Rubber Technologist's Handbook

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RAPRA
TECHNOLOGY LTD.

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First Published 2001 by

Rapra Technology Limited

Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK

A catalogue record for this book is available from the British Library.

ISBN: 1-85957-262-6

Typeset by Rapra Technology Limited
Printed and bound by Polestar Scientifica, Exeter, UK

Preface

From a materials point of view a rubber product is made from rubber and a host of other additives, including fillers, vulcanising agents and processing aids along with reinforcing materials such as textiles. From a manufacturing point of view, a rubber product is made by following several steps: mixing of additives with the rubber ('compounding') when the rubber is unvulcanised and in the plastic state; shaping the rubber compound and/or bonding it to a substrate; and finally vulcanising or curing the whole assembly, when chemical crosslinks are formed between the rubber molecules to give the material its 'elastic' recovery behaviour. The final properties of a rubber product depend on the type of rubber chosen and the additives used and their concentrations. The properties of the rubber can be further manipulated by varying the processing steps or manufacturing operations. The cost of a rubber product depends not only on the price of the raw materials but also on the efficiency of the processing operations. In the last few decades new materials have emerged and manufacturing has become increasingly automated and more efficient. This handbook aims to provide a basic foundation in rubber technology and to collate the most recent developments in the form of chapters, written by experts in their respective fields. The handbook is intended to serve the needs of those who are already in the rubber industry and of new entrants who aspire to build a career in rubber and allied areas. Materials Science students and researchers, designers and engineers should all find the handbook very helpful.

Fourteen chapters deal with natural rubber, synthetic rubbers, thermoplastic elastomers, fillers, compounding additives, mixing, engineering design, testing, tyre technology, automotive applications, footwear, rubbers in construction, durability of rubber products, and rubber recycling. It is obvious that several important topics could not be accommodated in the current volume and it is intended that a second volume of the handbook will be published by RAPRA Technology Ltd in the near future to extend the coverage. We gratefully acknowledge the cooperation from all of the contributors, without whom this handbook would not have been a reality. We are especially grateful to the commissioning editor, Ms Frances Powers, for her unique combination of professionalism and good humour: her prompt and pointed responses to all of our requests for assistance were invaluable. We wish to commend all of the staff at RAPRA Technology Ltd who contributed to the excellent production of the handbook, especially Claire Griffiths and Sandra Hall.

On a personal note, one of us (JRW) is grateful for being granted leave of absence from the University of Newcastle upon Tyne for a visit to the Rubber Technology Centre at the Indian Institute of Technology, Kharagpur in January 2001 during a critical stage of the preparation of the handbook. Although the purpose of the visit was to conduct research and teaching in the most stimulating surroundings of the RTC, time was found for the two editors to renew their friendship, tie up the loose ends of the handbook, and to lay plans for Volume 2. Finally we are extremely thankful to our wives, Prajna and Li Tong, for their patience and support during the preparation of the handbook.

S K De and J R White
August 2001

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1

Introduction

1.1 Brief historical review

Natural rubber obtained from trees was the only source of rubber until the advent of the synthetic polymers in the early part of the twentieth century. When Europeans first landed in South America, they observed the local people playing with a crude bouncing ball made by drying a material that oozed out of certain trees when their bark was cut. Locally it was known as ‘Cachuc’, meaning ‘weeping wood’, from which are derived the Spanish ‘Caucho’, French ‘Cauotchouc’ and German ‘Kautschuk’. The elasticity and waterproofing ability of the material attracted attention of the scientists in Europe. The English scientist Joseph Priestley coined the word ‘Rubber’, because the material could rub out pencil marks. In the early days, rubber products behaved like thermoplastics, which became hard in winter and soft and sticky in summer.

In 1839 Charles Goodyear in the USA, discovered that when rubber was heated with sulphur it became stronger and more elastic, but more importantly it was no longer susceptible to changes in temperature. At about the same time, Thomas Hancock in the United Kingdom made the same discovery independently. The process became known as vulcanisation (from ‘Vulcan’, the God of Fire). Hancock is also recognised as the pioneer in designing rubber processing machinery. He masticated rubber on two-roll mills, whereupon it became soft and tacky, and articles could be built up from multiple pieces of the masticated rubber.

Organic chemists made great strides in this period and it was found that isoprene (C_5H_8) could be obtained by cracking natural rubber, but attempts to duplicate rubber synthetically did not succeed. The pneumatic tyre was patented by John Dunlop in England in 1888. Up to 1890, the production of rubber was low and its cost was high. The only source of rubber then was the remote jungles of South America. In 1870 Sir Henry Wickham collected seedlings of *Hevea brasiliensis* from Brazil. He germinated them at Kew Gardens in London and then started planting them in Ceylon (Sri Lanka), Malay (Malaysia) and Indo-China (Vietnam). By 1920 these countries produced 90 per cent of the world’s supply of rubber. Soon other countries in the region, including the Philippines, Indonesia, Thailand and India became rubber producers. Over the years, production of natural rubber in Latin America became insignificant but the rubber industry continued to grow with the development of rubber plantations in Asia.

Synthetic rubbers were first produced in Germany in the 1930s. During the Second World War, interruption of the supply of natural rubber prompted the United States industry to take on the challenge of developing methods for bulk production of synthetic rubbers. The United States production of GR-S (Government Rubber Styrene also known as the general purpose styrene-butadiene rubber, SBR, used for tyres) was over 700,000 tonnes in 1945. In 1946 the world production of synthetic rubber had grown to over 900,000 tonnes in comparison to 555,000 tonnes of natural rubber. The present market share of synthetic rubbers is about 55% out of a grand total of about 15,000,000 tonnes of both natural rubber and synthetic rubbers.

Sulphur has been the principal vulcanising agent since its use by Charles Goodyear and Thomas Hancock, though the development of a variety of synthetic rubbers of varying chemical structures has led to the development of other types of vulcanising agents. The rate of vulcanisation with sulphur alone was very slow. George Oenslager discovered organic accelerators, which could speed up the vulcanisation process and improve the elastic properties of the rubber as well. Whereas the first generation tyres, in the 1910s, was reinforced by zinc oxide, the first use of carbon black in tyre treads was reported in 1912 and this led to a great improvement in tyre service life. Durable, high strength rubber articles can be made with judicious choice of fillers, vulcanising agents, accelerators and other additives.

Over the years, the importance of rubber to modern life has constantly increased. This is not always immediately apparent because the articles are often not colourful and eye-catching. For the most part, rubber components are used as components in cars or appliances in locations where they are not easily visible. Without rubber, the automobile as well as many other appliances and aids to everyday life such as footwear, foams, belting, seals, hoses, wires and cables, sporting goods and waterproof fabrics would not exist in the forms that are familiar to us today.

Although the rubber industry is now about 200 years old, research and developmental work still continue, with objectives that are constantly under revision, to meet current and projected needs. Existing rubbers are being modified, new rubbers are being discovered, new processing methods are being developed, new additives are being adopted, novel products are being engineered, existing products are being made more durable, and techniques for recycling and reusing waste rubber and worn out articles are beginning to meet environmental and commercial targets.

Finally, it is worth noting the importance of the body of knowledge that was built up among the scientists and technologists working on rubber prior to the advent of the spectacular expansion of the use of synthetic plastics and the corresponding interest in polymer science and technology after the Second World War. Apart from the immediate applicability of the results and techniques from rubber technology to the synthetic rubbers, an understanding of the behaviour of many other synthetic polymers has developed from seminal studies of rubbers. One example is the oxidation of polymers, which is a topic that attracted much attention in the 1990s [1, 2] and which used as its foundation the *basic auto-oxidation scheme* that was developed and refined by rubber scientists in the 1940s [3, 4].

1.2 The uniqueness of rubber

In most applications for rubber products there are no alternative materials except other rubbers. It has very high deformability. It consists of very high molecular mass molecules that can be crosslinked together to form a network. If the crosslink density is not too high the material will retain a memory of its original unstressed state and will return to its original dimensions when external forces are removed even after strains as high as 1000%. This ability to recover its original dimensions leads to many applications.

The mechanical properties of rubbers derive from the molecular chains that are assembled into a crosslinked network. When unstressed, the molecular segments between crosslinks are randomly coiled. When a tensile stress is applied, deformation is principally achieved by localised motions of the molecular segments that take on new shapes, in which they are stretched out in the direction of the tensile axis. Although the deformation process, involving countless random molecular segments, might appear to be difficult to model when compared to a metal crystal with a very well-ordered structure, the very elegant *theory of rubber elasticity,* gives a very good description of the behaviour [5]. It is based on a statistical description of the molecular states, and its relationship with the change in entropy on deformation. Some of the results of the theory of rubber elasticity find application in the wider context of synthetic polymers and, possibly more importantly, the way of thinking about the deformation behaviour of polymers often finds inspiration from the early rubber literature. In a similar way, the fracture of rubbers is quite different to non-polymeric materials and required novel methods of treatment that later found application to synthetic polymers.

Rubbers are usually formulated with a complex mixture of additives. These are included (i) to promote and control the crosslinking process; (ii) to impart beneficial mechanical properties; and (iii) to inhibit degradation caused by the working environment (including ultraviolet (UV) irradiation and vapour phase and liquid contaminants). Carbon black is a common additive and usually provides multiple benefits. The inclusion of carbon black causes an increase in stiffness and strength and provides abrasion resistance (which is especially useful in tyres); and it reduces UV degradation. This has permitted the development of a huge family of materials with a wide range of properties.

The uniqueness of rubbers extends not only to the end-use properties but also to the processing properties. This has resulted in the evolution of a collection of specialised mixing and processing methods.

1.3 Survey of the current Handbook

This volume addresses the basic chemistry of natural and synthetic rubbers; the physics and chemistry of their interactions with additives to improve processing and end-use properties; the mixing processes for the incorporation of additives; testing of rubbery materials for processability and end-use properties; design of engineering products; applications in a wide range of products; and techniques and strategies for recycling.

Chapters 2-4 deal with the production of the main classes of rubbers. In Chapter 2, Mathew deals with production of natural rubber and its modification. About 55% of all natural rubber produced is used in automotive tyres, for which its high resilience and excellent dynamic properties make it an ideal material. Major non-tyre applications include beltings, hoses, footwear, engineering products, latex products such as dipped goods, carpet backing and adhesives. Thermoplastic natural rubber (TPNR) is prepared by blending natural rubber with polyolefins such as polypropylene or polyethylene, so that the plastic phase is continuous. The elastic properties of TPNR can be considerably improved if the rubber phase is partially crosslinked during blending, a process called dynamic vulcanisation. Natural rubber can be blended with other rubbers to yield new materials or it can be chemically modified to make it more versatile.

Sudhin Datta discusses the developments of industrially important synthetic rubbers in Chapter 3, with special emphasis on synthesis and structure-property relations. The material sub-groups dealt with include diene elastomers, including polybutadiene, polyisoprene and SBR; saturated elastomers, including ethylene-propylene copolymers (EPM) and ethylene propylene diene terpolymers (EPDM), butyl and halobutyl rubbers, and ethylene-acrylic rubbers; solvent resistant rubbers including nitrile rubber and hydrogenated nitrile rubber, polychloroprene, acrylic elastomers and chlorosulphonated polyethylene; and temperature resistant elastomers including silicone rubber and fluorocarbon rubbers. Examples of other specialty elastomers are phosphazenes, polyethers and polyurethanes.

Thermoplastic elastomers (TPE) are a group of new materials, developed in the later part of the last century, which can be processed like thermoplastics but behave like vulcanised rubbers, without being vulcanised. Antony and De describe this novel family of materials in Chapter 4. There are three major classes of thermoplastic elastomers, namely, block copolymers; dynamically vulcanised rubber/plastic blends; and ionic thermoplastic elastomers. The phase structure of a TPE consists of hard glassy domains and soft rubbery segments, which must be thermodynamically incompatible with each other. The ratio of the soft and hard segments determines the hardness and elastic behaviour. Like thermoplastics, TPE are reprocessable. In contrast to conventional thermoset rubbers, there is little or no compounding required for TPE. Whereas the scrap generated in thermoset rubber processing requires special recycling methods, the scrap produced in the TPE process can be reprocessed directly. Furthermore, thermoplastic processing consumes less total energy than that required with conventional rubbers due to more efficient processing and shorter cycle times. Limitations of TPE include deformation during high temperature exposure and high set.

Without fillers, hardly any durable and useful rubber articles would exist. Development of new fillers, surface modification of existing fillers and understanding filler morphology and surface physics are as important as development of new polymers. Mouri has dealt with both carbon black and non-black fillers in Chapter 5. Since carbon black has become the most important filler in the rubber industry, the major emphasis has been given to carbon black in regard to particle structure and its influence on physical properties when added to rubber. Silica, calcium carbonate and clay are the next most popular fillers. The rubber compounder must select the right type of filler and its optimum loading to arrive at the best balance in compound quality. Carbon black is used as a reinforcing filler in a variety of rubber products including consumer products such as automobile tyres, footwear and shock absorbers, and industrial applications such as conveyor belts, dock fenders and roofing materials. The application of non-black fillers, especially the use of precipitated silica in passenger tyre treads, is growing.

Although the processing and final properties of rubber articles are highly dependent on the base polymer, the properties can be extensively manipulated by appropriate choice of compounding ingredients such as vulcanising agents, vulcanisation accelerators, activators and retarders, antireversion agents, and plasticisers. In Chapter 6, Rabin Datta and Ingham deal with the present status, recent developments, and the expected future developments of these additives. Developments are often driven by health concerns that may force the abandonment of a chemical, following new medical discoveries. For example, due to its suspected carcinogenic nature, there is growing concern in regard to presence of *N*-nitrosoamine in rubber articles. It is believed that accelerators containing secondary amines produce *N*-nitrosoamine. The alternatives that provide equivalent cure characteristics whilst safe with regard to carcinogenic nitrosoamine formation are *N*-*tert*.butyl-2-benzothiazole sulphenamide (TBSI), tetra benzyl thiuram disulphide (TBzTD) and dithiodicaprolactam (CLD). *N*-1,3-Dimethyl butyl-N′-phenyl-*p*-quinone diimine (QDI) is an example of recently commercialised bound antioxidant. Here the antioxidant becomes attached to the rubber chain during vulcanisation thus preventing its extraction during service and providing long-term protection. QDI functions also as a peptiser, a vulcanisation retarder and an agent to increase polymer-filler interaction. The most recently introduced antireversion agent is 1,3-bis(citraconimidomethyl) benzene also known as Perkalink 900. It compensates for the loss of polysulphidic crosslinks during the process of reversion with crosslinks based essentially on a carbon-carbon structure.

Once the choice of base polymer and compounding additives has been made, the ingredients must be mixed together. The degree of mixing has a profound influence on the rubber properties. Design of mixers, the mechanism of mixing, and rubber rheology form the basis of Chapter 7 by Freakley. Mixing processes can be broken down into the following steps: viscosity reduction, incorporation, dispersion, and distribution. In practical mixers, there are regions of high power density, in which the dispersive mixing is accomplished, and regions of low power density for distributive mixing. The proper balance and interaction of these regions determine whether the mixer can produce a rubber compound with uniform composition and a low level of undispersed agglomerates. In the case of blends, differences in flow behaviour and solubility parameter influence the location of fillers and other additives during incorporation. Very often, separate mixing of each rubber with a proportion of the compounding ingredients, followed by blending of the sub-compounds thus formed, is recommended. Transfer between phases does not occur, provided a moderate level of dispersion is achieved in each compound. However, great care should be taken with selection of the vulcanisation agent and accelerator to avoid migration between phases, both in mixing and subsequent operations. Continuous mixers, widely used for thermoplastics compounding, are now being increasingly used for rubber compounding. Co-rotating modular, twin-screw compounders are produced by a number of machinery manufacturers.

The very low Young's modulus of rubbers results in high deformations in load bearing applications. In a practical sense this is not a problem because of the relatively high strength of rubbers, permitting large deformations without failure. On the other hand, the large deformations that are common in many engineering applications of rubbers prevent the use of design calculations based on linear elastic behaviour, which are in turn based on Hooke's law. Interestingly, rubbers have a high bulk modulus, and this, combined with a very high recoverable deformation, leads to quite unique properties. This, in turn, gives rise to many vital engineering applications, one of which is reliable and maintenance-free bridge bearings. Stevenson reviews the basic principles for engineering design for applications such as this in Chapter 9. Other products made from rubber for which strict design codes must be observed include automobile suspension systems (which influence the ride, comfort and safety of the vehicle) and components for aerospace vehicles, such as seals, which may be in vital locations where the consequences of failure are catastrophic. More discussion is found in Chapters 11 and 14 where emphasis is placed on the service environment, which adds a new dimension to the mechanical design. Low temperatures, high temperatures, the presence of certain fuels, oils or other chemicals, can strongly alter the stiffness and other engineering properties, including fracture, thus influencing the life and performance of a rubber component.

In order to ensure suitability, quality and durability of a rubber product, laboratory testing of rubber is of prime concern. Tests are usually conducted on testpieces made to suit the laboratory test equipment and may not resemble the component for which the suitability of the material needs to be established and the test may not provide reliable information even when enshrined in standards. Similarly, accelerated tests are often applied to attempt to determine the durability of a product, and the ability of such tests to predict lifetime is often questionable. Brown has provided a critical review of the testing methods and has included a survey of the most important ISO standards and comments on their usefulness in Chapter 10. The topics covered include processability tests; measurement of curing or vulcanisation characteristics; mechanical property testing, including hardness, stress-strain properties, tear resistance, resilience, fatigue resistance, wear resistance, creep, stress-relaxation and set. Other test procedures measure characteristics such as friction, electrical properties, thermal properties, permeability, environmental resistance and fire resistance.

Chapter 11 is the first one that deals with a particular product type, and in view of the importance of tyres and because the tyre industry consumes more rubber than any other, it would be hard to choose any other product to be first. Tyres have evolved to become a unique product type, made from a family of complex rubber-based composites. There has been continuous research and developmental work in tyre materials, tyre construction and tyre manufacturing technology since the nineteenth century, but rapid changes were still taking place in the last part of the 20th century. In Chapter 11, Dryden, Luchini and Ouyang eloquently describe the latest developments, comparing new manufacturing processes developed by the leading tyre manufacturers. The most significant development in tyre materials in recent years is the complete replacement of carbon black by silica, which results in 20% reduction in rolling resistance, 8% improvement in snow traction and 5% improvement in wet traction, without change in tread life. Innovations continue to appear, such as the run-flat tyre, which is capable of operating without inflation pressure, at least for a limited duration at a modest speed. Another innovation is the development of ‘intelligent’ or ‘smart’ tyres where the signals from the pair of sensors in the sidewall provide information on the movements and deformations of the tyre in service.

In 1997 Continental AG started implementing its MMP (Modular Manufacturing Process), which utilises the present manufacturing capacity while minimising workforce reduction. In 1998 Goodyear announced their IMPACT (Integrated Manufacturing Precision-Assembled Curricular Technology Process), which is compatible with Goodyear’s conventional tyre manufacturing technology. Pirelli’s ‘Flexi’ system is fairly similar to

Continental's MMP process, while Bridgestone's ACTAS (Automated Continuous Tyre Assembly System) appears to be more like Goodyear's IMPACT. The most publicised of the new manufacturing technologies is 'C3M' process, which is the acronym for 'continous cold compounding' by Michelin. Reported advantages of the C3M process include: a 60% savings in energy requirement, a 90% reduction in work area, a 85% reduction in manufacturing time, reduction in work force and a highly uniform product. The C3M process integrates the rubber mixing, component preparation, tyre building and curing processes into a unified manufacturing cell.

Besides tyres, an automobile uses a variety of specialty rubbers in a large number of critical areas that demand service under aggressive conditions. Fuel lines, oil lines, air ducts, cooling lines, timing belts, seals, transmission bellows and electric insulation are examples where conventional rubbers or tyre rubbers such as natural rubber or styrene butadiene rubber cannot be used. Jaillet surveys the speciality automotive rubbers in Chapter 12, discussing how service requirements dictate the materials selection process for components from a list that includes EPDM rubber, nitrile rubber, hydrogenated nitrile rubber, chlorosulphonated polyethylene, epichlorohydrin rubber, fluorocarbon rubber, polychloroprene, acrylic rubber, nitrile rubber/poly(vinyl chloride) (PVC) blend and fluorosilicone rubber.

