dispersed in a copolyester–ether polymer matrix. The new products high-temperature, chemical, and oil resistance while maintaining a relatively low hardness in the Shore A range [6, 7].

In the field of *TPO materials* a major development has been the introduction of constrained site catalyzed polymerization (e.g., metallocene) [8], allowing the production of polyolefins with controlled structures. The new catalysts also enabled entirely heterophase block thermoplastic olefins (TPOs) to be made “ex reactor,” which can also be cross-linked to give thermoplastic vulcanizates (TPVs), and controlled isotactic/atactic polypropylene single-phase TPOs [1]. Specialty polyolefin elastomers (SPEs) are a family of polyolefin elastomers with isotactic polypropylene crystallinity. These polymers contain a predominant ($>80\%$) amount of polypropylene with isotactic crystallinity with the balance of the composition ethylene or other α-olefins. SPEs are highly elastic with an excellent recovery from deformation. Since they have processing characteristics similar to conventional polyolefins, they can be easily processed to cast and blow films with standard equipment [9]. Other products made from SPEs are elastic nonwoven (spunbond and melt-blown) fabrics [10]. When SPEs are blended with polypropylene it is possible to prepare soft elastic TPO formulations [11].

Aromatic *TPUs,* both polyester- and polyether-based, have been developed for high transparency and UV-light stability, and new polyester polyols are available for improved resistance to hydrolysis, heat, oxygen, and ultraviolet (UV) light and contribute to greater flexibility and softness of the final compositions. A new generation of soft thermoplastic polyurethane elastomers (TPUs) free of plasticizers and not compounded with any other materials has been developed recently [12]. Soft grades of TPUs (hardness values 70–85 Shore A) can be prepared from linear polybutadiene diols [13].

The use of *nanofillers* in TPEs, particularly in TPOs and TPVs, offers several benefits [14], such as the following:

- easy processing
- wider processing window (reduced scrap rate)
- improved scratch/mar resistance
- better dimensional tolerances (low coefficient of linear expansion).

An addition of as little as 4% by weight of *nanoclay* to SEBS and SEBS grafted with maleic anhydride results in an enhancement in the tensile modulus, dynamic modulus, elongation at break, and flexural strength. The hardness of the products has been unaffected [15].

TPVs based on natural rubber (NRTPVs) exhibit co-continuous phase morphology across a wide hardness range. They typically show lower moduli than other TPVs of similar hardness and exhibit excellent recovery properties as measured by conventional set measurements. A significant improvement in recovery performance can be achieved by brief application of prestrain [16].

Breathable films based on copolyether ester resins have been finding a wide use. The degree of permeation can be regulated by the selection of the soft block and hardness. Such breathable films find use in construction (e.g., roofing membranes), medical products (professional wound care coverings, transdermal patches, medical drapes, disposables, and reusable surgical gowns), consumer disposables (wound plasters, diaper backsheet, adult incontinence products, and feminine hygiene), consumer durables (shoe liners, sportswear, rainwear, and breathable car and boat coverings, antiallergic mattress coverings), and packaging (fruit and vegetable packaging) [17].

Organosilane technology has been proposed as a tailormade curing system for the preparation of TPVs. Besides the cross-linking, it enhances filler dispersion and mechanical properties and promotes adhesion of TPVs to different substrates [18].

17.4 Other New Developments

Some current biomedical applications for TPEs

- artificial implants
- drug delivery systems
- lubricious coatings for less invasive devices
- biological adhesives
- antithrombogenic coatings
- soft tissue replacements.

Blending of TPUs and polyether block amide copolymers with hydrophilic polymers (e.g., polyvinyl pyrolodone, polyethyl oxazilone) provide biocompatible materials [19].

Some other recently reported process and material developments:

- new application of living cationic polymerization for producing SBCs [20]
- soft touch TPVs (hardness Shore A 15–30) [21]
- dynamically vulcanized blends of oil-resistant elastomers with hydrogenated nitrile rubber (HNBR) with significant retention of properties after hot air and aging (22)
- flexible TPE based on ionomer technology [23]
- universal polyamide overmold TPE [24]
- high-performance styrenic thermoplastic vulcanizates (STPVs) for long-term high-temperature applications [25]
- the development of soft TPO for automobile interior skin that enhance recyclability [26]
- thermoplastic starch/natural rubber based nanocomposites [27]
- TPU/nanoclay composites produced via reactive extrusion [28]
- a novel isobutylene-based TPV [29]
- olefin block copolymers (OBCs) prepared by catalytic block technology [30]
- surface modification of automobile weather seals [31]
- optimization of twin-screw extruders with respect to torque, volume, and speed for TPEs [32]
- special TPE for fluid-resistant applications [33]
- reprocessable ionic TPE based on NR [34].

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Appendix 1 Books, Conferences, Major Review Articles

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Appendix 2 Major Suppliers of Thermoplastic Elastomers and Compounds

Company	Trade Name	TPE Type
Advanced Elastomer Systems, subsidiary of ExxonMobil	Dytron™ Geolast™ Santoprene™ Vistaflex™	TPV TPV (oil resistant) TPV TPO
Advanced Polymer Alloys	Alcryn® MPR DuraGrip® Duramax™	Melt processable rubber TPE compound TPV
API-Kolon Engineering Plastics	Kopel®	COPE
API spa	Apigo® Apilon 52® Megol® Raplan® Tivilon®	TPO TPU SEBS SBS TPV
Arkema	Pebax®	Polyether block amides
Asahi Kasei	Asaprene™ Tufprene™	SBC SBC
Basell	Hifax™ Hostacom™ Softell	TPO TPO TPO
BASF Corporation	Styrolux® Elastollan® TPU	SBS TPU
Bayer MaterialScience	Desmopan® Texin®	TPU TPU
Borealis	Daplen™	TPO
Dexco Polymers LP	Vector™	SBS
Degussa AG	Vestamid® E	Polyether block amide/PA12
The Dow Chemical Company	Engage™ Pellethane™ Versify™	TPO TPU Propylene/ethylene copolymer
Dynasol	Calprene® Solprene®	SBS, SEBS SEBS

Company	Trade Name	TPE Type
DSM	Arnitel®	COPE
	Keltaflex®	TPV
	Kelprox®	TPV
	Sarlink®	TPV
DuPont	DuPont™ ETPV	TPV
	Hylene®	TPU
	Hytrel®	COPE
Eastman Chemical Company	Ecdel/Elastomer	COPE
EMS Chemie AG	Grilon® ELX	COPA /PA6
	Grilamid® ELV	COPA /PA12
Equistar Chemical Company	Flexathene®	TPO
ExxonMobil Chemical	Vistamaxx™	TPO
Firestone Polymers	Stereon®	SBS, SB
GE Plastics	LNP*Lubricomp compounds	TPEE compounds
GLS Corporation	Dynaflex® compounds	SBC
	Kraton™ compounds	SBS, SIS
	Versaflex® compounds	SBC, TPV, TPU
	Versalloy® compounds	TPV
	Versollan® compounds	TPU
Huntsman	Irogran®	TPU (Extrusion and injection molding grades)
	Krystalgran®	TPU (aliphatic)
Japan Polyolefins Co.	Oleflex®	TPO (Dynamically cross-linked)
JSR Corporation	JSR TR	SBC
	JSR SIS	SIS
	JSR DYNARON	Hydrogenated polymer
	JSR RB	Syndiotactic 1,2 polybutadiene
Kraiburg GmbH	Thermolast® K	SBS or SEBS
	Thermolast® V	TPV (SEPS/PP)
	Thermolast® A	Acrylate based TPE
Kraton Polymers LLC	Kraton® D	SBS, SIS
	Kraton® G	SEBS, SEPS
	Kraton® FG	SEBS grafted with maleic anhydride
Kuraray Co. Ltd.	Hybrar™	SIS, special isoprene technology
	Septon™	S*EBS*, S*EEPS* reactive types
Merquinsa	Pearlthane®	TPU
	Pearlcoat®	TPU
LG Chem Ltd	Keyflex®	TPEE
Mitsui Chemicals	Milastomer®	TPO

Company	Trade Name	TPE Type
Multibase, Inc	Multifex® TEA	SEBS/SEEPS/Engineering thermoplastics
	TPSiV™	Silicone TPV
	Multiflex® TPE	SEBS/SEEPS/PP
	Multiflex® TPO	EP/EPDM/PP
Noveon	Estane®	TPU
	Estagrip®	TPU
	Polymedics®	TPU
Nycoa	Nycolastic®	Polyamide TPE
Polimeri Europe	Europrene® SOL T	SBS, SIS, SEBS
PolyOne	Sunprene™	SBS, SEBS, SEPS
	Elastamax™ XL, EB	TPO
	Elastamax™ HTE	PVC/NBR
Riken Technos Corporation	Actymer®	TPV
	Trinity®	TPV
	Leostomer®	Styrenic elastomer
	Multiuse Leostomer®	TPO
RTP	RTP 1200 Series	TPU
	RTP 1500 Series	COPE
	RTP 2700 Series	SBC
	RTP 2800 Series	TPO
	RTP 2900	COPA
	RTP 6000 Series	Specialty TPEs
A. Schulman Inc	Invision™	TPO
	Polytrope™	TPO
	Sunfrost™	Low gloss PVC TPE
	Sunprene™	PVC TPE
Solvay Engineered Polymers	Nexprene®	TPV
	Indure™	TPO
	Dexflex®	TPO
Sumitomo Chemical	Sumitomo® TPE	TPV, TPO
Ticona Engineering Polymers	Riteflex® COPE	COPE
Teknor Apex Company	Uniprene®	TPV
	Tekbond®	Proprietary compounds
	Elexar®	SEBS
	Monprene®	Saturated SBCs
	Tekron®	Block copolymers
	Telcar®	Proprietary compounds
Toyobo Co. Ltd.	Pelprene™	COPE
	Sarlink®	TPV

Company	Trade Name	TPE Type
UBE Industries Ltd.	PAE	COPA
Vichem Corporation	Ethavin™ Nitrovin™ Sevrene™ Sevrite™	TPO TPV SEBS SBS
VTC Elastotechnik	Dryflex® Vitaprene® Mediprene®	SBS, SEBS, TPO TPV SBS medical grades
Wacker Chemie AG	Goniomer®	Silicone TPE
Zeon	Quintac® Zeotherm® TPV	SIS TPV (PA/ACM)

Appendix 3 ISO Nomenclature for Thermoplastic Elastomers

In an effort to prevent the occurrence of more than one abbreviated term for a given thermoplastic elastomer term, and to prevent the interpretation of more than one meaning for a given abbreviated term, ISO (International Standard Organization) developed the International Standard ISO 18064 *Thermoplastic Elastomers—Nomenclature and Abbreviated Terms*, First Edition 2003-09-01 (Reference Number ISO 18064:2003(E)).

The established nomenclature system is based on the chemical composition of the polymer or polymers involved. It defines symbols and abbreviated terms used to identify thermoplastic elastomers in industry, commerce, and government.

A3.1 Generic Terms and Definitions

TPE—Thermoplastic elastomer (TPE), is defined as consisting of a polymer or polymers that has properties at its service temperature similar to those of vulcanized rubber but can be processed or reprocessed at elevated temperature like a thermoplastic

TP—Prefix used to identify the abbreviated term is for a thermoplastic elastomer.

A3.2 Nomenclature System

The prefix TP shall be followed by a letter representing each category of thermoplastic elastomers. The abbreviated term of each category of thermoplastic elastomers shall be followed, after a hyphen, by a combination of symbols to describe a specific member of each category. The categories are outlined below:

TPA—Polyamide thermoplastic elastomer, comprising a block copolymer of alternating hard and soft segments with amide chemical linkages in the hard blocks and ether and/or ester linkages in the soft blocks.

TPC—Copolyester thermoplastic elastomer, consisting of a block copolymer of alternating hard segments and soft segments, the chemical linkages in the main chain being ester and/or ether.

TPO—Olefinic thermoplastic elastomer, consisting of a blend of a polyolefin and a conventional rubber, the rubber phase in the blend having little or no cross-linking.

TPS—Styrenic thermoplastic elastomer, consisting of at least a triblock copolymer of styrene and a specific diene, where the two end blocks (hard blocks) are polystyrene and the internal block (soft block or blocks) is a polydiene or hydrogenated polydiene.

TPU—Urethane thermoplastic elastomer, consisting of a block copolymer of alternating hard and soft segments with urethane chemical linkages in the hard blocks and ether, ester or carbonate linkages or mixtures of them in the soft blocks.

TPV—Thermoplastic rubber vulcanizate consisting of a blend of a thermoplastic material and a conventional rubber in which the rubber has been cross-linked by the process of dynamic vulcanization during the blending and mixing step.

TPZ—Unclassified thermoplastic elastomer comprising any composition or structure other than those grouped in TPA, TPC, TPO, TPS, TPU, and TPV.

The above categories are further subcategorized as follows:

A3.3 Polyamide TPEs (TPAs)

The **TPA** group is subcategorized into groups according to the linkages in the soft blocks. The following symbols are used:

TPA-EE: Soft segment with both ether and ester linkages

TPA-ES: Polyester soft segment

TPA-ET: Polyether soft segment.

A3.4 Copolyester TPEs (TPCs)

The **TPC** group is subcategorized into groups according to the linkages in the soft blocks. The following symbols are used:

TPC-EE: Soft segment with ester and ether linkages

TPC-ES: Polyester soft segment

TPC-ET: Polyether soft segment.

A3.5 Olefinic TPEs (TPOs)

The **TPO** group varies according to the nature of the thermoplastic polyolefin being used and the rubber type.

A specific TPO is identified by a bracketed term comprising the standard abbreviation for the rubber type (see ISO 1629), a "+" sign, and the standard abbreviation for the thermoplastic type (see ISO 1043-1). The thermoplastic and the rubber type shall be listed in decreasing order of abundance in the TPO.

A commercially available TPO type is described as follows:

TPO-(EPDM + PP): Blend of ethylene-propylene-diene terpolymer with polypropylene, with no or little cross-linking of the EPDM phase, the amount of EPDM present being greater than that of PP.

A3.6 Styrenic TPEs (TPSs)

The following symbols are used for the **TPS** group:

TPS-SBS: Block copolymer of styrene and butadiene

TPS-SEBS: Polystyrene-poly(ethylene-butylene)-polystyrene

TPS-SEPS: Polystyrene-poly(ethylene-propylene)-polystyrene

TPS-SIS: Block copolymer of styrene and isoprene.

Note: TPS-SEBS is a block copolymer of styrene and butadiene in which the soft block comprises a mixture of hydrogenated cis-1,4-polybutadiene, and 1,2-polybutadiene units. TPS-SEPS is a block copolymer of styrene and isoprene in which the polyisoprene block has been hydrogenated.

A3.7 Urethane TPEs (TPUs)

The **TPU** group is subcategorized into types according to the nature of the hydrocarbon moiety (aromatic or aliphatic) between the urethane linkages of the hard blocks, and according to the chemical linkages (ether, ester, carbonate) in the soft blocks. The following symbols are used:

TPU-ARES: Aromatic hard segment, polyester soft segment

TPU-ARET: Aromatic hard segment, polyether soft segment

TPU-AREE: Aromatic hard segment, soft segment with ester and ether linkages

TPU-ARCE: Aromatic hard segment, polycarbonate soft segment

TPU-ARCL: Aromatic hard segment, polycaprolactone soft segment

TPU-ALES: Aliphatic hard segment, polyester soft segment

TPU-ALET: Aliphatic hard segment, polyether soft segment.

A3.8 Dynamically vulcanized TPEs (TPVs)

The **TPV** group varies depending on the nature of the thermoplastic material being used and the rubber type.

A specific TPV is identified by a bracketed term comprising the standard abbreviation for the rubber (see ISO 1629), followed by a "+" sign and the standard abbreviation for the thermoplastic type (see ISO 1043-1). The abbreviation for the rubber shall precede that for the thermoplastic.

Commercially available TPV types include:

TPV-(EPDM + PP): Combination of EPDM and polypropylene in which the EPDM phase is highly cross-linked and finely dispersed in a continuous polypropylene phase.

TPV-(NBR + PP): Combination of acrylonitrile-butadiene rubber and polypropylene in which the NBR phase is highly cross-linked and finely dispersed in a continuous polypropylene phase.

TPV-(NR + PP): Combination of natural rubber and polypropylene in which the NR phase is highly cross-linked and finely dispersed in a continuous polypropylene phase.

TPV-(ENR + PP): Combination of epoxidized natural rubber and polypropylene in which the ENR phase is highly cross-linked and finely dispersed in a continuous polypropylene phase.

TPV-(IIR + PP): Combination of butyl rubber and polypropylene in which the IIR phase is highly cross-linked and finely dispersed in a continuous polypropylene phase.

A3.9 Miscellaneous material (TPZ)

These thermoplastic elastomers do not fit into any particular class and are identified by the prefix TPZ.

