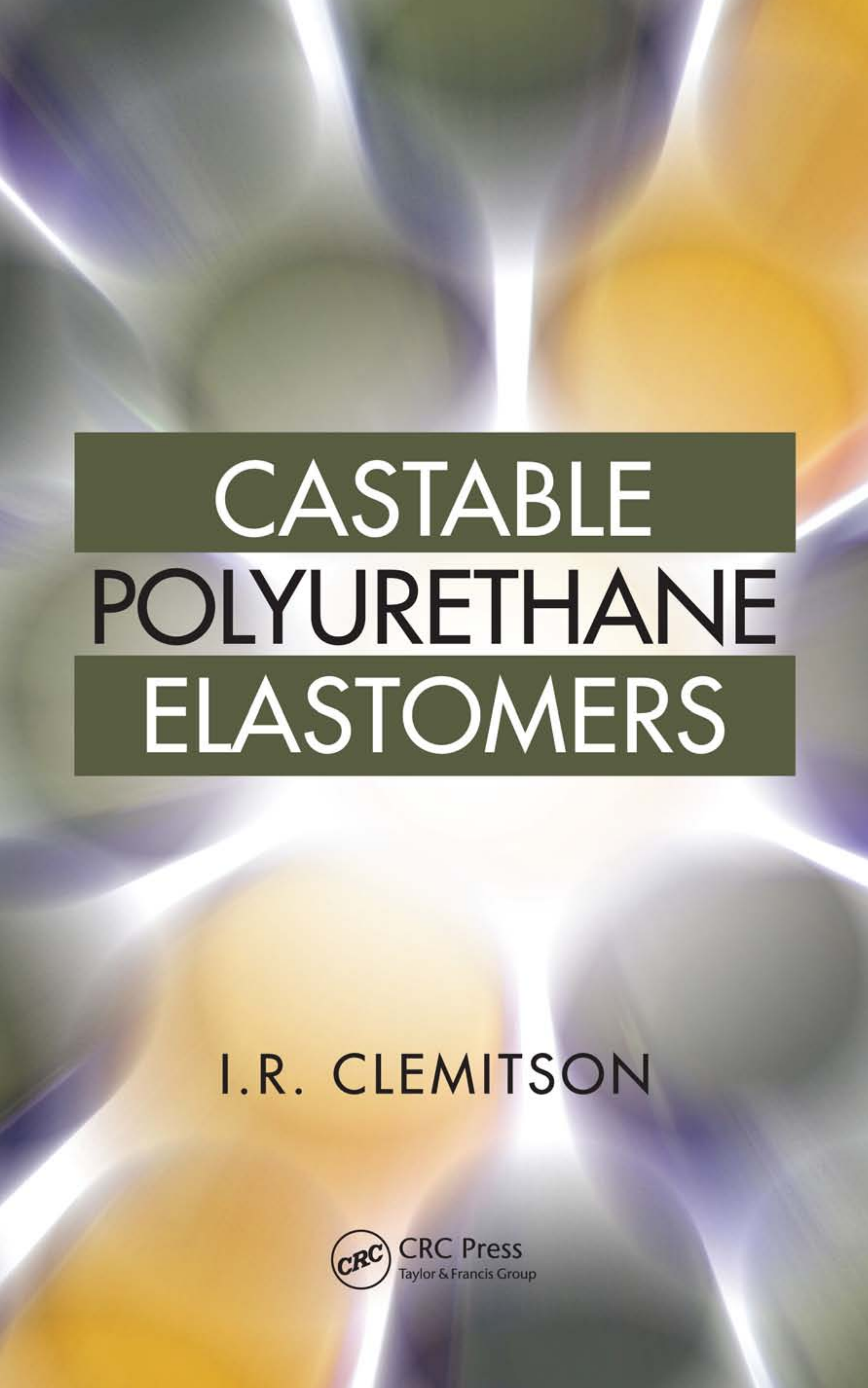

CASTABLE POLYURETHANE ELASTOMERS

I.R. CLEMITSON

CRC Press
Taylor & Francis Group

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IAN CLEMITSON

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Preface

Castable Polyurethane Elastomers is a practical guide to the production of castable polyurethane articles. These articles can be as simple as a doorstop to items used in nuclear and military industries. The book shows the progression from the raw materials needed to produce prepolymers to the production of prepolymers. This will include both the chemistry and the practical side of the production processes.

- The production of polyurethane components is explained from both theoretical and practical aspects, covering the different types of systems available and the reasons for choosing the right system, both on the micro and macro levels. Curing and post-curing operations are also covered.
- The traditionally quoted properties, for example, tensile strength and hardness, are often not the best for selecting the correct system to use. In the section on properties, the importance of using the correct property for the application is explained. The application of polyurethanes in various fields is expanded upon and logic for suitability is discussed. The effect of changes to the original application details is dealt with.
- As the world is not a perfect place, there are sections on problem solving and possible solutions. Throughout the book there is an emphasis on the health and safety aspects that should be observed at all times.
- The book is aimed at people entering the polyurethane world and those who work with it.

The Author

Ian Clemitson has worked in the chemical industry for all his working life. For many of these years he was involved with rubber and polyurethane production and developmental work. In 1999 he earned a master's degree from the University of Technology in Sydney, Australia. His thesis was titled "The Influence of Polyurethane Chemistry on Erosive Wear." During this time he was working at the R&D laboratory of Warman International in Sydney, doing research into polyurethanes and other elastomers. His final employment was with Chemind in Brisbane, Australia, where he worked setting up the manufacture of polyurethane elastomers. During this time he carried out more research (with a government grant) into wear-resistant polyurethanes. On a part-time basis, until his retirement, he lectured at the local Plastics Training Institute (PARTEC Brisbane) on polyurethane and rubber technology.

1

Introduction

1.1 What Are Polyurethanes?

Polyurethanes are part of a very versatile group of materials that find uses in a wide range of applications, both domestic and industrial. Polyurethanes are widely used in many applications such as paints and lacquers, foam mattresses, medical implants, and industrial applications such as rollers, electrical encapsulation, engineering components, shoe soles, seals, and in the mining industry.

Polyurethanes are organic polymers that contain the urethane group in the structure. They are typically made by the reaction of a polyol with a diisocyanate. Depending on initial reaction, the final product may require the addition of additives such as chain extenders, catalysts, and blowing agents. By careful arrangement of the chemistry, the entire process can be carried out in one step. Polyureas are similar in reaction to polyurethanes. They are made from polyamides and not polyols. They contain urea groups in place of urethane groups. Figure 1.1 illustrates the differences of the urethane and urea groups.

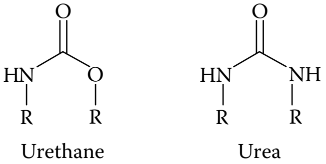


FIGURE 1.1

There are three main groups of engineering materials. These are:

- Ceramics
- Metals
    - Ferrous or iron based
    - Nonferrous

- Polymers
  - Organic (contain carbon)
  - Silicone

Polyurethanes are a group of organic polymers that are normally grouped with rubbers. Rubbers are often referred to as elastomers. Elastomers means stretchy materials. Elastomers/rubbers may be either thermoplastic or thermoset, depending on the chemistry and processing of the materials.

Some typical elastomers are natural rubber, which is gathered from trees, SBR rubber, which is used a lot in motorcar tires, neoprene, as in wet suits and oil seals, EPDM, a general purpose rubber, butyl, a heat-resistant rubber with the ability to keep the air in car tires, nitrile for oil seals, silicones for heat resistance, fluoro-elastomers for chemical resistance, and last but not least, polyurethanes, which cover a number of the above fields. Table 1.1 shows some of the advantages of castable polyurethanes over conventional rubbers.

TABLE 1.1

Advantages of Polyurethanes over Conventional Rubbers

	Polyurethane	Conventional Elastomers
Processing	Low-to-medium capital costs	High capital costs
Mixing	Bucket and stirrer	Open mill
	Machine optional	Intensive mixing; for example, Banbury
Molds	Lightweight	Heavy duty
	Made from a simple model	
Finishing	Repairs simple	Repairs complex

1.1.1 Discovery of Polyurethanes

Initial commercial developmental work on polyurethanes was carried out in Germany between World War I and World War II to find an alterative to nylon, which had been developed by E. I. du Pont de Nemours & Company. The research was based on urethane chemistry.

Intensive research discovered that there were many modifications that could be made to the chemistry surrounding the urethane linkage. During World War II (1942), William Hanford and Donald Holmes of E. I. du Pont de Nemours & Company developed a process for making and processing castable polyurethanes. The patent, Process for Making Polymeric Products and for Modifying Polymeric Products Polyurethane, #2,284,896, was granted.

1.2 Polyurethane Family

Polyurethanes can be produced in a large variety of different chemistries. Using different compounding techniques, polyurethanes with different final properties can be produced. The major groups are:

- Fibers
- Films
- Castables
- Thermoplastics
- Foams
- Millables

1.2.1 Fibers

The purpose of early work on the development of polyurethanes was to find an alternative to nylon. The early developments by Otto Bayer led to the first patents and to the development of fibers and foams. The most common fibers made from polyurethane are Perlon and Spandex.

1.2.2 Films

Films can be made from polyurethane in three main ways:

- **Two-part sprayable** polyurethanes are used in the production of chemical-resistant paints and coatings. The polyurethanes can be let down in some solvent to ease in the spraying. Polyureas are becoming important in this section of the market because of their very fast cure rates.
- **Single component** systems rely in most cases for the cure to take place by the reaction of moisture in the air with the prepolymer to form a solid polymer. Carbon dioxide gas is given off during this reaction and either escapes into the air or is trapped by fillers in the system. These systems are used to make waterproof barriers and single pack polyurethane paints.
- **Latex**: Fully cured polyurethane is made into latex, and on removal from the suspension medium is formed into a film. This system is used to make thin-walled items such as moisture barriers and adhesives. The environmental pressure for low volatile organic carbons (VOC) has led to a great interest in this field.

1.2.3 Castables Background

In 1952, castable polyurethanes first became commercially available. In 1956, the first polyethers were introduced by DuPont, followed by cheaper polyethers from BASF and Dow the following year. In subsequent years, developments have been made to cure systems and specialized isocyanates to optimize different properties. There are a multitude of different uses for castable polyurethanes, from domestic roller blades to military components.

1.2.4 Thermoplastics

Thermoplastic polyurethanes are designed to be processable by standard plastic machinery such as extruders and injection molding machines. Thermoplastic polyurethanes have been used in biomedical applications. They also can be used in the microcellular form where the apparent density can be reduced. Some applications include tubing, handles, automotive parts, and shoe soles and heels.

1.2.5 Foams

Foamed polyurethane was used during World War II in aircraft. Foams became popular when the low-cost polyether polyols became readily available. Much work has been carried out developing foamed polyurethanes. They have a three-dimensional network with an even cell structure. The cells may be either open or closed, depending on the application.

Polyurethane foams can be made into several distinct styles:

- **Rigid**: Rigid foams are used for both heat and acoustic insulation. They can be hand- or machine-processed or, alternatively, they can be sprayed on. They also can be used for buoyancy. They are used as insulation in walls and ceilings as well as in surfboards to provide the structure for the board. Their uses are varied and are limited by the imagination of the designer.
- **Flexible**: Flexible polyurethanes find many domestic applications such as mattresses, cushions, and carpet padding. This style of foam is normally bulk-processed and needs a large area for the finished product because of its very low density.
- **Integral skinned**: These integral skin urethanes are designed to have an outer layer that is not foamed, with a foamed inner section. This provides a firm feel without the dirt trapping of the cut cells. Typical examples of this style are steering wheels and motor car fascias.

1.2.6 Millable

Millable urethanes are processed on standard rubber-processing machinery. They may be either peroxide or sulfur cured. The sulfur-cured varieties have some chemicals added to enable sulfur curing to take place. These polyurethanes also have the properties of castable polyurethanes but need to be processed on standard rubber machinery.

1.3 Castable Polyurethanes

Castable polyurethanes form a part of the overall polyurethane industry. They are normally prepared by the mixing of two to five ingredients and introduced into a mold. The materials are cured by the application of moderate heat, approximately 100°C, for 6 to 18 hours. The finished parts can be post-machined to obtain the right size and shape.

Polyurethanes are made by extending chains of a prepolymer made from a macro diol and a diisocyanate. The prepolymer is further extended with a diol or an amine curative. The long chains form a solid which is relatively weak. When the part is given a longer heat treatment, the molecules align themselves and intermolecular bonds (hydrogen bonding) are formed. At this point the full mechanical properties are established and the material, if suitably formulated, has excellent mechanical and chemical properties.

Castable polyurethanes can be formulated to contain conventional cross-links, as in rubbers and epoxies. They may be either in the form of the liquid system or in the form that requires conventional rubber-processing equipment. The introduction of conventional cross-links will break the formation of the hydrogen bonds and normally reduce the hardness of the finished product. In very hard grades, they are used to increase the compression resistance.

1.3.1 Advantages of Polyurethanes

Because there is a large variety of different polyurethane materials that are excellent for specific applications, the right polyurethane for the particular application has to be selected. The type of polyurethane that is used has to be chemically stable and easy enough to process without giving large batch-to-batch variations that may cause service life problems. The application conditions may change greatly from those originally specified after several years of use, potentially causing changes to the service life.

1.3.2 Applications

Because there is a large variety of different materials that are excellent for specific applications, the right polyurethane for the particular application has to be selected. The base chemistry used in producing the polyurethane system can have a profound influence on the final properties of the part produced. The mechanical, thermal, and chemical properties of a cured system have to be selected for each application. A typical example is that certain amines cannot be used in applications where there is contact with food.

Domestic Applications

The major applications of polyurethanes in the domestic area are in the noncastable area, for example foam mattresses, cushions, and floor finishings. However, there are several everyday examples of polyurethanes in the domestic situation. Suspension bushes used in off-road vehicles can be made from polyurethanes. Boat trailer rollers, applications in engine mounts, and general finishing of crafts of all sizes are very important uses of polyurethanes in the maritime industry.

Skateboard wheels are often made from polyurethanes. Top-grade wheels are made from a highly resilient grade of polyurethane. Lifts in high-rise building blocks have centering polyurethane-rimmed wheels. Wheels on automatic closing gates can be made from very hard polyurethane. In office equipment, polyurethanes can be found in printers, in parts such as head drives and paper transport rollers.

Polyurethanes play an important role as molds for pavers used in gardening as well as molds for other concrete items with minimal undercuts.

Industrial Applications

Industrial uses of polyurethanes are wide and varied, from small components in machinery to large mining parts.

Polyurethane wheels may be small components in a piece of machinery or a large part of drive wheels on items such as forklifts or rod mills. Speed is the normal limiting factor in the use of polyurethane wheels. This is a result of heat buildup. Special polyurethanes find an application as spare motor car wheels.

Rollers of all shapes and sizes can be made from polyurethanes. They vary from very soft printing rollers to hard rollers used in the steel industry. The casting and trimming of these rollers are very suited to polyurethane manufacturing.

In the mining industry, the excellent wear resistance of polyurethanes provides financial and maintenance advantages to the mines. The mechanical and chemical resistance of the polyurethanes can be used to advantage in many applications. Applications are varied and include pump components, cyclones, conveyor belt idler wheels, belt heads, and scrapers. Specialized pipes and tubes, as well as tank linings, also use polyurethane.

Because of the radiation resistance of polyurethanes, they find use in the nuclear industry. Polyurethanes find an important use in short-run production where parts can be made accurately until more costly molds can be made, without the need for potentially expensive change. Polyurethanes can be used to make molds for casting polyurethane parts. A coat of mold release is required for easy part removal. These molds can be used for short-to-medium production runs. Polyurethane molds can be made from a variety of different materials. Only very low-density wood and high-moisture-containing materials such as plaster of Paris prove to be too difficult to prepare a mold.

2

Chemistry

2.1 Introduction

2.1.1 Background

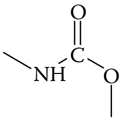
In 1849, Wurtz discovered the formation of aliphatic isocyanates when he reacted organic sulfates with cyanates. This represents the first recorded experimental work leading ultimately to the preparation of urethanes:

$$R_2SO_4 + 2KCNO \rightarrow 2RNCO + 2K_2SO_4$$

The first important commercial development was a result of the work of Professor Otto Bayer in 1937, who discovered how to make a polymer using diisocyanates employing an additional polymerization technique when working on a polymer fiber to compete with nylon. Initially, the development was considered impracticable. In 1938, Rinke and associates succeeded in producing a low-viscosity melt that could be formed into fibers. This led to the production of many different types of polyurethanes.

Polymer chemistry developed a nomenclature (language) different from the classical organic chemistry. The group "-NHCO-" in polymer chemistry is known as nylon, whereas in biochemistry it is known as a peptide, and in pure organic chemistry as an amide group. The urethane group "-NHCOO-" is called a carbamate in organic chemistry.

Polyurethanes are named because of the presence of the urethane linkage, which is illustrated in Figure 2.1. Intensive research discovered that there were many modifications that could be made to the chemistry surrounding the urethane linkage. During the 1940s and early 1950s, DuPont and ICI developed castable polyurethanes.



Urethane linkage

FIGURE 2.1

Wright and Cummins (1969) classified polyurethanes into eight different classifications. These are:

- Linear polyurethanes
- Castable polyurethanes
- Millable polyurethanes
- Thermoplastic polyurethanes
- Cellular polyurethanes
- Sprayable polyurethanes
- Porometric polyurethanes
- Spandex fibers

Of these groups, the castable, thermoplastic, and sprayable polyurethanes have the greatest abrasive and erosive wear resistance.

Within each family, there are various factors that give it particular properties and make it most suitable for various uses. The major factors are the degree of branching or cross-linking. This linking of the chains may either be permanent or hydrogen-bonding. This cross-linking interacts with the chain stiffness and the crystallinity of the polyurethane. Cast polyurethanes have a moderate degree of cross-linking in most cases because of interchain attractions. Rigid foams have high chain stiffness and a high level of branching and cross-linking. Millable polyurethanes, by contrast, have a limited degree of cross-linking and low chain stiffness, even lower than thermoplastic polyurethanes.

The castable and sprayable polyurethanes are commercially the most popular. They are easier to process, and parts can be made with an initially low capital expenditure.

The millable materials have a diene group (-CH=CH-) included in the polymer to allow for cross-linking by sulfur or by peroxides. However, the capital costs to use millable polyurethanes are high because rubber mills, presses, and heavy-duty molds are needed to produce an article.

A variety of polymeric subunits is used to make polyurethanes. These include polyesters and polyethers. The major interchain linkages are molecular forces such as hydrogen bonding and the London force. Depending on the type of chain extender and processing temperature, there also may be biuret or allophanate cross-links.

Polyesters make tough and wear-resistant urethanes. The one major drawback is the hydrolysis at the ester grouping. The hydrolysis can either be acid or alkali promoted. In more neutral conditions, the major breakdown product is normally adipic acid that catalyses further attack. The normal approach is to use carbodiimides to block further breakdown. Polyols made using polypropylene carbonate produce polyurethanes with polyester characteristics but with enhanced hydrolysis resistance.

Polyethers are not as tough as polyester urethanes. They do, however, provide a far greater degree of hydrolysis resistance as a result of the presence of an ether group instead of an ester grouping in the backbone.

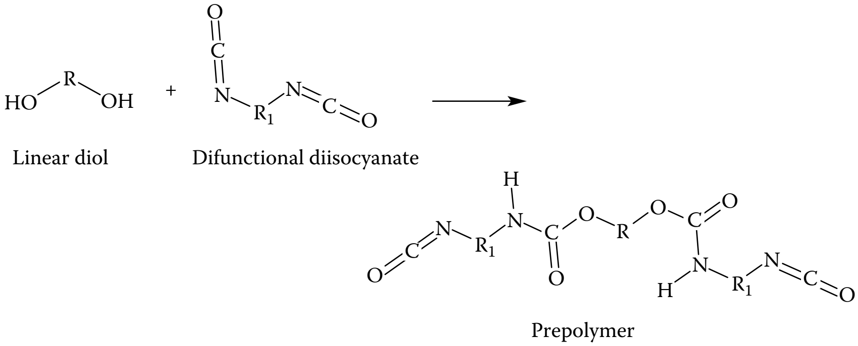


FIGURE 2.2

2.1.2 Basic Reactions of Urethanes

The urethane linkage is the fundamental group in polyurethane chemistry. The initial step in the preparation of a cast prepolymer is to react a suitable linear diol with a difunctional isocyanate, as illustrated in Figure 2.2.

The prepolymer is formed by addition polymerization, and there are no by-products formed that have to be removed. The prepolymer chains extend by the reaction of terminal isocyanate groups (-NCO) with the diol. The mole reaction ratio of the diol to diisocyanate is normally kept in the range of one mole diol to 1.6 to 2.25 moles of the diisocyanate. A reaction ratio of one mole diol to one mole diisocyanate will produce a linear material. This type of polyurethane is normally thermoplastic.

The molecular weight of the prepolymer is too low to form an elastic polymer. The overall molecular weight must be increased by joining prepolymer chains using either diols or diamines.

When the prepolymer chain is extended with a diol, the polymer formed has only urethane linkages. The polymer formed with the diamine chain extender is strictly a polyurethane polyurea. The first urethane component is from the initial chain extension when the prepolymer is prepared. A diamine curative will form urea linkages (Figure 2.3) between chains.

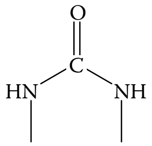


FIGURE 2.3 Urea Linkage

Reactivity of Isocyanate Group

The reactivity of the isocyanate group can be explained by its electronic structure (Wright, 1969). Several different electronic possibilities exist. The major resonance possibility shows that the oxygen will have the greatest electron density and the carbon will have the least. This results in the carbons′ having a net positive charge, the oxygen a negative charge, and nitrogen a slight negative charge. These structures influence the ways in which various active hydrogen compounds react with isocyanates. The attached group may speed up or slow down the reaction rate. The nature of the group attached to the isocyanate also changes the rate of reaction.

Chain Extension with a Diol

When a prepolymer is reacted with a diol, an extended chain is formed, as shown in Figure 2.4.

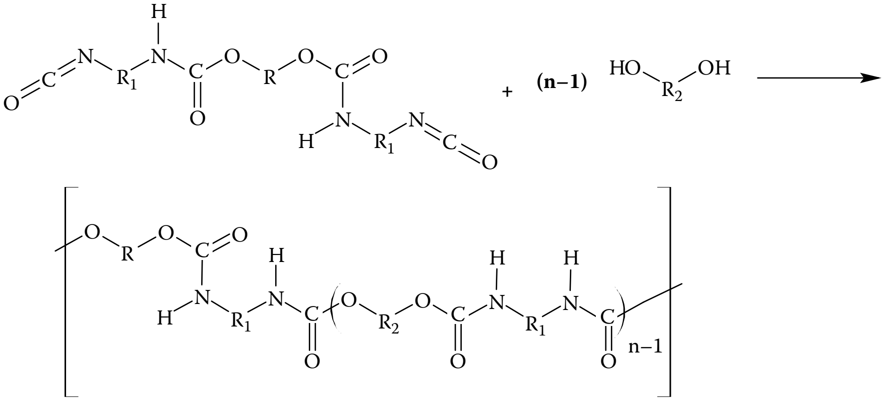


FIGURE 2.4

Chain Extension with a Diamine

If a diamine is used instead of a diol, a similar chain extension occurs with urea instead of urethane bonds. This is shown in Figure 2.5.

Side Reactions

Subsidiary chemical reactions can take place. The major of these is the formation of an allophanate cross-link, as illustrated in Figure 2.6. This reaction normally needs a temperature of between 120 and 140°C to take place. The presence of a urea group at 100°C can react with the isocyanate group to form a biuret linkage. This is shown in Figure 2.7.

Polyureas

If the hydroxyl group (–OH) in a conventional diol is replaced by an amine group (–NH_2), polyamines are formed. The polyamines can be used in a similar manner to polyols to form a polyurea on reaction with diisocyanate. These polymers do not have any urethane groups, only urea groups. Because

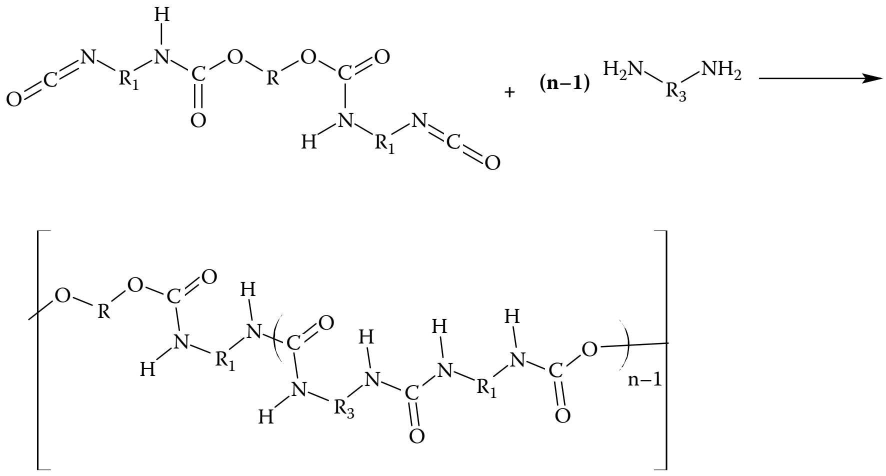


FIGURE 2.5

of their high curing speed, spraying is the best method of application. They are mainly used in thin coatings. Polyureas are used in the mining industry in wear applications. The basic reaction is shown in Figure 2.8. Further chain extension is carried out using diamine curatives such as DETDA or DMDTA. These are diamines used in both the polyurethane and epoxy industries.

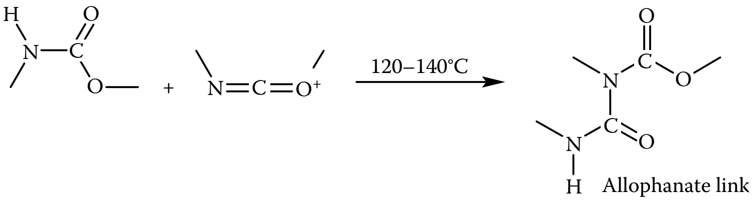


FIGURE 2.6

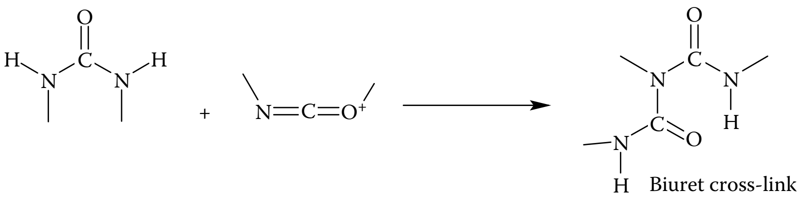


FIGURE 2.7

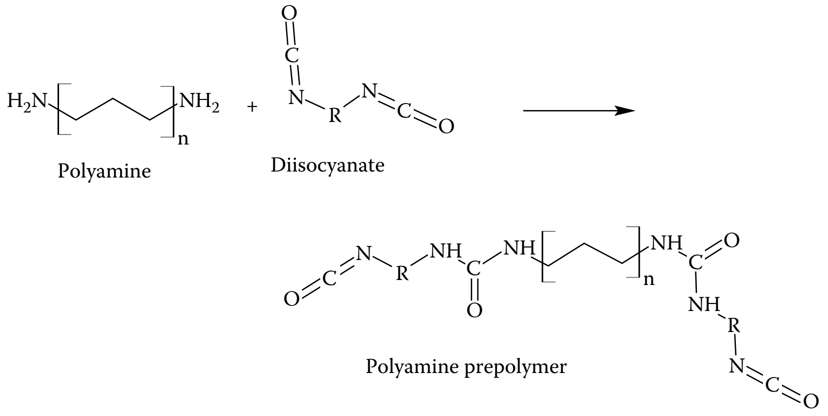


FIGURE 2.8

Water Reactions

When a polyurethane prepolymer is reacted with a substance containing a single hydroxyl group such as ethanol or water, reactions will take place that will give off carbon dioxide gas. In thin sections the bubbles may be able to escape or be held by inert fillers. They can also be trapped by pressure-molding the part.

The major problem is moisture that is absorbed into the polyurethane system or into the curative and auxiliary materials. Free water will liberate carbon dioxide when the chain extension is carried out. It is important to keep the reactants dry, as any moisture that may have come in contact with the prepolymer will react to give an amine and carbon dioxide. This amine reacts with more isocyanates to form a disubstituted diamine. The reaction is outlined in Figure 2.9.

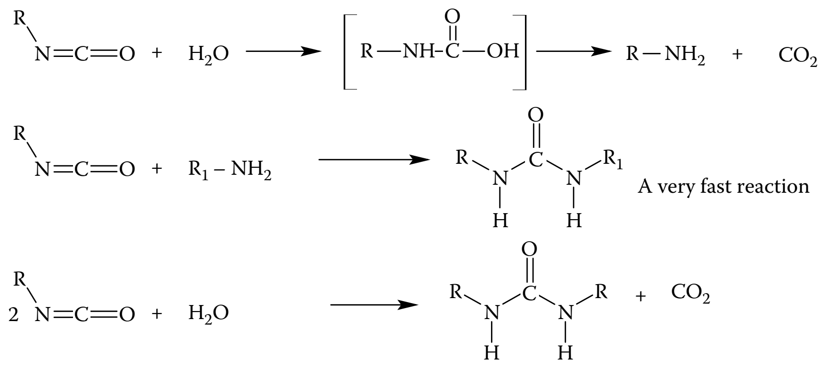


FIGURE 2.9

Two moles of isocyanate are used per one mole of water. The carbon dioxide released will form bubbles throughout the cast product, forming a spongy instead of solid material, thus detracting from the properties of the polyurethane. The physical properties will be lowered both from the chemical balance being incorrect and from the presence of the bubbles, which prevents the full strength from being developed.

2.2 Raw Materials

This book is studying the castable family of polyurethanes. The cured polyurethane elastomer is made from three main ingredients that are detailed in Table 2.1.

TABLE 2.1

Main Polyurethane Ingredients

1.	Polyols	Polyether Polyester
2.	Diisocyanate	Aromatic Aliphatic
3.	Chain extender	Diamines Hydroxyl compounds (glycols or water) Polyols
4.	Other chemicals	

2.2.1 Polyols

Flexibility in the polyurethane is provided by the backbone or "soft segment." Polyols provide the soft segment of the polymer and are capped with a hydroxyl group. Unless there are special requirements, the polyols are linear (i.e., no branching) of molecular weight between 400 and 7,000. The overall molecular weight of the soft segment controls the frequency of the hard phase and hence the hardness, resilience, and stiffness of the final product. The lower the molecular weight, the higher the occurrence of the hard phase. There are two main groups of polyols used to make castable polyurethanes, polyethers and polyesters.

Polyethers

Polyether diols form a very important segment of the diols used in the manufacture of polyurethanes. The normal route is by addition polymerization of the appropriate monomeric epoxide. The most important polyethers are polypropylene glycol (C3) and polytetramethylene glycol (C4). The manufacturing route is given in Figure 2.10.

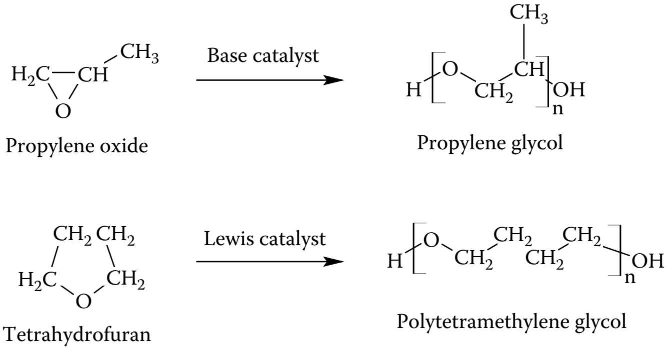


FIGURE 2.10

The polyether glycols produce polyurethanes that are not as strong and tough as the polyester-based polyurethanes, but they have far superior hydrolytic stability. The standard polyol in this group is polytetramethylene glycol (PTMEG), which gives compounds superior physical and mechanical properties to those produced with polypropylene glycol (PPG)-based systems. The PTMEG produces polyurethanes with excellent mechanical properties and very low abrasion loss.

Prepolymers based on polypropylene ether glycol (PPG) have excellent but not as good mechanical and wear properties as the PTMEG-based materials. Improvements to the performance of the PPG material were made by the end-capping of the propylene glycol chains with ethylene oxide. The modified PPG gave better processing and performance.

Newer polyethers have been introduced into the market. Based on polypropylene glycol, they have superior properties, especially in the high molecular weight range. The Acclaim® (Bayer Material Sciences PPL) polyethers are made by using an alkoxylation catalyst that yields a material with much higher diol content (Lawrey and Barksby, 2003). When high molecular weight PPG is made using potassium hydroxide catalyst, there is a large number of chains that have only one hydroxyl group (monol) instead of two. This will severely limit later chain extension. The monol content in a 2000 MW diol is reduced from 6 to 1 mole% using the new process, whereas with a 4000 MW diol the monol is reduced from 33 to 2 mole%.

The purchase cost of the polyols is as follows:

Classical PPG < EO tipped PPG < low monal PPG < PTMEG

Polyesters

The chemical structure of the prepolymer influences its chemical resistance. As a result of their structure, polyesters have inherently better oil resistance but lower hydrolytic stability. The ether groups in the polyether urethanes provide better hydrolytic stability and are more flexible. Polyesters have three different types: dibasic acid reacted with diol, polycaprolactone materials, and polycarbonate-based materials.

Dibasic Acid Type

The classical-based polyester is made by the reaction of a dibasic acid diol with the formation of a polyester and water. The water has to be removed. The general reaction equation is shown in Figure 2.11.

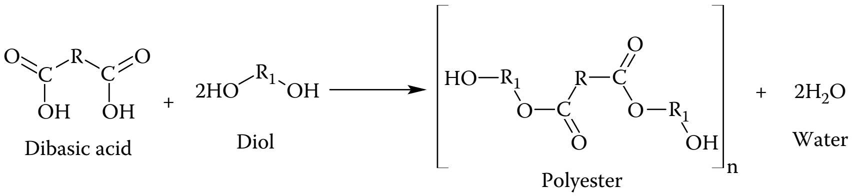


FIGURE 2.11

Polyesters produce strong, tough, oil-resistant materials. The major downside is a lack of hydrolysis resistance. The basic polyesters are prepared by the reaction of a dibasic acid (usually adipic, sebacic, or phthalic acid) with a diol such as ethylene glycol, 1,2-propylene glycol, and diethylene glycol. The polyesterification conditions must be such that only hydroxyl groups form the terminal groupings. The water of condensation formed must be removed to a level of 0.03% to produce good polyurethanes. Polyurethanes made from these ingredients suffer from relatively poor hydrolytic stability. The reaction between ethylene glycol and adipic acid is shown in Figure 2.12. They offer excellent heat and solvent resistance with high tear and sliding abrasion resistance. Their main drawback is poor hydrolytic stability and susceptibility to fungal attack.

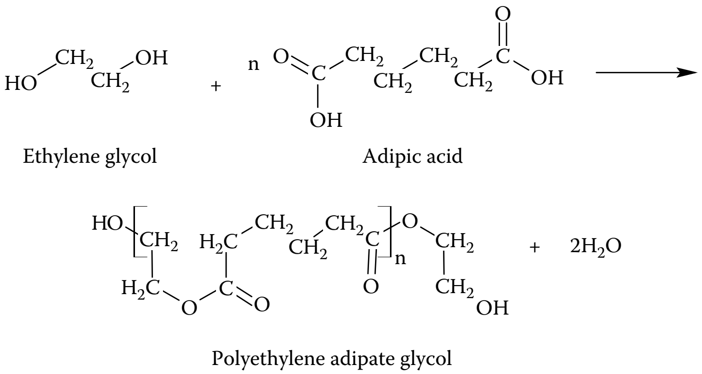


FIGURE 2.12

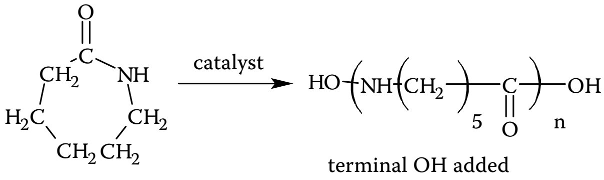


FIGURE 2.13

Polycaprolactone

This group of polyesters is made by the opening of the caprolactam ring. Caprolactam is also used in the production of nylon. Their structure appears to provide a degree of protection from hydrolytic attack. They are formed by the reaction shown in Figure 2.13 (Barbier-Baudry and Braachais, 2003). Their hydrolytic properties fall between those of PTMEG and other polyesters.

Polycarbonate

When reacting either ethylene carbonate or propylene carbonate with an aliphatic diamine, a polyurethane can be produced (Figure 2.14). Poly(ethylene ether carbonate) diols (Harris et al., 1990), when fabricated into polyurethanes using MDI and BDO, produce elastomers that have polyester polyol features. This was shown using ^{13}C NMR. The structure gives rise to potential for a very high virtual cross-linking density. These carbonate-derived polyesters have superior hydrolysis resistance compared to the traditional materials.

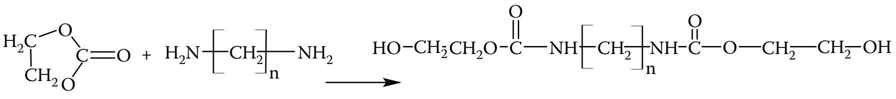


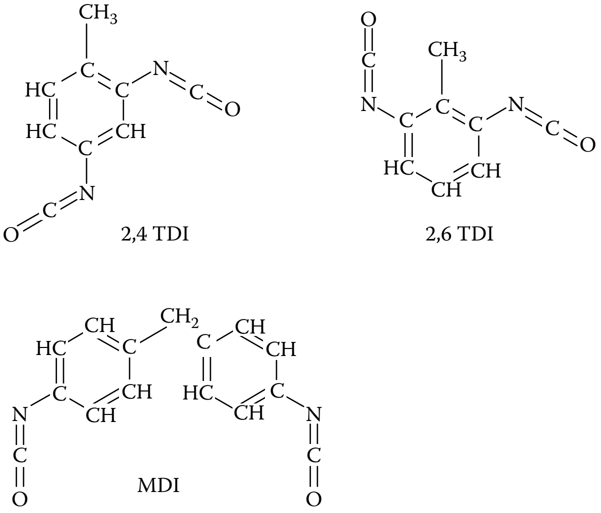
FIGURE 2.14

2.2.2 Diisocyanates

The isocyanates form the major part of the hard or rigid phase of the polyurethane. The three main isocyanates used in industry for castable materials are toluene diisocyanate (TDI), 4,4′ diphenylmethane diisocyanate (MDI), and 1,5-naphthalene diisocyanate(NDI). Aliphatic diisocyanates form a small segment of the diisocyanate market.

Aromatic Diisocyanates

In the production of polyurethane elastomers, only diisocyanates are of any important use. The major diisocyanates manufactured and used are the 2,4 and 2,6-toluene diisocyanates (TDI) and 4,4′-diphenylmethane diisocyanates (MDI). See Figure 2.15.


2,4 TDI

2,6 TDI

MDI

FIGURE 2.15

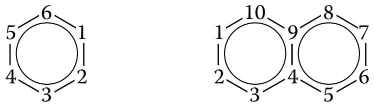
The reactivity of the various isocyanates is important in the processing of any system:

NDI> MDI > TDI

The aromatic diisocyanates are generally more reactive than the aliphatic diisocyanates. The position of the isocyanate group relative to surrounding groups controls the reactivity.

The velocity constant of 1,5 naphthalene diisocyanate, where both NCO groups are equal on the ring, is the same. The velocity constants of the 2,4 TDI are quoted by Saunders and Frisch (Saunders, 1962) as being $k_1 = 42.5$ and $k_2 = 1.6$. The 2,6 isomer of TDI has velocity constants of $k_1 = 5$ and $k_2 = 2$. This indicates that the initial reaction will be fastest with the 2,4 isomer at the 2 position. See Figure 2.16 for position numberings.

TDI is used either as an 80:20 mixture of the 2,4 and 2,6 isomers or as 100% 2,4-toluene diisocyanate. The current tendency is to use the 80:20 mixed isomers for normal work and the 100% 2,4 isomer TDI for high-performance material.



Benzene ring

Naphthalene

FIGURE 2.16

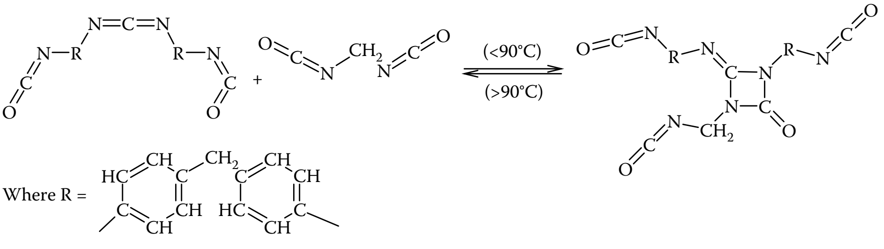


FIGURE 2.17

Pure MDI melts at 38°C. The MDI tends to dimerize readily, so it has to be stored at –4°C and melted just prior to use. The pure MDI can be modified so that it is liquefied at room temperature. The physical properties of the polyurethanes made from these modified isocyanates are inferior to the material made from pure MDI. The reversibility of the reaction is shown in Figure 2.17 (Dow Plastics, 2001).

Aliphatic Diisocyanate

Aliphatic diisocyanates belong to a different organic group. They do not contain the benzene (aromatic) ring. They may have a ring or a straight chain structure. See Appendix 7 for the formulas of typical aliphatic isocyanates. Figure 2.18 illustrates the difference in structure between the aromatic MDI and the aliphatic H_{12}MDI.

Because of their much higher costs, aliphatic diisocyanates find use mainly in specialized areas where their special properties such as nonyellowing in light are of great importance. The nonyellowing is a result of the aliphatic structure of the isocyanate. There are no series of double bonds that cause the yellowing.

The reactivity of aliphatic diisocyanates is low in comparison to aromatic isocyanates. It is a problem in the manufacturing stage when using the prepolymer route. Quasiprepolymers and one-shot reactions require the correct choice of curative and catalyst for the system to work.

Diisocyanates such as p-TMXDI do not form allophanates. This adds to their very stable storage life, even at slightly elevated temperatures. The

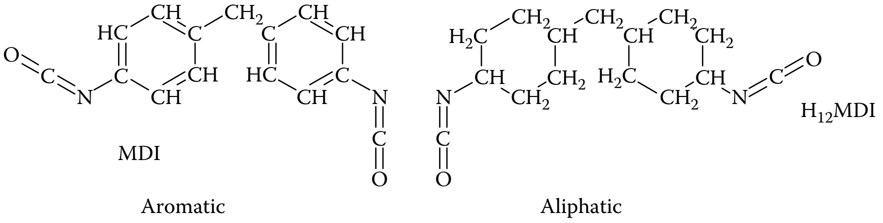


FIGURE 2.18

prepolymer has a shorter pot life and gel time compared to an equivalent prepolymer made with the aromatic MDI.

Aliphatic polyurethanes, with their nonyellowing, also provide sufficient impact resistance so that they can be used in face shields (U.S. Patent 3.866.242). Even with the nonyellowing properties, UV protection agents are often added to materials.

Other commercially available aliphatic and aromatic diisocyanates used in the polyurethane industry are listed in Table 2.2. These diisocyanates represent 3 to 4% of the market use. The remainder is TDI and MDI.

TABLE 2.2

Isocyanates Used in Lesser Quantities

Name	Abbreviation
4,4′-dicyclohexylmethane diisocyanate	H_{12}MDI
1,5 naphthalene diisocyanate	NDI
1,6 hexamethylene diisocyanate	HDI
xylene diisocyanate	XDI
isophorone diisocyanate	IPDI
3-isocyanatomethyl-3,5,5- trimethylcyclohexyl isocyanate	TMDI

2.2.3 Chain Extenders

The two main groups used as chain extenders are diamines and hydroxyl compounds. Triols are also used where some cross-linking is required. The choice of chain extender depends on the properties required and the process conditions. Diols are the most commonly used hydroxyl compound. In the normal course of events, diols provide good properties and processing speed with MDI-based prepolymers and diamines with TDI-terminated prepolymers.

The molecular shapes of the isocyanate and extender molecule often are considered to play a part in the ease of formation of hydrogen bonding. The molecules must be able to come closer to each other for hydrogen bonding to take place. There must be no steric hindrance to the two chains. Molecules with an even number of carbons are said to allow the hydrogen donor group (NH) to fit more easily to each electron donor group (C=O). When they are odd, the fit is poor, and many groups cannot participate in the hydrogen bonding. Experimentally it has been shown (Wright and Cummins, 1969) that the melting points of polyurethanes made with a series of aliphatic diisocyanates with different number of carbons in the chain varied with the number of carbons in the diisocyanate. Those made with an odd number of carbons in the isocyanate had a lower melting point than those on either side with an even number of carbon atoms in the isocyanate chain. This is shown in Figure 2.19.

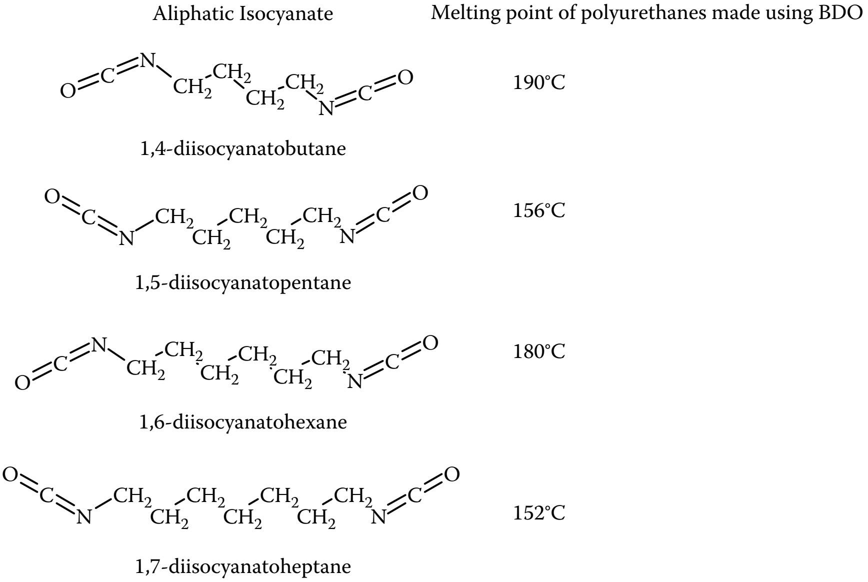


FIGURE 2.19

Diamines

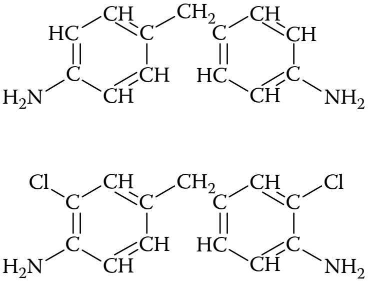
Aromatic diamines are the most commercially used chain extenders with TDI-based polyurethanes. The rate of reaction of a simple aromatic diamine is too great for normal use. Thus the rate of reaction is commonly controlled by having substitutes on the aromatic ring. An example is the simple diisocyanate MDA and MOCA with the chlorine atoms in MOCA slowing the reaction to a useable rate.

A chlorine or methyl group ortho (positions 1,2 = ortho) to the amine group gives optimum properties in a diamine-cured compound. It has been found that a methoxy group next to the aromatic amine gives polyurethane with inferior properties.

There are a number of different polyurethane curatives available based on methylene dianiline (see Figure 2.20) with different groups next to the amine group (NH_2). MOCA with the chlorine atoms has been the most successful.

Some aromatic diamines used as curing agents, such as 4,4′ diaminodiphenyl derivatives or 3,3′ Dichloro 4,4′ diaminodiphenylmethane (MOCA), have been investigated and have been declared to have suspect carcinogenic properties. All local rules and regulations must be adhered to if these materials are used.

The mixed isomers of di(methylthio)-toluene diamine are sold under the trade name Ethacure 300® (Albemarle, Baton Rouge, Louisiana) (Figure 2.21). The advantages of Ethacure 300 are that it is a liquid at ambient temperatures and does not have the suspect carcinogenic properties of MOCA.



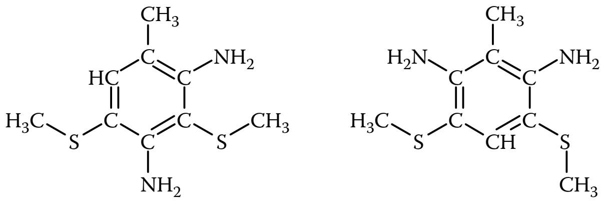
4,4'-methylenedianiline
(MDA)

4,4'-methylenebis(2-chloroaniline)
(MOCA)

FIGURE 2.20

Ethacure 300 is a liquid at room temperature, which has led to its favoritism in the marketplace for normal production runs. MOCA and Ethacure have advantages over each other in different aspects. In certain mechanical properties, Ethacure is superior, and in other aspects, MOCA is superior. Individual testing needs to be carried out to obtain the best curative for the situation. A newer diisocyanate, Lonzacure® (Lonza Ltd., Basel, Switzerland) M-CDEA, has superior properties to Ethacure or MOCA but has the processing disadvantage of being a solid. The melting point of Lonzacure M-CDEA is 88 to 90°C, which is slightly lower than that of MOCA. The structure of Lonzacure M-CDEA is given in Figure 2.22.

Amines produce polyurethanes with better mechanical properties than when diols are used for curing. Amines produce polyurethanes with a lower temperature resistance than when diols are used. The use of catalysts has been found to direct the cross-linking reactions away from the biuret to the allophanate reactions.



Di(methylthio)-2,4-toluene diamine Di(methylthio)-2,6-toluene diamine

Ethacure 300

FIGURE 2.21

Hydroxyl Compounds

Monols

The simplest hydroxyl compound that can be used is water. The two main disadvantages of water are the facts that carbon dioxide is liberated during

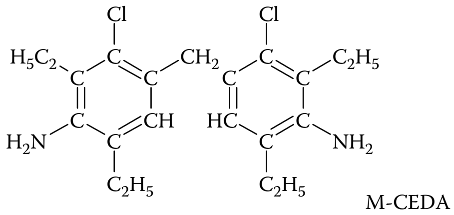


FIGURE 2.22

the reaction and the strength of the polymer formed is not very high. Polyurethanes also react with alcohols in a similar manner.

Cast polyurethanes cured with water would need the bulk of the carbon dioxide to be flashed off and the remainder held in place by compression molding.

Low-Molecular-Weight Diols

The chemistry is slightly different when diols are used. The bonds formed are urethane bonds. This means that the final product formed is pure polyurethane. No carbon dioxide is liberated during the reaction. The general reaction is shown in Figure 2.4.

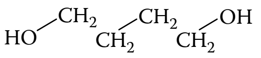
The shorter the linear diol chains, the better the compression set and the higher the melt temperature of the polyurethane elastomer. The hysteresis curve shows the least retained energy, thus giving a lower heat buildup under load. These desirable properties can be achieved more readily by the diols ranked in the following series:

Ethylene glycol> 1,3 propane diol> 1,4 butane diol>
1,5 pentane diol> 1,6 hexane diol

The most commonly used diol is 1,4 butane diol. It is generally referred to as just BDO or butanediol. The molecule is shown in Figure 2.23.

However, one of the main points to be considered in the making of a polyurethane elastomer (apart from the reactivities of the isocyanate and curative) is the water absorption. Special precautions must be taken to keep a diol curative (such as butanediol) sufficiently dry for use. Diols have to be kept dry with molecular sieves and dry nitrogen blanketing.

The solubility of the diols in the system must be carefully controlled so that phase separation does not occur. This is of great importance in quasiprepolymers.



Molecular weight = 90.1

Equivalent weight = 45.05

butane-1,4-diol

FIGURE 2.23

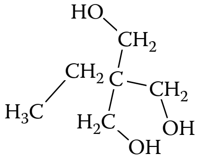


FIGURE 2.24 Trimethylol propane

Triols

Triols such as trimethylol propane (TMP) (Figure 2.24) provide sites for cross-linking to occur. Triols cause chemical cross-linking, which is not dependent on the reaction temperature, as is the case with allophanate and biuret reactions. This form of cross-linking leads to a lower density of the hard phase and softening of the material. These changes are a result of chain separation and a reduction in the hydrogen bonding. Other triols such as glycerol can be used. Glycerol is hygroscopic and is normally supplied with a water content of 2%. This causes problems in processing.

Polyols

Linear polyols of various molecular weights can be used in the chain extension of prepolymers. Their main use is to adjust the hardness of the final compound. They act as a reactive plasticizer, and their functionality and molecular weight must be taken into account in the curative calculations. Either polyether or polyester polyols can be used. The most important point is that they must be dry.

2.2.4 Other Chemicals

There is a group of chemicals used in polyurethanes that have an influence on the physical properties of the final product but do not take part in any chemical reaction.

Fillers

Fillers are not normally used in polyurethanes to bulk out the product, because they reduce the properties too drastically. This is in contrast to conventional elastomers, where they can be used to reinforce the product. Ultra fine silica is used as a thixotrophic filler in trowelable polyurethanes.

Nanoparticles are now being investigated and used to provide some extra stiffness to polyurethanes. These are very small, flat, claylike platelets of micron size. Montmorillonites of size 2 to 13 microns have been used. They can have functional groups such as amine attached to them. The particles have to be fully defoliated and wetted by the polyurethane. The functional groups will bond to the hard segments.

Plasticizers

Plasticizers can be either reactive or nonreactive. The nonreactive plasticizers are from the phthalate and ester groups. Typical plasticizers are DIOP, TCP, and Benzoflex 9–88. The level of plasticizer must be controlled because the physical properties decrease as the levels increase.

Moisture Scavengers

Molecular sieves are synthetic crystalline metal alumino-silicates that have very fine holes in their structure. The size of the holes is in the order of 4 to 5 angstroms (10^{-10} m) in diameter. The water molecules enter the holes and are trapped in them. Commercially, they are supplied in the form of a castor oil paste.

Ultraviolet Absorbers

Ultraviolet absorbers can be added to polyurethanes to lower the yellowing of the material. They are best used in the aliphatic materials to stop minor yellowing. In polyurethanes with aromatic diisocyanates, the attack is very fundamental and hard to stop.

Catalysts

Catalysts speed up certain reactions in the chain extension of polyurethanes. The catalysts used are those made by specialty suppliers for the polymer industry and include a range of amines and metal salts.

2.3 Prepolymers

2.3.1 Commercial Preparation of Prepolymers

Hepburn (1982) gives two main routes for the preparation of polyurethanes based on the relative activities of the various ingredients:

Prepolymers
  Unstable prepolymers
  Stable prepolymers
  Chain extension/cross-linking to complete production of polyurethane
One-Shot Systems

Unstable Prepolymers

The unstable prepolymers are typified by the Bayer Vulkalon polyurethane. Vulkalon is generally made by reacting naphthalene diisocyanate (NDI) and hydroxyl terminated polyesters to form a prepolymer. The reactivity of the prepolymer is such that it must be chain extended with a diol or water within a time span of 1 to 2 hours. After this time period, the prepolymer will react with itself to form an unsatisfactory product.

The best physical properties are obtained with polyethylene adipate as the backbone. After the manufacture of the prepolymer with the polyethylene adipate and NDI, the polyurethane was completed with the addition of BDO. The use of diamines gave too fast a reaction for successful processing. Water and glycols also were used for cross-linking. Glycols do not give the CO_2 gas the water chain extension does.