High performance athletic shoes have stimulated the development of new rubbers and these have proved to be attractive to the fashion footwear designer, opening up new possibilities and introducing new requirements. Outsoles are often intricately designed combinations of multicoloured compounds that must bond together and still perform adequately. In some ways, tyres and shoe outsoles have similar requirements in terms of wear resistance and traction, but there are differences in service conditions that limit the use of certain materials. Outsoles for running shoes need to provide good durability, good traction and high energy return (rebound). The polymers of choice for running outsoles are natural rubber and polybutadiene rubber. Under the category of safety shoes, chemical resistant outsoles are often based on nitrile rubber or PVC/nitrile rubber blend or polychloroprene. In the case of work shoes and other footwear for use under severe conditions (hiking boots, sports shoes used in outdoor basket ball or tennis) high abrasion resistance can be achieved through the use of carboxylated nitrile rubber (XNBR), polybutadiene rubber or natural rubber, in the presence of reinforcing fillers such as carbon black and reinforcing agents such as high styrene resin. Light weight and good cushioning are key properties for athletic as well as casual footwear. Low density of the rubber compounds can be achieved by adding a blowing agent and the resulting compound is microcellular. Ames reviews footwear rubbers in Chapter 13.

Rubbers are also used in construction. Building designers are interested in the following properties of rubbers: sound absorption, vibration isolation, sealing properties and easy fabrication and installation. In Chapter 14 Delgado and Paroli discuss rubber bearings to protect buildings from earthquakes; rubber-based flooring; adhesives and sealants; and roofing and water-proofing. New applications of rubbers in the construction industry are being developed. Rubber-based products can be used to create 'soft' environment in gymnasiums, houses, hospitals, etc., in order to minimise injuries in the event of falling. 'Soft' environments can be created in bathrooms, washrooms, kitchens or even around swimming pools. Both natural rubber and synthetic rubbers are used in the construction industry. Crumb rubber, obtained by grinding waste tyres, has been found useful in making floorings and pathways. EPDM rubber is popular in making sealing strips for windows and seals. Polychloroprene and chlorosulphonated polyethylene have been recommended for roofing and waterproofing.

Campion (Chapter 8) examines the factors responsible for the durability of engineering rubber products such as seals, hoses and cables. Fatigue life is not the only critical factor in assessing durability for some rubber components in service. Stress relaxation might be equally important (sometimes more important) in some applications as in seals, and the effects of fluids (liquids or gases) will probably dominate when a rubber comes in contact with harsh environments as in the case of gas/oil extraction. Hoses are rubber-based tubes used for transporting fluids, often at high pressures and high temperatures. A hose consists of an unbroken inner tubular liner, surrounded by a series of contacting concentric reinforcing layers and an outside cover along with suitable end-fittings. Besides bursting pressure and fatigue, durability tests here include stress relaxation near the end-fittings, effect of fluids and explosive decompression. Cables in service are often at risk of potential damage from the very high voltages to which they are subjected. Breakdown in the form of fine interlinked erosion channels, known as 'water treeing' occurs in the case of EPDM and crosslinked polyethylene (XLPE). Provided the design of the rubber component in service is correct, choice of the right type of rubbers and additives will ensure durability of the component. However, proper testing and appropriate life assessment methods are necessary to evaluate the required service lifetime.

Vulcanised rubbers are thermosets and it is not easy to break down the crosslinks. Among the various rubber wastes, worn out tyres create enormous environmental problems and health hazards. Isayev addresses this important topic in Chapter 15 with special emphasis on recycling methods and usage of recycled rubber. One of the most notable developments in rubber recycling is the solid-state shear extrusion pulverisation method of rubber waste. Microbial desulphurisation of waste rubber offers a biotechnological possibility of rubber recycling. The process of ultrasonic devulcanisation has shown great promise in the last two decades. Large scale utilisation of waste rubber is possible in blends with thermoplastics and in civil engineering applications such as rubber-modified asphalt and rubber-filled cement.

1.4 Closing remarks

In this volume we have assembled a collection of authoritative, up-to-date reviews that together form a coherent body of work that will provide new information for the experienced rubber technologist as well as providing a suitable introduction to those who are new to the field. We are conscious that the constraints of space have prevented the inclusion of some important topics, including detailed survey of the mechanical and fracture properties of rubbers, computer-aided design of rubber components made from rubbers, many aspects of processing, some important families of products, including those for medical applications, and degradation processes. We hope to remedy this by preparing a second volume in the near future.

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2 Natural Rubber

N. M. Mathew

2.1 Introduction

Natural rubber (NR) has been known to the civilised world ever since the year 1493, when Christopher Columbus found the natives of Haiti playing with balls made from the exudates of a tree called 'cau-uchu' or weeping wood. The term 'rubber' was coined by the English chemist Joseph Priestly for its ability to erase pencil marks. It was the French scientist Charles de la Condamine who first introduced NR to Europe in 1736 and published his observations in 1745. Industrial applications of rubber were found slowly after this. It was the discovery of vulcanisation by Charles Goodyear in 1841 that paved the way for the growth of the modern rubber industry.

2.2 Source

Natural rubber is *cis*-1,4 polyisoprene and is present as latex in a large variety of plants in many regions of the world. Latex containing appreciable quantities of rubber occurs in certain plant species belonging to the *Moraceae, Euphorbiaceae, Apocynaceae* and *Compositae* families as listed in Table 2.1. The most important source is the tree *Hevea brasiliensis*. Latexes from the other sources suffer from disadvantages such as low rubber content, high resin content and difficulties in extraction. However, *Parthenium argentatum*, which yields guayule rubber has gained some importance in the last two decades mainly

Table 2.1 Major plant sources of natural rubber

Family	Species	Popular name
Euphorbiaceae	*Hevea brasiliensis*	Para rubber
Compositae	*Parthenium argentatum*	Guayule rubber
Euphorbiaceae	*Manihot glaziovii*	Ceara rubber
Moracea	*Castilla elastica*	Panama rubber
Moracea	*Ficus elastica*	India rubber
Apocynaceae	*Funtumia elastica*	Lagos silk rubber

on account of the possibility of this shrub being cultivated in the semi-arid regions of South-Western USA and Mexico.

Hevea brasiliensis, the most widely exploited commercial source of NR, was introduced into tropical Asia in 1876 by Sir Henry Wickham. About 10 million hectares (100,000 km^2) are currently planted with it, producing around 6.7 million tonnes of NR annually. The rubber growing areas form a belt lying a few degrees north and south of the equator. Table 2.2 gives the major producing countries and their contribution to rubber production.

Table 2.2 NR production/consumption in major producing/consuming countries

Country	Production in 1999 (kilo tonnes)	Country	Consumption in 1999 (kilo tonnes)
Thailand	2265.5	USA	1093.0
Indonesia	1596.2	China	852.0
Malaysia	768.9	Japan	734.2
India	620.1	India	619.1
China	460.0	Malaysia	344.4
Vietnam	230.0	Korea	331.0
Ivory Coast	122.0	France	252.7
Sri Lanka	96.6	Thailand	226.9
Liberia	85.0	Germany	224.0
Brazil	70.0	Brazil	170.0
Philippines	65.0	Spain	162.0
Cameroon	63.0	Canada	141.0
Nigeria	50.0	Indonesia	116.0
Cambodia	40.0	Taiwan	111.0
Guatemala	31.3	Turkey	72.0
Myanmar	27.2	Sri Lanka	53.8
Others	159.2	Others	1186.9
Total	**6750.0**	**Total**	**6690.0**

2.3 Cultivation

Hevea brasiliensis is indigenous to the Amazonian rain forests, situated within 5° latitude and at altitudes less than 200 m. The trees evolved in this environment prefer a warm and humid weather [1, 2]. Rubber is grown predominantly in the tropics, where an equatorial monsoon climate prevails. The climatic conditions suitable for optimum growth of rubber trees include an annual rainfall of not less than 2000 mm, evenly distributed without any marked dry season and with 125 to 150 rainy days per year, a maximum temperature of 29 to 34 °C and a minimum of 20 °C or more with a monthly mean of 25 to 28 °C, high atmospheric humidity of around 80% with moderate wind, bright sunshine amounting to about 2000 hours per year at the rate of six hours per day throughout the year [3, 4]. Rubber needs a well-drained, fairly deep, loamy soil with a pH value of 4.5–6.0. South-East Asia is particularly suited for rubber cultivation as are countries in West Africa. Although not ideally suited, rubber is successfully cultivated even up to a latitude of 25°, well beyond the traditional latitude, in countries such as India and China.

Rubber is planted at a typical density of 450–500 trees per hectare (4500–5000 trees per km^2). Although the plants were earlier raised directly from seeds, the present method of propagation is a vegetative one, called budgrafting, in which buds taken from a selected high yielding mother plant are grafted to seedling stocks. The buds grow into plants which will have all the characteristics of the mother plant. All the trees that are derived by vegetative propagation from a single mother tree constitute a clone. Each clone has its own characteristics of growth, yield, tolerance to diseases and climatic stresses. Propagation of rubber is also possible by tissue culture. Although tissue culture methods have been evolved by many workers [5, 6], it has not yet been used on a commercial scale. The young plants are allowed to grow in a nursery bed or preferably in polyethylene bags in the first year and then transplanted to the field. Soil fertility is maintained by the use of fertilisers and by growing leguminous cover crops. Compared to many other crops, the nutrient requirement of rubber is very limited, since nutrient removal through the crop is very low and as the cultivation practices allow for nutrient recycling through litter disintegration and nitrogen fixation by the legume cover. The trees become ready for harvesting in 5–7 years when they attain a girth of 500 mm at a height of 1.25 m from the bud union.

The trees are affected by a number of diseases involving roots, stem and leaves. Effective control measures have been evolved for all these diseases except the South American Leaf Blight caused by the fungus *Microcyclus ulei*, which has caused extensive damage to the rubber plantations in South America. Fortunately Asia and Africa are free from this disease and a number of quarantine regulations are being implemented by Asian and African rubber growing countries to prevent any accidental introduction of the disease. The other major leaf diseases of rubber are abnormal leaf fall caused by different species of the fungus *Phytophthora*, powdery mildew caused by *Oidium heveae*, *Corynespora* leaf disease and *Gloeosporium* leaf disease. Pink disease caused by *Corticium salmonicolor* is a major problem affecting the stem while brown and white root diseases are the common problems affecting the root system. Copper-based fungicides are very effective in controlling most of these diseases [7].

The original plantings of rubber had an average annual yield of only 200 to 300 kg per ha (2000 to 3000 kg per km^2) [8]. Now there are clones with an annual production potential of 3500 kg per ha. This substantial improvement in productivity has been achieved mainly through breeding and selection programmes carried out in different countries. The successive cycles of breeding and selection have contributed to substantial gene erosion and the genetic base of *Hevea* has now become very narrow. However, efforts are being made to counter this shortcoming by incorporating freshly introduced wild *Hevea* genotypes from Brazil. Modern molecular approaches in breeding and use of genetic engineering techniques in *Hevea* will definitely yield still better performing rubber clones in future.

2.4 Harvesting

Natural rubber is present in the form of latex in a system of intercellular ducts called latex vessels which exist in the bark. The maximum number of such vessels is available close to the cambium, the outermost growing region of the wood. Latex is maintained in the vessels at a higher hydrostatic pressure called turgor pressure of approximately 1–1.9 MPa [9]. To extract latex from the tree, the vessels are opened by a process called tapping. A thin shaving of bark, about 1 mm thick, is removed with a sharp knife, to a depth very close to the cambium, but without injuring it. The tapping cut is made at an angle of approximately 30° to the horizontal from high left to low right. As latex vessels run in a spiral up the trunk at an angle of 2–7°, this severs the maximum number of vessels for a given length of cut. As turgor pressure is maximum just before sunrise, tapping is carried out early in the morning. Tapping is done at regular intervals, working down the trunk. Laticiferous bark grows again behind the descending cut so that the process can be continued indefinitely. There are variations regarding length of tapping cut and frequency of tapping. Common systems are half spiral alternate days, i.e., a cut extending halfway around the circumference, made every other day. This is abbreviated as 1/2S d/2. As high intensity tapping systems are believed to cause problems such as tapping panel dryness (TPD) in high yielding clones, lower intensity tapping systems such as 1/2S d/3 and 1/2S d/4 are being recommended. Yield varies with the clone, age of the tree, fertility and moisture content of the soil, climatic conditions, tapping system followed, skill of the tapper, etc. A tree can be economically tapped for a period of 20–

25 years, after which it is 'slaughter tapped', i.e., intensively tapped for about 2–3 years before it is replanted.

The first step in the tapping process is to peel off the coagulated rubber residue from the previous tapping before removing a shaving of bark. This is collected separately as 'tree lace'. After tapping, latex flows down the cut and is channelled into a plastic/ceramic cup through a short metal spout. The daily task of a tapper is usually 300–400 trees, which is completed late in the morning. Then the cups are emptied into buckets and the latex is then carried to the collection centre or the processing factory. If there is any spillage of latex, it is left to coagulate and is collected occasionally as tree scrap or earth scrap. Very often the tree will still be yielding at the time of latex collection. In such cases, the collection cup after emptying, is replaced on the tree to receive the late drippings. At the time of the next tapping, this latex would have spontaneously coagulated and this is collected by the tapper as 'cup lump'. The tree scrap, earth scrap, tree lace and cup lump together make the field coagulum, which constitutes around 20% of the crop. The remaining 80% is latex.

It is possible to increase the yield of latex by the use of chemical preparations called yield stimulants. The most widely used stimulant is 2-chloroethylphosphonic acid (ethephon) which was first introduced by Abraham *and others* [10]. Ethephon releases ethylene gas on hydrolysis, which acts as the stimulant. Ethylene is thought to act by inhibiting the plugging process which causes the latex flow to stop. Tapping at reduced frequency along with a low level of stimulation using ethephon has been suggested as an effective approach to increase productivity per tapper and thus to reduce production costs [11].

2.5 Biosynthesis of rubber

Natural rubber consists of thousands of isoprene units linked together to form a polymer. The individual steps in the synthesis of rubber from sucrose are well established by Lynen [12] and the pathway is illustrated in Figure 2.1 [13]. There are three stages: (1) generation of acetyl-coenzyme A, (2) conversion of acetyl-coenzyme A to isopentenyl pyrophosphate (IPP) via mevalonic acid and (3) polymerisation of IPP to rubber. Sucrose in latex is the primary source of acetate and acetyl-CoA essential for the biosynthesis of rubber. Acetate forms the basic precursor of rubber synthesis in all rubber yielding plants.

Hevea rubber differs from the majority of isoprenoid compounds in two respects. It has a high molecular weight, which varies from one hundred thousand to a few millions, and the geometric configuration around the double bond is exclusively *cis* 1, 4 [14].

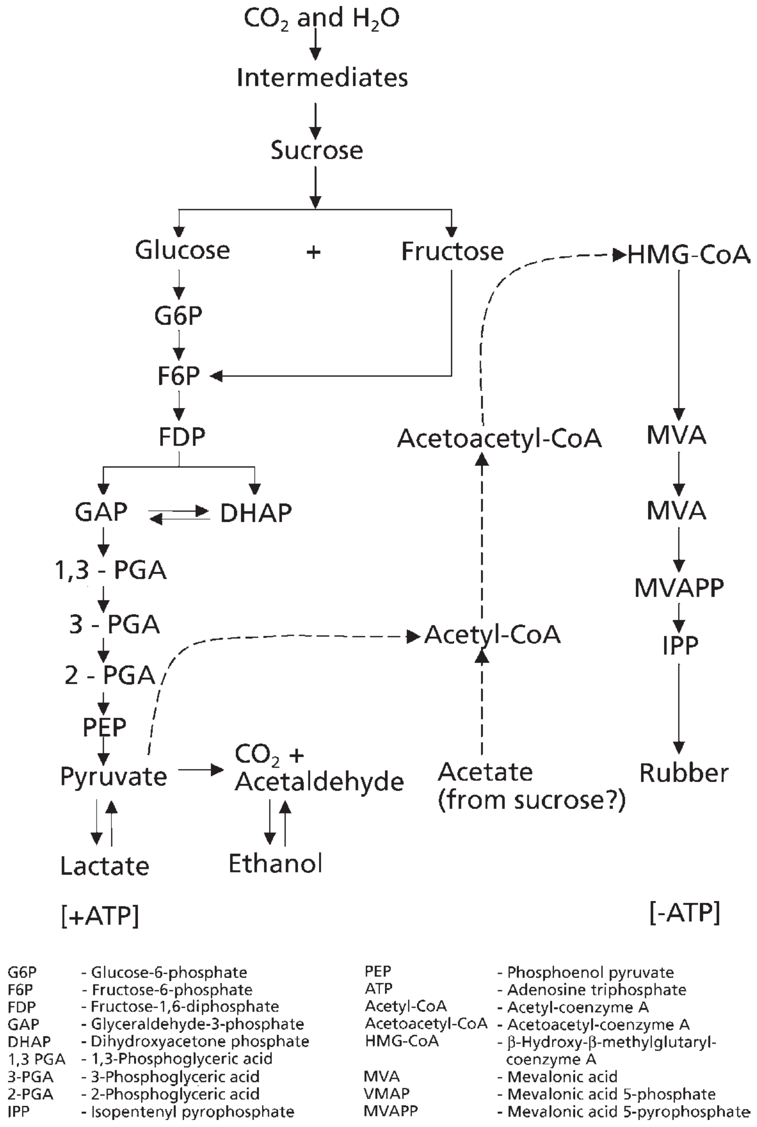

Figure 2.1 Pathway of rubber biosynthesis (adapted from Moir, [13])

2.6 Composition of latex

Natural rubber latex is a colloid with a specific gravity of 0.96 to 0.98 and a pH in the range of 6.5 to 7.0. The dispersed phase is mainly rubber and the dispersion medium is water. However, in addition to rubber and water, latex contains small quantities of proteins, resins including fats, fatty acids, other lipids, sterol and sterol esters, carbohydrates and mineral matter. The composition of field latex (latex as obtained from the tree) is given in Table 2.3. The dominant particulate constituent of fresh latex is the rubber hydrocarbon with a size ranging from 0.02 to 3.0 μm and shape mostly spherical and strongly protected in suspension by a film of adsorbed proteins and phospholipids [15, 16]. The other particles in latex comprise lutoids and Frey-Wyssling particles. The lutoids are subcellular membrane bound bodies ranging in size from 2 to 5 μm, containing a fluid serum known as B-serum, which is a destabiliser for rubber particles. Frey-Wyssling particles are spherical, larger in size and are yellow coloured. Quebrachitol (methyl-l-inositol), sucrose and glucose are the major carbohydrates in latex. Of the total protein content of fresh latex about 20% is adsorbed on the rubber particles, an equal quantity found in the B-serum and the remainder in the latex-serum. The adsorbed proteins and the phospholipids on the rubber particles impart a net negative charge, thereby contributing to the colloidal stability of latex. Lipids in fresh latex consist of fats, waxes, sterols, sterol esters and phospholipids. Lipids associated with the rubber and non-rubber particles in latex play a key role in the stability and colloidal behaviour of latex. Most of the classic amino acids have been found in latex. Nucleotides contained in latex are important as cofactors and are intermediates in the biosynthesis of rubber. Low molecular weight thiols such as glutathione and cysteine and ascorbic acid determine the redox potential of latex.

2.7 Crop collection

The crop is collected from plantations as latex and various forms of field coagulum. Generally latex accounts for about 80% of the crop, the rest being field coagulum. The proportion of the two forms depends on the age of the trees, tapping system, climatic

Table 2.3 Chemical composition of fresh latex

Constituent	Percentage
Rubber	30–40
Proteins	1–1.5
Resins	1.5–3.0
Minerals	0.7–0.9
Carbohydrates	0.8–1.0
Water	55–60

conditions, clone, stimulation, time of collection and stability of latex. Latex can be processed into ribbed sheets, pale latex crepe (PLC) or sole crepe, block or technically specified rubber (TSR) and speciality rubbers and preserved field latex and latex concentrate. Field coagulum is processed as crepe rubber or TSR.

Flow of latex usually stops 2 to 3 hours after tapping. The presence of proteins and carbohydrates in latex causes it to coagulate prematurely through bacterial activity. The tendency for precoagulation can be prevented using anticoagulants. These are chemicals added to latex in small quantities for preventing precoagulation for short periods. The most popular anticoagulants are ammonia, formalin and sodium sulphite. The usual dosages are 0.01, 0.02 and 0.05% in latex for ammonia, formalin and sodium sulphite, respectively. Hydroxylamine neutral sulphate along with ammonia is recommended as anticoagulant for latex to be used for the production of constant viscosity (CV) rubber. The preferred anticoagulant is sodium sulphite if the latex is meant for sheet rubber or PLC.

The different forms of field coagulum also need proper handling. Tree lace and cup lump are collected in baskets carried by the tappers. In high yielding trees, the quantity of cup lump is generally more. Field coagula are sorted and stored separately. It is preferable to process them fresh. This ensures proper dirt removal and better colour for the processed rubber. When field coagulum is to be stored, it is partially dried in smoke. Exposing it to direct sunlight or soaking in water for long periods accelerates degradation. Earth scrap is collected once a year or once in six months and may contain high levels of dirt.

Latex to be processed into sheet, PLC or light coloured block rubber is brought to the processing factory as early after collection as possible. In small and medium rubber estates, field latex is carried to the factory by the tappers themselves. Large estates have latex collection centres at suitable locations in the estate. The latex brought by the tappers is weighed and collected in a bulking tank in the collection centre and suitable anticoagulants are added. Latex intended for concentration is preserved using ammonia or low ammonia-tetramethylthiuram disulphide (TMTD)-zinc oxide (LATZ) system.