A commercially available TPZ type is described as follows:

> TPZ-(NBR + PVC): Blend of acrylonitrile-butadiene rubber and polyvinyl chloride.

Note: Many NBR + PVC blends are thermoset vulcanized rubbers, and with these the prefix TPZ should not be used.

Appendix 4
Processing Data Sheets for Commercial Thermoplastic Elastomers and Compounds

Note: Because of the very large total number of commercial grades and frequent changes due to product developments and/or discontinuation or changes in company ownership, the listings cannot ever be complete. However, they illustrate the typical processing equipment and/or conditions (temperature settings, pressures, etc.) used for individual classes of thermoplastic elastomers. The formats vary by individual suppliers and therefore it was not possible to have a completely uniform format. For details on the processing of specific grades the supplier should be contacted.

A4.1 Processing of Styrenic Block Copolymers

A4.1.1 Extrusion of SBS

Screw type: General purpose polyolefin screw, *L*/*D* ratio 24:1
Compression ratio: 2.5:1 to 3.0:1

Drying: Not required

Typical temperature settings, ±5°C (±10°F)[a]

	Material Hardness, Shore Durometer		
	45–55A	**60–65A**	**70A–45D**
Feed	65 (150)	65–150	80 (175)
Zone 1	160 (320)	165 (330)	170 (340)
Zone 2	165 (330)	170 (340)	175 (350)
Zone 3	170 (340)	175 (350)	180 (360)
Head	175 (350)	180 (360)	190 (370)
Die	175 (350)	180 (360)	190 (370)
Melt	175 (350)	180 (360)	185 (365)

Note: [a]These settings should be used as a starting condition and can be increased to a maximum +10°C (+20°F).
Source: Publication TPEPS-07–70060-C, PolyOne Corporation, Avon Lake, OH.

A4.1.2 Injection molding of SBS

Screw type: General purpose polyolefin screw, *L*/*D* ratio 20:1
Compression ratio: 2.5:1 to 3.5:1

Drying: Typically not required

Typical temperature settings, ±5°C (±10°F)[a]

	Material Hardness, Shore Durometer				
	00–25A	30–45A	50–55A	60–65A	70A–45D
Rear	65 (150)	65 (150)	80 (175)	80 (175)	80 (175)
Middle	165 (330)	170 (340)	170 (340)	175 (350)	180 (360)
Front	170 (340)	175 (350)	175 (350)	180 (360)	190 (370)
Nozzle	175 (350)	180 (360)	180 (360)	190 (370)	195 (380)

Mold temperature: 15–40°C (60–100°F)
Note: [a]These settings should be used as a starting condition and can be increased to a maximum +10°C (+20°F).
Screw speed: 30–50 rpm
Back pressure: 3–5 bar (50–75 psi)
Source: Publication TPEPS-08–70060-A, PolyOne Corporation, Avon Lake, OH, 2005.

A4.1.3 Extrusion of SEBS/SEPS

Screw type: General purpose polyolefin screw, *L*/*D* ratio 24:1
Compression ratio: 2.5:1 to 3.0:1

Drying: Not required

Typical temperature settings, ±5°C (±10°F)[a]

	Material Hardness, Shore Durometer					
	00–40A	45–55A	60–65A	70–75A	80–85A	45D
Feed	100 (210)	100 (210)	110 (230)	110 (230)	120 (250)	130 (265)
Zone 1	190 (375)	195 (385)	200 (395)	205 (405)	215 (415)	220 (425)
Zone 2	200 (395)	200 (395)	205 (405)	215 (415)	220 (425)	225 (435)
Zone 3	200 (395)	205 (405)	215 (415)	220 (425)	225 (435)	230 (445)
Head	205 (405)	215 (415)	220 (425)	225 (435)	230 (445)	235 (455)
Die	205 (405)	215 (415)	220 (425)	225 (435)	230 (445)	235 (455)
Melt	200 (395)	210 (410)	215 (420)	220 (430)	225 (435)	230 (445)

Note: [a]These settings should be used as a starting condition and can be increased to a maximum +10°C (+20°F).
Source: Publication TPEPS-07–70060-C, PolyOne Corporation, Avon Lake, OH, 2005.

A4.1.4 Injection Molding of SEBS/SEPS

Screw type: General purpose polyolefin screw, *L*/*D* ratio 20:1
Compression ratio: 2.5:1 to 3.5:1

Drying: Typically not required

Typical temperature settings, ± 5°C (± 10°F)[a]

	Material Hardness, Shore Durometer						
	00–25A	30–45A	50–55A	60–65A	70–75A	80–90A	35–45D
Rear	165 (330)	170 (340)	170 (340)	170 (340)	175 (350)	180 (360)	180 (360)
Middle	195 (380)	200 (390)	200 (390)	205 (400)	210 (410)	215 (420)	220 (430)
Front	200 (390)	205 (400)	205(400)	210 (410)	215 (420)	220 (430)	225 (440)
Nozzle	205 (400)	210 (410)	210 (410)	215 (420)	220 (430)	225 (440)	230 (450)

Mold temperature: 15–40°C (60–100°F)
Note: [a]These settings should be used as a starting condition and can be increased to a maximum +10°C (+20°F).
Screw speed: 30–50 rpm
Back pressure: 3–5 bar (50–75 psi)
Source: Publication TPEPS-08–70060-A, PolyOne Corporation, Avon Lake, OH, 2005.

A4.1.5 Thermolast® K (SEBS) General Injection Molding Procedure

Machine specifications
Standard injection molding machine
Compression ratio: at least 2:1
L/*D* ratio: at least 20

Guideline processing parameters
Melt temperature: 180–220°C (355–425°F); max. 250°C (480°F)
Mold temperature: 25–40°C (75–105°F)
Injection rate: high
Hold pressure: if possible, none

Molds
Balanced gate system:
  Gate point: Diameter 0.4–0.6 mm (0.016–0.024 in.), max. 1.0 mm (0.039 in.)
  Gate types: Pin gate, submarine gate, film gate
Venting: 0.01–0.02 mm (0.0004–0.001 in.) vent channels
Mold surface: eroded
Ejectors: large-area ejectors

Please always note that

- soft materials may be compressed, resulting in overfilling.
- the excellent flow characteristics of Thermolast K® compounds may cause obstruction of vents and therefore air entrapment.

Source: Kraiburg TPE GmbH.

A4.1.6 Overmolding of SBC

Screw type: General purpose polyolefin screw, L/D ratio 16:1 to 20:1
Compression ratio: 2.5:1 to 3.5:1

Drying: Typically not required

Temperature settings, ±5°C (±10°F)[a]

Substrate	SBC Material Hardness, Shore Durometer		
	PP, GFPP, PP	ABS, SAN, PC, HIPS	PA6, PA66, GFPA
	5A-90A	20A-70A	20A-70A
Rear	210 (410)	210 (410)	230 (450)
Middle	215 (420)	215 (420)	245 (470)
Front	225 (440)	215 (420)	250 (480)
Nozzle	230 (450)	220 (425)	255 (490)

Note: [a]These settings should be used as starting condition and can be increased to a maximum +10°C (+20°F).
Screw speed: 30–50 rpm
Back pressure: 3–7 bar (50–100 psi)
Source: Publication TPEPS-09–70060-B, PolyOne Corporation, Avon Lake, OH, 2005.

A4.2 Processing of Polyolefin-Based TPE (TPO)

A4.2.1 Extrusion of TPO

Screw type: General purpose polyolefin screw, L/D ratio 20:1 or higher
Compression ratio: 2.5:1 to 3.5:1

Drying: Not required

Typical temperature settings, ±5°C (±10°F)[a]

	Material Hardness, Shore Durometer		
	65–72A	77–82A	90A
Feed	150 (300)	150 (300)	150 (300)
Zone 1	150 (350)	180 (360)	190 (370)
Zone 2	180 (360)	190 (370)	195 (380)
Zone 3	190 (370)	195 (380)	200 (390)
Head	195 (380)	200 (390)	205 (400)
Die	195 (380)	200 (390)	205 (400)
Melt	195 (375)	195 (385)	200 (395)

Note: [a]These settings should be used as a starting condition and can be increased to a maximum +10°C (+20°F).
Source: Publication TPEPS-01–70059A, PolyOne Corporation, Avon Lake, OH, 2005.

A4.2.2 Injection Molding of TPO

Screw type: General purpose polyolefin screw, *L*/*D* ratio 20:1
Compression ratio: 2.5:1 to 3.5:1

Drying: Typically not required

Typical temperature settings, ± 5°C (± 10°F)[a]

	Material Hardness, Shore Durometer		
	65–72A	77–82A	90A
Rear	150 (300)	150 (300)	150 (300)
Middle	175 (350)	180 (360)	190 (370)
Front	180 (360)	190 (370)	195 (380)
Nozzle	190 (370)	195 (380)	200 (390)

Mold temperature: 10–32°C (50–90°F)
Note: [a]These settings should be used as a starting condition and can be increased to a maximum + 10°C (+ 20°F).
Screw speed: 50–150 rpm
Back pressure: 4–10 bar (50–150 psi)
Source: Publication TPEPS-02-70059B, PolyOne Corporation, Avon Lake, OH, 2005.

A4.3 Processing of Thermoplastic Vulcanizates

A4.3.1 Extrusion of TPV

Drying: 3 hr at 180°F (82°C)

Typical temperature settings

Feed section: 70–120°F (21–49°C)
Zone 1: 350–410°F (182–204°C)
Zone 2: 370–410°F (188–210°C)
Zone 3: 370–410°F (188–210°C)
Die: 380–420°F (193–216°C)

Melt temperature: 380–420°F (193–216°C)

A4.3.2 Injection Molding of TPV

Drying: 3 hr at 180°F (82°C)

Temperature settings

Rear barrel: 350–420°F (177–216°C)
Middle barrel: 350–420°F (177–216°C)
Front barrel: 350–420°F (177–216°C)
Nozzle: 370–420°F (188–221°C)

Melt temperature: 360–430°F (182–221°C)
Mold temperature: 50–120°F (21–49°C)
Injection pressure: 10–150 psi (0.7–10.3 bar)
Screw speed: 100–200 rpm

A4.3.3 Extrusion of ETPV

Drying: 3–4 hr at 180°F (82°C)

Screw type: *L*/*D* ratio 20:1 or higher, ideally 24:1, 3-zone
Compression ratio 2.5:1 to 3.5:1

Typical temperature settings

Zone 1: 410°F (210°C)
Zone 2: 425°F (220°C)
Zone 3: 435°F (225°C)
Zone 4: 445°F (230°C)
Head: 445°F (230°C)
Die: 435°F (225°C)

Melt temperature: 420–445°F (215–230°C)

Sources: Advanced Elastomer Systems, Kraiburg TPE GmbH.

A4.3.4 Injection Molding of ETPV

Drying: 3–4 hr at 180°F (82°C)

Screw type: *L*/*D* ratio 20:1 or higher, ideally 24:1, gradual transition
Compression ratio 2.5:1 to 3.5:1

Typical temperature settings

Rear barrel: 445°F (230°C)
Middle barrel: 465°F (240°C)
Front barrel: 480°F (250°C)
Nozzle: 480°F (250°C)

Melt temperature: 465–500°F (240–260°C)
Mold temperature: 50–120°F (40–60°C)
Hold pressure: 2,900–4350 psi (20–30 MPa)
Back pressure: 145–290 psi (1–2 MPa)
Screw speed: 100 rpm

Source: DuPont.

A4.3.5 Injection Molding of Silicone TPV

	TPSiV Grade								
Temperature Settings (°F)	**1180–50D**	**3010–50A 3010–60A**	**3011–50A 3011–60A 3011–70A**	**3011–85A**	**3040–55A**	**3040–60A 3040–65A 3040–70A**	**3040–85A**	**3111–70A**	**3340–55A 3340–60A 3340–65A**
Rear	446	356	356	401	338	356	392	356	338
Middle	464	374	374	410	356	374	410	374	356
Front	482	392	392	419	374	392	419	392	374
Nozzle	500	401	401	428	383	401	428	401	383
Mold	57–86	50–86	50–86	50–86	50–86	50–86	50–86	50–86	50–86
Injection Rate	Fast	Fast	Fast	Fast	Moderate to fast	Moderate to fast	Moderate to fast	Moderate to fast	Moderate to fast

Drying: 2.0–4.0 hr at 176°F.

A4.3.6 Extrusion of Silicone TPV

	TPSiV Grade		
Temperature settings (°F)	**1180–50D**	**3011–70A**	**3111–70A**
Cylinder, Zone 1	410	329	329
Cylinder, Zone 2	428	347	347
Cylinder, Zone 3	428	365	365
Cylinder, Zone 4	428	365	365
Cylinder, Zone 5	428	365	365
Melt (Aim)	455	374	374
Die	446	365	365

Source: Multibase Inc.

A4.4 Processing of Melt Processible Rubber

A4.4.1 Extrusion of MPR

Drying: Not necessary

Recommended screw: L/D ratio $>$20:1 (24:1 preferred), corrosion resistant.

Typical barrel temperature settings

Feed: 300°F (150°C)
Transition: 320–340°F (160–171°C)
Meter: 320–340°F (160–171°C)
Adapter: 325°F (163°C)
Die: 325°F (163°C)

Melt temperature: 356–365°F (180–185°C)
Screw speed: 20–60 rpm

Source: Advanced Polymer Alloys.

A4.4.2 Injection Molding of MPR

Recommended screw design: L/D 20:1 general purpose, gradual transition
Compression ratio 2.5:1 to 3.5:1 corrosion resistant material (e.g., Hastalloy C-276).

Typical barrel temperature settings

Rear: 340–350°F (171–177°C)
Front: 340–350°F (171–177°C)
Nozzle: 340–350°F (171–177°C)
Mold: 70–120°F (21–49°C)

Melt temperature: 340–375°F (171–191°C)
Injection speed: 1–3 cu.in./s (16–48 cm^3/s)
Injection pressure: 700–1,200 psi (48.2–82.7 bar)
Screw speed: 50–100 rpm
Back pressure: 30–80 psi (2–5.5 bar)

Source: Advanced Polymer Alloys.

A4.5 Processing of Thermoplastic Polyurethanes

A4.5.1 Extrusion of TPU

The extrusion temperatures for most TPUs are in the range between 320°F and 450°F (160°C and 230°C). The optimum melt temperatures for most TPU grades range typically from 390°F to 420°F (200°C to 220°C) and specific values can be found in the product information sheets.

Typical extruder temperature settings

Feed: 70–105°F (20–40°C)
Zone 1: 320–355°F (160–180°C) for grades with hardness 70–92 Shore A
355–390°F (180–200°C) for grades with hardness 93 Shore A to 53 Shore D

Zone 2: 340–375°F (170–190°C) for grades with hardness 70–92 Shore A
355–390°F (180–200°C) for grades with hardness 93 Shore A to 53 Shore D

Zone 3: 340–390°F (170–200°C) for grades with hardness 70–92 Shore A
355–410°F (180–210°C) for grades with hardness 93 Shore A to 53 Shore D

Zone 4: 320–355°F (170–210°C) for grades with hardness 70–92 Shore A
355–430°F (180–220°C) for grades with hardness 93 Shore A to 53 Shore D

Head: 340–390°F (170–200°C) for grades with hardness 70–92 Shore A
355–410°F (180–210°C) for grades with hardness 93 Shore A to 53 Shore D

Die: 340–410°F (170–210°C) for grades with hardness 70–92 Shore A
355–430°F (180–220°C) for grades with hardness 93 Shore A to 53 Shore D

Screw speed: Depending on the polymer grade, type and size of extrudate, the screw speed may be in the range 15–50 rpm.

A4.5.2 Injection Molding of TPUs

General purpose screws are satisfactory for use with TPU resins. The recommended screw length-to-diameter (L/D) ratio is 20:1 with a compression ratio of 2.5–3:1. Screws with a compression ratio greater than 4:1 should be avoided.

Typical barrel temperature settings

Rear: 360–390°F (180–200°C)
Middle: 360–400°F (180–205°C)
Front: 360–410°F (180–210°C)
Nozzle: 370–415°F (185–215°C)
Ideal melt temperature: 400°F (205°C)
Mold temperature:
  Stationary part: 60–110°F (15–45°C)
  Moving part: 60–110°F (15–45°C)

Injection pressure:
  1st Stage: 6,000–14,000 psi (41.4–96.5 MPa)
  2nd Stage: 5,000–10,000 psi (34.5–69.0 MPa)
  Clamp pressure: 3–5 ton/in.^{2} of projected part area
Shot weight: 40–80% of rated barrel capacity
Timers (per 0.125-in. cross section):
  Boost: 5–10 s
  2nd Stage: 10–20 s
  Cool: 20–30 s

Source: Bayer MaterialScience.