To improve the low temperature properties, a different backbone needs to be used. A mixture of polyethylene and polypropylene adipates has been found to be suitable. The physical properties are not as good as with the single polyol.

Stable Prepolymers

Following the early developments using NDI, it was found that by using TDI instead, a far more stable prepolymer could be made. Stable prepolymers are normally made using either polyesters or polyethers that have been reacted with a slight excess of a diisocyanate such as toluene diisocyanate (TDI) or methylene diisocyanate (MDI). Provided the storage is moisture free, the stable prepolymer may be kept for months before use. The polyurethane is prepared by chain extension with diols or diamines.

The starting point is to react two moles of the diisocyanate with one mole of the polyol (see Figure 2.25). The ratios of the two ingredients can be varied to change the overall properties.

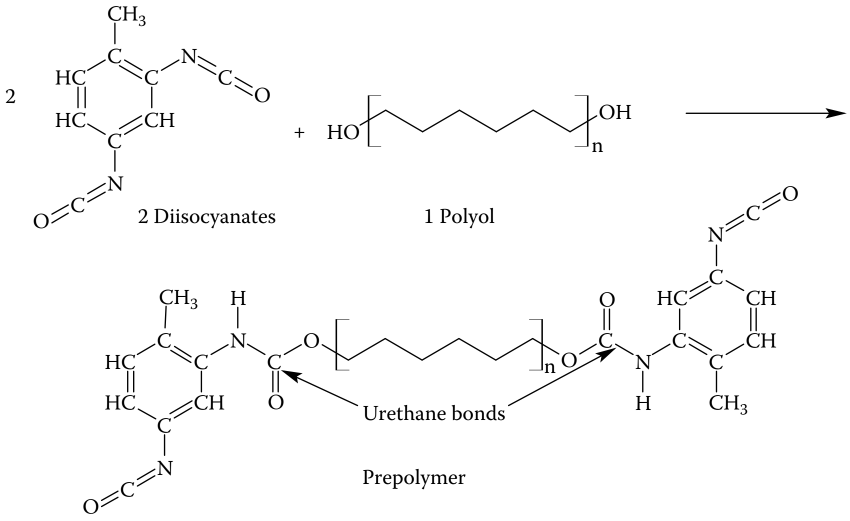


FIGURE 2.25

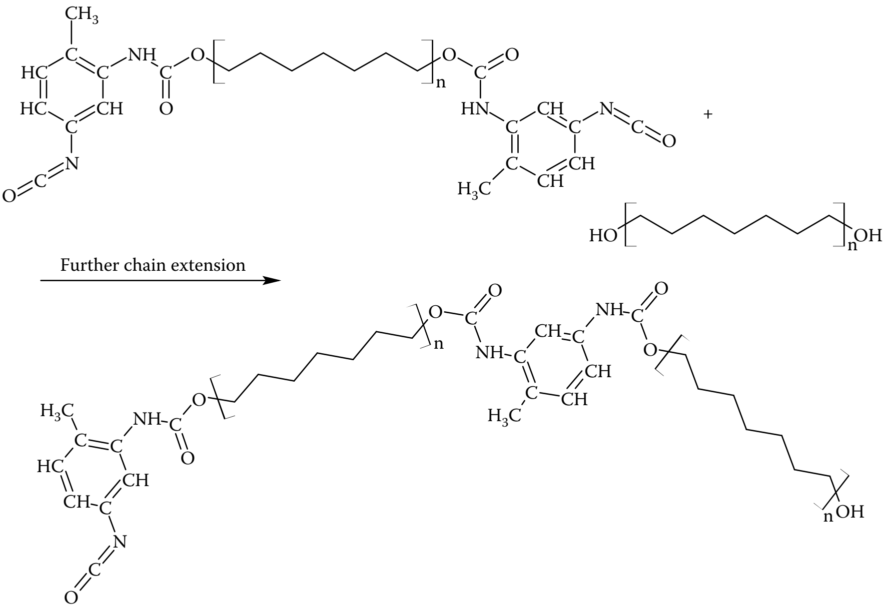


FIGURE 2.26

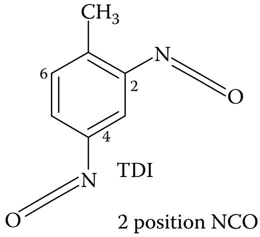
The chemical reaction proceeds with the terminal isocyanate of the initial prepolymer reacting with the available hydroxyl groups of the diol. This is illustrated in Figure 2.26.

When the diisocyanate and polyol are being reacted together, the diisocyanate is kept in excess as long as possible. The overall conditions are kept slightly acidic to reduce side reactions taking place. The acidity is a must when there is more polyol than diisocyanate present. The older-style PPG polyols may contain traces of potassium hydroxide (KOH). The KOH is a very active alkaline. Even small traces have a strong effect.

The most reactive isocyanate group (-NCO) in the structure will react with the hydroxyl (-OH) group first. The reaction will tend to favor the most reactive site. The reaction is allowed to proceed until almost all the diisocyanate is used up. The reaction is stopped before the viscosity increases too much. The temperature and speed of the reactions are such that catalysts are normally not used in these reactions.

The reaction rates at the various positions on the ring vary greatly. For example, with TDI, the relative rates are shown in Figure 2.27. The reactions are exothermic, so the rate of addition must be controlled to prevent side reaction.

Early work published in Saunders and Frisch, Volume II (Saunders 1962) shows how various properties change different diisocyanate-to-polyol ratios. As the NCO/OH ratio increases from 2 to 2.75, the main physical properties of tensile strength, modulus, tear strength, and hardness increase. Other positive improvements are compression set and resilience. The pot life and



TDI	Reaction Velocity Constant	
	73°C	100°C
2 position NCO	0.72	3.2
4 position NCO	3.4	8.5

FIGURE 2.27

Taber abrasion properties of the final polyurethane decrease as the ratio increases.

2.3.2 One-Shot System

Single Step

In the single-step system, the entire reaction takes place when all three basic components plus catalysts and pigments are mixed together. Careful use of catalysts enables the preparation of the prepolymer and the subsequent chain extension to take place in one step. As all the reactions are exothermic, heat is liberated and must be removed; otherwise, part distortion will take place.

The commercial use of this system requires the careful metering and temperature control of the various streams. As a result of the heat liberated, this system is best suited to long runs of thin wall products.

The systems may be either a three-dimensional network based on covalent bonding or linear extended chains bonding through hydrogen bonds.

Quasiprepolymers

The high exotherm and the number of feeds have led to the popularity of the quasiprepolymer variation of the one-shot technique. Quasiprepolymers are a version of the standard prepolymer method, where some of the polyol is reacted with an excess of diisocyanate. This is later reacted with the remainder of the polyols, including the chain extender and some catalysts. The advantage of this scheme is that the exotherm is spread between the preparation of the quasiprepolymer and the final cured part. In MDI systems, BDO is often used as the curative. As the molecular weight of BDOs is low, the amount added is low. By dissolving it in the polyol, a more even mix ratio can be obtained.

The polyol, the chain extender, and any catalysts are mixed and stored as a separate item. The second item, the diisocyanate prepolymer, is kept as a "B" part until the material is ready for use. When the two parts are mixed, the chain extension and cross-linking take place simultaneously. Methylene diisocyanate and a catalyst such as an organic tin or bismuth salt provide the required rate of reaction. The size of the exotherm is such that the reaction proceeds to its full extent.

2.4 Urea and Urethane Reactions

2.4.1 Introduction

Compounds that contain the N-H group are all potentially reactive toward isocyanates. Simple primary amine groups are very reactive, even at temperatures between 0 and 25°C, giving disubstituted ureas in high yields. Secondary aromatic amines are slightly less reactive. The basic reactions are given in Figure 2.28. Substitution on the aromatic ring is used to control the rate of reaction.

Compounds containing the O-H group such as diols will, under the appropriate conditions, react with isocyanates to give a urethane or, in pure organic literature, a carbamate. Secondary alcohols react at about one-third the rate of primary alcohols. Complex alcohols react very slowly with isocyanates and form a mixture of urethanes and olefins.

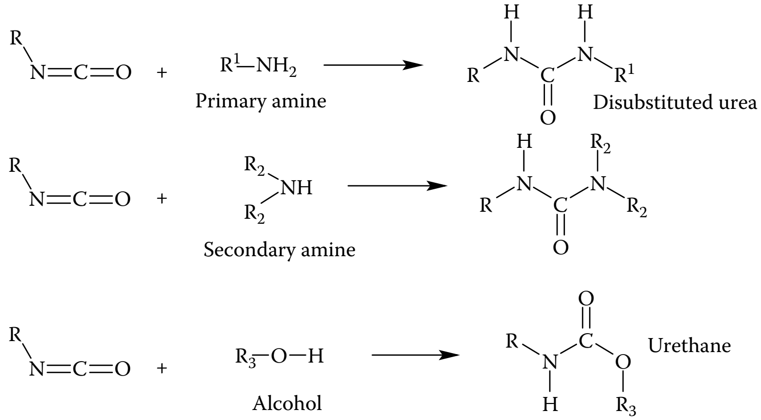
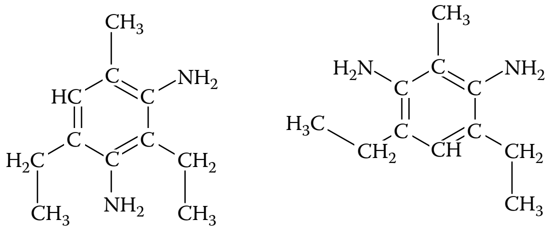


FIGURE 2.28

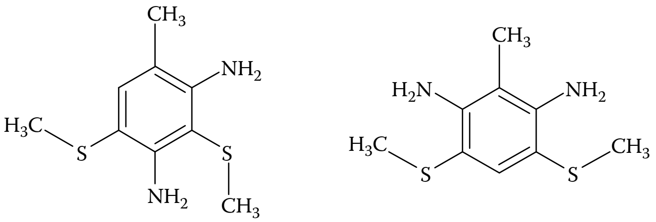
2.4.2 Speed

Isocyanates and amines react together to form ureas. Primary aliphatic amines react very quickly at temperatures down to ambient, whereas secondary aliphatic and primary aromatic amines react less quickly. The reaction rate of secondary aromatic amines is the slowest. The speed of the reaction can further be modified by the addition of substitutes near the amine group. The control of the speed can either be electronic, as illustrated by the effect of the chlorine in the MOCA ring, or by stereo chemical influences where the groups next to the amine group have a very strong hindrance to the curing. This is



3,5-Diethyltouene-2,4-diamine 3,5-Diethyltouene-2,6-diamine

DETDA (Ethacure 100)



3,5-(Dimetylthio)-2,4-diamine 3,5-(Dimetylthio)-2,6-diamine

DMTDA (Ethacure 300)

FIGURE 2.29

illustrated by the effect that the sulfur molecule has on the speed of DMTDA (Ethacure 300) to that of DETDA (Ethacure 100). The sulfur group slows the speed down to a level suitable for polyurethane processing. The structures of the aromatic amines and their isomers are shown in Figure 2.29.

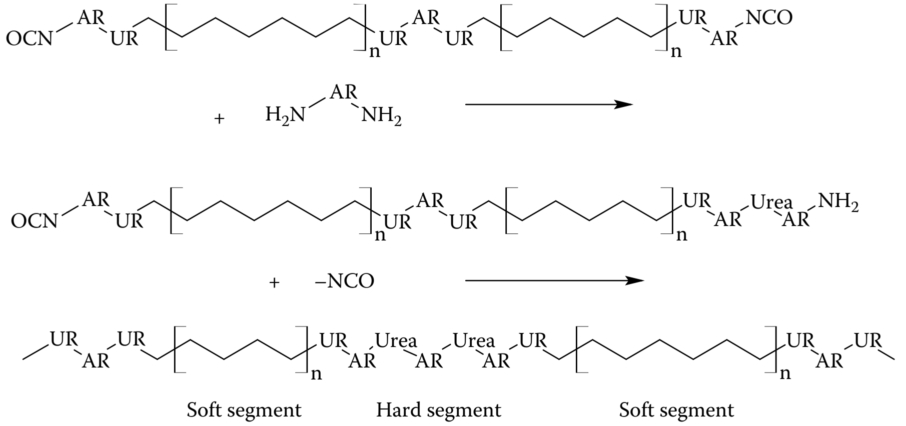
Amine curatives tend to give too fast a cure rate when used with MDI-based prepolymers and give the best results when used with castable systems based on TDI.

2.5 Chain Extension

In the preparation of a prepolymer, every effort is made to prevent the formation of any unplanned branching such as biuret groups. The prepolymer is essentially linear except when some cross-link sites have been introduced by using a multifunctional isocyanate or triol.

2.5.1 Urea

If a diamine curative is used, the amine groups (NH_2) will react with an isocyanate group of the prepolymer to form a urea bond. The remaining amine group will react with a further isocyanate group to extend the chain, as shown in Figure 2.30.



AR Aromatic or aliphatic group
UR Urethane group
Urea Urea group
NCO Isocyanate group

FIGURE 2.30

A diol such as PPG or PTMEG has 5 to 28 repeat units (382–1982 MW). On reaction with a diisocyanate, a urethane bond is formed. A further diol can react with the second isocyanate group, lengthening the chain. Final chain extension (curing) takes place when either a urethane or urea group is added on to form a longer chain. As the reaction proceeds, the mixture first thickens and then gels before becoming initially a brittle solid and then an elastomeric material on final curing. This is an ideal situation, but in practice, side reactions can occur.

The variation of the substitutes next to the amine group greatly affects the rate of reaction. A comparison between methylene diamine and MOCA shows the chlorine atoms adjacent to the amines slow the reaction rate down. This can be seen in Figure 2.31.

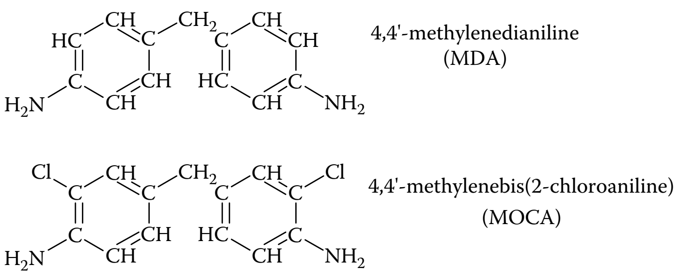


FIGURE 2.31

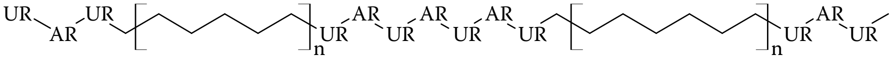
A polyurethane made from a 90 Shore A PTMEG prepolymer and the two curatives (DuPont) both had excellent physical properties, but the pot lives for the two were :

MDA curative	0.1 minutes
MOCA curative	15 minutes

2.5.2 Urethane

The use of hydroxyl compounds is normally with either MDI or NDI systems. The simplest hydroxyl compound, water, can be used. The disadvantage of this is the evolution of carbon dioxide. Water is normally only used in film-type situations or when the bulk of the gas can be removed.

Diols are predominantly used for chain extensions to give a product with only urea bonds. The progress is similar to the formation of the poly(urea–urethane), but with only urethane bonds. See Figure 2.32.



AR Aromatic or aliphatic group

UR Urethane group

FIGURE 2.32

All these reactions are idealized, and in reality there are some side reactions taking place. The materials in normal use are of commercial quality, and besides there being various isomers, there are a number of impurities. A change in supplier may give variations to the final properties. The reaction rates of both isocyanate groups, when using 4,4′ MDI (the normal pure MDI), are the same.

2.5.3 Hydrogen Bonding

The individual chains of polyurethane are composed of a large number of atoms joined together by covalent bonds. These chains consist of long sections of hydrocarbons (from the initial diols) joined by aromatic or aliphatic hard segments, which contain urethane or urea groups (from the isocyanate and chain extenders). The long, more flexible sections are called the soft segment and the urethane/urea sections the hard segment. See Figure 2.30.

These chains are separate except where joined by allophanate, biuret groups, or the use of triols in the system. In the hard segment, the urethane and urea groups have electrostatic charges on some of the hydrogen, oxygen, and nitrogen atoms. These charged atoms form dipoles (Figure 2.33), which attract another atom of opposite charge, forming a hydrogen bond (Boyd, 1983).

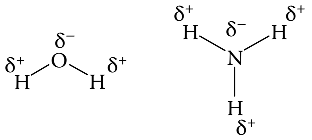


FIGURE 2.33

These hydrogen bonds are of lower strength than the covalent bonds in the rest of the chains but are still sufficient to form a strong compound. The hydrogen bond is approximately 5 kcals/mol, compared to the covalent bond of about 50 to 100 kcals/mol.

During the curing and postcuring, the molecules line up and the hard segments tend to agglomerate in groups where the hydrogen bonding takes place. See Figure 2.34. The size of these agglomerations is approximately 25 by 55 angstrom units in size. See also the illustrations (Figure 3.1 and 3.2). in Szycher's *Handbook of Polyurethane* (Szycher, 1999). It must be remembered that all of these reactions are in three dimensions.

Bulky side chains in the hard segment will tend to make the hydrogen bonding more difficult. The bulky side chains of Ethacure 300 will lower the hardness of a material by several points compared to that of a material cured with MOCA. The use of triols or macro diols in the curing phase will have a softening effect. If a trifuctional isocyanate or hydroxyl is used in the initial preparation of the prepolymers, this softening does not happen.

Studies in the mid-range infrared spectrum using Fourier Transform Infrared (FTIR) spectroscopy can show the course of the basic curing and the formation of hydrogen bonding. The NCO group has an intense band at the wave number 2273 cm^{-1} (note that this is near but not at the same number as carbon dioxide). As the final cure progresses, the band will decrease in intensity until it fully disappears. Figure 2.35 illustrates this.

Using a straight polyurethane system, for example, a PTMEG/MDI prepolymer, there will initially be an absorption band at approximately 1733 to 1725 cm^{-1} (Seymour et al., 1970). As the cure starts, this band will initially

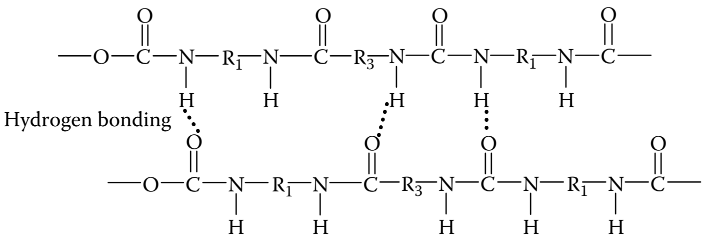


FIGURE 2.34

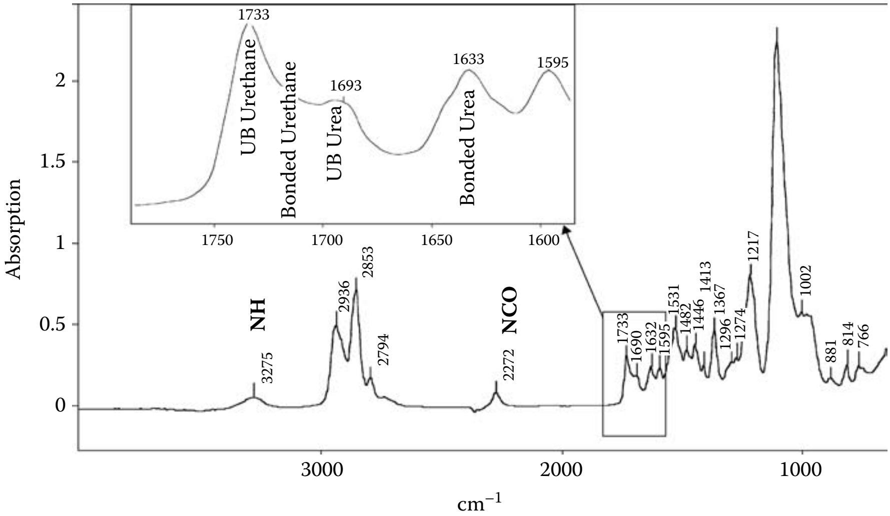


FIGURE 2.35

increase slightly in intensity. Then a second band at ~1700 cm^{-1} will appear due to hydrogen bonding. From the size of the split it is deduced that the bulk of the hydrogen bonding is in the hard segment. See Figure 2.36.

As a result of the shape of the molecules and the fact that they are twisted and bent, the bonding is in all three planes and not as a flat object.

When a diamine curative is used, urea bonds are formed. These bonds also play an important part in the hydrogen bonding process. The unbonded urea has an absorption band at approximately 1690 cm^{-1} and the bonded urea at 1682 cm^{-1}. The time sequence spectra (Figure 2.37) show the formation of the bonded urea bands over the first hours of curing.

Different references give variations to the values for the different bands. These vary depending on the calibration of the instrument used, the exact chemistry of the system, and the method of preparation and testing of the sample. Samples tested in a solvent may indicate the carbonyl band at a wave number of 1745 cm^{-1}, whereas the solid material will be at approximately 1730 cm^{-1}.

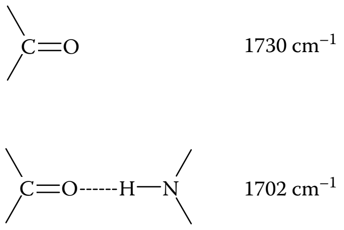


FIGURE 2.36

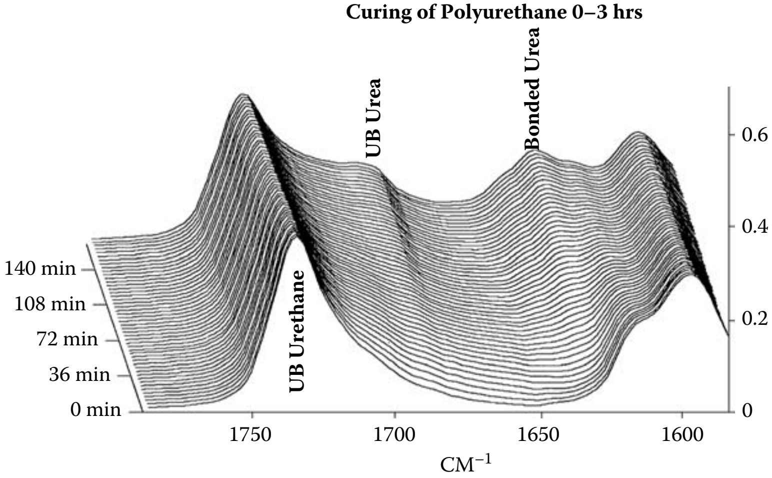


FIGURE 2.37

Maximum properties are formed during the postcuring as the molecules align themselves and the hydrogen bonding reaches a maximum. Some studies have shown that the 2,6 TDI isomer in polyurethanes is high hydrogen bonded. The 2,4 isomer, however, is only 50% hydrogen bonded (Ulrich, 1996).

The ability of the polyurethane chains to form zones with a high concentration of hard segments is vital for the formation of material that has excellent all-around properties. Some of the factors influencing the hydrogen bonding include:

- The use of long chain diols (macro diols)
- Chemical structure of curative
- The use of triols
- Plasticizers

Polyurethanes with a very high carboxyl (-C=O) content are also believed to start hydrogen bonding at the ether groups in the soft segment chain.

2.5.4 Three-Dimensional Cross-Linking

Hydrogen bonding takes place in three dimensions. Molecules are not planar but have various atoms and groups protruding at various angles. The hard segments tend to form cylindrical clusters with flexible chains in between.

Some cross-linking takes place in the form of side reactions such as biuret and allophanate bonds. Deliberate introduction of covalent cross-linking can be carried out by the introduction of multifunctional agents (mainly triols) into either the prepolymer or chain extension system.

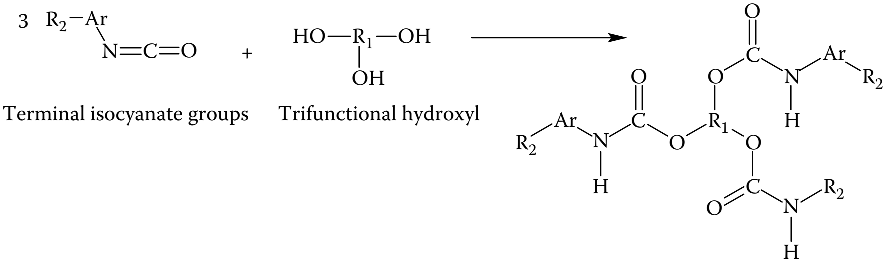


FIGURE 2.38

Triols

When triols are introduced into the prepolymer, they react in a slightly different manner when used as a curative. Prepolymers made containing some triols have a larger hard segment at the point where the triol reacts with the diisocyanate. The general reaction is given in Figure 2.38.

At this point, the chains have not fully developed and the hard segments will have the joined chain at random lengths in the structure. This has the effect of increasing the viscosity of the mix as well as improving the compression set and swelling in solvents. This is important in very hard compounds. A trifuctional isocyanate such as Tolonate HDT (Rhone Poulenc) will do the same as TMP but with less decrease in dynamic properties.

When the TMP is used as a curative, the reaction speed is slowed down and the material is softened as a result of the disruption of the chains. The bonds basically will only be at the end of the chains.

2.5.5 Catalysts

Catalysts have been defined as materials that, when present in relatively small amounts, influence the speed of a chemical reaction while not undergoing any permanent chemical change. A catalyst is generally considered to speed up a reaction. It also can slow it down.

There has been a group of catalysts developed by polyurethane raw material suppliers with the polyurethane market in mind. Mercury-based catalysts, because of their toxicity, have been banned in some countries or severe restrictions placed on their use. Bismuth-based catalysts are recommended in their place.

Catalysts influence specific reactions. The reactions in the polyurethane industry of interest are:

- Reactions with amines
- Reactions with diols OH-NCO
- Reactions with isocyanates and diols NCO-OH

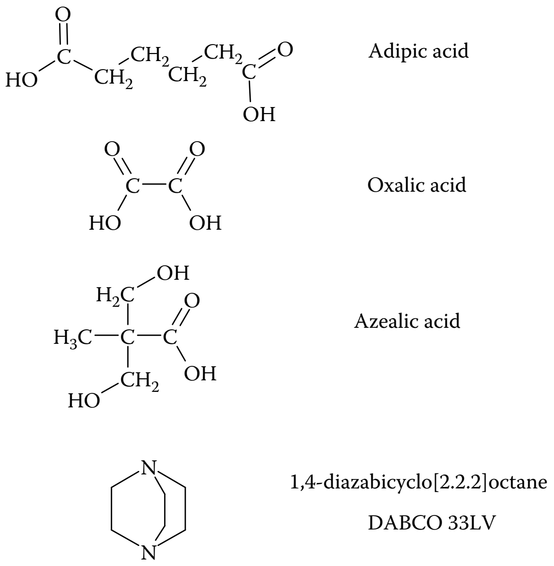


FIGURE 2.39

Reactions with Amines

When working with TDI/amine systems, the most commonly used catalysts are adipic acid, azealic acid, and oxalic acid. These acids are normally used at a rate of 0.3 to 0.6 part per 100 of prepolymer. Adipic acid is particularly effective if MOCA is being used. Diagrams of the acid catalysts are shown in Figure 2.39. Amine catalysts such as DABCO or DABCO 33LV® (Air Products) are also used with amine cures.

DABCO 33 LV is also known as triethylene diamine. It is a cage-like compound with no steric hindrance (Figure 2.39), which helps make it a very effective catalyst. It is reactive at close to ambient temperatures. The application range is in the range of 0.3 to 0.6 parts per 100 of prepolymer. To obtain the desired rate, a mixture of an acid (such as oleic) with a bismuth catalyst can be used. Bismuth catalysts include bismuth neodecanoate and bismuth ocotate.

Reactions with Diols

Tin-based salts such as stannous oleate or a dibutyl tin salt (Dibutyl tin dilaurate DBTL) will activate the OH-NCO reactions. This group speeds up the overall reaction rate as well. They also even out the reactivities of low- and high-molecular-weight polyols.

Compared to polyester-based systems, polyether diols require a greater degree of activation. The solution is to use a combination of a tin and an amine catalyst to obtain the required speed.

Reactions with Isocyanates and Diols NCO-OH

Traditionally, mercury catalysts have been the catalyst of choice, but because they are highly dangerous, they have, to a large degree, been replaced by bismuth-based catalysts. The mercury catalysts are both toxic and caustic.

Bismuth catalysts promote the isocyanate and OH reaction from the isocyanate side. This has the effect of reducing the water reaction and hence reduces the liberation of carbon dioxide gas. They are particularly useful in controlling the reactions when used in one-shot systems.

General

Catalysts are commonly used to control the pouring and gel times of polyurethane systems. As catalysts are used in small quantities, the addition must be carried out very carefully; otherwise, very erratic results may be obtained. Catalysts may be made into a concentrated solution with an inert carrier such as a plasticizer. This reduces a potential dispensing error. They also may be added to a liquid chain extender.

Tin catalysts are very moisture sensitive and, as only small quantities are used at a time, the bulk supply will deteriorate over time with repeated drum openings. The bulk container can be subdivided.

Raw material suppliers have a large range of catalysts available, each with special properties. They should be consulted when required. Some of the catalysts are heat-activated and start very slowly and then react more quickly as the temperature increases.

Catalysts to some degree have an effect on the final properties of the product. The most commonly affected properties are high-temperature heat stability and water resistance. If these are of importance, full evaluations should be carried out.

2.6 Degradation

2.6.1 Prepolymers

If the acidity of the prepolymer is not correct or if the material is stored at too high a temperature, the material will start to thicken. The level of isocyanate also falls under these conditions.

Isocyanates are not very reactive toward urethanes. Temperatures of 120 to 140°C are required for a significant reaction rate. Although not high, the reaction will proceed if the material is kept warm for a long period of time.

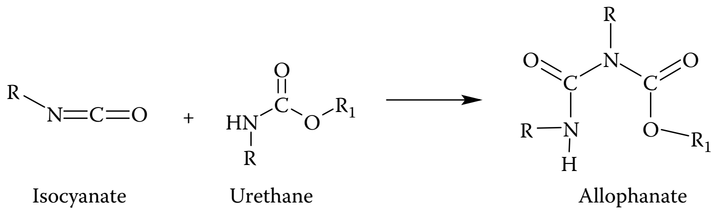


FIGURE 2.40

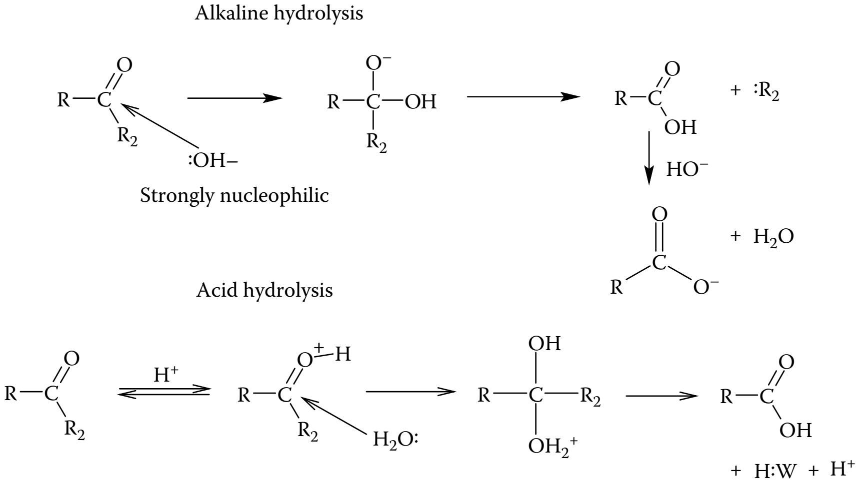


FIGURE 2.41

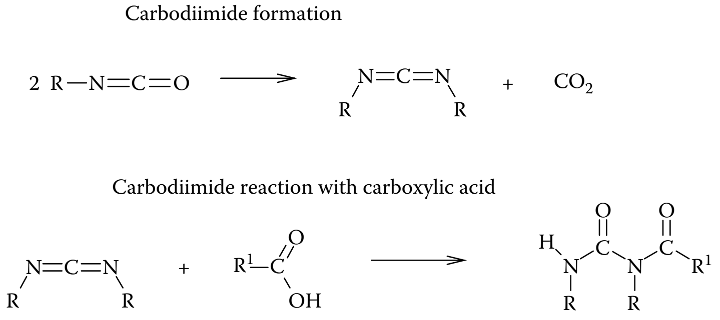


FIGURE 2.42

Figure 2.40 illustrates the formation of an allophanate bond formed between an isocyanate group and a urethane group.

2.6.2 Polyesters

Polyesters are attacked by both dilute acids and alkalis. At elevated temperatures, they are also attacked by water, which is normally either very slightly acid or alkaline. The method of attack is illustrated in Figure 2.41.

The presence of the carboxylic group will cause further breakdown. The removal of this group by the reaction with carbodiimide helps stop continued breakdown of the polyester. Carbodiimides are made from isocyanates. Their reaction with the carboxylic acid generated in the hydrolysis is illustrated in Figure 2.42.

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3

Prepolymer Production

3.1 Prepolymers

Prepolymers are formed by the reaction of an excess of diisocyanate with a polyol. One of the isocyanate groups (NCO) reacts with a hydroxyl group (OH) of the polyol. Another isocyanate group reacts with the second OH group. A very important feature of this reaction is that there are no by-products formed. The resultant product has isocyanate groups on both ends with urethane bonds between the original polyurethane and the diisocyanate group. Figure 3.1 shows the basic reaction.

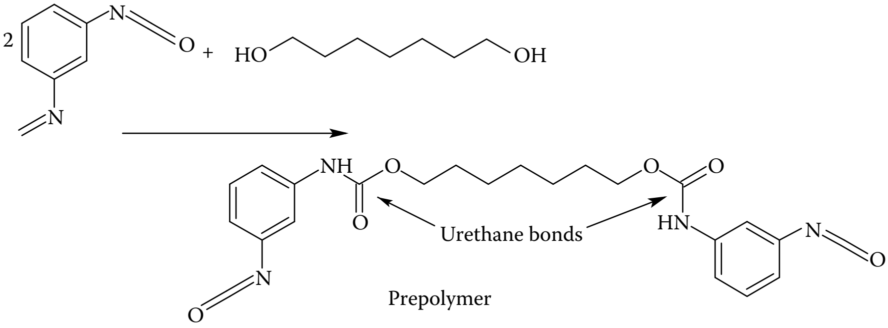

FIGURE 3.1

Prepolymers are normally produced with a mole ratio of approximately two moles of diisocyanate to one mole of polyol. If the ratio is very much larger (e.g., four to one), the resultant product is called a quasiprepolymer.

As the reaction proceeds, the chain length will increase as the hydroxyl groups react with the terminal NCO groups of the already formed prepolymer (Figure 3.2). Further extension of the chain can be carried out by reaction of the terminal hydroxyl group with either another diisocyanate molecule or an NCO from another prepolymer chain.

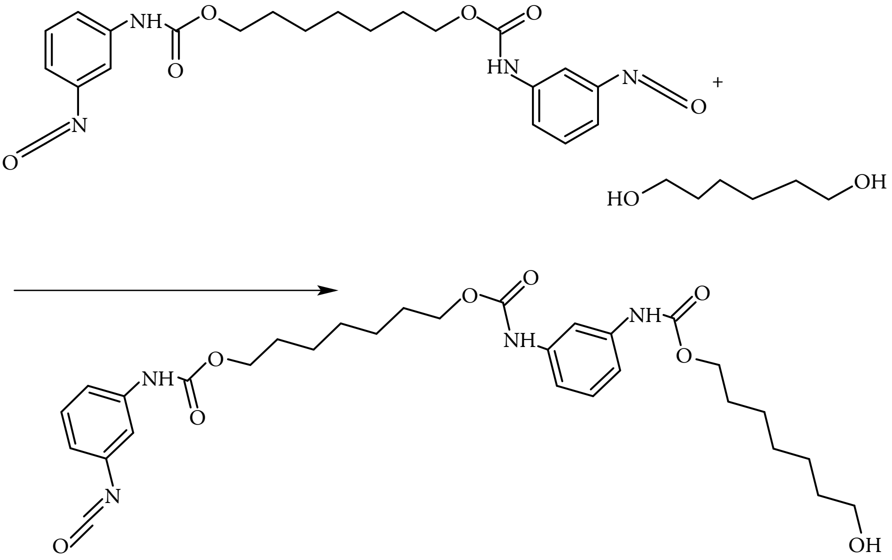

FIGURE 3.2

There are several reasons to work through the prepolymer route as opposed to the one-shot technique. These include:

- Ease in production
- Lower isocyanate vapour levels
- Designed structure
- Exotherm of final reaction reduced
- Easier handling of components
- Final properties of system

3.1.1 Ease in Production

The preparation of prepolymers and quasiprepolymers allows the production of polyurethane parts by component manufacturers without the large capital outlay required to produce materials from the basic raw materials. The production of any prepolymer requires a good understanding of the chemistry involved. The final quality of the polyurethane product is dependent on the initial control of the chemistry of the system and would be expensive for small operators to carry.

3.1.2 Isocyanate Levels

Free isocyanate vapors in the workplace are strictly controlled, because they are a health hazard. In the commercial production of prepolymers, the diisocyanates can be transferred in a closed system and the final prepolymer stripped of most of the free diisocyanate. Although the final prepolymer is strictly a diisocyanate, its molecular weight is so high that its vapor pressure is very low.

3.1.3 Structure of Polyurethane

Using controlled reaction conditions such as the temperature profile and rate and time of the addition of polyols, more uniform materials can be produced. The correct spacing of the hard segments required to produce the physical properties can be obtained. The controlled conditions will also help prevent the formation of undesirable side products such as allophanate, biuret, and trimers. These reactions will give branching of the polymer chains.

The reaction rates of the various ingredients must be understood to follow the probable course of the reaction. Certain polyols may have secondary hydroxyl groups that are very much slower in reaction than the primary hydroxyl groups. The preparation of a prepolymer will allow the secondary hydroxyls to fully react. The reaction of a 100-percent 2,4 TDI is much faster than the standard 80:20 TDI isomer blend. The reaction rate between the terminal NCO and chain extender can be adjusted to allow the prepolymer mix to fill the mold and allow entrapped air to escape before the material gels.

3.1.4 Reduction in Final Exotherm

The production of a polyurethane elastomer gives off heat when urethane and urea bonds are formed. This will cause shrinkage in the final part. The production of a prepolymer will allow part of the exotherm to be dissipated prior to the formation of the final elastomer. This will in turn result in a lower final exotherm and lower shrinkage.

3.1.5 Easier Handling of Components

In a number of applications, pure MDI has to be used. This chemical is solid at ambient temperature and melts at 38 to 40°C. The molten MDI is very prone to dimerization. These two factors make it very difficult to use. The normal storage rule of this material is to keep it at below –18°C.

Dow Chemicals (2001) gives the following storage life data regarding Isonate 125M, which is a pure MDI (Table 3.1). A prepolymer prepared with pure MDI does not have the dimerization problems of the diisocyanate.

In the preparation of elastomers, well-defined hard segments, in which hydrogen bonding can develop, are required. To produce the segments, low-molecular-weight diols and diamines are often used. These are not oversoluble in the high-molecular-weight polyols. They can be reacted with some diisocyanate to produce a prepolymer. This prepolymer is more compatible; therefore, less vigorous agitation is required to ensure the proper dispersion of the diols.

3.1.6 Final Properties

As the molecular weight of the polyurethane chains increases, the physical properties will change. Preparation of a prepolymer will allow the formation

TABLE 3.1

Storage Life of Pure MDI

Temperature (°C)	Storage Life (Days)
–17.8	300
–12.2	210
–4.4	68
10	33
25	*
40.6	31
43.3	35
46.1	35
48.9	28

* Temperature ranges between 21.1 and 37.8°C give a minimum dimer growth of 0.0114 percent per day and wildly erratic results in many recorded instances.

of an initial chain, which can be extended to its final length with a desired chain extender (curative). The heat given off during curing will not be as great as when the whole reaction is carried out in one step. This will reduce potential problems in the final product.

3.2 Laboratory Preparation

Before commencing any experimental work, the relevant up-to-date MSDSs must be studied and the appropriate safety requirements observed. There are often local or in-house regulations for handling certain materials such as MOCA. These must be strictly observed. All people near any isocyanate must take special care not to inhale any traces of its vapor, as these may cause respiratory problems.

If available, the analysis of the raw materials should be studied, especially with regard to purity, potential interfering contaminants, functionality, moisture, and acidity/alkalinity. The molecular weight is often not given directly but must be calculated from the "OH" value and the functionality of the polyol (see Appendix 5 for formula).

3.2.1 Equipment

Drying System

Polyols such as PTMEG may be a solid at ambient temperature and must be heated to allow further processing. This may be carried out in a convection oven set to 60°C. It must be remembered that there will be a pressure buildup in the container. The bung may be cracked slightly to vent the gasses given off.

The polyol must be dry prior to use. This is best carried out by heating the material under vacuum at 90°C for 1 to 2 hours to remove any moisture. It

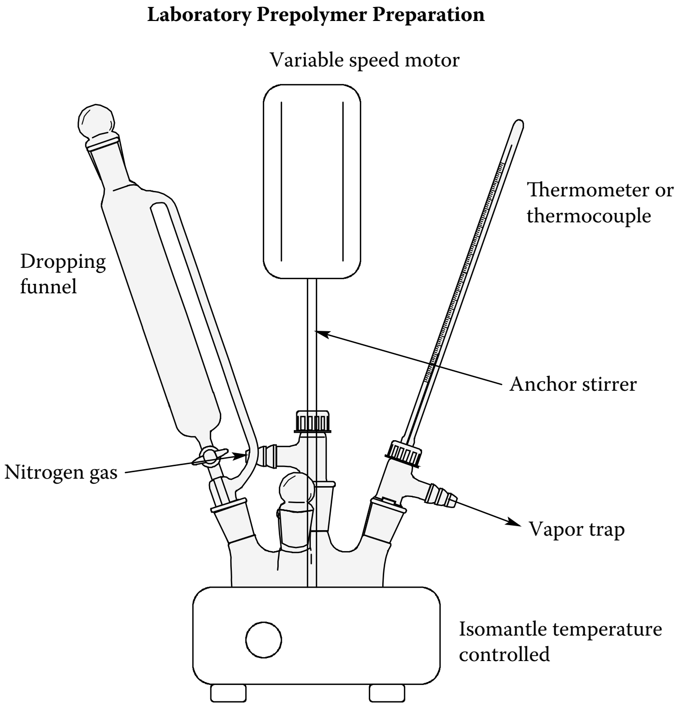

FIGURE 3.3
Laboratory scale prepolymer preparation.

must be allowed to cool in a dry atmosphere, for example, under a blanket of nitrogen gas. Figure 3.3 illustrates one form of a typical reaction vessel. The size and type will depend on the availability of equipment.

For laboratory-size experimentation, the most suited vessel is a wide-necked flask with a clamp-on lid. This style has several advantages, one being that fitting an anchor stirrer is much easier. The discharging of the final product is relatively quick with this type of vessel. When a batch has been prepared, all parts that have been in contact with the polyurethane must be thoroughly cleaned and dried. Polyurethanes are a very effective adhesive and can be formed by the reaction between the resin produced and the moisture in the air.

Heating

The heating of the reaction vessel may take one of several forms, namely:

- Heating mantle
- Oil bath
- Infrared heaters
- Sand bath

These heaters may be controlled by a thermocouple placed in the liquid coupled to a commercial temperature controller, preferably one that has ramping facilities. The application of heat must be able to be stopped and some form of forced cooling applied if the exotherm becomes too large.

3.2.2 Reactions

The aim when making prepolymers is for the majority of the terminal groups to be an isocyanate (NCO). By adding the diol to the isocyanate, the tendency will be for the product to have terminal isocyanate groups.

Most polyurethane systems tend to cling to the glass surface, so an anchor-style stirrer is the best to use. This provides a sweeping motion that helps prevent a very viscous layer from forming on the surface of the vessel.

The desired weight of diisocyanate is added to the flask plus any ingredients to either adjust the acidity or catalyze the reactions. See Appendix 5 for the required calculations. The diisocyanate is heated to the start temperature with gentle agitation. It is best to provide a complete blanket of nitrogen in the reaction setup from this point on.

The polyols are added at a rate so that the exotherm remains under control and the maximum temperature is such that side reactions are reduced to a minimum. Typically, the temperatures should be within the range of 60 to 90°C. As polyols are often viscous, care must be taken to ensure that the correct amount is added to the diisocyanate. This means either a long drainage time or weighing the amount added to the reaction.

Once all of the ingredients are added, the polyurethane must be held at temperature while the reactions proceed to completion. This may be in the order of 1 to 2 hours.

When more than one polyol is used, the structure of the final product can be controlled by the order in which the polyols are added. The varying reactivities of the isocyanate groups will also affect the structure of the final product.

On completion of the reaction, the material may be carefully degassed to remove any entrapped gasses and unreacted diisocyanate. Care must be taken to prevent foaming. Applying vacuum to the glassware does create the potential for it to implode. Suitable safety precautions must be taken. Table 3.2 indicates some typical time/temperature reaction conditions for some simple prepolymers.

Care must be taken when using polyols that have been made using a strong alkali as a catalyst. These are the standard polypropylene glycols (PPG polyols) made with a potassium hydroxide catalyst. Even though the level is low, the alkali is very reactive. There will be a point in the reaction when all the acidity of the diisocyanate is used up and the product is slightly alkaline. The excess alkali (base) will catalyze the reaction. This will not only speed up the reaction but also cause side reactions and the potential for gelation. The acid/alkali balance of the ingredients should be examined and a final acid excess of approximately 0.33 microequivalents per gram be obtained.

TABLE 3.2

Typical Reaction Conditions

	System One	System Two	System Three
Isocyanate	MDI	TDI	MDI
Initial temperature	55°C	40°C	55°C
Diol	PTMEG	PTMEG	PPG
Initial temperature	55–70°C	40°C	45°C
Final temperature	80–84°C	80°C	80°C
Hold time	1–2 hours	1–2 hours	1–2 hours

The acidity may be obtained by adding an organic acid such as benzoyl chloride or 85% phosphoric acid (see Appendix 5 for typical calculations).

3.2.3 Monitoring Reaction

The progress of the reaction can be followed in several different ways. The classical titration of the total available NCO level can be carried out. Initially, all of the NCO will be from the diisocyanate. When chain extension occurs, the NCO will be converted to urethane groups and the available NCO will decrease. The titration will have to be carried out rapidly to obtain a reasonably true result. The dry solvent used may have to be adjusted to give quick solubility. A general method is given in Appendix 6.

The reaction also may be followed by using a micro-temperature-controlled cone and plate viscometer. As the polyurethane chains increase in length, the viscosity will slowly increase. If side reactions take place, the viscosity will start to increase rapidly. This increase in viscosity is illustrated in Figure 3.4.

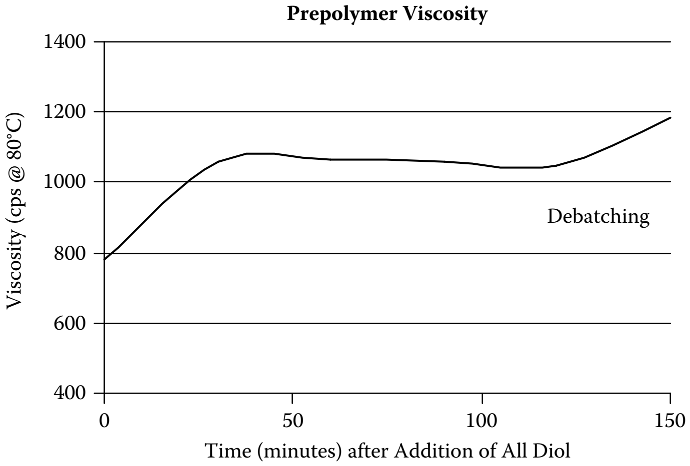

FIGURE 3.4
Prepolymer production final viscosity buildup.

Using Fourier Transform Infra Red (FTIR) spectroscopy, the reaction can be monitored. The progress of the reaction also can be followed by studying the reduction of the primary hydroxyl peaks in the mid-infrared spectra. The urethane band with the approximate wave number 1739 will be forming. The NCO band at 2273 will decrease from a maximum and then stabilize as the chain extension proceeds.

3.2.4 Prepolymer Storage

On completion of the reaction, the material (if not immediately used) must be stored in a clean, dry container. The material of construction must be able to withstand the heat of the material plus any further reheating required. If metal containers are used, they must be lined with an epoxy or similar material that is nonreactive to the polyurethane prepolymer. Any remaining air in the container must be replaced with dry nitrogen gas. All mating surfaces of the closure must be free of the polyurethane prepolymer.

3.3 Factory Preparation: Plant Production

In scaling up from laboratory size to large-scale production, the same chemistry takes place but the equipment used becomes far more complex. The capital costs are much larger and the financial consequences of a failed batch will run into thousands of dollars. There are several major components in the production unit:

- Safety considerations
- Raw material storage
- Raw material preparation
- Reactor
- Nitrogen
- Heating/cooling units
- Process control
- Vacuum
- Discharging batch
- Quality control and assurance

3.3.1 Safety

Safety requirements vary from state to state and from country to country. All local and national requirements need to be checked and taken into account

TABLE 3.3

Isocyanate Vapor Pressure Variations

Isocyanate	Vapor Pressure	Temperature
Toluene diisocyanate (TDI)	3 (10–2 mbar)	20°C
Methylene diisocyanate (MDI)	< 1 (10–5 bar)	20°C

prior to and during any large-scale production. The current MSDS for all chemicals must be available and all warnings be observed.

Isocyanates have acute and chronic safety problems. Elimination of isocyanate vapors must in the first instance be carried out by engineering methods. The ventilation of the area must be good. Transfer of the isocyanates must, wherever possible, be automated so that there is no human contact. If there is handling by humans, the proper protective equipment should be worn. The personal protective equipment must include safety goggles, vapor mask, impervious gloves, and disposable overalls. If vapor levels are expected to be high, a self-contained breathing hood must be used.

Splashes of isocyanate on the skin must be removed by copious flushing with water and then washing with soap followed by an application of barrier cream. Any splashes to the eye must be thoroughly washed out and medical advice must be obtained.

The level of isocyanate vapors in the air is specified by local authorities and refers to all isocyanates and not any individual isocyanate. Table 3.3 shows how the vapor pressure of the isocyanate varies from type to type as well as at different temperatures. Table 3.4 shows how the exposure limits vary from country to country.

Storage and production areas that contain isocyanate should have containment walls (bund) that will hold any spilled isocyanate. Spills of solid or liquid isocyanates must be cleaned up immediately. Oil-absorbent granules ("kitty litter") can be used to contain the spill and one of the following

TABLE 3.4

Occupational Exposure Limits

	Limit	Reference
TLV® (threshold limit value)	0.005 ppm as TWA; (skin)	ACGIH 2004
MAK (inhalable fraction)	0.05 mg/m^3;	
PEL (permissible exposure limit)	0.2 mg/m^3 (0.02 ppm)	OSHA
TWA (time-weighted average)	0.05 mg/m^3 (0.005 ppm)	NIOSH
	C 0.2 mg/m^3 (0.020 ppm)	REL: 10-minute
Sensitization of Respiratory Tract and Skin		*(Sah)*
IDLH	75 mg/m^3	NIOSH

or similar decontaminants used to neutralize the isocyanate. The material should be placed in a drum and allowed to react for a full 48 hours.

Liquid Decontaminant (Nonflammable)	
Water by volume	90%
Nonionic detergent (100%) by volume	2%
Concentrated ammonia by volume (specific gravity 0.880)	8%
Solid Decontaminant	
Sawdust by weight	20%
Kieselguhr, technical or China clay, or Fuller′s earth by weight	40%
Liquid decontaminant by weight	40%

If the spill is large, the staff must be evacuated and the emergency services called. All these procedures must be fully documented and the staff trained in their implementation.

Workers may become sensitized to isocyanates; therefore, they should be clinically monitored. An initial respiratory check should be carried out prior to commencement of work in the area and then at regular intervals after that.

The air around the production area must be vented out, flowing in the direction away from the workers. The isocyanate level should be monitored by an isocyanate detector such as the Remote Intelligent Sensor (RIS) by AFC International, Inc. Detector badges also can be used.

In designing a reactor, the vessel must be able to withstand both vacuum and a very slight positive pressure. The reactor must be fitted with a blow-off valve to vent any excess of nitrogen padding gas. In case the reaction runs out of control, the lid of the reactor also must be fitted with a pressure rupture disk. The fumes and product must be trapped safely.

Entry into the reactor must be strictly controlled and only carried out by suitably qualified and certified workers after complete flushing of the vessel with air. Air breathing equipment and safety equipment must be used. The power supply and feed valves must be safely isolated.

Auxiliary heating equipment such as steam generators must be maintained to the local safety requirements.

When preparing a batch of material, the reactor and the prepolymer are hot. Suitable heat-resistant gloves must be worn. It may be necessary to wear a pair of impervious gloves under the heat-resistant gloves to give both chemical and heat protection.

3.3.2 Raw Material Storage

The bulk raw materials such as polyols, isocyanates, and cleaning solvents are normally received in one of three ways:

- 200-liter drums
- 1000-liter IBC containers (intermediate bulk containers)
- Bulk delivery

The main aim of the storage is to keep the material in the same condition in which it was dispatched from the raw material manufacturer. All of the raw materials must be kept dry and away from extremes of heat. The temperature at which isocyanates are stored is of vital importance. Pure MDI needs to be kept frozen (–14°C) until just before use. This is to prevent the formation of dimers. The supplier's recommendations must be taken into account.

If 80:20 TDI is stored below 15°C, the material will partially crystallize. It can be melted again, but because the 2:4 isomer solidifies first, the material must be mixed well before use.

Chemical Incompatibilities

Small items such as organic acids (e.g., benzoyl chloride) and catalysts must be kept securely. They can be harmful if they are spilled. Their hazards include severe skin burns and damage to the eyes and respiratory systems. The MSDS for all items must be studied.

Chemicals such as ammonia, amines, and water must be kept away from all types of isocyanates, as they can react violently.

When receiving bulk raw materials, the grade of the material must be carefully checked before it is transferred to any tank. In addition to visual and paper checks, it must be impossible from an engineered aspect to add an isocyanate to a polyol tank or a polyol to an isocyanate tank, as there may be an extremely severe reaction.

General

On receipt of the raw material, the certificate of analysis must be checked. Any variations in molecular weight or NCO level must be evaluated and taken into account when the material is used.

It is good practice not to open any drums prior to use. Any partial drums should be flushed with nitrogen gas prior to resealing. All storage must work on a first-in, first-out basis.

The storage area must be secure and have large enough bunded (diked) areas to hold the material if a leak develops. Heating must be provided to the tanks if the local conditions are such that the material may become too cold. This could result in the material's being too viscous to pump or crystallization to take place.

3.3.3 Raw Material Preparation

Prior to the commencement of any production, all state and local regulations must be adhered to, as the operations may be hazardous from both a mechanical and chemical aspect. Safety and emergency protocols must be drawn up and checked out. All safety equipment must be thoroughly checked before commencement of any work.

The raw materials used must be kept in clean, dry surroundings at an appropriate temperature. The fitting used for isocyanates and polyols must be noninterchangeable. This is to prevent any unexpected reactions from taking place with drastic consequences.

The quantity of the raw materials kept in stock must be a function of both the straight economic cost and the storage life of the materials. The disposal cost of emptied containers must be taken into account. Many containers cost money to dispose of in a safe and legal manner, especially those that have contained isocyanates.