2.7.1 Pre-processing of latex

Latex brought to the factory is sieved and collected in a large bulking tank. Sieving is necessary to remove contaminants such as bark shavings, leaves, sand and small clots of rubber. Stainless steel sieves of 40 and 60 mesh size are preferred. As it is necessary to find out the rubber content of latex for its further processing, dry rubber content (DRC) is measured quickly using a metrolac (hydrometer).

2.8 Crop processing

Fresh field latex and the field coagula are not suitable for storage and are open to bacterial attack and degradation. Therefore, these two forms of the crop need processing into a form which is suitable for long-term storage and marketing. These primary processing operations are carried out in the plantation itself. The various marketable forms of raw natural rubber include preserved field latex and concentrated latex, ribbed smoked sheet (RSS) and air dried sheet (ADS), block rubber or TSR, PLC and estate brown crepe (EBC) and other low grade crepes made from field coagulum.

2.8.1 Preservation and concentration of latex

A number of rubber products such as gloves, condoms, rubber bands, balloons, foam mattresses, elastic threads, adhesives, etc., are made directly from latex. About 10% of the global production of NR is processed as preserved and concentrated latex.

Preservation of latex is aimed at preventing bacterial activity and enhancing its stability. This is achieved using preservatives such as ammonia. Apart from being a bactericide, ammonia enhances the colloidal stability of latex and deactivates certain harmful metal ions. For effective preservation of latex, ammonia is used at a concentration of 0.7 to 1.0% by weight. During storage, the higher fatty acid esters present in latex are hydrolysed into ammonium soaps, which improves the mechanical stability of latex.

Though ammonia is the most effective preservative for NR latex, its pungent smell, the low zinc oxide stability of latex and longer gel time of latex foams are disadvantages. But attempts to preserve latex entirely without ammonia have not been successful. However, many low ammonia preservative systems have been developed, in which the concentration of ammonia has been reduced to around 0.2% and supplemented with secondary preservatives such as zinc diethyldithiocarbamate, a TMTD-zinc oxide combination of boric acid, etc. Of these, a combination of 0.2% ammonia, 0.0125% each of TMTD and zinc oxide and 0.05% of lauric acid (LATZ system) is the most popular.

The process of latex concentration involves removal of a substantial quantity of serum from field latex, thus making latex richer in rubber. The main reasons for concentration of latex include a preference for high DRC by the consuming industry, economy in transportation and purification of latex. The major processes employed for the concentration of NR latex include evaporation, electrodecantation, creaming and centrifuging. Evaporation involves the removal of water only. Hence the ratio of non-rubber constituents to rubber and the particle size distribution remain unaffected. On the other hand, the other three processes involve the partial removal of non-rubber constituents and smaller rubber particles. Because of this, the range of particle size is reduced and a higher degree of purity is obtained. Centrifuging and creaming are more popularly used for the production of concentrated latex.

In any dispersion, the dispersed particles cream or sediment under the influence of gravity. In the case of latex the rubber particles, being lighter than serum, tend to cream up. The velocity of creaming depends upon a number of factors and can be deduced approximately from Stoke's Law [17], stated mathematically as

$$V = \frac{2g\,(Ds - Dr)\,r^2}{9\eta}$$

where V is the velocity of creaming (m/s)

g is the acceleration due to gravity (m/s^2)

Ds, Dr are the densities of serum and rubber particles, respectively (g/cm^3)

r is the effective radius of the particle (m) and

η is the coefficient of viscosity of serum (Pa-s)

In the creaming process, the creaming agent such as sodium alginate, forms an adsorbed layer over the rubber particles which reduces the Brownian movement and the intensity of the negative electric charge on the particle surface, thereby promoting temporary agglomeration of particles. Thus the effective size of the particle increases, favouring faster creaming. In the centrifugal process, when the latex enters the machine, rotating at a high speed of around 7000 rpm, the centrifugal force, which is several thousands greater than the gravitational force, replaces g and causes instantaneous separation of the latex into cream and skim. In creaming, the skim is almost clear serum and is therefore discarded. However, in the centrifugal process, the skim contains 3–8% rubber, which is recovered by coagulation using dilute sulphuric acid and processed as skim rubber, which is a low quality rubber. However, methods have been developed to improve the quality of skim rubber [18].

Natural rubber latex concentrate is marketed to strict technical specifications. The current ASTM specifications for latex concentrates are reproduced in Table 2.4.

2.8.2 Ribbed smoked sheet (RSS)

This is the oldest method of processing of NR latex and is still widely adopted by rubber growers owing to its simplicity, low cost and viability even when the quantity of latex is small. Even today RSS is the predominant form of NR in countries such as Thailand and

Table 2.4 Requirements for specified latex types (ASTM D1076-97) [19]

	Type 1	Type 2	Type 3
Total solids, min, %	61.5	66.0	61.5
Dry rubber content (DRC), min, %	60.0	64.0	60.0
Total solids content minus dry rubber content, max, %	2.0	2.0	2.0
Total alkalinity calculated as ammonia, as % on latex	0.60 min	0.55 min	0.29 max
Sludge content, max, %	0.10	0.10	0.10
Coagulum content, max, %	0.050	0.050	0.050
KOH number, max	0.80	0.80	0.80
Mechanical stability, S, min	650	650	650
Copper content, max, % of total solids	0.0008	0.0008	0.0008
Manganese content, max, % of total solids	0.0008	0.0008	0.0008
Colour on visual inspection	A	A	A
Odour after neutralisation with boric acid	B	B	B

A - No pronounced blue or grey
B - No putrefactive odour
Type 1 - Centrifuged natural latex preserved with ammonia
Type 2 - Creamed natural latex preserved with ammonia
Type 3 - Centrifuged natural latex preserved with low ammonia with secondary preservatives

India. Fresh field latex after sieving and bulking, is diluted to 12.5 to 15% DRC. Dilution improves the colour and transparency of the sheet and makes the sheeting operation easier, and allows denser impurities in latex to sediment on standing for 10–15 minutes. Sodium bisulphite is added to latex at the rate of 1.2 g per kg DRC to prevent the surface discoloration on wet sheet, occurring through enzyme catalysed oxidation of phenolic components in latex. *Para*-nitrophenol (PNP) is added to the latex at the rate of 1 g per kg DRC to prevent mould growth on the sheet surface during prolonged storage in humid weather. The diluted latex is then transferred to coagulation tanks or pans and coagulated with dilute formic or acetic acid. These acids are preferred on account of their volatile nature and being noncorrosive to the equipment used. However, because of their relatively high cost, alternative coagulants such as sulphuric acid and sulphamic acid have been recommended to be used under controlled conditions [20, 21, 22]. After a few hours, or the next day, the thick slab of coagulum is squeezed using a set of rollers to remove water and make it into sheet of approximately 3 mm thickness. The final set of rollers is grooved to introduce ribbed markings on the sheets. The ribbed markings increase its surface area and facilitate drying. The wet sheets are soaked in a 0.1% solution of PNP for a few minutes, if the latter has not been added to latex before coagulation. The sheets are then allowed to drip for a few hours before loading into the smoke house for drying.

Drying of sheets is ideally carried out in smoke houses or hot air chambers and the dried sheets thus obtained are termed ribbed smoked sheet or air dried sheet, respectively. Partial drying under the sun followed by smoke drying is practised widely in small holdings. Several types of smoke houses such as those with a furnace inside or outside the drying chamber, batch type or continuous type are in operation [23]. The temperature in the different regions of the smoke house is maintained in the range of 40–60 °C. The sheets are held on wooden or bamboo rods used for holding sheets in a smoke house (beroties) placed on trolleys which move on a central rail track in a large tunnel type smoke house. In smaller types of smoke houses, the beroties are placed on a framework inside the chamber. Drying of the sheets takes four to six days in a smoke house. The dried sheets are visually examined and graded adopting the norms prescribed by the International Rubber Quality and Packing Conference under the Secretariat of the Rubber Manufacturers' Association Incorporated and described in the 'Green Book'. Grading is done on the basis of colour, transparency, presence of mould, oxidised spots, blisters, bubbles, dirt, sand and other foreign matter, degree of drying, tackiness, etc. There are six grades of sheet rubber which are designated as RSS 1X and RSS 1 to RSS 5. These are graded according to the Green Book. RSS 1X is the best and RSS 5 the worst.

Dried sheets are packed by grade into bales of 111 kg. Wrapping of bales may be done on all sides with the same or higher grade of rubber. These bare back bales are coated with talc to prevent bale-to-bale adhesion. Appropriate markings about the manufacturer, grade, etc., of the rubber are stencilled on the bales, before these are shipped.

2.8.3 Pale latex crepe and sole crepe

NR latex contains certain yellow carotenoid pigments. PLC is a light coloured premium grade of NR from which the yellow pigments have been removed or bleached. It is preferred in products for which a light colour is important.

Pale crepes are made from latex of selected rubber clones such as PB 86, RRIM 600, etc., which give relatively white latex containing minimum β–carotenes and are less susceptible to enzymic discoloration. The latex is collected without any precoagulation and if necessary, sodium sulphite may be used as an anticoagulant. The latex is then bulked and diluted to a DRC of 20 and the yellow pigments are bleached with 0.05% of tolyl mercaptan or its water soluble alkali metal salt [24, 25]. Alternatively, the pigments are removed by fractional coagulation. A small quantity of acetic acid or oxalic acid (approximately 1 g per kg DRC) is added to the latex which is stirred well and then allowed to remain undisturbed for 1 to 2 hours. About 10% of the rubber coagulates, and the coagulum carries the bulk of the β–carotenes. The coagulum is removed and the remaining fraction of latex is processed further. In practice, a combination of bleaching and fractional coagulation is used. The treated latex is then coagulated and set into slabs which are passed several times through crepe rollers with liberal washing. The resultant thin crepes, 1–2 mm thick, are dried in hot air at about 33–35 °C for about two weeks. Pale crepe is also graded visually according to the Green Book. The main criterion is colour. The grades are PLC 1X, PLC 1, PLC 2 and PLC 3. PLC 1X is the best and PLC 3 is the worst. Thick and thin versions of these grades are available.

Sole crepes are used by the footwear industry and are made by laminating plies of pale crepe to the required thickness and consolidating them by hand rolling and finally through even speed rollers.

2.8.4 Field coagulum crepe

Among the various field coagulum materials, cup lump and tree lace are collected every tapping day and are processed fresh or after storage, into estate brown crepe. Earth scrap, tree scrap and scrap stored for long periods are lower quality materials and hence the crepe processed from these will be of inferior quality. Different grades of field coagulum crepe are used in appropriate proportions in blends with other forms of natural rubber to make products such as tyres, footwear, retreads or mechanical goods.

The selected field coagulum is soaked in water to make it soft and to remove surface dirt and is then thoroughly cleaned by passing through a battery of crepe rollers. Proper blending is carried out on the rollers to ensure uniformity. Simultaneously thorough washing is done by providing running water in every crepe roller. The crepe is dried in drying sheds at ambient or slightly elevated temperature.

Grading of field coagulum crepe also is done visually as per the norms prescribed in the Green Book. Here also the main criterion is colour. Different grades are available in each type.

2.8.5 Technically specified rubbers (TSR)

The disadvantages of the conventional forms of NR such as RSS and crepes became more evident with the advent of synthetic rubbers which were marketed in compact, uniform and medium-sized bales wrapped in plastic film and with technical specifications to suit the requirements of the manufacturing sector. This has necessitated R&D efforts to market NR also in more attractive forms. Consequently new methods of processing and presentation were developed to market NR as technically specified rubber in compact bales, wrapped in polyethylene film and graded adopting technical specifications. Technically specified rubbers are now being produced in almost all NR producing countries and are marketed under different names (Table 2.5).

The advantages of TSR include assurance of quality for important technical parameters, consistency in quality, minimum space for storage and clean and easy to handle packing. This method enables NR producers to process both latex and field coagulum using almost the same set of machinery and to minimise the processing time to less than 24 hours. Although different methods were developed to produce TSR, all these processes involve certain common steps such as coagulation of latex, processing of field coagulum, size reduction, drying, baling, testing, grading and packing. Differences among commercial processes lie in the method of coagulation or in the machinery used for crumbling the coagulum. Typical flow diagrams for processing of latex and field coagulum into TSR are given in Figure 2.2.

The major challenge in TSR production is ensuring consistency in quality [26]. Introduction of a slab cutter or pre-breaker in the initial size reduction stage, use of macro- and micro-blending tanks, transfer of raw materials from one tank to another while under motion by bucket elevator system and loading of final crumbs to the drier boxes with a slurry pump through a vibrating perforated screen and hopper are some of the recent developments in TSR production aimed at improving consistency and reducing cost.

Table 2.5 Nomenclature of TSR in different countries

Country	**Nomenclature**
Malaysia	Standard Malaysian Rubber (SMR)
Indonesia	Standard Indonesian Rubber (SIR)
Thailand	Standard Thai Rubber (STR)
India	Indian Standard Natural Rubber (ISNR)
Sri Lanka	Sri Lanka Rubber (SLR)
Singapore	Standard Singapore Rubber (SSR)
Papua New Guinea	Papua New Guinea Classified Rubber (PNGCR)

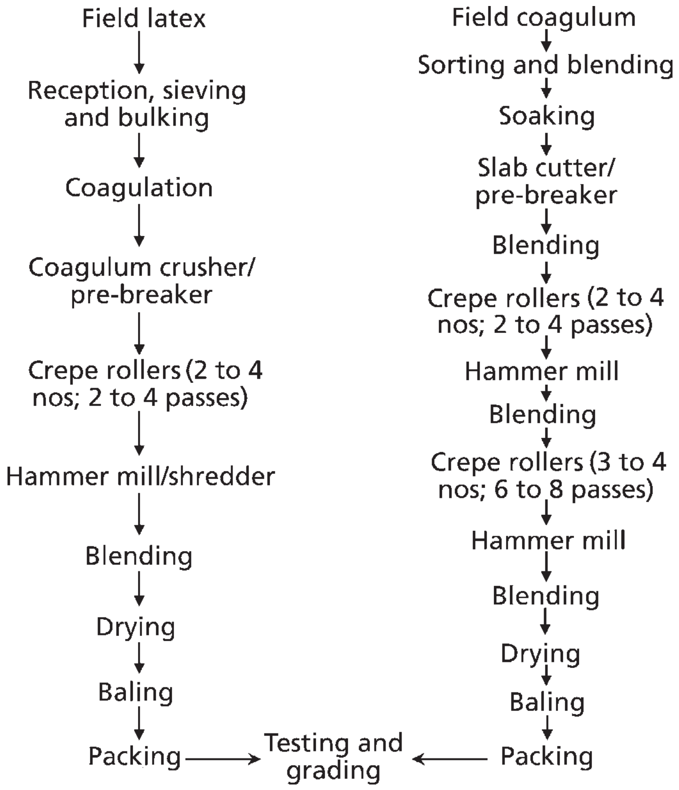

Figure 2.2 Flow diagram for processing latex and field coagulum into technically specified rubber

Since its introduction in the early 1960s, the specifications for TSR have been revised several times depending upon the requirements of the consuming industry. The specifications as per the latest revisions adopted by ASTM are given in Table 2.6 [27]. The development of TSR has helped the rubber plantation industry to improve the competitive position of NR by improving the quality of rubber and its consistency and introducing more efficient processing methods to meet the consumer requirements.

2.9 Modified forms of NR

With the development of synthetic rubbers, the monopoly enjoyed by NR until then, in the elastomer market was broken. Subsequently, a complex balance of technical properties and cost emerged as the decisive factor in its usage. Over and above the development of TSR, different special forms of NR have evolved to make it suitable for certain specific applications. Even before the 1939–1945 War, NR was found suitable for different types

Table 2.6 Specification for NR technical grades (ASTM D2227-96)

Property	Rubber grade				
	L	CV	5	10	20
Dirt retained on 45-micron sieve, max, %	0.05	0.05	0.05	0.10	0.20
Ash, max, %	0.60	0.60	0.60	0.75	1.00
Nitrogen, max, %	0.60	0.60	0.60	0.60	0.60
Volatile matter, max, %	0.80	0.80	0.80	0.80	0.80
Initial plasticity, P_0, min.	30	-	30	30	30
Plasticity retention index, PRI, min, %	60	60	60	50	40
Colour, Lovibond scale, max.	6.0	-	-	-	-
Mooney viscosity, ML(1+4) 100 °C	-	60 ± 5	-	-	-

L: light colour
CV: constant viscosity
The numbers 5, 10, 20 indicate the maximum permissible dirt content in the grade

of chemical modification, leading to the production of a number of polymeric materials of very interesting properties. Although many such materials lost their significance consequent to the development of totally synthetic counterparts, some are still technologically important. Moreover, the limited availability of petroleum-based feed stocks and the increasing awareness of the relevance of renewable and environment-friendly resources such as NR, have caused renewed interest in the development of modified forms of NR [28].

Natural rubber can be modified by physical and/or chemical means. Figure 2.3 gives an outline of the major modifications of NR. Some of these such as viscosity stabilised rubber, superior processing rubber, have been produced commercially. The commercial significance of the others depends mostly on emerging market forces.

2.9.1 Physically modified forms

The physical methods of modification of NR involve incorporation of additives which do not chemically react with rubber. The additives include various rubber compounding ingredients and polymers such as synthetic rubbers and thermoplastics. Some of the commercially important materials in this group are described in the following sections.

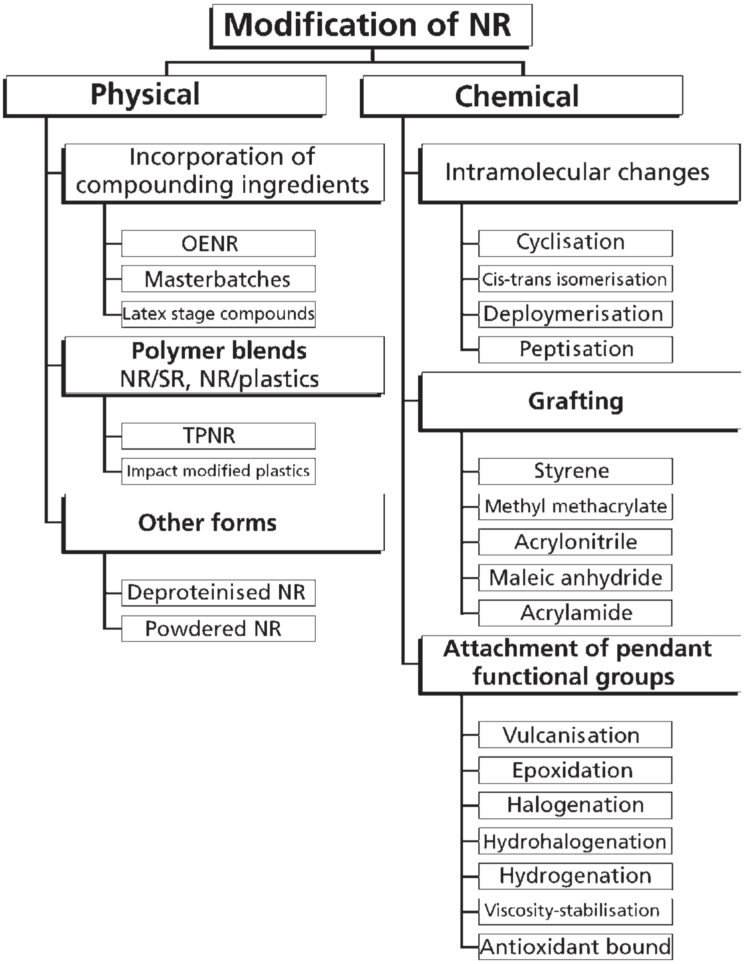

Figure 2.3 Modification of NR

2.9.1.1 Oil extended natural rubber (OENR)

This contains 20 to 25 phr of aromatic or naphthenic oil and is produced either in the latex stage [29] or in the dry rubber stage [30]. Extension in the latex stage is effected by adding an aqueous emulsion of the oil into latex followed by acid coagulation and processing into block rubber. In general, increasing oil content reduces tensile strength and resilience, but the vulcanisates retain good tear resistance and possess high wear resistance when blended with butadiene rubber. OENR also shows good skid resistance on wet surfaces when used in tyre tread.