A4.6 Processing of Copolyester Thermoplastic Elastomers

A4.6.1 Injection Molding of COPE

Screw design: *L*/*D* 17:1 to 23:1
Compression ratio 2.5:1 to 3.0:1

Drying: Not necessary unless bags remain open for extended period of time.

Typical temperature settings

Rear barrel: 380–450°F (195–235°C)
Middle barrel: 385–420°F (195–215°C)
Front barrel: 375–425°F (190–219°C)
Nozzle: 370–420°F (188–221°C)

Melt temperature: 375–480°F (190–250°C)
Mold temperature: 95–120°F (35–50°C)
Injection pressure: 7,500–10,000 psi (52–70 MPa)
Back pressure: 45–90 psi (3–6 bar)
Screw speed: 30–100 rpm

A4.6.2 Extrusion of COPE

Screw design: *L*/*D* 24:1 or higher three-section screw with gradual transition
Compression ratio 2.4:1 to 3.2:1

Typical temperature settings[a]

Rear barrel: 320–425°F (160–220°C)
Middle barrel: 340–435°F (170–225°C)
Front barrel: 340–435°F (170–225°C)
Adapter head and die: 320–465°F (320–465°C)

Melt temperature[a]: 330–500°F (165–260°C).

Note: [a]Depends on grade.

A4.7 Processing of Polyamide Thermoplastic Elastomers

A4.7.1 Extrusion of Polyamide Thermoplastic Elastomers

Drying temperature: 175–212°F (80–100°C)

Drying time: 4–12 hr

Screw design: *L*/*D* 24:1 or higher, three zone
Compression ratio: 2.5:1 to 3.5:1

Typical temperature settings[a]

Rear barrel: 340–475°F (170–245°C)
Middle barrel: 340–475°F (170–245°C)
Front barrel: 360–490°F (180–255°C)
Die: 370–500°F (190–260°C)

Melt temperature[a]: 372–509°F (190–265°C)

Note: [a]Depends on grade.

A4.7.2 Injection Molding of Polyamide Thermoplastic Elastomers

Drying temperature: 175–212°F (80–100°C)

Drying time: 4–12 hr

Screw design: *L*/*D* 18:1 to 22:1 three zone
Compression ratio: 2.0:1 or higher

Typical temperature settings[a]

Rear barrel: 320–425°F (160–220°C)
Middle barrel: 340–445°F (170–230°C)
Front barrel: 355–460°F (180–240°C)
Nozzle: 355–465°F (180–240°C)

Melt temperature[a]: 355–465°F (180–240°C)
Mold temperature: 60–105°F (15–40°C)

Clamping force: 2,900–8,700 psi (200–600 bar)

Note: [a]Depends on grade.

Source: Arkema Inc.

Appendix 5
Technical Data Sheets for Commercial Thermoplastic Elastomers and Compounds

Note: Because of the very large total number of commercial grades and frequent changes due to product developments and/or discontinuation, the listings cannot ever be complete. However, they illustrate the basic properties of individual classes of thermoplastic elastomers. The formats vary by individual suppliers and therefore it was not possible to have a completely uniform format. For further details the vendor should be contacted.

A5.1 SBC Data Sheets

Elastamax^{TM} Styrenic Block Copolymers Typical Properties

Property	Test Method	Unit	HTE 1101	HTE 1102	HTE 1104	HTE 1105	HTE 1106
Tensile Strength (psi)	ASTM D412	psi	800	1200	1320	1290	590
Elongation (%)	ASTM D412	%	550	900	1000	1060	189
Modulus @100% Elongation	ASTM D412	psi	—	—	250	230	510
Modulus @ 300% Elongation	ASTM D412	psi	—	—	455	330	—
Compression Set[a]	ASTM D395[a]	%	—	—	16	—	—
Hardness Shore A (5 s Dwell)	ASTM D2240	—	41	50[b]	45[b]	43[b]	65[b]
Specific Gravity	ASTM D792	—	1.00	0.92	0.93	0.94	1.03
Tear Strength, Die C, 20 in./min	ASTM D624	pli	192	300	170	170	117
Applications			GP	GP	FDA[c]	GP	GP

Notes:

[a] Method B, 22 hr @ 73°F

[b] Instantaneous hardness reading.

[c] Food contact; contact the company for details.

GP: general purpose.

Source: Technical Data Sheet, PolyOne Corporation, 2005.

Hybrar™ Triblock Copolymer Typical Properties

Property	Method	Unit	Hydrogenated			
			5127	5125	7125	7311
Styrene Content		Wt%	20	20	20	12
Specific Gravity	ISO 1183	—	0.94	0.94	0.90	0.89
Glass Transition Temperature	DSC	°C	8	−13	−15	−32
Hardness		Shore A	84	60	64	41
100% Modulus	ISO 37	MPa	2.8	1.6	1.7	0.6
300% Modulus		MPa	4.7	2.5	2.7	0.9
Tensile Strength		MPa	12.4	8.8	7.1	6.3
Elongation at Break		%	730	730	680	1050

Source: Hybrar, High Performance Thermoplastic Rubber, Kuraray Co., Ltd., 2004.

Kraton® D (IR) Polymer Grades Typical Properties

Property	IR305 Linear	IR307 Linear	IR 309[a,b] Linear	IR310[a,c] Linear	IR 401[d] Latex Linear
Specific Gravity	0.91	0.91	0.91	0.91	—
Intrinsic Viscosity (dl/g)	7.8	7.8	8.0	8.0	7.8
Mooney Viscosity @ 212°F	—	—	45	45	—
Oil Content (%wt)	3.6	—	3.6	0	—
Styrene/Rubber Ratio	0/100	0/100	0/100	0/100	0/100
Comments	—	FDA[e]	Bimodal MW distribution	FDA[e]	FDA[e]

Notes:

[a] Lower viscosity.

[b] Easy processing version of IR305.

[c] Easy processing version of IR307.

[d] 63% solids in latex (aqueous dispersion).

[e] Contact the vendor for details.

Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® D Oiled Polymer Grades

Property	D4141K (SBS) Linear	D4150K (SBS) Linear	D4158K $(SB)_n$ Radial	D4433P (SIS) Linear
Tensile Strength[a] (psi)	2,750[b]	2,800[b]	1,330[b]	900[c]
300% Modulus[a] (psi)	250	160	230	150
Elongation[a] (%)	1,300	1,400	1,110	1,450
Set @ Break[a] (%)	20	25	10	24
Hardness Shore A[b] (10 s)	50	45	41	29
Specific Gravity	0.93	0.92	0.92	0.92
Brookfield Viscosity[d] cP @ 77°F	1,000	850	4,800	350
Melt Index (200°C/5 kg), g/10 min	11	10	<1	29
Oil Content (%wt)	28.5	33	33	23
Styrene/Rubber Ratio	31/69	31/69	31/69	22/78
Diblock (%)	17	17	16	20
Comment	FDA[e]	FDA[e]	FDA[e]	FDA[e]

Notes:

[a] ASTM D412 tensile tester jaw separation speed 10 in./min.

[b] Typical values on polymer compression molded at 350°F.

[c] Typical properties determined on film cast from toluene solutions.

[d] Oil extended polymer concentration 25%wt in toluene.

[e] Contact vendor for details.

Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® D (SBS) Radial Polymer Grades Typical Properties

Property	D1403P Radial	D1493P Radial
Tensile Strength[a,b] (psi)	4,000	4,000
Elongation[a,b] (%)	200	200
Flexural Modulus[a,b] (psi)	270,000	270,000
HDT[b] @ 66 psi °C	80	80
Hardness Shore D[b] (ASTM D2240)	65	65
Specific Gravity	1.01	1.01
Brookfield Viscosity[c] cP @ 77°F	220	220
Melt Flow Index (200°C/5 kg), g/10 min	11	11
Oil Content (%wt)	0	0
Styrene/Rubber Ratio	75/25	75/25
Comment	FDA[d]	FDA[d]

Notes:

[a] ASTM D638 tensile tester jaw separation speed 2 in./min.

[b] Injection molded sample

[c] Neat polymer concentration, 25%wt in toluene.

[d] Contact vendor for details.

Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® D (SIS) Polymer Grades

Property	D1111K (SIS) Linear	D1113P (SIS) Linear	D1114P (SIS) Linear	D1117P (SIS) Linear	D1119P (SIS) Linear
Tensile Strength[a,b] (psi)	2,900	600	4,600	1,200	350
300% Modulus[a,b] (psi)	200	50	275	60	160
Elongation[a,b] (%)	1,200	1,500	1,300	1,300	1,000
Set @ Break[a,b] (%)	10	20	—	15	20
Hardness Shore A[c] (10 s)	45	23	42	33	30
Specific Gravity	0.93	0.92	0.92	0.92	0.93
Viscosity[d] cP @ 77°F	1,100	600	900	500	340
Melt Index (200°C/5 kg), g/10 min	3	24	9	33	25
Oil Content (%wt)	0	0	0	0	0
Styrene/Rubber Ratio	22/78	16/84	19/81	17/83	22/78
Diblock (%)	18	56	<1	33	66
Comment	FDA[e]	FDA[e]	FDA[e]	FDA[e]	FDA[e]

Notes:
[a] ASTM D412 tensile tester jaw separation speed 10 in./min.
[b] Typical properties determined on film cast from toluene solutions.
[c] Typical values on polymer compression molded at 350°F.
[d] Neat polymer concentration 25%wt in toluene.
[e] Contact vendor for details.
Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® D (SIS) Polymer Grades (Continued)

Property	D1124K $(SI)_n$ Radial	D1126P $(SI)_n$ Radial	D1161P (SIS) Linear	D1162BT (SIS) Linear	D1163P (SIS) Linear	D1164P (SIS) Linear
Tensile Strength[a,b] (psi)	2,100	1,120	3,100	4,000	1,500	4,000
300% Modulus[a,b] (psi)	430	360	130	—	70	445
Elongation[a,b] (%)	1,100	1,400	1,300	—	1,400	1,000
Set @ Break[a,b] (%)	26	—	—	—	—	—
Hardness Shore A[c] (10 s)	54	44	32	—	25	53
Specific Gravity	0.94	0.92	0.92	0.95	0.92	0.94
Brookfield Viscosity[d] cP @ 77°F	340	500	1,200	120	900	300
Melt Index (200°C/5 kg), g/10 min	4	15	12	35	23	12
Oil Content (%wt)	0	0	0	0	0	0
Styrene/Rubber Ratio	30/70	19/81	15/85	44/56	15/85	29/71
Diblock (%)	30	30	19	<1	38	<1
Comment	FDA[e]	FDA[e]	FDA[e]	FDA[e]	FDA[e]	FDA[e]

Notes:
[a] ASTM D412 tensile tester jaw separation speed 10 in./min.
[b] Typical properties determined on film cast from toluene solutions.
[c] Typical values on polymer compression molded at 350°F.
[d] Neat polymer concentration 25%wt in toluene.
[e] Contact vendor for details.
Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® G Polymer Grades Typical Properties

Property	G1641H[a] (SEBS) Linear	G1650M (SEBS) Linear	G1651H (SEBS) Linear	G1652M (SEBS) Linear	G1654H (SEBS) Linear	G1567M (SEBS) Linear
Tensile Strength[b,c] (psi)	>2,500	>4,000	>4,000	4,500	<4,000	3,400
300% Modulus[a,c] (psi)	630	800	—	700	—	350
Elongation[b,c] (%)	>800	500	>800	500	>800	750
Hardness Shore A[d] (10 s)	52	72	61	70	63	47
Specific Gravity	0.92	0.91	0.91	0.91	0.91	0.89
Brookfield Viscosity[e] cP @ 77°F						
25%wt	>50,000	8,000	>50,000	1,800	>50,000	4,200
10%wt	80	50	1,800	30	410	65
Melt Index (5 kg), g/10 min						
200°C	<1	<1	<1	<1	<1	8
230°C	<1	<1	<1	5	<1	22
Oil Content (%wt)	0	0	0	0	0	0
Styrene/Rubber Ratio	34/66	30/70	33/67	30/70	31/69	13/87
Diblock (%)	<1	<1	<1	<1	<1	29
Comment	FDA[f]	FDA[f]	FDA[f]	FDA[f]	FDA[f]	FDA[f]

Notes:

[a] Enhanced rubber segment (lower viscosity, lower hardness, and more compatibility with PP).

[b] ASTM D412 tensile tester jaw separation speed 10 in./min.

[c] Typical properties determined on film cast from toluene solutions.

[d] Typical values on polymer compression molded at 350°F.

[e] Neat polymer concentration 25%wt in toluene.

[f] Contact vendor for details.

Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Kraton® G Polymer Grades Typical Properties (Continued)

Property	G1701M SEP Diblock	G1702 SEP Diblock	G1726M SEBS Linear	G1730M SEPS Linear	G1750M (EP)n Star	G1765M (EP)n Star
Tensile Strength (psi)[a,b]	300	300	350	—	<50	<50
Elongation@ Break (%)[a,b]	<100	<100	200	—	—	—
Hardness, Shore A (10 sec)[c]	64	41	70	61	11	12
Specific Gravity	0.92	0.91	0.91	0.90	086	0.86
Viscosity (Toluene Solutions), cP @ 77°F						
25% wt[d]	>50,000	50,000	200	1,980	8,700	12,800[e]
10% wt[d]	—	280	10	35	140	1,805[e]
Melt Flow Index (5 kg), g/10 min						
200°C	<1	<1	65	3	8	4
230°C	<1	<1	<100	13	—	—
Oil Content (%wt)	0	0	0	0	0	12
Styrene/Rubber Ratio	37/63	28/72	30/70	20/80	0/100	0/100
Diblock (%wt)	100	100	70	<1	—	—
Comments	FDA[f]	FDA[f]	FDA[f]	FDA[f]	FDA[f]	FDA[f]

Notes:

[a] ASTM Method D412 tensile tester jaw separation speed 10 in./min.

[b] Typical properties determined on films cast from toluene solution.

[c] Typical values on polymer compression molded at 350°F.

[d] Neat polymer concentration in toluene.

[e] Oil extended polymer.

[f] Contact vendor for details.

Source: *Kraton® Polymers and Compounds, Typical Properties Guide*, Publication K0137, Kraton Polymers LLC, 2006.

Vector® Styrenic Block Copolymers Typical Properties

Property	Test Method	Unit	2411 (SB)n Radial	2518 SBS Linear	4113A SIS/SI[a] Linear	4114A SIS/SI[a] Linear	4211A SIS Linear	4215A SIS/SI[a] Linear
Tensile Strength[b] (psi)	ASTM D412	psi	4,000	4,500	2,900	1,700	3,500	2,600
300% Modulus[b] (psi)	ASTM D412	psi	650	550	—	—	275	500
Elongation[b] (%)	ASTM D412	%	725	725	1,300	1,500	900	1,000
Hardness Shore A (1 s Dwell)	ASTM D2240		71	78	32	24	62	58
Specific Gravity	ASTM D792		0.94	0.94	0.92	0.92	0.94	0.94
Viscosity, 5wt% in toluene	ASTM D2196	cP	21	—	—	—	—	—
Melt Flow Index (200 °C/5kg)		g/10 min	<1	6	10	25	13	9
Styrene Content	Dexco	wt%	30	31	15	15	30	30
Diblock (%)	Dexco		30	<1	18	42	<1	18

Notes:
[a] Triblock/diblock copolymer blend.
[b] Typical values on compressed plaques.
Source: Technical Data Sheet, Dexco Polymers, LLC, 2005.

Vector® Styrenic Block Copolymers Typical Properties (Continued)

Property	Test Method	Unit	4230 (SIS)n Radial[a,e]	4411A SIS Linear	4461 SBS Linear	6241 SBS Linear	6507 SBS Linear	7400 SBS Linear[b]
Tensile Strength[c] (psi)	ASTM D412	psi	1,940	300	4,500	4,500	4,500	2,900
300% Modulus[c] (psi)	ASTM D412	psi	—	1,300	1,200	1,275	1,275	380
Elongation[c] (%)	ASTM D412	%	1075	750	700	800	700	1,220
Hardness Shore A (1 s Dwell)	ASTM D2240		45	87	87	87	88	47
Specific Gravity	ASTM D792		0.94	0.96	0.96	0.96	0.96	0.90
Viscosity, 5wt% in Toluene	ASTM D2196	cP	—	—	—	—	—	—
Melt Flow Index (200°C/5 kg)		g/10 min	14	40	23	23	23	18
Styrene Content	Dexco	wt%	20	44	43	43	43	31
Diblock (%)	Dexco		30	<1	<1	<1	<1	<1
Mineral Oil	Dexco	wt%	—	—	—	—	—	33
Comment			—	—	FDA[d]	FDA[d]	—	—

Notes:
[a] Four-arm radial.
[b] Oil extended polymer.
[c] Typical values on compressed plaques.
[d] Contact Company for details.
[e] Triblock/diblock copolymer blend.
Source: Technical Data Sheet, Dexco Polymers, LLC, 2005.