For all raw materials, the current Material Safety Data Sheets and any other handling and storage information must be obtained from the raw material supplier, studied, and kept on hand. The recommendations contained in this data must be complied with.

Raw materials received in damaged containers must be isolated and rendered safe as soon as possible. Wearing full protective clothing, workers must lay drums with a puncture hole in the side (e.g., from a forklift prong) on their side with the hole on top. The hole can then be sealed and any spilled material neutralized. The pressure in a drum with a bulging end must be carefully released, taking all precautions. The material should be returned to the supplier for correct disposal.

Bulk supplies of liquid isocyanates and polyols must be delivered into their own bulk storage containers. The size of the tank must be large enough to take the new consignment, allowing for some of the previous batch to be present. There must be sufficient ullage to cover temperature expansion. Guidelines for the receipt of bulk TDI are given in supplier and organizational guidelines (Alliance for the Polyurethane Industry, 2002).

The tanks must have a regulated nitrogen gas pad to prevent any moisture from entering and reacting with the material. A pressure relief valve must be built into the system to enable excess pressure to be relieved when the tank is being refilled or the material becomes hot.

If the ambient temperature falls too low, gentle heating must be provided to the tank to keep the material liquid. TDI starts to crystallize at 15°C (Huntsman International, 2000). The lines to the processing reactors also may have to be heated. A low temperature may cause the material either to become too viscous or to freeze. The transfer pump must be set up to be able to recirculate the material to help keep the temperature constant.

The isocyanate and polyol storage units must not share pumps or any fittings. The fitting must be such that there is no way that the wrong material can be added to a tank. All tanks must be clearly labeled with their contents and the appropriate safety signs, for example, isocyanate hazard signs. Most regulatory authorities will require the tanks to be in a suitably sized bunded (diked) area.

The transportation and storage of pure MDI must be carefully controlled. For transportation between a depot and the factory, the MDI may be kept at –18 to –4°C for up to 2 days. For long-term storage of approximately 300 days, the MDI must be held at –18°C. This is the total of the warehouse and factory storage times. If MDI has to be held in the liquid form, it must be kept at 43 to 48°C for a maximum of 4 weeks. These requirements are to reduce the formation of dimers.

The most commonly approved method for melting solid MDI prior to use is a drum roller in a steam (Dow Chemical Company, 1990) or hot air (BASF Corporation, 2000) atmosphere. Requirements are:

- Drums free from dents
- Previously opened drums flushed with nitrogen gas (dew point −40°C)
- All bungs tightly closed
- Rolling speed 5 rpm
- Atmospheric steam pressure or hot air
- Normal time to reach 70°C briefly 4 to 5 hours

The aim is to melt the material quickly but evenly with the least formation of dimers.

Polyol can be either a liquid or a semisolid at ambient temperature. These materials will have to be kept in heated bulk containers. Drum stock will have to be melted in a similar manner to pure MDI. To ensure that the material does not absorb moisture from the air, the drums must be blanketed with nitrogen and the bungs properly closed. Table 3.5 shows the melting range of some common diols.

The higher the molecular weight, the higher the melting point and the more viscous the material. The polyol needs to be heated to provide a good flow of material and to have no tendency to solidify in the feed pipes. A maximum temperature of 70°C is normally recommended to prevent too high an exotherm.

Stabilizers are added to the system to prevent side reactions and gelation. The aim is to have the final system very slightly acidic (0.33 microequivalents

TABLE 3.5

Melting Range of Some Common Diols

Diol Type	Molecular Weight	Melting Point (°C)
Esters		
Polyethylene adipate glycol	1000	45
	2000	50
Ethers		
PPG	4000	Liquid at ambient
PTMEG	1000	14–23
	2000	26–30
Caprolactones		
Polycaprolactone glycol	830	35–45
	2000	45–55

per gram). The two most popular materials are benzoyl chloride and 85% phosphoric acid (see Appendix 5 for calculations). The degree of alkalinity of the polyol will depend on the chemistry of the polymerization. If an alkaline catalyst such as potassium hydroxide is used to make the polypropylene glycols, the alkalinity may be relatively high. Some new polyols, such as the Bayer Acclaim® (Bayer Material Science LLC, Pittsburgh, Pennsylvania) range, have some phosphoric acid added.

For the best effect, the stabilizers must be added to the reactants before the point of acid/base equilibrium is reached. Catalysts are normally not added to the prepolymer, as they may be rather basic and may cause the reactions to proceed too swiftly.

3.3.4 Reactor

Design

A typical reactor is illustrated in Figure 3.5. The reactor needs to be built from a grade of stainless steel that can withstand mild acidic conditions. Traces of hydrochloric acid may be present in the isocyanates and in some cleaning solvents. The side and bottom of the vessel must be fitted with either heating coils or a suitable jacket. Depending on design considerations, the jacket may be either plain or dimpled. If at all practicable, the lid should be completely removable. This is important for major cleaning or if a batch should gel. It does, however, make the maintaining of positive pressure or vacuum more difficult.

The lid of the reactor will have ports to cover the following functions:

- Isocyanate in
- Polyol in
- Outlet port
- General purpose port (for minor ingredients)
- Nitrogen in
- Vacuum
- Pressure rupture disk
- Low-pressure relief valve
- Pressure gauge
- Recycle port (if needed)
- General viewing (entry manhole)
- Agitator gland

Thermocouple probe pockets also need to be fitted. Their location needs to be in conjunction with the design of the agitator and the need to obtain, as accurately as possible, the true temperature of the prepolymer as it is

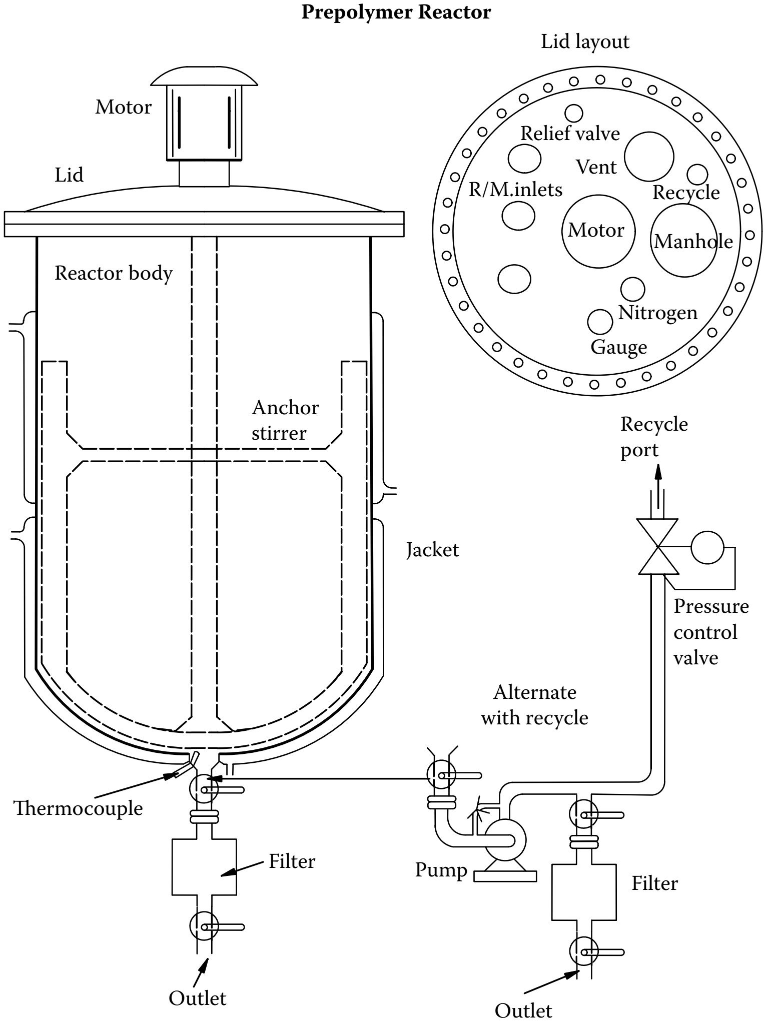

FIGURE 3.5
Factory prepolymer reactor.

being made. The lowest probe must be low enough to measure the temperature of the initial isocyanate that is added to the reactor.

The main outlet of the vessel should be at least 75 mm in diameter to allow for a fast flow of the prepolymer. The outlet can be connected either to a recirculating pump or directly to a filter prior to the drum filling. The pump must be capable of pumping the most viscous material quickly. Another key point to be noted when selecting a pump is that it has to have suitable glands. It also must be able to withstand the cleaning solvents and be readily stripped for clearing any buildup in the pump.

Because of the physical size of the reactor, it is normally mounted with the top of the reactor at a mezzanine floor level. This allows easy access to the inlet ports. The reactor can be mounted at this point on a number of load cells. The load cells must be of such capacity to take the whole weight of the reactor when it is full of prepolymer. In this case, all connectors to the reactor must be flexible.

Agitation

The agitation of the material is important, as quick and efficient mixing is required to allow the reaction to proceed correctly. The speed must be such that a vortex is not formed and gasses entrapped into the mix, because they would need to be removed at a later stage. Anchor-style mixers have proven popular in this application.

Keeping the walls clean of buildup is important, because buildup would cause heat transfer problems as the production proceeds. The polyurethane prepolymer builds up in viscosity as the chain length increases and tends to hang onto the wall of the reactor. The heat of the wall will increase the speed of the reaction and hence increase the reaction rate and viscosity. Viscosities in the reactor will be generally between 30 and 4,000 MPa.s at a temperature of approximately 90°C.

The surface of the agitator must be as smooth as possible to prevent unnecessary hang-ups but also must be strong enough to take the torque required. The design and sizing of the motor are best carried out by a company that is experienced in these matters.

As the unit will work under vacuum and a slight pressure, the sealing gland must be able to take both vacuum and pressure. As polyurethane is a very effective adhesive, the seals must be readily replaceable. If a mechanical seal is used, great care must be taken to prevent any product from coming onto a contact surface.

Dispensing Ingredients

The addition of the correct quantity of each ingredient is important. The dispensing equipment must be suitably sized to cope with the various weight ranges involved.

The entire reactor may be mounted on load cells and the weight indicated on a visual display with outputs to logging and other control units. The weight of the reactor with agitator and motor may be on the order of tons. The weight of the heating and cooling jackets also must be taken into account. If a combined heating and cooling system is used, there will be a difference if the jacket has steam, condensate, or water in it. The initial isocyanate may be weighed directly into the reactor and any acidity controlling agents separately added by volume or by weight using a more sensitive weighing system.

The system for dispensing the polyols must be flexible to enable both the rate and the quantity to be varied. The addition of the polyol may have to be slowed down or stopped and restarted if the reaction becomes too vigorous and the temperature increases. As the addition will be over 1 to 2 hours, it is also important to keep the temperature of the polyol constant.

3.3.5 Nitrogen

Nitrogen is used to blanket the reaction and the raw materials to stop the absorption of moisture and to prevent oxidation of the product. The dew point of a gas is the temperature at which the water vapor present in the gas saturates the gas and begins to condense. Dew points of below 0°C are sometimes called the hoar-frost point. Industrial-grade nitrogen gas normally is dry enough for use.

In these applications, nitrogen is needed in volume but at a very low pressure, slightly above atmospheric. The supply must be set up to prevent overpressurization of the containers. Suitable pressure relief valves must be installed to vent any excess pressure. The three main routes to supply nitrogen to the system are:

- Compressed gas cylinders
- Evaporated liquid nitrogen
- On-site preparation

Compressed gas cylinders have the lowest capital cost of the three systems. Cages of four or more cylinders are supplied as a group and the system connected to the cylinder manifold. The gas cylinders are supplied at a high pressure and the gas has to be reduced to just above atmospheric pressure for use.

Liquid nitrogen is stored in large vacuum vessels (cryostats). The liquid nitrogen is evaporated through a heat exchanger and the gas used in the factory. The units are normally supplied and maintained by the gas company. The cryostats can be easily topped up by a road tanker. This system is more economic in medium to large units.

Dried compressed air can be passed through molecular sieve tubes, where the nitrogen is separated from the oxygen and inert gasses present in the air. The advantage of this system is that the production of the nitrogen is on site. The rate of take-off will affect the final purity of the gas. The units will have to be sized for the application. A buffer may have to be built into the system. This means that output from the unit is compressed into gas cylinders to buffer the peak demand. Nitrogen is an "on cost," but it is of vital importance for a quality product. Removal of air from the reactor by vacuum will save on the use of nitrogen to replace all the air.

3.3.6 Heating/Cooling

The temperature of the reactor needs to be controlled for several vital steps in the reaction:

- The reactor needs to be brought to the start temperature.
- The isocyanate needs to be heated to the initial temperature.
- Heat must be available to raise the temperature to the final holding temperature.
- Cooling must be available to cool the reactor if the temperature rises too high.

Heating also may be required to keep the polyols fluid and to melt pure MDI if used.

There are two major alternatives in the heating, namely, steam or a heat transfer medium such as Dowtherm® (Dow Chemical Company) heat transfer fluid. The system must be such that the heating medium must be rapidly replaced by a cooling medium. The switching must be on a fail-safe sequence.

If steam is used for heating, all pressure must first be vented safely prior to water being used to cool the reactor. Steam is introduced at the top of a jacket and the condensate released from the bottom. Water normally flows from the bottom to the top. The moist air needs to be vented prior to circulation.

If a pump is fitted to the discharge of the reactor, it can be used to fast-circulate the hot prepolymer through cooling tubes to rapidly reduce the temperature. When the temperature probes indicate a too-rapid temperature rise, the addition of polyol must be slowed down immediately. If the temperature still rises too quickly, the addition of the polyol must be stopped until the temperature is brought back under control. The temperature probes must be positioned so that the temperature of the prepolymer indicated is unaffected by the wall temperature of the reactor. A second thermocouple positioned elsewhere in the reactor can be used to detect runaway reactions.

Dow Chemical Company (1990), in their pamphlet on prepolymer production, gives a formula to calculate the total heat given off by the instantaneous reaction of polyol with an isocyanate. Figure 3.6 indicates the instantaneous heat rise generated when polyols of different molecular weights are reacted with TDI and MDI. The slow addition of the polyol will allow heat to be dissipated, and thus the full rise in temperature will not be realized.

3.3.7 Process Control

The aim of the factory production is to produce, as economically as possible, a consistent product with the specified properties. The key points in achieving this are:

- The correct weight of each ingredient added
- The addition in the correct order

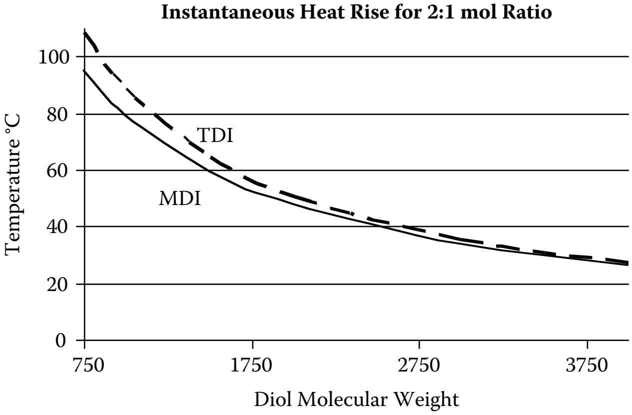

FIGURE 3.6
Instantaneous heat rise on mixing isocyanates and diols.

- The rate of addition correct
- The heat history of each batch the same
- Minor variations in raw material values accounted for

A set procedure for each grade must be set up and strictly adhered to. For normal quality assurance, the weights, temperatures, and times must be logged. The degree of sophistication of each plant can vary from a purely manual system to a computer-controlled, fully automated unit.

Temperature control is normally carried out using thermocouples in a stainless steel pocket. The type of thermocouple used is either a platinum resistance detector (RTD) or a thermocouple using two dissimilar metals that produce a voltage (EMF). The indicators for these thermocouples must match the probe type and grade. The positioning of the probes is very important as well as any lag (delay) in the system. The output from the probe is connected to the indicator and/or controllers. Most indicators have at least a set point with an on/off output. The more advanced units will allow anticipated switching, more than one set point, temperature ramping between temperatures, time, and hold facilities. Thermocouple break and over-temperature alarm outputs are also commonly provided features.

The output from the temperature controller can be fed into control valves, either on/off or proportional, or into a PLC, which can be programmed to turn off the polyol feed and heat and start the cooling cycle.

The amount of material added can be measured by either weight or volume. If the material added is by weight, the size and capacity of the scale must be taken into account. Electronic scales are based on the number of counts in a given range. Typical figures may be 1 in 3,000, 1 in 10,000, or 1 in 20,000. For a given range, these will control the readability of the scale. The control is illustrated in Table 3.6.

TABLE 3.6

Readability of Scale Ranges

	Count		
Load Cell Range	**1:3000**	**1:10000**	**1:20000**
0–300 kg	0.1 kg	0.03 kg	0.015 kg
0–1000 kg	0.3 kg	0.1 kg	0.05 kg
0–6000 kg	2.0 kg	0.6 kg	0.30 kg

Scales currently used are usually based on load cells. Modern weight indicators/controllers have outputs that can be connected to valves that control the flow of the material. Batch weights can also be stored in some units.

When the material is measured out by volume, the density of the feed must be known, as the weight is a direct function of the density and volume.

$$\text{Density} = \text{weight/volume} \quad \text{or} \quad \text{Volume} = \text{weight/density}$$

The density at any given temperature will have to be obtained either experimentally or from the raw materials supplier.

3.3.8 Vacuum

Reducing the pressure of the reactor serves three main purposes:

- Removal of moist air/gasses from the reactor
- Removal of isocyanate vapors after the batch is complete
- Removal of any gasses in the prepolymer

The reduction of pressure in the reactor will decrease the boiling point of any unreacted chemicals in the batch. This is increased with elevated temperatures. Care must be taken to prevent foaming. Apply the vacuum slowly and release if required to break the foam.

Direct contact of the isocyanate vapours to the pump must be avoided. The fumes must be frozen out with a liquid nitrogen trap and/or a trap containing a plasticizer such as Messamol or a phthalate plasticizer.

The resistance of the materials of construction and the seals of the pump must also be resistant to isocyanate vapors. The final exhaust fumes must be vented well away from all operations. Valving must be installed to prevent pressure in the system from being forced into the vacuum system.

3.3.9 Discharging Batch

When the batch is complete, the material must be discharged as soon as practical into the dispatch container. The viscosity at this point will be low to assist in flow.

The drums must be clean and dry before being filled. The inside of the drums must be coated with either a phenolic or epoxy resin to provide resistance against attack from the prepolymer. The wall thickness must be sufficient to prevent collapse due to a vacuum being formed as the material cools and contracts. Prior to sealing the drum, nitrogen should be introduced into the free space in the drum.

IBCs (intermediate bulk containers) must be clean and dry and made from material that can resist the temperatures when filling the container. The discharge temperature may have to be lowered to cope with the initial temperature of the prepolymer.

If a recirculation pump is fitted to the reactor, the material may be discharged from the pump circuit. The valving must be such that the material is recirculated when not being discharged. Pressure relief valves also must be fitted to the pump.

The prepolymer also may be discharged by gravity into the container. Nitrogen gas pressure may be used to assist the flow of prepolymer.

The prepolymer is dispersed by weight into the containers. The scales used must be trade certified and filled to the specified weight. This may be carried out either manually or automatically with controlling output from the scales.

Depending on the smoothness of the reactor and heat uniformity, solid polyurethane is sometimes formed and may be discharged with the material. These lumps must be removed by passing the material through a free-flowing filter. The filter material must be resistant to both the temperature and prepolymer. Polypropylene filter material has been successfully used. The filters must be cleaned after use.

The reactor needs to be kept clean to keep the heat transfer optimal and to prevent solid material in the prepolymer. The method employed is to use an appropriate solvent such as methyl ethyl ketone (MEK), methylene chloride, or m-pyrol (NMP). To prevent an explosive vapor mixture from being formed when the solvent is added to the reactor, the air must be replaced by nitrogen gas. The solvent needs to be heated to just above its boiling point and kept there until the solid material has been softened and removed from the metal. A second rinse with clean solvent may be needed.

As this process is an "on cost" to production, the cleaning must be done in a manner to keep the costs down while still maintaining quality. Dirty solvents can be reused until they will not clean efficiently. The solvents must be kept dry to prevent the dissolved prepolymer from coming out of solution. All final waste material must be disposed of in accordance with local regulations.

3.3.10 Quality Control and Assurance

The process of producing a prepolymer is one of adding two or more liquids together under controlled conditions to obtain a prepolymer. To maintain the quality of the product, the following areas need to be addressed and controlled:

- Raw materials
- Process instrumentation
- Process conditions
- Final tests

The raw materials need to be of a suitably consistent quality and maintained in the same quality as they were received. Every effort must be made to prevent the ingress of moisture into any raw material. The moisture content of the major raw materials should be 0.05%, or preferably less than 0.03%. Manufacturers' certificates of analysis must be obtained for all materials purchased and the values used to make fine adjustments to the batches. In-house confirmation of quality of the raw materials may include:

- FTIR confirmation of identity of raw material
- Moisture analysis by the Karl Fischer method
- Viscosity–capillary method or spindle viscometer
- Hydroxyl number (for polyols)
- Isocyanate content (for isocyanates)
- Acidity (pH, 10 percent neutral alcoholic solution or titration)

With the widespread acceptance of the independently assessed ISO 9000 scheme, many companies will accept the analysis of the raw material supplier. Once the quality and consistency of the raw material are proven, only vital tests may be carried out. Because of the moisture sensitivity, opening and sampling of the drums may lead to faulty material if the drums are not properly resealed. The three vital control instruments are:

- Weight
- Temperature
- Time

The weights of the raw materials added must be recorded either manually or by printout from the scales display unit. The weighing units must be regularly checked and recalibrated if needed. The capacity of the scale must be of a suitable size for the material being added. The low quantity of acid adjustment material needed requires the use of a lower total capacity scale.

If the liquid materials are being volumetrically pumped in, the amount must be correct for the temperature of the material to obtain the correct weight.

The basic position of the temperature probe will be determined in the construction stage of the reactor. The correct function of the actual probes must be checked on a regular basis. The actual temperature may be randomly checked by using a noncontact infrared thermometer. The time/temperatures obtained must be either recorded manually or logged automatically from the temperature controller. The point of any addition changes must be noted.

If the batch is produced on a manual system, more detailed readings and times need to be added to the batch sheet. With minimal equipment the weight and temperature instrumentation will provide either hard copy or computerized records of the time, temperature, and weight of each batch. If a batching controller is used, the program for each grade must be routinely verified for a continued lack of corruption or unauthorized change.

Prepolymer production is a time-dependent operation that reaches an optimum point, after which the properties are reduced. The production control must be such that the critical parameters of temperature and time are closely monitored.

The prime control is the viscosity of the material. This is best carried out using a temperature-controlled cone and plate viscometer. The sample volume needs to be small to allow quick stabilization of the material to a temperature of 23°C. A secondary test to determine the NCO content using a titration method based on that given in Appendix 6 must be carried out as rapidly as possible.

The day after production, more extensive tests can be carried out to confirm the quality of the batch. The tests must be carried out by approved local or international methods (e.g., ISO or ASTM). Final release of the prepolymer is based on these results and the data obtained during the production of the prepolymer.

3.3.11 Typical Process

The general procedure to produce a batch consists of several steps:

1. Prepare the batch card.
2. Program the batch controller if used.
3. Check that the reactor is clean.
4. Bring the raw materials to starting temperature (MDI may need to be melted).
5. Turn on the reactor heating and bring to the starting temperature.
6. Check all the valves for correct functioning.
7. Flush reactor with nitrogen.
8. Weigh in the isocyanate and record weight.
9. Bring the isocyanate to start temperature (40 to 50°C).
10. Adjust acidity if required and record amount.
11. Slowly add polyol(s) over 1 to 2 hours.
12. If temperature rises too rapidly, slow down or stop polyol addition.
13. If temperature goes above 85°C, stop polyol addition and start external cooling.

14. After all the polyol is added, slowly ramp the temperature up to the end temperature and keep it at this level while the reaction comes to completion.
15. Apply vacuum to reduce isocyanate vapors and entrapped gasses.
16. Monitor viscosity and NCO levels over final period.
17. When the viscosity is correct (and NCO, if tested), discharge the batch under slight positive pressure. Label batched material.
18. Proceed with second batch if required after reducing reactor temperature, or else clean reactor and valves.
19. Test the prepolymer fully prior to release.

3.4 Quasiprepolymers

Polyurethane systems can be produced to have near-equal or easy mixing component ratios (by either weight or volume). The prepolymers in this type of system are called quasiprepolymers. Quasiprepolymers are normally taken as having at least a fourfold molar excess of isocyanate in the isocyanate side of the system. The other side contains the remainder of the polyol, curative, and any catalysts.

The preparation of the isocyanate side is similar to that of a standard prepolymer, with the difference being that only some of the polyol is reacted with isocyanate. All handling procedures are the same as for the normal prepolymer except the application of a vacuum at the end of the reaction. As there is an excess of isocyanate in this side, the exotherm is generally not as large as for a full prepolymer. Viscosity and NCO checks need to be carried out.

In the United States, the isocyanate side is called the "A side." If the material comes from Europe, the reverse is true and the material may be called the "B side." Care must be taken and the appropriate checks made.

In the preparation of the polyol or "B side," the curative is dissolved in the remainder of the polyol. Care must be taken that the curative (often BDO) is fully soluble in the remainder of the polyol at all temperatures. It is essential to examine the material over time to check for any phase separation. Manufacturers provide solubility data for BDO in various polyols, but it is best to check your own system.

Depending on the temperature at which the material is processed, various amounts of a metallic catalyst are added. Tin-based catalysts, such as Air Products T12, catalyze the OH-NCO reactions. The metallic catalyst increases the total reaction speed but also equals out the reaction rates of the high molecular polyols and the low molecular polyols. Bismuth catalysts are now preferred to the previously used mercury catalysts. Polyether polyols are slow in reaction, and both a tin and an amine catalyst may be needed to obtain the best speed and properties.

3.5 One Shot

With the use of suitable catalysts, it is possible to produce a polyurethane product in a single step. This involves the mixing in the correct ratios of the polyol(s), isocyanate, catalyst, and any pigment and plasticizer.

A major problem is the exotherm that is given out in the reaction. The heat generated must be removed in the molding. The total amount of heat given out is the sum of the heat from the initial prepolymer reaction and the final chain extension stage. This leads the process to be used in relatively thin-walled products.

The major problem is to have all the materials at the correct temperatures and the flow rates set correctly. The machine must be purged until the mix is constant and correct. Figure 3.7 illustrates the ingredient flow in the one-shot method.

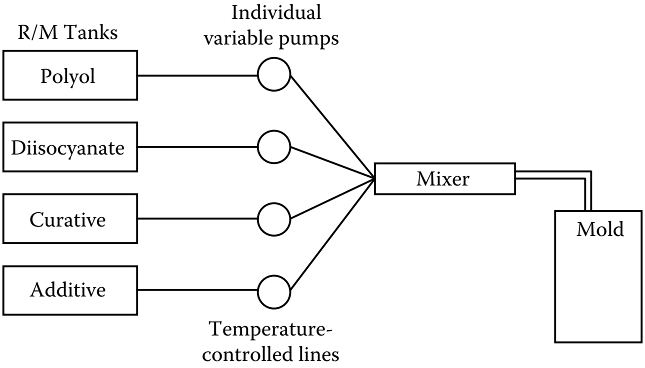

FIGURE 3.7
Ingredient flow in one-shot polyurethane production.

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4

Hand Processing

4.1 Introduction

4.1.1 Process Definition

The production of solid polyurethane parts of the correct engineering quality requires the conversion of either the prepolymer or quasiprepolymer to a solid material. The grade and chemistry of the material must be carefully considered in order to obtain a material that can be reproducibly processed and that has the correct final properties. The correct application of heat also must be used to obtain the best product.

4.1.2 Importance of the Process

Curing—or, more correctly, chain extension—is required to convert the material from a semisolid or liquid into a solid material that possesses elastomeric or rubbery-type properties. The definition of an elastomeric polyurethane is that on the application of a strain, the material will stretch, and when the strain is removed it will rapidly return to approximately the original length. This increase in length should be less than 1%. In the case of fully cured polyurethane, the material is normally very tough and the extension can only be made by a machine. In a thin sheet, it may be illustrated by folding it double and then letting it snap back. The three main groups of polyurethanes are:

- Thermoplastic polyurethanes
- Castable polyurethanes
- Cross-linked polyurethanes

Thermoplastic polyurethanes are normally processed in conventional plastic machines and when heated to above 120 to 150°C will soften and can be processed. By definition, this process can be repeated over and over. The TPU is supplied as a polymer chain extended to a suitable length with terminal groups that do not allow any further chain extension.

Castable polyurethanes are supplied as a prepolymer with an active terminal isocyanate group to the polymer chain. These isocyanate groups are reacted with either a diamine or a diol. Alternatively they can be supplied as a quasiprepolymer, the prepolymer is made and the chain extension carried out at the same time. As the chain becomes longer the viscosity increases, and at a certain point it becomes a solid. On further heating, extra strength is developed by a type of physical chemical bond (hydrogen bonding). In castable polyurethanes, the actual chains will break down on heating before the physical chemical bonds give way. The material therefore cannot be re-formed after the chain extension is complete.

In cross-linked polyurethanes, there are actual chemical bonds formed in a three-dimensional manner. The main difference is that with the castable polyurethanes the actual chemical structure consists of two major zones, a hard zone and a soft zone. This is not as pronounced in the cross-linked polyurethanes. A typical example is the addition of TMP (trimethylol propane) to polyurethane to make it softer. This curative will make the material much softer as it breaks the hard segment zoning up to a certain degree. They do, however, give a material with improved compression set properties.

4.1.3 Changes in Material Properties Before, During, and After Curing

The process of curing polyurethane elastomers depends to a large degree on initially having a material with a reasonably low viscosity. This is to allow the flow of the material into the mold and the ability for any entrapped air to rise to the surface. Once the mold has been filled and the air allowed to escape, the increase in viscosity should be rapid to prevent excessive leakage through any parting lines in the mold.

Heat plays an important part in the curing of polyurethanes. The reaction itself gives out heat, so this must be taken into account in determining the temperature of the mold. The mold should be at the maximum temperature the curing prepolymer will reach. An MDI-based system will release heat more rapidly than a TDI-based system; therefore the mold has to be hotter than when using a TDI-based material.

It also must be noted that there is a certain amount of shrinkage because of the actual reaction. The harder the fully cured polyurethane, the more the final shrinkage will be.

During the curing process, the material builds up a degree of strength. The strength after several hours is usually sufficient to allow the product to be removed from the mold without any damage to it. At this point full mechanical properties have not yet developed. Further heating of the material at 80–100°C for 16–24 hours is required for all the properties to be fully obtained. The purist of the polyurethane processors will maintain that the polyurethanes should then be rested at room temperature for 1 to 2 weeks for the ultimate in properties. The explanation for this is that the polyurethanes will slowly absorb water from the air, which will assist the formation of very strong bonds.

4.1.4 Stages of Curing and Factors Affecting Cure

Prepolymer Curing or Chain Extension

The prepolymer as received from the manufacturer has a simple chain that has been terminated with an isocyanate. The isocyanate ends with this magical NCO group. The NCO is the reactive part of it. The higher the percentage of NCO in the prepolymer, the harder the material will be. An 80 Shore A will have an NCO of approximately 3.1 to 3.2%, whereas a 75 Shore D will have an NCO content of about 11.2%. To obtain the chain extension, one must add an appropriate amount of an amine or diol curative. For every curative, there is a different amount that must be added. The manufacturers of the prepolymers and curatives will give the appropriate factors for mixing the polyurethane. The prepolymer must be heated before use. This is to reduce the viscosity of the material as well as to obtain the correct cure rate and complete cure time.

The amine and the prepolymer each have two available sites for reaction. The amine will react with one isocyanate (NCO), and then the second amine will react with another isocyanate. This reaction will in effect double the length of the chain. The reaction will continue until all the amine has been used up. As the chains become longer they become more entangled and the viscosity of the material increases. At a certain point, some order begins to appear in the mixture, and the hard segment areas all tend to agglomerate into a group and the soft or body section of the prepolymer remains separate. These agglomerated areas form hydrogen bonds and begin to give the material strength. Careful experimentation will show that after 2 to 3 hours, 95% of the available isocyanate groups have been used up (at 80°C). After 14 to 16 hours, more than 99% have been used up.

The final properties of the polyurethane can be enhanced by using slightly more or less than the theoretical amount of curative needed to react with all the available isocyanate groups. Table 4.1 details the changes in properties with respect to the level of curative.

The theoretically calculated value of the amount of curative needed to react with all the available isocyanate is called the 100% theoretical, or stoichiometric, value.

Quasiprepolymers (Cold Cure Materials)

One of the major advantages of quasiprepolymers is the ability to produce parts using a system with very even mixing ratios. The reduction in errors when using small quantities of highly hydroscopic materials such as BDO is very important. Unless prepared in-house, the disadvantage is that the chemistry is controlled by the manufacturer of the system.

When using these systems, one must always ensure that both sides are individually very well mixed prior to the final blending. The manufacturer of the system will make every effort to ensure that the components are all fully soluble in each other, but on occasion, they will separate out.

TABLE 4.1

Property Changes with Different Curative Levels

Property	Effect of Changes in Mixing Ratios
Physical Properties	
Hardness	Remains unchanged between 85–100% theory
Tensile strength at break	Maximum physical properties are achieved between 90–95% theory
Modulus	Stable; minor change over the range of 85–100%; decrease outside this range
Elongation	Maximum elongation at 100–105% theory
Tear strength	Maximum properties at 100–105% theory
Compression set	Best at 85–95% theory
Dynamic Properties	
Flex life	Maximum property at 100–105% theory
Abrasion resistance	Remains relatively unchanged between 85–105% theory, although 100–105% is the best
Resilience	Maximizes at 85–90%; slight decrease above this range
Hysteresis, dynamic mechanical	Low percent stoichiometry is preferred
Other	
Heat resistance	Best at 85–95% theory

When these materials are processed, two reactions take place. The polyol side will react with the isocyanate, and the curative will extend the polymer chains to their maximum length.

4.2 Introduction to Molding Process

The distinction between advantages and limitations of batch and continuous processes is given in Table 4.2. Continuous processing machines allow for the dispensing of many small items, with the output being stopped for a

TABLE 4.2

Comparison between Batch and Continuous Processing

Batch	Continuous
Low capital cost	Cost of machine $40,000+
Able to change grades rapidly	Suitable for long runs on one grade
Minor variations batch to batch possible	If machine running well, uniform quality
Large job requires many batches	Continuous pour (within limitation of machine)
Manual process	Process can be automated
Operators more exposed to chemicals	Can be completely self-contained

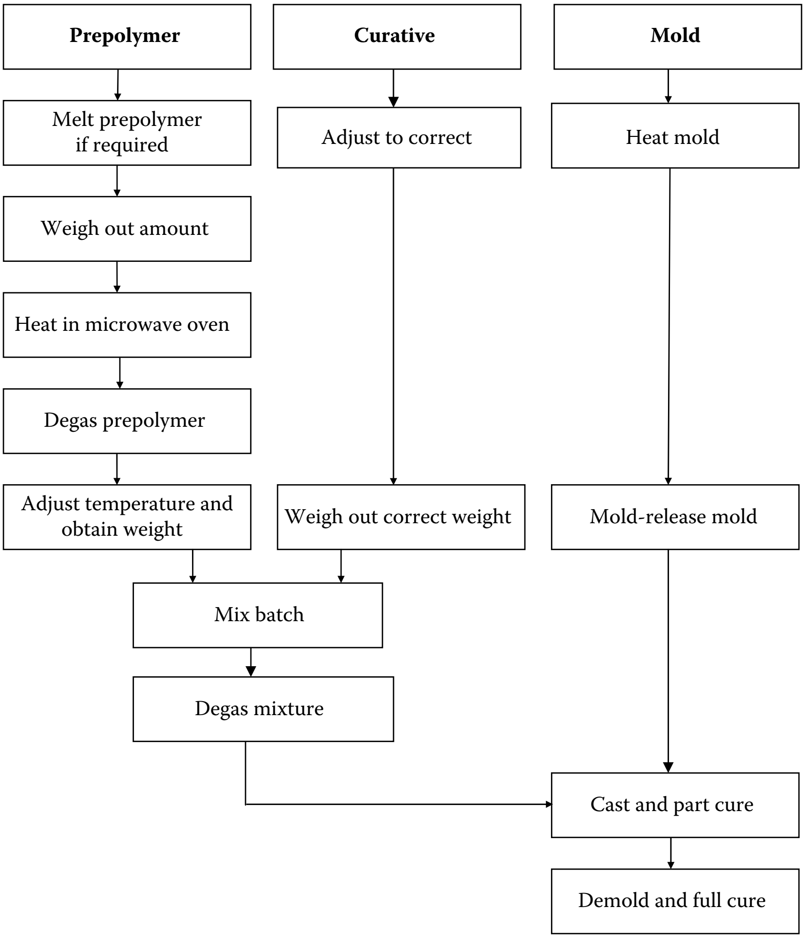


FIGURE 4.1
Hand casting of polyurethane elastomers.

short period in between each mold. The maximum size pour is dependent on the size of the feed tanks.

Hand casting of polyurethane elastomers is summarized in Figure 4.1, and more details are given in subsequent sections. Before commencing any casting operations, the people involved must be fully conversant with the health and safety requirements of the operations that they are about to carry out. They must be familiar with the MSDS details of all products being used as well as the engineering and personal protective equipment required. There are seven main steps in hand-casting polyurethane parts:

- Prepare and mold-release mold.
- Preheat prepolymer if required and degas.
- Add pigment and any other additive to prepolymer.

- Prepare curative.
- Mix prepolymer and curative.
- Pour into mold where curing will commence.
- Trim article and fully cure molding.

4.2.1 Prepare Mold

Molds must be checked for damage prior to use and preheated to a temperature equal to the maximum that the exotherm will reach when the prepolymer and curative are reacted together. If required, a thin coating of mold release is applied to the mold to assist in the demolding process. It is often found that more that one release can be obtained from the mold that has previously been prepared.

4.2.2 Preheat Prepolymer

The prepolymer must be melted so that all solid material is liquid. (A lump of unmelted prepolymer is sometimes seen in the middle of the drum.) It must be remembered that excessive heating irreversibly ages the material. Once a drum or pail has been melted, it can be kept in that state by keeping it in a warm spot in the factory. The prepolymer can be weighed out and heated in a microwave or conventional oven to the required temperature. The material should be degassed under a high vacuum prior to use. This helps to remove any gases and moisture in the material. If the material is very foamy, breaking of the vacuum during the operation will help. Manufacturers will provide material that is both very dry and gas free. For articles that are noncritical, this step is often left out. The operator must ensure that it is safe to eliminate this step.

4.2.3 Add Pigment or Other Additive

If required, pigment and any other additive may be added and predispersed. The pigments used must be in a dry, nonreactive medium. If the pigments are dispersed in a polyol, the paste may absorb moisture and will react with some of the isocyanate groups. Some yellow pigments need to be added to the prepolymer prior to its final heating, as they disperse poorly.

4.2.4 Prepare Curative

Curatives may be either solid or liquid at the processing temperature. Solid curatives such as MOCA or MCEDA are normally melted under controlled conditions prior to use. The manufacturers' recommendations must be taken into account as to the temperature to which the material is heated. Excessive heating can cause breakdown of the materials, which is dangerous from a health and technical point of view. MOCA, if heated to 140°C, will start to decompose and give off dangerous fumes. The molten curatives can cause severe burns to the skin and absorption into the blood stream.

Solid curatives may be dissolved in a liquid solvent to eliminate handling of the hot molten material. The solvent may be a nonreactive plasticizer such as a phthalate (for example, DIOP) or an ester such as a benzoate (for example, Benzoflex 9–88). These will soften the product but not take part in any reaction. If a diol or triol of high molecular weight is used, it will take part in the curing reaction. The equivalent weight of the system must be taken into account when calculating the weight of curative required. In both cases, the hardness as well as the physical properties will be changed.

Liquid curatives are sometimes very hygroscopic, and great care needs to be taken to prevent the absorption of moisture vapor from the air. The material needs a constant blanket of nitrogen, and, if required, dried molecular sieves to keep the material dry.

4.2.5 Mix Prepolymer and Curative

Mixing tools used should be of dry, impervious materials. Wood is not considered to be a good mixing tool material. The mode of mixing should be such that there is a minimum of air entrapped in the blend. The mixing may be in either a figure of eight or a zigzag motion across the container (see Figure 4.4). The sides and bottom of the container must be scraped to help remove the prepolymer from the walls and bottom of the container. There must be no swirl lines in the blend when the mixing is finished. These lines represent bad dispersion. If power mixing is used on large batches, the mixing head must always be immersed and the speed adjusted to prevent inclusion of an excess of air. If air is introduced into the mix and there is sufficient time, the mix may be degassed for a second time. The mixing technique must be adjusted to add the minimum amount of air that is possible.

4.2.6 Cast into Mold

Once the prepolymer and catalyst are added together, the chain extension (curing) reactions will commence. The time taken to mix must be carefully monitored. It must be sufficient to allow complete mixing, but there must be enough pot life left to allow pouring into the mold while the material is at the lowest viscosity possible. This is to allow the polyurethane to fill the mold completely and any entrapped bubbles to reach the surface.

Polyurethanes tend to trap air very easily. The method of pouring must be such that the mix will flow down a surface and across the bottom and fill the mold upward, displacing the air ahead of it. The pouring should be in one continuous stream. It may be advantageous to raise the height slowly during the pour to improve the flow of the material into the mold.

Any exposed bubbles may be gently popped using a soft gas flame or a hot air gun. The heat source must be used to a minimum and kept moving to prevent damage to the surface.

When the material has gelled sufficiently for the mold to be moved, it should be placed in an oven heated to the curing temperature for the initial curing to take place. The reaction proceeds and the structure begins to develop. When the material has sufficient strength, the article can be demolded. MDI/BDO polyurethanes normally need more initial cure time to build up sufficient structure to allow for successful demolding.

4.2.7 Trim Article and Fully Cure Molding in Oven

The state of cure at this point allows for the easy removal of a large proportion of any flash that may be present. This can be carried out using a sharp knife with the material under slight tension. The material at this point will appear to have sufficient properties for use, but the full cure cycle is needed to bring about the complete cure. The article needs a further 2 weeks at ambient temperature to reach its absolute maximum properties.

Postmolding operations such as final cleanup, trimming to size, or minor repairs can be carried out immediately after the full cure cycle.

4.3 Casting Health and Safety

The casting operation will expose the personnel involved in close proximity to both chemical and physical hazards. Copies of MSDSs for all the various chemicals used must be available at all times. These documents must not be more than 3 years old. They include all prepolymers, curatives, solvents, plasticizers, adhesive paints, blast cleaning agents, solid and liquid additives, and any gasses used.

Inserts that are to be used in the molding have to be prepared by either grit blasting or chemical treatment. The grit blasting operations must be carried out in a sand blast cabinet or the operator must be in an approved air-supplied garment. If solvent-based adhesives are used, appropriate personal protective equipment must be worn (chemical mask, gloves, and apron) and the operation carried out in a fume extraction hood.

Molds can be made from either metallic or nonmetallic materials. Metallic and nonmetallic molds are heated to the same temperature, which can be up to 120°C. Metallic molds are much more heat conductive than molds made from polyurethane or epoxy. When handling the metal molds, clean, heat-resistant gloves must be worn to prevent burning of the skin. The weight of these molds must be taken into account when handling them. Suitable lifting equipment such as a crane, block and tackle, or a forklift must be used.

When the prepolymer is melted, it and any gas in the container will expand. Care must be taken to prevent excessive pressure buildup. The container must be vented to reduce the pressure buildup; otherwise, it may rupture. After use, the can must be flushed with nitrogen to remove any moisture-containing air.

Vessels used for the degassing of prepolymers must be designed to withstand the 250 to 280 Pa gauge vacuum applied. The exhaust fumes from the vacuum pump must either be trapped or exhausted safely, because they will contain isocyanate vapors.

If silicas are being used as a filler, proper handling and mixing equipment must be employed, as these materials are extremely fine. Both engineering and personal protective measures must be used.

MOCA is classed as a suspect carcinogen, so its handling must be in straight accordance with the local safety rules and regulations. The manufacturer's recommendations must be observed for the use of all curatives.

During the casting process, care must be taken to not inhale any vapors from the mix (use a suitable respirator) and to prevent any burns or absorption through the skin. All solvents must be removed before the flaming off is carried out to reduce the fire hazard risk. Both cast and cured polyurethane moldings are hot and may give off fumes. Heat, chemical, and weight considerations must be taken into account when handling the filled molds.

The degree of difficulty in demolding the parts is a function of the design of the mold and the correct functioning of the mold release. Any levers used must be free of burs and cracks. Compressed air is often used to assist in breaking the seal between the polyurethane and the mold. The air lines and gun must always be in good order. Accidental misuse of the compressed air is very dangerous.

4.4 Mold Preparation

4.4.1 Molds

Molds used in the processing of polyurethanes can be made from a variety of materials. These include:

- Aluminum
- Polyurethane
- Silicone
- Epoxy
- Hard thermoplastics
- Steel

The polymer molds may or may not be filled. The filling material can be a metal such as iron shot or silica particles.

The first consideration is to check that the mold is the correct one for the product that is planned to be made. The molds should be permanently identified.

Before using a new mold, the dimensions should be checked. The coefficient of expansion of the mold material must be balanced against shrinkage of the cast polyurethane (normally 1.0 to 1.5%). It is normally much easier to remove material from a mold or master piece than to add to it. This should be taken into account when designing the mold.

The first part produced from any new mold should be fully cured, allowed to cool, and then fully checked for dimensions. Polyurethanes absorb moisture at high humidity and will expand. At ambient temperature and 100% humidity the expansion may be +0.6%.

The presence of any air pockets formed on the casting should be noted in relationship to their position in the mold. Additional vents may need to be added at this point if required.

4.4.2 Cleaning and Repair

Before reusing a mold, it should be physically cleaned to remove any grime or protective materials. Buildup on the surface should be cleaned off without damaging the surface of the mold. Location pins must be checked and repaired if needed. Any damage caused during demolding also must be repaired if in a critical area. The repairs must be such that they do not leave any marks on the surface of the part.

4.4.3 Mold Release

There are three main groups of mold releases:

- One-shot
- Semipermanent
- Durable film

A selection of commercial mold release materials are listed in Appendix 3.

All mold-release agents should be applied in accordance with the manufacturer's instructions. Thin coats of the mold release should be used. Great care must be taken not to get any mold release onto any inserts that have been coated with a bonding agent. This will prevent the bonding of the urethane to the insert.

One-Shot Mold Release

This group is commonly based on silicones and needs to be applied on a regular basis. Initially the release agent needs to be used after every pour, but there is often a buildup, and several pours may be done between applications.

Water-based mold releases are available. Care must be taken with these materials to ensure that the water used to carry the release agent is completely evaporated before use.

Semipermanent

These materials can provide many releases from a mold (20+) before recoating is required. They often require more preparation before use, such as baking on. The agents are often based on fluorine polymers.

Durable Film

These films can be based on Teflon® (DuPont, Wilmington, Delaware) film, polypropylene, or Mylar® (DuPont, Wilmington, Delaware) polyester film. These release materials are normally used where the surface of the material must be free of any contamination and defects. An example of the application is in the preparation of test sheets for determining mechanical properties.

4.4.4 Assembly

After the mold has had a coat of mold release applied, it must be fully assembled. Inserts must be correctly placed in the mold and fully secured. In a complex mold it may be necessary to temporary lock the insert into place with a removable pin that is taken out after the mold is full but before the material has gelled. Any join lines that may be prone to leakage must be sealed with a silicone sealant.

4.5 Batch Size Adjustment

4.5.1 Quantity of Polyurethane

If the mold has been made from a CAD/CAM design, there is often a facility in the package to estimate the volume of material to use. The weights of the smaller and larger parts in a series can be used for gauging the amount of material required.

Sufficient material to overfill the mold should be prepared for the first pour so that the mold will definitely be filled. Noncritical molds should be available to use up any excess material prepared.

4.5.2 Weight Calculations

The next step in the process is to calculate the quantity needed to make the articles. The main factors to be considered are:

- Volume of the mold
- Density of the final polyurethane
- Formulation of the material

A simple example is given here.

Formula

Prepolymer	100
Curative	10.0
Pigment	0.5
Total:	110.5

The density of the polyurethane needs to be known. This may be determined experimentally or from the material suppliers data used. In this example, the volume is assumed to be 1.10 liters and the density of the polyurethane is 1.07 g/m^3.

The most important point is that all the data must be in the same units. After doing the calculation, make sure the result you get is logical.

1.10 liters is 1100 cm^3
Density = weight/volume
Hence, weight = volume × density
= 1100 × 1.07
= 1177 grams

Always allow for some material to remain on the inside of the container. A starting point is 5%. This should be cut back as experience is obtained. The adjusted batch size will be:

$$(1177 \times 105)/100 = 1236\ \text{g}\ (1240\ \text{g})$$

Calculate the quantities of materials required:

Prepolymer resin = (100/110.5) × 1236 = 1119 grams (1120)
Curative = (10.0/110.5) × 1236 = 111.9 grams (112)
Pigment = (0.5/110.5) × 1236 = 5.59 grams (5.6)

4.6 Prepolymers

Polyurethane prepolymers are supplied in a variety of sizes, from small 1-kg cans up to 1-ton IBC containers. The available isocyanate (%NCO) level should be marked on every container of conventional prepolymers. Quasiprepolymers do not have individual batch levels supplied, as the overall reaction levels are factory adjusted.

The level can be confirmed by a standard dibutyl amine titration. A typical method is given in Appendix 6. Depending on the type of isocyanate used, the exact solvent for dissolution of the sample may have to be determined.

The prepolymer should be used on a first-in, first-out (FIFO) basis, as it may deteriorate slowly on standing. During the normal manufacturing process, the system is stabilized to reduce the aging process. Systems based on the unstable prepolymers (such as NDI-based materials) only have a life of several hours, so this must be taken into account.

Once a container has been opened, care must be taken to prevent moisture from the air affecting the material. This may be done simply by replacing any air in the container with dry nitrogen gas prior to resealing or, in a more permanent situation, keeping a supply of nitrogen gas over the prepolymer. The pressure in the drum cannot be allowed to build up when being heated, as this may cause the possible rupture of the drum. Industrial-grade nitrogen with a dew point of –40 to –50°C is sufficiently dry for this purpose.

The threads of the bungs must be cleaned after material has been decanted from the container to prevent sealing of the bung. If the bung cannot be opened, the gentle application of heat around the bung is often sufficient to soften the partially cured polyurethane and to allow the reopening of the container. Excessive heat must not be applied and any seals must be checked after this method is used.

Polyurethane prepolymers may be liquid or semisolid at ambient temperatures. Before further processing can take place, they must be heated so that the material is fully melted and the viscosity reduced to a point that it can be dispensed successfully.

The container may be heated in a thermostatically controlled hot room or with a heating band. Care must be taken to prevent localized overheating. As the thermal conductivity of the material is poor, there is often a temperature gradient in the container leading to the outside being melted and the center being still solid. This can be corrected by roll-mixing the container. All the material needs to be molten prior to use. The can must not have any translucent lumps in it.

This melting of the material adds to the heat history of the prepolymer. Table 4.3 is a general guide to the heating that a typical prepolymer can withstand.

The polyurethane prepolymer will slowly increase in viscosity on prolonged heating. It is a result of a chemical reaction between the polyurethane chains. The chemical reaction is irreversible. The available isocyanate is used up; therefore, the stated %NCO is reduced.

Small volumes can be heated in a microwave oven. Amounts of polyurethane too large for the microwave oven will need to be heated in a forced draft oven. The prepolymer must be heated to slightly above the required temperature. The required temperature depends on the prepolymer and

TABLE 4.3

Prepolymer Life

Temperature (°C)	Time
25	1 year
60	2 weeks
70	3 days
80	36 hours
90	12 hours
100	8 hours

TABLE 4.4

Typical Suppliers' Data

Polymer Type	Polyester Based	Polyether Based	Polyether Based	Polyether Based
Prepolymer level	100	100	100	100
%NCO	3.3	5.5	4.15	6.3
Curative	MOCA	MOCA	MOCA	MOCA
Curative % stoichiometry	95	95	90	90
Curative level	10.0	16.6	11.9	18.1
Processing temperature				
Prepolymer (°C)	93	82	93	83/93
Curative (°C)	113	113	113	113
Pot life of mix (minutes)	8	4	10	5.5

curative system being used. The basic data is normally supplied by the manufacturer of the prepolymer or curative. Typical data is shown in Table 4.4.

The larger the part, the lower the temperature at which the material must be processed. This is because as the material cures, heat is given off. In the center of thick cross-sections the heat cannot escape, because the thermal conductivity of the material is poor. Undesirable reactions may take place at these temperatures. There also will be thermal stresses induced into the molding.

A balance has to be reached between having a low viscosity to allow easy pouring and the speed of reaction. There may be other materials available that will give a lower viscosity while still having the required properties. The changes in viscosity with heat are shown in Figure 4.2.

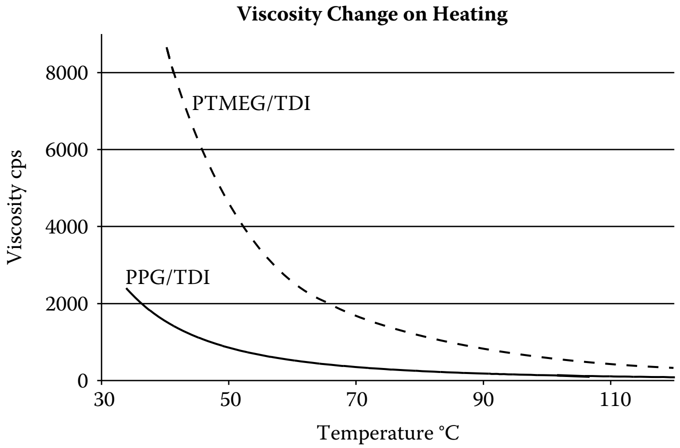


FIGURE 4.2
Short term viscosity change on heating prepolymers.

To determine the quantity of curative that has to be used, there are three main variables in the calculations:

- NCO level of prepolymer
- Type of curative used
- Index value

When prepolymers are manufactured, they do not always come out exactly the same. The viscosity and the isocyanate level can vary within the specified limits. The manufacturer determines the exact level of the NCO that is in that batch and supplies it on the container.

Each type of curative on the market has a different factor (molecular weight/functionality). This value changes according to the basic chemical composition and the fundamental activity of the curative; for example:

Material	Equivalent Weight (EW)
MOCA	133.5
Ethacure E300	107.8
BDO	45.0

The term *equivalent weight* (EW) is given to the factor of the molecular weight/functionality. The functionality is the number of appropriate active sites in the molecule.

Index value: By experience and research, it has been found that to obtain the best results for an application, slightly more or less than the theoretical amount of the curative needs to be used. The value is obtained by evaluating the most important physical properties required for the application in which the product will be used. This is discussed further in Chapter 7, Section 7.1.4.

4.6.1 Calculations

There are different methods of doing the calculations. Most commonly used are the %NCO method and the amine equivalent method.

%NCO Method

The calculation is to determine the amount of curative needed for 100 parts by weight of the prepolymer.

$$\text{Parts curative used per 100 parts polymer} = \frac{\%\text{NCO of prepolymer} \times \text{EW of curing agent} \times \text{desired index}}{\text{EW of NCO} \qquad 100}$$

The percentage NCO can be obtained from the container, certificate of analysis, or the manufacturer's data sheet.