2.9.1.2 Thermoplastic natural rubber (TPNR, see also Chapter 4)

Thermoplastic natural rubber blends are prepared by blending NR and polyolefines, particularly polypropylene and polyethylene in varying proportions. As the ratio varies, materials with a wide range of properties are obtained. Rubber-rich blends are thermoplastic elastomers while those with lower rubber content are impact-modified plastics. The mechanical properties of rubber–thermoplastic blends depend on the proportion of the rubber and thermoplastic components. In order to get reasonably good mechanical properties, the hard phase must be continuous. The soft phase, providing elastic properties, need not be continuous, provided it is sufficiently small and adheres to the matrix under stress. The elastic properties of TPNR are considerably improved if the rubber phase is partially crosslinked during mixing, a process called dynamic vulcanisation. The effect is pronounced in relatively soft blends. The blends are prepared in internal mixers at temperatures above the melting point of the plastic component. After blending the material is immediately sheeted and then granulated. TPNR is more resistant to heat ageing than NR vulcanisates. Ozone resistance of TPNR is also very high [31]. The soft grades of TPNR can replace vulcanised rubber and flexible plastics for applications in footwear, sports goods, seals and mountings and a wide range of moulded and extruded goods. The automotive industry is the largest potential market for the hard grades in applications such as automotive bumpers and body protection strips.

2.9.1.3 Deproteinised natural rubber (DPNR)

This is a purified form of NR with low protein and mineral content. The proteins and other hydrophilic non-rubbers can absorb moisture leading to reduction in modulus and electrical resistance and increase in stress relaxation and creep. Absorption of water by unvulcanised rubber can affect its degree of crosslinking and other cure characteristics. Deproteinisation of NR reduces moisture sensitivity thereby improving consistency and modulus. The general method of deproteinisation involves treating the latex with an enzyme preparation followed by dilution and coagulation. The enzyme hydrolyses the proteins into water soluble forms which are then washed away during subsequent processing [32].

2.9.2 Chemically modified forms of NR

Being an unsaturated organic compound, natural rubber is highly reactive and several chemical reactions can be carried out in NR resulting in materials having entirely different properties. These reactions can take place by the attachment of pendant functional groups, grafting of different polymers along the rubber molecule or through intra-molecular changes. The products of the reactions possess properties which are different from those of NR and therefore, can find use in applications where other materials are being used. Some of the important chemically modified forms of NR are described in the next sections.

2.9.2.1 Constant viscosity (CV) rubber

NR undergoes hardening during storage especially under low humidity. The increase in viscosity is caused by a crosslinking reaction involving the randomly distributed carbonyl groups on the rubber molecule [33]. The reaction can be prevented by the addition of small quantities of hydroxylamine salts to the latex before coagulation. The rubber so treated retains its original viscosity for a long time and is marketed as CV rubber. The controlled and stable viscosity favours easy and uniform processing. Premastication can be minimised or even avoided. This form of rubber is available mostly in the Mooney viscosity range of 60–65. Stabilisation of viscosity is evaluated by an accelerated storage hardening test. The increase in initial plasticity should be less than eight units.

2.9.2.2 Graft copolymer rubbers

Graft copolymers are prepared from natural rubber by polymerising vinyl monomers either in latex or in solution. Methyl methacrylate (MMA) and styrene are the common monomers used for grafting onto NR. Poly(methyl methacrylate) (PMMA) graft NR has been commercially produced since the mid-1950s in Malaysia. Generally, grafting can be achieved using free radical initiation by chemical method or by irradiation.

MMA graft NR is a self-reinforcing agent for NR with which it is compatible in all proportions. The graft rubber or its blends with NR can be compounded and vulcanised in the same way as rubber. The vulcanisates have excellent physical properties at high hardness levels with good hardness retention at elevated temperatures and good electrical properties. The major use of the MMA graft copolymer is in adhesives. It gives exceptionally good bond strength for bonding NR onto PVC which is particularly useful in the footwear industry. The adhesive property can also be exploited in tyre cord dipping.

Polystyrene is also grafted onto NR by polymerising styrene in NR latex. Various levels of modification can be achieved according to the proportion of grafted polystyrene. The modified rubber can be blended with NR, compounded and vulcanised in the usual manner. The graft rubber containing 50 parts of styrene (SG 50) is used in microcellular soles in place of high styrene grade of SBR.

2.9.2.3 Epoxidised natural rubber (ENR)

The mechanical properties of NR are superior to those of most synthetic rubbers. However, with regard to special properties such as oil resistance and gas permeability, NR is inferior to the special purpose synthetic rubbers. Baker and others [34] and Gelling [35] reported that epoxidation of NR in the latex stage, under controlled conditions, gives epoxidised NR with improved resistance to hydrocarbon oils, low permeability to air, increased damping and good bonding properties while retaining the high strength properties of NR. Improvement in these properties depends on the degree of epoxidation and two grades of ENR with 25 and 50 mole% epoxidation (ENR 25 and ENR 50) have gained commercial importance.

ENR is produced from NR latex by performic acid formed *in situ* by the reaction of formic acid with hydrogen peroxide [35, 36]. The reaction is carried out under carefully controlled conditions to avoid secondary ring opening reactions. The epoxide groups are randomly distributed along the NR backbone and ENR retains the stereoregular *cis*-1,4 configuration of NR. A wide range of applications are envisaged for ENR including accessories for milking machines, pharmaceutical and food contact applications, shoe soles, floor coverings and high damping engine mountings. ENR 50 or its blends with suitable rubbers can be used in inner tubes for bicycles and light agricultural vehicles. ENR has considerable potential in adhesives and sealants. Varkey *and others* [37] have reported that ENR can be used as a reinforcement modifier for silica filled rubber vulcanisates.

2.9.2.4 Superior processing (SP) rubber

This is an intimate mixture of vulcanised and unvulcanised rubber obtained by mixing vulcanised latex with normal latex in the desired proportions, before coagulation. It can be compounded in a similar manner to ordinary grades of NR with little loss of physical properties of the final vulcanisates. Improved processing characteristics and the ability to retain dimensional stability make it an ideal material for calendered and extruded products. The SP rubber that contains 20 parts of vulcanised and 80 parts of unvulcanised NR is termed SP 20 and is generally used to replace NR completely. SP 80 contains 80 parts of vulcanised rubber and 20 parts of unvulcanised rubber. When one part of SP 80 is blended with three parts of NR, the resultant material is equivalent to SP 20.

Superior processing rubbers can be used with great advantage in extrusion processes, especially at lower filler loading due to its low die swell, less affected by extrusion conditions and better surface finish and higher stock viscosities permitting easier handling and better open-steam curing characteristics. It also allows use of a wider range of extrusion temperatures and roll speeds for smooth extrusion leading to increased productivity. The superior processing quality and better extrusion properties of SP rubber [38] can also be imparted to synthetic rubbers like ethylene-propylene-diene terpolymer (EPDM) by blending in suitable proportions [39].

2.10 Properties of natural rubber

Natural rubber is a high molecular weight polymer having the chemical structure, *cis*-1,4 polyisoprene. The raw rubber contains, in addition to the rubber hydrocarbon, small quantities of proteins, fats, fatty acids, carbohydrates, mineral matter. The rubber hydrocarbon content is about 94%. The physical and chemical properties of the rubber are influenced by the presence of the non-rubber substances. The properties of NR depend very much upon the degree of crosslinking. Therefore, the important properties of the raw and vulcanised rubber are discussed separately.

2.10.1 Raw rubber

Being a linear long chain polymer, NR is composed of molecules of different sizes. The weight average molecular weight ($\overline{M}_w$) of NR ranges from 30,000 to about 10 million. A random blend would have an $\overline{M}_w$ of about 2×10^6 and a number average weight ($\overline{M}_n$) of 5×10^5. Subramaniam [40] demonstrated that the molecular weight distribution (MWD) of unmasticated NR is distinctly bimodal. The clonal variation in molecular weight and MWD was also studied by Subramaniam [41]. A small portion of the rubber undergoes crosslinking even in the latex present within the latex vessels of the tree. The usual concentration of this microgel is 7–30% and influences the melt viscosity of the rubber. The gel content of raw NR which has been stored for some time is much higher and is known as macrogel, and is responsible for the increased viscosity during storage. The presence of certain active chemical groups such as carbonyl groups on the rubber chain is believed to cause formation of branched chains. Mastication reduces the gel content. The rheological properties of NR are strongly influenced by long chain branching. The slow rate of stress relaxation of *Hevea* rubber compared to guayule and synthetic polyisoprene rubber has been attributed to chain branching [42].

Storage of NR at subzero temperatures causes stiffening of the rubber and the maximum rate of crystallisation occurs at –24 °C. Such stiffened rubber requires thawing at 40–50 °C before processing. The temperature at which the last traces of crystallinity disappears is described as the melting temperature, T_m. Although a value of 28 °C has been assigned for the T_m of NR, values of 30 °C and higher depending on storage temperature and duration, have been occasionally reported.

All polymeric materials will, at some temperature, undergo a glass transition (T_g), and change from a glassy to a rubbery state. Specific volume measurements on NR have established a T_g of –72 °C. While carbon black has relatively little influence on T_g of NR, plasticisers depress it considerably and crosslinking increases it.

2.10.1.1 Processing properties

The processing characteristics of NR are considered to be excellent. Although it is tough and nervy at temperatures below 100 °C, it breaks down easily to a workable viscosity. The normal fabrication techniques can easily be adopted for NR. Although premastication is not required for the viscosity stabilised grades, mastication is commonly practised for the normal grades. The efficiency of mastication is temperature dependent and is the least at around 100 °C [43]. Chemical peptisers allow mastication to be carried out at lower temperatures and are useful for increasing the efficiency of mastication. Rubbers with high initial viscosity tend to break down faster mostly due to the high shearing forces realised. The break down behaviour also depends on the plasticity retention index (PRI) of the rubbers and it is generally found that latex grades with high PRI values break down more slowly than field coagulum grades. It is observed that because of the faster break down behaviour of NR compared to SBR, the average viscosity of a NR mix during mixing is lower than that of a similar SBR mix, although the initial viscosity is much higher for NR. This leads to lower energy consumption for mixing the NR compound.

The batch viscosity is the main factor controlling die swell and the stress developed while extruding a fully mixed compound. Thus viscosity is a useful guide to assess the processing behaviour of masticated rubbers. A masticated rubber has better extrusion properties than an unmasticated rubber of the same viscosity.

The most important aspects of processability of NR are its high inherent tack and green strength. These two characteristics are of utmost importance in the manufacture of products such as tyres. Tack is important as it holds the compounds of green tyre together until moulding. Green strength is needed so that the uncured tyre will not creep and hence distort excessively before moulding or tear during the expansion that occurs upon moulding. A practical definition of tack is the ability of two similar materials to resist separation after they are brought into contact for a short time under a light pressure. The higher tack of NR compared to SBR has been attributed to its greater ability to flow under compressive load and its higher green strength. NR is an ideal material for developing high tack. It can be processed to a low viscosity and still maintain high green strength. Furthermore, the mechanism responsible for high green strength is strain crystallisation which is not active in the bond formation stage and hence does not interfere with contact and interdiffusion, but rather develops upon stretching.

2.10.2 Vulcanised rubber

The physical properties of vulcanised natural rubber are dependent on several factors such as degree and type of crosslinking, type and amount of fillers, degree of filler dispersion and presence of plasticisers. Some of the important properties of vulcanised NR are discussed in the following sections.

2.10.2.1 Strength

As in the case of other engineering materials, strength properties are of great importance in most of the practical applications of rubber. Many of these properties can be defined and measured. The most widely measured among these are tensile strength, tear strength and resistance to fatigue.

Perhaps the most striking characteristic of NR, compared with most synthetic elastomers is its high tensile strength even without the help of any reinforcing agent. This is undoubtedly due to its ability to undergo strain-induced crystallisation. The tensile strength of NR vulcanisates frequently exceeds 30 MPa, which is almost ten times the values reported for gum vulcanisates of non-crystallising rubbers such as styrene butadiene rubber (SBR) under similar test conditions. The effect of reinforcing fillers on the tensile strength of NR vulcanisates is not as significant as in the case of non-crystallising rubbers. Temperature is found to influence the tensile strength of NR gum vulcanisates significantly and there is a critical temperature of around 100 °C, above which the strength falls abruptly, crystallisation being suppressed at that temperature. However, tensile strength of filler-reinforced NR vulcanisates is found to be less temperature dependent. Strength of NR is also characterised in terms of tear resistance. Over wide ranges, the catastrophic tearing energy is insensitive to rate and temperature for a crystallising rubber like NR [44]. It appears that in such materials the effect of crystallisation which can induce substantial hysteresis at high strains, overshadows viscoelastic effects. It is also observed that tear resistance is greatly increased by reinforcing fillers.

2.10.2.2 Resistance to abrasion

The mechanisms by which abrasion occurs when a rubber is in moving contact with any surface are somewhat complex, involving principally, cutting of the rubber and fatigue. These mechanisms have been reviewed by Gent and Pulford [45]. It is generally accepted that some of the synthetic rubbers such as SBR and BR are superior to NR in abrasion resistance. However, it may be pointed out that the relative wear rating of compounds depends on the nature of the track as well as load. On smooth surfaces SBR is superior to

NR, but on increasing roughness the difference between the two is reduced and reversal of ranking can be observed. Tyre surface temperature is another important factor influencing the relative wear rating of NR and SBR. At low tyre surface temperature, as encountered during winter, NR is superior. At high surface temperature the reverse is true, the reversal occurring at about 35 °C.

2.10.2.3 Resistance to skidding

This is important in applications such as tyre tread. In tread compounds of the same hardness, skid resistance depends on viscoelastic properties. The highly resilient NR compounds show lower skid resistance than SBR compounds at temperatures above 0 °C. The wet skid resistance of NR above 0 °C can be improved by extending with oil. Treads from OENR are as good as oil extended styrene-butadiene rubber (OESBR) on wet roads and are superior on icy roads [46]. OENR blended with butadiene rubber is most suitable for treads of winter tyres.

2.10.2.4 Dynamic properties

The crack growth behaviour and fatigue of rubber vulcanisates are intimately related. The strain dependence of fatigue life of different elastomers vary widely. NR is very good at high strains, compared with non-crystallising elastomers. The difference is more pronounced under non-relaxing conditions. For a crystallising rubber, the much larger enhancement is attributed also to an effective increase on the threshold energy required for crack initiation and a reduction in the rate of growth once the threshold energy is exceeded. It is also known that the threshold energy for NR increases substantially if atmospheric oxygen is excluded and/or if certain antioxidants are incorporated in the compound. This behaviour is reflected in enhanced life, particularly in the region of the fatigue limit, that is the strain below which the fatigue life of elastomers is very long.

Frequency of deformation is found to have very little influence on the fatigue life of NR vulcanisates. The effect of temperature on crack growth and fatigue is also found to be much less for NR than for non-crystallising elastomers. Resistance to crack growth can be increased by fine particle size fillers, the effect being attributable to blunting of the crack tip due to branching. The resilience of NR vulcanisates is very high, with values exceeding 90% in well-cured gum vulcanisates. However, the values, in general, are 1–2% lower than those of synthetic *cis*-1,4 polyisoprene, the difference being attributed to the presence of proteins in NR. In carbon black-filled vulcanisates the difference is negligible. Good resistance to flexing and fatigue together with high resilience makes NR useful in applications where cyclic stressing is involved.

2.10.2.5 Creep, stress relaxation and set

One of the notable features of NR, compared with most other elastomers, is its good elastic behaviour. This means low creep and low stress relaxation. If the stress relaxation rate is expressed as per cent stress relaxation per decade of time, a typical NR gum vulcanisate may give a value of about 2% per decade. If carbon black is present, the rate will be higher, about 7% per decade for a 70 IRHD rubber containing 50 phr of a non-reinforcing black. However, pre-stressing of such a filled rubber can reduce the stress relaxation rate to little more than the gum value. This superior elastic behaviour of NR is a consequence of the high mobility of the molecules, which is also reflected in the relatively low glass transition temperature. Stress relaxation rates are substantially independent of the type or amount of deformation, but creep rates depend on both the rate of stress relaxation and the load-deflection characteristics. In tension the creep rate may reach double the rate of stress relaxation. In shear it is about the same and on compression it is lower.

Measurement of set under compression provides a practical evaluation of either the creep or the stress relaxation of rubber and has been very useful for those purposes where a high degree of precision is not required. Compression set and creep are poorer in NR than in synthetic polyisoprene. This is mostly due to the presence of non-rubber constituents. In this respect DPNR is found to be better than the normal grades of NR. A high state of cure is found to reduce set. Creep, stress relaxation and set are important in load bearing applications such as springs. Partly because of this NR is the most widely used rubber in this field.

2.10.2.6 Resistance to ageing

Being an unsaturated polymer, NR is highly susceptible to degradation by oxygen, ozone, radiation, heat and chemicals. The naturally occurring antioxidants present in the rubber protect it from degradation during coagulation and subsequent processing and drying of the coagulum and also during storage. These antioxidants are partially lost and/or used up during further processing and hence additional antidegradants are needed to ensure adequate service life of end products. The changes occurring during degradation of rubber include chain scission, crosslinking and introduction of new chemical groups. Natural rubber degrades mostly by chain scission, resulting in a weak softened stock, often showing surface tackiness.

Oxygen is considered to be the most powerful degradant for NR. A small amount of 1–2% of combined oxygen in rubber serves to render it useless for most applications. The oxidation of rubber is believed to take place through a free-radical chain reaction. In order to prevent extensive degradation of rubber, it is necessary to interrupt the chain reaction and stop autocatalysis. This could be accomplished by either terminating the free radicals or by decomposing the peroxides into harmless products. Antioxidants, in fact, function this way. Amine antioxidants act both by reacting with free radicals and by decomposing peroxides. Phenolic antioxidants, on the other hand, react primarily as free radical sinks or chain stoppers. Phosphites react readily with free peroxides. The attack by oxygen on raw rubber is different from that on vulcanised rubber. In the former case an initial induction period is followed by rapid uptake of oxygen. With vulcanised rubber, there is no induction period and oxygen uptake is essentially linear with time. The net result of oxygen attack on NR is an overall decrease in all properties [47]. Heavy metal ions such as copper, manganese and iron and peroxides catalyse oxidative ageing of rubber and these are called pro-oxidants. Some of the standard antioxidants, notably the aromatic diamines are effective against metal catalysed oxidation of rubber. The effect of heat and oxygen on rubber are never separated and the practical result of heat ageing on rubber is a combination of crosslinking and an increase in the rate of oxidation.

Ozone reacts readily with NR and the effect manifests itself as cracks on the surface perpendicular to the direction of stress and as a silvery film on the surface in unstressed rubber. The mechanism of ozone attack is thought to involve the reaction of ozone with the double bonds in rubber to form ozonides. These are easily decomposed to break the double bond, and under strain, cracks appear which become deeper as the reaction proceeds. Two factors influencing the rate of ozone cracking are ozone concentration and the strain in the rubber. Protection of NR stocks from ozone cracking is accomplished using antiozonants. Under static conditions physical antiozonants such as wax which forms a surface bloom can be used. Under dynamic conditions, waxes are unsuitable and hence, chemical antiozonants are employed. Blending of NR with a more saturated rubber such as EPDM has also been found to be effective in protecting NR from ozone attack [48].

Some of the important physical constants of unvulcanised and vulcanised NR are summarised in Table 2.7.

2.11 Vulcanisation

Compounding is the process of formulating NR for its final application. Vulcanisation is the most important aspect of NR processing. This is generally achieved by reaction with sulphur and accelerators at an elevated temperature. Vulcanisation transforms the linear polymer into a three-dimensional macromolecule by the insertion of a relatively few crosslinks between the polymer chains. Other aspects of compounding include incorporation of additives to protect rubber from degradation, addition of fillers to reinforce the rubber and to reduce cost, addition of oils to improve processing. Some of the requirements can

Table 2.7 Physical constants of natural rubber*

Property	Unvulcanised	Pure gum vulcanisate
Density, $Mg.m^{-3}$	0.913 (0.906–0.916)	0.970 (0.920–1.000)
Coefficient of volume expansion, $\beta = (I/V)\ (\delta V / \delta T),\ (°C)^{-1}$	670×10^{-6}	660×10^{-6}
Glass transition temperature, °C	–72 (–74 to –69)	–63 (–72 to –61)
Specific heat, Cp, $Cal.g^{-1}\ (°C)^{-1}$	0.449	0.437
Thermal conductivity, $W.m^{-1}\ (°C)^{-1}$	0.134	0.153
Heat of combustion, $J\ kg^{-1}$	4.52×10^6	4.44×10^6
Equilibrium melting temperature, °C	28	
Heat of fusion of crystal, $kJ.kg^{-1}$	64.0	
Refractive index, n_D	1.5191	1.5264
Dieletric constant (1 kHz)	2.37–2.45	2.68
Dissipation factor (1 kHz)	0.001–0.003	0.002–0.04

** The figure in parentheses indicate the range*

even be conflicting and hence it is often necessary to arrive at a compromise. Over the last few decades considerable progress has been achieved in understanding the science of compounding NR, which has been reviewed by Crowther *et al* [49].