A5.2 TPO Data Sheets

Dow^{TM} ENR TPO Typical Properties

Property	ASTM D Method	Unit	ENR 7256.00	ENR 6386.00	ENR 7086.01	ENR 7256.00	ENR 7380.00	ENR 7387.00
Melt Index, 190°C/2.16 kg	1238	dg/min	2.0	2.9	< 0.5	2.0	< 0.5	< 0.5
Density	792	g/cm^3	0.885	0.875	0.901	0.885	0.870	0.870
Mooney Viscosity, @ 121°C	1646	—	13	26	28	13	54	51
Tensile Strength	638	MPa	11.2	4.5	23.3	11.2	9.1	5.2
Elongation @ Break	638	%	850	870	740	850	810	500
Modulus @ 100% Elongation	638	MPa	3.9	—	8.0	3.9	2.9	2.6
Hardness	2240							
Shore A			82	75	90	82	66	74
Shore D			28	—	41	28	22	22
Tear Strength, Die C	624	kN/m	—	—	92.2	56.2	40.6	38
Melting Point (DSC, 10°C/min)	Dow Method	°C	55	55	95	75	50	51

Source: Technical Information, Dow Chemical Company, 2005.

Elastamax^{TM} EG Series Typical properties

Property	ASTM D	Unit	EG-9065	EG-9072	EG-9077	EG-9082	EG-9090
Durometer Hardness, Shore A	2,240						
Instantaneous		—	66	71	76	82	88
After 15 s		—	64	69	74	80	86
Specific Gravity	792	—	0.88	0.88	0.88	0.88	0.88
Tensile Strength	412	psi	430	520	570	650	960
Elongation @ Break	412	%	420	450	460	440	430
Modulus @100% Elongation	412	psi	325	380	430	475	790
Modulus @ 300% Elongation	412	psi	450	510	580	620	1,020
Tear Strength, Die C	624	pli	135	150	—	—	—
Melt Flow Rate, Procedure A, 374°F	1,238	g/10 min	35	26	20	15	6

Source: PolyOne Corporation, Technical Data Sheets, 2005.

Engage^{TM} 8100 Series Typical Properties

Property	ASTM D Method	Unit	ENGAGE 8100	ENGAGE 8107	ENGAGE 8130	ENGAGE 8137	ENGAGE 8150	ENGAGE 8180
Melt Index, 190°C/2.16 kg	1,238	dg/min	1.0	1.0	13	13	0.5	0.5
Density	792	g/cm^3	0.87	0.87	0.864	0.864	0.868	0.863
Mooney Viscosity, @ 121°C	1,646	—	24.1	25	4	3	33	37
Tensile Strength	638	MPa	9.76	5.4	2.4	1.9	9.5	6.3
Elongation @ Break	638	%	810	600	800	580	810	910
Modulus @ 100% Elongation	638	MPa	2.9	2.8	1.8	1.4	2.6	1.9
Hardness	2,240							
Shore A			73	73	63	57	70	63
Shore D			22	22	13	9	20	16
Tear Strength, Die C	624	kN/m	40	38.8	26.4	20.1	37.3	32.0
Melting Point (DSC, 10°C/min)	Dow Method	°C	60	59	56	50	55	47

Source: Technical Information, Dow Chemical Company, 2005.

A5.3 TPV Data Sheets

DuPont™ ETPV Typical Properties

Property	Test Method	Unit	Grade				
			60A01L NC010	**60A01HSL BK001**	**80A01 NC010**	**90A01HS BK001**	**95A01HS BK001**
Tensile Strength (23°C)	ISO 527	MPa (kpsi)	6 (0.87)	6 (0.87)	7.8 (1.13)	10 (1.45)	13.5 (1.96)
Elongation @ Break (23°C)	ISO 527	%	50	50	123	200	223
Flexural Modulus (23°C)	ISO 178	MPa (kpsi)	13 (1.9)	13 (1.9)	28 (4)	50 (7.25)	—
Hardness, Shore A	ISO 868						
15 s		—	54	54	72	82	96[a]
Maximum		—	60	60	78	90	—
Brittleness Temperature	ISO 812	°C (°F)	–40	–40	—	–40	—
Tear Strength	ISO 34–1, Method B/b	kN/m (pli)	16 (91.4)	16 (91.4)	43 (246)	29 (165.5)	—
Melting Temperature 10°C/min	ISO 11357–1/–3	°C (°F)	205 (401)	205 (401)	205 (401)	205 (401)	216 (420)
Density	ISO 1183	kg/m^3 (g/cm^3)	1,080 (1.08)	1,080 (1.08)		1,120 (1.12)	—
Dielectric Constant 1 kHz	ASTM D150	—	—	4.6	—	4.4	—
Compression Set	ASTM D 395B	%					
22 hr @ 100°C (212°F)			—	34		54	70
22 hr @ 150°C (212°F)			—	67		85	52

Notes:
[a] ASTM D2240.
Source: Technical Data Sheets, DuPont, 2006.

Geolast^{TM} TPV, Typical Properties

Property	ASTM Method	Unit	Grade			
			701-70	701-80W183	701-87W183	703-45
Durometer Hardness, Scale A	D2240	—	70	80	84	45 (Scale D)
Density	D792	—	1.00	1.02	1.01	0.97
Tensile Stress @ 100%	D412	psi	480	680	730	1,640
Tensile Strength	D412	psi	860	1,200	1,310	2,470
Elongation @ Break	D412	%	260	300	330	365
Tear Strength (Die C)	D624	lbf/in.	108	154	194	497
Compression Set, 22 hr @ 158°F	D395	%	25	30	39	—
Compression Set, 70 hr @ 257°F	D395	%	33	37	50	—
Brittle Temperature	D746	°F	–35	–31	–31	–17
Aging in Air 168 hr @ 257°F	D573					
Change in Durometer Hardness		%	+1	+5	–2	+1
Change in Tensile Strength		%	+13	+1	+15	+3
Change in Elongation @ Break			–4	–29	–26	–18
Aging in IRM 903 oil, 70 hr @ 257°F	D471					
Change in Tensile Strength		%	–25	–27	–17	—
Change in Elongation @ Break		%	–27	–38	–31	—
Change in Mass		%	–2	+3	+5	—

Source: Technical Data Sheets, Advanced Elastomer Systems LP, 2006.

Santoprene$^{\mathrm{TM}}$ TPV, Typical Properties

Property	ASTM Method	Unit	Grade TPV					
			101-45 W255	101-55	101-64	101-73	101-80	101-87
Durometer Hardness, Scale A	D2240	—	44	55	64	73	80	87
Density	D792	—	0.98	0.97	0.97	0.97	0.96	0.96
Tensile Stress @ 100%	D412	psi	200	300	380	520	680	1,030
Tensile Strength	D412	psi	580	750	1,010	1,280	1,610	2,550
Elongation @ Break	D412	%	400	400	450	490	540	580
Tear Strength (Die C)	D624	lbf/in.	−2	91	131	154	200	297
Compression Set, 22 hr @ 158°F	D395	%	—	22	18	28	41	36
Compression Set, 70 hr @ 257°F	D395	%	—	38	44	37	47	44
Brittle Temperature	D746	°F	—	−76	−76	−76	−76	−65
Dielectric Constant	D150	—		2.40	2.50	2.50	2.60	2.60
Aging in Air 168 hr @ 257°F	D573							
Change in Durometer Hardness		%	—	+3	+2	+7	+5	+2
Change in Tensile Strength		%	—	−7	−12	−1	−5	−15
Change in Elongation @ Break			—	+13	+6	−3	−12	−16
Aging in IRM 903 oil, 70 hr @ 257°F	D471							
Change in Tensile Strength		%	—	−8	−30	−31	−25	−29
Change in Elongation @ Break		%	—	−48	−49	−47	−43	−32
Change in Mass		%	—	+97	+87	+72	+64	48
Continuous Upper Temperature Resistance	SAE J2236	°F	—	275	275	275	275	275

Source: Technical Data Sheets, Advanced Elastomer Systems LP, 2005.

Santoprene^{TM} TPV, Typical Properties (Continued)

Property	ASTM Method	Unit	Grade TPV	
			103-40	103-50
Durometer Hardness, Scale D	D2240	—	40	50
Density	D792	—	0.95	0.95
Tensile Stress @ 100% Elongation	D412	psi	1,310	—
Tensile Strength	D412	psi	3,000	—
Elongation @ Break	D412	%	610	—
Tear Strength (Die C)	D624	lbf/in.	377	497
Tensile Strength @ yield	D638	psi	—	1,740
Tensile Elongation @ yield	D638	%	—	30
Compression Set, 22 hr @ 158°F	D395	%	54	59
Compression Set, 70 hr @ 257°F	D395	%	61	74
Brittle Temperature	D746	°F	−58	−18
Dielectric Constant	D150	—	2.60	2.40
Aging in Air 168 hr @ 257°F	D573			
Change in Durometer Hardness		%	+4	+5
Change in Tensile Strength		%	−11	−32
Change in Ultimate Elongation		%	−15	−27
Aging in IRM 903 Oil, 70 hr @ 257°F	D471			
Change in Tensile Strength		%	−27	−23
Change in Ultimate Elongation		%	−29	−27
Change in Mass		%	+41	+35

Source: Technical Data Sheets, Advanced Elastomer Systems LP, 2005.

Santoprene$^{\text{TM}}$ TPV, Typical Properties (Continued)

Property	ASTM Method	Unit	Grade TPV						
			111-35	**111-45**	**111-55**	**111-64**	**111-73**	**111-80**	**111-87**
Durometer Hardness, Scale A	D2240	—	35	45	55	64	73	80	87
Density	D792	—	0.95	0.96	0.97	0.97	0.97	0.97	0.96
Tensile Stress @ 100%	D412	psi	150	200	270	380	490	640	940
Tensile Strength	D412	psi	420	510	670	900	1,070	1,360	1,810
Elongation @ Break	D412	%	330	340	400	430	460	460	510
Tear Strength (Die C)	D624	lbf/in.	—	63	—	—	—	—	—
Compression Set, 22 hr @ 158°F	D395	%	10	11	12	33	37	38	32
Compression Set, 70 hr @ 257°F	D395	%	31	35	34	42	43	64	63
Brittle Temperature	D746	°F	−81	−80	−76	−78	−74	−67	−76
Dielectric Constant	D150	—	—	—	2.60	—	2.60	2.70	2.60
Aging in Air 168 hr @ 257°F	D573								
Change in Durometer Hardness		%	−1	+1	+3	+6	+6	—	+ 2
Change in Tensile Strength		%	−29	−23	−12	+2	+12	—	−15
Change in Elongation @ Break			−1	+26	+16	+16	+6	—	−24
Aging in IRM 903 Oil, 70 hr @ 257°F	D471								
Change in Tensile Strength		%	−61	−39	−44	−38	−24	—	−30
Change in Elongation @ Break		%	−65	−54	−59	−49	−48	—	−43
Change in Mass		%	+108	+116	+102	+87	+62	—	+ 51
Continuous Upper Temperature Resistance	SAE J2236	°F	—	—	275	257	257	—	275

Source: Technical Data Sheets, Advanced Elastomer Systems LP, 2005.

Sarlink® 3139 D Typical Properties

Typical Properties*	Test Method	SI System		US System	
		Typical Values	Units	Typical Values	Units
Hardness Shore D (5 s)	ASTM D-2240,				
Injection Molded Sample	5 s delay	42	—	42	—
Extruded Sample	5 s delay	38	—	38	—
Specific Gravity	ASTM D-792	0.94	—	0.94	—
Stress/Strain Properties	ASTM D-412, Die C				
Flow Direction					
Tensile Strength		14.6	MPa	2117	psi
Modulus at 100%		10.1	MPa	1465	psi
Elongation at Break		625	%	625	%
Cross Direction					
Tensile Strength		16.2	MPa	2349	psi
Modulus at 100%		9.4	MPa	1363	psi
Elongation at Break		714	%	714	%
Tear Strength	ASTM D-624, Die C				
Cross Direction					
Unnicked		76	kN/m	433	pli
Compression Set	ASTM D-395, Method B				
72 hr/23°C		43	%	43	%
22 hr/70°C		61	%	61	%
22 hr/100°C		70	%	70	%
Hot Air Aging,	ASTM D-573				
168 hr/150°C, Cross Direction					
Change in Hardness		.9	—	.9	—
Retention Tensile Strength		93	%	93	%
Retention Modulus at 100%		111	%	111	%
Retention Elongation at Break		84	%	84	%
1,000 hr/125°C, Cross Direction					
Change in Hardness		4.6	—	4.6	—
Retention Tensile Strength		93	%	93	%
Retention Modulus at 100%		116	%	116	%
Retention Elongation at Break		89	%	89	%
Volume Swell	ASTM D-471				
24 hr/121°C Oil #3		46	%	46	%
70 hr/125°C Oil #3		55	%	55	%

Note:
*Tests are conducted on injection-molded plaques unless indicated otherwise.
Source: Product Data Sheet, DSM, 2006.

Thermolast® Typical Properties

Grade	Color	Hardness DIN 53505/ ISO 868 Shore A	Density DIN EN ISO 1183-1:2004 (g/cm^3)	Tensile Strength DIN 53504/ ISO 37 (N/mm^2)	Elongation at Break DIN 53504/ ISO 37 (N/mm^2)	Tear Resistance ISO 34-1 method B (b) (Graves) (N/mm)	Compression Set ISO 815 (%)			
							72 hr/23°C	22 hr/70°C	22 hr/100°C	22 hr/120°C
T V 5 L V Z	Black	50	1.05	4.7	520	12.4	12	33	43	55
T V 6 L V Z	Black	60	1.05	6.0	470	15.0	13	35	38	47
T V 7 L V Z	Black	70	1.05	8.0	470	15.4	14	36	37	44
T V 8 L V Z	Black	80	1.05	11.0	480	23	19	37	41	48
T V 9 L V Z	Black	90	1.05	14.3	460	32	26	51	52	63
T V 5 L V N	Natural	50	1.05	4.7	520	12.4	12	33	43	55
T V 6 L V N	Natural	60	1.05	6.0	470	15.0	13	35	38	47
T V 7 L V N	Natural	70	1.05	8.0	470	15.4	14	36	37	44
T V 8 L V N	Natural	80	1.05	11.0	480	23	19	37	41	48
T V 9 L V N	Natural	90	1.05	14.3	460	32	26	51	52	63

Source: Technical Data Sheets, Kraiburg TPE GmbH, 2006.

Zeotherm® Typical Properties

Property	ASTM Method	Unit	Grade			
			100-70B	100-80B	100-90B	130-90B
Density	D792	—	1.15	1.15	1.13	1.10
Durometer Hardness, Scale A	D2240	—	75	85	95	95
Stress @ 100% elongation	D412	psi	725	870	1,160	1,305
Tensile Strength	D412	psi	1,160	1,305	1,595	1,885
Elongation @ Break	D412	%	200	200	185	200
Compression Set, 70 hr @ 125°C	D395 Method B	%	60	60	75	—
Low Temperature	D1053					
Gehman T10		°C	−35	−35	−43	−45
Gehman T100		°C	−50	−35	−42[a]	−44[a]
Melting Temperature	—	°F	428	428	428	428
Heat Aging in Air, 168 hr @ 125°C						
Change in Tensile Strength		%	−10	−10	−10	0
Change in Elongation @ Break		%	−20	−30	+30	−35
Change in Durometer Hardness						
Heat Aging in SF 105 Oil, 168 hr @ 150°C						
Change in Tensile Strength		%	+10	+10	+10	+20
Change in Elongation @ Break		%	−30	+30	+30	−20
Change in Volume		%	−4	−4	+3	+1

Note:

[a] Brittle point (ASTM D2137).

Source: Technical Data Sheets, Zeon Chemicals LP, 2006.