EW of the curative is as given earlier, and a more complete list is given in Appendix 2. The EW of NCO is 42.02.

The desired index is normally in the range of 80 to 115%. Normally, the index value is between 90 and 105%. As there are several semiconstants, the calculation can be simplified. The formula is normally used in a simplified form. For example, if we are using MOCA as the curing agent:

$$\text{Parts curing agent used per 100 parts polymer} = \frac{\%NCO\ of\ prepolymer \times 133.5 \times 95}{42.0 \quad 100}$$

$$\begin{aligned}\text{Parts curing agent used per 100 parts polymer} &= \%\text{NCO of prepolymer} \times 3.18 \times 0.95 \\ &= \%\text{NCO of prepolymer} \times 3.02\end{aligned}$$

Amine Equivalent Method

The other method that is sometimes proposed is the "amine equivalent" (AE) method.

$$\text{Parts curative} = \frac{(\text{curative EW}) \times (\%\ \text{theory})}{\text{prepolymer AE}}$$

The amine equivalent is given by:

$$\begin{aligned}\text{Amine equivalent} &= \text{formula weight NCO}/\%\ \text{NCO} \\ &= 42.02 \times 100/\%\text{NCO}\end{aligned}$$

Manufacturers of prepolymers will often provide the weight of curative per 100 units of prepolymer. This is based on the midpoint NCO for the grade and the normal index value for the curative. The calculations can readily be carried out using a calculator or spreadsheet. From a practical point of view, a set of shop scales with a discount function has been used to provide the weight required.

After dispensing a run of prepolymer from a container, the prepolymer must be resealed in a state that will prevent attack by moisture in the air. A blanket of dry nitrogen gas must be used to displace any air present in the container. Any bungs or taps must be properly cleaned using a dry solvent such as MEK or MIBK to prevent traces of polyurethane from reacting with the moisture in the air and sealing the container.

4.7 Pigments and Additives

Pigments are used to color polyurethanes, basically for appearance. Normally, cured MDI- and TDI-based polyurethanes yellow on exposure to ultraviolet light. The product will change color, becoming more yellow and darker where the light strikes the object. White or pale-colored pigments in polyurethane are not normally recommended for this reason.

Raw pigments will have to be ground in a dispersing medium to develop the full color of the pigment. The dispersing medium is normally a nonreactive plasticizer that is both dry and nonhygroscopic. The cost of a pigment system is a function of both the light and heat stability of the particular pigment and its tinting strength. The light and heat resistance is normally given as a ranking out of 5. A ranking of 1/5 is very poor, and 5/5 is excellent.

The chemical nature of the pigment also must be considered when using it in a system that requires FDA or equivalent approval. Cadmium- and chromium-based pigments are often suspect.

The quantity of pigment used should be kept to a minimum, normally in the range of 0.25 to a maximum of 5%. The pigmenting effect will reach a maximum and then stay relatively constant. Too much pigment will only degrade the quality of the part and add extra cost.

The ability of the pigment system must be checked prior to full production. Some pigments do not disperse well if introduced late in the mixing. Some yellows need to be predispersed prior to final heating for the maximum effect. Poorly dispersed pigments will appear either as flakes in the system or as swirls. The flaky material needs to be dispersed in the prepolymer before the final heating. Swirl marks normally indicate lack of proper mixing, although some marks are very difficult to remove in certain red pigments.

Pigments can be dispensed using plastic squeeze bottles with long nozzles. If the viscosity of the material is too high, it may be diluted with some plasticizer. If larger amounts need to be used, tinting machine dispensers are an option.

Plasticizers can perform several rolls in a polyurethane compound. There are two major groups of plasticizers used. The most common is the nonreactive plasticizers such as the ester group, and the second is the long-chained diols that act as a combined curative and plasticizer. In the case of the reactive material, this must be taken into account when calculating the amount of curative to be used (see Appendix 2).

Nonreactive plasticizers will soften the polyurethane as well as extend the polyurethane's pot life. The mixture has a reduced viscosity, which assists in the ease of flow of the mixture and the removal of any entrapped air. This is of great importance in the casting of rolls where the final product must be bubble free.

The use of fire-retardant plasticizers, such as Fyrol PCF at levels of 5 to 10 parts, will reduce the hardness by 3 to 4 points while providing improved fire resistance.

4.8 Curatives

Curatives are used to enlarge the prepolymer chain either by extension or by cross-linking. Materials with two active groups will extend the length of the chain by joining two chains together. Triols will provide the means to form permanent covalent bonds between different chains.

TABLE 4.5

Common Curatives

Type	Name	Equivalent Weight
Diol	BDO	45
High M/W Diols	PPG 1000	500
	PTMEG 1000	500
Triols	TIPA	63.7
	TMP	44.7
Diamine	Ethacure E100	89.3
	Ethacure E300	107
	MCEDA	187
	MOCA (MBOCA)	133

There are two main groups of curatives that are used. These are either hydroxyl- or amine-terminated compounds.

Table 4.5 gives a selection of some of the more common curatives. See Appendix 2 for a more comprehensive list.

If a blend of curatives is used, the equivalent weight of the blend must be calculated, taking into account the individual equivalent weights.

$$\text{EW of Blend} = \frac{\text{Weight of A} + \text{Weight of B} +}{\dfrac{\text{Weight of A}}{\text{EW of A}} + \dfrac{\text{Weight of B} +}{\text{EW of B}}}$$

For example, if a mixture of 3 parts of TMP is used with 1 part of TIPA:

$$\text{EW of TMP/TIPA blend} = \frac{3 \;+\; 1}{\dfrac{3}{44.7} + \dfrac{1}{63.7}} = 48.3$$

The above calculation gives a working EW of 48.3.

Certain amine-based curatives such as MOCA are classed as suspect carcinogens. Extra care must be taken to observe all safety requirements both as required by local regulations and as specified on the MSDS. In all cases, the requirements of the MSDS must be obeyed.

Curatives can be either liquid or solid. The solid curatives such as MOCA and MCEDA need to be melted prior to use. The prepolymer and melted curative need to be at a temperature that will prevent any crystallization of the curative when added to the prepolymer.

The supplier's recommendations should be noted so that an adequate pour time is obtained. Pot life times quoted on the specification sheet are in many cases determined by laboratory size samples where the effect of the bulk of material is less than in a large mix. In a large mix, the poor conductivity of the material will cause the center of the mix to become hotter than the material on the side of the container.

Overheating the melted curative will result in partial decomposition of the material, giving off dangerous fumes. Care must be taken to keep the temperature stable and to melt only sufficient curative needed for the current run.

Protective clothing as recommended by the material supplier must be worn when handling molten curatives. The gloves must be impervious to the liquid curative. There is often a conflict at this point, as heat-resistant gloves are also needed for handling of the mold. Curative entrapped in cotton-style gloves can be absorbed into the skin.

Hydroxyl materials (diols and triols) are very hygroscopic, and the absorption of moisture must be prevented. Positive nitrogen blanketing is often required. All air must be displaced by dry nitrogen gas and the material stored under a slight positive nitrogen pressure. The use of dried 5A molecular sieve in BDO is also advantageous.

4.9 Degassing

There are two main times during the processing of polyurethane where vacuum degassing may be required. The first is the prepolymer as supplied by the manufacturer. The second is after mixing the prepolymer with the rest of the system (curative, pigment, extenders, and fillers).

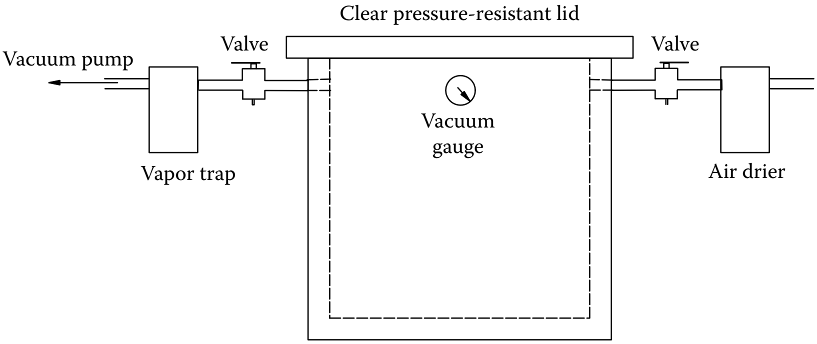


FIGURE 4.3
Vacuum degassing pot.

The manufacturer of the prepolymer endeavors to supply a low-moisture, low–free isocyanate, gas-free material. Moisture may be introduced with repeated opening of the prepolymer container. Contaminants will form bubbles in the final material. Any moisture or free isocyanates will have an effect on the reaction ratios as well as change the chemistry to a degree.

There are two main methods to "de-gas" the prepolymer. The first is a simple batch system composed of a vacuum pump and a pot designed to withstand vacuum. Figure 4.3 illustrates a simple vacuum pot. The alternate is a thin film evaporator. In this system, the heated prepolymer is allowed to flow in a thin film in a vacuum. Under these conditions, the volatile material will be readily removed.

For safety reasons, the pot must be specifically designed for vacuum use and any replacements be made from the same materials and the same size and design. A simple replaceable liner such as plastic wrapping in the pot will help keep the system in good condition.

The prepolymer is normally heated 5 to 10°C higher than the final temperature. The volume of prepolymer in the mixing container should be approximately 25 to 30% of the total volume, as the material tends to foam as the volatile components escape. The viscosity of the material will drop as the temperature is increased. The lower viscosity and reduction of the boiling points of the materials under vacuum will allow the volatiles to escape more easily. A suitable silicone defoamer (Dow Corning® [Dow Chemical Company, USA] 200 Fluid) may be used if known not to give problems later in the process. These problems may include knitting, bonding to metal, or creating a surface film that interferes with coatings. A few drops of a nonreactive dry solvent such as MEK may also be used.

The degassing should be continued until vigorous foaming ceases. There will always be some small bubbles showing in the polymer. The foam can be broken and knocked down by breaking the vacuum during the process. The inflowing gas should be dry. The material normally takes approximately 5 to 10 minutes at a vacuum of 250 to 280 Pa. The exact time will depend on the quantity, temperature, quality, degree of vacuum, and shape of container used. The time needs to be determined experimentally for each set of conditions.

A second degassing may be carried out after the addition of all the ingredients to remove any bubbles introduced into the mix. It must be remembered that this takes up part of the available casting time.

4.10 Mixing and Casting

4.10.1 Premixing

It is most important that all materials be dry before any weighing and mixing are carried out. As polyols may be rather hygroscopic, they should not be dried in an oven, because they can absorb moisture from the oven. Fillers such as the very fine amorphous silica have a very large surface area which can hold a large quantity of moisture.

Pours requiring more than one container must be carefully preplanned. The material must all be weighed out into separate containers and heated to the correct temperature. The auxiliary materials must be added to the correct containers and preblended. In large pours, it is very important to add the next addition before the previous one has gelled. If the material has gelled too far, a knit line will form, with consequent poor mechanical properties. Some time must be allowed, however, for entrapped air to escape.

4.10.2 Curatives

Plasticizers and catalysts can be mixed into the liquid curative prior to addition to the prepolymer if required. They must be well blended so that there is a uniform mix. The correct weight of the curative or blend must be accurately weighed in a clean, dry container or with great care directly into the prepolymer. The material must be added in a thin, continuous stream that will form a single phase. The addition must be done rapidly.

4.10.3 Mixing

Before the commencement of the final mixing, a last check of the mold must be made and the following points verified:

- Inserts prepared and seated properly
- Mold at correct temperature
- Thin film of mold-release agent applied
- All joint lines properly sealed
- Pouring hole and vents open

When hand mixing is used, the stirrer must be made from a nonreactive material and of suitable size for the mixing container. The stirrer should have a straight edge that can scrape the sides and bottom of the vessel. Wood is generally not suitable as a stirrer.

The motion of the mixing can be of any pattern, as long as the material is completely mixed. Care must be taken not to whisk air into the mixture. There are two main patterns used, namely the figure of eight and the zigzag pattern. The sides, bottom, and corner must be scraped, as prepolymer tends to hang onto the container. The two mixing patterns often used are illustrated in Figure 4.4.

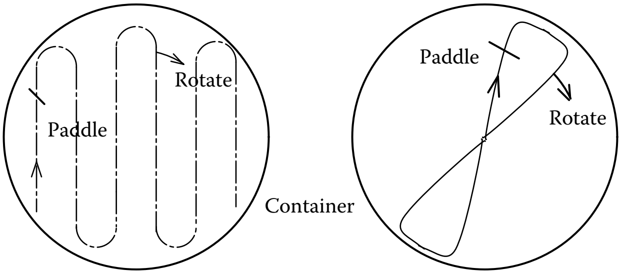


FIGURE 4.4
Hand mixing patterns.

The mixing must be complete, with no signs of color streaks in the mix. Inexperienced operators should initially do mixes without any pigmentation. The mix in the container should be completely uniform, with no lines. After pouring, the remaining material should be cured off. When the cured dregs are removed, there must be no signs of wetness. Any wetness is an indication of incomplete mixing.

If a mechanical mixer is used, a "Zippy" style head (such as used in the fiberglass industry) has been found suitable. The speed of mixing is important, and the formation of a vortex must be prevented. Care must be taken with this style of mixer that air is not whipped in. If necessary, the mixture can be degassed for a short period at this time.

The time available for mixing is a function of the system and can vary from less than 30 seconds to 4–5 minutes. Once the prepolymer and curative are added, a chemical reaction commences. In very hard materials, the time available is very short. After mixing, the material must still be poured into the mold and any entrapped air allowed to escape.

4.10.4 Casting

Time

The mixing and degassing must be completed in sufficient time to allow complete filling of the mold and for any air bubbles to rise to the surface. The hotter the material, the lower the initial viscosity will be. However, the viscosity will increase more rapidly and the material will gel off more quickly. This is shown in Figure 4.5.

Pouring

The mixed polyurethane must be poured in a continuous stream from as low a height as possible. The polyurethane must be allowed to flow down

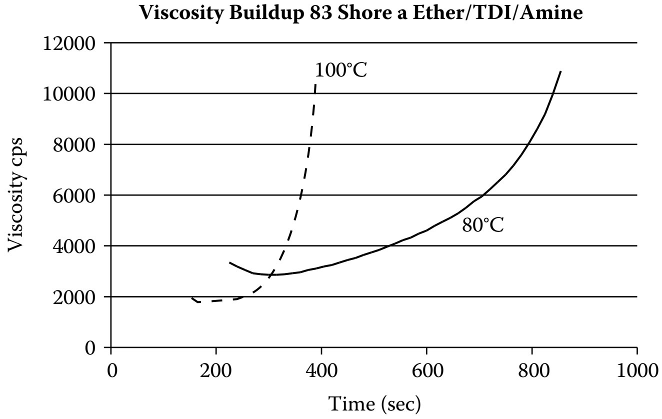


FIGURE 4.5
Viscosity buildups during initial curing of prepolymer.

a surface to the bottom of the mold. The bottom of the mold must be fully wetted by the mixture before the mold is filled from the bottom up, sweeping any air out before it. Polyurethane will fold over on itself, entrapping air very readily. The pour hole should be 2 to 3 times the area of the vent holes. The mold may have to be held at an angle to allow a top corner to be fully filled by the material. The remaining material is added as the mold is slowly brought to the vertical.

The mold should be completely filled before the material has gelled. During the period that the polyurethane is still fluid, any air bubbles that have been introduced will slowly rise to the surface. The bubbles can be readily removed by briefly passing a soft butane gas flame over the surface to pop the bubbles. The flame must be kept moving and not allowed to degrade the surface of the material.

The onset of gelation can readily be checked by trying to draw a thread of material from the surface with a piece of wire about the thickness of a paper clip. When a thread can be drawn, a lid can be placed on the mold or the mold transferred to an oven for curing.

4.11 Curing and Post Curing

On mixing all the ingredients, chemical reactions commence and the material will become more and more viscous and eventually solidify. The full physical properties of the material are not developed at this point, and the polyurethane will break very easily.

The mold containing the polyurethane should be placed in an oven that is set to a temperature 5 to 10°C higher than the casting temperature. The ideal temperature is the maximum the molding will reach. This will reduce the shrinkage in the mold.

The casting is kept in the oven long enough to develop sufficient strength to allow the part to be successfully demolded without any damage or distortion. Careful removal of risers and sprues may now be carried out.

It is most important to realize that at this time the full properties of the material are not yet developed, and the molded polyurethane has to be returned to the curing oven for the period recommended by the system supplier. The curing time varies depending on the chemistry of the system. The maximum properties of the cast polyurethanes are developed after a further 1 to 2 weeks at ambient temperature.

Polyurethanes with a hardness of 60 Shore D and above will often indicate full hardness, but they are very brittle. Extra postcuring cycles of ambient temperature to 120°C will develop the toughness of the material.

5

Processing

5.1 Molding Methods

Along with the simple open-mold casting method, there are several other methods of casting polyurethanes. They include:

- Rotational casting
- Centrifugal casting
- Vacuum casting
- Compression molding
- Liquid injection
- Complex shapes

5.1.1 Rotational Casting

In rotational casting, the heated mold is rotated in one or more planes at the same time. The viscosity buildup of the polyurethane is very important. In normal casting, it is desirable to have the mix at a low viscosity for as long as possible before a rapid gelation. In rotational molding, the viscosity needs to build up continuously at a steady rate. The pot life needs to be as long as practicable and in the order of 8 to 12 minutes to allow for full and even coverage of the mold surface. Figure 5.1 illustrates the type of viscosity buildup required.

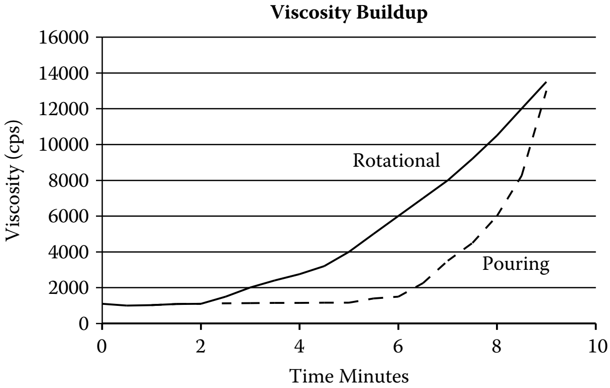


FIGURE 5.1
Viscosity buildup required for rotational casting.

Flat sheets can be made using a rotating cylinder with lips on the ends. The cylinder must be level to ensure even thickness. The polyurethane mixture is added to the bottom of the horizontal drum, which is rotated at a speed of between 2 and 15 revolutions per minute. The thickness of the sheet is controlled by the weight of polyurethane added. The speed of rotation must be adjusted to suit the diameter of the cylinder and the viscosity of the mixture. The cylinder must be fully coated before gelation starts.

When the material has built up sufficient strength, the casting can be removed and a sheet produced by cutting along the cylinder's length. The sheet is then allowed to fully cure on a flat surface in an oven. This method allows sheets of even thickness to be produced without the need for a large flat heated table that must be level in both horizontal planes. Different shapes including hollow spheres can be produced using this method. The major point is to obtain the correct rotation in the *x*, *y*, and *z* planes.

5.1.2 Centrifugal Casting

Centrifugal casting is used to produce parts with fine detail relatively free from included air. The mold is attached to a horizontal spinning disk which rotates at a speed of 5 to 30 m/s. The mold must be capable of having the polyurethane added from the center of the disk. The centrifugal forces move the denser polyurethane to the circumference of the mold and the air moves to the center. Some air vents may be required, as air can be trapped on horizontal surfaces.

The material needs to be added at a steady rate to allow it to flow evenly to the outside of the spinning mold. When full, the mold and the material gelled may be removed and placed in an oven for the initial cure before demolding.

It is important that the mold be dynamically balanced and securely locked in place on the spinning plate. The safety guards around the equipment must be capable of retaining the mold if it comes loose from the spinning plate. The polyurethane mixture must be carefully added to the center of the mold. If it hits the edge of the inlet, strands of "fairy floss-like" polyurethane may be formed.

5.1.3 Vacuum Casting

In parts where amounts of entrapped air must be kept to an absolute minimum, the process may be carried out under full vacuum. The unit consists of two chambers, one for mixing the prepolymer, curative, and other ingredients, and the lower chamber for the mold.

The mixing is done under vacuum, and the fully degassed mix is poured into the mold using remote handling equipment. As both chambers are under vacuum, there is no air to be displaced and the mold is filled completely with no entrapped gasses. In certain units, the mix can be pressure-transferred to the mold. A pot life of at least 5 to 6 minutes is needed for this method. The equipment is expensive and needs careful maintenance to keep the vacuum seals in good order.

5.1.4 Compression Molding

In this process, the polyurethane mix is poured into a mold that can be placed into a compression molding press with heated platens. The material is allowed to gel, and a top plate is placed on the material. The molding press is fully closed. The pressure applied is normally on the order of 1.50 to 2.0 MPa (250–300 psi) based on the projected area of the molding; e.g., a parts plan area is 300 × 400 mm in size. Its area is $0.300 \times 0.400\ \mathrm{m}^2 = 0.12\ \mathrm{m}^2$; therefore, a pressure of $1.500 \times 0.12 = 0.18$ MPa on the mold is required. The molds must be capable of withstanding the direct heat and pressure of the press. Aluminum or steel molds are preferred for this process.

Air vents are not strictly required in this process, but it may be advantageous to briefly release the pressure and then reapply it to the molding. The exact time to apply the pressure varies from system to system and must be determined by experimentation.

A variation of the compression molding technique is to use transfer molding. In this method the liquid polyurethane mix is placed in a pot and allowed to thicken. The polyurethane semi-gel is forced through sprues into the mold, and the air is allowed to escape through vent holes. The part is allowed to cure sufficiently so that it can be removed. Figure 5.2 shows the general layout of a compression and transfer mold.

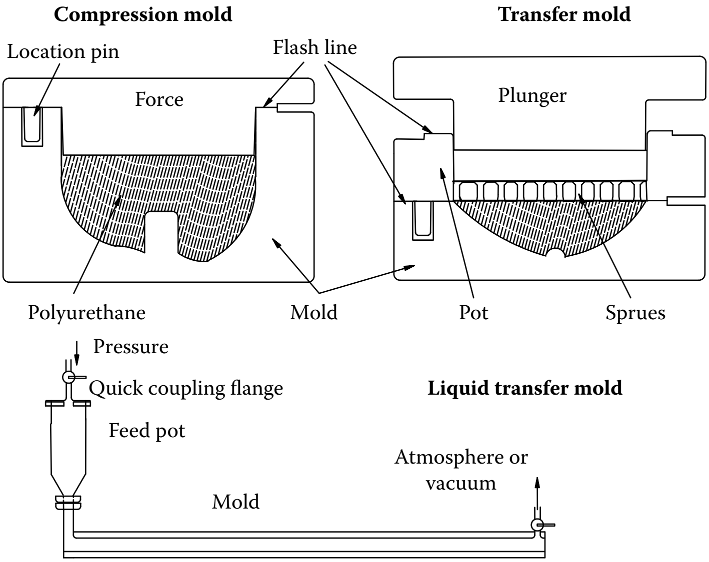


FIGURE 5.2
Compression and transfer molds.

There are several key points in these methods to allow proper success. The pot, and if possible the sprues, must be mold-released to ease demolding. The sprues must be designed so that the remaining pad in the pot can be cut off. The taper of the sprues must be such that they are wider on the part side than the pot side. It is normally best to trim the sprues and material in the vents straight after demolding to ease the later trimming and cleaning of the part.

5.1.5 Liquid Injection

In this method, the polyurethane is assisted in the flow by the application of gas pressure to the surface of the material. Parts where there is a long flow are particularly suited to this method.

The air ahead of the flow of polyurethane must be removed, and other vents in the parts must also be used. Applying a vacuum ahead of the polyurethane will also help the flow and will help prevent trapped air. Typically, pressures of 0.4 to 0.8 MPa are needed. The lower the viscosity, the lower the pressure required.

5.1.6 Complex Shapes

Tall items with complex internal shapes that can easily entrap air are best filled from the bottom up. By introducing the polyurethane at the bottom of the mold, the polyurethane mix will rise, sweeping the air out ahead of the polyurethane. The easiest method is to have a removable delivery tube that reaches the bottom of the mold. When the polyurethane mix has filled the mold, the tube is removed before the material starts to gel.

5.2 Bonding

Polyurethane can be bonded to most materials either during the initial casting or after full curing. In both cases, the most important consideration is that the surface must be clean and dry without any surface contamination.

5.2.1 Precasting

The polyurethane is normally bonded to a metal reinforcing or a rim of a wheel or gear. All bonding consists of four basic steps:

- Removal of gross contamination
- Preparation of surface (mechanically or chemically)
- Application of bonding primer
- Casting and curing of polyurethane

Cleaning Components

Reinforcings may be coated with a protective layer of grease that must be removed by an environmentally suitable method using either a locally approved solvent or a chemical alkaline wash. Gross scale and welding scatter must be mechanically removed.

Old polyurethane on rims may be removed either on a lathe, by solvent attack, or by freezing in liquid nitrogen. For more complex shapes, the reinforcing may be recovered by the above methods as well as by pyrolysis in a specially designed chamber, where the material is heated in the absence of air to above the decomposition temperature of the polyurethane. The fumes are then burned using special after-burners.

A metallurgist should be consulted regarding both the freezing and the pyrolysis methods, as the reinforcing may pass through phase-change temperatures that may change the properties of the metal.

Surface Preparation

The surface of the metal must be treated to form a layer to which the primer can successfully adhere. The treatment may be mechanical, or the surface may be treated chemically. Mechanical treatment is the most common and is by either grit blasting or hand abrasion. The grit or shot used must be clean, dry, and free from any grease or oil. The blasting of the surface must be carried out in an approved grit blast chamber by a suitably protected operator. The operator must wear appropriate protective clothing to prevent inhalation of the fumes and dust developed during the process.

The surface of the part, when the blasting is complete, must be matte grey with all the surface contamination just removed (Sa2.5 ISO 8501–1). It need not be over-rough. The surface must be cleaned of excess dust from the operation. If needed, the surface may be cleaned with a solvent such as toluene or MEK. Solvents that evaporate too quickly may, under some conditions, cool the part and cause condensation to form. The primer should be reapplied before reoxidation and contamination can take place.

The blasting medium used must be compatible with the material being prepared. The potential for chemical corrosion must be avoided. Copper slag should be avoided, as it can react with steel and aluminum to form chemical cells later when the polyurethane absorbs moisture if standing or immersed in a liquid. Steel shot must also be avoided on aluminum. Aluminum oxide is a popular choice as the blasting medium.

5.2.2 Chemical Treatment

To obtain optimum adhesion onto a wide range of materials, chemical treatment of the surface is often recommended. The first action, as with the mechanical treatment, is to remove surface contamination such as grease with a clean solvent. The surface of the material is then modified to provide a layer for the primer to bond to. The chemical treatment varies greatly with the type of surface. Some typical methods are:

Steel	The surface is subject to a phosphate treatment
Stainless steel	Dichromate treatment
Cast iron	Solvent and abrasion; carbon nodules in SG cast iron is a problem
Magnesium and its alloys	Dilute silicate/phosphate rinse followed by chromium treatment
Nickel	Nitric acid passivating
Titanium and its alloys	Chromic acid treatment
Zinc and galvanized metals	Dilute hydrochloric acid treatment
Concrete	Hydrochloric acid etch
Glass	Suppliers' special primer

These chemicals are dangerous, and full protective equipment must be used when carrying out the treatments. The appropriate MSDS must be consulted prior to use.

Immediately after these chemical treatments, all excess treatment solution must be washed off and the part well dried. The supplier of the primer should be consulted for current formulations to carry out chemical surface preparations.

5.2.3 Bonding Primer

There are specialist primers on the market for bonding polyurethane to metals. The three most popular brands are:

- Chemlok® (Lord Chemical Products, Erie, PA)
- Conap® (Cytec Conap, Olean, N.Y.)
- Thixon® (Rhom and Hass, Philadelphia, PA)

The prepared metal surface is coated with one or two coats of the primer, depending on the grade and the chemical and water resistance required. The coats must be applied at the recommended thickness. There is normally a minimum and maximum thickness. The aim is to fully wet the metal surface but not have too thick a layer. All the solvents in the primer must be evaporated before use. If the coated metal part is not used immediately, it must be carefully covered in polythene film to prevent surface contamination.

The primer can be applied by brush, roller and doctor blade, or spraying. To lower the viscosity for spraying, the recommended solvent must be used. The most important point when applying the primer by spray is to ensure that the spray is still solvent-wet when it reaches the part. Dry material can cause poor bond strength.

Once a part has been coated with a primer, it must be handled only with clean cotton gloves, preferably in a noncritical area. Parts that have had a long period between coating and molding may have to be freshened with a thin coat of primer.

Certain primers require a prebake prior to use. This can at times be achieved while the reinforcing is being heated in the mold.

5.2.4 Casting and Curing of Bonded Prepolymer

The polyurethane mix must flow over the part that has been primed and fully wet it. The presence of air pockets will prevent adhesion. It is most important that the primed part of the molding reaches the full cure temperature so that proper bonding will take place.

It is also very important to ensure that mold release does not come into contact with primer when the mold is being assembled. This will result in no bonding to all the contact areas. Care must be taken, especially of overspray, if the mold release is sprayed on.

When the bonded part is tested using the 90° Peel test (ASTM D429 method B), readings of more than 53 kN/m (300 lb/in) are usually obtained. When the bonding is good, the polyurethane will break (stock break) rather than actually peel at the bond line. However, it is recommended that the bond still be evaluated under appropriate field conditions. Without the use of the bonding primers, some adhesion is obtained, but the strength is far too low for it to be considered as an engineering-grade bond.

The strength of the bond will drop off as the temperature is raised. The strength decreases slowly until approximately 100°C, after which it declines rapidly.

5.2.5 Postcasting

Postcasting bonding of polyurethanes can be for two main reasons:

- Repairs to existing parts, for example, filling in air pockets on surface of molding
- Attaching polyurethane to another surface

Filling in defects should be done as soon as possible. The surface must first be solvent-cleaned to remove any traces of mold release and then slightly roughened with a barrel grinder. The area is then coated with some primer. A small dam is made around the part with a silicone sealant. A slightly catalyzed version of the same grade is used in the defect area. This process is best carried out between demolding and the final cure, with some heat initially still in the part. Color matching is a major problem.

Bonding-cured polyurethane requires that both surfaces be clean and free from contamination, especially traces of mold release. The surface of the polyurethane should be roughened slightly and must be capable of making proper contact with the other piece. The polyurethane should be primed with the adhesive manufacturer's primer. The normal suppliers of polyurethane bonding agents can supply suitable adhesives and primers. Loctite also provides a range of bonding agents.

When the component is used in a chemical environment, the effect of the chemicals involved must be taken into account. Some cyanoacrylates have poor hydrolytic stability. If the bond line is not fully protected, the bond may break down over time.

5.3 Finishing

Most normal metal machining operations can be carried out on polyurethanes with some minor modifications to technique. With some experience, polyurethanes harder than 90A can be machined relatively easily. Materials softer than 80A require more skill and experience.

The machining techniques used are like that employed with rubbers—for example, "knifing"—and in extreme cases the polyurethane may have to be taken to subzero temperatures. Using standard stock polyurethane sections, it is possible to machine prototypes using modified metal working techniques.

5.3.1 Differences from Metals

Before commencing any machining operations, it is best to consider how polyurethanes differ from metals and the general effect this difference has on the process.

Heating

The thermal conductivity of metals is much greater than that of all polyurethanes. The impact of this is that in the case of metals the heat is readily removed by the coolant into the stock and machine. The lower thermal conductivity of the polyurethane means that the heat remains near the surface of the part. Without proper care, the part can melt quite easily. Most polyurethanes start softening at about 135°C and melt to a gummy state by 180°C.

Dimensional measurements taken when the material is hot will be much larger than when the material is at room temperature and 50% relative humidity. This means that parts that may be in specification if measured during machining may be too small when reinspected later. Experience is needed to know how much extra must be allowed so that on cooling the dimensions will be correct.

The use of water-based oil coolants and light oils will help to remove some of the heat generated at the cutting tool. Care must be taken to match the coolant to the next process in the production; for example, if the part is to be bonded or painted next, do not use any oil, as it will have to be fully removed.

Memory and Modulus of Polyurethanes

When subjected to force, polyurethanes will distort. When compressed, the volume of the polyurethane remains, for practical purposes, the same. If the polyurethane is attached too firmly to the machine, it may be distorted. After machining when the part has been removed, the shape will change, giving a faulty part.

Polyurethane has a memory, and when a force is removed the material will return to its previous shape. A cutting tool will distort the polyurethane. After the tool has moved on, the material that has not been removed will return to its original shape. The swarf can foul the tool and generate more heat. The clearances on the tool must allow for the swarf to clear easily.

This memory effect can cause dimensions to change. Outside dimensions can increase while internal dimensions will decrease.

Safety Considerations

Standard safety precautions for the operation of the machine must be adhered to at all times, and the guarding of the machine must be operational and used. Personal protective equipment must also be used. Eye protection is particularly important. The part must be correctly mounted on the machine with just sufficient force to prevent it from moving and coming loose during the operation. The tool and its holder must not interfere with the part when internal work is being done. This may cause the part to come loose under speed.

The smoke and/or dust generated during machining should not be inhaled, as it is dangerous to health. Smoke generated during any operation means that the operation is not being carried out correctly, and the machining conditions must be changed immediately.

Softer grades of polyurethanes must be suitably supported to prevent undue distortions. Sharper tools with more clearance also need to be used.

5.3.2 Machining Conditions

Cutting, Shearing, and Splitting

Recommended tools	Abrasive cutting machines with knife blades or shears up to 9 mm knife blade or water jet cutters.
Size limitations	Sheets up to 13 mm.
Grades of polyurethanes	All grades.
Work holding suggestions	Friction-type clamps.
Note	Use bevel-edged knives to prevent uneven cuts.

Drilling

Recommended tools	High-speed twist bits with 90° or more points. Thick materials angle 90° to 110°. Thin materials angle 115° to 130°. The drill should have slow spirals to allow easy removal of swarf.
Size limitations	9.5 mm diameter. Smaller diameters should be clamped between plates to prevent distortion.
Grades of polyurethanes	All grades.
Operation speeds	600–800 rpm.
Work holding suggestions	Clamp or vice.
Notes	It is hard to obtain close tolerances on softer grades. Oversized drills may have to be used. The drills must be kept very sharp.

Tapping

Recommended tools	Regular high-speed taps.
Size limitations	None.
Grades of polyurethanes	All grades.
Operation speeds	600 to 800 rpm.
Work holding suggestions	Clamp or vice.
Note	Softer grades very difficult.

Turning and Boring

Recommended tools	High-speed tool steel or carbide bits with a positive rake of 5° to 10°. Must be razor-sharp.
Size limitations	Any diameter may be machined. Length maximum 250 mm unsupported. Softer grades will flex under cutting.
Grades of polyurethanes	Increase rake with softer grades.
Operation speeds	The speed should be high, with a slow feed rate 70 to 89 Shore A cutting speed approx. 7 m/s 90 Shore A and harder cutting speed approx 2 m/s.
Work holding suggestions	Angle of cut to work 90° to 120°.
Notes	Form tools can be used with the shore D grades. The chip material should be in a long, continuous strand. As the hardness increases, the surface finish improves. The tool should be just below the center line of the work.

Milling

Recommended tools	Single-bladed flycutters or a two-fluted end mill cutter with 10° back rake and maximum clearance.
Size limitations	Minimum of 9 mm thick.

Grades of polyurethanes	Shore D grades the best (90 to 95 Shore A grades need extreme back clearance). Milling of material softer than 80A is not normally recommended.
Operation speeds	900 to 1200 rpm with a 75-mm cutter, with a feed rate of up to 8 mm/sec.
Work holding suggestions	Vice or double-facing clamping tape.
Note	Fly cutting at approximately 75 mm diameter is the best.

Sawing

Recommended tools	Sharp 2–4 hook blades with raker set (teeth set to right and left).
Size limitations	200 mm diameter with cut 3 mm thick.
Grades of polyurethanes	All grades.
Operation speeds	1800 sfpm for shore D grades to 1200 sfpm for softer grades.
Work holding suggestions	Hand or vices.
Notes	Rotate round pieces to even out heat generated. Keep blade tension high to reduce friction on parts.

Grinding

Recommended tools	The grinding wheels should be coarse in texture and fine grained. Carborundum (43 grit size) is a suitable medium.
Size limitations	Wheel size to suit diameters of job.
Grades of polyurethanes	All hardnesses. Softer grades can deflect more.
Operation speeds	Part-approximately 150 rpm. Some recommendations of reverse direction. Grinding wheel 2250 to 3250 rpm.
Work holding suggestions	Mount on lathe with grinder on tool post.
Notes	Coolants such as water normally required in form of fine mist or brush. If no cooling, collect dust when grinding. Lower feed or use finer grit to obtain smoother finish.

5.3.3 Painting

Polyurethanes produced with aromatic isocyanates tend to yellow rather badly when exposed to the UV rays in sunlight. Internal pigmentation is not always successful in parts that are exposed to the sun. Polyurethanes pigmented with colored pigments (especially white) still change color drastically. The two main problems in obtaining good adhesion of paint to the surface of the part are:

- Remaining mold release on the material
- Plasticizers that migrate to the surface

The use of a nonsilicone mold release (such as a vegetable oil spray) in an aluminum mold may help. The mold release must be removed with a solvent such as isopropanol and water scrubbing.

The paint used must be flexible enough to withstand all repeated movements in the material. The most suited paint is a nonyellowing polyurethane paint, which can normally be applied to the well-cleaned surface. If required, the surface can be primed with a special primer that is obtainable from the larger suppliers such as Loctite® (Henkel Loctite Corporation, Dusseldorf, Germany).

5.4 Plasticized Polyurethanes

There are two methods to soften (plasticize) polyurethanes. The first is to use reactive plasticizers such as long-chain hydroxyl or amine-based materials, and the second is to use a compatible nonreactive plasticizer such as DIOP or Benzoflex 9–88.

Systems can be designed to work in the 25 to 35°C temperature range. A catalyst is added to the part containing the curative. The amount of catalyst added must be adjusted to give the required gel and demold time.

The addition of plasticizer disrupts the hydrogen bonding in the system and, hence, the physical properties decrease. To overcome this, at low harnesses, some long-chained material can also be added. A simple system is shown in Figure 5.3, where some additional plasticizer such as DIOP is added to a 95 Shore A polyether prepolymer, which has been cured with Ethacure 300.

Similar systems can be developed with polyester prepolymers with the addition of an ester-based plasticizer. Polyesters are very much tougher than polyether so they make better, softer materials. One commercial system uses a blend of a short-chain triol with either MOCA or Ethacure 300, with the addition of some plasticizer for the very softest material. The most-used triol is Isonol 93, which is now known as Conap AH50.

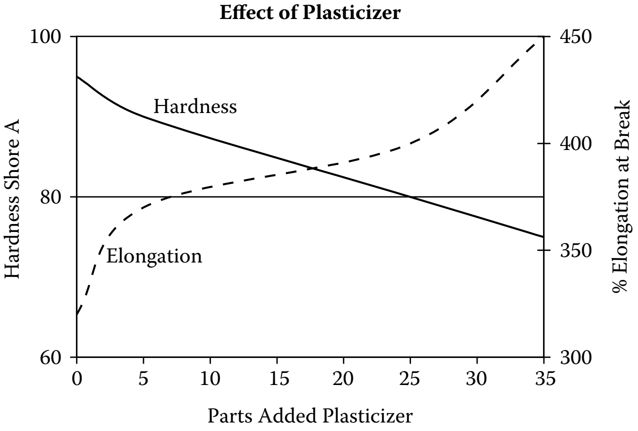


FIGURE 5.3
Effect of plasticizer on properties of polyurethanes.

When adding reactive plasticizers to polyurethane systems, the reactivity of the plasticizer must also be taken into account when calculating the amount to be added. The formula to calculate the equivalent weight of the blend is given in Appendix 5.

Nonreactive plasticizers are held within the structure of the polyurethane. On prolonged heating, they may slowly vaporize and the material will become harder.

The addition of phosphorous-based plasticizers will provide a degree of fire retardancy to the polyurethane. Fryol PCF and CEF have been used in polyurethane systems. Most phosphorus-based fire retardants are thin liquids that are compatible with polyurethanes. Because of the very varied nature of fire-resistant tests, the material made must be tested to the appropriate standard.

5.5 Epoxy–Polyurethane Blends

Epoxy resins when cured are very hard. Their toughness can be improved by adding some polyurethane to the epoxy resin during curing. The polyurethane imparts more impact and a higher level of toughness to the epoxy. The blends maintain most of the epoxy's electrical and chemical properties.

Epoxy resins are made with a reaction producing a resin with a molecular weight between 350 and 6000. These resins are terminated with an epoxide group. Figure 5.4 illustrates a basic unhardened epoxy resin.

Hardening of the resin can be carried out using a diamine to open the epoxide ring. Aromatic diamines can be used to harden the epoxy by using heat to activate the reaction. Diamine curatives such as MOCA and Ethacure 300 (DMDTA) can be used. Ethacure 300 is slightly on the slow side, so a blend of Ethacure 300 and Ethacure 100 (DETDA) can be used. Ethacure 100 is very fast when used with polyurethanes on its own.

In the reaction between diamines and epoxys, all four hydrogen atoms in the amine group react with the epoxide groups; therefore the functionality is four. (With polyurethanes, each amine group reacts with an isocyanate

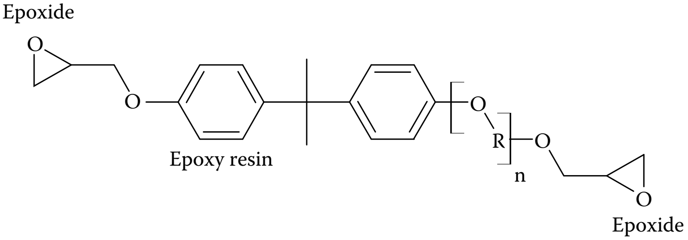


FIGURE 5.4

TABLE 5.1

Curative Factors

Material	Molecular Weight	Equivalent Weight for Polyurethanes	Amine Hydrogen Equivalent Weight (AHEW)
MOCA	267	133.5	66.75
Ethacure 100	178.3	89.2	44.6
Ethacure 300	214	107	53.5

group; hence, the functionality is two.) The basis of the calculations are that one epoxide group reacts with one hydrogen from the diamine. Table 5.1 gives the factors for some diamine hardeners/curatives of interest.

As with polyurethanes, the amount of hardener is calculated on 100 parts by weight (pbw). Epoxies are supplied with the epoxide value (EEW) of each batch. The basic calculation is

$$\mathrm{AHEW}/\mathrm{EEW} = X/100$$

or

$$X = (\mathrm{AHEW} \times 100)/\mathrm{EEW}$$

For an epoxy resin with epoxide value of 183 if hardened with Ethacure 100, one would need $(44.6 \times 100)/183 = 24.5$ ppw of E100 for 100 pbw of resin. The required amounts of curative for the polyurethane and the epoxy are calculated separately.

The amount of curative/hardener added is normally higher than the calculated value. Up to 140% of the nominal amount for the epoxy is often used.

6

Polyurethane Processing Problems

6.1 Introduction

Faults encountered when hand-casting polyurethanes can often be a result of one or more problems. A complete review must be carried out when solving any irregularities. When defects appear in products that previously were good, it may be the interaction of several factors. The weather may have changed, affecting the dew point. This may cause moisture to condense on the reinforcings. A second effect is the processing temperatures becoming too low. Table 6.1 indicates some general causes of problems.

6.2 General Problem Solving

6.2.1 Low NCO Level

Result

Low Durometer
Poor tear
Low tensile strength

The NCO level is normally specified by the prepolymer manufacturer but can slowly be reduced if the material has not been properly stabilized or if it has been stored for a long period at elevated temperatures. This will effectively give off ratio mixes, the consequence of which could be low Durometer readings, poor tear strength, or low tensile strengths.

6.2.2 Off Ratio

Result

Low Durometer
Wet spots
Poor tear
Cheesy appearance

TABLE 6.1

Problem Solving

Problem	Observation	Cause
Short pot life	Faster increase in pot viscosity	Curative contamination Incorrect temperature
Striations	Initial mix	Poor mixing
	Finished product	Poor mixing Off ratio
Voids in material	Fine bubbles	Moisture in system
	Small bubbles randomly in part	Pouring technique Dirty mold
	Large voids	High exotherm Casting technique Dirty molds Mold design
Foaming	In solid materials	Moisture in curative Very moist prepolymer
High shrinkage	Level of material lower than design in molds and vents	Incorrect temperatures of mold and polyurethane High exotherm Wrong ratios System contaminated
Cracking of part	On demolding	Low green strength Incorrect temperatures of mold and polyurethane High exotherm Wrong ratios Poor mixing Casting method
Wet spots	On surface of part	Poor mixing Off ratio
Snowflake or white skin	Normally MDI systems	High exotherm Casting technique
Cheesy appearance	Often MDI systems	Low green strength Insufficient cure Off ratio Poor mixing Incorrect temperatures
Physical properties	Durometer hardness, tensile strength, tear strength all low	Wrong curative ratios Prepolymer degraded Not fully cured Poor mixing
Failure to bond to insert	Lumps when material hot	Incorrect bonding preparation
	No strength in bond	Surface contaminated

High shrinkage
Cracking
Striations
Low tensile strength

Off-ratio mixes can be a result of the NCO level in the prepolymer being too low. If the prepolymer is stored at too high a temperature for an extended period, the isocyanate at the end of the chains reacts with itself to form multifunctional chains. Thus when the curative is added, it will be in great excess as a result of the isocyanates having used themselves up.

The fundamental calculations of the ratios of prepolymer, curative, and the rest of the system must be checked. The wrong EW or NCO levels may have been used. Alternatively, the weights for a different curative could have been substituted. The correct functioning of the scales used also must be confirmed.

6.2.3 High Exotherm

Result

High shrinkage
Snowflake or white skin
Voids
Cracking

Too high a mixing temperature will have two major effects: one, the exotherm will be way too high, and two, the time available for casting will be too short. Too high an exotherm or processing temperature will cause high shrinkage. With MDI-based materials, the surface will have a snowflake-type effect or it may have a white skin on it. In extreme cases, one may find a void or small crack internally in the part.

6.2.4 Incorrect Temperature

Result

High shrinkage
Voids
Short pour life
Cracking

Temperatures

High

When the temperature of the mixture is too high, the reactions will take place more rapidly. The heat given off by the reaction cannot escape as a result of the low thermal conductivity of the polyurethane. This can cause wrong chemistry. The initial viscosity of the mix will be lower.

The size and shape of the article will also affect the temperature required. A sphere may require a lower casting temperature to prevent overheating in the center.

Low

If the temperatures are too low, the viscosity of the prepolymer will make the mixing of the curative very much harder. The mixed prepolymer also will not flow easily into the mold and will tend to trap air against the mold surface. Another effect is that one can find a roll-type situation with the prepolymer's not joining on itself.

Mold

A mismatch of mold temperature against the prepolymer and the maximum exotherm can cause shrinkage. In a closed mold, internal pressures can cause damage.

6.2.5 Curative Contamination

Result

High shrinkage
Air bubbles
Short pour life
Unexpected foaming

Moisture in the curative or prepolymer manifests itself by very fine bubbles. Diols are particularly prone to moisture absorption. The moisture can be prevented from getting into the material by good housekeeping. The material must have a positive blanket of dry nitrogen over it at all times. If the material is properly degassed at an elevated temperature, these gas bubbles will be greatly reduced in number. Care must be taken at all times to prevent cross-contamination of curatives by items such as catalysts, mold-release agents, or bonding agents.

6.2.6 Poor Mixing

Result

Low Durometer
Wet spots
Poor tear
Cheesy appearance
Cracking
Striations
Low tensile strength

If the batch of material is incorrectly mixed, there will be zones of material that will have either too much or too little curative. This will result in a number of potential problems, such as:

- Low hardness
- Mechanical properties being off specifications
- Internal stresses in the component

Very poor mixing will be evident by areas of uncured prepolymer appearing as wet sticky zones. Mixing containers should be cured off and checked for any wetness on the edges between the container and the cured polyurethane.

The mixing technique should be such that all the surfaces of the vessel and mixing utensils are well scraped off and that the curative is well mixed in. For smaller batches, a spatula-type instrument is normally used. Poor mixing is evident by the formation of striations in the mix. These are lines of different color or intensity that are evident in both the unpigmented and pigmented mixtures. The hand mixing should be such that the color or clarity of the mix is completely even. For large batches, an electric mixer may be used, but in this case care must be taken that air is not sucked down and whipped into the mix.

6.2.7 Casting Technique

Result

Air bubbles
Snowflake or white skin
Voids
Cracking

When pouring the polyurethane mix, care must be taken so that the polyurethane flows down to the base of the article and displaces the air as it fills from the bottom. If the polyurethane rolls over itself, it will trap air and form a void. The vent holes should be positioned such that the polyurethane can fill the whole mold. If required, additional holes should be inserted. The mold may have to be tilted to help with its complete filling.

If more than one mix is required to complete the pour, the second mix must be commenced while the first is still very tacky and not surface-cured; otherwise, it will not fully blend together and will form a crack or knit line.

A balance has to be reached between various competing factors when casting polyurethanes. These competing factors are:

- The temperature of the mix and the mold must be suitable for the part.

- The viscosity of the material must be as low as practicable to allow easy filling and release of entrapped air.
- The polyurethane temperature must not be too high to cause too fast a gelation.

6.2.8 Dirty Molds

Result

Air bubbles
Voids

All molds must be mold-released with a suitable mold-release agent. This agent must be applied very sparingly. If there is too much mold release, some of it may be wiped off during the pouring and cause faults in the polyurethane. Too little or no mold release can make the part virtually nonremovable from the mold. After several castings, a mold will have sufficient buildup of mold release that one may not have to apply more for each subsequent casting. Only apply more mold release if one feels that the molding is becoming more difficult to remove.

6.2.9 Insufficient Cure

Result

Low Durometer
Poor tear
Cheesy appearance
Low tensile strength

The molded part can be removed from the mold as soon as it has sufficient strength not to break on demolding. The material should be postcured at the specified temperature, normally 100°C, for at least 16 hours. If this is not carried out, the physical properties will not be as high as they should. It must always be remembered that in the case of high Durometer TDI-based materials, although they are very hard soon after casting, they are very glasslike and will shatter readily. When they have had their full cure, they are both hard and tough.

6.2.10 Low Green Strength

Result

Cheesy appearance
Cracking

MDI-based materials go through an initial cheesy state with very poor tear and tensile strengths. Once they have had their full cure, they are also very tough.

6.3 Ratios

The material can be off-ratio for a number of causes other than the low NCO mentioned earlier. These may be incorrect weighing or calculation of the amount to be added. Always make sure that the scales are checked regularly and that the calculations are verifiable and within the normal limits suggested by the raw material suppliers. A number of problems are caused, including low Durometer readings and poor tear and tensile strengths. The pour life of the mixture will be quite different. If MDI materials are used, they will have a more cheesy appearance with a higher shrinkage.

6.4 Bond Failure

There can be a number of reasons for bond failure. The type of failure can be established by examining where the bond has failed. Polyurethane will stick to a metal surface, but the strength is very much lower than a proper engineering grade bond, where the strength will be greater than the tear strength of the polyurethane. The standard terminology representing descriptions for bond failures are:

RC	failure at the polyurethane cement interface
CP	failure at the cover cement primer interface
CM	failure at the metal primer interface
R	failure in the polyurethane

The polyurethane failure can be further broken down into a number of subgroups. These classifications are based on normal rubber, and that is why the "R" appears frequently. These include:

SR: spotty polyurethane. This appears on the metal surface looking like splattered-on polyurethane. It is caused by either surface contamination with dust or the fact that the sprayed-on adhesive has dried as it leaves the spray nozzles.

TR: thin polyurethane. There is an even but very thin residue of polyurethane on the metal surface. It is normally found with either butyl or polyurethane stocks that are very highly oil (or plasticizer) extended. The oil migrates to the surface and forms a layer that is part adhesive, part oil, and part polyurethane but is fairly weak.

HR: heavy polyurethane. A thick or heavy layer of polyurethane remains on the metal surface and indicates a very good bond.

SB: stock break. This is when the polyurethane appears to have folded back on itself and then broken off. This also shows very good bonding.

6.4.1 Bond Failures at the Metal-to-Primer Interface

Table 6.2 indicates the possible causes and solutions of metal-to-primer interface failures.

TABLE 6.2

Metal-to-Primer Failures

Possible Causes	Remedies
Poor metal surface—oil or powdery residue evident	Better mechanical or chemical cleaning Check degreasing operation
Contamination of treated metal part before bonding agent application	Eliminate source of contamination Cover or remove parts to clean area
Surface oxidized before application of bonding agent	Speed up coating process
Manual handling of cleaned part	Automate or supply clean gloves for operators
Environmental destruction; i.e., salt spray, oils, etc.	Check surface preparation techniques Use robust metal primer
Galvanic decay	Avoid dissimilar metal contacts upon installation of finished bonded parts
Sacrificial metal activity	Avoid dissimilar metals in abrasion cleaning operation, i.e., steel grit with aluminum
Bonding agent predried before reaching metal (spray application)	Reposition spray gun in relation to part Check bonding agent viscosity Add higher boiling diluent
Solvent trapped in bonding agent film	Increase time or temperature between application and bonding
Destruction by solvents from protective paints or rust preventatives applied after bonding	Ketone types usually responsible
Trapped air forced through bonding agent film	Improve mold ventilation

6.4.2 Bond Failures in the Polyurethane–Cement Interface

This failure mode is where a layer of primer is visible on the reinforcing but not on the polyurethane. The possible causes and solutions are given in Table 6.3.

TABLE 6.3

Polyurethane–Cement Failures

Possible Cause	Remedies
Precure of polyurethane	Pour polyurethane when the viscosity is low
	Transfer molding—start transferring earlier
Precure of bonding agent	Speed up transfer cycle
	Lower molding temperature
Leakage	Check mold for any sign of leaks
	Ensure all split lines are well sealed
Incorrect molding cycle	Check mold temperature
	Check cure rate of polyurethane
Low bonding agent film weight	Use heavier or multiple adhesive coats
Migration from polyurethane	Substitute more compatible ingredients
Contamination of bonding agent-coated parts	Check unbonded specimens for oil or dust
	Avoid overspray or excessive use of mold release agents
	Check for possible contamination from nearby equipment or agents
Cement–polyurethane incompatibility	Use other bonding agent

7

Properties

7.1 Introduction

There are a number of major factors that influence the final properties of polyurethanes. The most important of these are:

- Type of backbone used
- Length of backbone
- Type of isocyanate
- Ratio of reactants
- Type and concentration of curative (chain extender)
- Final processing conditions

Careful choice of the polyurethane is needed to obtain a cost-effective article. Just as underspecifying an item can result in failure, overspecifying can result in the product no longer being viable.

7.1.1 Type of Backbone

Polyethers give good mechanical properties with excellent hydrolysis resistance. PTMEG (C4) ether is generally superior to those of the PPG (C3) ethers. The properties of polyurethanes made with PPG ethers have been brought closer to the PTMEG materials with the use of end capping with ethylene oxide (EO) and the low monal materials (Acclaim).

Polyesters produce tough, oil-resistant polyurethanes, with the major drawback being lower hydrolysis resistance compared to polyurethanes made using polyethers. The two newer groups of polyesters (polycaprolactone- and polycarbonate-based) both have better resistance to hydrolysis. Their toughness is very close to the basic polyester polyurethanes. Their disadvantage is cost.