2.11.1 Vulcanisation with sulphur

As per the generally accepted mechanism of reaction of sulphur with NR, the first step is the formation of an active sulphurating agent from sulphur, accelerators and activators [50]. After abstracting a hydrogen atom from the rubber, a polysulphidic rubber-bound intermediate is formed which initially forms polysulphidic crosslinks. The polysulphide in the crosslinks and network-bound accelerator fragments shorten at a rate depending on the ratio of sulphur to accelerator, the cure temperature and time. Vulcanisation systems using a high ratio of accelerator to sulphur which give predominantly monosulphidic crosslinks are called efficient vulcanisation (EV) systems. Those using low ratio are known as conventional vulcanisation systems. A compromise between the two systems is also used as a semi-EV system.

The structure of the crosslinks and the extent and type of main chain modifications have important effects on the physical properties of a vulcanisate. High levels of polysulphidic crosslinks confer high tensile and tear strength particularly in unfilled vulcanisates. High resistance to fatigue is also obtained together with high resilience and high elastic recovery at ambient temperature. However, resistance to heat and oxidation is limited as is resistance to set at elevated temperatures. In contrast, monosulphidic crosslinks give rise to high thermal stability and resistance to oxidation and reversion. However, EV vulcanisates possess marginally reduced strength, but exhibit substantially improved resistance to creep, stress relaxation and set at elevated temperature. The rate of low temperature crystallisation of such vulcanisates is higher than that of conventional vulcanisates, due to the low level of main chain modification.

2.11.2 Non-sulphur vulcanisation

These systems are reviewed by Kemperman [51] and are of far less industrial significance. Of the many systems investigated, only two have achieved practical significance, vulcanisation with organic peroxides and urethane. Vulcanisation by organic peroxides such as dicumyl peroxide, is a free radical process. The effective crosslinking can take place in the complete absence of oxygen, otherwise peroxy radicals would be formed leading to the oxidation of the rubber. Peroxide vulcanisation is, therefore, limited to products made by press moulding. The structure of peroxide vulcanisate is relatively simple compared with that of a sulphur vulcanisate, as rubber chains are crosslinked by simple carbon-carbon linkages, which are highly stable towards heat. Therefore, these vulcanisates possess extremely good thermal ageing characteristics, superior to those of even EV systems, and also lower compression set at elevated temperature. However, fatigue resistance and resistance to low temperature crystallisation are low. Another major disadvantage of the peroxide system is its lack of processing safety.

Urethane vulcanising systems available under the trade name Novor, developed by Baker [52] are now being used in a variety of applications, particularly in those demanding high temperature vulcanisation and service. The crosslinks formed are mainly of the urea-urea type. The principal benefits of these systems are outstanding reversion resistance and good ageing resistance, coupled with good physical properties. It is also possible to use these systems in combination with sulphur vulcanisation to give a range of systems designed to vary in cost, cure behaviour and properties.

2.12 Applications

Natural rubber is a general purpose elastomer. Its high resilience, low heat build-up and excellent dynamic properties coupled with outstanding processability, make it an ideal rubber for automotive tyres. Therefore, it is no surprise that around 55% of all the NR is used in tyres. The major non-tyre applications include beltings, hoses, cycle tyres, footwear, engineering products, latex products such as dipped goods, rubber backed carpets and adhesives. Consumption of NR in major countries is shown in Table 2.2.

Since the development of synthetic rubbers and their large-scale production since the 1939–1945 World War, the share of NR in the total elastomer consumption decreased from 100% in 1940 to almost 30% in 1978. However, its share has increased since then and at present is nearly 40%. This increase is mostly attributed to the large-scale switch over to radial tyre construction in the major rubber consuming countries. A higher proportion of NR is necessary in the manufacture of radial tyres. The increase in the relative price of synthetic rubbers compared to NR has also contributed to the increase in the share of NR in the overall elastomer consumption.

2.12.1 Tyres (see also Chapter 11)

Use of NR is preferred in tyres because of its high strength combined with high elasticity and outstanding tack and green strength. The repeated deformation of a tyre as it runs, together with distortion arising from acceleration, braking and particularly cornering, causes energy dissipation in the tyre because of imperfect elasticity. This leads to considerable temperature rise, which is naturally higher in the interior of the tyre and increases with increasing tyre size. Damage caused by overheating is generally separation between carcass and tread and constitutes catastrophic failure. At high temperatures, maintenance of adhesion between the plies of carcass and breaker (restraining belt of rubber and reinforcing fabric, placed around the edge of a tyre carcass to provide increased lateral stiffness and improved control and steering properties to an otherwise flexible radial tyre) and to the adjacent parts of the tyre is very important. This and the excellent tack of NR are the main reasons for the use of at least a portion of NR in the carcass. Generally a blend of NR and SBR is used in the carcass of a passenger tyre, the proportion of NR in radial tyre carcass being higher. To keep heat generation within acceptable limits, the rubber in carcass and breaker must have high resilience. In current practice a minimum of 30% NR is used in the carcass of radial passenger tyres. The formulation of carcass rubbers appears to be a compromise between technical and economic considerations. The carcass of truck tyres contains more NR and the proportion varies between 50 and 100%. The rubber in the carcass of earthmover and other giant tyres is almost exclusively NR. Aircraft tyres carry a heavy load for their size and suffer severe service conditions, especially when landing and hence their carcass is almost entirely NR.

In a tyre, sidewalls are the most strained elements and are susceptible to flex cracking and ozone cracking. The sidewalls of radial tyres flex more than those of bias ply tyres and their formulation must take account of this fact. The flex-cracking behaviour of NR is better than SBR at higher strains and therefore, sidewalls of radial tyres incorporate substantial proportions of NR.

The main requirements for treads are resistance to wear, to skidding on wet and icy surfaces and to groove cracking at the bottom of the tread profile. The thick treads of truck tyres contribute very well to heat build-up and impose an additional condition on the choice of rubber. Tread wear depends on the ambient temperature and on the severity of service and magnitudes of these two factors depend on the tread material. NR treads wear less than SBR treads at low temperature. However, when the overall tread wear ratings are considered, NR is inferior to SBR. However, blends of OENR and BR are found to be competitive with SBR-based treads of passenger tyres. Truck tyres and off-the-road tyres are exposed to coarse mechanical damage, in which large chunks of tread are torn and removed. Resistance to this type of chipping and chunking calls for high resistance to tear which can be met only by NR. The proportion of NR in the treads of large commercial tyres increases with size and roughness of service and treads made entirely of NR are not uncommon. Treads of aircraft tyres are made entirely from NR. Skid resistance of tyres is important for safety. On wet roads, skid resistance increases with the hysteresis of the tread compound and for this SBR has been preferred to NR in passenger tyres. Here again oil extension has greatly improved the position of NR and NR/BR blends. On icy roads skid resistance of NR is better than that of synthetic rubbers. The low skid resistance in combination with high wear resistance of NR at low temperature, makes OENR particularly suitable for winter tyres.

2.12.2 Engineering applications

Most engineering applications of NR involve its use as a spring. The main reasons for using NR in springs are:

1. Excellent resistance to fatigue, cut growth and tearing,

2. High resilience,

3. Low creep,

4. Low heat build-up,

5. Reasonably good bonding with metals/fibres,
6. Wide temperature range of use,
7. Low cost, and
8. Good processability.

In comparison with metal springs, NR springs require no maintenance, have high energy storage capacity and non-linear load deflection characteristics, can accommodate a certain amount of misalignment and are easier to install. Although NR is highly resilient, the small amount of inherent hysteresis serves to dampen resonant vibrations. The typical engineering applications of NR include antivibration mountings, flexible couplings, bridge bearings, bearings for buildings for protection from earthquakes, dock fenders and rail pads.

2.12.3 Conveyor beltings

Top grade conveyor beltings can be made from NR except for those used in underground mines (problems of inflammability). In belt manufacture good tack and adhesion are very important. Good control of compound viscosity is also important in the proper compaction of the belt carcass. In service, NR offers reasonably good resistance to wear and chipping by such abrasive materials as stone, coal and ores. For moderate heat resistance NR is blended with SBR.

2.12.4 Linings

Linings based on NR are ideal for protection against corrosion and abrasion of chemical plant. NR is resistant to most inorganic acids, salts and alkalies except the concentrated materials and is widely used for linings of tanks, especially those containing caustic solutions. Soft linings from NR are highly resistant to abrasion, even better than mild steel in that respect and hence are ideal for equipment used for handling slurries and sand blasting.

Thus NR is an ideal elastomer suitable for most general purpose and engineering applications. However, the most important aspect of NR is that it is environmentally friendly. It is a product of nature and the energy requirement for its production is only a small fraction of that required for synthetic rubbers [53]. While production of synthetic rubber causes large-scale pollution including release of large quantities of carbon into the atmosphere, production of NR starts with fixing up of the carbon from the atmosphere. Therefore, use of NR has a definite positive impact on the environment.

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3 Synthetic Elastomers

S. Datta

3.1 Synthetic and natural elastomers

3.1.1 Synthesis

The worldwide capacity (see Table 3.1) for all synthetic elastomers is about 13,000 kilotonnes per year and is comparable to natural rubber which is estimated to be 17,000 kilotonnes per year. Elastomers such as butadiene rubber (BR), isoprene rubber (IR), ethylene propylene rubber (EPM)/EPDM, styrene-butadiene rubber (SBR), halogenated isobutylene isoprene rubber/chlorinated IIR (BIIR/CIIR) and styrene-butadiene-styrene block copolymer (SBS) comprise a majority of this volume. This capacity is evenly distributed between solution polymerisation and emulsion polymerisation. These synthetic processes are suited for both efficient removal of heat of polymerisation as well as isolation of the elastomer without residues. The solution process is also used for the modification of elastomers in an organic solvent.

The recent growth in synthetic elastomers made in solution reflects some inherent advantages for this compared to bulk processes such as slurry polymerisation. Solution polymerisation leads to a) greater control of both intermolecular and intramolecular composition, b) attenuation of competing intermolecular reactions, e.g., branching, c) easier removal of catalyst residues, d) easier diffusion of monomers for elastomers with high melting point (T_m), high glass transition temperature (T_g) or very high bulk viscosities and e) easier removal of the heat of polymerisation. Chemical modification of elastomers is almost exclusively conducted in solution or emulsion. Notable examples are chlorination of polyethylene (PE), bromination of IIR, hydrogenation of NBR and hydrogenation of SBS. In addition to the preceding reasons, solution and emulsion procedures are used here for uniform (intra and intermolecular) reactions of the polymer.

Another conclusion from the description of synthetic elastomers is that the usage is closely governed by the price. The price of common elastomers spans the range of \$1.10 to \$550/kg. There is sharp decrease in the volume for elastomers at prices greater than approximately \$2.20/kg. This is indicated by the shaded row in Table 3.1. Elastomers below this delineation are specialty polymers.

Table 3.1 Worldwide capacity for major elastomers in kilotonnes

Elastomer	Capacity, kt per year
NR (for comparison)	5,500,000 trees
Polybutadiene	2600
Polyisoprene	1500
Ethylene-propylene polymers	1150
Styrene-butadiene rubber	5300
Styrene block copolymers	650
Halobutyl rubber	315
Butyl rubber	800
Ethylene-olefin plastomers	300
Epichlorohydrin rubbers (and propylene oxide)	11
Chlorosulphonated PE	35
Trans-cyclooctenamer	2.5
Chlorinated PE	20
Polychloroprene	310
Nitrile rubber	280
Hydrogenated nitrile rubber	40
Acrylate rubbers	75
Thermoplastic polyurethane	80

3.1.2 Mechanical properties

According to ASTM D1566 [1] the term 'elastomer' describes a material that exhibits quick and forcible recovery of most of its original dimensions after extension or compression and can be vulcanised. Early pioneers such as Staudinger [2, 3] showed that this mechanical property was due to cross-linked, long-chain, flexible polymer molecules. When such a material is stretched, the individual molecules partially uncoil, but retract when the force is removed. The flexibility arises from ability of the atoms in the polymer backbone chain to rotate around single bonds.

Elastomer properties are also influenced by the presence of intermolecular forces leading to crystallisation. An important class of elastomers are those which can temporarily crystallise at a high elongation but retract to their original dimension in non-crystalline form when the force is removed. Such 'strain-crystallising rubbers' demonstrate unusually high tensile strength though they are soft and rubbery in the undeformed state. In addition the properties of elastomers are also affected by the T_g. Below T_g all intramolecular motion is inhibited and the elastomer properties are significantly reduced. In summary, the best synthetic elastomers are those with a molecular design such that while they are not crystalline under ambient conditions they do undergo stress crystallisation and have a T_g much below the use temperature of the elastomer.

3.1.3 The need for synthetic elastomers

A wide variety of synthetic elastomers have been developed to overcome some of the performance deficiencies of natural rubber (NR). Some of these deficiencies are i) poor resistance to light, oxygen and ozone weathering, ii) poor heat resistance, iii) poor resistance to organic fluids. In addition synthetic elastomers have supplanted many of the applications of NR since the properties of NR cannot be modified. An example of this is the partial replacement of NR by BR in sidewalls of tyres since the latter offers lower rolling resistance. Similarly, treads of tyres are made with SBR since they last longer than treads made with NR.

There are four distinct and important tools in matching the structure of the synthetic elastomer to its intended use. These are:

1. composition of the elastomer,
2. the micro structure and orientation of the monomers,
3. the use of a combination of monomers, and
4. segregation of the different monomers into portions of a single chain (block co-polymers).

The use of the composition of the synthetic elastomer as a tool in matching the properties of the polymer is shown in Figure 3.1. Two of the most important properties of elastomers are the ability to withstand weathering due to oxygen, ozone and light as well as the ability to withstand organic fluids. Figure 3.1 shows graphically the weathering resistance of a variety of synthetic elastomers. Elastomers with a saturated backbone are more resistant to weathering than those that are unsaturated. Thus EPM is significantly better than BR or NR. The ultimate weathering is for elastomers where the C-C backbone is

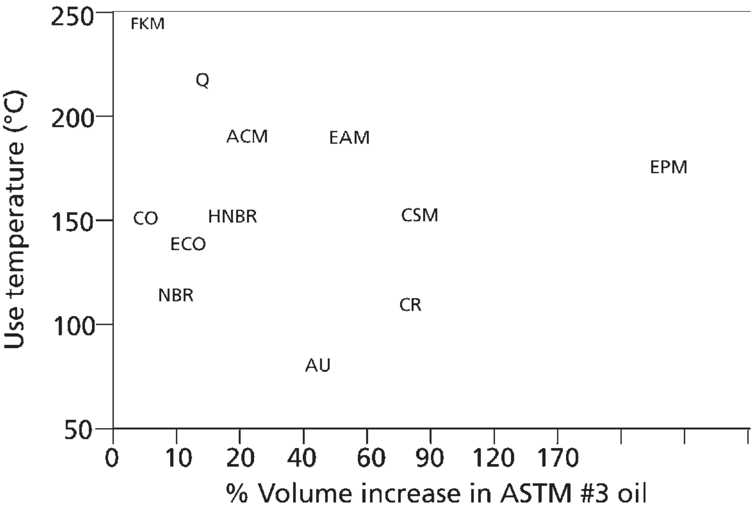


Figure 3.1 Weathering and fluid resistance of elastomers (see Abbreviations and Acronyms (p.549) for materials codes)

replaced with the Si-O-Si backbone of the Q elastomers. Figure 3.1 also shows the ordering of these elastomers with respect to resistance to organic solvents. Elastomers with strong polarity are more resistant to apolar organic fluids and oils than those that are composed entyrely of hydrocarbons. Thus NBR, acrylic rubber (ACM) and fluorinated rubber (FKM) are more solvent resistant than SBR, EPDM or IIR. Chlorinated polymers, such as CR, which are intermediate in polarity are intermediate between these extremes. The use of NR alone does not allow such a wide change in the properties of the vulcanisates.

The microstructure and the orientation of the monomer units in the synthetic elastomer can be altered by the choice of the reaction conditions and catalysts. NR exists as a single, naturally derived isomer. The manipulation of the properties of NR by changes in the stereochemistry is impossible. *Cis*-1,4 isoprene rubber (IR) is the synthetic analogue of NR while its isomeric form *trans*-1,4 IR is a tough, semicrystalline polymer. IR polymers containing intermediate amounts of these isomers display intermediate properties. A similar example is the difference between isotactic and atactic polypropylene. These isomers differ in the stereochemical orientation of the methyl group on the propylene monomer. The former is a thermoplastic while the latter can be used as an elastomer. In general, the ability of a polymer to exhibit elastomeric properties depends on the flexibility of rotation around the backbone. Rigid, stereo chemical isomers prevent this and often crystallise in ordered crystals: this prevents these polymers from exhibiting elastomeric properties.

In contrast to NR which is a homopolymer of isoprene, most synthetic elastomers contain two or more monomers. EPM which contains ethylene and propylene and SBR which contains styrene and butadiene are examples. The mixture of monomers is used either to lower the T_g (for SBR) or the crystallinity (for EPM). In addition, the presence of the two monomers allows a tailoring of the properties of the synthetic elastomer that cannot be attempted with homopolymers such as NR. Normally the two monomers are randomly mixed in the copolymer, however the presence of two monomers also allows a geometrical isomerisation where they are segregated into different sections of the copolymer backbone. These sections may be small portions of the chain of several monomers in length as in thermoplastic polyurethane elastomers (TPU-E) or sections which are several hundred monomer units long as in SBS. These segregated copolymers ('block co-polymers') show unexpected elastomeric properties such as extreme elongation (>1000%) and excellent tensile strength even when unvulcanised. An example of this is the difference in the mechanical properties of SBS, a block co-polymer, and SBR, the corresponding random copolymer, composed of the same monomer units in essentially the same ratio. This segregation in structure is possible because of the corresponding segregated polymerisation process where one monomer is added in preference to the other. These architectural details of the elastomers are important in fulfilling the needs of particular applications and are impossible for NR where neither the selection of the monomer nor the polymerisation condition can be altered.

3.1.4 Compounding and vulcanisation

Vulcanisation of elastomers is a chemical reaction leading to crosslinked macromolecular chains. Elastomers are vulcanised after compounding with fillers, plasticisers, curatives, accelerators and minor amounts of antioxidants and flow improvers. The vulcanisation reaction is conducted by heating the formed or extruded rubber part to a temperature such that the crosslinking reaction initiates. Most synthetic elastomers have specific curing sites, formed by the introduction of a special monomer, where the crosslinking occurs. These special monomers include isoprene for IIR, halogens for HIIR, diene for EPDM and alkenoic acids for ethylene acrylate rubber (EAM). Since the amount of crosslinking sites are limited, the conditions and chemistry for crosslinking are typically more severe for synthetic elastomers than NR. The reaction conditions are maintained until a significant extent of the crosslink density is achieved before the temperature is lowered. Press cure, transfer moulding, steam cure, hot-air cure, and injection moulding are acceptable methods of curing.

3.1.5 Synthetic elastomer polymerisation

Synthetic elastomers are mostly made by addition polymerisation where individual monomers are incorporated into a growing polymer chain. Polymer chains which terminate can almost never reparticipate in the polymerisation. A feature of this type of polymerisation is that the average molecular weight of the elastomer does not change during the course of the polymerisation. The alternate is step growth polymerisation where individual monomer molecules are incorporated into small prepolymer units which are dormant for a while and then assemble into high molecular weight polymers. Several intermediate molecular weight polymers often exist simultaneously and the average molecular weight increases continuously during polymerisation. Polysulphide rubber (TM), polyurethane rubber (AU), and polysiloxane rubber (Q) are examples of polymers obtained by condensation polymerisation. In all of these polymerisations, multifunctional compounds react to form elastomers. If bifunctional compounds are used exclusively, linear molecules result. The presence of at least one trifunctional component per macromolecule yields branched or crosslinked elastomers (see Figure 3.2).

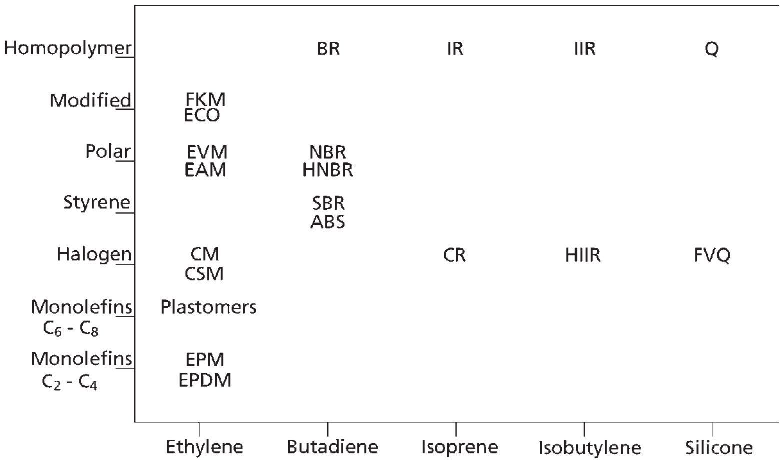


Figure 3.2 Composition map of major elastomers
EVM: ethylene-vinyl acetate rubber. CM: post chlorinated PE

Copolymerisation of two or more monomers can lead to several geometric isomers of the same polymer, giving rise to variations of the three limiting cases:

a) alternating polymerisation - the two types of monomer units alternate in the polymer chain until the monomer in the minor concentration is exhausted,

b) statistical polymerisation - the two monomers enter into a polymer chain in a statistically random manner with their average concentration in the chain corresponding to their feed ratio, and

c) block polymerisation - complete polymerisation of one monomer prior to polymerisation of the second. Only in statistical polymerisations do reactivity ratios and concentrations of both monomers determine the average chemical composition, the average sequence length, and sequence distribution of the monomers.