A5.4 MPR Data Sheets

Table 1. ***Alcryn***® **General Purpose Grades**

Property[a]	Test Methods				1000 Series			3000 Series		
	ASTM	ISO	DIN	Unit	1060 BK	1070 BK	1080 BK	3055 NC	3065 NC	3075 NC
Mechanical										
Specific Gravity	D471	2781	53479		1.19	1.23	1.25	1.18	1.26	1.35
Hardness, Durometer A	D2240	48	53505	Shore A	62	72	78	57	67	76
Tensile Properties	D412	37	53504							
100% Modulus				MPa	3.9	5.3	7.9	2.8	4.1	5.9
Tensile Strength				MPa	9.6	12.4	13.1	8.2	8.9	9.8
Elongation at Break				%	300	270	210	440	400	360
Torsion Modulus										
At 24°C	D1043	—	—	MPa	1.9	2.2	2.9	1.3	2.1	3.4
At −20°C	—	—	—	MPa	7.5	14.3	19.9	17.2	45.5	127.5
Tear Strength										
Graves (Die C), at 24°C	D624	—	53507	KN/m	26.3	28.0	24.5	28.9	35.9	49.0
Permanent Set (Tension)	D412	—	—	%	8	10	8	6	9	11
Compression Set, Method B[b]	D395	815	53517							
After 22 hr at 24°C				%	15	15	15	17	17	23
After 22 hr at 100°C				%	55	55	55	65	69	67
Heat Aging Resistance										
Tensile Properties After 7 Days at 125°C	D573	188	53508							
100% Modulus				MPa	3.9	5.3	9.4	2.5	4.5	6.6
Tensile Strength				MPa	10.6	13.1	14.0	8.7	8.9	10.5
Elongation at Break				%	325	235	190	450	370	350
Hardness, Durometer A				Shore A	67	70	77	58	65	74

Low Temperature Properties										
Brittleness Temperature	D746	812	—	°C	−51	−53	−44	−54	−45	−30
Clash-Berg Stiffness Temperature, 10,000 psi (69 MPa)	D1043	—	—	°C	−38	−34	−30	−28	−23	−17
Taber Abrasion, Cs-17 Wheel, 1,000 g Load	D3389	—	53516	mg/1,000 cycles	7	7	5	<1	<1	<1
Chemical										
Fluid Resistance—Volume Change	D471	1817								
After 7 Days in Water at 100°C			—	%	12	8	10	15	14	13
After 7 Days in IRM 901 Oil (ASTM No. 1 Oil) at 100°C			—	%	−10	−9	−8	−12	−9	−6
After 7 Days in IRM 903 Oil (ASTM No. 3 Oil) at 100°C			—	%	27	25	23	25	30	29
After 7 Days in ASTM Reference Fuel B at 24°C			—	%	30	30	29	30	32	36
Rheological										
Viscosity at 300 s^{-1} at 190°C	D3835	—	—	Pa.s	545	740	800	465	580	840
Typical Processing Temperature	—	—	—	°C	177	177	177	177	177	177

Notes:

[a] All properties measured on specimens cut from 1.9 mm (75 mil) thick compression-molded plaques.

[b] Type 1 pellets, 12.7 mm (0.5 in.) diameter, plied up from 1.9 mm (75 mil) slabs.

Table 2. *Alcryn*® **Injection Molding Grades**

Property[a]	Test Methods				2000 Series							
	ASTM	ISO	DIN	Unit	2060 NC	2070 NC	2080 NC	2060 BK	2070 BK	2080 BK	2250 UT	2265 UT
Mechanical												
Specific Gravity	D471	2781	53479		1.12	1.20	1.26	1.10	1.14	1.17	1.06	1.08
Hardness, Durometer A	D2240	48	53505	Shore A	59	68	76	59	68	78	47	62
Tensile Properties	D412	37	53504									
100% Modulus				MPa	3.0	4.0	5.3	2.9	4.2	6.2	1.9	3.5
Tensile Strength				MPa	7.9	8.6	9.9	8.0	8.7	12.1	6.8	9.7
Elongation at Break				%	420	400	400	410	320	320	420	470
Torsion Modulus												
At 24°C	D1043	—	—	MPa	2.3	2.2	2.9	2.2	2.3	3.2	1.9	2.5
At −20°C	—	—	—	MPa	4.8	8.5	14.3	5.9	10.2	27.5	2.6	5.5
Tear Strength												
Graves (Die C), at 24°C	D624	—	53507	KN/m	28.0	29.7	33.3	27.1	28.0	35.0	19.2	26.3
Permanent Set (Tension)	D412	—	—	%	8	9	11	9	9	10	7	6
Compression set, Method B[b]	D395	815	53517									
After 22 hr at 24°C				%	13	16	17	13	14	14	15	12
After 22 hr at 100°C				%	62	64	61	62	64	62	56	54
Heat Aging Resistance												
Tensile Properties After 7 Days at 125°C	D573	188	53508									
100% Modulus				MPa	2.7	3.5	4.4	2.7	4.4	5.2	1.6	4.4
Tensile Strength				MPa	6.5	5.5	5.5	7.6	8.4	11.0	6.4	11.5
Elongation at Break				%	340	220	135	390	280	235	450	405
Hardness, Durometer A				Shore A	60	65	71	63	70	76	45	66
Low Temperature Properties												
Brittleness Temperature	D746	812	—	°C	−85	−85	−76	−87	−79	−86	−91	−91
Clash-Berg Stiffness Temperature, 10,000 psi (69 MPa)	D1043	—	—	°C	−42	−40	−32	−40	−40	−17	−26	−50
Taber Abrasion, Cs-17 Wheel, 1,000 g Load	D3389	—	53516	mg/1,000 cycles	5	9	10	5	5	3	5	7

Chemical											
Fluid Resistance—Volume Change	D471	1817									
After 7 Days in Water at 100°C			—	%	8	7	8	8	6	5	7	6
After 7 Days inIRM 901 Oil (ASTM No. 1 Oil) at 100°C			—	%	−21	−16	−14	−19	−17	−8	−39	−21
After 7 Days in IRM 903 Oil (ASTM No. 3 Oil) at 100°C			—	%	17	18	23	16	19	31	32	23
After 7 Days in ASTM Reference Fuel B at 24°C			—	%	17	22	29	25	25	32	24	19
Rheological											
Viscosity at 300 s^{-1} at 190°C	D3835	—	—	Pa.s	350	465	640	365	410	700	115	390
Typical Processing Temperature	—	—	—	°C	177	177	177	177	177	177	166	166

Notes:

[a] All properties measured on specimens cut from 1.9 mm (75 mil) thick compression-molded plaques.

[b] Type 1 pellets, 12.7 mm (0.5 in.) diameter, plied up from 1.9 mm (75 mil) slabs.

Table 3. *Alcryn*® General Purpose Grades

Property[a]	Test Methods				4600 Series					
	ASTM	ISO		Unit	4660 NC	4670 NC	4680 NC	4660 BK	4670 BK	4680 BK
Mechanical										
Specific Gravity	D471	2781			1.17	1.25	1.27	1.17	1.25	1.27
Hardness, Durometer A	D2240	48		Shore A	57	70	78	57	70	79
Tensile Properties	D412	37								
100% Modulus				psi	380	570	740	430	580	860
Tensile Strength				psi	1225	1280	1600	1125	1310	1570
Elongation at Break				%	440	440	360	390	420	380
Torsion Modulus										
At 75°F (24°C)	D1043	—		psi	250	350	600	250	350	600
At −4°F (−20°C)	—	—		psi	1000	4000	10,000	1000	4000	10,000
Tear Strength										
Graves (Die C), at 75°F (24°C)	D624	—		Ib/in.	170	220	310	190	220	300
Permanent Set (Tension)	D412	—		%	7	9	12	7	9	12
Compression Set, Method B[b]	D395	815								
After 22 hr at 75°F (24°C)				%	16	21	25	16	20	24
After 22 hr at 212°F (100°C)				%	72	74	74	72	75	75
Heat Aging Resistance										
Tensile Properties After 7 Days at 257°F (125°C)	D573	188								
100% Modulus				psi	370	730	1260	400	700	1100
Tensile Strength				psi	1200	1380	1680	1210	1320	1600
Elongation at Break				%	400	380	350	460	420	380
Hardness, Durometer A				Shore A	54	64	71	55	64	76
Low Temperature Properties										
Brittleness Temperature	D746	812		°F(°C)	−92(−69)	−76(−60)	−65(−54)	−101(−74)	−80(−62)	−75(−58)
Clash-Berg Stiffness Temperature, 10,000 psi (69 MPa)	D1043	—		°F(°C)	−40(−40)	−4(−20)	39(−4)	−31(−35)	−4(−20)	34(1)
Taber Abrasion, Cs-17 Wheel, 1,000 g Load	D3389	—		mg/1,000 cycles	4	4	9	1	2	6

Chemical Fluid Resistance—Volume Change	D471	1817								
After 7 Days in Water at 212 °F (100°C)				%	9	11	11	10	12	10
After 7 Days in IRM 901 Oil (ASTM No. 1 Oil) at 212°F (100°C)				%	−19	−17	−10	−19	−15	−9
After 7 Days in IRM 903 Oil (ASTM No. 3 Oil) at 212°F (100°C)				%	14	17	26	12	17	24
After 7 Days in ASTM Reference Fuel B at 75°F (24°C)				%	13	16	26	11	14	22
Rheological										
Viscosity at 300 s^{-1} at 374°F (190°C)	D3835	—		Pas	400	500	870	370	510	780
Typical Processing Temperature	—	—		°F(°C)	330(166)	330(166)	330(166)	330(166)	330(166)	330(166)

Notes:

[a] All properties measured on specimens cut from 1.9 mm (75 mil) thick compression-molded plaques.

[b] Type 1 pellets. 12.7 mm (0.5 in.) diameter, plied up from 1.9 mm (75 mil) slabs.

Source: Alcryn Product and Properties Guide, Advanced Polymer Alloys, 2005.

A5.5 TPU Data Sheets

Desmopan® 445

Property	Test Conditions	Unit	Standard	Value
Specific Gravity			ASTM D792	1.22
Hardness Shore D			ASTM D2240	45
Flexural Modulus	73°F	lb/in.^{2}	ASTM D 790	8,400
Flexural Modulus	158°F	lb/in.^{2}	ASTM D 790	5,450
Flexural Modulus	–22°F	lb/in.^{2}	ASTM D 790	37,200
Tensile Strength		lb/in.^{2}	ASTM D 412	4,500
Ultimate Elongation		%	ASTM D 412	500
Tensile Stress at 50% Elongation		lb/in.^{2}	ASTM D 412	1,250
Tensile Stress at 100% Elongation		lb/in.^{2}	ASTM D 412	1,400
Tensile Stress at 300% Elongation		lb/in.^{2}	ASTM D 412	2,500
Compression Set, as Molded	22 hr at 73°F	%	ASTM D 395-B	16
Compression Set, as Molded	22 hr at 158°F	%	ASTM D 395-B	65
Compression Set, Postcured	22 hr at 73°F; postcured 16 hr at 230°F	%	ASTM D 395-B	12
Compression Set, Postcured	22 hr at 158°F; postcured 16 hr at 230°F	%	ASTM D 395-B	30
Compressive Load	5% deflection	lb/in.^{2}	ASTM D 575	275
Compressive Load	10% deflection	lb/in.^{2}	ASTM D 575	500
Compressive Load	15% deflection	lb/in.^{2}	ASTM D 575	750
Compressive Load	20% deflection	lb/in.^{2}	ASTM D 575	975
Compressive Load	25% deflection	lb/in.^{2}	ASTM D 575	1,250
Compressive Load	50% deflection	lb/in.^{2}	ASTM D 575	3,625
Tear Strength, Die C		lbf/in.	ASTM D 624	700

Source: Desmopan® Data Sheet, Bayer MaterialScience, 2006.

DESMOPAN® 453 Properties

Property	Test Conditions	Unit	Standard	Value
Specific Gravity			ASTM D792	1.22
Hardness Shore D			ASTM D2240	53
Flexural Modulus	73°F	lb/in.^{2}	ASTM D 790	15,000
Flexural Modulus	158°F	lb/in.^{2}	ASTM D 790	7,390
Flexural Modulus	–22°F	lb/in.^{2}	ASTM D 790	110,000
Tensile Strength		lb/in.^{2}	ASTM D 412	5,000
Ultimate Elongation		%	ASTM D 412	500
Tensile Stress at 50 % Elongation		lb/in.^{2}	ASTM D 412	1,800
Tensile Stress at 100 % Elongation		lb/in.^{2}	ASTM D 412	2,000
Tensile Stress at 300 % Elongation		lb/in.^{2}	ASTM D 412	3,100
Compression Set, as Molded	22 hr at 73°F	%	ASTM D 395-B	17
Compression Set, as Molded	22 hr at 158°F	%	ASTM D 395-B	62
Compression Set, Postcured	22 hr at 73°F; postcured 16 hr at 230°F	%	ASTM D 395-B	15
Compression Set, Postcured	22 h at 158°F; postcured 16 hr at 230°F	%	ASTM D 395-B	35
Compressive Load	5% deflection	lb/in.^{2}	ASTM D 575	350
Compressive Load	10% deflection	lb/in.^{2}	ASTM D 575	650
Compressive Load	15% deflection	lb/in.^{2}	ASTM D 575	950
Compressive Load	20% deflection	lb/in.^{2}	ASTM D 575	1,250
Compressive Load	25% deflection	lb/in.^{2}	ASTM D 575	1,550
Compressive Load	50% deflection	lb/in.^{2}	ASTM D 575	4,550
Tear Strength, Die C		lbf/in.	ASTM D 624	900

Source: Desmopan® Data Sheet, Bayer MaterialScience, 2006.

Estane® Ester-Based Products Typical Properties

Property	ASTM Method	Unit	5703	58680	58213	58224	58238	5719
Hardness, Shore	D2240	—	70A	74A	75A	75A	75A	80A
Specific Gravity	D412/D638	—	1.19	1.21	1.18	1.18	1.17	1.19
Tensile Strength	D412/D638	psi	4,500	6,300	5,600	3,600	7,000	7,300
Elongation @ Break	D412/D638	%	630	660	780	800	680	430
Tensile Set	D412/D638	%	—	5	12	18	3	—
Compression Set	D395	%	—	21	34	37	21	—
T_g (by DSC)		°F	–24	–	–15	–18	–49	66

Source: ESTANE® Product Selection Guide, Noveon, Inc., 2003.

Estane® Ester-Based Products Typical Properties (Continued)

Property	ASTM Method	Unit	5713	5701	5708	58206	58271	58132
Hardness, Shore (A or D)	D2240	—	40D	85A	85A	85A	85A	88A
Specific Gravity	D412/D638	—	1.20	1.21	1.20	1.20	1.21	1.21
Tensile Strength	D412/D638	psi	5,500	7,100	6,100	6,500	6,000	5,100
Elongation @ Break	D412/D638	%	600	460	490	550	550	645
Tensile Set	D412/D638	%	—	11	—	10	11	—
Compression Set	D395	%	—	23	—	20	23	16
T_g (by DSC)		°F	−45	−18	−27	−26	−25	−56

Source: ESTANE® Product Selection Guide, Noveon, Inc., 2003.

Property	ASTM Method	Unit	58226	5707	58092	58277	58134
Hardness, Shore (A or D)	D2240	—	92A	93A/45D	93A/45D	93A/45D	94A/45D
Specific Gravity	D412/D638	—	1.22	1.22	1.22	1.21	1.21
Tensile Strength	D412/D638	psi	7,900	7,100	4,600	8,000	5,500
Elongation @ Break	D412/D638	%	500	460	450	450	575
Tensile Set	D412/D638	%	16	11	17	17	—
Compression Set	D395	%	—	23	28	18	16
T_g (by DSC)		°F	—	−18	1	27	−44

Source: ESTANE® Product Selection Guide, Noveon, Inc., 2003.

Estane® Ether-Based Products Typical Properties (Continued)

Property	ASTM Method	Unit	75AT3	58245	58370	58881	5714
Hardness, Shore (A or D)	D2240	—	74A	80A/31D	80A	80A	82A
Specific Gravity	D412/D638	—	1.08	1.21	1.18	1.10	1.11
Tensile Strength	D412/D638	psi	3,800	4,000	4,300	3,400	4,500
Elongation @ Break	D412/D638	%	660	800	690	710	530
Tensile Set	D412/D638	%	6	10	15	10	15
Compression Set	D395	%	24	17	33	18	24
T_g (by DSC)		°F	−89	–	−58	−61	−36

Source: ESTANE® Product Selection Guide, Noveon, Inc., 2003.

Estane® Ether-Based Products Typical Properties (Continued)

Property	ASTM Method	Unit	58300	58630	58202	58284
Hardness, Shore (A or D)	D2240	—	82A	82A	85A	85A
Specific Gravity	D412/D638	—	1.13	1.14	1.25	1.10
Tensile Strength	D412/D638	psi	4,500	5,000	4,000	7,000
Elongation @ Break	D412/D638	%	700	670	650	550
Tensile Set	D412/D638	%	15	14	17	8
Compression Set	D395	%	24	24	25	19
T_g (by DSC)		°F	−58	−56	−49	−47

Source: Estane® Product Selection Guide, Noveon, Inc., 2003.

Pellethane® TPU 2102 Series Typical Properties

Property	ASTM Method	Unit	2102-55D	2102-65D	2102-75A	2102-85A	2102-90AR	2102-90AE
Hardness Shore (A/D)	D2240	—	58D	65D	77A	86A	94A	94A/58D
Specific Gravity	792	—	1.21	1.22	1.17	1.18	1.2	1.2
Melt Flow Rate, 224°C	1238	g/10 min	14	49	25	35	15	29
Modulus @ 100% Elongation	D412	psi	2,350	2,900	680	1,050	1,600	1,450
Modulus @ 300% Elongation	D412	psi	5,200	4,500	1,400	2,200	4,000	3,000
Tensile Strength	D412	psi	7,180	6,400	5,400	5,850	7,100	6,100
Elongation @ Break	D412	%	415	390	535	525	440	540
Elongation Set after Break	D412	%	30	110	30	50	30	60
Tear Strength, Die C	D624	pli	1,020	1,500	500	520	810	750

Source: Technical Information, the Dow Chemical Company, 2006.