7.1.2 Backbone Length

The length of the backbone will control the frequency of the hard segments that are present in the polyurethanes. The most obvious of this is the overall hardness of the material. The longer the backbone, the more flexible it will be. Short backbones with a degree of coordinate cross-linking (i.e., some short-length trifunctional groups) will produce material with high hardness and good compression set.

7.1.3 Type of Isocyanate

TDI-based polyurethanes produce the best properties when further chain-extended with amine-based curatives. The overall properties can be increased if only the 100% 2,4 isomer is used. These materials are generally not suited for use with food. MDI-based polyurethanes have good overall properties and as they are predominately cured with a diol, they can obtain FDA approval more readily.

In order to obtain an increase of 10 to 20°C in useable temperature, isocyanates such as PPDI and CHDI need to be used.

Aromatic isocyanates, due to their structure, will yellow when exposed to light. The use of aliphatic isocyanates enables nonyellowing materials to be produced. The downside is the increase in cost.

7.1.4 Ratio of Reactants

Both the ratios in the prepolymer production and the curing ratios will affect the final properties of the polyurethane. In the initial prepolymer production, the properties vary according to the molar ratios of the prepolymer. This is illustrated by the graphs compiled in Saunders and Frisch (Saunders, 1962).

The effect of varying the mixing ratios of the chain extender has a number of different influences on some of the more common properties. The changes depend on the effect at the molecular level.

The most commonly quoted property (hardness) remains relatively constant between 85 to 100% of the theoretical curative addition. This is due to the fact that the hard segments will provide the bulk of the stiffness to the product. Even when there is some hydrogen bonding, the hardness will stay approximately the same. Compression set needs a lower level of curative (85 to 95%) with some covalent cross-linking to develop the lowest set.

Properties such as abrasion resistance, resilience, and heat buildup are normally the best at a lower level of curative. These properties rely on unhindered flexibility of the backbone chain.

Tensile strength needs a level just below the nominal level (90 to 95%), as the strength relies on both the hard and the soft segments without the effects of uneven chain lengths. Purely physical properties such as tear strength, flex, and elongation all require the curative index to be either at or slightly above the theoretical level. These properties need the strongest overall bonding in the matrix.

7.1.5 Type and Concentration of Curative

Within the same group of curatives, some properties may be enhanced by using a certain curative. MOCA and Ethacure 300 both produce very good elastomers, but each may give certain properties that are superior to the other's. MOCA gives a higher nicked tear strength but a lower unnicked tear than Ethacure 300. MOCA also has better compression set. The tensile properties produced using Ethacure 300 are also slightly higher than those from MOCA (Albemarle Corporation, 1999). Ethacure also has production advantages such as being a liquid at room temperature and being not subjected to as many controls as MOCA.

7.1.6 Final Processing Conditions

All polyurethanes need the complete cure as specified to develop the properties fully. If the product is allowed to stand for a week at ambient temperature, the full properties will be developed.

A further heat treatment (sometimes referred to as annealing) or a longer, slightly hotter cure (18 hours at 130°C) will also improve properties such as tensile, tear, and overall toughness.

Very hard compounds (80 Shore D and above) need this extra heat treatment to fully develop the bonding network and to prevent cracking under load or impact. The products will form glasslike fragments unless the extra heat treatment is complete.

7.2 Physical Properties

There are a number of other physical properties that are very important to the optimum performance of polyurethane other than the normally quoted ones in trade literature. These include temperature, dynamic, and hysteresis properties.

7.2.1 Temperature

Physical

The effect of temperature on polyurethanes has a number of zones (Garret, 2003):

below –80°C	The material is a hard solid and in a glassy state.
–80 to +20°C	The hard segments of the urethane begin to rotate and move.
20 to 130°C	The material is useable.
130 to 180°C	The polyurethane starts to soften severely.
above 180°C	The polyurethane starts to break down irreversibly.

Within each of these zones, the temperatures can be changed depending on the exact nature of the backbone, isocyanate, and curative.

The polyurethane becomes harder as the temperature decreases from 20 to 0°C. The environmental effects on the urethane decrease below 0°C. At these temperatures the hardness, tensile and tear strengths, and torsional stiffness increase. The largest increase is to the Young's modulus. The resilience of the polyurethane will decrease as the temperature is lowered.

The normal operating temperature of polyurethane is between ambient and 120°C (dry conditions). At these temperatures, the properties are normally at their best. The envelope can be increased by the use of the most appropriate curative and backbone. For moist conditions, the normal maximum temperature is 80°C using a PTMEG polyether, whereas it drops to 50°C for conventional polyesters. The newer esters have more hydrolysis resistance and can be used at slightly higher temperatures. The dry and moist temperatures can be extended by using newer isocyanates such as PPDI.

Oxidative effects of air are greater on polyether-based materials compared to the polyester grades. This effect is due to the attack by the oxygen on the ether bonds.

Dimensional

Polyurethanes have changes in their dimensions during curing, subsequent heating, and cooling. The shrinkage of hot-cast polyurethanes is a function of the temperature of the reaction. For a reaction temperature of 50°C, the linear shrinkage is approximately 1%. At 90°C it is close to 1.5%, and at 130°C it is 2.5%.

Cold-cast materials will have very minimal shrinkage. This is useful where an exact-size copy must be made. Some postcuring may be carried out by using a stepwise process, for example, 4 hours at 50°C followed by 2 to 3 hours at 100°C.

It must be remembered that shrinkage takes place in all three planes. It is present but not normally detectable in thin cross-sections. In hollow items, the dimensions of the finished article will be smaller in the outside diameter. The inside dimension will be larger. This must be taken into account when a mold is designed.

The coefficient of thermal expansion of fully cured polyurethane is between 11×10^{-5} and 8×10^{-5} in/in/°F. There is also an expansion of polyurethane at ambient temperature when the relative humidity increases. The major effect is between 70 and 100% RH, where it can swell up to 0.6%.

7.2.2 Resilience

The resiliency quoted for an elastomer is normally a single expression of the result of a specified test. The results quoted will vary according to the method used. To compare results, elastomers must be tested by the same method.

An explanation of resiliency is based on the conservation of energy. When an object strikes a polyurethane with a certain mass and velocity, the energy must remain the same. The mass of the object leaving the polyurethane is the same, but its velocity is lower. The difference is retained in the polyurethane as heat energy.

$$M1 \times V1 = cf \times (M1 \times V2)$$

The factor cf is called the coefficient of restitution.

A second explanation (Wright and Cummins, 1969) is that when a stress (force) is applied, there is a small but measurable time lag before the material takes on the strain (change in shape). This is due to the need of the intermolecular forces to overcome the vibrational energy of the atoms. The warmer the polyurethane, the quicker the vibrational energy will be overcome and the polyurethane will become more resilient. If a stress–strain graph is produced, the applied stress and the recovery graphs are not the same. This is called hysteresis. Figure 7.1 illustrates the typical curves for a resilient and a nonresilient polyurethane. The curves become more constant after three or four applications of stress. The molecules of all rubbers (elastomers), when allowed to rest undisturbed, align themselves in a dormant position. They become more active when some stress is applied. This can be illustrated when a ball that has not been used for some weeks is bounced. The first bounce will be much lower. After three to four bounces, the rebound height becomes constant. The difference between the applied energy to the returned energy is stored in the part as heat.

The polyurethane can be considered to consist of two components, somewhat like the physics spring and dash pot model for viscous materials. The elastic component (spring) stores and returns the energy. The second or viscous area (pot) converts the retained energy into heat. This is an important property in the design and selection of polyurethanes. The design of the

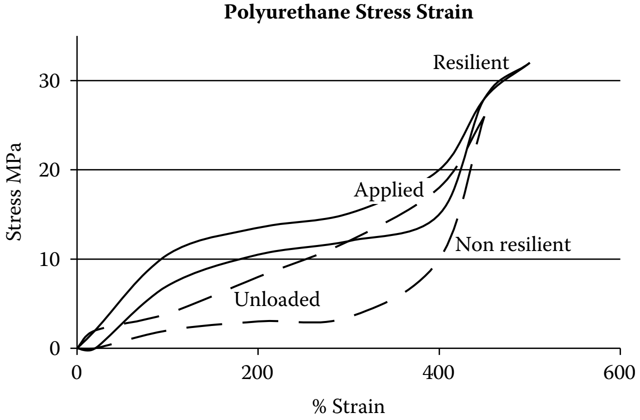


FIGURE 7.1
Polyurethane stress-strain curves.

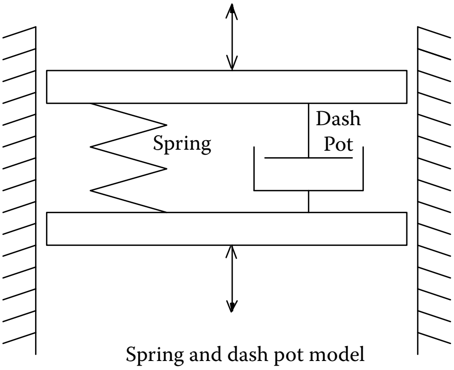


FIGURE 7.2
Spring and dash pot model for energy absorption.

polyurethane system can be adjusted to give varying amounts of resilience or absorption of energy. Figure 7.2 illustrates the spring and dash pot model.

The current method of determining the energy properties of polyurethane is the Dynamic Thermal Mechanical Analyzer (DTMA). This instrument applies a cyclic stress/strain to a sample of polyurethane in a tension, compression, or twisting mode. The frequency of application can be adjusted. The sample is maintained in a temperature-controlled environment. The temperature is ramped up over the desired temperature range. The storage modulus of the polyurethane can be determined over the whole range of temperatures. Another important property closely related to the resilience, namely tan delta (δ), can also be obtained. Tan (δ) is defined in the simplest terms as the viscous modulus divided by the elastic modulus.

In practice, a material that is "dead" will store much of the applied energy and has a low resilience and a relatively high tan delta. A material that returns much of the energy has a high resilience and a low tan delta. These properties have an influence on the grades used for shock absorbers, springs, bushes, or wheels.

7.2.3 Thermal Conductivity

The heat generated when work is done to the polyurethane must be removed or the material will become overheated. The thermal conductivity of polyurethane is poor compared to metals. Unless the product is properly designed, there can be failures in some polyurethane applications.

Thermal conductivity is expressed in several different internationally recognized ways. One method of expressing thermal conductivity (λ) is in terms of the heat flux under steady conditions per square meter for one meter of thickness of one degree Kelvin difference in temperature. Kelvin is a thermodynamic scale and is centigrade starting at absolute zero.

Thermal conductivity = W/m.K.

Another method for expressing thermal conductivity is to determine the quantity of heat passing through a unit area of the material, when the temperature gradient (when measured across unit thickness in the direction of the heat flow) is unity (Smith, 1993). The thermal conductivity of a polyurethane is on the order of 0.1 to 0.3 W/m.K. Other references give a value of approximately 1.7 to 3.5×10^{-4} cal.-cm/sec. cm^2.°C (Gallagher Corporation, 1994).

The low thermal conductivity of polyurethanes must be taken into account in the design of parts. The efficient dissipation of the heat must be allowed for when any part is subject to vibration, flexing, or impact.

7.2.4 Stress–Strain Properties

The term elastomer is normally used to describe a material that will stretch when placed under load and will retract to approximately the original shape when the load is removed. The solid polyurethanes described so far have this elastic property. The elasticity differs from that of ordinary rubbers due to the nature of the bonds in the polyurethane matrix.

The chains that make a polyurethane elastomer have many polar groups with hydrogen bonding occurring throughout the chains. Natural rubber has many long, entangled chains with some sulfur or peroxide crosslinks. On applying a stress, the chains can straighten out and slide over each other. Reinforcing fillers such as carbon black are needed to reduce the elongation under load and produce a material with a high "modulus." Modulus is the stress required to produce a certain strain. Expressed differently, it is the tensile stress (strength) at a specified elongation. Normally it is at 100, 200, or 300% elongation. Polyurethanes with the hydrogen-bonded polar groups prevent the chains from sliding over each other and give a material with a higher modulus. Polyurethanes' "high modulus" means that reinforcing fillers are not needed to achieve the same properties.

Polyurethane, like rubbers, has its tensile strength calculated using the initial cross-sectional area and not the area at break, as with metals. Therefore, the ultimate strength is much higher than conventionally quoted.

With metals, the modulus is stress divided by strain (Young's modulus) and is both a ratio and a constant. In the case of polyurethanes, the load defection curve is linear only over the first few percent. The Young's modulus is calculated in this area. As the curve passes through the origin, the modulus is the same in compression as in tension. Work has also shown that the Young's modulus is three times shear modulus (Wright and Cummins, 1969).

In practice, up to 90% of polyurethanes are used in compression, a few percent in torsion, and very little in tension. There is considerable data on the tensile stress against tensile strain (elongation) for polyurethanes. Most polyurethane specification sheets provide this data. Figure 7.3 and Figure 7.4 show typical stress–strain curves for both polyester and polyether polyurethanes.

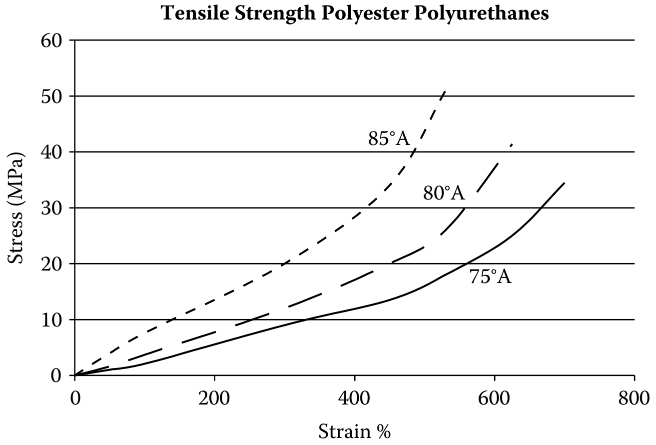


FIGURE 7.3
Tensile strengths of polyester polyurethanes.

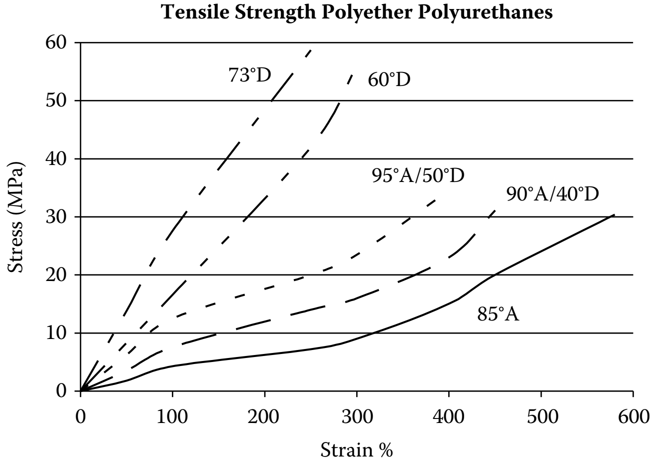


FIGURE 7.4
Tensile strengths of polyether polyurethanes.

7.2.5 Hardness

Hardness is measured by a specially shaped indentor that protrudes from a flat base. The other end is held against a spring. When held against a sample, the indentor is pressed into the case. The movement of the spring is measured either by analogue dial or by a digital display. The harder the sample, the more the indentor moves into the case. In all scales, 0 is very soft and 100 very hard. The two scales used in polyurethanes are the A and the D Durometer scales. Figure 7.5 shows the relationship between the Shore A and D scales.

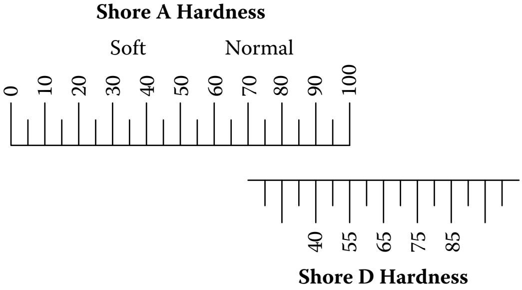


FIGURE 7.5
Shore A and D hardness scale overlaps.

Hardness is a stiffness measurement. Stiffness is a stress/strain relationship. In load-carrying applications the stiffness is a bulk property, whereas measuring hardness is only a surface measurement. Two polyurethanes with completely different chemistries can have the same hardness. There are up to six completely different chemistries that are in common use (as shown in Table 7.1) that can give the same hardness.

In processing polyurethanes, the hardness is not greatly affected by the mixing ratios. A material mixed at 80% of the theoretical curative level has greatly different overall properties to one mixed at 100%. The hardness is still at the same level. Figure 7.6 shows the hardness variations with different curative variations.

To measure the hardness, one needs to have a sample that is at least 5 mm thick and has a flat-enough surface for the base of the Durometer to rest on. For the most accurate measurements, a dead load instrument should be used.

The compressive strain properties of urethanes show that polyurethanes have very good load-bearing properties. Softer materials (below shore hardness of 75 A) all have very similar response curves. The shape of these curves is influenced to a large degree by the ratio of the constrained polyurethane to the free area. The ratio is commonly called the shape factor. In calculating the shape factor, only the area of one loaded surface is taken. The

TABLE 7.1
Basic Structure Combinations

Base	Curative	Comments
Ether polyol/TDI	Diamine cure	Both C3 and C4 subtypes
Ester polyol/TDI	Diamine cure	Traditional, Caprolactone, polycarbonate subtypes
Ether polyol/MDI	Hydroxyl cure	Both C3 and C4 subtypes
Ester polyol/MDI	Hydroxyl cure	Traditional, Caprolactone, polycarbonate subtypes
Ether polyol/PPDI	Diamine cure	Mainly C4 subtype
Ether polyol/PPDI	Hydroxyl cure	Mainly C4 subtype

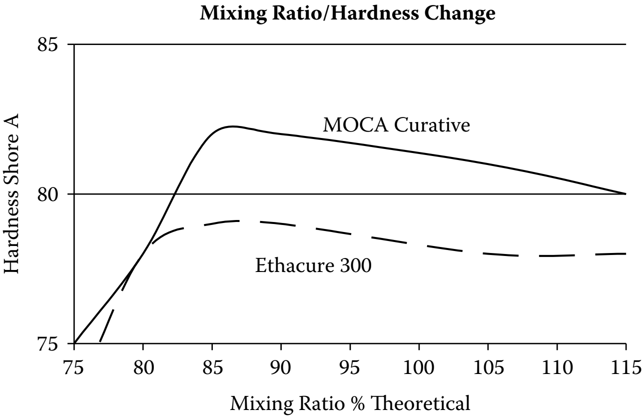


FIGURE 7.6
Effect of mixing ratio on Shore hardness.

total area that is free to deform (expand) is calculated. Figure 7.7 illustrates shape factors.

The compression stress–strain graphs are normally determined using samples that are bonded to steel plates. If there is any lubrication, the results are completely different due to slippage that may take place.

Compared to conventional rubbers, polyurethanes retain their elastic properties at Shore hardnesses of 85 A and above. At Shore hardness of 50 D, the

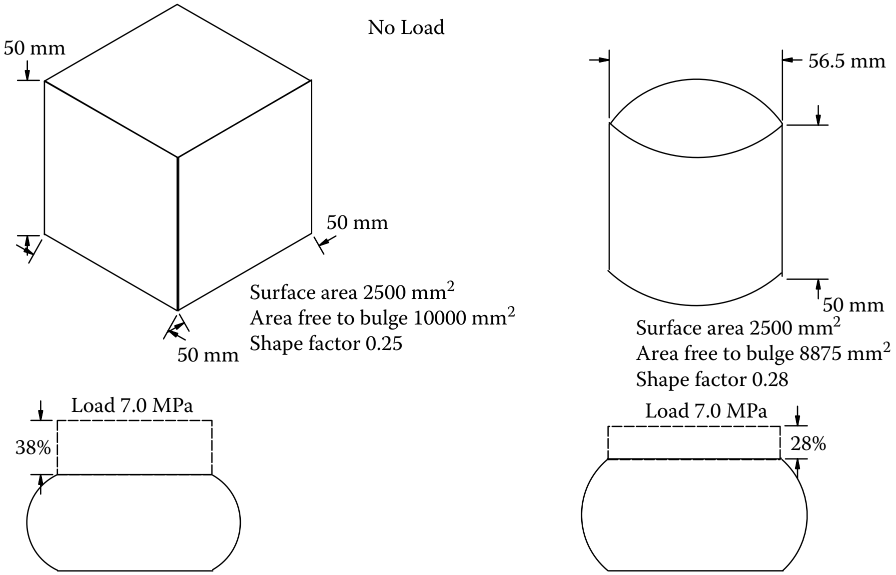


FIGURE 7.7
Shape factor determination.

elastic properties are still retained. When the polyurethanes are in compressive stress as well as shear, the load-bearing properties are still retained.

7.2.6 Tensile

The tensile strength of polyurethanes is dependent on the resistance of the cross-linking bonds that are either covalent bonds or hydrogen bonds to prevent the chains from slipping completely and the material from breaking. The harder the material, the more densely the cross-linking will be. This produces a material that is not only strong but also has a high modulus.

When operating below the ultimate tensile strength, the harder materials retain their elastic properties and do not behave like a thermoset. If a tensile test piece is allowed to recover, the sample will return close to its original size, but there will be a degree of permanent set.

Polyurethanes under tension are very "notch" sensitive and when used as a spring, a nick will propagate and cause failure. Under long-term tension, polyurethanes will suffer from creep (strain relaxation) and set.

Fully postcured polyurethanes will lose both tensile and modulus properties when heated in the short term (30 minutes) to temperatures above ambient and below their breakdown point. These effects are detectable both in classical testing and when using DTMA techniques. These short-term effects are normally reversible at temperatures up to 120°C, with some changes to the hydrogen bonding possible. Prolonged heating will cause breakdown. This is shown in Figure 7.8. The elongation at break increases as the temperature is raised. This is due to the secondary bonds' being able to move more easily.

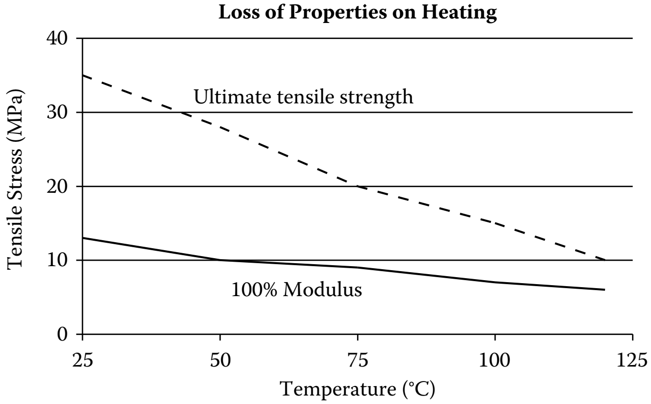


FIGURE 7.8
Loss of properties on heating polyurethanes.

7.2.7 Tear

The higher the modulus of polyurethane, the higher the tear strength. The density of the cross-links appears to increase the tear strength. There are a number of recognized tests to determine the tear strength, namely, nicked (notched) and unnotched. The nicked samples give a much lower tear strength result than the unnicked samples. Soft samples are very pronounced, with the ratio approximately 10:1, whereas medium hardness (90 A) gives a ratio of 5:1. Hard materials maintain the same ratio as the medium hardness grades.

Polyester polyurethanes have higher tear strength than their polyether counterparts. The nicked tear strength is much closer to that of the polyethers. As with the tensile strength, the tear strength decreases rapidly as the temperature increases (see Figure 7.8).

Lubrication of the sample under tension while being torn reduces the tear strength greatly. This has a major effect in wear applications where fine-nicked tears play an important role.

7.2.8 Coefficient of Friction

The coefficient of friction of polyurethanes has been found to be similar to that of rubbers. The coefficient is the resistance to sliding or rolling of the surfaces of two bodies in contact with each other. It has been found that the softer the material, the higher the coefficient of friction. The values vary from 0.2 for the harder grades to approximately 3 for the softer grades. This is thought to be due to the higher actual area of contact between the elastomer and the second surface. A hard material under moderate loads will not deform and follow the surface profile of the second material. The coefficient of friction reaches a maximum at approximately 60°C.

Laboratory tests must be taken only as a general guide. In practice, surface cleanliness and lubrication by dust, moisture and oil traces will greatly affect the actual friction properties.

The speed of friction will increase the coefficient slightly as it increases. The coefficient of friction will reduce over the course of time when the material is under load. It is thought that this may be due to the development of abrasive debris.

As the coefficient of friction can be reduced by the use of a lubricant, it is generally beneficial to use a suitable oil or grease when required. The addition of a modifier to the prepolymer itself must be done with care, as the material will reduce the overall properties including aging and may influence the bond ability of the material. Additives that have been employed in this application include molybdenum disulfide, graphite, and silicone oil. They must be used at the lowest level possible.

7.2.9 Compression Set

When polyurethane is subjected to a compressive force, it will deform. When the force is removed, the material will recover some of its original shape. The amount of the deformation that does not recover is known as the permanent set (see Figure 7.9).

The normal method of evaluation is to measure the amount of permanent set with the constant strain of 25%. That means that the thickness is compressed by

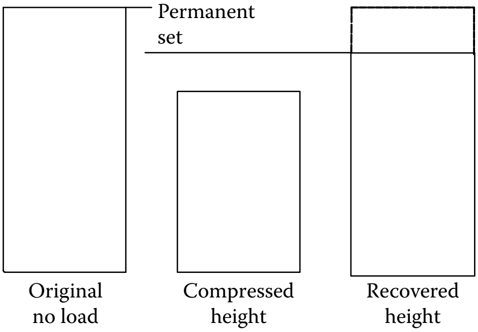


FIGURE 7.9
Determination of permanent compression set.

25%. The ability of the material to recover is important in sealing applications, where the compression forces may change due to temperature fluctuations.

Softer materials normally have better compression set results than the harder grades. This is due to the chains being able to move more readily over each other. Compression set values can also be improved by introducing some degree of permanent cross-linking at the prepolymer stage. If polyurethane is placed under a constant stress, it will creep slowly over the course of time due to strain relaxation.

7.2.10 Permeability to Water

Polyurethane, like all other plastics, consists of chains that are always moving on the molecular scale. The polyurethane has molecular-size voids in which it will allow small molecules to enter the material. The material breathes and allows moisture to enter.

This moisture has several effects. Initially, it will react with any remnants of isocyanates and curatives. Moisture acts like a plasticizer, helping to give the final properties of the polyurethane. Under the influence of heat, it will cause some breakdown of the material, especially in the polyesters.

When polyurethanes are used in the lining situation, this permeability of water can cause major problems in the form of blisters. The thin coating allows the moisture to reach the support layer. If the bonding is incomplete or the water attacks the bonding agent, some of the moisture can condense if the outer layer is cool enough. This has two effects. First, there is a greater driving force for more moisture to enter the polyurethane as the equilibrium has been disturbed. Second, as the metal support heats up, again the moisture is vaporized and there is a high internal pressure. The pressure will extend the plastic polyurethane layer and a blister will form. This action will also cause an enlargement to the disrupted bond area (see Figure 8.7).

In all such applications, the bonding surface must be correctly prepared, and the correct bonding agents must be used, allowed to dry, and, if needed, activated properly.

7.3 Environmental

Polyurethanes need to have the right mechanical, temperature, chemical resistance, and wear properties to be successful in any application. In real-world applications, there is normally more than one influence that will affect the properties of the polyurethanes.

7.3.1 Thermal

Cold

As the temperature decreases, the degradation effect on the polyurethane chain also reduces to virtually nil. Physical properties change, but these changes are reversible. The major changes are:

- Increase
  - Young's modulus
  - Hardness
  - Tensile strength
  - Torsional stiffness
- Decrease
  - Resilience

The stiffness increases slowly from 20 to approximately –25°C, after which it increases rapidly. At –30 to –40°C, there are molecular changes to parts of the polyurethane chain. These changes are dependent on the regularity of the molecule. The use of mixed polyesters will give lower results than the straight polyethylene adipate. The ester-based polyurethanes will become brittle at about –60 to –80°C. If polyester polyurethanes are held at low temperature, crystallization can occur. They are very much harder and much stiffer than normal. This state can be reversed by gentle heating or work such as slight flexing.

Polyether-based urethanes do not become brittle until approximately –87°C. DuPont (now Uniroyal) polyurethanes indicate an elongation at break of 200% at –73°C (Uniroyal Chemicals, 1993).

Heat

Short- and long-term application of heat to the polyurethane has different effects.

Short-Term Effect of Heat

If kept within the range of ambient to 110°C, there is a temporary falloff in most properties, except the Young's modulus, as the bonds become weaker.

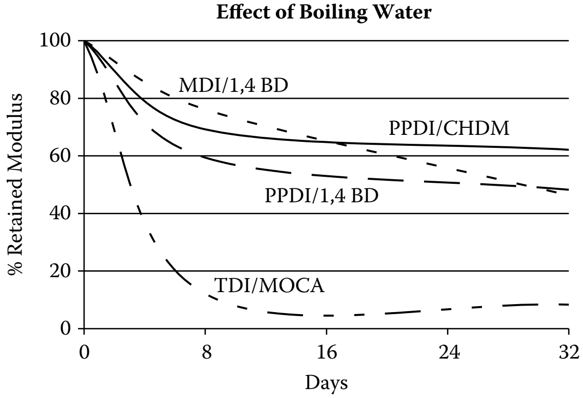


FIGURE 7.10
Effect of boiling water on different polyurethanes.

For polyether-based polyurethane at 70 to 80°C, the properties are only 50% of the original, whereas at 110°C the value drops to about 20%. This gives a normal safe working temperature of 80°C. Figure 7.10 illustrates the aging effect on different cure systems. This working range can be increased by the use of isocyanates such as PPDI in the polyurethane (Chin et al., 1992).

The second heat-related effect normally under dry conditions starts at temperatures higher than 80°C. Above 80°C, there is a gradual decrease in properties over time, and the rate increases with more elevated temperatures. Figure 7.11 shows the effect of dry heat aging on a typical polyether polyurethane.

Polyether polyurethanes are less stable to higher temperatures than the polyester-based materials. The ether linkage in the soft segment is attacked

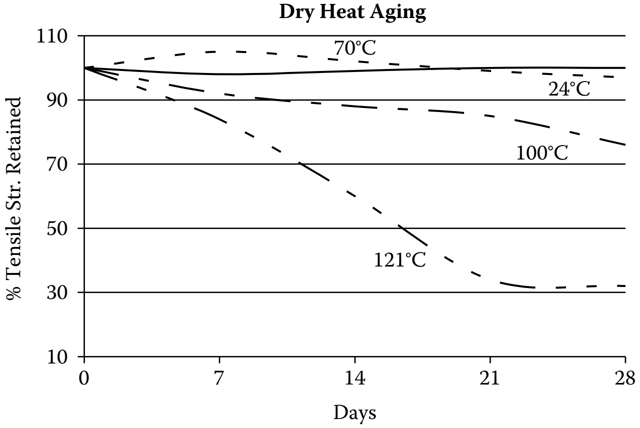


FIGURE 7.11
Dry heat aging of polyether polyurethanes.

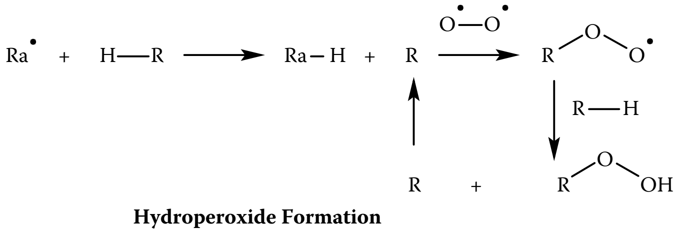


FIGURE 7.12

by the oxygen in the air while under the influence of heat. The order of resistance is:

ester > urea > urethane > ether

The mechanism is believed to be that a hydrogen atom next to the ether linkage is attacked. This radical reacts with oxygen from the air to form a peroxide radical, which in turn takes another hydrogen atom from the backbone of the chain to form a hydroperoxide. This hydroperoxide breaks down into two more radicals (see Figure 7.12). When polyether polyurethanes are heated in an atmosphere of nitrogen, this thermal degradation does not take place and the material retains its properties.

7.3.2 Ozone Resistance

Ozone is found in the atmosphere, especially around electrical appliances such as motors. Empirically, it has been found that exposure to 3 ppm ozone under 25% strain gives a good indication of ozone resistance. At this level the material does not crack after 500 hours of exposure. If the level is increased to 100 ppm, some cracking is observed after 45 hours, and the sample breaks after 460 hours.

7.3.3 Hydrolysis

Hydrolysis can be defined as the decomposition of a compound by reaction with water, the water taking part in the reaction. The effect is enhanced by the presence of either acids or alkalis. The chemistry of polyurethanes leads to the probability of hydrolytic attack. The mechanism is illustrated in Figure 2.41.

Applications of polyurethane are often in moist air and water. Polyurethanes are frequently used in acid or alkaline solutions; even plain water is never actually neutral. Water is also present in the air and is absorbed into the polyurethane.

Early work by Athey (1965) and Magnus et al. (1967) evaluated a range of polyurethanes for their resistance to moisture and dry and moist air environments. Athey showed that polyether urethanes were 5 to 10 times more resistant to hydrolysis than polyurethanes made from polyadipate urethanes. Further work showed that polycaprolactone polyurethanes were more resistant than polyadipate polyurethanes. Polyurethanes made from polycarbonate diols have been found to be more hydrolytically resistant than the polycaprolactone polyurethanes. This leads to the series:

ether > polycarbonate > caprolactone > ester

Chemistry books show that the neighboring groups have an influence on the hydrolysis effect and diminish as the ester groups become further apart.

Work showed that moist air (100% relative humidity) will cause more damage than moist conditions. This can be due to a combined effect of thermal oxidation and hydrolysis. In moist air, the acid generated by the hydrolysis is not removed. The acid will catalyze the reaction further. In a liquid environment the acid generated will be washed away by the water solution.

Carbodiimides have been found to stabilize the polyester polyurethanes by blocking the carboxyl group formed when the chain has been broken. This helps prevent further autocatalytic degradation. The action is most pronounced when amines are used as the curative in caprolactone polyurethanes.

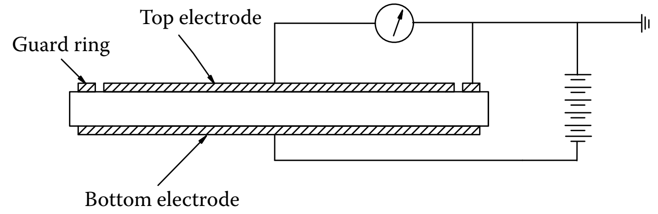
The loss in properties of polyethers at 70°C (when in water) is evident with the life expectancy of 12 months. At temperatures above 50°C, the hydrolysis of polyadipate polyurethanes is such that their useful life is limited unless stabilization is used.

A 10-year long-term study was carried out in Panama on diamine cure polyether polyurethanes to examine their long-term resistance in wet humid conditions. The 10 years of exposure was found to have little effect on the samples that had been stored in the sea, jungle, soil, sun, and in a hut. The samples exposed to the direct sun had the greatest loss of properties. Those in the sea had minimal loss in properties after the barnacles had been removed (Cumberland, 1960–1985).

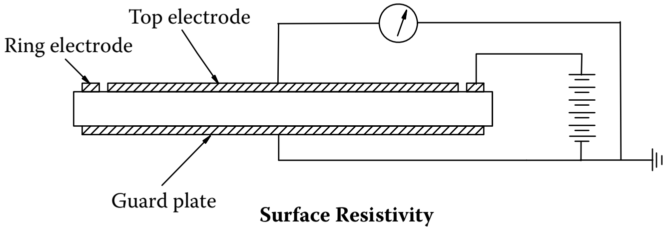
7.4 Electrical

The basic electrical properties of polyurethanes are good, but the polymer's tendency to absorb moisture can change the properties considerably. Polyurethanes are therefore not normally used as electrical insulators. They can be used in potting and encapsulating applications. Any applications involving mains power must be evaluated and approved by the relevant local electrical authority before use in the application.

There are several important electrical properties. Insulation resistance is the resistance of polyurethane to the flow of electricity. The insulation resistance is composed of two main components. The "volume resistivity" is the resistance to flow through the bulk of the material and is a function of the composition of the polymer. The second component is the "surface resistivity,"



Volume Resistivity



Surface Resistivity

FIGURE 7.13
Volume and surface resistivity measurements.

which is controlled by the condition of the surface of the polyurethane (see Figure 7.13). The cleanliness of the surface, purity (bleeding or surface breakdown), and amount of moisture absorbed into the surface layer affect the surface resistivity. Moisture is slowly absorbed by the polyurethane and moves inward toward the center of the material.

The electrical resistivity of materials can vary from being an insulator through semiconductors to conductors of electricity. By careful adjustment to the chemistry and the use of additives, the resistivity can be controlled from being an insulator to a semiconductor. Figure 7.14 illustrates the change from a conductor to an insulator.

Arc resistance is the tracking of an electrical arc over the surface of a polymer. The arc will initially track through the air, but, depending on the composition of the polyurethane surface, decomposition of the polymer can take place and a more conducting track formed. The polyurethane will decompose to carbon that will readily carry the current. Figure 7.15 illustrates the diagrammatic method of how to determine the tracking resistance of polyurethanes.

Dielectric factors include the dielectric constant. This constant is the ability of a material to hold an electrical charge, as in a capacitor. The two other factors related to the dielectric constant are the "dissipation factor," which relates to the rate at which the charge is lost from the polyurethane, and the "power factor," which relates to the amount of heat generated in the storage of electricity.

The resistivity of polyurethanes changes with both temperature and relative humidity (RH). The typical volume resistivity value at 50% RH is 3.6×10^{12} ohm-cm at 23°C, whereas at 100°C it drops to 1.2×10^{11} ohm-cm.

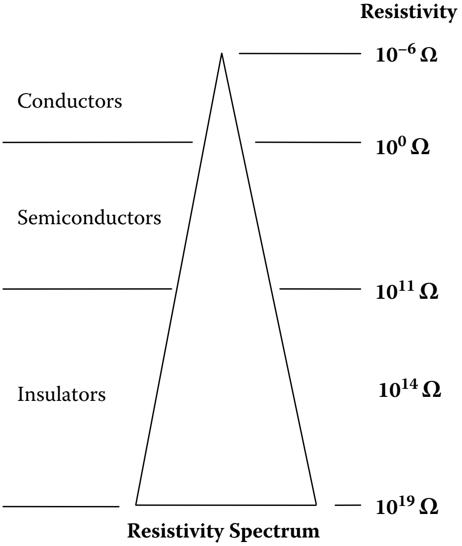


FIGURE 7.14
Resistivity spectrum.

Another grade changes its resistivity from 3.5×10^9 ohm-cm at 20% RH down to 1.4×10^9 ohm-cm at 90% RH.

Polyurethanes find an application where they dissipate electrostatic charges generated in rollers and items such as chute liners. There are two main routes to obtain these properties. The classical method is to add conductive graphite or fine metal to the polyurethane. The major disadvantage is the high loading of the material, which reduces the physical properties. The viscosity of the mix is also drastically increased, and nonuniform mixing is often the result. The alternative is to use an anionic or cationic antistatic

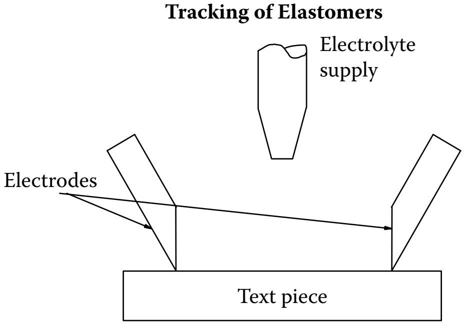


FIGURE 7.15
Electrical tracking of elastomers.

liquid. The agents are liquid surfactants such as quaternary ammonium salts, alkyl sulfonates, ethoxylates, and ethanolamides. The liquid antistatic agents are hydroscopic, and care must be taken to keep them dry. Some agents in the market are supplied in a water alcohol mix. These are not suitable. The initial addition of up to 1% of the liquid has the greatest effect.

7.5 Radiation

Polyurethanes have been reported to be one of the most resistant polymers to gamma radiation. Early work by Harrington (1960) comparing the effect to tensile strength and hardness found that it is the total dosage rate that is the controlling factor. High dosages of 258kC/kg (Roentgens) had some effect on tensile strength, but the material was still serviceable. Initial work was done using thermoplastic polyurethane (Estane). The exposure to the gamma radiation caused cross-linking in the material after initial chain scission. The polyurethane was found to be more resistant to flex cracking than other polymers and retained its toughness and flexibility.

7.6 Chemical

The chemical resistance of polyurethanes allows them to be used extensively in industry. The individual chemistry of each grade must be used to optimize the use. For example, polyesters are tough and oil resistant. This makes them ideal for wiper blades on metal-working machinery.

7.6.1 Inorganic Chemicals

Inorganic salts normally do not have adverse effects on polyurethane beyond that discussed under hydrolysis. If the pH of the solution is kept within the normal "neutral" range of pH 5.5 to 8.0, they usually have no catalytic effect on the degradation of the polyurethane. If the concentration is increased, the material will become either more acidic ($pH < 5.4$) or more alkaline ($pH > 8.0$). The acidity or alkalinity will promote the hydrolysis of the polyurethane.

The temperature also plays a large part in the speed of the hydrolysis. Polyethers are also more resistant to hydrolysis than polyester-based polyurethanes.

In the following sets of data, the grading is:

A: No/little effect

B: Moderate effect

C: Probably unsatisfactory

D: Unsatisfactory

Inorganic Salts

Material	Grading	Comments
Ammonium nitrate	D	Acts more like nitric acid than a salt
Barium chloride	A	
Barium sulfate	A	
Barium sulfide	A	
Calcium chloride	A	
Calcium nitrate	A	
Copper chloride	A	
Copper cyanide	A	
Copper sulfate	A	
Magnesium chloride	A	
Potassium chloride	A	
Potassium nitrate	A	
Potassium sulfate	A	
Sodium chloride	A	
Sodium phosphate	A	
Sodium sulfate	A	
Salt water	A	Brine or sea water

Inorganic Acids

Strong acids such as sulfuric and nitric acid have different forms of attack. Strong sulfuric acid will dehydrate the structure, whereas nitric acid will oxidize it.

Material	Grading	Comments
Boric acid	A	Weak acid
Nitric acid concentrated	D	
Nitric acid diluted	C	
Oleum spirits	B	Sulfur trioxide in sulfuric acid
Phosphoric acid 20%	A	
Phosphoric acid 45%	A	Note upper operating temperature
Sulfuric acid concentrated	D	
Sulfuric acid diluted	B	

Alkali

Material	Grading	Comments
Ammonium hydroxide	A	
Calcium hydroxide	A	Very weak alkali–lime
Lye	A, B	Crude sodium hydroxide
Potassium hydroxide	A	Dilute solutions/Polyethers
Sodium hydroxide	A	Dilute solutions/Polyethers

In dilute hydrogen peroxide (less than 10%) there is a slight attack, whereas with the strong peroxide (30%) the degradation is fast. This also applies to 12% bleach (sodium hypochlorite).

Inorganic Gases

Material	Grading	Comments
Carbon dioxide	A	
Carbon monoxide	A	
Chlorine wet, dry, or gas	D	Very aggressive gas will react with any moisture
Hydrogen gas	A	
Nitrogen	A	
Oxygen 95°C	A	

7.6.2 Organic Chemicals

The term "organic" is used in the traditional chemical interpretation. Depending on the structure of the organic material, there will be varying effects on the polyurethane. Alcohols, organic acids, ketones, and esters can cause swelling and degradation at higher temperatures.

Hydroxyl

Material	Grading	Comments
Ethyl cellulose	B	Complex hydroxyl
Ethylene glycol	B	Complex hydroxyl
Glucose	A	Complex hydroxyl
Glycerine	A	Complex hydroxyl
Glycols	B	Complex hydroxyl
Ethyl alcohol (ethanol)	B	Simple hydroxyl
Methyl alcohol (methanol)	D	Simple hydroxyl
Whisky, wines	A	Simple hydroxyl

Ketones

Material	Grading	Comments
Acetone	D	
Methyl ethyl ketone	D	50°C

Esters

Esters and aliphatic hydrocarbons do not affect the polyurethane to a great degree.

Aromatics

Aromatic hydrocarbons need to be used with careful consideration. At ambient temperatures, they can cause swelling, and at higher temperatures there is a slow breakdown. It has been found that in uses up to 40 or 50°C, polyurethane can be used in petroleum pump valve seats.

Material	Grading	Comments
Diesel oil	B	
Hydraulic oil (petroleum based)	A	
Kerosene	B	Paraffinic
Petrol (with alcohol)	D	Alcohol makes it more aggressive
Petroleum > 121°C	D	
Petroleum < 121°C	B	
Petroleum < 71°C	A	
ASTM Fuel No. 1 < 70°C	A	
ASTM Fuel A	A	Standard test fuels
ASTM Fuel B	B	Standard test fuels
ASTM Fuel C	C	Standard test fuels

Natural Oils and Fats

Natural oils and fats have little to no effect on polyurethanes. Use of food grades will often be required.

Material	Grading	Comments
Animal fats	A	Animal
Butter	A	Animal
Cod liver oil	A	Animal
Lard	A	Animal
Coconut oil	A	Vegetable
Corn oil	A	Vegetable
Cottonseed oil	A	Vegetable
Linseed oil	B	Vegetable
Olive oil	A	Vegetable
Peanut oil	A	Vegetable
Soybean oil	B	Vegetable
Stearic oil	A	Vegetable
Tung oil	B	Vegetable

Oils and Greases

Oils and greases find a good application with polyurethanes at lower temperatures when the total wear, oxidation, and degradation are taken into account.

Material	Grading	Comments
Asphalt	B	
Bunker oil	B	
Mineral oil	A	
Transmission fluid type A	A	

Chlorinated Materials

Chlorinated solvents cause varying damage, from weak to relatively strong. Methylene chloride is very aggressive, whereas carbon tetrachloride and trichloroethylene are relatively inert.

Material	Grading	Comments
Methylene chloride	D	This is a very aggressive solvent
Ethyl chloride	B	

Numerous tables of chemical resistance are available in the marketplace, but there are a number of points to be considered prior to use:

- Concentration of material
- Whole composition of the material being used (e.g., a defoaming agent dissolved in diesel)
- Temperature of use
- Extreme conditions (e.g., dilute sodium hydroxide normally but strong caustic at 120°C for cleaning)

Before any final recommendation can be made, the entire application must be considered, from a normal operating situation to extreme conditions, including changes to the material under operating conditions.

7.7 Wear

Wear is not a direct property of polyurethane but is the result of a complex system of materials being in contact, geometry of contact, operating conditions, and environment (Mardel et al., 1995). Polyurethanes find successful use in applications where resistance to wear is required. The choice of the correct grade is vitally important, as the resistance to wear is a complex problem involving knowledge of the wear mechanism, the wear environment, and the properties of the grade of urethane. The two types of wear associated with polyurethanes are:

- Abrasive wear
- Erosive wear

ASTM G40-83, "Standard Terminology Relating to Erosion and Wear," defines abrasion as "wear due to hard particles forced against and moving along a solid surface." Erosion is defined as the "progressive loss of original material from a solid surface due to mechanical interaction between that surface and a fluid, a multi-component fluid, or impinging liquid or solid particle."

Abrasive wear is a two-bodied wear that is found in a large number of applications where polyurethane is moving over a second object without lubrication. Wheels used on forklifts, trolleys, or any other situation under load are typical examples of abrasive wear.

Erosive wear is a three-bodied wear, which is found in pump and cyclone linings, impellers, and screens. The polyurethane is attacked by a solid object that is being transported by a third medium such as process water. The temperature and chemical composition of the process liquid also play an important part in the life of the component.

The process conditions, such as fluid composition and temperature, often have a far greater effect on the maximum useable life than the normal dry mechanical properties of the material. A typical change is from 120°C maximum temperature for dry applications to 75°C for wet applications.

7.7.1 Abrasive Wear

Abrasive wear is a complex combination of a number of factors, including resilience, stiffness, thermal resistance, thermal stability, resistance to cutting, and tearing (Smith, 1993). There are a number of laboratory tests, both international standards and commercial tests, for the evaluation of abrasive wear. The results from these tests normally represent only an indication of the actual wear that can be found in practice. The test equipment generally has a loaded sample against course abradant or, in the case of a Taber abrader, a loaded abrasive wheel against a flat sample (see Chapter 8).

The wear rate can be considered to be composed of three factors. The first is the properties of the material being worn, the second the angularity of the abrasive, and the third the nature and servility of the interaction of the abrasive and the material being worn (Gates, 2001).

A comparison of the abrasive wear by Böhm (1990) found that the hard and more brittle plastics, such as polyacetals, polyamide-imide, and polycarbonates, are less abrasion resistant than softer and tougher materials such as the polyethylenes and polyurethanes. Table 7.2 details some comparative

TABLE 7.2

Abrasive Wear Comparisons

Material	Abrasion mm^3.cm^{-2} (3.66 m)
Polyurethane 70 Shore A Ester	4.6
HD Polyethylene	6.7
UHMWPE	6.8
Nylon 66	7.5
PET	8.1
Polyurethane 80 Shore A Ester	9.0
Polypropylene	9.4
Polyurethane 80 Shore A Ether	10.1
Polycarbonate	11.8
Polyvinylidene fluoride	12.1
Polysulfone	12.5
Polyacetal	14.4

figures. Within the polyurethane group of materials, the harder and tougher polyurethanes have the better abrasive wear resistance.

Trofimovich et al. (1987) considered polyurethanes to be a mixture of two insoluble materials, namely, the hard and the soft phases. He found that with simple thermoplastic systems a relationship could be found, with the density of the hard segment being a controlling factor. With the more complex cross-linked materials, the relationship was harder to establish. In filled compounds, the filler can protrude above the surface and change the wear conditions. The abrasive wear will reach a minimum depending on the concentration of the hard segment and the type of backbone.

Examination using a scanning electron microscope (SEM) of the surface of abraded polyurethane shows cutting and gouging marks on the surface. The surface can deteriorate further, and fatigue cracks can start to appear. If the conditions are extreme, the surface can soften drastically and molten/decomposed polyurethane can be seen under the SEM.

The heat generated by the abrasive wear is not as readily dissipated as with the erosive wear.

7.7.2 Erosive Wear

Erosive wear can be considered to be an interfacial wear where the energy evolved in the wear is dissipated. The third component in the wear process removes some of the frictional heat generated when the wear particle strikes the surface of the sample.

Erosion studies have shown that the softness and resilience of elastomers handle wear better in a number of cases than hard metals (Ephithite, 1985). In dry applications, the heat dissipation is poor and can result in rapid degradation of the elastomer. However, in slurry applications the lubrication of the water changes the friction resistance greatly.

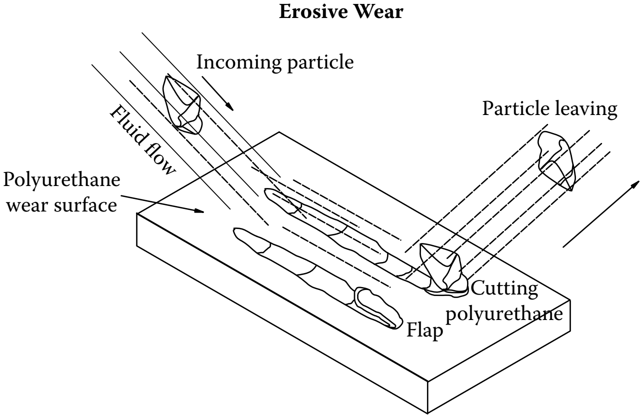


FIGURE 7.16
Erosive wear mechanisms.

Mode of Wear

Arnold and Hutchings (1990) found that the normal erosive wear of elastomers is characterized by fine cracks being formed under impact. These grow incrementally under cyclic impact loading. When these cracks intersect, small particles are removed. Cracks will form and grow when the rate of elastic energy increases due to impact and exceeds surface energy associated with crack formation. As cracks grow, elastic energy is released.

Microcutting of Polyurethane

A mode of wear is microcutting, where a sharp edge will cut through the surface. The general mechanism is shown in Figure 7.16. Polyurethane under tension will wear at a greater rate than one that is under slight compression. This is similar to other polyurethane properties such as cut and ozone resistance.

An elastomer with a low modulus will often have far better erosive wear than material with a higher modulus. An abrasive wear test (such as the DIN abrader) will show a poor result for a soft elastomer. This is also shown in field applications such as tire wear. When the application is changed from abrasive to erosive wear, the softer elastomer will wear very well. The reason for this is that the low modulus of the soft elastomer allows the stresses from each impact to be dissipated more readily than for hard polyurethanes. The soft material will stretch further and then snap back before damage is done. Any microcracks formed will have a slower growth rate and hence less erosion will occur.

Resilient elastomers will give a pattern of ridges approximately 15 to 30 micrometers apart across the elastomer at right angles to the direction of wear (Hutchings, 1987). Attached to the ridges will be globules of worn polyurethane. Low-resilience elastomers have higher wear rates. The surface is rough and does not show the same ridges.

Studies of the properties of polyurethanes, both physical and physicochemical, showed only that resilience had some direct relationship to wear. A relationship of $(1\text{- resilience})^{1.4}$, where resilience is expressed as a fraction, has been shown (Hutchings, 1987). No other relationship has been found for other properties for erosive wear between 30° and 90° (Hutchings, 1987).

External factors that affect the erosive wear of the elastomers include:

- Angle of impact
- Particle velocity
- Particle size
- Particle shape
- Presence of lubricant

Angle of Impact

The angle of impact of the particles on the polyurethane has a major effect on the erosive wear. Both Hutchings and Deuchar (1987) and Li and Hutchings (1990) found that the wear of polyurethane was 10 times greater at 30° than at 90°. The wear mechanism did not change with different mechanical properties. Figure 7.17 shows the erosive wear variations between impingement angles and prepolymer type. At a 90° impact angle, the mode of wear is one of many direct cuts and not the "rolling" of the surface. The number of interparticle collisions also increases greatly.

Velocity of Particles

At high particle velocity (above 50 m/s), the wear rate increases more than what would be expected from straight kinetic modeling (Arnold and Hutchings, 1990). This is believed to be from higher formation and propagation of microcracks.

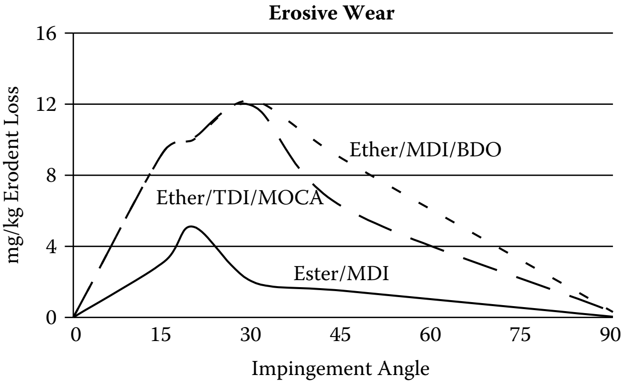


FIGURE 7.17
Effect of impingement angle on erosive wear of polyurethanes.

The rate and amount (flux rate) of material impinging on the elastomer have an effect on the wear rate of the elastomer (Arnold and Hutchings, 1989). With flux rates of between 500 and 5000 kg m^{-2} sec^{-1}, the erosive wear decreased with flux rate at low velocities and low angles of incidence. At higher flux rates (1000 to 10000 kg m^{-2} sec^{-1}), the wear rate decreased when the velocity was lower and the angle of impact was more normal to the surface.