3.1.6 Mechanisms

There are several processes for the production of synthetic elastomers. These are:

i) Free radical polymerisation,

ii) Ionic polymerisation,

iii) Coordination or metal complex polymerisation.

In free radical polymerisations heat, light or electrochemical reactions produce free radical generators (initiators) from molecules added to the monomer for this purpose. The best chemical initiators are formed by the decomposition of peroxides, hydroperoxides, or azo compounds. The most frequently used electrochemical initiators are redox-systems, where the reaction of a reducing and oxidising agent forms free radicals. After initiation of the polymerisation, the propagation step occurs, where the polymer chain grows through stepwise addition of monomer molecules, until the chain is terminated. The growing polymer chain can react with other molecules, ('chain transfer agents'), which are also present, to start new chains. The polymer radical becomes deactivated, and a chain transfer radical forms, which, in turn, starts a new monomer radical and thus a new polymer chain. Alcohols, alkyl halides, mercaptans, and xanthogen disulphide are examples of practical chain modifiers.

Anions or cations, as opposed to free radicals, are used as chain initiators in ionic polymerisation. In ionic polymerisation, there is a transfer of charge from the initiator ion to the monomer. Therefore, positively or negatively charged initiator ions result in cationic or anionic polymerisations, respectively. A cationic polymerisation can be initiated by *Bronsted* or *Lewis* acids, e.g., $AlCl_3$, BF_3, $C_2H_5AlCl_2$. For anionic polymerisations, initiators such as alkyl lithium compounds are used. The activation energies for the initiation and polymerisation reactions are often small and ionic polymerisations can often be conducted at low temperatures. The extent of formation of the dissociated initiator, and thus its efficiency, is dictated by the dielectric constant of the solvent. Chain transfer or termination is the principal feature of ionic polymerisation which limits molecular weight of the elastomer. However, at low polymerisation temperatures for cationic polymerisation or for ambient conditions for anionic polymerisation these chain transfer or termination processes do not occur. Thus, very narrow molecular weight distributions can be obtained.

A particular case of coordination polymerisation is commonly known as anionic polymerisation. This is mostly used for the polymerisation of conjugated dienes and styrenes. These polymerisations are initiated by a carbon centred organic anion of an alkali metal. Polymerisation proceeds by step wise addition of the diene to the anion which always leaves the growing terminus as an anion coordinated to the alkali metal cation. Homopolymers and copolymers of styrene and 1,3 dienes are made by this procedure. A recent innovation has been living anionic polymerisation. Under carefully selected polymerisation conditions where the initiation of polymerisation is instantaneous and all termination pathways are supressed the polymerisation leads to intermolecular uniform polymers, similar in both composition and molecular weight ($M_w/M_n \approx 1$). However, the intra molecular composition can be changed by modifying the composition of the monomers during polymerisation. These techniques lead to formation of styrene butadiene block polymers [4, 5].

In coordination polymerisation reactions, the initiator exists as a metal centred complex attached to the polymer chain and the polymerisation progresses by insertion of new monomer molecules into this complex. The most common initiators for these insertion reactions are the Ziegler-Natta catalysts. These are reaction products of aluminum alkyl halides with transition metal salts of Group IV to VIII elements. Since a monomer unit enters the polymer chain in a stearically controlled coordination, stearically and geometrically regular polymers are obtained with coordination catalysts. Thus in the polymerisation of butadiene, pure *cis*-1,4, *trans*-1,4, or 1,2 microstructures can be made.

3.1.7 Polymer synthesis processes

There are several processes for the production of synthetic elastomers. These are

i) Emulsion,

ii) Bulk,

iii) Solution, and

iv) Suspension.

Emulsion polymerisation is primarily used in free radical chain polymerisation. At least four components are required here: water insoluble monomers, water, emulsifiers, and water soluble initiators in addition to chain modifiers and polymerisation stoppers. The emulsifier causes the monomer to be emulsified into small droplets which aggregate into micelles. Initiator radicals react with the monomer in the micelles. The micelles grow larger by absorbing new monomer from the surroundings to form a latex. Emulsion polymerisation leads to very high conversion of monomer since the termination reactions are avoided. In comparison with homogeneous polymerisation processes emulsion polymerisation provides the following: a) water is efficient at dissipating the heat of polymerisation, b) viscosity is independent of the molecular weight of the polymer leading to elastomers with very high molecular weight and c) polymerisation can be conducted in simple reaction vessels. Although originally developed for use of peroxide initiators (reaction temperature >100 °C) to form 'hot polymers' the use of redox initiators at low polymerisation temperatures (near room temperature) has led to more uniform and thus, more valuable, 'cold polymers.'

In bulk polymerisation, the polymerisation takes place in the pure, liquid monomer as reaction medium. The heat of polymerisation is dissipated through external or evaporative cooling. The first synthetic BR elastomers were made by bulk polymerisation.

In polymerisation, the monomer is dissolved in an organic solvent. After initiation of the polymerisation reaction, the viscosity of the reaction medium rises with the degree of polymerisation, and this limits the extent of chain growth.

Suspension polymerisation is carried out using a liquid monomer as the solvent. However, in contrast to bulk polymerisation, the resulting polymer is insoluble in the monomer, and precipitates as a suspension in the reaction medium. In suspension polymerisation, the viscosity of the reaction medium increases only slightly and thus very high molecular weight elastomers can be made. For instance, suspension polymerisation processes are of importance for the production of ultra high molecular weight EPDMs where ethylene, the diene monomer, and polymerisation aids are dissolved in the liquefied propylene, and then polymerised.

3.2 Diene elastomers

Most unsaturated rubbers contain 1,3-butadiene or isoprene as a major component. 1,2 or 1,4 insertion of either diene leaves an unsaturation on the chain. The synthetic elastomer produced in greatest volume is SBR and was first commercialised as Buna S in 1937. The homopolymer polybutadiene (BR) is second in importance to SBR. Polyisoprene (IR) is the homopolymer of isoprene. Both of these dienes can insert into the chain in different stereochemical and geometric isomers. These stereo isomers (*cis* and *trans*) as well as regio isomers (1,2 and 1,4 insertion) lead to a multiplicity of microstructure structures. Each microstucture or combination of different microstructures has different elastomeric properties. NR is 100% *cis*-1,4 IR

3.2.1 Polybutadiene (BR)

3.2.1.1 Producers

The worldwide capacity for BR elastomers is about 2,600 kilotonnes. Four companies account for about 50% of the world capacity for BR - Bayer (17%), Goodyear (13%), Michelin (11%) and Bridgestone/Firestone (8%). Other producers include Petrochim NV, Shell Buna AG, Degussa-Hüls AG, EniChem, Repsol Quimica SA, Petkim Petrochemicals, Asahi, Showa Denko, Japan Synthetic Rubber, Nippon Zeon, Ube Synthetic Rubber, Australian Synthetic Rubber, Coperbo, Indian Petrochemicals, Kumho Petrochemical Co., Karbochem and Taiwan Synthetic Rubber.

3.2.1.2 Microstructures of polybutadiene

1,3-BR can be polymerised to produce a variety of isomers and only some of them are elastomers. The isomers differ in the position of the insertion (1,2 versus 1,4), see Figure 3.3. 1,4 polymerised BR can exist in *cis* or *trans* form depending on the orientation of the substituents across the enchained double bond. Similarly, 1,2-BR can be differentiated by the tacticity of the substituents containing the pendant double bond. Each of these isomeric forms are different BR elastomers with unique physical, mechanical, and rheological properties. A mixture of these isomers on a single chain also leads to different elastomeric properties.

3.2.1.3 Structure and properties of 1,2-BR

The 1,2-BR exists as three isomers. The 1,2 insertion forms a chiral carbon attached to the pendant vinyl group. The tacticity of this group can be either exclusively meso or racemic or a mixture of the two. This orientation corresponds to syndiotactic, isotactic

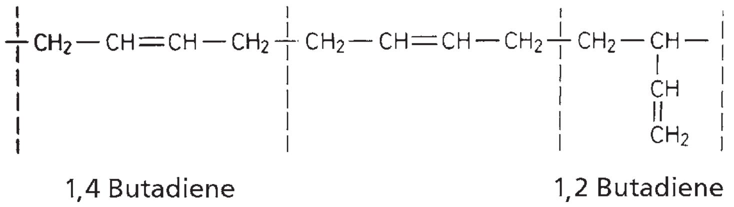


Figure 3.3 Monomers constituting BR

or atactic BR, respectively. Syndiotactic BR is made with cobalt Ziegler-Natta catalyst and is a crystalline thermoplastic melting at about 220 °C. It is compatible with NR and the blends are excellent thermoplastic elastomers. Intrachain mixtures of syndiotactic and atactic isomers lead to lower melting points and a variety of BRs containing different fractions of syndiotactic sequences are commercially available.

Amorphous 1,2-BR is made by an anionic lithium alkyl polymerisation modified by a chelating diamine. This leads to BR with ≈ 99% of the butadiene inserted at the 1,2 position. Intermediate structures having a greater amount of 1,4 insertion are obtained by controlling the ratio of chelating modifier to the anionic lithium catalyst as well as the polymerisation temperature. Raising this ratio increases the vinyl content and T_g of the BR. Amorphous 1,2-BR has become important to the tyre industry for tread formulations since it has a low hysteresis loss and excellent wet skid resistance characteristics.

3.2.1.4 Structure and property of 1,4-BR

1,4-BR in both *cis* and *trans* forms is made with a transition metal coordination catalyst, closely related to the Ziegler-Natta catalysts for polyolefins. The *trans*-1,4-BR has a melting point between 50 °C and 150 °C and is not used as an elastomer. An alternate synthesis of an amorphous *trans*-1,4-BR, useful as a tyre rubber, has been made using an alkoxide of group II, reduced with organolithium or organomagnesium compounds. A similar amorphous 1,4-BR containing 90% of a mixture of *cis* and *trans* 1,4-BR has been made with a living anionic catalyst. This polymer is used in tyres since it shows low hysteresis combined with good wear characteristics. An advantage of the anioic polymerisation is that these BRs can be terminated during polymerisation with a ketone, aldehyde, amine or tin/silicon halides. The presence of a this functionality (maximum 1/ per chain) leads to strong interactions with fillers and leads to even lower hysteresis.

3.2.1.5 Uses of BR

Use of BR showed a rapid and uninterrupted growth from its introduction in 1960 until 1975. The principal uses were partial replacement for NR in the tyre treads and, to a lesser extent, in carcass and sidewall formulations. Since the mid-1970s, growth has averaged 1–2% per year. Technological and economic trends in the automotive and tyre industries, e.g., smaller cars and radial tyres, are major determinants. In recent years, impact toughening of polystyrene and acrylonitrile-butadiene-styrene rubber (ABS) has become a major growth market for BR. In 1997 impact toughening of plastics accounted for 30% of total BR consumption. The prices for almost all grades of BR are listed at between $1.5 to $2.00/kg. These prices have not varied over time and negotiated costs may be as low as 75% of these prices.

3.2.2 Polyisoprene (IR)

3.2.2.1 Producers

The worldwide capacity for IR is approximately 1,500 kilotonnes and is concentrated in Asia and Eastern Europe. The principal Japanese producers are Japan Synthetic Rubber Co (2%) and Nippon Zeon Company (3%). In Europe Shell Nederland Chemie BV (3%), Brazi (Romania) (3%), Onestl (Romania) (7%), V/O Raznoimport (Confederation of Soviet States) (81%) are the principal manufacturers. The manufacturer of IR in USA is Goodyear Tyre and Rubber (4%).

3.2.2.2 Microstructure of IR

IR, like BR, can be polymerised to produce a variety of isomers depending on the polymerisation conditions. These differ in the position of the insertion (1,2 or 1,4 or 3,4). 1,4-IR can exist in *cis* or *trans* forms depending on the orientation of the substituents across the enchained double bond. These elastomers are commercially important since *cis*-1,4-IR is a synthetic analoge of NR. *Trans*-1,4-IR is a tough semicrystalline polymer. The 1,2-IR and 3,4-IR isomers are of less importance. In the commercial production of 1,4-IR, the isomer distribution of the elastomer depends on the catalyst system and reaction conditions. Stereospecific (*cis* versus *trans*) and regio specific (1,2 versus 1,4) catalysts include anionic lithium-alkyl systems as well as coordination catalysts similar to Ziegler-Natta catalysts. All synthetic IR elastomers are produced by solution polymerisation using either C_5-C_7 alkanes or aromatic compounds as the solvent.

3.2.2.3 Cis 1,4-IR

Cis-1,4-IR was first made in 1954 using a Ziegler-Natta catalyst consisting of $TiCl_4$ in conjunction with trialkyl aluminum. Later *cis*-1,4-IR was made by alkali metal polymerisation to give >90% *cis*-1,4-IR. *Cis*-1,4-IR of predictable molecular weight can also be prepared by anionic polymerisation.

3.2.2.4 Trans-1,4-IR

Trans-1,4-IR is a thermoplastic and is made using a different Ziegler-Natta catalyst with vanadium as the transition metal. The annual production of 1,4-IR is only 2% of the total worldwide production of IR.

3.2.2.5 Mixed (cis/trans) isomer 1,4-IR

This is made using a free radical emulsion polymerisation.

3.2.2.6 Uses of IR

There is a clear distinction between the properties and uses of *cis*-1,4-IR and *trans*-1,4-IR. *Cis*-1,4-IR is an elastomer and is used mainly in i) tyres and tyre products (66% of all IR use), ii) belts and gaskets (combined 8%), iii) hoses (4%), iv) foam rubber, moulded and mechanical goods (combined 11%), v) baby bottle teats, gloves, caulking, sealants, footwear and sporting goods (combined 2%), vi) rubber bands, erasers, and rubber sheeting (combined 8%). *Trans*-1,4-polyisoprene is a crystalline thermoplastic with a melting point around 60 °C. It resists abrasion, scuffing, and cutting, and is used mainly in high quality golf ball covers and orthopeadic devices and splints, and to some extent in transmission belts, cable covering, and adhesives. 3,4-IR is finding some applications in specialty tyre rubber compounds.

In the early 1990s about 66% of the US consumption of IR elastomers went into tyres and tyre products. IR, in conjunction with NR, is used for passenger car tyre carcasses due to good green strength, building tack and resilience. These IR-based polymers are generally not used for passenger car tyre treads, however they are used for the manufacture of heavy-duty truck and bus treads. This application requires a high resistance to wear and low hysteresis under heavy load conditions. A continuing increase in demand for radial-ply truck tyres is likely to increase the use of isoprenic elastomers for tyres.

3.2.3 Styrene-butadiene rubber (SBR)

3.2.3.1 Producers

The worldwide production of SBR is about 5,300 kilotonnes. In the USA the main producers are Bridgestone/Firestone (25% of the worldwide capacity)) and Goodyear (3%). In Mexico the manufacturer is Industrias Negromex (8%). In Europe the main manufacturers are Repsol Quimica SA (10%), Shell (5%), Michelin (5%), Petrochim NV (3%), Bayer (3%) and EniChem (2%). In Japan the main producers are Asahi Chemical (10%), Japan Elastomer (5%), Nippon Zeon (5%), Nippon Solution Rubber (3%) and Japan Synthetic Rubber (2%). In USA, the SBR is synthesised by tyre manufacturers (88% of capacity), operating large plants. In Western Europe and Japan, chemical and/or rubber companies dominate the supply of SBR, and most plants are somewhat smaller than the plants in the US.

3.2.3.2 Structure and synthesis of SBR

SBR contains about 25% styrene and the balance is butadiene (see Figure 3.4). The mode of insertion of the 1,3-butadiene is predominantly at the 1,2 insertion point. The two processes for making SBR are emulsion polymerisation and solution polymerisation. These processes are analogous to those for BR.

3.2.3.3 Emulsion SBR

Emulsion polymerisation originated in the work done in 1920s at Bayer [6]. Emulsion polymerisation produces SBR of high molecular weight. Because it is a free-radical-initiated process, the composition of the resultant chains is governed by the statistics of polymerisation, with units of styrene and butadiene randomly spaced throughout. Further there is little stereochemical control of the insertion of the butadiene. The microstructure is not amenable to manipulation, although the temperature of the polymerisation affects the ratio of *trans* to *cis* forms. SBR production is dominated by the emulsion process, though the S-SBR process is rapidly replacing it, particularly in Europe.

3.2.3.4 Solution SBR

In the 1960s, anionic polymerised S-SBR began to challenge E-SBR in the automotive tyre market. This has been now been complemented by solution polymerisation using Ziegler-Natta transition metal catalysts. In S-SBR, use of the anionic or coordination initiators allows control of the *trans/cis* microstructure and the 1,2 content of the polymerised butadiene. S-SBR is similar to E-SBR in terms of tensile strength, modulus and elongation, but it has better flex resistance, lower heat buildup, higher resilience and lower rolling resistance in tyres. As a result, S-SBR is slowly replacing E-SBR in tyre applications. In 1997, S-SBR (used primarily

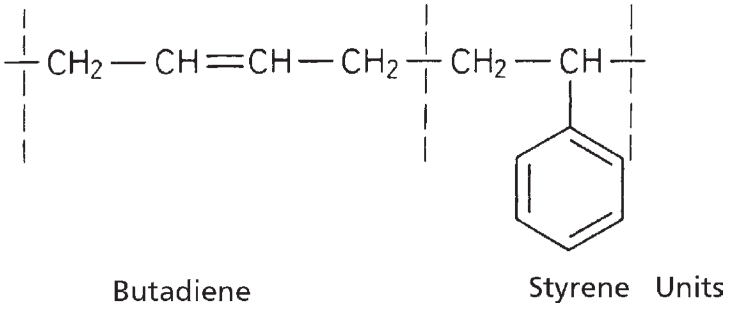


Figure 3.4 Monomers constituting SBR

for original equipment tyres) accounted for an estimated 20% of world capacity for SBR. Most future capacity expansions are expected to utilise the solution process, except for some developing regions where E-SBR capacity may be added.

3.2.3.5 Uses of SBR

The distribution of SBR among the principal end uses is passenger car tyres (45% of the worldwide capacity), truck and bus tyres (9%), retread tyres (16%), other automotive (6%) and mechanical goods (16%). Tyres and tyre products are the major end use for SBR, accounting for 70–75% of SBR consumption throughout the 1980s and the early 1990s. SBR is used to such a large extent in tyres and tyre products because of its excellent abrasion resistance and its cost/performance/processing balance relative to BR and NR. The tread-wear and heat-ageing properties of SBR are superior to those of NR, and it generally has better crack (or cut) growth initiation resistance than either NR or BR. Somewhat poorer building tack and green strength, particularly compared to NR, present some problems with SBR, particularly in tyre manufacture. This is generally overcome by blending with NR or with the use of appropriate tackifiers or tackifying resins (phenolic resins, hydrocarbon resins, or resin and its derivatives).

S-SBR usually sells at a premium over E-SBR, especially in original equipment tyre markets, where its low rolling resistance is an advantage. This premium may be of the order of 2–7 cents/kg. A typical SBR is sold for about $1.65/kg.

3.3 Saturated elastomers

Elastomers with saturated backbone polymer chains yet having a small amount of pendant unsaturation (for vulcanisation) resist environmental ageing better than diene elastomers. Degradation by oxygen, ozone and light is slow on the saturated backbone and cause only infrequent chain cleavage.

3.3.1 Ethylene-propylene copolymers (EPM) and ethylene-propylene-diene terpolymers (EPDM)

3.3.1.1 Producers

The worldwide production of EPR and EPDM is approximately 1,150 kilotonnes. In the USA the producers are Uniroyal (11% of worldwide capacity), Exxon Chemical (11%), DuPont/Dow Elastomers (12%) and Copolymer/DSM (9%). Western European producers are Exxon Chemical (10%), DSM (7%) and Degussa-Hüls (5%). In Japan the producers are Mitsui Petrochemical (8%) Japan Synthetic Rubber (7%), DSM/Idemitsu (6%) and Sumitomo Chemical (5%). There are additional smaller capacities in Brazil (2%), Korea (2%) and India (2%). In addition to these solution plants, Polysar/Bayer (7%) and EniChem (10%) have suspension plants in the US and Europe, respectively. Additional US capacity (12% of worldwide capacity) has been announced by Union Carbide using a novel gas phase process.