Property	ASTM Method	Unit	2103-55D	2103-65D	2103-70A	2103-80PF	2103-80AEN	2103-90A
Hardness Shore D	D2240	—	96A/55D	64D	72A	84A	83A	92A
Specific Gravity	792	—	1.15	1.17	1.06	1.1	1.13	1.14
Melt Flow Rate, 224°C	1238	g/10 min	15	35	11	39	20	23
Modulus @ 100% Elongation	D412	psi	2,400	2,800	440	750	870	1,630
Modulus @ 300% Elongation	D412	psi	4,600	4,800	750	1,150	1,600	3,600
Tensile Strength	D412	psi	6,400	5,750	3,580	3,800	4,200	6,500
Elongation Set after Break	D412	%	30	360	730	660	650	450
Elongation @ Break	D412	%	425	80	50	50	40	30
Tear Strength, Die C	D624	pli	900	1,100	380	450	500	760

Source: Technical Information, the Dow Chemical Company, 2006.

Pellethane® TPU 2355 Series Typical Properties

Property	ASTM Method	Unit	2355-55D	2355-75A	2355-80AE	2355-95AE
Hardness Shore D	D2240	—	53D	83A	85A	94A
Specific Gravity	792	—	1.19	1.19	1.18	1.22
Melt Flow Rate, 224°C	1238	g/10 min	—	28	7	13
Modulus @ 100% Elongation	D412	psi	1,750	710	900	1,400
Modulus @ 300% Elongation	D412	psi	3,600	1,530	2,200	3,100
Tensile Strength	D412	psi	6,000	5,130	5,700	5,650
Elongation @ Break	D412	%	500	525	550	450
Elongation Set after Break	D412	%	80	30	60	60
Tear Strength, Die C	D624	pli	650	450	720	600

Source: Technical Information, the Dow Chemical Company, 2006.

Texin® TPU 200 Series Typical Properties

Property	ASTM Method	Unit	Texin 245	Texin 250	Texin 255	Texin 260	Texin 270	Texin 285
Hardness Shore (A/D)	D2240	—	45D	52D	55D	60D	70D	85A
Specific Gravity	792	—	1.21	1.22	1.21	1.22	1.24	1.2
Modulus @ 100% Elongation	D412	psi	1,300	1,600	2,000	3,000	4,300	775
Modulus @ 300% Elongation	D412	psi	2,800	3,500	4,000	4,300	5,700	1,700
Tensile Strength	D412	psi	6,000	6,000	7,000	6,000	6,000	5,000
Elongation @ Break	D412	%	500	450	500	400	250	500
Tear Strength, Die C	D624	pli	700	775	900	1,000	1,300	500
Glass Transition Temperature	DMA	°F	−51	−4.0	−15	5.0	32	−44

Source: Texin® Data Sheets, Bayer MaterialScience, 2006.

A5.6 COPE Data Sheets

Hytrel® Typical Properties

Property	Test Method	Unit	3078	4056	4068	4069	4556	5526
Hardness Shore D	ISO 868	—	30	40	40	40	45	55
Density	ISO 1183	g/cm^3	1.07	1.15	1.10	1.11	1.14	1.19
Melt Flow Rate, 190°C	ISO 1133	g/10 min	5.0	5.6	8.5	8.5	8.5	18
Tensile Strength	ISO 527	MPa	24	30	22	31	34	44
Elongation @ Break	ISO 527	%	740	424	620	612	550	500
Tear Strength, Die C	ISO 34-1, Method B/a	kN/m	80	98	95	98	122	133
Glass Transition Temperature	ISO 11357-1/-2	°C	−60	−50	—	−50	−45	−20

Source: DuPont™ Hytrel® Product Information, DuPont, 2005.

Property	Test Method	Unit	5556	6356	6358	7246	8238
Hardness Shore D	ISO 868	—	55	63	63	72	82
Density	ISO 1183	g/cm^3	1.19	1.22	1.22	1.26	1.28
Melt Flow Rate, 190°C	ISO 1133	g/10 min	8.1	9	9	12.5	12.5
Tensile Strength	ISO 527	MPa	42	46	46	53	50
Elongation @ Break	ISO 527	%	500	490	490	450	400
Tear Strength, Die C	ISO 34-1, Method B/a	kN/m	137	158	158	200	228
Glass Transition Temperature	ISO 11357-1/-2	°C	−20	0	0	25	50

Source: DuPont™ Hytrel® Product Information, DuPont, 2005.

Kopel® KP Polyester Elastomers Typical Properties

Property	ASTM Test Method	Unit	KP3340	KP3355	KP3363	KP3372	KP3755
Specific Gravity	D792	—	1.15	1.19	1.23	1.27	1.18
Hardness, Shore D Scale	D2240	—	40	55	65	72	55
Melt Flow Index (230°C)	D1238	g/10 min	12	18	20	17	12
Melting Point	DSC	°C	170	200	210	218	199
Tensile Strength (23°C)	D638	MPa	25	35	37	39	36
Elongation @ Break	D638	%	850	650	550	400	650
Abrasion Resistance, CS-17 Wheel	D1044	mg/1,000 cycles	3.0	5.0	7.0	10	5.0
Resilience		%	67	50	43	—	56

Source: Property Information, Kolon Industries Inc., 2006.

A5.7 COPA Data Sheets

Pebax® Typical Properties

Properties/Grades	4033	6333	7033	7233	MX1205	MV1074	MH1657
Hardness (Shore D)	42	63	69	72	42	40	42
Flexural Modulus (MPa)	75	290	390	730	78	90	80
Tensile Strength (MPa)	—	17	24	34	—	—	—
Density	1.01	1.01	1.02	1.02	1.01	1.01	1.14
Melting Point (°C)	168	169	172	174	147	158	195
Typical Application Areas	Mechanical parts	Mechanical parts	Mechanical parts	Mechanical parts	Impact modifier	Breathable film	Antistatic additive

Source: Technical Data Sheets, Arkema Inc., 2006.

UBE PAE Typical Properties

Property	ASTM Test Method	Unit	Grade	
			PAE 1200U	PAE1201U
Melting Point	D3418	°C	154	165
Density	D792	g/cm^3	1.00	1.00
Tensile Strength @ Yield	D638	N/mm^2	9	19
Elongation @ Break	D638	%	> 300	> 300
Flexural Strength	D790	N/mm^2	7	16
Flexural Modulus	D790	N/mm^2	150	360
Shore D Hardness	D2240	—	58	65
Izod Impact Strength (Notched)	D256	J/m	No break	170
Heat Deflection Temperature (0.45 N/mm^2)	D648	°C	82	110
Melt Flow Index (235°C, 2,160 g)	D1238R	g/10 min	14	8.6

Note: All data measured at 23°C and 65% relative humidity.
Source: Technical Data Sheets, UBE Industries, Ltd., 2006.

UBESTA XPA 9044 X2 Typical Properties

Properties	Test Method	Unit	Value
Melting Point	ISO 11357-3	°C	150
Density	ISO 11 83-3	g/cm^3	1.01
Tensile Strength @ Yield	ISO 527-1, 2	MPa	8
Tensile Strain @ Yield	ISO 527-1, 2	%	44
Tensile Strain @ Break	ISO 527-1, 2	%	>400
Flexural Strength	ISO 178	MPa	5
Flexural Modulus	ISO 178	MPa	80
Shore Hardness (Scale D)	ISO 868	—	44
Heat Deflection Temperature (0.45 MPa)	ISO 75-2	°C	51
(1.80 MPa)			—
Mold Shrinkage In Flow Direction	ISO 294-4	%	0,2
In Transverse Direction			0,8
Abrasion Loss (CS-17 Wheel, 1,000 Revolutions)	ISO 9352	mg	9
Coefficient of Linear Expansion	ISO 11 359-2	10^{-4}/K	2.3
Moisture Absorption (24 hr in Water @ 23°C)	ISO	%	2.5
Melt Flow Index (190°C; 2,160 g)	ISO 1133	g/10 min	13

Source: Technical Information [041024], UBE Industries Ltd., 2006.

A5.8 Silicone TPE Data Sheets

Geniomer® Typical Properties

Property	Test Method	Unit	Grade		
			60	80	200
C_p spec. (25°C)	DSC	[Jg^{-1}K^{-1}]	1.5–1.6	1.5–1.6	1.5–1.6
C_p spec. (200°C)	DSC	[Jg^{-1}K^{-1}]	2.0–2.4	2.0–2.4	2.0–2.4
Compression Set (−18°C)	ISO 815	[%]	22	20	10
Compression Set (5°C)	ISO 815	[%]	52	52	23
Compression Set (23°C)	ISO 815	[%]	75	75	44
Compression Set (40°C)	ISO 815	[%]	96	95	66
Tensile Strength	DIN 53504 S2	[N/mm^2]	4.0–5.5	4.0–6.0	3.0–5.0
Elongation at Break	DIN 53504 S2	[%]	>400	>400	>400
50% Modulus	DIN 53504 S2	[N/mm^2]	0.6–1.0	0.6–1.0	1.2–1.4
100% Modulus	DIN 53504 S2	[N/mm^2]	1.5–2.0	0.9–1.5	1.5–1.7
Hardness, Shore A	DIN 53505	—	40–55	45–55	55–65
Refractive Index	—	—	1.42	1.42	—
Tear Strength	ASTM 624, Die B	[N/mm^2]	20–30	20–30	20–30
Water Content	Thermogravimetry	[%]	<0.3	<0.3	<0.3

Source: Technical Data Sheets, Wacker Silicones, 2006.

TPSiV^{TM} 3010 Series Typical Properties

Property	Test Method	Unit	Grade	
			3010-50A	3010-60A
TP Matrix			Polyurethane	Polyurethane
Specific Gravity, 23/23°C	ASTM D792	—	1.12	1.20
Taber Abrasion Resistance	ASTM D1044	mg	21.0	21.0
Tensile Strength	ASTM D412	psi	1,030	2,320
Elongation at Break	ASTM D412	%	470	500
Tensile Set	ASTM D412			
At Break		%	24	24
After 100% Extension			6	6
After 300% Extension			20	20
Compression Set	ASTM D412	%		
22 hr @ 73°F			14	12
22 hr @ 158°F			49	—
22 hr @ 248°F			74	70
Tear Strength	ASTM D624	lbf/in.	140	170
Durometer Hardness (10 s), Scale A	ASTM D2240	—	52	65
Dielectric Strength	ASTM D149	V/mil	483	457
Dielectric Strength at 100 Hz	ASTM D149	kV/mm	19	18
Dielectric Constant	ASTM D150	—	4.34	4.13

Note: Bonds to PC, ABS, PU, and PVC.
Source: Technical Data Sheets, Multibase Inc., 2006.

TPSiV^{TM} 3011 Series- Properties

Property	Test Method	Unit	Grade			
			3011-50A	3011-60A	3011-70A	3011-85A
TP Matrix			Polyurethane	Polyurethane	Polyurethane	Polyurethane
Specific Gravity, 23/23°C	ASTM D792	—	1.14	1.20	1.20	1.15
Taber Abrasion Resistance	ASTM D1044	mg	60.0	37.0	38.0	—
Tensile Strength	ASTM D412	psi	1,600	1,740	2,320	2,320
Elongation at Break	ASTM D412	%	680	720	600	600
Tensile Set	ASTM D412					
At Break		%	60	68	24	—
After 100% Extension			10	10	6	—
After 300% Extension			34	37	20	—
Compression Set	ASTM D412	%				
22 hr @ 73°F			18	21	23	—
22 hr @ 248°F			84	95	95	—
Tear Strength	ASTM D624	lbf/in.	230	260	260	260
Durometer Hardness (10 s), Scale A	ASTM D2240	—	58	65	71	82
Flame Rating, UL	UL 94	—	—	—	—	HB

Note: General purpose grades.
Source: Technical Data Sheets, Multibase Inc., 2006.

TPSiV^{TM} 3040 Series Typical Properties

Property	Test Method	Unit	Grade				
			3040-55A	3040-60A	3040-65A	3040-70A	3040-85A
TP Matrix			Polyurethane	Polyurethane	Polyurethane	Polyurethane	Polyurethane
Specific Gravity, 23/23°C	ASTM D792	—	1.15	1.15	1.15	1.15	1.15
Tensile Strength	ASTM D412	psi	725	1,020	1,600	1,700	1,730
Elongation at Break	ASTM D412	%	450	450	600	600	280
Tear Strength	ASTM D624	lbf/in.	140	170	260	260	290
Durometer Hardness, 10 s	ASTM D2240	—	58A	61A	65A	68A	84A
Flame Rating, UL	UL 94	—	HB	HB	HB	HB	FB

Note: For overmolding on PC, ABS.
Source: Technical Data Sheets, Multibase Inc., 2006.

TPSiV^{TM} 3340 Series Typical Properties

Property	Test Method	Unit	Grade		
			3340-55A	3340-60A	3340-60A
TP Matrix		—	Polyurethane	Polyurethane	Polyurethane
Specific Gravity, 23/23°C	ASTM D792	—	1.15	1.15	1.15
Tensile Strength	ASTM D412	psi	435	435	580
Elongation at Break	ASTM D412	%	400	400	360
Tear Strength	ASTM D624	lbf/in.	88	86	110
Durometer Hardness (10 s), Scale A	ASTM D2240	—	55	60	63
Flame Rating, UL	UL 94	—	HB	HB	HB

Note: UV stability, overmolding on PC and ABS.
Source: Technical Data Sheets, Multibase Inc., 2006.

TPSiV^{TM} 1180-50D Typical Properties

Property	Test Method	Unit	Nominal Value
TP Matrix—Polyamide			
Specific Gravity, 23/23°C	ASTM D792	—	1.09
Tensile Strength	ASTM D412	psi	3,480
Elongation at Break	ASTM D412	%	200
Tear Strength	ASTM D624	lbf/in.	140
Durometer Hardness (10 s), Scale D	ASTM D2240	—	52
Dielectric Strength	ASTM D149	V/mil	569
Dielectric Strength at 100 Hz	ASTM D149	kV/mm	22.4
Dielectric Constant	ASTM D150	—	4.04
Flame Rating, UL	UL 94	—	HB

Source: Technical Data Sheets, Multibase Inc., 2006.

TPSiV^{TM} 3111-70A Typical Properties

Property	Test Method	Unit	Nominal Value
TP Matrix—Polyurethane			
Specific Gravity, 23/23°C	ASTM D792	—	1.15
Taber Abrasion Resistance	ASTM D1044	mg	35.0
Tensile Strength	ASTM D412	psi	2,180
Elongation at Break	ASTM D412	%	600
Tear Strength	ASTM D624	lbf/in.	260
Compression Set (22 hr @ 73°F)	ASTM D395	%	20
Durometer Hardness (10 s), Scale A	ASTM D2240	—	70

Note: Good stability in water.
Source: Technical Data Sheets, Multibase Inc., 2006.

Appendix 6 Recent TPE Patents

Kawakami, T., et al., U.S. Patent 7,171,142 (January 30, 2007), to Canon Kasei, Kibushiki Kaisha, "Conductive roller, and process cartridge, and electrophoretic apparatus, which have conductive roller."

Gramespacher, H., et al., U.S. Patent 7,170,004 (January 30, 2007), to ABB Schweiz AG, "Surrounding Body for a high voltage cable and cable element, which is provided with a surrounding body."

Papke, N., U.S. Patent 7,169,887 (January 30, 2007), to Ticona GmbH, "Thermoplastic molding material and molded bodies produced therefrom."

Starzewski, O., et al., U.S. Patent 7,169,866 (January 30, 2007), to Bayer Aktiengesellschaft, "Process of preparing homopolymers, copolymers and/or block copolymers by living polymerization with metallocenes having a donor–acceptor interaction."

Ikeda, S., U.S. Patent 7,169,851 (January 30, 2007), to Zeon Corporation, "Thermoplastic elastomer molding."

Ikuji, M., et al., U.S. Patent 7,169,849 (January 30, 2007), to Kuraray Co. Ltd., "Process of production of thermoplastic elastomer composition."

Ninomiya, N., et al., U.S. Patent 7,169,065 (January 30, 2007), to Mizuno Corporation, "Multi-piece golf ball and manufacturing method thereof."

Walak, S., U.S. Patent 7,168,605 (January 30, 2007), to Boston Scientific Scimed Inc., "Microtubes for therapeutic delivery."