At the high flux rate, there will be a large number of particle-to-particle collisions that will decrease the wear rate. Water and air will be forced into the surface of the polyurethane. Hydroperoxides can be formed under these conditions, resulting in breakdown of the polyurethane in a similar manner to that described for hydrolysis.

Particle Size

The load applied to the surface of the polyurethane by the impinging particle is considered to be an important factor in the wear process (Ephithite, 1985). The force is a product of the mass and velocity. The mass of the particle increases greatly as it becomes larger (the volume increases by the cube of its dimensions). When a certain force is reached, rolling wear will commence. Depending on the force, either the elastomer will deform or, if the force is large enough, a particle of polyurethane will be removed in a scallop-like piece or a curled-up leaf.

Particle Shape

Particles can be any shape, from round to knife- or dagger-shaped. The shape can also change during the wear process. The way particles break on impact is very important. The edge of the particle can vary from being blunt to razor-sharp. Sharp-edged and flaky particles are considered to be the most abrasive (Ephithite, 1985). The sharp edges often have a slashing effect.

The Presence of Lubricant

The largest effect of water or any other liquid is that it acts as a lubricant and reduces the erosive rate by reducing the frictional forces. This effect is greatest at angles between 30° and 90°. If water instead of air is used, the wear rate is reduced by 50% (Arnold and Hutchings, 1990). To a lesser degree, the lubricant will enhance any cutting that may take place. The formation of hydroperoxides is another effect caused by water on the polyurethane.

Summary

The wear of polyurethanes is a complex combination of a large number of influences, from both the polyurethane and the material that is doing the wearing. Over the course of the life of the polyurethane, the properties can change and the wear rate altered. Flow patterns can also change, affecting the wear to a large degree.

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8

Applications

8.1 Introduction

Polyurethanes find applications in a wide range of industries in competition with other plastics, ceramics, and metals. Cast polyurethanes are tough, abrasion resistant, have load bearing properties, and are chemical resistant. That makes them the first-choice materials in certain situations. The ability to be easily prototyped and have short production runs is a major positive factor for polyurethanes.

The correct choice of the type and grade of polyurethane is important to produce a successful product and a happy customer. Some of the important criteria are:

- What is the main purpose of the application?
- Are the conditions static or dynamic?
- In what environment will the part work?
  - Heat
  - Cold
  - Chemical
  - Food/drugs
- Electrical, radiation, and so on.
- What are the expected extremes in working conditions?
- Will there be any abrasive or erosive wear?
- Is there a potential internal heat buildup?
- Is there any history of previous use of polyurethanes in similar situations?

When selecting polyurethanes for any application, a full understanding of the working conditions should be obtained to prevent overspecifying the grade and type. These conditions may include the interaction of temperature, hydrolysis, and wear in a dynamic situation. The limitations of polyurethanes also must be taken into account and some redesign carried out if needed.

8.2 Major Type and Grade Selection

A number of traditional factors are often specified for polyurethanes, such as hardness and tensile strength, that do not control the final performance properties.

8.2.1 Hardness

The hardness of polyurethanes can be obtained by either the density of the hard segments, the choice of curative, or the addition of plasticizer. The importance of hardness is to control the rigidity of the part (if not reinforced) or its softness to conform to the shape of some other object it passes over. For very low hardness (< 60 A) applications such as rolls, TDI esters are the most suited, whereas ether-based materials are least suited. Hard materials do have better abrasive resistance than soft materials.

8.2.2 Tear Strength

Tear strength is important where there is any tension and the potential for "nicking" of the surface. The structure and internal bonding in the polyurethane give the tear properties. The high toughness of the esters makes them most suited, whereas materials made from the low-cost ethers have the worst resistance.

8.2.3 Temperature

Low-temperature applications are controlled by the stiffening of the polyurethane as the temperature goes from 20°C down to –20°C. In these applications, MDI ethers are the most suited, whereas ester-based materials become very stiff. At very low temperatures, esters have a lower brittle point than ethers but they must be kept from crystallizing.

In high-temperature applications, the use of the newer isocyanates such as PPDI and CHDI provide a higher maximum temperature range of up to 110 to 120°C dry, but they do come at additional cost. For materials in the slightly lower temperature range, TDI-based materials give better heat resistance than MDI-based materials. With sustained heat, aging esters will maintain their properties longer than with ethers. The older-style PPG-based materials have the least heat resistance.

8.2.4 Heat Buildup

Heat buildup is closely related to resilience and a low tan (δ) value. The design of the part is vital to allow heat that is built up to dissipate successfully. Ether-based materials have a lower heat buildup than esters.

8.2.5 Hydrolysis Resistance

In any choice of material involving hydrolysis resistance, the time–temperature relationship with regard to hydrolysis must be known and appreciated. The newer types of esters offer better resistance than the traditional grades. This means that the newer material can operate in higher temperatures than the previous maximum of 50°C. MDI-ether-based materials are classed as the most hydrolysis-resistant polyurethanes.

8.2.6 Compression Set

Compression set is controlled by the cross-linking in the material. This may be carried out during the design of the prepolymers or by using some short-chain cross-linking agents. TDI-based polyurethanes have better compression set than the MDI-based materials.

8.2.7 Tensile Strength

Polyurethanes are occasionally used in the tensile mode. In these applications, the strength and toughness of ester-based materials are superior to those made from ethers. The ultimate elongation of all polyurethanes far exceeds any application, so the choice is not of any major consideration.

8.2.8 Oil Resistance

The oil and grease resistance of the ester group of polyurethanes, together with their toughness, makes them most suited to these applications.

8.2.9 Wear Resistance

For sliding abrasive resistance, the tough polyesters are the best suited. This also must be balanced against the hardness of the material. The older style PPG materials do not have the physical properties to provide outstanding resistance to abrasive wear.

When there is impinging erosive wear, MDI-based polyethers are normally classified as the most suited because hydrolysis resistance is also taken into account. Certain of the more sophisticated esters have better erosive wear than the high-cost ethers (PTMEG) under hydrolysis conditions. The temperature limitation, however, is still just below that of the ether-based materials. The angle of impingement also must be taken into account.

8.2.10 FDA Approval

MDI-diol-cured polyurethanes generally can receive FDA approval for use, provided no mercury catalysts are used. Polyurethanes made from most amine-cured TDI material will not meet the requirements for FDA approval. Trimetyleneglycol di-p-aminobenzote (Versalink 740M) of the diamine curatives has, however, been approved. If additives (e.g., catalysts and plasticizers) are used with the polyurethanes, these also must be considered in the approval process. Appropriate local and state approvals must be obtained prior to use where food or drugs come in contact with the polyurethane.

8.2.11 Flexibility in Adjustments to Formula

Polyurethanes based on MDI have the greatest flexibility in the choice of curatives and blends of curatives that can be used to obtained the desired properties. In cast elastomers, the hygroscopic nature of the curatives must be taken into account and proper handling and storage used; otherwise, there may be a very high reject rate. Catalysts are also more readily used with the MDI materials. Organic acids such as adipic or oleic acids work better with TDI materials than MDI systems.

TDI-based materials are normally cured with a range of amine-based curatives. The current most popular are Ethacure 300, followed by MOCA. MOCA is still popular despite the carcinogenic concerns associated with it.

For soft materials, extension with either a reactive or nonreactive plasticizer is best with an ester-based material. The toughness of the ester helps keep the properties usable at lower hardness.

8.2.12 Cost

The unit cost of polyurethanes varies greatly from the lowest raw material cost of the PPG/TDI based systems to a heat-resistant, optically clear aliphatic grade. The actual lowest volume cost is the cost of a system that will fully meet the needs of a specified item. The use of a grade that is too good for the application wastes money. Conversely, a grade that is not suited also costs money.

8.3 Polyurethane's Role in the Materials Field

Polyurethanes have several advantages over competing material in the materials field. The major items of competition are metal, other plastics, and rubbers. Ceramics offer some competition to urethanes. Each of the above groups of materials, including polyurethanes, requires its own design adjustments for successful use in any application.

8.3.1 Comparison to Metals

The very much lower density of polyurethanes (1.0 to 1.2g/cm^3) compared to the lightest of standard metals, namely aluminum (~2.7 g/cm^3), gives it great weight advantages. The difference is magnified even more when compared to steel. Parts can be made so much lighter that they can be handled with ease.

The fabrication of polyurethanes into complex shapes is much easier than with metals. Large casting of up to 500 to 1,000 kg can be made from relatively simple molds and buckets, with minimal labor. The energy input into the production of a cast polyurethane part is low compared to the melting of a metal alloy. The actual molding costs are also lower.

Polyurethanes provide a large package of chemical resistance to metals within the operating temperature of the polymer. By careful selection, alloys can be used to provide the desired chemical resistance, but normally at a cost disadvantage.

Choosing the polyurethanes with the correct resiliency property can be made to be either resilient or energy absorbing. The operations do not produce the noise levels that metals produce when they strike each other. The design of the polymer parts must be such that the heat buildup due to the lower heat conductivity is removed. This is often achieved by using a thinner cross-section and bonding the material onto metals.

For smaller particle sizes (~1,000 microns), polyurethanes provide a superior erosive wear resistance to metals at most normal velocities of up to 20m/s. Outside these limits, the materials need to be evaluated in a manner that is as close to real conditions as possible.

Polyurethanes can flex and deform to assist in any movement of parts. The elastic nature means that the polymer will return to close to its original shape after any minor deformation. The flexibility can be a disadvantage in certain situations and the positive attributes (e.g., better wear) nullified. In such situations, the casting of an outer surface of polyurethane over a metal reinforcing is advantageous.

The chemical structure of the polyurethanes make them relatively nonconductive and, with suitable modification, semiconductive, allowing for the controlled discharge of static. Polyurethanes will not produce a spark when they are struck by another object.

8.3.2 Advantages over Plastics

Within the polymer group, there may be certain plastics that have specific superior individual properties to polyurethanes. In the overall situation, the total requirements of the application must be considered.

The ability to produce polyurethane parts with a large cross-section (>30 mm) easily is a major advantage over other polymers. A conventional polymer such as polyethylene requires heat under pressure to form a thick cross-section with a long, slow cooling/annealing cycle to prevent stress and voids in the part. The production of other than simple-shaped articles is very difficult. After this molding process, postmachining also needs to be carried out.

Tooling cost for the production of all polyurethane parts is much lower than that for making plastic parts by either compression or injection molding. The molds do not have to withstand the pressures involved when compression and injection molding is carried out. These lower molding costs can be used to prepare prototypes of a new concept for general evaluation prior to the expense of an injection molding die.

The wear resistance is better than most plastics, except for UHMWPEin sliding wear applications such as chutes. Polyurethanes can be made in thick-sectioned intricate shapes. This makes them a very good choice in wear-resistant applications.

The thermoset component in polyurethanes gives them better compression set than most thermoplastic polymers. They also have better cold flow properties. Polyurethanes are tough and more resilient than a large number of other plastics.

The radiation resistance of polyurethanes is better than that of other polymer materials and makes them a good candidate in applications where there is gamma radiation.

Most polyurethanes need UV additives to stop yellowing, except for the specialized nonyellowing clear grades. These grades are far more expensive than the standard materials.

8.3.3 Advantages over Rubber

Rubber can be formulated to meet most of the properties of polyurethanes. This is a complex capital and labor-intensive procedure. In most applications more than one property is needed, and polyurethanes provide many of these properties at one time. Rubbers that have the same or better properties than polyurethanes are detailed below.

Property	Rubber Group
Resilience	Natural and chloroprene (neoprene)
Load bearing	Polyurethane is superior to all
Bonding to metal	Natural, chloroprene, SBR, and nitrile
Compression set	Silicone and fluoroelastomers
Electrical	Natural, SBR, and silicone rubbers
Impact resistance	Natural and SBR
Abrasion resistance	Natural, chloroprene, SBR, and nitrile
Tear resistance	Natural rubber
Cut growth	Natural rubber
Radiation resistance	Polyurethane best
Weather resistance	Neoprene, silicone, fluoroelastomers, and polyacralates
Oxidation	Silicone, fluoroelastomers, and polyacralates
Ozone resistance	Neoprene, silicone, fluoroelastomers, and polyacralates
Grease and oil	Neoprene, nitrile, and fluoroelastomers
Water resistance	Natural, chloroprene, SBR, and nitrile

In all these comparisons, the overall properties must be taken into account. Although fluoroelastomers have excellent compression set properties, the other poor physical properties and cost also must be considered.

The capital and process control costs to prepare rubbers must be considered against the cost to process the polyurethanes. The straight raw material cost of the standard rubbers (natural, SBR, and chloroprene) will be less than the polyurethanes' cost, but the overall processing cost of the polyurethanes will be lower.

The load-bearing properties of polyurethanes are superior to that of conventional rubbers. The properties of the harder polyurethanes are superior to that of a rubber with the same hardness. To reach the 60 D to 70 D range, the conventional rubbers have to be very highly loaded or in the form of an ebonite (25% sulfur). Polyurethanes can be produced in this high range while maintaining the elastic properties that are also present in the lower-hardness materials.

Rubbers rely on fillers (both reinforcing and nonreinforcing) to obtain their properties. The curing system also produces a dirty-colored material. To color a rubber is difficult, and only a few basic colors are used. To obtain a transparent rubber, special latex or synthetic cis-polyisoprene must be used, and the use of a peroxide cure is normal. Polyurethanes can be colored any color, but the yellowing of aromatic systems must be taken into account. Aliphatic systems can give transparent nonyellowing systems.

Latex rubber can be poured like polyurethanes, but they generally are only poured in thin sheets. Even thicker sheets such as Linatex require a very long cure time. Pouring is the method of choice for cast polyurethanes. Normally, rubbers require a compression molding press or injection molding machine to produce parts. This has high capital and mold costs.

8.3.4 Limitations of Polyurethanes

Polyurethanes can be used over a temperature of –40°C to a maximum of 120°C. The normal working range has a lower maximum temperature of 70°C.

Hydrolysis is a major problem for polyurethanes, even with the right choice of polyurethane and the use of antihydrolysis agents such as polycarbodiimides. Care and experience are needed in these conditions.

Certain chemicals such as the ketones (acetone and MEK), polar solvents, and concentrated acids affect polyurethanes badly.

A major consideration in all dynamic applications is the buildup of heat. The low conductivity of the polyurethanes does not allow for rapid removal of heat. The design of the part and the grade choice are very important. The part must not be allowed to deflect too much, and a heat sink must be provided. It is desirable to keep the cross-section of the polyurethane at a minimum.

8.4 Polyurethane Selection Criteria

Selecting a polyurethane for any application is composed of two stages.

Properties Required for Application

Every application needs to be evaluated on its merits for the range of properties required. A database of previously successful applications is a distinct advantage. An analysis of the main attributes of an application is needed, e.g., compression, shear, static, dynamic, or wear. Many of these factors are not on the supplier's data sheets and the information needs to be obtained from the supplier or by experimentation.

The overall environmental conditions also must be evaluated. Some of the information may be hard to obtain from the customer due to commercial secrecy. Knowledge of the general type of application needs to be known; for example, a simple defoaming agent may be let down in diesel, which has a moderate effect on polyurethanes. The effect of the overall concentration then needs to be evaluated.

Changes in temperature are an important limitation. The temperature may be from the process stream or it may be generated internally by dynamic work.

Processing of the Polyurethane System

Several factors must be taken into account when the exact grade of material is chosen. The first is the pot life of the system. The pot life controls the time it takes to fill the mold, allowing any entrapped bubbles to rise and to gel off so that it can be placed in the curing oven. This represents a large portion of the physical cycle time.

Very hard polyurethanes gel rapidly (< 1 minute). Hand casting needs to be carried out at as low a temperature as possible to allow for complete filling of the mold. These polyurethanes are normally of a reasonably low viscosity. The pour hole in the mold must be as large as is practical to allow for the speedy addition of the mix. Care must be taken not to allow any folding of the mix in the mold.

PTMEG-based systems are normally much more viscous than PPG-based materials. They must be processed at as high a temperature as possible (at the upper limit of the manufacturer's range). The temperature, however, must not be so high as to cause problems in the chemistry during curing.

MDI-based systems often are slow in setting up. The addition of a catalyst may be needed to speed the reaction. Catalysts such as tin salts (Polycat® T12 or equivalent) or an amine-based catalyst (Polycat® [Air Products and Chemicals, Allenstown, PA] 33LV or equivalent) can be used. Care also must be taken in the demolding of MDI-based systems, as they take longer to build up enough strength to be demolded. Insufficiently cured parts will break easily. The surface of the break looks like shattered glass.

8.4.1 Applications in Tension

The ultimate tensile strength and the modulus at various strains are always quoted in technical literature. These are very good quality control values and give an indication to the type (ether, ester, MDI, IDI) and nature of the prepolymer system used. These tests are also valuable in evaluating the chemical and aging effects on polyurethanes. Where polyurethanes are used in tension, the amount they are stretched is normally no more than 30%. The highest extension is on the order of 100%.

Using polyurethanes as a spring is an application where there is a tension and a compression cycle. The ability of the polyurethane under stress–strain cycling to reach a steady state is important. The material must reach equilibrium after the first couple of cycles to give a constant spring rate. TDI-ether-based materials are best suited for shock mounts or die springs. Applications such as sprockets need a tougher material such as an MDI-ester-based material.

Polyurethanes do not need fillers to give the hardness required as do rubbers. This means that they will keep their resiliency properties over a larger temperature range than conventional rubbers.

In all cases in which polyurethanes are used under tension, the part must be designed to fail in a safe mode. Any internal defects can severely affect the life of the spring, as failure is often developed around these points.

8.4.2 Load Bearing

Polyurethanes have very good load-bearing properties under compression, and this is used in a number of applications. The ability to take the load and then to recover is superior to all other plastics. In all considerations, it must be remembered that polyurethanes are virtually incompressible; that is, they change shape but keep the same volume. The parts must be designed so that the bulge does not become too large and put undue stress on the edges. Examples of successful applications include wheels, tires, cutting and feed rolls, and metal-forming pads.

The shape factor is an important consideration in the response to any applied load. Shape factor is defined as the ratio of the area of one loaded surface to the total of the unloaded surface that is free to bulge. The ability of the part to move when placed under load is important. If the surfaces are bonded to metal plates, the compressive stress to the compressive strain relationship is quite different. Figure 8.1 illustrates the load bearing of a series of polyurethanes compared to SBR and neoprene rubber compounds.

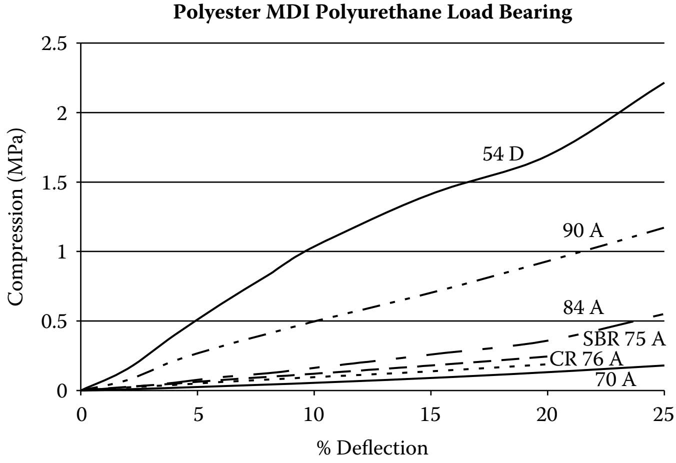


FIGURE 8.1
Polyester versus rubber load bearing.

Wheels

Polyurethanes are used in a variety of wheels, from small wheels in machinery to large wheels such as forklift and rolling wheels on mills. The high degree of natural hardness of polyurethanes, together with its excellent dynamic properties, makes it ideal for load-bearing wheels, with the heat dissipation being the controlling factor. This limits the speed and amount of time that the wheels can work. The very high resiliency grades of MDI-based systems make the use of polyurethane a very good material for rollerskate wheels and similar applications.

In applications using polyurethane wheels, the normally used compression of the polyurethane is 10% of its original thickness. This can be obtained by adjustments to the hardness grade and compression modulus. Polyurethanes in the hardness range of 90 A to 50 D normally have enough load-bearing potential for applications in wheels (see Figure 8.2). The next factor to be considered is the heat buildup in the tire. Polyurethanes with a high resilience (low tan [δ]) are the best suited. Other properties that must be optimized are nick resistance and abrasive wear.

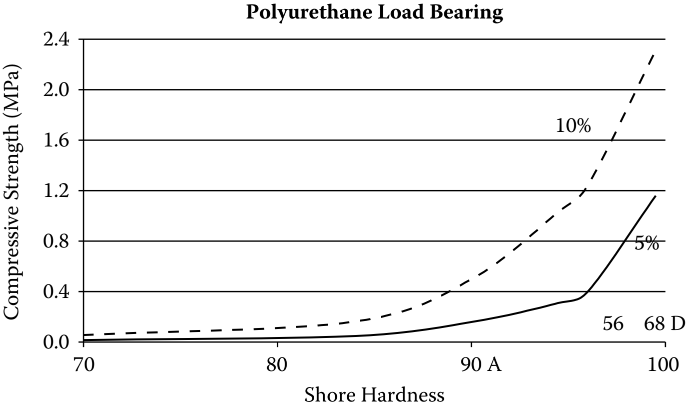


FIGURE 8.2
Polyurethane load bearing for wheels.

There are two normally quoted formulas for the calculation of wheel parameters. The first is the classical formula, which is still quoted in imperial units:

$$U = [(0.75\ W\ (b-a))/(ES\ (8b)^{1/2})]^{2/3}$$

Where U = deflection in inches, W = load in pounds, E = compression modulus in psi, a = inside radius, b = outside radius of polyurethane in inches, and S = actual width in inches. The value of U must be less than 10% of the thickness of the polyurethane (b-a). This, as in all calculations, is the starting

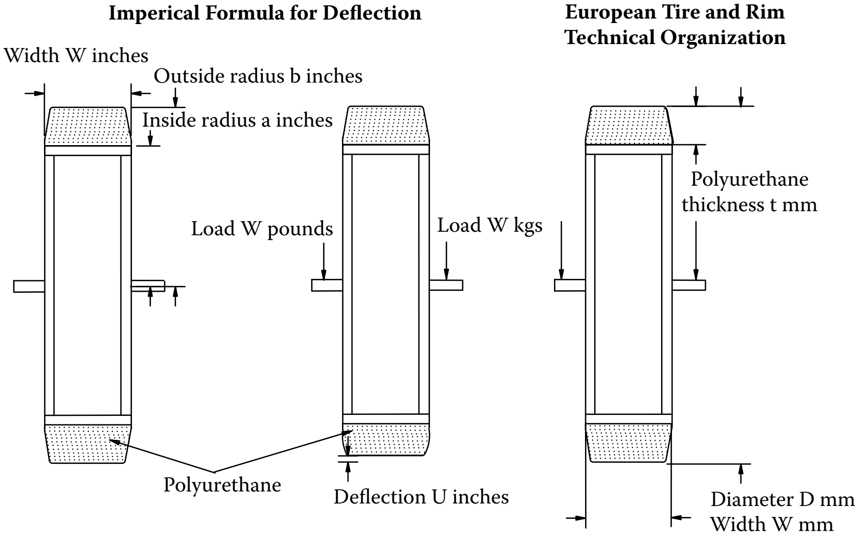


FIGURE 8.3
Wheel deflection formulas.

point. The suitability of the selected grade should be evaluated in either real or simulated tests.

The second formula quoted is that of the European Tire and Rim Technical Organization. This is used for polyurethanes in the hardness range of 92 to 95 A:

$$L = k \times 0.238 \times 10^{-8} \times (628–2t)^2 \times D \times W$$

Where L = load in kg, k = speed/use rating factor, t = polyurethane thickness in mm, D = outside diameter of polyurethane in mm, and w = width of polyurethane in mm. The calculations are illustrated in Figure 8.3.

The k factor varies from 115 to 70, depending on speed and whether any side forces are applied to the wheel. For example, at 10 kph the load wheel of a forklift has a k factor of 100. If the speed is increased to 16 kph, the factor drops to 85. The steering wheel has a lower factor of 70 at 10 kph.

The heat generated in the tire must be able to be dissipated at below the maximum temperature of the bonding agent (approximately 115°C). If the tire overheats and decomposes, it will be from the inside of the wheel.

Care must be taken in using polyurethane wheels in areas that are smooth and wet, as the coefficient of friction is very low and stopping and steering can be a problem.

8.4.3 Applications in Shear

In certain applications, there are not only compressive loads but also a stress function (see Figure 8.4). Even though the polyurethanes have very good

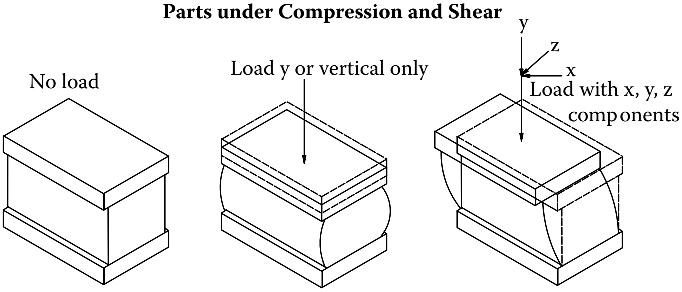


FIGURE 8.4
Parts under compression and shear.

stress (tensile strength) properties, they deflect more under stress than compression. To overcome this problem, the materials need to be bonded to metal plates to ensure that they do not slide out of place. The limiting factor now becomes the bond strength. The standard 90° peel test shows that the material breaks before the bond fails. In this situation, the peeling component is nearer 180° and the stress is more on the bond line. (See Figure 8.5)

The bonding material traditionally is a thermoplastic, and it softens as the temperature increases. The bond strength decreases as the material becomes warmer.

The shear component in a compression mount is often a result of misaligned components in a system. Differential thermal expansion of a steel girder compared to a concrete base will also give this effect.

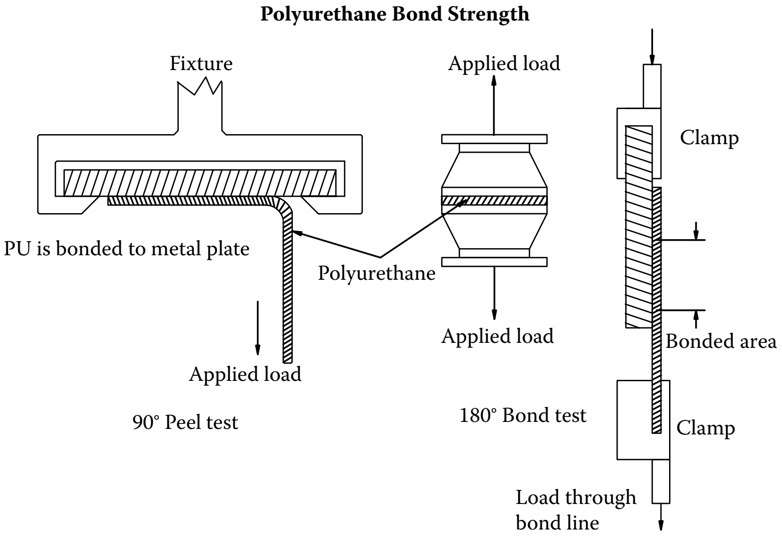


FIGURE 8.5
Polyurethane bond strength loadings.

8.4.4 Wear Resistance

The most important factor in any application is to determine the nature of the wear. Is the wear abrasive or is it erosive? When polyurethanes are used in a dry screening application, the particles move through the air and are not blown along in a current of air. This application is abrasive wear. In a dry cyclone where the air blows the particles, it is an erosive wear situation. The basic layout of a cyclone is given in Figure 8.6.

The centrifugal effects on impeller parts must be taken into account when using elastomers. Soft elastomers will tend to expand slightly when the speed is too high. It is advisable to reinforce the polyurethane part. The flow patterns in a pump are very complex and need to be evaluated very carefully. Incorrectly adjusted clearances can lead to turbulent flow and unexpected wear patterns. High-resiliency polyurethanes with hardness between 82 and 92 A prove to be satisfactory.

In an industrial situation, the following factors affect the choice of material:

- Size and shape of the solids
- Velocity of the particle
- Angle of impingement
- Operating temperature
- Chemical composition of process medium
- Flexibility of polyurethane

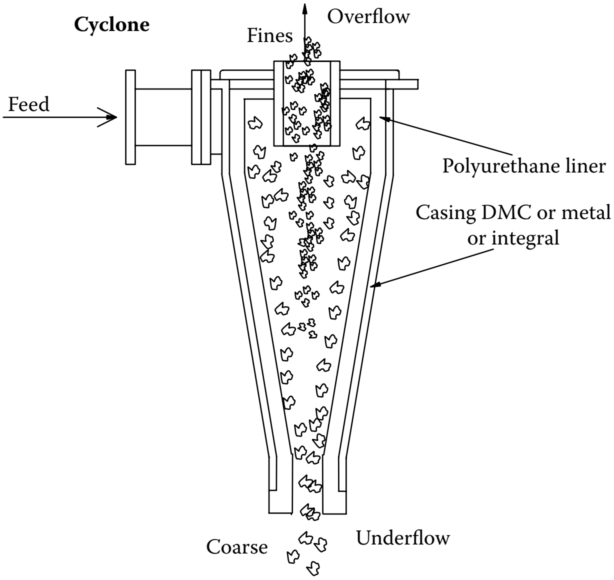


FIGURE 8.6
Basic cyclone layout.

The chemical composition and temperature of the process medium greatly influence the choice of material. The acidity or alkalinity, together with the standard operating and maximum temperature, must be taken into account when the material is selected. The toughness and excellent wear of the polyesters must be balanced against maximum working temperature, ease of processing, and the cost.

The presence of a reinforcing will increase the stiffness in situations such as screens and pump parts. This will also act as a heat sink. In cyclones there are a number of approaches:

- All solid polyurethane
- Polyurethane liners in metal casing
- Polyurethane liners in composite (DMC) casing

The under- and overflow spigots are normally made from a harder material, and the angle of wear is much more sliding and almost abrasive in nature.

8.4.5 Vibration Damping

The hysteresis property of any polyurethane is composed of two components, namely the spring and the viscous component. The viscous component is responsible for the absorption of the force and the conversion of the energy into heat. Any deflections must be within the limits where Hookes Law is obeyed (i.e., only 1 to 10%). The ratio between the forced and natural frequencies needs to be determined. The natural frequency is a function of the static deflection of the system. The damping ratio of the polyurethane also must be known. This can vary from 0.05 for highly resilient materials to 0.15 for low-resiliency materials. To obtain damping, the forced-to-natural damping frequency ratio must be greater than 1.4.

Polyurethanes can be used to develop vibration isolation pads to isolate movements generated in the machinery. Absorption of acoustic vibrations also can be done with polyurethanes. This finds application in submarine coatings for certain temperature conditions.

8.4.6 Electrical

Polyurethanes are not suited as an insulation material in mains voltage situations due to the ability of the polyurethane to absorb moisture and lower its resistivity. Polyurethanes alone or in a combination with an epoxy can be used as a potting material.

Polyurethanes can be modified to be semiconductive throughout the whole volume of the material, which allows them to be used in applications in which generated static electricity has to be dissipated. Typical examples of these applications are textiles or paper passing between rollers at speeds where an electrical charge can be developed, leading to poor handling and the risk of electrical sparks. Grains flowing down a polyurethane chute also can build up an electrostatic charge. As there is normally a large amount of organic dust in the area, any discharge could potentially cause an explosion.

Antistatic polyurethanes find applications in electronic and business machines when there are moving parts that can generate static. They also can be used where bench tops need to be kept at zero electrical potential.

8.5 Design

8.5.1 Bonding

Bonding of polyurethane to metal is needed to keep the part in the correct position and to provide a continuous layer between the reinforcing material and polyurethane.

Large flat objects require holes in the reinforcing to allow the air to escape when the part is poured. Holding the part at an angle also helps. The result of not getting rid of all the air is to have large areas with no bond. On heating over time, moisture can permeate and blisters may be formed. The formation of a blister is shown in Figure 8.7.

When parts are to be used in tension, the polyurethane should be bonded onto a tag rather than a flat plate. This helps eliminate stresses on the bonded surface.

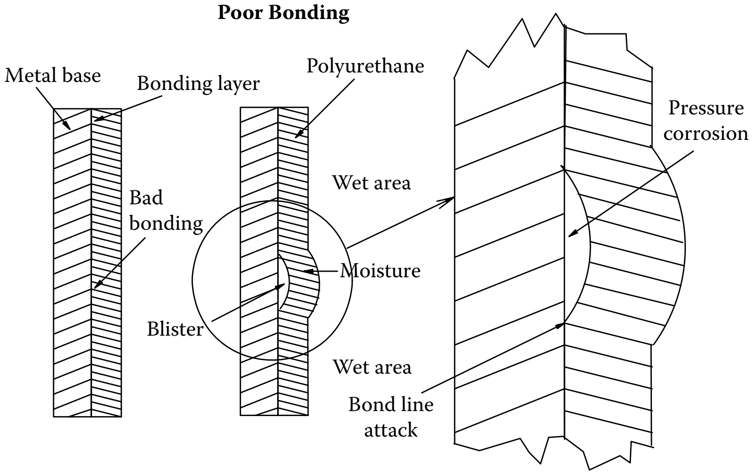


FIGURE 8.7
Poor bonding causing blisters.

8.5.2 Fillets

The reduction of potential stress points in any part is very important. The use of fillets in the junction between the polyurethane and the reinforcing is

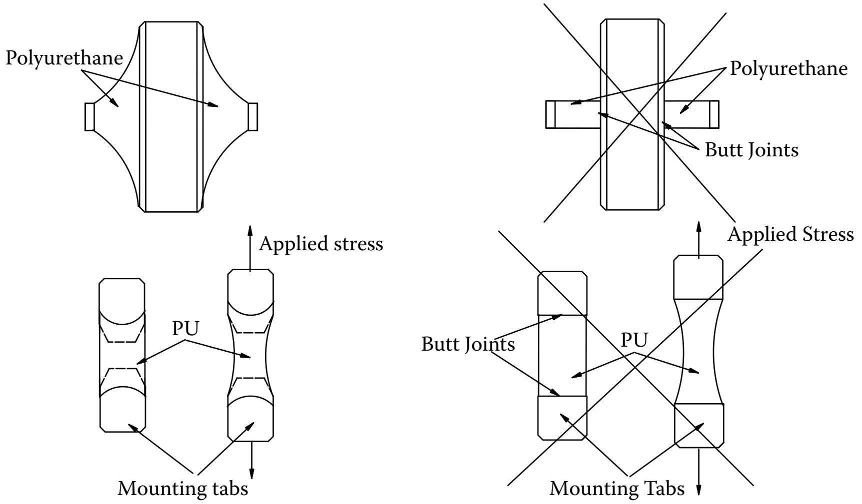
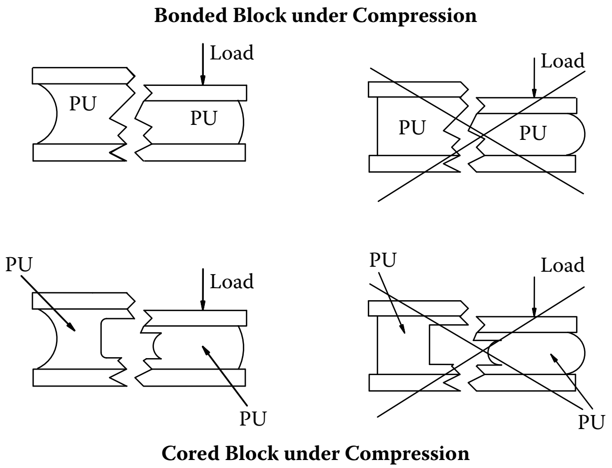


FIGURE 8.8
Reduction of stress by use of fillets.

important in limiting stress concentration. Right-angled joints are not desirable. The use of fillets to reduce stress is shown in Figure 8.8.

8.5.3 Shape

The correct choice of the shape factor in polyurethane parts can help the bulging of parts under compression. This is shown in Figure 8.9. A cylindrical part with the same loaded area will deflect less than a rectangular part


Bonded Block under Compression

Cored Block under Compression

FIGURE 8.9
Bonded and cored blocks under compression.

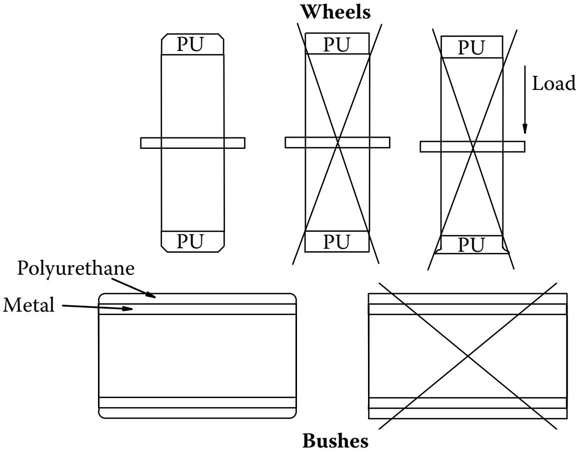


FIGURE 8.10
Correct and incorrect edges.

under the same load. Any surface that is bulged due to compressive forces will be more prone to failure due to nicking or fatigue. A simple solution is to design the part so that the material under no load has a slight "waist." On compression the material will give an item with more parallel sides.

Radius or chamfer the outermost edges of wheels and bushes. Square edges will bulge out under load and tend to break off. This will give more sites for further damage. This effect on wheels and bushes is shown in Figure 8.10.

To increase the vertical stiffness of any load-bearing component, multiple layers of steel plates can be inserted into the molding. This will increase the vertical stiffness while having no influence on the shear properties. There will be more bulges of smaller magnitude than if a single unit is poured.

8.6 Summary

Polyurethanes find many different uses in a wide variety of industries. Their applications are only limited by the ability to use the right grade with an appropriate design change. The major limiting factors are the operating temperature range and any specific chemical attack.

Appendix 8 lists a number of common applications of polyurethanes. This list is by no means complete, as there are many unpublicized applications.

9

Tools for Evaluation

9.1 Introduction

The five main points in the evaluation of polyurethanes are:

- Verification of selected grade
- Quality control tests
- Type tests
- Prototype and service tests
- Investigative research

Full chemical and physical testing is often outside the scope of many processors of polyurethanes. Firms will mainly be equipped to carry out tests relating to their main product line. Many of the other tests may be carried out by specialist consulting laboratories or by local universities with an interest in the field that the article will be used in.

Wherever possible, testing should be carried out in accordance with an approved standard. These include the standards issued by the International Standards Organization (ISO), the American Society for Testing and Materials (ASTM), and the Deutsches Institut für Normung (DIN). There are many other standards of international repute, such as the NF, JIS, and BS standards. Most countries have their own standards. These are adjusted to suit local requirements but are based on the main international standards. Evaluations carried out to these standards in a laboratory compliant with the ISO 9001 quality standard carry more weight than those tested under other conditions. Other standards, such as aviation and maritime specifications, are also recognized in their fields. In all cases, the most recent issue of the standard or specification must be used.

These standard tests do not cover all situations. Simulated service tests or in-service evaluations also need to be carried out. In-service tests should only be carried out if the potential for a positive result is very high or if requested by the customer.

9.2 Verification of Selected Grade

There are two main factors to be checked:

- Is it the right material for the application?
- Are there any processing changes to be made?

These two factors are interrelated, as the material needs to be processed before the evaluation can be carried out. Successful casting may require adjustments to the mold, processing conditions, and postcuring operations. Dimensional testing should be carried out at this point to check the need for any mold alterations that may be required.

Prior to any production for complex and critical applications, theoretical calculations should be carried out to assess the properties of the selected grade. Computerized mathematical techniques such as finite element analysis can be carried out to determine potential stress points. There are also mold-filling programs that can be used. Both these methods are expensive and need specialized staff.

The evaluation process consists of several stages, with reassessment if the initial results are not satisfactory. The molding process or the grade of polyurethane may need to be changed. This may have to be repeated when service tests are carried out.

9.3 Quality Control Tests

9.3.1 Weighing Equipment

All scales must be kept clean and free from any buildup of polyurethane raw materials. The level and zero must be checked daily. A weight check also must be available in the normal weight range. The scales must be checked annually by a suitably qualified technician.

9.3.2 Temperature

The correct indication of temperature is important and the probes must be checked on a regular basis. Temperature indicators should have an internal check of the continuity of the probe's wires. Any breakage should be indicated on the display. The probe's sheath should be made from a material that is not attacked by any vapors that are present. Both RTD and "K" type probes have been shown to be satisfactory.

Prepolymers heated in a microwave oven, even using a rotating table, will have uneven temperatures, and the material needs to be mixed well before taking a temperature reading.

There are two main ways of calibrating the temperature-indicating system. The first is to use a specialized test box that will give either a known voltage or resistance to the indicator. The output from the box corresponds to a known temperature. The output from the probe also can be checked. The second method is to check the melting point of ice, which should give zero on the scale. The boiling point of water is very close to 100°C and varies depending on the atmospheric pressure. The probe should be placed in steam at atmospheric pressure. There are tables available that correlate the atmospheric pressure to the boiling point of water.

The location of the temperature probes is very important to obtain the correct temperature of the curing ovens. They must be in the air, away from direct heat from any elements.

Measuring the temperature of cured polyurethanes requires a special technique. Polyurethanes are a poor conductor of heat and the probe will locally heat or cool the surface of the material. Once a temperature is obtained, the probe must be quickly moved to a second and third spot to obtain the correct temperature. The use of a noncontact thermometer (such as an infrared thermometer) can eliminate this problem. The instrument must be of the correct range and resolving power.

9.3.3 Linear Dimensions

Before carrying out any measurements, the material must be at ambient temperature and stabilized at a relative humidity of approximately 50%. Measurements may need to be taken during processing such as machining. In this case, the expansion of the polyurethane by heat needs to be taken into account.

The very hard materials can be checked using the standard pressure settings. For softer materials, this will cause undue distortions. The micrometer or vernier calipers need to be gently passed over the item. The faces of the instrument must just touch the surface. This can be felt through the instrument as a very mild resistance. The measurements will represent the high points on the surface.

The micrometers and calipers must be zero-checked before use and regularly checked against standard test blocks. Standard tests for taking dimensions include:

Method	Details
ASTM D3768–03	Standard practice for rubber-measurement of dimensions
BS 903: PA38	Methods for determination of dimensions of test pieces and products for test purposes

9.3.4 Density

The density, or more correctly the apparent density, of polyurethanes can be determined in a number of ways. Density is defined as the weight of the material in air divided by its volume.

The determination of the volume is the most complicated. The sample of polyurethane must be free from all internal bubbles or other voids. If the sample is of a uniform shape, the volume can be determined geometrically by measuring its dimensions and then calculating its volume.

If the sample is irregular in shape, the traditional Archimedes principle must be employed. The sample is first weighed in air on a laboratory scale and then suspended by a fine thread in water. The density is given by:

$$\text{Sample density} = (M_1 \times Q_f)/(M_1 - M_2)$$

M_1 = weight of sample in air
M_2 = weight of sample in liquid
Q_f = density of liquid—if water is used, $Q_f = 1.0$

Standard tests for the determination of density include:

Method	Details
ISO 2781	Rubber, vulcanized Determination of density
ASTM D1817	Standard test method for rubber chemicals Density
BS 903: PA1	Physical testing of rubber; part A1 Determination of density
AS 1683.4	Methods of test for elastomers Rubber, vulcanized Determination of density

There are other methods for the determination of density. These include the specific gravity balance and the use of a pycnometer (weighing bottle).

9.3.5 Hardness

Although not greatly influenced by the mixing ratio of prepolymer and curatives, hardness is one of the most frequently specified and carried-out tests. The two main handheld units are the Shore A and D range Durometers.

The construction constraints and the test methods are detailed in the following specifications.

Method	Details
ISO 7619	Rubber, vulcanized or thermoplastic Determination of indentation hardness Part 1: Durometer method (Shore hardness)
ASTM D2240	Standard test method for rubber property Durometer hardness
DIN 53505	Shore A and Shore D hardness testing of rubber
BS 903: PA57	Physical testing of rubber; Part A57 Determination of indentation hardness by means of pocket hardness meters

For the most accurate results, dead-load instruments should be used. Traditionally, all of the instruments have been analog, but currently both analog and digital units are available. The most important features of the instruments are:

- Size and shape of the indentor
- Distance the indentor protrudes from the base
- Characteristics of the spring

The A scale instruments have a frustoconical indentor, whereas the D scale has a pointed conical indentor. The scales overlap but the stresses on the material are different. There are also micro units available for measurements on small pieces of material, including "O"-rings. Figure 9.1 illustrates the method of operation of the Durometer hardness testers.

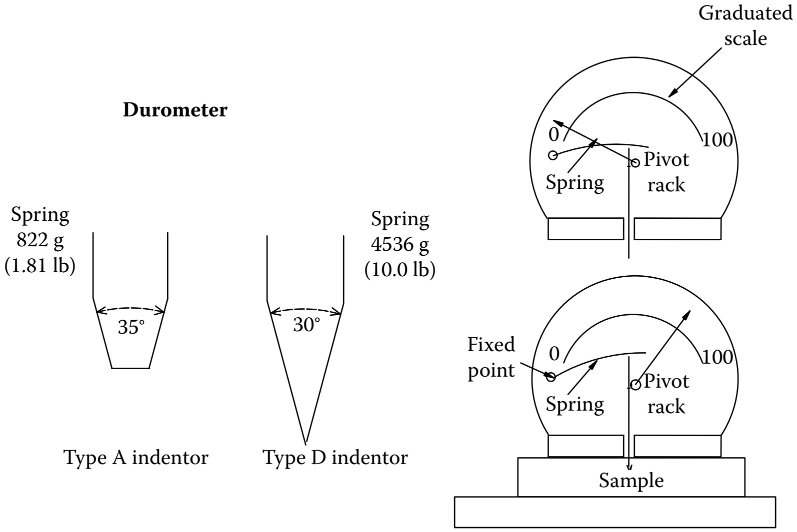


FIGURE 9.1
Durometer construction layout.

New electronic units claim to have an accuracy of ±1 unit, which is much better than the previous ±3 units. An experienced operator can obtain more consistent results than the ±3 units range quoted. Results may vary from operator to operator.

A check spring is supplied with the Durometer and can be used for day-to-day checks. A series of standard rubber blocks also can be purchased for checking over the full range. The blocks need to be rechecked every 2 years. Durometer suppliers also offer a recalibration service.

9.3.6 Curative Level

Certain curatives such as those containing either chlorine or sulfur can be tested using x-ray fluorescence (XRF) techniques. The principle of XRF is that the electrons in the atoms become excited when exposed to the x-rays. As the electrons move in the atoms, they emit x-ray light (photons). The wavelength is characteristic of the element and the intensity proportional to the concentrations in the sample. Elements with an atomic number greater than 15 (magnesium) can be determined by this method. Standards have to be made for the different levels and types of curative.

As the method is independent of how the atom is attached, chlorine-containing plasticizers such as TCP will interfere with the result if MOCA is used.

There are some simple units that use a radioactive source instead of an x-ray generator. These have problems of handling and storing the source, as well as the disposal of the spent source after a number of years.

9.3.7 Surface Porosity

When a thin layer of polyurethane is cast over a metal reinforcing, the thickness of the polyurethane must be even and sufficient to prevent moisture from getting to the reinforcing and causing corrosion. A potential cause of problems is if an air bubble is trapped between the reinforcing and the cast polyurethane.

The entire thickness of the polyurethane over the reinforcing can be measured using an ultrasonic gauge. The correct head and sound velocity will have to be used, as polyurethanes require different conditions than metals.

An alternative method is to use high-voltage spark testing (500 V to 30 kV) either in the DC or the AC mode. There are several methods for carrying out these tests, shown here.

Method	Details
ISO 2746	Vitreous and porcelain enamels Enameled articles for service under highly corrosive conditions High voltage test
DIN 55670	Paints and varnishes Method for testing paint coatings and similar coatings for pores and cracks, using high voltage
ASTM D4787	Standard practice for continuity verification of liquid or sheet linings applied to concrete substrates
ASTM G62–87	Standard test methods for holiday detection in pipeline coatings (withdrawn 2007)

The voltage in the units needs to be set to enable the detection of a defect, but it must not be so strong that it burns a hole in the polyurethane. Either a brush or wand can be used to check the continuity of the surface. This type of test can be used with different fittings to check the interiors of items such as pipes.

9.4 Type Tests

Type tests of polyurethanes are used to evaluate polyurethanes using standardized methods. The tests are a characteristic of the polyurethane being evaluated but do not represent actual field conditions.

The samples need to be brought to controlled test conditions before the test is carried out. If they were used as a quality control test, the product in many cases would be at the customer before the test was completed. A typical example is that tests such as the tensile tests require a week to settle down before the test is carried out after the 18-hour cure cycle. In many cases an approximate value is obtained by testing as soon as the sample has reached room temperature after it has had its full cure.

9.4.1 Tensile Stress–Strain

Tensile properties are used in the evaluation of batches of material as well as in determining the aging effects on polyurethane. Currently, the time taken for the preparation and stabilization of the samples does not make this test ideal for a batch-to-batch real-time quality control tool. Testing is normally carried out to one of the following standards:

Method	Details
ISO 37	Rubber, vulcanized or thermoplastic Determination of tensile stress–strain properties
ASTM D412	Standard test methods for vulcanized rubber and thermoplastic elastomers-tension
DIN 53504	Determination of tensile strength at break, tensile stress at yield, elongation at break, and stress values of rubber in a tensile test
BS 903: PA2	Physical testing of rubber: Part A2: Method for determination of tensile stress–strain properties

There are a number of different terms for the strength of the polyurethanes, including:

- Tensile strength
- Breaking stress
- Breaking load
- Ultimate tensile strength

Tensile strength is the highest tensile stress reached before the sample breaks. Conventionally, the result is expressed as the force required per unit area. The area is taken as the original cross-sectional area. The sample is dumbbell shaped and the area is measured in the waist of the sample.

The preparation of the sample is important. There should be no gas bubbles or other imperfections in the test sheet. The cutting knife must be sharp and free from any nicks. The sides of the sample must not be concave or have any fine ridges. Tensile samples from hard grades may be milled out.

Clamps used to hold the sample must be self tightening as the polyurethane shrinks under load. Any traces of mold release act as a lubricant and make the holding of the sample difficult. The flat tag ends of the dumbbell can be slightly roughened. Pneumatic clamps can help keep the samples in place.

As the samples are dumbbell shaped, the movement of the crosshead of the tensile machine cannot be used to determine the elongation. Extensometers of various designs are used to measure the elongation in the waist area of the sample. One method is to have two clamps set to the desired distance apart. As the sample stretches, the movement is measured by a system of counterweights and cords. Another method is to use light/laser beams reflecting from pieces of reflective tape on the sample.

The "elongation at break" or "ultimate elongation" is the elongation expressed as a percentage at the point of rupture.

The modulus (or tensile stress) at various elongations is the load at the elongation divided by the original cross-section. This is expressed in terms of force per unit area (MPa). The normally used elongation values are 50%, 100%, 200%, and 300%.

When using the tensile strength or modulus at a certain elongation to investigate change in properties, it is better to use relative changes to the ultimate values. A material that has changed from 28 MPa down to 15 MPa has suffered more damage than one that has changed from 21 MPa to 14 MPa (54% and 67% retained).

9.4.2 Set Tension Compression

Tension Set

The test involves stretching the sample to a constant strain (generally 100% or 25%, 50%, 200%, or 300%). The sample is held at the desired strain for a fixed period before the load is removed and the sample allowed to stabilize. The increase in length of the markers is the permanent set. The methods are detailed below.

Method	Details
ISO 2285	Rubber, vulcanized or thermoplastic Determination of tension set under constant elongation, and of tension set, elongation, and creep under constant tensile load
ASTM D412	Standard test methods for vulcanized rubber and thermoplastic elastomers-tension
DIN 53518	Testing of rubber and elastomers Determination of tension set after constant deformation
BS 903: PA5	Physical testing of rubber; part A5: Method for determination of tension set at normal and high temperatures

The test is composed of marking the desired length on the dumbbell, stretching the sample to the desired elongation, and holding at that elongation for a set period of time. The time duration may be 24, 72, or 168 hours. The temperature may be ambient, 70, 85, or 100°C. The test time starts 30 minutes after the sample is introduced, and the final measurements are made after 30 minutes of recovery.

$$\text{Tension set} = ((L_1—L_0)/(L_S—L_0)) \times 100$$

where L_0 = original unstrained length, L_1 = reference length after recovery, and L_S = strained reference length.

Compression Set

Samples of polyurethane are clamped between two plates so that they are compressed by 25%. The samples may be tested at ambient or 70°C. They are compressed for either 24 or 72 hours. After compression they are allowed to recover for 30 minutes and then remeasured. The methods are detailed below.

Method	Details
ISO 815	Rubber, vulcanized or thermoplastic Determination of compression set at ambient, elevated, or low temperatures
ASTM D395 method B	Standard test methods for rubber property Compression set
DIN 53517	Testing of rubber and elastomers Determination of compression set after constant strain
BS 903: PA6	Physical testing of rubber Part A6: Method for determination of compression set at ambient, elevated, or low temperatures

If there is no recovery, the compression set is 100%, and with full recovery it will be 0%.

$$\text{Compression set at constant strain} = ((T_O—T_R)/(T_O—T_S)) \times 100$$

where T_O = original thickness of piece, T_R = thickness after recovery, and T_S = thickness of spacer.

Figure 9.2 illustrates the sample sizes and basic test equipment for the compression set test.

The main problem with the compression set results is that the time period of testing is short in relation to the real-life situation; for example, a gasket seal may be in service for one or more years before it is removed. It is also found that if left for longer periods than the 30 minutes specified, the compression set becomes less.

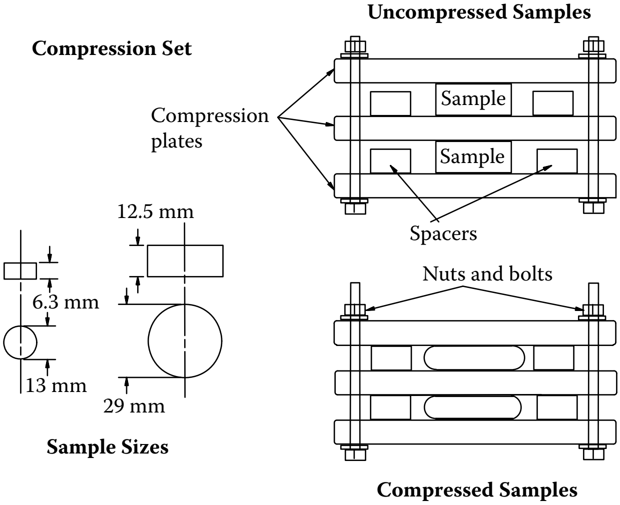


FIGURE 9.2
Compression set layout.

9.4.3 Tear Strength

In tensile strength determinations, the material has to completely break through the cross-section, whereas the tear strength test indicates the resistance to the propagation of a defect, such as a nick, in the polyurethane. The way that elastomers tear under different conditions has led to a number of different tests.

There are three main configurations for the tear test. In the first two a tensile force is applied to the sample. In one configuration, the force is vertical to the plane of the sample, and in the second it is at right angles. In the third style, an element of shear is also introduced. Figure 9.3 shows the basic configuration of the tear test pieces.

There are a number of different standard test methods, some of which are shown below.