3.3.1.2 Processes

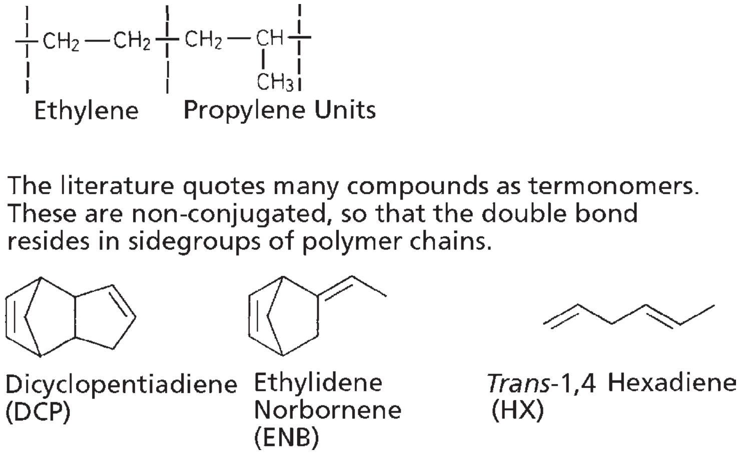
Even though EPM and EPDM elastomers have been available for more than 30 years, the technology for these products, both their production and their application, is still under development. The most widely used process is a solution polymerisation, in which the polymer is produced in a hydrocarbon solvent. EPM and EPDM rubbers are produced in continuous processes. Slurry polymerisation is conducted in liquid propylene. Special reactor designs with multiple feeding locations to achieve special molecular structures have been developed. Gas-phase polymerisation of EPDM is possible as an extension of the ubiquitous gas-phase processes for polyethylene and polypropylene.

3.3.1.3 Structure

EPM and EPDM as manufactured today are rubbers based on the early work of Natta and co-workers [7]. Generically an EPM contains 60 mol% of ethylene, 40 mol% of propylene. Analogous EPDM polymer contains in addition, 1.5 mol% of non-conjugated diene such as ethylidene norbornene or dicyclopentadiene. The co-monomers are statistically distributed along the molecular chain (see Figure 3.5).

3.3.1.4 Properties

EPM is a saturated synthetic elastomer since it does not contain any unsaturation. It is inherently resistant to degradation by heat, light, oxygen, and, in particular, ozone. EPDM which contains pendant unsaturation, is only slightly less stable to ageing than EPM. The properties of EPM copolymers are dependent on the relative content of ethylene units in the copolymer chain and the variation in the comonomer composition of different chains. EPM and EPDM polymers with greater than 60 mol% ethylene are increasingly crystalline and are tough.



The literature quotes many compounds as termonomers. These are non-conjugated, so that the double bond resides in sidegroups of polymer chains.

Figure 3.5 Structure of EPDM

EPM can be vulcanised radically with peroxides. A small amount of a third diene monomer in EPDM permits conventional vulcanisation with sulphur and other vulcanisation systems like resins at the pendant sites of unsaturation. EPM/EPDM grades have to be compounded with reinforcing fillers, e.g., carbon black, if enhanced mechanical properties are required. Paraffinic oils are widely used as plasticisers. In EPM/EPDM compounds mechanical properties depend on the composition of the elastomers and the type and amount of fillers. In general, the elastic properties are better than many other synthetic rubbers, but they do not reach the level of NR or SBR.

The resistance to heat and ageing of EPM/EPDM is much better than that of SBR and NR. EPM/EPDM vulcanisates have an excellent resistance to inorganic or highly polar fluids, such as dilute acids, alkalies and alcohol. However the resistance to aliphatic, aromatic, or chlorinated hydrocarbons is very poor. The electrical-insulating and dielectric properties of the pure EPM/EPDM are extraordinary, but in compounds they are also strongly dependant on the choice of compounding ingredients.

Among the synthetic elastomers, EPM and EPDM are the fastest growing elastomers, due to their excellent ozone resistance in comparison to the diene elastomers. This growth still comes from replacement of these commodity rubbers by virtue of their better ozone and thermal resistance. Another facet of the growth is that EPDM rubber can be extended with fillers and plasticisers to an extremely high level in comparison with the other elastomers, and still maintain excellent processibility and properties in end use articles.

3.3.1.5 Uses

The main uses of EPM or EPDM are in i) automotive applications as profiles, hoses, and seals (41% of the worldwide uses); ii) building and construction as profiles, roofing membranes, and seals (21%); iii) in cable insulation and jacketing (6%); and in appliances as moulded articles. An important application for EPDM is blends with general purpose rubbers. Considerable amounts of EPM and EPDM are also used in blends with thermoplastics (28%). Substantial amounts of EPM are also used as additives to lubrication oils (12%) because of its excellent heat and shear stability under the operating conditions of automobile engines. The list prices of EPM are $2.85/kg for EPM and $3.20/kg for EPDM.

3.3.2 Butyl and halobutyl rubbers (IIR and BIIR/CIIR)

3.3.2.1 Producers

The worldwide capacity for IIR and BIIR/CIIR is about 1,100 kilotonnes. Exxon Chemical is the largest producer for isobutylene-based elastomers with 50% of the worldwide capacity. Polysar/Bayer have 38%, the remaining 12% being in Commonwealth of Independent States (CIS) and Romania. In addition, a new plant by Sovbutital, in CIS, will add about 15% to the worldwide capacity.

3.3.2.2 Processes

The bulk of the world production of IIR is made by a precipitation (slurry) polymerisation process. Isobutylene and a minor amount of isoprene are cationically copolymerised with aluminum chloride in methyl chloride at –100 °C to –90 °C. Even at these temperatures the rates of polymerisation are very high. Alternately, IIR can be made in hydrocarbon solution at similar temperatures. BIIR/CIIR is produced by dissolving IIR in an hydrocarbon solvent and contacting the solution with elemental chlorine or bromine.

3.3.2.3 Structure

Isobutylene polymerises in a head-to-tail sequence and has a T_g –70 °C. In IIR, isoprene is enchained by a *trans*-1,4 addition (see Figure 3.6). In the formation of BIIR/CIIR, halogenation at the isoprene site in IIR proceeds via a halonium ion. This leads to a shift in the double-bond and formation of an exomethylene alkyl halide.

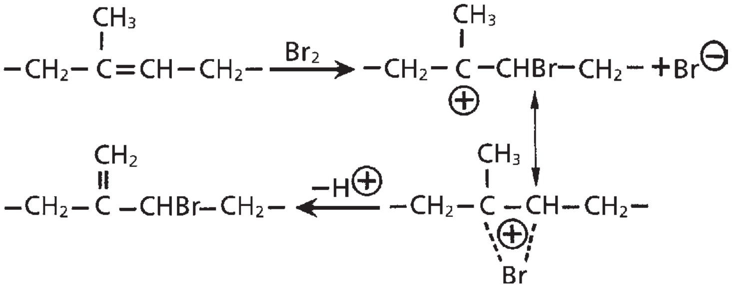


Figure 3.6 Halogenation of IIR and structure of BIIR

3.3.2.4 Properties

The most important physical properties of the IIR and BIIR/CIIR vulcanised compounds are high loss modulus and low permeability to air. Crosslinking reactions for these polymers depend on reaction at either an allylic hydrogen (IIR) or halogen (BIIR/CIIR). These reactive sites allow vulcanisation with sulphur and accelerators (IIR) and metal oxides (BIIR/CIIR). Halogenated versions of IIR have greatly extended the usefulness of IIR by providing higher vulcanisation rates and improving the co-cure compatibility with highly unsaturated elastomers. BIIR/CIIR undergoes vulcanisation by different mechanism using non-migratory ingredients compared to either SBR or NR. These properties have permitted the production of tubeless tyres with halogenated IIR in contact with diene rubbers.

Polyisobutylene is readily soluble in non-polar organic liquids. The solution properties of polyisobutylene, IIR and BIIR/CIIR are very similar.

3.3.2.5 Uses

The first use for IIR was in inner tubes where the low air permeability is the major factor. Good weather and ozone resistance, and oxidative stability properties make it useful in mechanical goods and elastomeric sheeting. Tyres, tubes and other tyre products have traditionally been the largest end use for IIR, generally accounting for 83% of total consumption. Halogenated IIR, used for liners on tubeless tyres, accounted for an estimated 55–60% of total IIR consumption.

In addition to tyres, isobutylene elastomers find uses in automotive mechanical goods (6% of worldwide capacity), adhesives, caulks and sealants (6%) and pharmaceutical applications (4%). The remaining 1% use is accounted for by hoses, ditch and reservoir liners, chewing gum and plastic blends.

Polyisobutylene has a set of uses distinct from tyres. The low molecular weight liquid polybutenes have applications as adhesives, sealants, coatings, lubricants, and plasticisers, and for the impregnation of electrical cables. High molecular weight polyisobutylene is used to make uncured rubbery compounds, and as an impact additive for thermoplastics

The cost of IIR is generally listed at $2.30/kg while halogenated IIR is listed about $0.10–0.20/kg above IIR.

3.3.2.6 Other isobutylene elastomers

A partially cross-linked isobutylene-isoprene-divinylbenzene terpolymer is available. It is used in the manufacture of sealant tapes and caulking compounds. Low molecular weight IIR is made by degradation of an IIR at high shear and temperature. The principal uses of this are in sealant, caulks, potting compounds, and coatings. Star-branched butyl rubber has a bimodal molecular weight distribution with a minor high molecular weight branched mode and a low molecular weight linear component. The polymer is prepared by a conventional cationic copolymerisation in the presence of a polymeric branching agent. It offers a balance of viscoelastic properties resulting in significant processability improvements as well as improved extrusion rates.

A recent innovation has been the introduction by Exxon Chemical of a copolymer of isobutylene (>95 mol%) and *p*-bromo methylene styrene (BIMS). These polymers are made by a free radical bromination of preformed copolymer of iso butylene and *p*-methyl styrene under conditions where only a fraction of the *p*-methyl groups are halogenated. These polymers are analogous to the more common brominated isobutylene copolymer BIIR except that the backbone is saturated. This leads to much greater thermal and oxidative stability for these polymers comparable to EPDM [8, 9].

3.3.3 Ethylene-acrylic elastomers (EAM)

3.3.3.1 Producers

The worldwide capacity for acrylate rubbers is about 75 kilotonnes. E. I. DuPont is the sole producer of EAM polymers.

3.3.3.2 Processing

EAM polymers are made by the free radical polymerisation of ethylene, methyl acrylate and an alkenoic acid

3.3.3.3 Structure

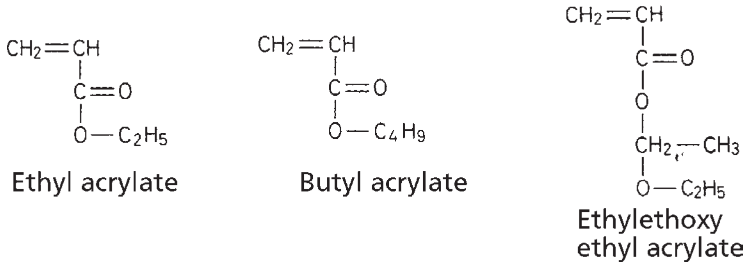
EAM elastomers are random copolymers of ethylene and methyl acrylate (see Figure 3.7). A small amount (1–5 mol%) of an alkenoic acid is incorporated to provide sites for cross-linking with diamines. Recently copolymers of ethylene and methyl acrylate have been commercialised.

3.3.3.4 Properties

EAM is an amorphous polymer due to random placement of the acrylate comonomer along the ethylene backbone. The polymer is saturated, making it highly resistant to ageing and weathering even in the absence of antioxidants. In addition, the methyl acrylate to ethylene ratio determines both the low temperature properties and the resistance to organic fluids. EAMs have ageing, heat and fluid resistance in addition to acceptable elastomeric properties. In particular, they show largely temperature stable vibrational damping properties and the ability to form flame-resistant elastomeric compounds with combustion products having low toxicity and corrosiveness.

3.3.3.5 Uses

EAM polymers are used in automotive applications in the USA, Europe and Far East.



Ethyl acrylate

Butyl acrylate

Ethylethoxy ethyl acrylate

Figure 3.7 Structure of EAM

3.4 Solvent resistant elastomers

Solvents encompass a broad class of apolar organic fluids. This includes paraffins, aromatics, cycloalkanes, olefins, chlorinated hydrocarbons, fatty acids and their esters but not small polar molecules such as methanol. Vulcanisates of hydrocarbon elastomers easily swell in these solvents and lose most of their tensile, elongation and resistance to set or abrasion. Thus synthetic elastomers which resist these hydrocarbon solvents are an important commercial development. The class of solvent resistant elastomers incorporates large amounts of strongly polarising groups such as esters, nitriles or halogens to raise the solubility parameter of the elastomer such that it is no longer miscible with the solvents.

The polarity of the acrylonitrile makes NBR resistant to common hydrocarbon solvents. However, NBR is an unsaturated elastomer and is easily degraded by weathering. Most of these shortcomings can be alleviated by hydrogenating the double bonds to form hydrogenated NBR (HNBR). Acrylic elastomers (ACM) are copolymers of various alkyl acrylates differing in the nature of their alkyl group. They contain the strongly polar ester group. Acrylate elastomers are saturated. Chloroprene rubber (CR) is prepared by emulsion polymerisation of chloroprene. It resists hydrocarbon solvents and shows improved flame resistance due to the incorporated chlorine. In addition, it is also more resistant to oxidation than NR. Saturated chlorinated synthetic elastomers such as chlorinated polyethylene (CPE) are made by reacting polyethylene with chlorine. Chlorosulphonated polyethylene (CSM) is also made similarly by reacting polyethylene with both chlorine and sulphur dioxide.

3.4.1 Nitrile rubber (NBR)

3.4.1.1 Producers

The worldwide production of NBR and HNBR is about 320 kilotonnes. Nippon Zeon is the largest worldwide manufacturer with about 22% of the capacity, including the sole capacity for HNBR, and has plants all over the world. Goodyear (18%), Uniroyal (15%) and Bayer (17%) are all major producers of nitrile elastomers.

3.4.1.2 Structure and synthesis of NBR

NBR is a copolymer of 1,3-butadiene and acrylonitrile (ACN) (see Figure 3.8). The copolymer can be largely linear to highly branched depending on the conditions of polymerisation. NBR containing 8 to 27 wt% of ACN is available. NBR is used for its resistance to various organic oils, fuels, and chemicals in seals, gaskets and hose. NBR containing higher amounts of ACN is more resistant to fluids but has a higher T_g. Virtually all nitrile elastomers are manufactured by emulsion polymerisation. The primary steps in the process include polymerisation into a latex form, coagulation of the latex into a wet crumb, and then drying into a final product.

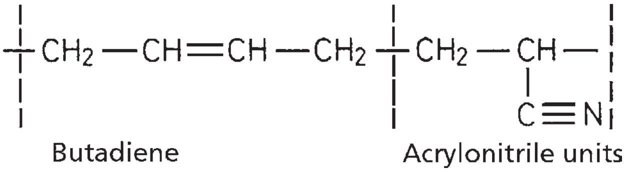


Figure 3.8 Structure of NBR

3.4.1.3 Uses

Common applications for NBR take advantage of the chemical resistance of the rubber. Seals, O-rings, gaskets, oil field parts, diaphragms are the principal uses of NBR. Gloves, pump stators, belts, wire and cable insulation, hose tubes/covers, rolls, sound insulating gaskets, footwear/shoe products, and miscellaneous moulded rubber goods are some of the minor applications. Nitrile rubber is also used for modification of plastics, adhesives coatings, and friction materials.

3.4.1.4 Chemically modified NBR-Hydrogenated NBR (HNBR)

The most important chemical modification is hydrogenation of the NBR so that little of the unsaturation remains. This results in a product with much improved resistance to oxidation and weathering, but with little or no sacrifice of other useful properties. Hydrogenated nitrile rubber (HNBR) is produced by a catalytic solution hydrogenation of the butadiene unsaturation in the polymer. Owing to the largely saturated backbone of the rubber it has significantly better high temperature and ageing resistance compared to NBR. As in NBR, HNBR with different ACN contents is also available. Finally, versions of HBNR containing incorporated methacrylic acid are available. This acid functionality leads to excellent polymer-filler interaction in compounds. Applications for HNBR take advantage of the excellent resistance to organic fluids. However, the increased high temperature performance of the HNBR makes it far superior to NBR in critical applications.

3.4.1.5 Chemically modified NBR-acid functional NBR

Chemically modified NBR containing pendant carboxylic acids are made by copolymerising methacrylic or acrylic acid with the butadiene and acrylonitrile. These polymers which contain 2–6 wt% of the acid monomer, can be vulcanised with polyvalent metal ions. This results in a large improvement in abrasion resistance.

3.4.2 Polychloroprene (CR)

3.4.2.1 Producers

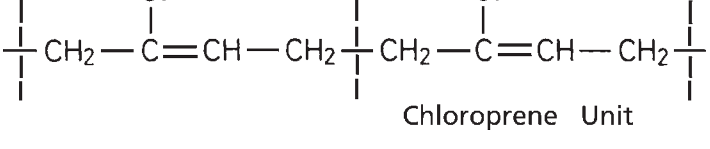
CR was the first commercially developed synthetic elastomer. The current worldwide capacity of CR is 310 kilotonnes. DuPont Dow has 49% of the capacity with facilities in USA, UK, and Japan. There are five other producers of CR.

3.4.2.2 Synthesis and structure

Commercial CR polymerisation is typically conducted in aqueous emulsion. The molecular weight is controlled with chain transfer agents. Mercaptan chain transfer agents are used, but other materials such as xanthogen disulphides have also been used. The latter provide reactive end groups. Molecular weight is also controlled by copolymerisation with sulphur. This copolymer contains polysulphide units that are then cleaved chemically to lower the molecular weight.

The predominant microstructure of CR is the head to tail *trans*-1,4-CR although other structural units are also present (see Figure 3.9). The high concentration of this repeat unit is responsible for crystallinity of CR and for the ability of the material to crystallise under strain. Other structures, e.g., 3,4-insertion, in minor amounts lead to easily vulcanisable sites on the polymer. The presence of these structural irregularities does lead to lower crystallinity and tensile strength. The total amount of insertion modes other than *trans*-1,4 increases with polymerisation temperature from 5% at –40 °C to about 30% at 100 °C. CR made with high *trans*-1,4 content is tough and is used for adhesives. CR made at higher temperature, with more chain irregularities, tends to be much slower-crystallising, and is more suitable for elastomer uses.

CR polymers are often differentiated by the use of an appended letter. These designations reflect not the composition of the polymer but are derived from the manufacturing and



$$\left[CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2 \right]\left[CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2 \right]$$

Figure 3.9 Structure of CR

process conditions. Ultimately, these process conditions affect the microstructure, i.e., branching, molecular weight distribution, isomer distribution, and thus the compounding and the ultimate physical properties of the polymer. The G family of polymers, containing residual thiuram disulphide, can be cured with metallic oxides. The W, T and xanthate modified families require addition of an organic accelerator, often in combination with a cure retarder, for practical cures. G, W, T are trade designations.

There are a only a few uses of bulk or solution polymerisation of CR. These involve production of liquid polymers.

3.4.2.3 Properties

CR has been successful, since it combines both environmental resistance and toughness, especially in dynamic applications involving heat buildup and resistance to flex cracking. The high strength of CR vulcanisates is a result of its tendency to crystallise under stress. The rate of crystallisation and the melting point of CR both increase with increasing amount of *trans*-1,4 micro structure. The resistance of CR to ageing is higher, compared to other diene elastomers, because of the presence of an electronegative chlorine atom on the repeat unit double bond.

Polyester plasticisers are more effective than hydrocarbon oils in reducing the T_g of vulcanisates. However, the plasticisers are also effective in promoting crystallisation. For many applications, where cost and processibility are the objective, naphthenic and aromatic oils are used.

3.4.2.4 Uses

CR has a well-balanced combination of properties including processibility, strength, flex and tear resistance, flame resistance, and adhesion, together with sufficient heat, weather and ozone resistance for most applications. Typical applications involve power transmission and timing belts, automotive boots (rubber piece around the constant velocity joint in the front wheels of cars), airsprings, and truck engine mounts.

A large amount of CR is used as adhesives. CR tends to have high uncured strength due to stress induced polymer crystallisation. CR latex and solvent adhesives have been used in foil laminating adhesives, facing adhesives, and construction mastics. CR latex can be used in a variety of special applications to make binders, coatings, dipped goods, elasticisers, and foam where either dry or solvent-based processes would be impractical. The water-based systems are now preferred since they have high solids content and minimal solvent emissions, but are unaffected by polymer rheology, and have extremely small particle size.