Robinson, C., et al., U.S. Patent 7,168,605 (January 23, 2007), to Rexam Medical Packaging Inc., "Closure for a retort processed container having a peelable seal."

Ganachaud, P., and Covet, J., U.S. Patent 7,168,466 (January 30, 2007), to Inergy Automotive System Research, "Safety systems for liquid fuel tank."

Worrick III, C.B., U.S. Patent 7,168,466 (January 30, 2007), to Gilette Company, "Shaving system."

Datta, S., et al., U.S. Patent 7,166,674 (January 23, 2007), to ExxonMobil Chemical Patents Inc., "Elastic blends comprising crystalline polymer of polypropylene."

Van Schaftlingen, J.-J., et al., U.S. Patent 7,166,253 (January 23, 2007), to Solvay (Societe Anonyme), "Process of manufacturing hollow bodies."

Devens, Jr., D.A., U.S. Patent 7,166,099 (January 23, 2007), to Boston Scientific Scimed Inc., "Multilayer medical devices."

Grogl, F., and Mehl, A., U.S. Patent 7,168,078 (January 16, 2007), to Nexans, "Abrasion resistant jacket."

Kanae, K., et al., U.S. Patent 7,163,983 (January 16, 2007), to JSR Corporation, "Olefinic thermoplastic elastomer sheet, process for production thereof, and laminates."

Khadpur, A.K., et al., U.S. Patent 7,163,741 (January 16, 2007), to 3M Innovative Properties Company, "Adhesive for bonding to low surface energy surfaces."

Murata, A., et al., U.S. Patent 7,163,597 (January 16, 2007), to Nitto Denko Corporation, "Heat peelable pressure-sensitive adhesive sheet."

Devens, Jr., D.A., U.S. Patent 7,163,523 (January 16, 2007), to Scimed Life Systems Inc., "Baloon catheter."

Wang, L., and Chen, J., U.S. Patent 7,163,522 (January 16, 2007), to Scimed Life Systems Inc., "Block copolymer elastomer catheter balloons."

Hayashi, J., et al., U.S. Patent 7,160,940 (January 9, 2007), to Bridgestone Sports Co. Ltd., "Multipiece solid golf ball."

Lee, J., U.S. Patent 7,160,508 (January 9, 2007), to Gilette Co., "Personal care products having elastomeric portions."

Chen, J.Y., U.S. Patent 7,159,259 (January 9, 2007), to Applied Elastomerics Inc., "Gelatinous elastomer compositions and articles."

Kennedy III, T.J., and Binette, M., U.S. Patent 7,156,755 (January 2, 2007), to Callaway Golf Company, "Golf ball with thermoplastic material."

Moeller, T., et al., U.S. Patent 7,156,944 (January 2, 2007), to Hemkel Kommanditgesellschaft auf Aktien, "Fusible adhesives crosslinkable by radiation."

Park, E.H., and Walker, F.J., U.S. Patent 7,151,134 (December 19, 2006), to Freudenberg-NOK General Partnership, "Dynamic vulcanization of polyurethane elastomer in the presence of thermoplastics."

Hoerner, P., and Sidey, T., U.S. Patent 7,148,283 (December 12, 2006), to Hutchinson, "Thermoplastic elastomer thin-walled film, method for preparing same as uses thereof."

Kirstin, C., U.S. Patent 7,147,742 (December 12, 2006), to Henkel Kommanditgesellschaft (Henkel KGAA), "Method of accelerating the curing of adhesives."

Nakabayashi, H., et al., U.S. Patent 7,144,961 (December 5, 2006), to Kaneka Corporation, "Thermoplastic elastomer composition."

Court, F., et al., U.S. Patent 7,144,952 (December 5, 2006), to Arkema France, "Compositions based on semicrystalline thermoplastic resins and block copolymers, resulting materials and methods obtaining same."

Shin, G., U.S. Patent 7,144,623 (December 5, 2006), to Mitsubishi Chemical Corporation, "Thermoplastic elastomer composition and sheet and laminate."

Yamamoto, S., and Takayanagi, K., U.S. Patent 7,141,300 (November 28, 2006), to Nitto Denko, "Adhesive sheet for dicing."

Saito, H., U.S. Patent 7,138,447 (November 21, 2006), to Kuraray Co. Ltd., "Thermoplastic polymer composition."

Chen, J.Y., U.S. Patent 7,134,929 (November 14, 2006), to Applied Elastomerics Inc., "Tear resistant gels, and diving apparel articles."

Chen, J.Y., U.S. Patent 7,134,236 (November 14, 2006), to Applied Elastomerics Inc.,"Gelatinous elastomer compositions and articles for use as fishing bait."

Datta, S., et al., U.S. Patent 7,132,478 (November 7, 2006), to ExxonMobil Chemical Patents Inc., "Elastic blends comprising crystalline polymers of propylene."

Kanenari, D., and Yamakawa, K., U.S. Patent 7,117,911 (October 10, 2006), to Yokohama Rubber Co. Ltd., "Pneumatic tire having run flat capability."

Glossary

A

Abrasion Resistance—Wear rate or abrasion rate is an important property of materials during motion in contact with other materials. Abrasion or wear resistance is measured by a number of methods such as ASTM D3389, also known as the *Taber Abrasion Test*.

ACM—Acrylate rubber consists of the basic monomer (rubber base) containing different acrylate esters, which influence the physical properties of the compound and of a curing monomer needed for cross-linking. Current commercial products include *ethyl acrylate rubber* that has a good resistance to heat and mineral oils, and *butyl acrylate rubber* that has a better low-temperature flexibility.

Adhesive—A material, usually polymeric, capable of forming permanent or temporary surface bonds with another material as-is or after processing such as curing. The main classes of adhesives include hot melt, pressure sensitive contact, UV cured, EB cured, emulsion, etc.

Adherend—A part to be covered by an adhesive and then joined into an adhesive joint.

Adhesive Bonding—A method of joining two plastic or other materials in which adhesive is applied to the surfaces of the parts to be joined. Bonding occurs through mechanical or chemical interfacial forces between the adhesive and adherend and/or by molecular interlocking. Surface preparation of the adherends and curing of the adhesive may be required.

Adhesive Bond Strength—The strength of a bond formed by joining of two materials using an adhesive. Bond strength may be measured by peeling or shearing the two adherends using extensiometry.

Adhesive Failure—Failure of an adhesive bond at the adhesive–adherend interface. An example is a failure that leaves adhesive all on one adherend, with none of the other adherend. Adhesive failure is less desirable than cohesive failure because it is indicative of joint with lower adhesive strength. See also ***Cohesive Failure***.

Amorphous Phase—See ***Amorphous Polymer*** and ***Semi-crystalline Polymer***.

Amorphous Polymer—A polymer having a noncrystalline or amorphous supramolecular structure or morphology. Amorphous polymers may have some molecular order but usually are substantially less ordered than crystalline polymers and subsequently have inferior mechanical properties.

Annealing—A process in which a material, such as plastic, metal, or glass is heated and then cooled slowly. In plastics and metals, it is used to reduce stresses formed during fabrication.

ASTM International—is an international voluntary standards organization that develops and produces technical standards for materials, products, systems, and services; developed from the original ASTM (acronym for American Society for Testing and Materials).

ASTM D471—Standard Test Method for Property-Effect of Liquids; commonly used test for swelling of elastomeric materials in oils, fuels etc.

ASTM Oil No. 2—See ***IRM 902.***

ASTM Oil No. 3—See ***IRM 903.***

Attractive Intermolecular Forces—See ***van der Waals forces.***

B

Bar—A metric (SI) unit of pressure, equal to 1.0×10^6 dynes/cm^2 or 1.0×10^5 pascals (Pa). It has a dimension of unit of force per unit of area and is used to denote the pressure of gasses, vapors, and liquids.

Biaxial Orientation—Orientation in which the material is drawn in two directions, usually perpendicular to one another. Commonly used in films and sheets.

C

Calender—This is equipment used to form a thermoplastic material into a film or sheet. The equipment consists of two or more steel (often heated) rolls with adjustable gap between them.

Carbon Black—A black colloidal carbon particles produced by partial combustion and/or thermal cracking of natural gas, oil, or another hydrocarbon. Depending on the starting material and the method of manufacture, carbon black can be called acetylene black, channel black, furnace black, etc. The properties and uses of each carbon black type can also vary. Carbon black is used mainly as reinforcing agent of elastomers, as a black pigment in rubber and plastics, and also as an additive increasing UV resistance of polyolefins and other polymers. Special conductive carbon blacks are used to introduce electrical conductivity to polymeric compositions.

Cast Film—Film produced by pouring or spreading resin dispersion, resin solution, or melt over a suitable temporary substrate (carrier), followed by curing via solvent or water evaporation or melt cooling, and removing of the film from the substrate.

Coalescence—Refers to a mechanism of consolidation of polymer particles in solvents, aqueous dispersions into a coherent system. After the polymer melts, adjacent particles begin to combine (i.e., coalesce) to form a film.

Coefficient of Thermal Expansion—The change in unit of length or volume that occurs due to a unit change in temperature. The expansion and contraction of a material with temperature depends on its coefficient of linear expansion (CLTE).

Cohesive Failure—Failure of an adhesive bond that occurs within the adhesive layer, leaving adhesive attached on both adherends. Optimum failure is 100% cohesive failure when both shear areas are completely covered. See also ***Adhesive Failure.***

Cold Flow—See ***Creep.***

Conduction—In heat transfer, migration of energy due to a temperature gradient. Heat is transferred by the movement of molecules at hotter or colder temperatures, with different degrees of thermal motion, into colder or hotter regions, respectively.

Contact Adhesive—An adhesive that will adhere to itself on contact. When applied to both adherends, it forms a bond without sustained pressure on the adherends. See also ***Pressure Sensitive Adhesive.***

Contact Angle—The angle a droplet or edge of a liquid forms with the solid plane of a substrate. A contact angle of zero degree indicates complete wetting, larger contact angle values represent limited wetting.

Convection—The mass movement of particles arising from the movement of a streaming fluid due to difference in a physical property such as density, temperature, etc. Mass movement due to a temperature difference results in heat transfer, as in the upward movement of a warm air current.

COPA—Polyamide thermoplastic elastomers with polyamide hard segments and soft segments based on aliphatic polyesters, aliphatic polyesters, or aliphatic polycarbonates.

COPE—Copolyether-ester block thermoplastic elastomers with ester hard segments and ether soft segments.

Copolymer—See ***Copolymerization.***

Copolymerization—A polymerization where more than one monomer takes part in the reaction and forms the polymer chain. The result is a *copolymer*.

Corona Treatment—A process commonly used in non-polar polymers (e.g., polyethylene) to increase wettability and surface reactivity. The result is an increased affinity to inks, adhesives, and coatings. Plastic films and sheets are passed over a grounded metal cylinder with a pointed high-voltage electrode above it to produce an electrostatic discharge. The discharge oxidizes the surface of the film, making it more receptive to finishing.

Covalent Bond—A bond formed by the sharing of two or more electrons between two atoms. Covalent bonds can be single (two electrons shared), double (four shared electrons), or triple (six shared electrons).

Creep—Nonrecoverable deformation in a part subjected to a continuous load. Creep is dependent on temperature, and on the duration and the amount of the load.

Critical Shear Rate—Thermoplastic materials must be processed below the velocity, at which the *melt fracture* occurs. The shear rate at that velocity is referred to as the *critical shear rate*.

Cross-linking—Reaction resulting in the formation of covalent bonds between chain-like polymer molecules. As a result of cross-linking, polymers such as thermosetting resins become hard and infusible. Thermosetting (conventional) elastomers become stronger and more elastic and cannot be dissolved.

When immersed into solvents, they only swell. Besides this, so-called chemical cross-linking, physical cross-linking results from glassy or crystalline domains attached to elastomeric domains as is the case with most thermoplastic elastomers. Unlike chemical cross-links, physical cross-links are reversible, that is, can be removed by heating above corresponding melting temperature and restored by cooling below it.

Crystalline Melting Point—The temperature of melting of the crystalline phase of a semi-crystalline polymer. It is higher than the melting of the surrounding amorphous phase.

Crystalline Phase—It is an organized structural arrangement of polymeric molecules. In this arrangement, polymer chains are aligned into a closely packed ordered state called *crystalline phase*.

Crystallization Temperature—Temperature, or temperature range at which a polymer crystallizes. The polymer chains, which were randomly distributed in the melt become aligned into a close packed ordered arrangement during the crystallization process.

Crystallinity—Crystalline content of the polymer expressed in weight percent. See also ***Crystalline Phase.***

D

Deflection Temperature under Load—See ***Heat Deflection Temperature.***

Deformation under Load—See ***Creep.***

Degradation—Loss of or undesirable change in polymer properties as a result of aging, chemical reactions, wear, use, exposure, etc. The properties include color, size, strength, etc.

Density—The mass of any substance (gas, liquid or solid) per unit volume at specified temperature and pressure.

Die Land—The part of the extrusion die (orifice) that is downstream from the convergent section where both cross-sectional area and shape are constant.

Dielectric Breakdown Strength or Voltage—The voltage (minimum) required to breakdown through the thickness of a dielectric insulation material (i.e., create a puncture). ASTM D149 is used to measure dielectric breakdown strength of plastic insulation material.

Dielectric Constant—The dielectric constant of an insulation material is the ratio of the capacitance of a capacitor insulated with that material to the capacitance of the same capacitor insulated with a vacuum.

Dielectric Dissipation Factor—The ratio of the power dissipated in a dielectric to the product of the effective voltage and the current; or the tangent of the dielectric loss angle; or the cotangent of the dielectric phase angle. Also called *tan delta* or *dissipation factor*.

Differential Scanning Calorimetry—Differential scanning calorimetry (DSC) is a technique in which the energy absorbed or produced is measured by monitoring the difference in energy output into the substance and a reference material as a function of temperature. Absorption of energy produces an endotherm; production of energy produces an exotherm. The method is used for processes involving energy change, such as melting, crystallization, resin curing, and loss of solvents, or for processes involving a change in heat capacity, such as the glass transition.

DSC—See ***Differential Scanning Calorimetry.***

Durometer Hardness—Indentation hardness of a material as determined by either the depth of an indentation made by an indentor under specified load or the indentor load required to produce a specified indentation depth. The tool used to measure indentation hardness of polymeric materials is called a *durometer* (e.g., *Shore Durometer*).

E

Elasticity—Property whereby a solid material changes its shape and size under action of opposing forces but recovers its original configuration when the forces are removed.

Electron Beam Radiation—Ionizing radiation propagated by electrons accelerated by very high voltage (typically kilovolts to megavolts). This radiation is used frequently for cross-linking, modification, or degradation of polymeric materials.

Elongation at Break—The increase in distance between two gauge marks, resulting from stressing the specimen in tension, at the exact point of break.

Measurement taken at the exact point of break according to ASTM D638.

F

Fatigue—Process of progressive localized permanent structural change occurring in a material subjected to conditions that produce fluctuating stresses and strains at some point or points and that may culminate in cracks or complete fracture after a sufficient number of fluctuations, according to ASTM E1150.

Fatigue Life—Number of loading–unloading cycles of a specified type of material that can endure before failing in a fatigue test.

Fatigue Strength—The limiting value of the median fatigue strength as the number of loading cycles sustained before failure becomes very large. Fatigue strength, here is the maximum stress that can be sustained without failure at this number of loading cycles.

Filament—A filament is a small individual strand that is melt extruded during fiber spinning. Bundles of filaments are called fiber or yarn.

Film—A product, for example, plastic that is extremely thin compared to its width and length. There are supported and unsupported films such as coatings and packagings, respectively.

Flexural Modulus of Elasticity—The ratio, within the elastic limit of the applied stress on a test specimen in flexure to the corresponding strain of the outermost fibers of the specimen.

Free Radical—An atom or group of atoms with an odd or unpaired electron. Free radicals are highly reactive and participate in free radical chain reactions such as free radical polymerization, combustion, and polymer oxidation. Scission of a covalent bond by thermal degradation or radiation can produce a free radical.

G

Gamma Radiation—Ionizing radiation propagated by high-energy protons, that is, emitted by nucleus in transition between two energy levels.

Gamma Ray Irradiation—A technique for crosslinking or reduction of molecular weight of polymers by exposing them to a source of gamma rays such as ^{60}Co.

Graft Copolymer—A chain of one type of polymer to which side chains are attached or grafted. Such copolymers are generally formed by generating active sites on one polymer A in presence of a monomer B. The monomer B is then polymerized to form side chains (see ***Grafting***).

Grafting—A process to attached side chains to chain of a polymer or copolymer. First active sites are generated chemically or by ionizing radiation. During the grafting process a monomer can react with the active site and form side chains by polymerization. Other methods, such as transfer or activation grafting are often accomplished by the use of ionizing radiation.

Graphite—A crystalline form of carbon. It occurs in nature but can also be produced by heating petroleum coke, carbon black, and organic materials. Used mainly as lubricating filler or as additive introducing electrical conductivity.