Method	Details
ISO 34	Rubber, vulcanized or thermoplastic Determination of tear strength Part 1: Trouser, angle, and crescent test pieces; Part 2: Small (delft) test pieces
ASTM D624	Standard test method for tear strength of conventional vulcanized rubber and thermoplastic elastomers
DIN 53507	Testing of rubber and elastomers Determination of the tear strength of elastomers Trouser test piece
BS 903 PA3	Physical testing of rubber; part A3: Determination of tear strength [trouser, angle, and crescent test pieces; Section 3.2: Small (Delft) test pieces

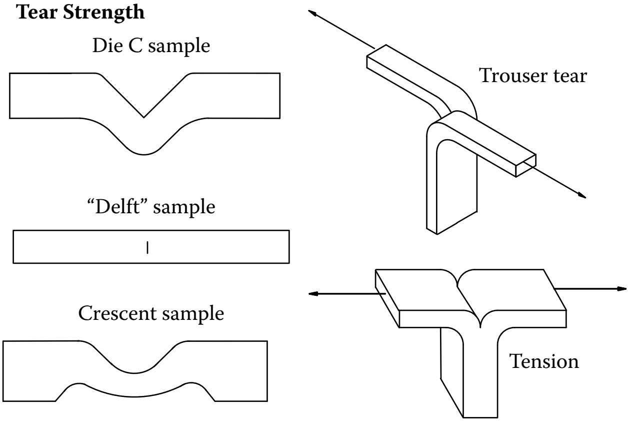


FIGURE 9.3
Tear strength test pieces.

There are a number of different-shaped samples that are specified for carrying out the tear strength determination. The exact shape and test method used needs to be specified for any values quoted.

The two most commonly specified tests are the Die C test and the "trouser tear" (D470) test. Both of these tests measure resistance to tear propagation. Other test shapes include the crescent tear with or without end tabs. This sample shape is often nicked. The "Delft" (IS0816) sample with its internal nick is often used from samples taken from finished products. The exact size of the nick does not appear to be critical to the result.

The standard calculation is based on the force required for the tear (in Newtons) divided by the thickness of the sample in millimeters. When carrying out the trouser tear, the median force must be taken, as the load varies during the test.

In practice, there are many factors that may cause a sample to fail. These include nicking under tension, impurities in the material, and air bubbles.

9.4.4 Adhesion

Very strong bonding between polyurethane and metal is needed in items such as polyurethane mounts. When metal is used as reinforcement or for location and stabilization, a very good bond is needed to form the bridge between the rigid metal and the elastic properties of the polyurethane. Ideally, a test that could be performed on the finished product is desirable, but in practice this is often not the case.

Air pockets or blisters can be detected by using ultrasonic test methods. The correct head and frequency need to be used, as the speed of sound through elastomers is very different than through metals.

9.4.5 Peel Tests

Peel tests, or the "one plate" method, are commonly used. These are specified in the following standards:

Method	Details
ISO 813 (one plate)	Rubber, vulcanized or thermoplastic Determination of adhesion to a rigid substrate 90-degree Peel method
ASTM D429 (method B)	Standard test methods for rubber property Adhesion to rigid substrates
DIN 53531: part 1	Determination of adhesion of rubber to rigid material by the one plate method
BS 903 PA21	Physical testing of rubber; Part A21: Determination of rubber to metal bond strength; Section 21.1: Adhesion to rigid substrates, 90-degree Peel method.

In peel tests, the polyurethane is bonded to a metal strip. The bonded area is 25 × 25 mm. The sample is conditioned, and an initial length of approximately 1.5 mm is stripped from the plate using a knife. The sample is mounted in a tensile strength machine and the polyurethane stripped from the plate. Figure 9.4 shows the sample configurations used.

The adhesion is calculated by dividing the maximum force recorded by the sample width in millimeters. With the current bonding technology, the polyurethane will, in most circumstances, break before the sample starts to peel. This is referred to as a stock break (SB).

If the sample does peel off, the zone where the peeling takes place is recorded. If the peeling occurs between the metal plate and the bonding

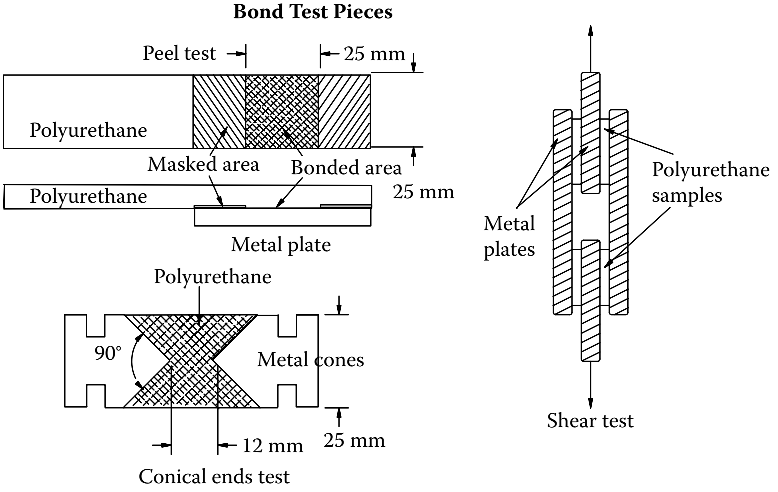


FIGURE 9.4
Bond test sample configurations.

medium, the surface preparations need to be examined. The bonding may fail between the bonding medium and the polyurethane. This could be caused by either poor activation of the bonding agent or contamination of the surface by mold release. For multilayers of bonding agent failure, there may also be contamination or improper activation.

It has been suggested that the test angle be changed from 90 to 45° to give more realistic and reproducible results. This has not met with official approval.

Tension Tests

There are two main types of tension tests that are in use, namely, the "two plates" test and the "conical ends" test.

Method	Details
ISO 814 (two plates)	Rubber, vulcanized Determination of adhesion to metal Two-plate method
ISO 5600 (conical ends)	Rubber Determination of adhesion to rigid materials using conical-shaped parts
ASTM D429 (methods A and C)	Standard test methods for rubber property Adhesion to rigid substrates
DIN 53531: part 2 (conical ends)	Determination of the adhesion of rubber to rigid materials using conical-ended cylinders
BS 903 PA21 (method A)	Determination of rubber to metal bond strength
BS 903 PA40	Determination of adhesion to rigid materials using conical-shaped parts

Care must be taken to align the samples exactly vertically in the tensile strength machine; otherwise, shearing is introduced into the mechanism. In the conical test, high concentration of stress is placed at the apex of the cones and any failure starts at this point.

9.4.6 Shear Tests

In this test, multiple bond points are used and a quadruple bond test is performed. These tests are illustrated in Figure 9.5. Shear tests are specified in the following specifications:

Method	Details
ISO 1827	Rubber, vulcanized or thermoplastic Determination of modulus in shear or adhesion to rigid plates Quadruple shear method

The test pieces are similar to that used to determine shear modulus. The results are taken by dividing the maximum force required by the total bonded area of one pair of samples.

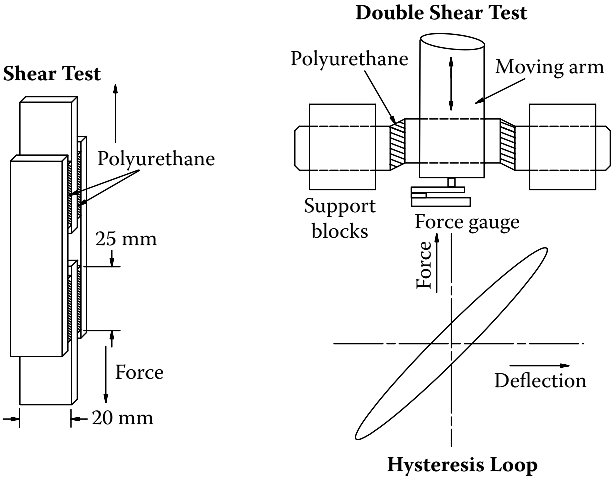


FIGURE 9.5
Double shear tests.

All these tests are carried out under relatively slow conditions (50 mm/minute) and do not represent normal service conditions. There are no standard tests to simulate these real life conditions. Equipment is available to perform these dynamic tests.

These tests are useful as a screening test to evaluate new bonding agents and methods of surface preparation. It must be remembered that polyesters have a bond strength three times that of polyethers.

9.4.7 Compression Modulus

Polyurethanes are more often used in compression or in the shear than in the tensile mode. There are a number of standard tests that may be used.

Method	Details
ISO 7743	Rubber, vulcanized or thermoplastic Determination of compression stress–strain properties
ASTM D575	Standard test methods for rubber properties in compression
BS 903: A4	Determination of compression stress–strain properties

The test piece is a cylinder of 29 ±0.5 mm diameter by 12.5 ±0.5 mm height. The sample is compressed in a tensile strength machine. The sample must not be allowed to move on the compression anvils (fine emery paper is suggested between the anvil and sample).

The result of the third compression on the sample is taken. During the first two, the sample is compressed 5% more than the maximum to be recorded.

It is recommended that the results be given graphically of compression strain against compression stress.

In the compression modulus test, the movement of the crosshead can be taken. Precautions also must be taken to prevent overrun of the crosshead by having stops installed to prevent damaging the load cell with an overrun.

9.4.8 Shear Modulus

Applications where there is compression will often have a shear component, even if not by design. The following methods detail the determination of shear modulus.

Method	Details
ISO 1827	Rubber, vulcanized or thermoplastic Determination of modulus in shear or adhesion to rigid plates Quadruple shear method
BS 903: PA14	Method for determination of modulus in shear or adhesion to rigid plates quadruple shear method

The ISO 1827 method has four blocks 4 mm thick by 20 mm wide and 25 mm long bonded to plates as shown in the sketch (Figure 9.5). The samples are cycled five times in a tensile machine before the results are taken. A micrometer or the movement of the crosshead can be used to measure the strain. The speed of the machine is 25 ±0.5 mm per minute.

The shear stress results are expressed in Pascals (N/m^2). The calculation is obtained by dividing the applied force indicated by the tensile machine by twice the actual bonded area of one block in square meters (nominally $20 \times 25 \times 10^{-6}$). The shear strain is obtained by dividing half the actual deformation by the actual thickness of one block. All measurements must be in the same units.

9.4.9 Dynamic Mechanical Testing

Tests such as the tensile strength and tear strength tests evaluate polyurethanes to destruction. When polyurethanes are used in a practical situation, the aim is for them to have as long a life as needed in the application. Stress, strain, and shear are applied to the polyurethane at various frequencies and at different temperatures. There may also be dynamic variations on top of a static load, for example, vibrations on a loaded isolation pad.

ISO 2856 and ASTM D2231 outline general requirements for dynamic testing but with no descriptions of actual method or equipment. The tests are divided into three main groups:

- Test methods where there is free vibration applied and then allowed to decay.

- Tests where the vibrations are maintained from an external source. The frequency can be adjusted to be either resonant or nonresonant.
- Propagation of either continuous or pulsed waves below the kHz or MHz range.

These tests form the classical methods of testing, but the use of dynamic mechanical analyzers are becoming more popular, especially those that can operate from subambient temperatures to 150°C and above.

9.4.10 Resilience

Resilience is one of the most common rebound tests. It is fundamentally a deformation of the material for half a cycle. The rebound resilience basically is the ratio of the indentor after to before impact expressed as a percentage. There are a large number of methods for this test, including the following.

Method	Details
ISO 4662	Rubber, vulcanized Determination of rebound resilience
ASTM D1054	Standard test method for rubber property-resilience using a Goodyear–Healey rebound pendulum
ASTM D2632 (falling weight)	Standard test method for rubber property Resilience by vertical rebound
BS 903: PA8	Method for determination of rebound resilience
DIN 53512	Rubber, vulcanized Determination of rebound resilience

The tests all have different test conditions, and only results from the same type of instrument can be compared. The instruments are all simple in design but with different degrees of complexity.

ISO 4662 details testing by the pendulum method. There are a number of different machines that conform to the specifications for impacting mass, velocity, and the apparent strain energy density. The types of suitable instruments mentioned in the specification include the Lüpke, Schob, and Zerbini. Some modern instruments have electronic outputs giving either digital or printed results.

Falling plunger and ball machines are generally not popular in Europe, but one design is specified in ASTM D2632. ASTM 1054 describes the Goodyear–Healey rebound tester. Figure 9.6 shows the principles of some of the tests.

Free Vibration Testing

The torsion pendulum is detailed in ISO 4663, where one end of the sample is fixed and the other can rotate freely. Frequencies of vibration of between 0.1

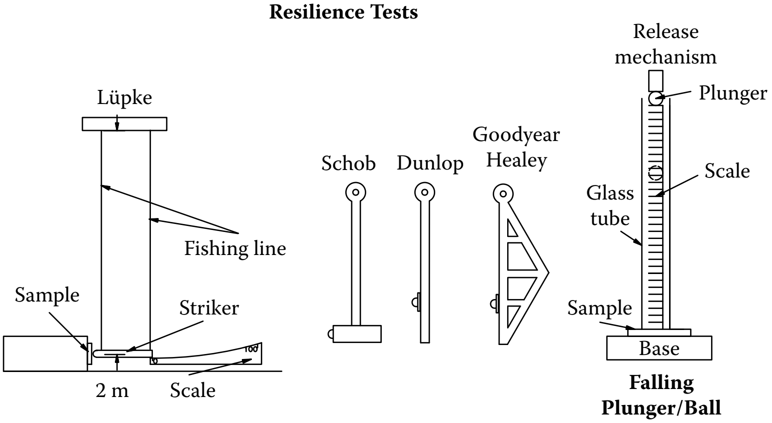


FIGURE 9.6
Resilience test methods.

and 10 Hz are possible with this method. An older method specified under ASTM D945 is the Yerzley oscillograph, where a beam can oscillate vertically. The die off the vibrations are recorded on a drum. Resilience results can be calculated.

Forced Vibrations

Tests based on forced vibrations are preferred when parts are being designed. The relationships are still very complex and only approximate. If experimental tests can be carried out close to actual service conditions, better results can be obtained. Forced vibration testing is detailed as follows.

Method	Details
ISO 4664	Rubber, vulcanized or thermoplastic Determination of dynamic properties Part 1: General guidance; Part 2: Torsion pendulum methods at low frequencies
BS 903: PA24	Guide to the determination of dynamic properties of rubbers
DIN 53513	Determination of the viscoelastic properties of elastomers on exposure to forced vibration at nonresonant frequencies

There are a number of different types of machines available to perform the tests based on either a mechanical, hydraulic, or electromagnetic method to obtain the dynamic movement in the samples. The frequency of the applied force can vary between 2 Hz and 10,000 Hz using an electromagnetic vibrator. A typical machine is the Rhiovibron™. In the test the samples are bonded onto the fixture either during curing or by using cyanoacrylate glue.

From the results obtained when used in a dynamic stress–strain mode, a hysteresis graph can be generated. As the machines were developed and computerized results obtained, a new group of instruments was developed, namely, the dynamic mechanical analyzers.

9.4.11 Dynamic Mechanical Analysis (DMA)

Polyurethanes have a combination of elastic and viscous properties that can be explained in standard engineering terms using DMA methods. Information can be obtained on the properties of polyurethanes that relates to the storage and dissipation of energy applied during use.

The equipment can operate in several different modes, over various frequencies, and over a wide temperature range. Typical modes that can be used are:

- Tension
- Compression
- 3-Point bend
- Single or dual cantilever
- Shear sandwich (for very viscous materials)
- Submersed sample cups

The manner in which these modes are carried out can further be modified by some of the following methods:

- Multistress–strain applications
- Multifrequencies
- Creep/stress relaxation
- Constant strain
- Controlled force/strain

The instruments can operate from –150°C to well above the melting point of polyurethanes.

Samples that are used must be free from any defects such as bubbles and must be uniform in size and measured accurately. The size of the samples is reasonably small, approximately 3 mm thick by 12 mm wide and 50 mm long. The exact size will depend on the instruments and the test being carried out. The basic results generated are:

- Storage modulus (energy stored)
- E' Stretching
- G' Twisting or torsional

- Loss modulus (energy lost—generally as heat)
- E'' Stretching
- G'' Twisting or torsional
- Tan delta ($\tan \delta$) = $E''/E' = G''/G'$

Other outputs from a typical instrument include complex modulus, creep compliance, relaxation modulus, sample stiffness, and all the basic data including instrument parameters.

The operation of the instrument involves the selection of the correct mode and the frequency and method of application. The sample is cooled to the start temperature and allowed to stabilize. A small deformation is applied and the results obtained. The temperature is raised and the process is repeated until the final temperature is reached.

The uses of such a technique include:

- Studies of the effect of changes in chemistry on the properties of the polyurethane
- Determination of the lower and upper useful temperatures of the polyurethane
- Provision of dynamic engineering properties
- Creep determination
- Coefficient of expansion

These instruments are high precision, with state-of-the-art force and position measurement technology. Modern computer power enables the storage of data obtained during the test as well as its mathematical manipulation and presentation. Interpretative skills are required to obtain the best results from the techniques used. Comparison to results obtained in the field should always be made.

9.4.12 Electrical Properties

Polyurethanes can be used in applications where electrical properties are important. They are not normally used for high-voltage insulation. Polyurethanes are often used directly or in combination with epoxies for encapsulation. The addition of antistatic agents to polyurethane gives a product with the correct electrical properties while retaining the excellent wear needed for a number of roller-type applications.

Testing of polyurethanes for their electrical properties due to the voltages required must be carried out using properly designed equipment. The electrical tests that are normally carried out are resistivity, insulation resistance, electric strength, tracking resistance, power factor, and permittivity.

Volume and surface resistivity tests for conductive and antistatic materials include:

Method	Details
ISO 1853	Conducting and dissipative rubbers, vulcanized or thermoplastic Measurement of resistivity
ISO 2878	Rubber Antistatic and conductive products Determination of electrical resistance
ASTM D991	Standard test method for rubber property–volume resistivity of electrically conductive and antistatic products
BS 2050	Specification for electrical properties of conducting and antistatic products made from flexible polymeric material

Any application involving mains power must be approved by the local state authorities before use.

Polyurethanes with antistatic properties are suitable for use where static electrical charges must be dissipated. The polyurethane must be compounded to provide the antistatic properties throughout the whole bulk of the material. The antistatic agent, if a liquid, must not migrate to the surface readily. Surface coating the item is not desirable, as the effect is only temporary.

9.4.13 Environmental Resistance

Weathering Resistance

The Panama weathering study (Cumberland, 1960–1985) has shown polyurethanes to be very resistant to the long-term effects of weather. There are a number of short-term effects that must be noted. Aromatic polyurethanes will yellow and become dark on exposure to light. These changes can have a drastic effect to the color of pigmented polyurethanes. Light colors should be avoided. There is often some surface crazing and chalking found in some samples when exposed to the weather.

The effect of ultraviolet (UV) light on aliphatic clear polyurethanes or aromatic polyurethanes that have had UV stabilizers added can be evaluated using Weather-Ometer™. The tests are performed to ASTM D750 or to ISO 4665/3.

In evaluating polyurethanes in weather exposure situations, care must be taken to consider the bulk of the material and not just the surface. The surface may be affected by the weathering, but this may only be very shallow and not represented by the bulk of the material.

9.4.14 Chemical

Because of its molecular size and polarity, water is absorbed into polyurethane and an equilibrium set up. The presence of water in the urethane will aid in certain external attacks by dilute acids and alkalis.

When carrying out chemical resistance tests, it is advisable where possible to use the same solution that the product is going to be used in. This will help cover the interpretation of the effects of several different chemicals that may be in a commercial mixture.

In the evaluation of the effect of chemicals on polyurethanes, there are two main test methods used. The first is the change in tensile properties, and the second is the absorption into the material. The following test methods deal with the resistance to liquids.

Method	Details
ISO 1817	Rubber, vulcanized Determination of the effect of liquids
ASTM D471	Standard test method for rubber property-effect of liquids
ASTM D1460	Standard test method for rubber property Change in length during liquid immersion
DIN 53521	Determination of the behavior of rubbers and elastomers when exposed to fluids and vapors
BS 903: PA16	Determination of the effect of liquids
BS 903: PA18	Determination of equilibrium water vapor absorption

Changes in Volume and Dimensions

In order for samples to reach equilibrium with the test solution, the samples should not be more than 2 mm thick. The width and length should be 25 by 50 mm.

The samples are completely immersed in the liquid, with no touching of the sides or bottom. Laboratory glass beads will assist with this. If the test is carried out near the boiling point of the liquid, it must be carried out in a container that is fitted with a reflux condenser.

The change in volume can be determined gravimetrically. The change in the sample is determined by weighing in air and in a suitable liquid such as water. The volume is given by the difference in the weight in air to the weight in water. These changes also can be calculated by measurements. The thickness is determined by using a micrometer and the width and length by a traveling micrometer. The results are expressed as a percentage change in volume. The volume swell in water is normally very low. In ketones, it will be high.

Changes in Physical Properties

The changes in properties are determined by preparing a number of dumbbell-shaped samples of the material under test from the same mix of polyurethane. A reference set of dumbbells is stored in the dark. The test samples are placed in a container containing at least 15 times their volume of test liquid and kept at the desired temperature for the test period. Before immersion in the test liquid, the dimensions of the pieces must be taken.

There are two alternative test procedures. The first requires the tensile and modulus tests to be carried out immediately after removal from the test solution, and the second after drying and stabilization of the sample. The results obtained, like all tensile results, are arbitrary and used for comparison purposes. The percentage changes in properties are normally reported.

The standard hardness blocks are too thick to reach equilibrium in the normal test period, so the hardness readings are taken on a stack of 2-mm-thick pieces.

The second method is applicable to situations where there is attack only from one side of the polyurethane. Typically, this would be in pipe linings or thin layers of polyurethane bonded onto reinforcings.

There are two basic test configurations. The first is a blind flange setup where the sample is clamped between a glass tube containing the liquid and a temperature-controlled heater. In this test, two samples can be tested under identical conditions. The second is a retaining cup clamped onto the sample. Figure 9.7 illustrates the two types of test cells.

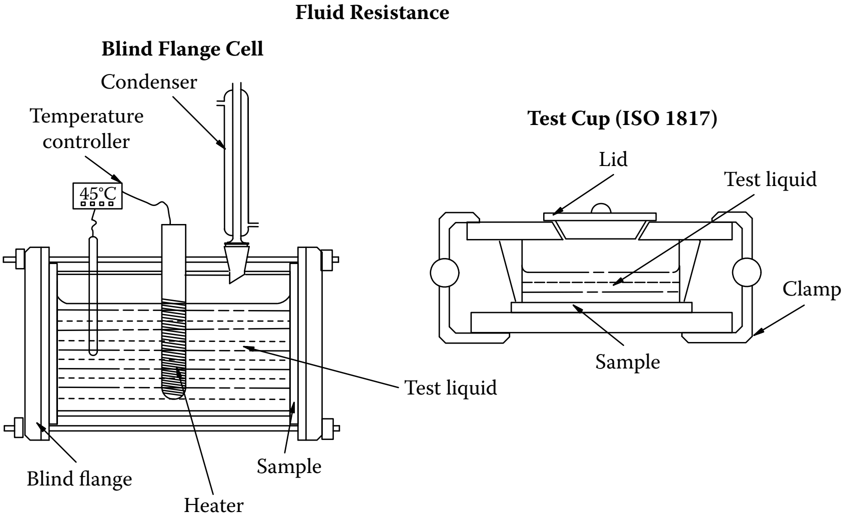


FIGURE 9.7
Fluid resistance test cells.

These tests can also be used to study the effect of the test liquid on the bonding of polyurethane to a reinforcing plate. In applications such as tank and pipe lining, the complete and correct bonding to the substrate is of vital importance.

9.4.15 Heat Aging

The correlation between dry heat aging and field aging results is poor. The tests are carried out to obtain some indication of the effect of heat on the polyurethane. The sample dimensions are small compared to most applications. This causes oxidative effects to be pronounced. There are a number of international tests for the determination of heat aging properties:

Method	Details
ISO 188	Rubber, vulcanized Accelerated aging or heat resistance tests
ASTM D454	Standard test method for rubber deterioration by heat and air pressure
ASTM D572	Standard test method for rubber Deterioration by heat and oxygen
ASTM D573	Standard test method for rubber Deterioration in an air oven
ASTM D865	Standard test method for rubber Deterioration by heating in air (test tube enclosure)
DIN 53508	Rubber, vulcanized Accelerated aging or heat resistance tests
BS 903: PA19	Heat resistance and accelerated air aging test

In these tests, the samples are placed in an oven at the set temperature (70°C or 100°C) for the required period of time. A control set of samples is kept in the dark at ambient temperature. The volume of the samples in the oven should not exceed 15% of the oven's working volume. Depending on the expected results, the samples are exposed for 1, 3, 7, 10, or multiples of 7 days.

On completion of the aging tests, physical tests such as tensile, modulus at various strains, elongation at break, and hardness tests may be carried out. Modern testing such as DMA tests also can be performed. The results are often plotted as a graph against time for the properties examined.

9.4.16 Fungal

The Panama weathering study has shown polyester polyurethanes to be prone to fungus attack within 6 months. Polyether-based polyurethanes are resistant to such attacks. If specific work is required, it is best that it is carried out by a suitably competent consulting laboratory.

9.4.17 Wear Resistance

Abrasion

Abrasion tests indicate the relative resistance of the polyurethane to two-bodied wear. When choosing a test, the test most suited to the application should be used. The ranking of the results varies with the type of test used. Many of the standards for the tests are based on commercial units.

Method	Details
ISO 4649	Rubber, vulcanized or thermoplastic Determination of abrasion resistance using a rotating cylindrical drum device
ISO 5470–1	Rubber- or plastic-coated fabrics Determination of abrasion resistance Part 1: Taber abrader
ASTM D1630	Standard test method for rubber property-abrasion resistance (footwear abrader)
ASTM D2228	Standard test method for rubber property-relative abrasion resistance by the pico abrader method
ASTM D3389	Standard test method for coated fabrics abrasion resistance (rotary platform, double-head abrader)
DIN 53516	DIN abrader "Rubber and elastomer abrader"
BS 903: PA9	Determination of abrasion resistance

The DIN abrader is used extensively for wear testing. The test uses a metal drum (150-mm diameter) that is covered with a 60 mesh corundum abrasive cloth. The drum revolves at 40 revolutions per minute and the sample moves down the length of the drum. The 16-mm-diameter sample travels a distance of 40 m during the test. From the loss in weight of the sample and its density, the volume loss is calculated. Three runs are normally carried out to obtain an average result.

The Taber abrader is another popular tester. It is used in a variety of different fields such as the paint, textile, and metal industries. A weighed sample is clamped onto a revolving table and abrasive wheels are placed onto the sample. The load on the free rotating wheels can be varied. The loss after a specified number of revolutions is recorded. The type and load on the wheels must also be stated with the result.

Erosive Wear

The evaluation of erosive wear of elastomers has not been standardized, and most industries test the erosive wear by using methods designed to simulate conditions relevant to their operations.

Organizations involved in the evaluations of erosive wear in pipes will often have a replaceable section of pipe that can have the experimental lining in it. Alternatively, there may be a side loop where the experimental material may be placed.

The use of pumps running in a process stream under good supervision and instrumentation can give good results. The ideal situation is two pumps pumping the same slurry, running in parallel.

Work under I.M. Hutchings and A.C. Arnold (Zu et al., 1990; Hutchings and Deuchar, 1987; Arnold and Hutchings, 1989; Arnold and Hutchings, 1990; Arnold and Hutchings, 1992) developed the slurry jet erosion tester. In this style of tester, a stream of erodent impinges on the surface of the sample at a predetermined angle. The mechanisms of erosive wear can be established at various angles of impingement. Quantitative work needs very careful post-cleaning of the sample, and the moisture equilibrium of the sample needs to be the same before and after the test.

Hector McI. Clark and associates (Clark et al., 2000; Clark and Wong, 1995) developed a wear tester based on a high-speed disk and on a slurry pot to evaluate the nature of erosive wear. Another type of slurry pot test was described by the U.S. Bureau of Mines (Blickensderfer et al., 1987) where only a very low angle of incidence was observed.

Walker and Bodkin (1993) discuss the advantages and limitations of a number of the commonly used erosive wear testers. The influence of particle size and shape are very important as well as the impingement angle and concentration of the slurry. They found that the wear rate increases with the jet velocity to the power of 2.2 (Mens and de Gee (1986) gives 2.8–3.2.). Wear rate is at a maximum at 30° impingement angle. The mechanism is mainly cutting. The rate increases with the size of the particle.

There are a number of other erosive wear testers used in industry to suit the type of product being evaluated. All the testers must be compared to actual field results. A major problem with many of the methods is the degradation of the slurry under test. The erosive wear of polyurethanes is very good, so extended testing often needs to be carried out.

9.4.18 Dynamic Heat Buildup

Dynamic heat buildup in applications such as wheels is important. Polyurethanes with a high resilience or a low tan δ in the operating range are important. Polyurethane elastomers used in wheel applications can be evaluated using a test rig where the urethane can be run under load for a fixed period or until failure.

A typical test speed is 32 kph at a load of 55 kg. The surface temperature of the wheel can be measured using an infrared thermometer. Failure will be due to hysteresis work, and the part will decompose from the inside out.

9.5 Prototype and Service Tests

The amount of testing and verification carried out depends largely on the importance of the part being produced and its future function. An end stop for a tube may only need the appearance, hardness, and the fact that it will correctly fit the tube checked. A flexible mounting of similar size also will need extensive testing to prove that it has the correct dynamic properties and can take the load and vibrations and not fail due to excessive heat buildup.

9.5.1 First Part Evaluation

The first part produced must be checked for a number of basic points:

- Correct polyurethane system used
- Molding of correct color
- Molding free of defects
- All dimensions in accordance with drawing/sketch
- Part fits correctly into rest of system

Any minor adjustments to the mold need to be made at this time, for example, the dimensions or any air pockets being removed by adding suitable sprues and or bleed holes.

9.5.2 Verification of Design

The basic design needs to be confirmed by the customer. Does the proposed part actually look like what is required, and will it fit into the rest of the equipment if it is part of a larger assembly? If not previously discussed with the supplier, any potential trouble points like sharp corners or butt joints should be brought to the attention of the customer and the potential problems resolved. If the part is a noncritical item or if there is knowledge available from previous similar items, the part can be evaluated by the customer. Flexibility, deformation under load, and correct functioning in an assembly can be verified using the part.

9.5.3 Simulated Tests

Standard laboratory dynamic tests provide screening of grades only. They do not verify how the full-scale part will perform. Some of these tests have been developed from a generalized product situation.

The aim of the tests should be to verify the correct functioning of the part at normal and at the limits of the operating conditions. By carrying out the tests under laboratory conditions, the potential for problems in the real world is reduced. In critical applications, the potential for major problems has to be eliminated. There is a large variety of service-style testing that can be carried out. These may range from very simple rigs to complicated test setups.

A roller may be subjected to pressure in a hydraulic press to simulate actual service conditions. The deflection at various loads can be noted. Wheels can be run on a test rig at service speeds under a load and the life and heat buildup recorded.

Antivibration mounts can be tested by measuring the reduction in the forces through the part under simulated working conditions. Any heat buildup also must be monitored. The tests may be carried out in an environmental chamber if nonambient temperatures are being used.

The properties of large pads can be tested in hydraulic presses such as those used to cure elastomers. Any shear factors can be added by using side rams. Seals can be tested under all potential conditions of pressure, speed, and environmental conditions.

The major problem in any simulated test is that of shortening the life span of the part. If a part is expected to last several years, an increase in operating temperature may introduce other aging problems than those experienced by operating at standard temperature. Similar considerations need to be applied to other variable factors such as load, vibrations, or concentration of chemicals.

9.5.4 Field Trials

In certain cases, more information may be obtained from field trials than by laboratory testing. Certain important criteria must always be observed before field trials are commenced:

- The potential for success must be very high.
- Failure of the test must not adversely affect the organization or person carrying out the test.
- The tests must be statistically designed to prevent bias.
- The length of the test must be such that an outcome can be reached.

The time span taken for a field trial to reach conclusion is important. If a part takes a considerable time to wear out, intermediate evaluations must be carried out to estimate the overall life. Improvements on short-life parts are easer to evaluate.

In certain cases, field trials can provide information that testing cannot. The feel to a golfer of a polyurethane cover on a golf ball is very important to the acceptance of the new cover stock.

Field trials on mining sites and large industrial complexes have several problems of their own. The part will be required to last a long time, so the continued knowledge of the item must be known. A trial part on service for 12 or more months may be changed by the night shift and scrapped before being assessed. Another major problem is to ensure that the trial part and its control both see the same feed and the operating times and conditions are rigorously recorded.

9.6 Investigative Research

There are a number of instrumental techniques that can be used to elucidate the structure of polyurethanes. These are often expensive and need specialized operation and interpretation of results.

9.6.1 Infrared Studies

The development of Fourier transform techniques with infrared spectra has made the use of infrared spectroscopy available to many more polymer chemists.

There are three main infrared bands, namely, the near, mid-, and far infrared zones. The most commonly used band is the mid-range band covering 50 to 2.5 µm or, in wave numbers, 200 to 4000 cm^{-1}. The near infrared band that covers the range of 0.8 to 2.5 µm (wave numbers 12500 cm^{-1} to near 4000 cm^{-1}) has overtones that have some importance to polyurethane processing. In this region, real-time studies have been carried out to follow the course of a reaction. (Wave numbers (in cm^{-1}) = 10000/wavelength (in µm).) The far infrared range does not have information that is relevant to polyurethane studies.

In the mid-range, the major technical problem is the fact that glass absorbs the infrared strongly so that special crystals such as potassium bromide, dried sodium chloride, or silver chloride need to be used. In the near range there are special glasses that can be used, for example, special black glass.

Infrared spectroscopy studies the effect on the molecules by infrared radiation. In the mid-range it is the fundamental vibrations of atoms and groups of atoms. Every group has its own specific wave number. At the high frequency end (of the mid-range), there are hydrogen-stretching vibrations (from O-H, N-H, C-H, and others). As the frequencies become lower, the double bonds start absorbing (C=O and N=C=O). At still lower frequencies, there are bands due to hydrogen bending (Pruckmayr, 1993).

The most commonly used technique for obtaining a spectrum is the attenuated total reflectance (ATR) method in the multiple internal reflectance (MIR) mode. In this method, the infrared beam is passed into a special crystal of a selenide (KRS-5). The angle of incidence is such that the beam will bounce along the crystal. A sample of the polyurethane is placed hard up against the crystal. The infrared just penetrates into the material before it continues down the crystal. A number of internal bounces are obtained along the crystal. Up to 25 reflectances are obtained from a 2 mm crystal. Figure 9.8 illustrates the infrared path in an ATR cell.

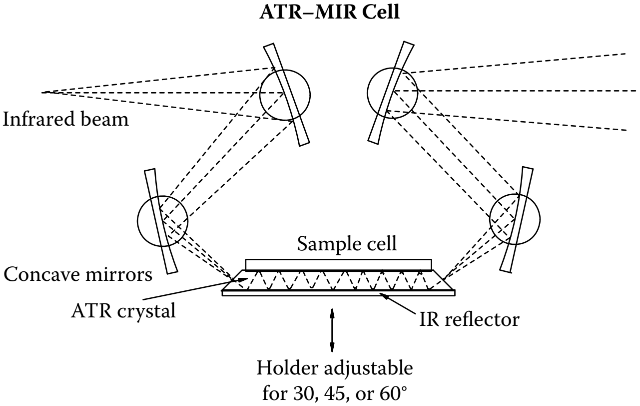


FIGURE 9.8
Infrared light path in an ATR cell.

There are two ways of viewing the spectrum produced, either in the percent transmitted or in the absorption mode. For work involving the formation of urethane and urea groups, the absorption mode appears to be easier. Some important wave numbers in the polyurethane work are as follows.

Functional Group	Wavelength (μm)	Wave Number (cm^{-1})
-NH	3.0	3333
-NCO	4.4	2273
-C=O in esters	5.71–5.83	1751–1715
-C=O in allophanate and urea	5.71–5.85	1751–1709
	8.85–6.06	1709–1650
-C=O in urethane	5.75	1739
-C=O in urea	5.9–6.1	1694–1639
Amide II band (NH)	6.5	1538
C-O in ethers	9.3	1075

Textbooks dealing with infrared will have tables with the wave numbers for various groups. There is often confusion between "-OH" bands near the –NH band at 3333 cm^{-1} and a band from atmospheric contamination near the –NCO at 2273 cm^{-1}.

It always must be noted that the wave numbers will vary from instrument to instrument. There are also influences from other functional groups attached to the group that will change the exact position.

A qualitative use for infrared spectra is the identification of the type of system used based on standard databases such as the Sadler library of reference spectra or by comparing to a database developed internally. A large library of spectra taken on the same instrument and under the same conditions will give the best results.

The type of TDI used can be determined by studying the bands at 810 cm^{-1} and 782 cm^{-1}. One hundred percent 2–4 TDI has a peak at 810 cm^{-1} and no peak at 782 cm^{-1}. As the percentage 2–6 isomer increases, the band at 782 cm^{-1} intensifies. The ratio of these two bands indicates the grade of TDI used.

The reaction rates of systems can be measured. Using heated cells, the reaction between mixtures of polyols and isocyanates can be followed. There are a number of changes to the infrared spectrum that take place. The "-OH" band at 3460 cm^{-1} will decrease, as will the "-NCO" band at 2270 cm^{-1}, as the diisocyanate reacts with the polyol, leaving only the terminal isocyanate groups. Other urethane bands at 3289, 1730, 1534, and 1230 cm^{-1} will increase. The ether group (1112 cm^{-1}) will stay the same, because it does not take part in the reaction. It can be used as a reference to normalize the other bands. If a polyol and MDI are studied, it is found that there is only one rate constant, whereas when using 80:20 TDI there are two rate constants.

Similar work can be carried out during the curing by studying the reaction rate between the curative and the prepolymer. The "-NCO" band at 2270 cm^{-1} will decrease and the urethane or the urea bands will increase, depending on the type of curative used.

This also shows the development of hydrogen bonding in the system. The urethane and urea bands will split into bonded and nonbonded bands. Work by Seymour, Estes, and Cooper has shown how the percentage of hydrogen bonding can be calculated (Seymour et al., 1970).

The effect of temperature on hydrogen bonding can also be examined. It has been found that the bonding disappears on heating and returns as the material cools. With moderate heating, the level of hydrogen bonding will increase when the material cools down.There are glasses that are transparent to infrared in the near-infrared range. The special glass is made into a fiberoptic cable, enabling some flexibility. Overtones from the mid-infrared range can be used to monitor reactions. A disposable probe can be inserted in or at the surface of a polyurethane molding. This technique is particularly suited to very fast cures.

9.6.2 Gas Chromatography

ASTM standard method D3432 describes how to determine the amount of unreacted TDI in prepolymers and coating solutions. An internal standard is used to normalize the results. Care has to be taken not to get any prepolymer onto the main column. This test is important, as the unreacted isocyanate is a prime cause of health problems.

9.6.3 Nuclear Magnetic Resonance (NMR)

This method relies on the fact that the isotopes of certain atoms have electrons that will flip under certain conditions. This change in state can be detected, and how they are connected can be shown. The ^{1}H and ^{13}C isotopes are able to produce resonance spectra for polyurethane raw materials and cured samples. ASTM method D4273 details a method to determine the primary hydroxyl content of polyether polyols.

Any fluid samples can be tested on standard NMR machines. The structure of the polyol can be calculated and any branching will be shown. The approximate size and structure of prepolymers can also be determined by using both ^{1}H and ^{13}C NMR methods.

Solid polyurethanes can be tested using specialized NMR instruments and the overall structure determined.

9.6.4 X-Ray Diffraction

Various x-ray diffraction techniques have been used to study the size and distribution of hard and soft segments near the surface of the polyurethane.

9.6.5 Differential Scanning Calorimetry (DSC)

The amount of heat absorbed or given out by a sample of polyurethane is measured as the sample is heated over a range of temperatures. Changes in the state of the polyurethane occur at various temperatures. Changes occur when the hard, then soft, segment becomes mobile and when hydrogen bonding starts to break down.

Samples are normally heated to just above softening point and then allowed to cool down before a test is carried out. With castable polyurethanes, decomposition takes place when the sample is softened, so either the annealing cycle must not be used or the temperatures must not be taken up as high.

9.6.6 Atomic Force Microscopy

Atomic force microscopy has been used to evaluate the nature and size of the polyurethane structure at the surface of a sample. In this method, the surface of the sample is coated with a layer of gold and a probe scans over the surface. As the nature of the chemistry below the probe changes, the force field acting on the probe changes. The hard segment clusters can be visualized.

9.6.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is an important tool when examining the mode of wear of any sample. The surface of the sample is coated with a very thin layer (only several atoms thick) of a conductive material such as gold. The surface is scanned using a beam of electrons and the image magnified and recorded.

SEM microscopy gives results with a much greater depth of field than conventional optical microscopy. When wear surfaces are being examined, a full depth image of the wear damage can be seen. The representation gives a three-dimensional effect, allowing for very good visualization.

9.6.8 High Performance Liquid Chromatography (HPLC)

HPLC instrumentation and methods have taken over from many GLC methods, and using the correct methods gives better resolution and accuracy. HPLC methods are used in the urine analysis of people who have been exposed to MOCA.

HPLC techniques have been developed to analyze for free TDI in prepolymers as an alternative to the official GLC method.

If the HPLC is set up for the determinations of anions and cations, the metallic catalyst level in quasiprepolymers can be determined.

9.6.9 Size Exclusion Chromatography

In this variation of high performance liquid chromatography (HPLC), the columns are packed with material that will hold back molecules dependent on the molecular size. Using the correct solvent system and column types, the molecular weight and distribution of the polyols can be determined. Standard samples are needed to calibrate the system. The molecular weight distribution of prepolymers can also be determined. This will enable an estimation to be made of the number of soft segment chains there are.

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10

Health and Safety

10.1 Introduction

Socially, economically, and legally, it is important to have a workplace that is a safe and healthy environment in which to work. If chemicals used in polyurethane manufacturing are not used in a safe and careful manner, they can cause harm to workers in the short and long term. Laws and regulations exist regarding the use of polyurethane ingredients and the associated machinery. Local laws and regulations must be studied, implemented, and adhered to when working with polyurethanes and all auxiliary materials.

10.1.1 Rationale

There are two major chemical areas of health concern in the polyurethane industry. The first is isocyanates, in their free form as a liquid or in the vapor form. The second is amines. These can be either curatives or catalysts. One curative, MOCA (CAS number 101–14–4), is classed as a suspect carcinogen in most parts of the world and is subject to many rules and regulations regarding its use. MOCA (MBOCA) is known by many different names, which are listed on various websites such as www.chemindustry.com/chemicals.

Even traces of isocyanate vapor in the atmosphere can cause bronchial troubles, either in the short or long term. Operators who have asthmatic problems are extremely sensitive to isocyanate vapors and must be kept clear of any exposure.

All chemicals used in the polyurethane industry can cause some harm and must be treated with both care and respect.

10.1.2 Work Environment

The overall work environment of a polyurethane workshop is prone to becoming untidy and hazardous due to the nature of the operations being carried out; e.g., there may be hot, slippery chemicals; hot molds; and curing ovens. The layout of the workflow must be under constant review as the emphasis of the product range changes. It is also important that safety of the operation is controlled to a large extent by the inclusion of engineering methods of hazards reduction rather than relying mainly on personal protective equipment (PPE).

10.1.3 Acute Exposure

Acute exposure generally refers to single-dose, high-concentration exposures over short periods. Some of the chemicals used in the polyurethane industry can cause acute health problems and have an immediate effect on the health of people exposed to it. The most prominent of the chemicals are the isocyanates. People with bronchial problems can have an immediate attack. It is often suggested that all employees be screened for lung function and for potential problems. Isocyanates also have the potential to sensitize people, and they can develop problems in the future.

If mercuric catalysts are used, they must be handled with great care. They can cause burns to the skin that will develop over the next 12 hours subsequent to handling.

10.1.4 Chronic Exposure

Chronic exposure refers to repeated or continuous exposure over long periods of time. Amine-based materials, such as amine curatives and catalysts, have a potential for problems to occur after a number of years. The highest-profile potential problem material is MOCA, which has been subject to numerous studies. There have been very few cases of fatalities due to exposure to MOCA. The initial casualties also had exposure to precursor materials that were known carcinogens. Further details are very scant.

10.2 The Workplace

The workplace environment can be divided into the following sections:

- Chemicals
  - Solid
  - Liquid
  - Vapors
- Heated areas
- Finishing
- Engineering

10.2.1 Information Sources

Material Safety Data Sheets

Material Safety Data Sheets (MSDS) are a means of communicating properties and safe-handling procedures to users of industrial and laboratory chemicals.

They also give professionals such as doctors, paramedics, firefighters, and emergency services, information regarding the nature of any problem situations that they may be called on to assist in.

Initially, MSDSs were in many different formats and levels of completeness. They have now been standardized into a recommended format so that the information is readily available.

There are national codes of practice for the preparation of MSDSs. The current trend is to use an internationally recognized 16-point standard. This is a comprehensive document referring to how and where to obtain the information as well as including approved terms and forms of wording that must be avoided, for example, the use of N/A, which could mean either "not applicable" or "not available." Such terms should be written out in full. An outline of the international standard is included at the end of this chapter.

There are rules governing classification of materials that contain a percentage of hazardous materials. These are given in the criteria for determining hazardous materials and are a function of the degree of hazardousness and the concentration of the ingredient. In the case in which there are several different hazardous materials, the various factors are summed up and a total degree established. These factors are also used to determine what risk and safety phases are applicable to the particular material.

An MSDS should be written in a clear and understandable manner, and unnecessary technical terms should be avoided. Layman's terms rather than complex medical terms should be used.

All MSDS documents have to be updated every 3 years and fresh versions issued. With the first delivery or sample of any material, a copy of the MSDS must be received and studied before use. The documents must be available to all people coming in contact with the material. The terms used therein should be fully explained and understood by all.

Governments

Governments at various levels issue rules and regulations controlling many aspects of the operation of the polyurethane industry. Some of the typical information available includes:

- Uses, sale, and storage of MOCA
- Health surveillance of people using MOCA
- Use and storage of solvents
- Use and storage of diisocyanates
- Safety in transport
- Monitoring of diisocyanates
- Format of MSDS documents
- Definitions of dangerous and hazardous chemicals

- Workshop safety requirements
- Forklift driving and crane driving

There are also the local government rules and regulations regarding the location of factories making and processing polyurethanes. These regulations vary from state to state and country to country, so the local requirements must be considered and implemented.

Standards are issued by both the standards organizations (e.g., ANSI, BS, or AS) and the professional industry associations regarding the recommended procedures for handling diisocyanates and materials such as MOCA. The Polyurethane Alliance has issued guidelines for the transportation of TDI (Alliance for the Polyurethane Industry, 2002).

Suppliers

Suppliers of polyurethane raw materials issue MSDSs for all their products as well as data sheets on the individual materials with additional information about the material concerned. This may be important, as in the case of pure MDI, where the storage conditions are vital.

Suppliers of bulk raw materials will provide instructions for handling their material, including details of transfer procedures from the supply vehicles. The information also may include the suggested correct valves, blanketing, and heating if required.

All MSDS documents must be read from a practical as well as scientific viewpoint. The most appropriate grade of safety equipment must be used. The equipment must stop the offending material from reaching the person it is protecting. The useful life of the equipment must not be exceeded. Engineering the problem out is the best solution. An example is the fully automated system for handling MOCA.

Signage

Internally, all permanent pipe work should be plainly labeled with its contents, for example, compressed nitrogen, steam, polyol, or diisocyanates. The signs must be clearly visible and in accordance with local regulations and also indicate the direction of flow.

The entrance to the plant must be distinctly placarded with a permanent sign indicating the nature of the dangerous and hazardous materials in the factory, with the basic emergency response to each. The "UN number" for each should be indicated on the sign as well as the appropriate emergency and contact numbers; for example, the UN number for TDI is UN 2078. Hazard information cards also should be available and sent with each load of isocyanate.

Outside storage containers also must have hazard information relating to their contents attached.

10.3 Prepolymer Preparation

10.3.1 Isocyanates

Isocyanates must be used strictly in accordance with the government's and supplier's recommendations. The material is in the unreacted form with the potential for the presence of vapors. MDI at temperatures above 50°C has a substantial vapor pressure compared to when it is at ambient temperature. Care must be taken if work is carried out using PPDI, as it has a very high vapor pressure. The fumes will bring tears to the eyes if contact is made.

If the presence of isocyanates can be smelled, this means that the safe exposure limits have been exceeded.

Engineering controls must be the first line of safety when using any diisocyanate, followed by the strict use of personal protective equipment (PPE). There also have to be strict engineering protocols so that cross-connection between sources of polyols and diisocyanates cannot be made. Personal and atmospheric monitoring must be carried out. It is important that the operators in this area be under medical screening.

Isocyanates are also strong skin sensitizers and can cause irritation to the eyes and mucous membranes. The correct protection equipment must be worn and there must be thorough washing of the hands and arms after exposure to isocyanate liquid or its vapors.

The factory should have the correct hazardous chemical signage at every entrance to the shop floor. Protocols must be set up to handle any spilled isocyanates. Minor spills in-house must be correctly neutralized and the waste disposed of according to local regulations. The local fire and emergency authorities must be made aware of the presence of isocyanates in the factory and have the appropriate documentation of how to handle any emergency. The industry professional body should have this information available for the fire and emergency authorities.

10.3.2 Polyols

Polyols do not have the same extreme toxic properties as isocyanates but must still be treated with care. They are not treated as hazardous but may cause some skin and eye irritation. Basic precautions such as impervious gloves and eye protection must be worn.

Care must be taken when melting any solid polyols not to overheat the drum. This can cause an explosive drum rupture.

Heat

Steam is often used to melt frozen MDI and PTMEG. The steam generators and associated controls must be maintained according to the local regulations to prevent major problems, including a possible explosion. Steam carries far more energy than hot water. It must be treated with care to prevent severe burns.

Areas where there are hot drums and pipes must be clearly labeled with appropriate signage. Hot polyurethane prepolymer can cause severe burns, and the potential for free isocyanate vapors is very high.

10.3.3 Prepolymers

Free Isocyanates

Free isocyanates are unreacted diisocyanates left over after the production of prepolymers. The manufacture of prepolymers is normally stopped prior to the consumption of all the diisocyanate. This is so that the material is at the optimum point for further processing. This free isocyanate may either be left in the product (at a level of 0.1 to 0.8%, depending on grade) or removed by the manufacturer to a lesser or greater degree. Special low free isocyanate grades (LF grades) are available. These grades have health and safety as well as some technical advantages.

Monitoring must be carried out to check that the levels of isocyanate vapors do not exceed the local limits. These limits vary from area to area. In some areas of the world, only the isocyanate level is specified and is not controlled by the type of isocyanate. Care must be taken, as the vapor pressure of different isocyanates may vary by a factor of 100 or more. Plants that may comply with the atmospheric isocyanate levels when using MDI-based material may have too high a level when using TDI-based prepolymers.

Certain blocked prepolymers contain chemicals such as methyl ethyl ketoxime. The blocking is on the isocyanate (NCO) groups. When the prepolymer is heated, the vapors of the blocking agent are given off. These vapors can cause irritation if inhaled.

10.3.4 Curatives

The two main groups of curatives used in the castable polyurethane industry are:

- Amine-based
- Diol-based

Amines

Amine-based curatives are a popular choice when working with TDI-terminated prepolymers. The two most used amine-based curatives are MOCA and Ethacure 300. Other amine curatives used include Versalink 740M, MCEDA, and Cyanacure.

MOCA is technically a good curative, but it is a classified Class 2 suspect carcinogen and is listed in the safety regulations as a chemical along with such materials as asbestos. MOCA has to be used under a strict code of practice.

The workers using it must be health-screened quarterly by a competent medical authority. The level of MOCA in the urine has to be tested and the results evaluated by a competent physician in this field.

There is a feeling in the industry that MOCA is not as dangerous as claimed, and the concerns are based on old information. There is, however, a large body of information that shows that MOCA reacts with DNA to form an adjunct. There is also evidence that Ethacure 300 has some mutagenic effects, but to a much lower degree. The risks involved are of a chronic nature; they may not be evident for many years after the initial exposure. It is most important that the code of practice be strictly adhered to. There was a reported case in 1988 of two nonsmoking males under the age of 30 who developed bladder cancer. They were exposed to MOCA during its manufacture but also had worked in other sections with another carcinogen.

Ethacure 300 is a much easier material to handle, as it is a liquid at room temperature. It is classed as a hazardous substance according to the safety authorities' criteria. As with all chemicals, it must be treated with respect and used in accordance with the MSDS, which suggests that there should be sufficient ventilation. Neoprene gloves must be worn with disposable or impervious clothing.

Amine curatives that are solid at room temperature need to be melted prior to use. The hot molten material must be handled with care, as it can cause severe burns and may be absorbed into the skin.

Data for MCEDA published by its manufacturer (Lonza Fine Chemicals, 1992) indicate that it is not as hazardous as MOCA or MDA, with lower toxicity and irritation.

Diols

These curatives are normally hydroxyl (OH) based. Although not as dangerous as the amine-based curatives, these materials are still hazardous, as are all hydroxyl-based materials, with the exception of ethanol in small quantities. Safety precautions such as gloves and impervious clothing should be worn. All chemicals must be treated with respect.

10.3.5 Catalysts

There are three main groups of catalysts used in the casting industry:

- Organometallic materials (mercury or tin soaps)
- Amine-based material (Dabco 33LV)
- Organic acids (adipic, oleic acid)

Metallic

These materials provide an extremely fast gel rate of castable polyurethanes. They are the most hazardous of the three groups. Mercury-containing catalysts must not be used in any systems that will come in contact with food. The local limits (if allowed) for mercury-based catalysts must be adhered to.

Metallic catalysts will cause rapid poisoning if ingested. Some catalysts—for example, phenyl mercuric acetate—will result in strong caustic burning. Contact with the skin will cause a dangerous burn. Care must be taken with these materials even though they are only used in very small quantities. These catalysts are extremely toxic if digested.

Amine

Dabco 33LV is classified as hazardous according to the criteria of safety authorities. The material has a typical ammonical odor and can be absorbed through the skin. If accidental contact is made, medical attention should be sought after flushing with water. Inhalation of the vapors should be avoided by use of correct engineering practices or the use of a respirator.

Other Organic Acids

Organic acids such as adipic acid and oleic acid are the slowest working of the group, but they are the least hazardous. Normal procedures should be taken when using them, such as wearing gloves and avoiding inhalation of any dust. These catalysts are normally used with TDI-based systems.

10.3.6 Other Additives

Plasticizers

Plasticizers such as DIOP, TCP, and Benzoflex 9–88 should be handled with gloves, as they may cause minor skin irritations when small concentrations come in contact with the skin. Large-scale exposure to TCP must be avoided, as absorption through the skin can cause nerve damage. If exposure occurs, the material must be removed immediately and the area washed with copious quantities of water. Medical advice should be sought.

Spills of plasticizers must be cleaned up immediately by absorption, using standard oil-absorbent granules. These must be disposed of according to local rules and regulations.

The use of simpler phthalates (such as Dibutyl phthalate) must be carried out with care because of their higher vapor pressure and greater potential for hazardous health effects.

Silica

Silica is used as a thickening agent in polyurethanes. The grade of silica is a fine, anhydrous silica typically sold under the name of Aerosil (Evonik. Degussa. Essen, Germany). The particle size is very fine, normally less than 40 millimicrons. The bulk density of the material is extremely low and it is very light and fluffy. Inhalation of the dust must be avoided. From the method of manufacture, there should not be any crystalline material in it. Unless properly contained, the very fine material also is a dust problem.