Gravure Coating—A coating technique using engraved rolls capable of picking up a precise amount of coating (dispersion or ink) from a trough and transferring it to a web that is in contact with the roll. The engravings on the surface act as small reservoirs for the coating.

H

Heat Deflection Temperature—The temperature at which a material specimen (standard bar) is deflected by a certain degree under specified load. Also called *Heat Distortion Temperature (HDT).*

Hot Melt Adhesive—An adhesive that is applied in a molten state, which forms a bond after cooling to a solid state unlike other adhesives that achieve bond strength through evaporation of solvent or through a chemical reaction.

Hysteresis—Incomplete recovery of strain during unloading cycle due to energy consumption. This energy is converted from mechanical to frictional energy (heat).

Hysteresis Loop—In dynamic mechanical measurement, the closed curve representing successive stress-strain status of the material during cyclic deformation; it is the cyclic non-coincidence of the elastic curves. The area of the resulting loop is equal to the heat that is generated in the system.

I

Impact Strength—The energy required to break a specimen, equal to the difference between the energy in the striking member of the impact apparatus at the instant of impact with the specimen and the energy remaining after complete fracture of the specimen.

Injection Molding—A molding procedure in which heat-softened plastic material (melt) is forced from a cylinder into a cavity, which gives the article the desired shape. It is used for thermoplastics and for some thermosets.

Ionomeric Elastomers—Ionomeric elastomers have essentially acidic groups polymerized into the backbone chain and these are neutralized by metallic counterions (e.g., by sodium or zinc). The counterions associate together to form *ionic clusters* that can behave like the hard domains in block copolymers thus forming physically cross-linked network. Examples of the backbone chains are ethylene-methacrylic acid copolymer and ethylene-acrylic acid copolymer.

Ionizing Radiation—Any electromagnetic or particulate radiation, which in its passage through matter is capable of producing ions directly or indirectly. Examples are electron beam and gamma radiation.

IRM 902—Industry Reference Material—replacement for ASTM Oil No. 2, but not exact equivalent; used for immersion tests (according to ASTM D471).

IRM 903—Industry Reference Material—replacement for ASTM Oil No. 3, but not exact equivalent; used for immersion tests (according to ASTM D471).

L

Lap Joint—A joint, in which one adherend is placed partly over the other adherend; overlapped areas are bonded together.

Laser—A device used to produce an intense light beam with a narrow band width. Laser is an acronym for *light amplification by stimulated emission of radiation*.

Lewis Base—A substance that donates a pair of electrons in a chemical reaction to form a bond with another substance.

Limiting Oxygen Index (LOI)—LOI is defined as the required minimum percentage of oxygen in a mixture with nitrogen, which allows a flame to be sustained by an organic material such as a plastic.

M

Matched Die Forming—A type of thermoforming process consisting of preheating the plastic sheet prior to forming and then subjecting it to simultaneous motion of two mold halves.

Melting Point—The temperature at which the solid crystalline and liquid phases of a substance are in thermodynamic equilibrium. The melting point is usually referred to normal pressure of 1 atm.

Melt Processible Polymer—A polymer that melts when heated to its melting point and forms a molten material with definite viscosity value at or somewhat above its melting temperature. Such a melt can be pumped and should flow when subjected to shear rate using commercial processing equipment such as extruders and molding machines.

Micron—A unit of length equal to 1×10^{-6} m. Its symbol is Greek small letter mu (μ).

MPR—Melt-processible rubber; described as alloys of proprietary ethylene interpolymers and chlorinated polyolefins in which the ethylene polymer component has been partially cross-linked *in situ*. These comprise of blends of molecularly miscible polymers having a single glass transition temperature (T_g).

N

Nanometer—A unit of length equal to 1×10^{-9} m. Often used to denote the wavelength of radiation especially UV and visible spectral region. Its symbol is nm.

Newtonian Fluid—A term to describe an ideal fluid in which shear stress is proportional to shear rate. The proportionality coefficient is called viscosity, which is independent of shear rate, in contrast to nonideal fluids where viscosity is a function of shear rate. Paints and polymer melts are non-Newtonian fluids.

O

Offset Printing—A printing process in which the image to be printed is first applied to an intermediate carrier such as roll or plate, then is transferred to the surface of a substrate such as paper or plastic.

Olefins—The group of unsaturated hydrocarbons of the general formula C_nH_{2n}., and named after the corresponding parafins by the addition of "ene" "ylene" to the stem. Examples are ethylene, propylene, or butenes. Polymers of olefins are polyolefins.

Orientation—A process of drawing or stretching of thermoplastic films or as-spun synthetic fibers to orient polymer molecules in the direction of stretching. The fibers are drawn uniaxially, whereas films may be drawn in one direction (uniaxially, either longitudinally or transversely) or two directions (biaxially). Oriented films and fibers have enhanced properties in the direction of stretching. The film will shrink in the direction of stretching, when reheated in the direction of stretching.

Ozone—A molecule consisting of three atoms of oxygen, that is, O_3.

P

Paraffins—Linear saturated hydrocarbons with the general formula C_nH_{2n+2}.

Parison—Parison is a tube used for blow molding, which in principle at least has a constant wall thickness at all points around its circumference and along its length. Thickness along the parison may vary due to tensile thinning caused by its own weight.

Pascal—An SI unit of measurement of pressure equal to the pressure resulting from a force of one Newton over an area of one square meter. Used to denote the pressure of gases, vapors, or liquids and the strength of solids. The symbol is Pa.

Peel Strength—The strength of an adhesive bond between two flexible substrates or between one flexible and one rigid substrate measured by peeling. The resistance of the bond to separation by peeling is measured on an extensiometer.

Pendant Methyl Group—A methyl group (CH_3) attached to the main chain of a polymer molecule.

PEO—Abbreviation for *polyethylene oxide*. Low molecular weight polymers of ethylene oxide are viscous liquids or waxes. Those of high molecular weight are tough, crystalline ductile thermoplastics. All PEO resins are soluble in water.

Permeability—The capacity of a material to allow another substance to pass through it; or the quantity of a specific gas or other substance, which passes through under specific conditions.

Poisson's Ratio—This ratio is defined as the ratio of the change in the width of a material to the change in its length per unit length, as a result of strain in the length direction. It is designated by the Greek letter ν. Poisson's ratio values always fall within the range 0–0.5. The value for rubber is 0.5.

Polar Molecule—A molecule, in which the positive and negative electrical charges are permanently separated. Polar molecules ionize in solution and impart electrical conductivity to the solution. Water, alcohol, and sulfuric acid are examples of polar molecules; hydroxyl and carboxyl are polar functional groups.

Polyethylene (PE)—A family of polyolefins consisting of linear and branched polyethylenes. Polyethylenes are thermoplastic but can be readily cross-linked by irradiation or chemically.

Polyolefins—Polyolefins are a large class of carbon-chain elastomeric and thermoplastic polymers usually prepared by addition polymerization or copolymerization of olefins or alkenes such as ethylene. The most important representatives of this group are polyethylene and polypropylene.

Polypropylene (PP)—Polypropylene is a carbon-chain thermoplastic comprised of polypropylene homopolymer prepared either by stereospecific polymerization using Ziegler-Natta catalysts or by the polymerization using metallocene catalysts.

Polytetrafluoroethylene (PTFE)—Thermoplastic prepared by free-radical polymerization of tetrafluoroethylene. It has a superior chemical resistance, very high thermal stability, very high weather resistance, low friction coefficient, low flammability, very good release properties, and a low dielectric constant. On the other hand, it has a low creep resistance, relatively low strength, and high permeability. Because of its high melt viscosity, PTFE can be processed either by sinter molding, powder coating, and coating from aqueous dispersions.

Polyvinyl Chloride (PVC)—PVC is a thermoplastic prepared by free-radical polymerization of vinyl chloride in dispersion (emulsion), bulk, or suspension process. Unmodified PVC is very rigid and requires plasticizers to make it more flexible. The main end forms are rigid PVC and flexible PVC. The flexible form is often made from plastisols, suspensions of PVC in plasticizers. Flexible form is also obtained when PVC is blended with nitrile rubber (NBR).

Polyvinylidene Fluoride (PVDF)—Thermoplastic prepared by free-radical polymerization of vinylidene fluoride. It has a very high tensile strength, wear and creep resistance, high dielectric constant and dielectric loss factor. PVDF is nonflammable, resists most solvents, and has excellent weather resistance. It exhibits piezoelectricity and pyroelectricity.

Pressure Sensitive Adhesive—An adhesive that requires applied pressure to the parts for the bonding to occur. It is usually composed from an elastomer and modifying tackifiers. Pressure sensitive adhesives are applied as melts or solvent-based or water-based systems. In most cases curing of the adhesive does not usually occur.

Primer—In adhesive bonding a special reactive chemical dispersed in organic solvent or water is applied to the substrate prior to the application of an adhesive or a coating. A primer acts as a chemical bridge between the substrate and the adhesive or coating. Examples of primers are organ-silanes and isocyanates.

R

Radiation Dose—Amount of ionizing radiation energy absorbed by a material during irradiation. The unit of radiation is a gray (Gy) defined as 1 joule per kilogram (J/kg). In practical application a larger unit, namely kGy (10^3 Gy) is used. Previously used unit, no longer official since 1986, is megarad (Mrad), equal to 10 kGy. See ***Ionizing Radiation***.

Reference Fuel A—100% isooctane; used frequently for immersion tests (according to ASTM D471).

Reference Fuel B—70% isooctane, 30% toluene (by volume); used frequently for immersion tests (according to ASTM D471).

Reference Fuel C—50% isooctane, 50% toluene (by volume); used frequently for immersion tests (according to ASTM D471).

Reference Fuel D—40% isooctane, 60% toluene (by volume); used frequently for immersion tests (according to ASTM D471).

Rheology—A science that studies and characterizes flow of polymers, resins, gums, and other materials.

S

SBC—Styrenic block copolymer, general.

S-B-S—Styrene-butadiene-styrene block copolymer, a triblock copolymer with polystyrene hard segments and polybutadiene soft midblock.

S-EB-S—Styrene–(ethylene- butylene)–styrene block copolymer, a triblock copolymer with polystyrene hard segments and poly(ethylene-butylene) soft midblock. S-EB-S is prepared by hydrogenation of S-B-S.

Semi-Crystalline Polymer—A polymeric material characterized by localized regions of crystallinity. See also ***Amorphous Polymer***.

S–EEP–S—Triblock styrenic copolymer with (ethylene-ethylene/propylene) elastomeric midblock; frequently used as compatibilizer.

S–EP–S—Styrene–(ethylene-propylene)–styrene block copolymer, a triblock copolymer with polystyrene hard segments and poly(ethylene-propylene) soft midblock. S–EP–S is prepared by hydrogenation of S–I–S.

Shear—Displacement of a plane of solid body parallel to itself, relative to other parallel planes within the body; deformation resulting from this displacement.

Shelf Life—Time during which a physical system such as material (solid compound, adhesive, coating, etc.) retains its properties during a long-term storage under specified conditions.

Shore Hardness—Indentation hardness of a material as determined by the depth of an indenter of the Shore-type Durometer. The scale reading on this Durometer is from 0, corresponding to 0.100 in. (2.5 mm) depth to 100 for zero depth. The Shore A indenter has a sharp point, is spring-loaded to 822 gf, and is used for softer plastics and rubber. The Shore D indenter has a blunt point, is spring-loaded to 10 lbf (4,540 gf), and is used for harder plastics.

S–iB–S—Styrene–isobutylene–styrene block copolymer, a triblock copolymer with polystyrene hard segments and polyisobutylene soft midblock. Prepared by carbocationic polymerization.

S–IB–S—Styrene–isoprene/butadiene–styrene block copolymer with polystyrene hard segments and a hybrid isoprene/butadiene soft midblock with controlled distribution of monomeric units.

S–I–S—Styrene–isoprene–styrene block copolymer, a triblock copolymer with polystyrene hard segments and polyisoprene soft midblock.

Softening Point—Temperature at which a material changes from rigid to soft or exhibits a sudden and substantial decrease in hardness.

Solubility—The solubility of a substance is the maximum concentration of the material in a binary mixture at a given temperature forming a homogeneous solution.

Solubility Parameter—Solubility parameter characterizes the capacity of a substance to be dissolved in another substance, for example, of a polymer in a solvent. It represents the cohesive energy of molecules in a substance and determines the magnitude and the sign of the heat of mixing two substances in given concentrations. The magnitude and the sign of the heat of mixing determine the sign of the free energy of mixing. The solution occurs when the sign of the free energy of mixing is negative. The symbol used is δ.

Spherulite—In polymers, a rounded aggregate of radiating lamellar crystals with amorphous materials between the crystals. It has the appearance of a pom-pom. Spherulites exist in most semi-crystalline polymers and usually impinge on one another to form polyhedrons. They range in size from a few tenths of a micron in diameter to several millimeters.

Star Block (Radial) Copolymers—Block copolymers consisting of a core and three or more arms emanating from the core.

Strain—The per unit change, due to force, in the size or shape of a body as referred to its original size or shape. *Note*: Strain is nondimensional but is often expressed in unit of length or percent.

Stress Relaxation—Time-dependent decrease in stress in a solid material as a result of changes in internal or external conditions.

Surface Tension—The surface tension is the cohesive force at a liquid surface measured as a force per unit length along the surface or the work, which must be done to extend the area of a surface by a unit area, for example, by a square centimeter. Also referred to as *free surface energy*.

T

Taber Abrasion Resistance—The weight loss of a plastic or other material specimen after it was subjected to abrasion in the Taber Abraser for a prescribed number of specimen disk rotations, usually 1,000. A Taber Abraser consists of an idling abrasive wheel, designated depending on the type and grit of abrasive used as CS-10F, H 22, etc. and a rotary disk with the specimen mounted on it. The load is applied to the wheel. The produced motion simulates that of rolling with slip.

Tensile Strength—The maximum tensile stress that a specimen can sustain in a test carried to failure. Measured according to ASTM D638.

Tensile Strength at Yield—The maximum load per original minimum cross-sectional area of the plastic specimen in tension within the gauge length, when the maximum load corresponds to the yield point. Measured according to ASTM D638.

Tensile Stress—The force related to the smallest original cross-section of the specimen at any time of the test.

Thixotropic Liquid—This liquid exhibits lower viscosity as shear rate increases. A practical example is house paint, which appears thinner when stirred.

TPE—Thermoplastic elastomer, consisting of a polymer or blend of polymers that has properties at its service temperature similar to those of vulcanized rubber but can be processed and reprocessed at elevated temperature like a thermoplastic.

TPO—Polyolefin-based thermoplastic elastomers, blends of isotactic polypropylene and ethylene-propylene copolymers.

TPU—Thermoplastic elastomers based on polyurethanes, prepared from long-chain diols, short-chain diols chain extenders and isocyanates. There are essentially random block copolymers with crystalline hard segments and soft flexible polyester or polyether segments.

TPSiV—Thermoplastic elastomer based on dynamically vulcanized silicone elastomer and polyamide or other thermoplastic matrix polymer.

TPV—Thermoplastic elastomers based on dynamically vulcanized elastomer-plastic blends, such as EPDM elastomer and polypropylene or acrylic rubber and polyamide.

U

Ultraviolet (UV) Radiation—Electromagnetic radiation in the 40–400 nm wavelength region. Sun is the main natural source of UV radiation on the Earth. Artificial sources are many, including special UV lamps of different designs. Ultraviolet radiation causes polymer degradation and other chemical reactions, including polymerization and crosslinking of monomeric and oligomeric systems.

V

van der Waals Forces—Weak attractive forces between molecules, weaker than hydrogen bonds and much weaker than covalent bonds.

Viscosity—The internal resistance to flow exhibited by a fluid, the ratio of shear stress to shear rate. A viscosity of one Poise is equal to a force of one dyne/square cm that causes two parallel liquid surfaces one square cm in area and one cm apart to move past one another at a velocity of one cm/s. The SI unit of viscosity is Pa.s (Pascal second).

W

Wetting—The spreading out (and sometimes absorption) of a fluid onto (or into) a surface. In adhesive bonding, wetting occurs when the surface tension of the liquid adhesive is lower than the critical surface tension of the substrates being bonded. Good surface wetting is essential for high strength adhesive bonds; poor wetting is evident when the liquid beads up on the part surface. Wetting can be increased by preparation of the part surface prior to adhesive bonding.

Y

Yield Deformation—The strain at which the elastic behavior begins, while the plastic is being strained. Deformation beyond the yield deformation is not reversible.

Young's Modulus—In the elastic region, the relationship between stress and strain of a polymer, undergoing tensile or compressional strain is linear (i.e., follows Hooke's law). In this relation the stress is proportional to strain. Young's modulus is the coefficient of proportionality in this stress–strain relationship.

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