Pigments

Pigments that are used should not contain cadmium, which has hazardous properties. Pigments will normally be supplied in a paste form let down in either polyol or a plasticizer. Pigments can be very messy and stay on the skin for a period of time if not removed promptly. Disposable impervious gloves should be used when using pigment concentrates.

10.3.7 Solvents

Mold Release

Mold-release agents are supplied in either a solvent or water. The solvent-based materials present handling problems, as they are flammable. There are two potential sources of ignition: (1) flames used to pop bubbles that come to the surface of the casting, and (2) arcs from electrical contacts that can also set the solvent vapor off.

Water-based mold-release agents need more heat to dry the coating and to reheat the reinforcing. Solvent-based mold-release agents tend to flash off and leave a coating with greater ease. The operation with the solvent-based material needs to be carried out away from any flames.

Cleaning Solvents

Only sufficient solvents for immediate use should be kept on the shop floor. The bulk of the stock must be kept in a special flammable storage container.

Besides the fire hazard that they present, any solvent that is spilled on clothing or the skin presents a health problem. Suitable impervious gloves and eye protection must be worn when using any solvent. Contaminated clothing must be removed and the contact area washed well. As the solvents will remove the natural oils from the skin, they must be replaced by an industrial grade of barrier cream.

Any spills of solvent on the floor should be absorbed into "kitty litter" and disposed of in an approved manner.

10.3.8 Heat

Prepolymer/Curative

When handling heated prepolymers or molten prepolymers, impervious gloves must be worn. These materials can cause severe burns, as they are poor conductors of heat. In this condition, they can readily be absorbed into the body. If MOCA is overheated to above 140°C, dangerous fumes will be given off.

Molds

A hot metal mold will feel much hotter than a hot polyurethane or epoxy mold. This is because of the thermal conductivity of the mold material. For light metal molds, heat-resistant gloves must be worn. For larger molds, suitable mechanical handling must be employed. The handling equipment must be of suitable size and in good condition.

Dermatitis can result from using a heat glove (nonimpervious) that has been contaminated with either a solvent or polyurethane prepolymer. The same applies to gloves used in the manufacture of prepolymers.

Curing Ovens

Everything inside an operating oven must be considered to be at the set temperature. Large walk-in ovens could have high concentrations of solvent or isocyanate vapors. Proper PPE must be worn when entering them. If too long a time is spent in a curing oven, dehydration can occur.

10.3.9 Products of Combustion

Polyurethane products, including isocyanates, produce dangerous fumes when involved in a fire. Polyurethanes and diisocyanates, like other nitrogen-containing materials such as wool, will produce both carbon monoxide and hydrogen cyanide gas when burned.

Reports (Boettner et al., 1973; DuPont, 1981) on the combustion products of polyurethanes show that the levels of carbon monoxide in an oxygen-deficient burning condition can reach 290 to 640 mg per gram of sample burned, with cyanide (as HCN) up to 34 mg per gram of sample burned. This data is from laboratory tests and may not represent actual combustion conditions. Professional firefighters should be involved in all situations in which there is an uncontrolled fire in a polyurethane plant.

10.4 Engineering

10.4.1 Gases

Gases used in a processing plant will be received either as a cylinder or as a liquid in a cryostat (large vacuum flask).

Cylinders

Gases that are used in a polyurethane factory include nitrogen, butane, or LPG for heating, and oxygen and acetylene for welding. Compressed air is used to remove parts from molds and can be generated on site with a small compressor.

All cylinders must be stored in an appropriate manner and properly secured. The supplier of the gas can provide local details of any requirements.

Compressed Gases

Nitrogen is often used to blanket prepolymers and curatives after the container has been partially used. The blanketing system, if left in place permanently, must be so engineered that the container cannot build up a level of pressure in it that renders the situation unsafe.

It must always be taken into account that polyurethane prepolymers are messy materials, and they will cure in the air to form a solid mass. A major precaution would have to be that the gas being delivered to the vessel is at a very low pressure and there is a safe continuous bleeding point.

The pipelines used to convey compressed air or nitrogen must be designed to carry pressure. Low-pressure flexible PVC tubing is not suitable. Where the gases are carried for long distances, solid metal lines with takeoff junctions should be provided. Flexible lines should be kept clear of heated ovens and open flames. Kinks and other mechanical damage should be avoided, and when it occurs it should be immediately repaired.

From a work point of view, it is far better to have the compressed air coming down from the ceiling than lying either on the benches or across the floor, where it can easily be damaged and trip one up.

Any line, whether it is gas or water that is under pressure and is not secured, will slash around like a snake and can cause considerable damage and harm to a person.

Compressed air should have any free water removed to prevent contamination of prepolymers.

Liquid Nitrogen

In production units where polyurethane prepolymers are used, liquid nitrogen is an option to provide an inert atmosphere in the reactors. The unit should be set up professionally by a supplier and the liquid nitrogen unit properly maintained.

If it stays in contact with the skin, liquid nitrogen can cause freezing burns due to its extremely low boiling point (–195°C). Evaporating nitrogen can cause the oxygen in the air to freeze out.

It must be remembered that nitrogen when mixed with oxygen (that is, as in air) is nontoxic, but when oxygen is not present it will cause suffocation. Any entry into a reactor that has been filled with nitrogen must be fully flushed with air. Only people who are licensed to enter enclosed vessels and are wearing the correct respiratory gear, with qualified backup, may enter the vessel.

10.4.2 Machinery

Workshop

Electrical Equipment

Electrical equipment is the field of qualified electricians; therefore any changes, repairs, or modifications should be done by an approved electrician.

The overall condition of electrical equipment, including extension leads, must always be observed and any wear and tear replaced or made good by a qualified person. Leads should not be allowed to drape all over the floor or in areas where a hot or heavy mold may be accidentally placed on them.

Lifting Gear

Large molds must only be moved by approved lifting gear. The mold should have "eyes" attached of size and number to take the weight of the mold. The weight of the mold should be clearly marked on its side. Certified chains and hooks should be used. The capacity of the chain must be sufficient to take the load applied to it.

When lifting the load, it must be kept as close to the floor as practicable to prevent harm in case of gear failure. All equipment must be fully checked and replaced if damaged.

Forklifts

Forklifts must only be operated by qualified personnel and all standard precautions taken. Load limits must always be carefully obeyed, taking into account the effects of high lifts. Speed must be kept to a minimum when working inside the building.

Proper drum-handling equipment, such as drum clamps or parrot beak clamps, must be attached and used when moving drums.

There is poor air circulation in shipping containers; therefore, there is a potential for heat and fume buildup that makes it hazardous when working inside it. All drums must be inspected for leaks or bulging as they are being unloaded.

Machinery

Workshop machinery is used either for the finishing operations on polyurethane castings or in the production of prototypes and molds. All people using the machinery must have had safety training in the operation of the equipment.

All safety guards, where fitted by the manufacturer, must be kept in use. The cutting equipment must be sharp and the clearances suitable for polyurethane. Poor machining practices can cause localized heating, and the decomposition fumes are dangerous.

Appropriate PPE must be worn during any operation. This includes safety glasses with side shields and a face shield in case chips or pieces fly off the machine.

The correct attaching of the piece to the machine is important to prevent accidents. The machine must not be started until one is sure that the work will not become dislodged during machining operations.

The dust from any dry grinding operations must be removed as it is formed. The dust must not be inhaled.

10.5 Material Safety Data Sheet Format

The following is the basic layout of the 16-point MSDS.

1. Product and Company Identification
    - Product information
    - Product identifier
    - Manufacturer's name, street address, city, state, postal code, and emergency telephone number
    - Supplier identifier, supplier's street address, city, state, postal code, and emergency telephone number
    - Product use
2. Hazards Identification
    - Emergency overview
    - Regulatory status
    - Potential health effects
    - Toxicological Information
    - Route of entry (including skin contact, skin absorption, eye contact, inhalation, or ingestion)
    - Effects of acute exposure to product
    - Effects of chronic exposure to product
    - Irritancy of the product
    - Sensitization to the product
    - Carcinogenicity
    - Reproductive toxicity
    - Teratogenicity
    - Mutagenicity
    - Names of toxicologically synergistic products
    - Potential environmental effects
3. Composition/Information on Ingredients
    - Hazardous ingredients
    - For each ingredient, the concentration expressed as percent weight/weight, percent volume/volume, or percent weight/volume must be indicated
    - CAS registry number (for each ingredient) and product identification number
    - Confidential business information (trade secrets)

4. First Aid Measures
    - First aid procedures
    - Specific first aid measures
    - Note to physicians
5. Firefighting Measures
    - Flammable properties
    - Conditions of flammability
    - Flash point and method of determination
    - Upper flammable limit
    - Lower flammable limit
    - Auto-ignition temperature
    - Explosion data—sensitivity to mechanical impact
    - Explosion data—sensitivity to static discharge
    - Extinguishing media
    - Suitable extinguishing media
    - Means of extinction
    - Unsuitable extinguishing media
    - Protection of firefighters
    - Specific hazards arising from the chemical
    - Hazardous combustion products
    - Protective equipment and precautions for firefighters
6. Accidental Release Measures
    - Procedures to be followed in case of a leak or spill
    - Personal precautions
    - Environmental precautions
    - Methods for containment
    - Methods for cleanup
    - Other information
7. Handling and Storage
    - Handling
    - Handling procedures and equipment
    - Storage
    - Storage requirements
8. Exposure Controls/Personal Protection
    - Exposure guidelines
    - Exposure limits
    - Engineering controls

    Specific engineering controls to be used
    Personal protective equipment (PPE)
    Personal protective equipment to be used
    Eye/face protection
    Skin protection
    Respiratory protection
    General hygiene considerations

9. Physical and Chemical Properties
    - Physical state (i.e., gas, liquid, or solid)
    - Odor and appearance
    - Odor threshold
    - Specific gravity
    - Vapor pressure
    - Vapor density
    - Evaporation rate
    - Boiling point
    - Freezing point
    - pH
    - Coefficient of water/oil distribution
10. Stability and Reactivity
    - Chemical stability
    - Conditions to avoid
    - Conditions under which the product is chemically unstable
    - Incompatible materials
    - Name of any substance or class of substance with which the product is incompatible
    - Hazardous decomposition products
    - Possibility of hazardous reactions
    - Conditions of reactivity
11. Toxicological Information
    - LD_{50} (species and route)
    - LC_{50} (species and route)
    - Effects of acute exposure to product
    - Effects of chronic exposure to product
    - Irritancy of product
    - Sensitization to product
    - Carcinogenicity

  Reproductive toxicity
  Teratogenicity
  Mutagenicity
  Name of toxicologically synergistic products

12. Ecological Information
13. Disposal Considerations
    Waste disposal
14. Transport Information
    Basic shipping information
    Special shipping information
    Additional information
15. Regulatory Information
    Material safety data sheets should include a statement such as "This product has been classified in accordance with the hazard criteria of the country of issue and the MSDS contains all of the information required by those regulations."

    It is advisable to include the WHMIS classification here as well.
16. Other Information
    Preparation information
    Name and phone number of the group, department, or party responsible for the preparation of the MSDS
    Date of preparation of the MSDS

References

Alliance for the Polyurethane Industry. "TDI Transportation Guidelines." Arlington, VA: American Plastics Council, 2002.

Boettner, E.A., G.L. Ball, and B. Weiss. "Combustion Products from the Incineration of Plastics." 1–140: Michigan University, 1973.

DuPont. "Combustion Products of a Urethane Vulcanizate Cured with MBCA." 1. Wilmington, Deloware: DuPont, 1981.

Lonza Fine Chemicals. "Lonzacure® M-CEDA "The Superior Curative for the Polymer Industry." 1–7. BASLE: Lonza, 1992.

Appendix 1

Abbreviations and Trade Names

Name	Description
Acclaim Polyol	Low monal PPG
BDO	1,4-butane diol
Benzoflex-9–88 SG	Dipropylene glycol dibenzoate
CHDI	Cyclohexyl diisocyanate
Crosslink 30/10	HQEE
DABCO	DABCO 33LV
DABCO 33LV	1,4-diazabicyclo[2.2.2]octane/triethylene diamine
DIOP	Di iso octal phthalate
Ethacure 300	3,5-dimethyl-2,4-toluenediamine and 3,5-dimethyl-2,6-toluenediamine
Fyrol PCF	Tri(b-chloroisopropyl) phosphate
HDI	Hexamethylene diisocyanate
HQEE	Hydroquinone bis (beta hydroxyethyl)ether
Isonol 93	Ether triol; now Conap AH50
Lonzacure M-CEDA	4,4′-methylenebis(3-chloro-2,6-dichloroaniline)
MBOCA	3,3′-Dichloro-4 ,4′ diaminodiphenylmethane
MDI	4,4′-Diphenylmethane diisocyanate
Messamol oil	Alkyl sulphonic acid ester of Phenol (Miles)
MOCA	3,3′-Dichloro-4 ,4′ diaminodiphenylmethane
m-Pryol	2–methyl-2-pyrrolidone (CAS872–50–04)
NDI	1,5-naphthalene diisocyanate
NMP	2–methyl-2-pyrrolidone (CAS872–50–04)
Polacure	Trimethylene glycol di-p-aminobenzoate
PPDI	Para-phenylene diisocyanate
PPG	Polypropylene ether glycol
PTMEG	Polytetramethylene ether glycol
Santicizer 160	Butyl benzyl Phthalate
Stabaxol	Anti-hydrolysis agent Rhein Chemie
TDI	Toluene 2,4-diisocyanate and Toluene 2,6-diisocyanate
Terathane	Polytetramethylene ether glycol
THF	Tetrahydrofuran
TMP	Tri methylol propane
TODI	3,3 ′-Dimethyldiphenyl 4, 4′diisocyanate

Appendix 2

Polyurethane Curatives

Curative	Equivalent Weight	Comments
BDO	45	1,4 Butane diol
Conap AH50	90	Previously known as Isonol 93
Conap-AH33	280	
Cyanacure	138	1,2-bis[2-amino-phenylthio]ethane
DEG	53	Diethylene glycol
DETDA	89.3	Diethyltoluene diamine
Ethacure E100	89.3	DETDA
Ethacure E300	107	Di-(methylthio)toluene diamine DMDTA
Ethylene glycol	31.03	
HER	99	
HQEE	99	Hydroquinone bis (beta hydroxyethyl)ether
MCEDA	187	Lonzacure
MOCA (MBOCA)	133.5	
TIPA	64	Tri iso propane amine
TMP	45	Trimethyol propane
Versalink P650	415	
Versalink P-1000	600	
Plurocol TP-440	145	Range 139–145 Triol
Conap AH-40	133.5	Commercial formula
1,4 Butane diol	45.1	BDO
Isonol 93	90	Range 88–93 Triol
Versalink 740M	157	
Poly-cure 1000	155	
PPG 1000	500	Polypropylene glycol
PTMEG 1000	500	
Curene 3005	280	

Appendix 3

Mold Release Agents

Name	Manufacturer	Comments
200® and 20	Dow Corning®	
3422 polyurethane release	Dow Corning	Water-based
Cilrelease 910	Chemical Innovation	Concentrated mold +50°C
Crystal 4000	TSE Industries	
Eralease	Era Polymers	
Freecote #1 NC	Loctite	Teflon-based
Freecote Aqualine® PUR 100	Loctite	
Freecote FRP-NC	Loctite	
Freecote® WOLO	Loctite	
Gorapur®	Degussa	
Mavcoat™ mold release	Marerix Solutions, Inc.	
Mold release 81801	Chesterton	
Mylar Film	DuPont	
Nonstikenstoffe	Freekote	
Rhodosil 47V50	Rhodia	

Appendix 4

Technical Terms

Term	Description
Abrasion	Wear due to friction.
Activator	A compounding material used in small proportions to increase effectiveness of an accelerator.
Additive	A material combined with the prepolymer and curative to modify the final properties of the casting. This includes plasticizers, fillers, and stabilizers.
Adhesive failure	A separation of two bonded surfaces within the bonding material.
Aliphatic	A class of open chained compounds containing straight, branched, or cyclic fragments.
Amine	A class of compounds used as catalysts or curatives in polyurethane elastomer and foam reactions. Amines are characterized by having N, NH, or NH_2 groups in the molecule.
Amine equivalent	Used in the same manner as the equivalent weight of the prepolymer and equal to formula wt. NCO/%NCO.
Annealing	The process of heating and cooling metals and some plastics to reduce brittleness and/or improve strength.
Antioxidant	Compounding material used to retard deterioration caused by oxidation.
Antiozonant	Compounding material used to retard deterioration caused by ozone.
Aromatic	A class of organic compounds containing a resonant, unsaturated ring of carbon atoms. The benzine ring is the basic structure.
Bench marks	Marks of known separation applied to a specimen and used to measure strain.
Bloom	A discoloration or change in appearance of the surface of a polyurethane product caused by the migration of a liquid or solid to the surface.
Blowing	The process of foaming polyurethane.
Blowing agent	A substance incorporated in a mixture for the purpose of producing foam. Polyurethane foam can be produced using a physical blowing agent or a chemical blowing agent.
Bund	Low enclosure around tanks or drums to prevent escape of liquid.
Certificate of Analysis (C of A)	Documentation of analytical test results for a chemical or chemical system.
CAS number	A number assigned by the Chemical Abstract Service that is a unique identifier for each chemical.
Catalyst	A chemical that initiates or speeds up a chemical reaction.
Cell	A single small cavity surrounded partially or completely by walls.

(*Continued*)

Term	Description
Cell closed	A cell totally enclosed by its walls and not interconnecting with other cells.
Cell open	A cell not completely enclosed by its walls and interconnecting with other cells.
Chain extenders	Low-molecular-weight molecules that usually react with isocyanates. They form rigid, crystalline, hard segments in the polyurethane and lengthen the main urethane chain by end-to-end attachment.
Coefficient of friction	A material property of the contacting surfaces and/or of the contaminants and other films at their interface.
Coefficient of thermal expansion	The rate at which a material expands per degree of temperature.
Cold cure	Casting process for the production of elastomers, in which the elastomer is mixed, dispensed, and cured at or near room (ambient) temperature.
Compound	An intimate admixture of a polymer(s) with all the materials necessary for the finished article.
Compression set	A measure of permanent deformation remaining in an elastomer or flexible foam after a deforming force is removed. For most applications, a low degree of compression set is desirable.
Crazing	Fine cracks on surface of a material.
Creep	Compressive deformation occurring over time in both cured and uncured polyurethane, resulting from the application of a constant load or stress.
Cross-linking	Formation of chemical bonds or bridges between separate polymer chains, resulting in a three-dimensional polymer network.
Curative	Materials that react with an isocyanate prepolymer to produce the final elastomer.
Cycle time	The amount of time required to complete a molding cycle including mold preparation, insert loading (when applicable), release agent application, mixing and dispensing of components, reaction, and demolding.
Cyclone	A tapered piece of equipment to separate fine and coarse material by centrifugal spinning.
Degassing	Also known as deaeration or vacuuming—removing air from a liquid material.
Demold	The process of removing a specimen or cast from a mold.
Density	The mass per unit volume of a material.
Dew point	The temperature at which the water vapor present in the gas (e.g. air or nitrogen) saturates the gas and begins to condense.
Diamine	Organic compound containing two NH_2 groups.
Dielectric strength	The measure of polyurethane's ability as an insulating compound to resist the passage of a disruptive discharge produced by an electric potential.
Diisocyanate	A chemical compound, usually organic, containing two reactive isocyanate groups. Isocyanate groups consist of a nitrogen atom bonded to a carbon atom bonded to an oxygen atom, $-N{=}C{=}O$. It is often abbreviated as isocyanate or iso in the polyurethane industry.
Dike	Low enclosure around tanks or drums to prevent escape of liquid (bund).
Dumbbell	A flat sample having a narrow straight central portion of a uniform cross-section with elongated ends.

Term	Description
Durometer	An instrument for measuring the hardness of rubber and plastics.
Elastomer	A term often used for rubber and similar polymers.
Elongation (E@B %)	Extension produced by a tensile stress.
Elongation ultimate	The elongation at the time of break.
Endothermic	A chemical reaction that absorbs heat from the environment around it.
Epoxy	Synthetic resin compounds, usually thermosetting, which are capable of forming tightly cross-linked polymer structures characterized by toughness, strong adhesion, and high corrosion and chemical resistance. Used for making casts, coatings, and high-strength adhesives.
Exotherm	The liberation of heat during the course of a chemical reaction.
Filler	A solid compounding material, usually fine, which may be added to a polymer for technical or economic reasons.
Filler, inert	A filler having no reinforcing effect.
Flame retardant	An added substance that inhibits the initiation and/or spread of flame and/or amount of smoke generated during combustion.
Flammable limits	The concentration of flammable vapor in air, oxygen, or other oxidant that will propagate flame on contact when provided with a source of ignition. The lower explosive limit (LEL) is the concentration below which a flame will not propagate; the upper explosive limit (UEL) is the concentration above which a flame will not propagate. A change in temperature or pressure may vary the flammable limits.
Flash	The excess material protruding from the surface of a molded article at the mold junctions.
Flash point	The lowest temperature at which a flammable liquid will give off enough vapor at or near its surface to form an ignitable mixture with air.
Flexural modulus	The ratio, within the elastic limit, of the applied stress on a test specimen in flexure to the corresponding strain of the specimen.
Flexural strength	The maximum stress required to be applied to the center of a test specimen (a bar-shaped test specimen that is positioned on two supports, one either side of the load) required to crack or break the specimen.
Free isocyanate	A measure of the free, unreacted diisocyanate monomer present in an isocyanate prepolymer. Low free isocyanate prepolymers are desirable, as they contain very low levels of volatile isocyanate, making them inherently safer for the end user.
Gel time	For polyurethanes, the interval of time between mixing together the polyol and diisocyanate or prepolymer and curative and the formation of a nonflowing, semisolid, jelly-like system.
Glass transition temperature (Tg)	A reversible change that occurs when plastic is heated to a certain temperature range, characterized by a rather sudden transition from a hard, glassy, or brittle condition to a flexible or elastomeric condition.
Green strength	The rate of development of initial strength properties of polyurethane, soon after reaction completion. Rapid green strength development is desirable in molding operations, as it allows early removal of the molded part from the mold, decreasing molding cycle times and increasing productivity of the molding operation.

(*Continued*)

Term	Description
Hard segment	One of the two phases that make up polyurethane. The hard segment is made from isocyanates and chain extenders. The hard segment controls many of the polyurethane properties such as tensile, tear strength, hardness, compression set, abrasion/erosion resistance, and thermal stability.
Hardness	The resistance to indentation as measured under specified conditions.
Hazardous goods	A classification for chemicals that describes the Workplace Health & Safety issues associated with its handling by end users.
HDI	An abbreviation for hexamethylene diisocyanate.
Heat buildup	The temperature rise within an elastomer due to hysteresis. In many end-use applications, an elastomer can be subjected to repeated cycles of deformation–relaxation. As this occurs, friction between the elastomer molecules generates heat. As elastomers have relatively poor thermal conductivity, the heat generated builds up over time, progressively increasing the internal temperature of the elastomer. If the temperature increases above 70°C, the elastomer physical properties can begin to reduce. Design of the elastomer part can play an important role in minimizing the effects of heat buildup.
HMDI	An abbreviation for hydrogenated diphenylmethane-4,4′-diisocyanate.
Homogeneous	A term describing the uniform composition of a material. It can be used to describe complete and thorough mixing of polyurethane or uniform physical properties throughout a cured polyurethane.
Hot cure	Casting process for the production of high-performance elastomers in which the elastomer is mixed, dispensed, and cured at elevated temperature.
Hydrolysis	The effect experienced particularly by polyester-based polyurethanes, where prolonged contact with water or water-based liquids causes breakdown and failure of the polyurethane.
Hydrophilic	Water-soluble or water-attracting molecules or systems that strongly interact with water.
Hydroxyl group	The combined oxygen and hydrogen radical (-OH) that forms the reactive group in polyols.
Hydroxyl number	The number of mg of potassium hydroxide (KOH) equivalent to the hydroxyl content of 1.0 g of polyol.
Hygroscopic	A material that absorbs moisture readily.
Hysteresis	The ability of polyurethane to absorb and dissipate energy due to successive deformation and relaxation. A measurement of the area between the deformation and relaxation stress–strain curves.
Inert gas	A gas that exhibits great stability and extremely low reaction rates under normal temperature and pressure conditions, for example, nitrogen, argon, and helium. Nitrogen is commonly used in polyurethane processing.
IPDI	An abbreviation for isophorone diisocyanate.
Isocyanate	The name of the chemical group containing a nitrogen, carbon, and oxygen atom (-NCO).
Isocyanate decontaminant	A liquid material consisting of 90% water, 8% concentrated ammonia, and 2% detergent, used to neutralize isocyanate spills and decontaminate used isocyanate drums before disposal.

Term	Description
Knit line	A visible line seen in a molded polyurethane part that indicates where two flows of reacting polyurethanes have come together and joined. Often caused by flow turbulence, incorrect pour point placement, or poor polyurethane flow. Depending on the severity, the knit line can be a weak point in the molding that may cause future delamination, structural failure, or poor dimensional stability.
Master cast	A flawless cast that is set aside to take the place of the specimen, should it need to be molded in the future.
Master pattern	A flawless pattern similar in function to a master cast. The pattern preserves the detail of the mold, as well as the detail of the specimen. There is one master pattern for each side of a mold. Therefore, a two-part mold would have two master patterns.
MDI	An abbreviation for diphenylmethane-4,4′-diisocyanate.
MEK	Methyl Ethyl Ketone
MOCA (MBOCA)	Trade name for methylene bischloroaniline, which is a widely used curing agent for hot cure polyurethane elastomers. There are ongoing debates about health risks associated with its use, as it is a suspected carcinogen.
Modulus	The tensile stress at a given elongation.
Molecule	A group of atoms held together by chemical forces. Each type of molecule is composed of a specific arrangement of atoms. It is the smallest quantity of matter which can exist by itself and retain the properties of the original substance.
Monomer	The smallest repeating structure of a polymer. Usually a relatively simple compound containing carbon that can react with itself or with other molecules or compounds to form a polymer.
Mold	A manufactured cavity which preserves a negative impression of a specimen. The cavity can be filled with uncured polyurethane blends. Can be manufactured from a variety of materials depending on the production requirements, such as steel, aluminum, polyurethane, epoxy, FRP, silicone rubber, or latex. It can be manufactured in "one piece" or in multiple interlocking pieces. Multi-piece molds are used when the cast has a complex shape or undercuts which would make demolding from a one-piece mold difficult or impossible.
Mold release agent	A lubricant that prevents the casting from adhering to the mold.
Molding	The process of forming a material to a desired shape by flow induced by force after the material is placed in the heated mold cavity.
MSDS (Material Safety Data Sheet)	A document required by law to be supplied to a user of a hazardous product, to assist the user in safe use and handling of the hazardous product.
MW	Abbreviation for molecular weight. The sum of the atomic weights of all the atoms that constitute a molecule.
NCO	Nitrogen carbon oxygen (the isocyanate group)
NDI	The abbreviation for naphthalene diisocyanate.
Nonreactive	Does not react in the situation.
On cost	Non-capital or raw material cost associated with production.

(*Continued*)

Term	Description
Open pour	The process of filling a mold by pouring polyurethane directly onto the lower surface of an open mold.
Optimum cure	The state of cure at which a desired property value or combination of property values is obtained.
Orange-peel (alligator) skin	Term used to denote a typical surface texture caused by the settling of fillers from a batch during casting.
Overcure	The state of cure beyond the state of optimum cure.
Part line	The surface at which the various pieces of a mold come together when re-assembled. The part lines of a mold determine the flash lines of the casts produced from that mold.
Pigment	A powdered or liquid substance used in resins that imparts coloration to the cured item. Can be organic or inorganic.
Plasticizer	A compounding material used to enhance the deformability of a polymeric compound.
PLC	Programmable logic controller
Polycaprolactone	A polymer made by ring opening caprolactam.
Polyester polyol	A chemical building block. The polyester provides good solvent resistance and good mechanical properties in the final polyurethane.
Polyether	A chemical building block. The polyether provides good resilience, hydrolytic stability, mechanical properties, and cost advantages.
Polyisocynanurate	A polymer containing multiple isocyanate-to-isocyanate bonds.
Polymer	A material consisting of molecules characterized by the repetition of one or more types of chemical units (poly = many, mer from monomer, mono = one).
Polyol	An organic compound having more than one hydroxyl (-OH) group per molecule. The term includes monomeric and polymeric compounds containing hydroxyl groups such as polyethers, glycols, glycerol, and polyesters.
Polyurea	A polymer containing the urea group –NH-CO-NH-.
Polyurethane	A polymer containing the urethane group –NH-CO-O-.
Porosity	The presence of numerous small cavities.
Post cure	Heat treatment to which a cured or partially cured thermosetting plastic or rubber composition is subjected to enhance the level of one or more properties.
Pot life	The period of time during which a reacting thermoset plastic remains suitable for processing after mixing with a reaction-initiating agent.
PPDI	An abbreviation for paraphenylene diisocyanate.
PPG	Polypropylene glycol.
Prepolymer	The product from reacting a polyol with an isocyanate.
Processability	The relative ease with which a raw or compounded polymer can be handled.
Processing aid	A compounding material that improves the processability of a polymeric compound.
PTMEG	Polytetramethylene glycol.
PU (R)	An abbreviation for polyurethane.
Purging	Process of expelling an unwanted gas or vapor from a system through the introduction of a different gas or vapor until all traces of unwanted gas or vapor have been removed.

Term	Description
Recovery	The degree to which an elastomeric product returns to its normal dimensions after being distorted.
Registration	The active alignment of the various pieces of a mold by tabs or locator pins, so that no portion of the mold will stray from the position it was in when it was initially formed around a specimen.
Relative humidity	The ratio, expressed as a percentage, of the amount of moisture the air actually contains to the maximum amount it could contain at that temperature.
Release agent	A substance put on a mold surface or added to a molding compound to facilitate the removal of the molded product from the mold.
Resilience	The ratio of energy output to energy input in a rapid full recovery of a deformed specimen.
RIM	Abbreviation for reaction injection molding. The RIM process involves the rapid metering and mixing of polyurethane reaction ingredients, followed by their injection into a mold. It allows the rapid production of molded polyurethane components.
Sealants	A liquid, paste, coating, or tape that fills holes, joints, or gaps between mating surfaces, stopping leakage of gas, liquids, or solids.
Set	Strain remaining after the complete release of the force producing the deformation.
Shore hardness	The hardness of a material as determined by either the size of an indention made by an indenting tool under a fixed load or the load necessary to produce penetration of the indenter to a predetermined depth.
Shot	The accurate dispensing of a pre-calculated quantity of mixed polyurethane from a polyurethane-dispensing machine. The shot can be expressed in seconds or by weight of polyurethane dispensed.
Shrinkage	A measure of a material's reduction in size after setting or curing. Usually expressed as a dimensionless ratio of the amount of shrinkage over a unit length. Dimensionally stable materials have shrinkages very close, or equal, to 0.
Silicone rubber	A two-component synthetic rubber capable of curing at room temperature by chemical means into a solid elastomer. Commonly used as a mold-making compound where a soft, pliable mold is required. Silicone rubbers offer advantages of very low hardness, high flexibility, and self-releasing properties but have the disadvantages of high cost, high viscosity, and low strength, which limit their application and longevity.
Soft segments	One of the two phases which make up polyurethane. The soft segment is composed of long-chain polyether or polyester polyols. The soft segment controls many of the polyurethane properties such as tensile and tear strength, hydrolysis and chemical resistance, glass transition temperature, and flexibility.
Sprue	The opening, or hole, through which the casting medium is poured into some molds and from which the excess is allowed to escape.
Strain	The unit of change, due to force, in the size or shape of a body referred to its original size or shape (e.g., elongation).

(*Continued*)

Term	Description
Stress	The intensity, at a point in the body, of the internal forces that act on a given plane through the point. (This is expressed as a force per unit area, e.g., pounds per square inch or MPa.)
Striations	Lines of different color or intensity that are evident both in the unpigmented and pigmented polyurethane mixtures.
Swelling	The increase in volume of a specimen immersed in a liquid or exposed to a vapour.
Taber wear index	The ability of a material to withstand mechanical action such as rubbing, scraping, or abrasion that tends to progressively remove material from its surface. Usually expressed in milligrams loss per number of cycles per a given load.
Tan delta(δ)	The viscous modulus/elastic modulus.
TDI	An abbreviation for toluene diisocyanate.
Tear strength	The maximum force required to tear a specified specimen, the force acting mainly parallel to the major axis of the test specimen.
Tensile modulus	The ratio of stress to corresponding strain below the proportional limit of the material. Normally expressed in MPa (megapascals).
Tensile strength	The maximum tensile stress applied during stretching a sample to break.
Thermoplastic	A resin or plastic compound that can be repeatedly softened by heating and hardened by cooling. Examples of thermoplastics are: acetal, acrylic, chlorinated polyether, fluorocarbons, polyamides (nylons), polycarbonate, polyethylene, polypropylene, polystyrene, some types of polyurethanes, and vinyl resins.
Thermoset	A resin or plastic compound that in its final state is substantially infusible and insoluble. It cannot be repeatedly softened by heating and hardened by cooling. Examples of thermosets are: epoxy, phenol-formaldehyde, some types of polyester, some types of polyurethane, and urea-formaldehyde resins.
Thixotropy	A flow characteristic of certain fluids where a decrease in viscosity of the fluid occurs when it is stirred at a constant or increasing rate of shear. When the stirring or shearing is discontinued, the apparent viscosity of the fluid gradually increases back to the original value. Changes in both directions are dependent on time as well as shear.
Toxic	A substance that has the ability to produce injurious or lethal effects through its chemical interaction with the body.
TMXDI	An abbreviation for meta-tetramethylxylene diisocyanate.
TPU	Thermoplastic polyurethane.
Triol	A polyol containing three reactive hydroxyl groups.
Trowelable	Capable of being applied using a trowel and having thixotropic proprieties.
Turbulence	Used to describe an erratic, tumbling flow of liquid elastomer through a mold or cavity during filling. Usually caused by poor mold design, incorrect location of the polyurethane pouring point, obstructions in the mold or cavity, or high polyurethane viscosity.
UHMWPE	Ultra high molecular weight polyethylene.
Undercure	The state of cure between the onset of curing and the state of optimum cure.
Undercut	A part of a mold, cast, or specimen which deviates from a sloping or vertical surface and turns back onto itself.
Urethane	The chemical group –NH-C=O-O-.

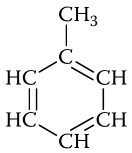
Term	Description
UV stabilizers	Additives incorporated into a polymer that prevent or slow the degradation of the polymers caused by exposure to light.
Venting	The displacement of air from the mold cavity as the cavity is filled by polyurethane. Venting normally occurs through small holes or seams in the mold located at strategic positions around the mold to ensure that all air is vented. When the mold is completely air free and polyurethane filled, a small amount of polyurethane also vents, further ensuring a complete air-free filling of the mold.
Viscosity	The resistance of a material to flow under stress.
Water absorption	The amount of water absorbed by a material under specified conditions.
Weathering	The surface deterioration of a rubber article during outdoor exposure.
Wetting	The process by which a liquid spreads over a solid surface.
Young's modulus	The modulus where stress/strain is both a ratio and is constant. (This is only at very low elongations in elastomers.)

Appendix 5

Calculations

Molecular Weight

The mole (mol) is the fundamental unit describing the amount of a chemical species. The weight of a mole of a substance is its gram formula weight (fw), which is the summation of the atomic weight in grams for all the atoms in the chemical formula of the species (Skoog and West, 1982).



Molecular Formula = C_7H_8
Formula Weight = 92.14
Nominal Mass = 92

Equivalent Weight

The equivalent weight is based on the behavior of the substance in any particular reaction. The equivalent weight of a substance is the result of the formula weight (molecular weight) divided by the number of reactive sites in it taking part in the reaction.

The equivalent weight of a diol with a molecular weight of 1500 will be 1500/2 = 750.

If it is a triol with three reactive sites, the equivalent weight will be 1500/3 = 500.

Specification sheets will often give the equivalent weight of the polyol in terms of the hydroxyl number ("OH" value). The hydroxyl number is defined as "the number of milligrams of potassium hydroxide (KOH) equivalent to the hydroxyl content of 1.0 grams of polyol." Manipulation of this definition gives the follow equation:

Equivalent weight of any polyol = (56.1)(1000)/OH number
where 56.1 g = equivalent weight of KOH
1000 = mg/1.00g

If the "OH" value of a polyol is given as 28.05, the equivalent value will be

$$EW = ((56.1)(1000))/28.05 = 2000$$

If the molecular weight is known to be 4000, the number of functionality or reactive sites will be

$$\text{Functionality} = \text{molecular weight/equivalent weight} = 4000/2000 = 2$$

Equivalent Weight of Blends of Polyols or Curatives

If a blend of items is used, the equivalent weight of each item must be taken into account when calculating the final value.

$$\text{Equivalent wt of blend} = \frac{\text{Weight of A} + \text{Weight of B}}{\dfrac{\text{Weight of A}}{\text{EW of A}} + \dfrac{\text{Weight of B}}{\text{EW of B}}}$$

Weight Calculations

There are two main methods to calculate the weight of the polyol and diisocyanate to use in a reaction:

- Molecular ratios
- To fixed NCO level

Molecular Ratios

In this method, the number of gram moles of each item is taken into account when making the first approximation of the weight ratios.

For example, if two moles of TDI were to be reacted with one mole of 1000 MW PPG:

	TDI	+	PPG	+	TDI
Ratio	1		1		1
EW	87.1	+	500	+	87.1

$$\begin{aligned}\text{Total gram EW} &= 87.1 + 500 + 87.1\\ &= 174.2 + 500\\ &= 674.2\end{aligned}$$

If it is desired to make 2.5 kg of the prepolymer, the following portions would have to be reacted together:

Weight mixture in grams = 2.5 × 1000 = 2500
TDI = (174.2/674.2) × 2500 = 646 grams
PPG = (500/674.2) × 2500 = 1854 grams

It must be remembered that these are theoretical calculations, and final results may be different due to raw material purities, transferring efficiencies, and the degree of conversion.

Fixed NCO Levels

To produce a prepolymer with 0% free isocyanate (NCO), one equivalent of the polyol with one equivalent of the isocyanate must be reacted together.

From first principles:

$$\%\ \text{NCO of prepolymer} = \frac{\text{wt of terminal NCO} \times 100}{\text{Total wt}}$$

The equivalent weight of NCO = 14 + 12 + 16 = 42 (more exactly, 42.02)

$$\text{The}\ \%\ \text{NCO in an isocyanate} = \frac{42 \times 100}{\text{Equivalent wt isocyanate}}$$

$$\text{EW TDI} = 87 \qquad \%\ \text{NCO (Z)} = 42/87 = 48.3$$

$$\text{EW MDI} = 125 \qquad \%\ \text{NCO (Z)} = 42/125 = 33.6$$

If a 500-MW diol is used,	D = 500 g EW
and pure MDI is used	I = 125 g EW
total g EW	T = 625 g EW

If a final NCO (N) level of 20 % is desired, Y g EW of the isocyanate must be added.

$$\frac{Z \times Y}{T + Y} = N \qquad \frac{33.6 \times Y}{625 + Y} = 20$$

$$Z \times Y = N(T + Y) \qquad 33.6Y = 20\ (625) + 20Y$$

$$Z \times Y - Y \times N = NT \qquad 13.6Y = 12500$$

$$Y = 12500/13.6 = 919$$

The total MDI = 125 + 919 g = 1044 g
The total polyol = 500 g

These calculations provide a starting point. Final adjustments need to be made depending on raw material and processing conditions.

Acid Levels

To prevent gelation and side reactions, it is normally recommended that the reaction be kept very slightly acid. The level is 0.33 microequivalents per gram of prepolymer. The acidity of the diisocyanates is normally specified in terms of parts per million of isocyanate acid in the diisocyanate. To convert to microequivalents:

$$\text{Isocyanate acid} = \frac{\text{specified ppm} \times \text{wt diisocyanate (in grams)}}{\text{Equivalent g EW of hydrochloric acid}}$$

$$\text{EW HCl} = 36.5$$

The acidity may also be expressed as a percentage. The calculation would have to be adjusted.

$$\text{ppm} = \frac{X\% \times 10^6}{10^2} \quad 0.004\%\text{HCl} = 0.004 \times 10^4 = 40 \text{ ppm}$$

$$\text{Polyol base level (mg KOH/g)} = \frac{(\text{mg KOH/g}) \times 10^6 \text{ ppm}}{1000}$$

$$\text{Polyol base level} = \frac{\text{ppm base} \times \text{wt polyol (in grams)}}{\text{Equivalent g EW of KOH}}$$

$$\text{EW KOH} = 56.1$$

Using the previous example for 20% total NCO:

MDI	Weight = 1044g	Acidity 5ppm as HCL
Diol 500 EW	Weight = 500g	Acid value 0.0015 mg KOH/g

$$\text{Acidity of MDI} = \frac{5 \times 1044}{36.5} = 143.0 \text{ microequivalents of acid}$$

$$\text{Polyol base level ppm} = \frac{0.015 \times 10^6}{1000} = 15 \text{ ppm}$$

$$\text{Polyol base level} = \frac{15 \times 500}{56.1} = 133.7 \text{ microequivalents of base}$$

To have the desired level of 33 microequivalents/g, there must be 0.33 × 1544 = 510 micro equivalent of acid. Without any additions, there will be a very slight excess of acid but less than the desired level of 0.33 per gram. Therefore, more acid must be added, using benzoyl chloride (EW 140.6) as the acid.

$$(510-(143-134) \times 140.6)/1000 = 70.4 \text{ mg benzoyl chloride}$$

needs to be added. If 86% strong phosphoric acid (EW 98) is used instead, the formula must be adjusted.

Reference

Skoog, D.A, and D.M West. *Fundamentals of Analytical Chemistry*. 4th ed: Saunders College Publishing, 1982.

Appendix 6

Isocyanate Calculation

Determination of % NCO in Prepolymer

The method for the determination of the isocyanate level is based on that given by Wright and Cummins (1969).

The NCO content of diisocyanates can be determined by the reaction with an excess of a standard solution of dibutylamine in chlorobenzene (or dry toluene) and titration of the excess with hydrochloric acid. The dibutylamine is prepared by dissolving 129 g of freshly distilled dibutylamine in 871 g of redistilled chlorobenzene and storing the resultant solution in the dark. The solution is relatively stable, but it is advisable to determine the amine content weekly by titration with 1 N hydrochloric acid in methanol.

In the determination, 2 g of the diisocyanate should be accurately weighed out into a conical flask and 5 ml of chlorobenzene added. In the case of naphthalene diisocyanate, it is recommended that the mixture be warmed slightly to assist dissolution. To this mixture there is then added 25 ml of the standard dibutylamine solution. The reaction is rapid and takes only a few minutes for completion, when a clear solution is obtained. After adding 2 or 3 drops of a 1% alcoholic solution of bromophenol blue and 100 ml of methanol, the excess dibutylamine can be titrated with 1 N hydrochloric acid.

If W = weight of sample in grams
V_1 = volume in ml of HCl solution required for titration of the sample
V_2 = volume in ml of HCl solution required for 25 ml of dibutylamine solution (blank)

$$\%\text{NCO} = 4.20 \times \text{N} \times \frac{V_2 - V_1}{1000\,\text{W}} \times 100$$

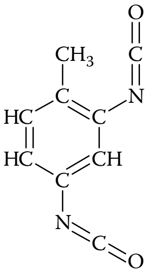
Reference

Wright, P., and A.P.C. Cummins. *Solid Polyurethane Elastomers.* 1st ed. London: MacClaren and Sons, 1969.

Appendix 7

Chemical Structures

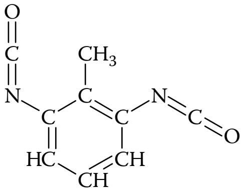
A7-1 Aromatic Isocyanates



2,4 TDI

Formula Weight = 174.2

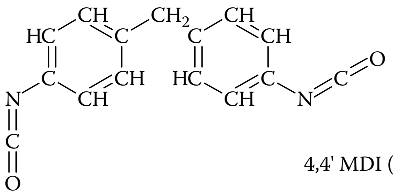
2,4-diisocyanato-1-methylbenzene



2,6 TDI

Formula Weight = 174.2

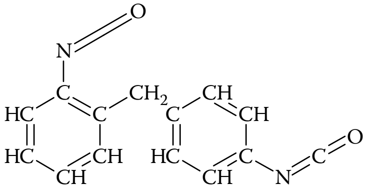
1,3-diisocyanato-2-methylbenzene



Formula Weight = 250.3

1,1'-methylenebis(4-isocyanatobenzene)

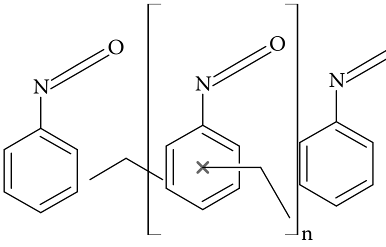
4,4' MDI (MDI)



Formula Weight = 250.3

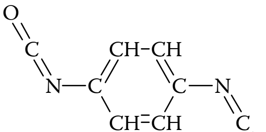
1-isocyanato-2-(4-isocyanatobenzyl)benzene

2,4' MDI



Polymeric methylene diisocyanate

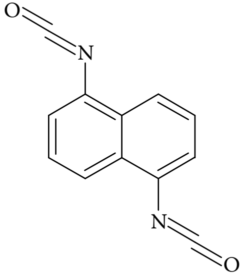
PMDI



Formula Weight = 160.1

1,4-diisocyanatobenzene

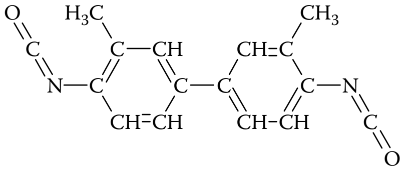
PDI



Formula Weight = 210.2

1,5-diisocyanatonaphthalene

NDI



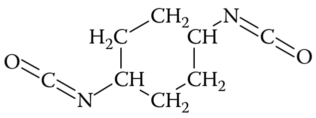
Formula Weight = 264.28

4,4'-diisocyanato-3,3'-dimethylbiphenyl

TODI

FIGURE A7.1
(*Continued*)

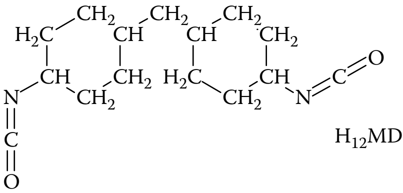
A7-2 ***Aliphatic Isocyanates***



CHDI

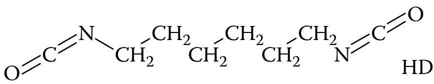
Formula Weight = 166.2

1,4-diisocyanatocyclohexane



Formula Weight = 262.3

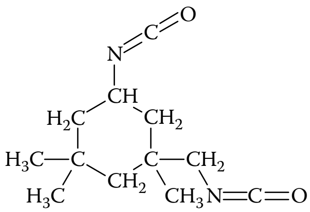
H_{12}MDI 1,1'-methylenebis(4-isocyanatocyclohexane)



HDI

Formula Weight = 168.2

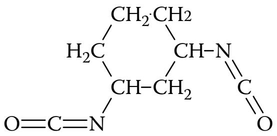
1,6-diisocyanatohexane



IPDI

Formula Weight = 222.3

5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane

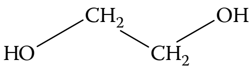


H_6XDI

Formula Weight = 166.2

1,3-diisocyanatocyclohexane

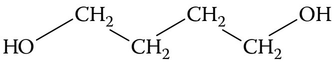
A7-3 Hydroxyl Curatives



ethylene glycol

Formula Weight = 62.1

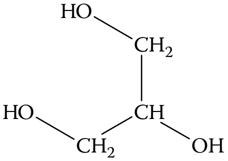
ethylene glycol



1,4 Butane Diol

Formula Weight = 90.121

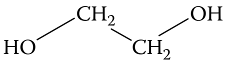
butane-1,4-diol



Glycerine

Formula Weight = 90.1

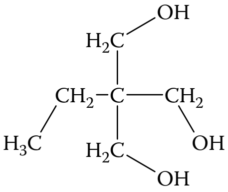
glycerol



ethylene glycol

Formula Weight = 62.1

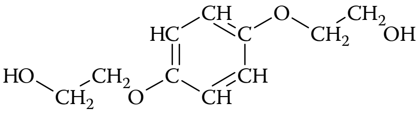
ethylene glycol



TMP

Formula Weight = 134.2

2-ethyl-2-(hydroxymethyl)propane-1,3-diol

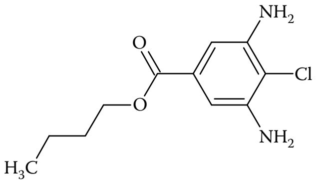


HQEE

Formula Weight = 198.2

2,2'-[1,4-phenylenebis(oxy)]diethanol

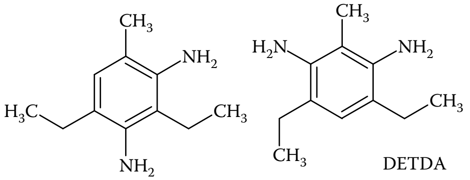
A7-4 Amine Curatives



Baytec 1604

Formula Weight = 242.7

butyl 3,5-diamino-4-chlorobenzoate

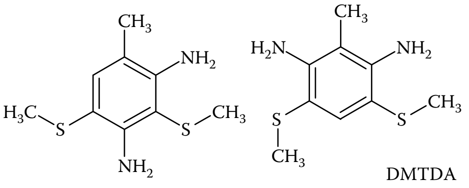


DETDA

(Ethacure 100)

Formula Weight = 178.3

2,4-diethyl-6-methylbenzene-1,3-diamine
4,6-diethyl-2-methylbenzene-1,3-diamine



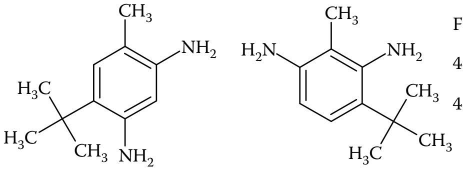
DMTDA

(Ethacure 300)

Formula Weight = 214.4

4-methyl-2,6-bis(methylthio)benzene-1,3-diamine

2-methyl-4,6-bis(methylthio)benzene-1,3-diamine

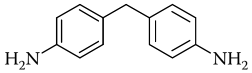


t-BTDA

Formula Weight = 178.8

4-*tert*-butyl-6-methylbenzene-1,3-diamine

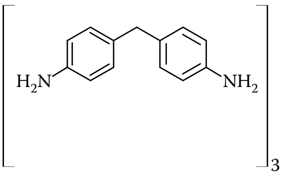
4-*tert*-butyl-2-methylbenzene-1,3-diamine



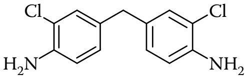
Formula Weight = 198.3

1,1'-methylenebis(4-isocyanatobenzene)

MDA



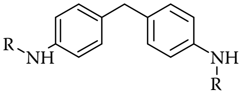
Caytur 21



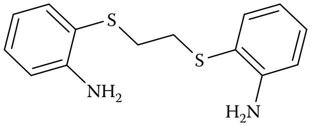
Formula Weight = 267.2

1,1'-methylenebis(3-chloro-4-isocyanatobenzene)

MOCA



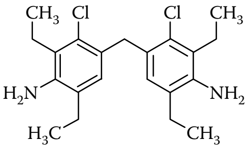
Unilink 4200



Formula Weight = 276.4

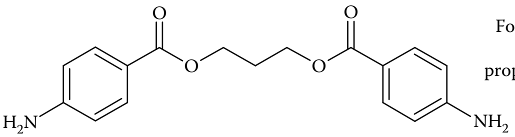
2,2'-[ethane-1,2-diylbis(thio)]dianiline

Cyanacure



Formula Weight = 379.36642

MCEDA



Formula Weight = 314.3

propane-1,3-diyl bis(4-aminobenzoate)

Polacure 740M

FIGURE A7.4
(*Continued*)

Appendix 8

Applications

Typical Applications

Industry	Application	Comments
Automotive	Bearings	
Automotive	Flexible couplings	
Automotive	Grommets	
Automotive	Suspension bushes	
Building and Construction	Concrete panel molds	
Building and Construction	Gate seals	
Building and Construction	Lift centralizing wheels	
Building and Construction	Paver molds	
Chemical processing	Hydrocyclones	
Domestic	Automatic gate wheels	Very hard—good compression set
Domestic	Bowling balls	
Domestic	Golf ball cleaners	
Domestic	In-line roller wheels	
Domestic	Roller skate wheels	High-resilience MDI ether
Electrical	Antistatic pads	
Electrical	Potting	
Engineering	"O" rings	
Engineering	Flange seals	
Engineering	Gear wheels	
Engineering	Hydraulic forming diaphragms	
Engineering	Lip seals	
Engineering	Location fixtures	
Engineering	Press brake pads	
Engineering	Shock absorption pads	
Engineering	Stripper plates	
Engineering	Vibration absorption pads	
Engineering	Wiper blades	
Food	Food conveyor systems	FDA wet food contact—MDI ester
Food	Grain handling equipment	FDA approval, abrasion resistance MDI ester
Food	Meat processing equipment	FDA wet food contact MDI ester
Industrial	Cable guides	
Industrial	Flattening rollers	
Industrial	Fork-lift tires	Low heat buildup TDI ether
Industrial	Hammers	Tear resistance, low resilience TDI ester
Industrial	Log pushers	

(*Continued*)

Typical Applications

Industry	**Application**	**Comments**
Industrial	Printing rolls	Solvent resistance at low Durometer TDI ester
Industrial	Sand blast curtains	High resilience—impingement abrasion MDI ether resistance
Industrial	Wheels and castors	
Mining	Bucket liners	
Mining	Chute linings	
Mining	Conveyer heads	
Mining	Crossover pads	
Mining	Cyclone spigots	
Mining	Cyclones	
Mining	Filter press parts	
Mining	Flotation cell liners	
Mining	Flow control valves	
Mining	Grading screens	High abrasion resistance
Mining	Idler wheels	
Mining	Launder equipment	Hydrolysis resistance MDI ether
Mining	Pipe linings	
Mining	Pump impellers	
Mining	Pump liners	
Mining	Pump throat and back plates	
Mining	Scraper knives	
Oil	Oil pipeline pig	Oil abrasion resistance TDI ester
Paper Mills	Rolls	Hydrolysis resistance, hardness stability TDI ether
Pipelines	Cleaning pigs	
Pipelines	Sealing rings	

Index

Materials Science

CASTABLE POLYURETHANE ELASTOMERS

I.R. CLEMITSON

Currently, raw material suppliers are the sole providers of polyurethane processing information. In most cases, they give instruction only on how to mix products and do not always include an explanation of the accompanying logic as to why these recommendations are being made.

Castable Polyurethane Elastomers explains the production process of polyurethane components from both the theoretical and practical points of view. It describes the underlying concepts for the raw material supplier recommendations and explains how to achieve application-specific properties in polyurethane. The book explains the production of prepolymers with special focus on health and safety issues. It presents the different types of methods available on both the micro and macro levels and explains the rationale behind choosing the system needed to create a cost-effective, application-specific product.

Offering an inside look at the logic behind the formation of polyurethane components, ***Castable Polyurethane Elastomers*** enables material scientists, engineers, and chemists to understand the total production process and reproduce the procedures to achieve desired results.

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6000 Broken Sound Parkway, NW
Suite 300, Boca Raton, FL 33487
270 Madison Avenue
New York, NY 10016
2 Park Square, Milton Park
Abingdon, Oxon OX14 4RN, UK