3.4.2.5 Copolymerisation

Over the years, almost every vinyl and diene monomer has been tested with CR in free-radical polymerisation. Copolymers usually contain only a limited amount of random co-monomer. Methacrylic acid, for example, promotes adhesion and increases cohesive strength. An exception to the reactivity deficiency is 2,3-dichlorobutadiene, which is even more reactive than CR and is often used to improve the crystallisation resistance of the polymer. A large number of graft polymers of CR have been described, but the only ones of commercial significance are those made with acrylates and methacrylates. These are particularly useful for adhesion to plasticised poly(vinyl chloride) (PVC). The graft polymers may be made either in solution or emulsion polymerisation.

3.4.3 Acrylic elastomers (ACM)

3.4.3.1 Producers

ACM elastomers are a limited volume specialty elastomer with a worldwide capacity of about 8 kilotonnes. This volume is included in the worldwide capacity for the more common EAM. ACM manufacture is distributed among USA, Western Europe, and Japan. Its production is intimately associated with automotive production. The major producers for EAM include Enichem Elastomers and Zeon Chemical with approximately equal market share. Ricon Resins produces a small amount of low molecular weight EAM polymer for adhesive applications.

3.4.3.2 Process

ACM elastomers are produced by free radical polymerisation using principally aqueous suspension and emulsion polymerisation.

3.4.3.3 Structure

ACM elastomers consist of a majority (≈97–99 wt%) of ethyl acrylate, butyl acrylate, and 2-methoxy ethyl acrylate monomers (see Figure 3.10). In addition a small amount

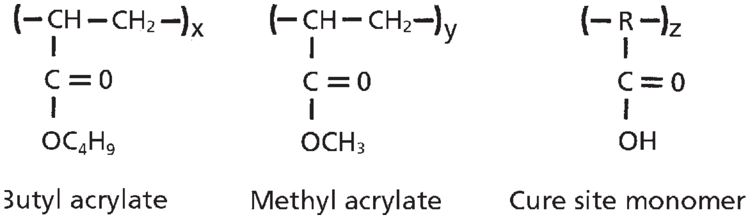


Figure 3.10 Structure of ACM monomers

(≈1-3 wt%) of cure site monomers are added to facilitate vulcanisation. The acrylic esters constituting the majority of the polymer chain determine the physical, chemical and mechanical properties of the polymer and its vulcanisates. Cure site monomers have an acrylate double bond for polymerisation into the ACM and a reactive group for the vulcanisation process. Two of the most important classes of cure site monomers are reactive chlorine-containing monomers and epoxy/carboxyl-containing monomers.

3.3.3.4 Properties

ACM has both a saturated backbone, which is responsible for the heat and oxidation resistance, as well as the ester side groups, which contribute to the marked polarity.

The cure sites present in the ACM also affect the expected properties. Reactive chlorine cure sites generally give excellent heat ageing as shown by retention of elongation. The alkali metal carboxylate-sulphur cure system is widely used for this type of cure monomer since its introduction in the early 1960s. Epoxy/carboxyl cure monomers give good compression set and good resistance to hydrolysis. New vulcanisation systems based on quaternary ammonium salts have been introduced to vulcanise epoxy/carboxyl cure sites. These have been found to be effective also in chlorine containing ACM.

3.4.3.5 Uses

The resistance to ageing at high temperatures and the insensitivity to organic fluids, e.g., oils, makes ACM useful in automotive underhood parts. These include lip and shaft seals, O-rings, oil pan and cover valve gaskets, and hoses. The list price of ACM is \$8.80/kg, which is midway between the general purpose elastomers, e.g., SBR, and the small volume specialty rubbers, e.g., HNBR.

3.4.4 Chlorosulphonated polyethylene (CSM)

3.4.4.1 Producers

The worldwide capacity of CSM elastomers is about 55 kilotonnes. E. I. DuPont is the principal manufacturer with >90% of the share with plants in USA and Northern Ireland. Toyo Soda in Japan provides the balance of the capacity.

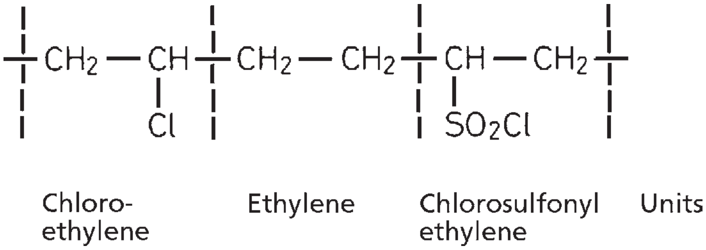
3.4.4.2 Processing

CSM is not made from the component monomers but from the chemical modification of polyethylene. The chlorination and chlorosulphonation reactions of polyethylene are carried out simultaneously or sequentially using carbon tetrachloride as the reaction solvent.

3.4.4.3 Structure

The elastomer character of CSM arises from inherent flexibility of the polyethylene chain due to reduced crystallinity. Substitution of chlorine in the polymer chain provides sufficient molecular irregularity to reduce crystallinity (see Figure 3.11). The sulphonyl chloride groups provide cross-linking sites for non-peroxide vulcanisation. CSM properties can vary from elastomeric to plastic depending on the amount of chlorine and sulphonyl chloride substitution.

The presence of chlorine and sulphonyl chloride in the chain requires weak bases in CSM compounds to react with acidic by-products. Acceptable bases include magnesia, litharge, organically bound lead oxide, calcium hydroxide, synthetic hydrotalcite, and epoxy resins.



$$-\left|\, CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}} \,\right|\, CH_2-CH_2 \,\left|\, \underset{\displaystyle SO_2Cl}{\underset{|}{CH}}-CH_2 \,\right|-$$

Figure 3.11 Structure of CSM

3.4.4.4 Properties

Resistance to thermal degradation and ageing, particularly attack by ozone, results from the absence of unsaturation in the CSM backbone. The presence of sulphonyl chloride groups contribute to adhesion and mechanical reinforcement by reaction with fillers. In addition, the presence of chlorine imparts significant flame and light resistance to CSM compounds. However, all of these properties depend on the extent and distribution of chlorination and chlorosulphonation. CSM polymers can be easily functionalisd by replacement of the halogen either on the backbone or on the sulphonyl group. Acid, ester, and amide derivatives of the sulphonyl chloride groups have been prepared.

The sulphonyl chloride group is the cure site for CSM and determines the rate and state of cure. Carbon black fillers give the best reinforcement as well as significant resistance to photochemical degradation. Ester plasticisers provide the best combination of low temperature flexibility, heat resistance, and mechanical properties.

3.4.4.5 Uses

CSM is used in specialty end use applications such as coating, adhesives, roofing membranes, pond and reservoir liners, electrical wiring insulation, automotive and industrial hose, tubing and belts, and in moulded goods. The list price of CSM is about $4.40/kg.

3.5 Temperature resistant elastomers

The truly temperature resistant elastomers are those that have replaced the hydrocarbon structure with more refractory building blocks. The commonest of this is silicone rubbers (Q). These are based on chains of Si-O-Si rather than C-C units, and owe their temperature resistance to their unique structure. Silicone rubbers are almost exclusively polydimethylsiloxanes. The other heat resistant elastomer, fluorocarbon elastomer (FKM), is derived from perfluorinated versions of common polyolefins such as polypropylene and polyethylene. Their thermal resistance arises from the nonreactivity of the carbon-fluorine bond .

3.5.1 Silicone rubber (Q)

3.5.1.1 Producers

The majority of silicone rubber elastomers (~60%) are made by General Electric. Laur and Dow Corning have about 10% of the remaining capacity while smaller manufacturers (Wacker, Bayer and Rhône-Poulenc) have the balance of the production.

3.5.1.2 Process

Q rubbers are made commercially by the either the multistep hydrolysis of dimethyldichlorosilane or by the ring opening polymerisation of the cyclic oligomer octamethylcyclosiloxane. In the hydrolysis procedure the chlorine atoms are hydrolysed and replaced with a oxygen atoms bonding a pair of silicon atoms. Water is frequently replaced with methanol which leads to the formation of methyl chloride rather than the more corrosive hydrochloric acid. In the ring opening polymerisation strong acid or base catalysts are used to produce high molecular weight Q. The ring opening polymerisation process can be conducted in an aqueous emulsion procedure using dodecylbenzenesulphonic acid as the catalyst.

3.5.1.3 Structure

Most Q polymers have the repeat unit empirical formula of ((CH3)$_2$SiO) and are referred to as polydimethylsiloxanes (see Figure 3.12). The elastomer consists of alternating silicon and oxygen atoms with two methyl groups on each silicon. A significant departure from most other elastomers is the absence of carbon in the backbone. Three reaction types are predominantly employed for the formation of vulcanised Q: peroxide-induced free-radical vulcanisation, hydrosilylation addition cure, and condensation cure. Silicones have also been cross-linked using radiation to produce free radicals or to induce photoinitiated reactions.

3.5.1.4 Properties

Q does not crystallise even under strain and has very poor physical properties. Unfilled silicone rubber has only a 0.345 MPa tensile strength. Q vulcanisates are reinforced with <25% finely divided fumed silica. This reinforcing filler increases tensile strength, tear

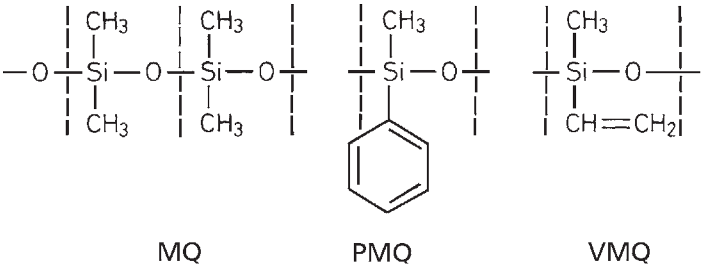


Figure 3.12 Structure of some silicone rubbers
MQ: silicone rubber with methyl substituent. PMQ: silicone rubber with methyl and phenyl substituents. VMQ: silicone rubber with methyl and vinyl substituents

strength, and abrasion resistance. The Si-O-Si bonds in Q have a much lower energy of activation for rotation than C-C bond or C-O bond. This makes Q elastomers flexible and rubbery even at very low temperatures and this elastomeric property is less affected by temperature changes. This feature combined with the refractory characteristics of Q makes these elastomers useful over a wide temperature range.

3.5.1.5 Liquid injection moulding

Liquid injection moulding is the process for forming vulcanised elastomer articles by combining two low viscosity streams. One of these contains a linear polydimethysiloxane polymer with pendant Si-H functionality. The other contains a linear polydimethylsiloxane with terminal and pendant vinyl groups and a platinum hydrosilylation catalyst. On contact, the hydrosilation of the vinyl groups occurs by addition of silcon hydride. This leads to cross-linking. This reaction may be delayed to allow for a thorough mixing by adding small amounts of amines or phosphines.

3.5.1.6 Uses

Q elastomers are used for electrical insulation, medical devices, seals, surface-treated fillers, elastic textile coatings and foams. Liquid injection moulding is used for electrical connectors, O-ring seals, valves, electrical components, health care products, and sporting equipment such as goggles and scuba diving masks.

3.5.2 Fluorocarbon elastomers (FKM)

3.5.2.1 Producers

The principal producers of FKM polymers are 3M, Ausimont, E. I. DuPont in USA. In the Far East production is maintained by Asahi Glass and Daikin. The annual worldwide FKM usage is about 8 kilotonnes. About 40% of this is in USA, 30% in Europe, and 20% in Japan.

3.5.2.2 Processing

These elastomers are typically prepared by high pressure, free-radical, aqueous emulsion polymerisation. The initiators are organic or inorganic peroxides, e.g., ammonium persulphate. The emulsifying agent is usually a fluorinated acid soap.

3.5.2.3 Structure

FKM elastomers are the perfluoro derivatives of the common polyolefins (see Figure 3.13). The monomers are the perflourinated derivatives of ethylene and propylene. Copolymers of different olefins are available. They are non crystalline polymers that are elastomeric when crosslinked.

3.5.2.4 Properties

The vulcanised FKM polymers are dimensionally stable and chemically inert in hostile environments and in a variety of organic fluids such as oils and solvents. This chemical resistance spans a wide temperature range. In addition, vulcanised FKM polymers show extraordinary self-lubricating properties due to the low surface energy. FKM elastomers can be vulcanised with one of three distinct procedures. These include diamine, bisphenol-onium, and peroxide curing agents. The bisphenol-onium cure system is the most widely used.

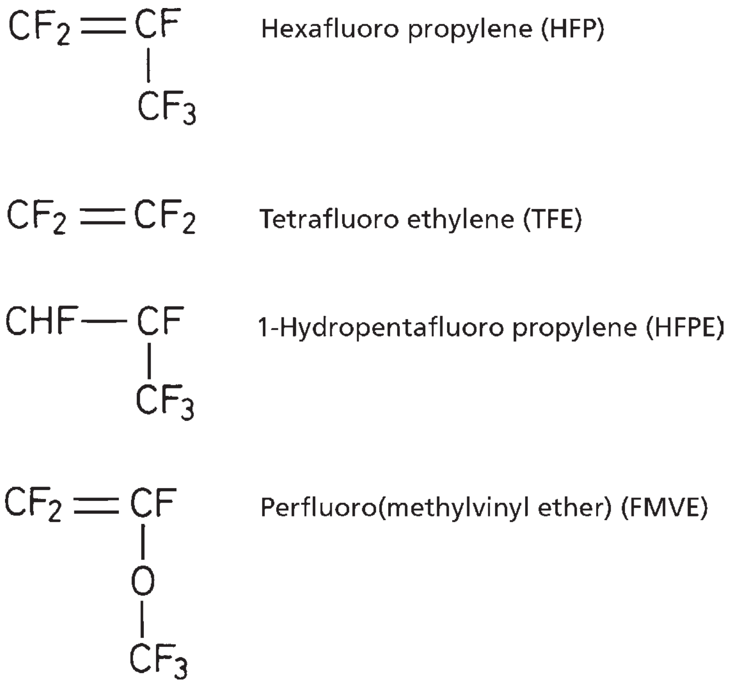


Figure 3.13 Structure of FKM

3.5.2.5 Uses

FKM elastomers are resistant to heat, chemicals, and solvents. The major use of FKM polymers is automotive. These include engine and gaskets and fuel system components (hoses and O-rings). This application is fueled by increased demands from higher use temperatures, alcohol containing fuels, and aggressive lubricants. Other major segments include petroleum, petrochemical and industrial pollution control, and industrial hydraulic and pneumatic applications. The list price for FKM polymers is about $55/kg.

3.6 Specialty elastomers

3.6.1 Phosphazenes (FZ)

3.6.1.1 Producers

The worldwide capacity for phosphazenes is less than 0.1 kilotonnes. Albemarle (Ethyl Corporation) is the sole supplier.

3.6.1.2 Processing

Phosphazene polymers are made in a two-step process. First, the trimer hexachlorocyclotriphosphazene is polymerised in bulk to poly(dichlorophosphazene), chloropolymer. The chloropolymer is then dissolved and reprecipitated to remove unreacted starting material. After redissolving in solvent, nucleophilic substitution with alkyl or aryloxides substitution of the halide provides the elastomer.

3.6.1.3 Structure

Polyphosphazenes have a backbone of alternating nitrogen and phosphorus atoms with two substituents on each phosphorus atom. The backbone is isoelectronic with that of silicones; these polymer backbones share the characteristics of thermal stability and high flexibility.

3.6.1.4 Properties

Two elastomers have been commercialised with unique property profiles. One has fluoroalkoxy substituents that provide resistance to many fluids, especially to hydrocarbons.

FZ elastomer is a translucent pale brown gum with a T_g of –68 °C to –72 °C. The gum can be crosslinked using peroxides such as dicumyl peroxide and a,a´-bis(*t*-butylperoxy) diisopropylbenzene. FZ elastomers have excellent resistance to hydrocarbons and inorganic acids, as is expected for a fluorinated elastomer. They are strongly affected by polar solvents, but are more resistant to amines than most other fluorinated elastomers. This material also has a broad use temperature range and useful dynamic properties.

The other elastomer (aryloxyphosphazene) has phenoxy and *p*-ethylphenoxy substituents. It has flame retardant properties without containing halogens. It may be cured using either peroxides or sulphur.

3.6.1.5 Uses

Coatings, fluids, elastomers, and thermoplastics can be produced by varying the polymer molecular weight and the substituents on the phosphorus. These materials have been suggested for use in biomedical devices, including implants and drug carriers [10]. However initial applications have been largely in military and aerospace areas.

3.6.2 Polyethers

3.6.2.1 Producers

Nippon Zeon with plants in the US and Japan, has a near monopoly on polyether rubbers. These include epichlorohydrin homopolymer rubber (CO), epichlorohydrin/ethylene oxide copolymer (ECO), epichlorohydrin (ECH)/ethylene oxide terpolymers (ETER), propylene oxide homopolymer rubber (PO) and propylene oxide/allyl glycidyl ether copolymers (GPO). There are no production facilities in Western Europe for these elastomers. The worldwide capacity for these polymers is about 11 kilotonnes/year with Nippon Zeon having about 90% of the market share and Daiso the balance.

3.6.2.2 Processing

Polymerisation is conducted either as a solution or in a slurry at 40–130 °C in toluene, benzene, heptane, or diethyl ether. Trialkylaluminum/water and trialkylaluminum/water/acetylacetone catalysts are used. Chain propagation is by a cationic charge transfer mechanism.

3.6.3 Structure

The polyethers include a group of minor elastomers made by ring opening polymerisation of epoxides and includes CO, ECO, ETER, PO and GPO. CO and ECO are linear and amorphous. Since it is unsymmetrical, ECH monomer can polymerise in the head-to-head, tail-to-tail, or head-to-tail fashion. The commercial polymer is 97–99% head-to-tail and atactic. The commercial products are essentially amorphous.

3.6.2.4 Properties

Polyethers are remarkable because of an exceptional combination of properties. The CO has low gas permeability and is better than IIR. It is resistant to ozone and has low hysteresis. The polymer is flame retardant due to its high chlorine content. It has poor resilience at room temperature, but this improves upon heating. ECO is less flame retardant due to its lower chlorine content. It has some impermeability to gases but has better low temperature flexibility. It also exhibits good heat resistance. The family of polyethers are resistant to apolar organic fluids like oils and aliphatic/aromatic solvents.

3.6.2.5 Uses

The polyethers are important in automotive applications such as fuel, air, and vacuum hoses, vibration mounts, and adhesives. Other uses include drive and conveyor belts; hoses, tubing, and diaphragms; pump parts including inner coatings, seals, and gaskets; printing rolls and blankets; fabric coatings for protective clothing; pond liners, and membranes in roofing material. In the automotive areas they are used as constant velocity boots, dust and fuel hose covers, mounting isolators, and hose and wire covers. The list price of polyethers is about $6.60/kg.

3.6.3 Ring opened polymers (TPA, TOR)

Ring opening metathesis polymerisation of cyclopentene is carried out in either chlorinated or aromatic solvents to give *trans*-polypentenamer (TPA). This polymer is not commercially available. The same polymerisation technique is used to convert cyclooctene to *trans*-cyclooctenemer (TOR). Degussa-Hüls is the sole producer of TOR. Their capacity is estimated at 13.5 kilotonnes. The list price of TOR is about $4.40/kg.

3.7 Thermoplastic elastomers

Examples of thermoplastic elastomers which are made by polymerisation from constituent monomers include styrene-butadiene block elastomers (SBS) and thermoplastic polyurethanes (TPU). In both cases they are copolymers of at least two kinds of monomers. One forms a hard thermoplastic homopolymer due to either a high T_g or a high melting point (T_m). The other forms a soft elastomeric polymer with a low T_g and an absence of crystallinity. The synthetic procedure consists of a segregated polymerisation where sections of the polymer containing only one of the above monomer units is constructed and then joined to the other polymer. This results in a polymer having an extremely non-uniform distribution of composition along the backbone. For styrene-butadiene block copolymer this is done by sequentially adding styrene and then finally butadiene. The styrene block copolymer contains a few distinct but very long blocks. For the TPU this is done by polymerising the monomers individually to oligomers, followed by copolymerisation of the oligomers. Thus they contain a large number of alternating blocks of different compositions with each being of fairly short length.

The chemical bonds between these blocks prevent a gross phase separation as would happen on mixing the individual homopolymers of the hard and soft block components. Instead the separation of the phases into very small domains (less than 0.1 μm) occurs, resulting in an elastomer matrix strongly reinforced with the hard domains and having properties comparable to vulcanised elastomers. This occurs since the hard domains act as virtual though thermally reversible crosslinks. At temperatures above the T_g or T_m of the hard segment, the polymer can easily be melt processed.

3.7.1 Styrene block copolymers

3.7.1.1 Producers

The principal suppliers of styrene block polymer are Shell (47% of the worldwide capacity), EniChem (18%), other Phillips process licensees (18%), Dexco (6%), Bridgestone/Firestone (5%) and Japanese and Taiwanese operations (6%).

3.7.1.2 Processes

Styrenic block copolymers are manufactured by solution polymerisation in cyclohexane or other suitable solvents. Organometallic anionic catalysts such as butyl lithium are used. Under these reaction conditions the termination rates for the polymerisation are extremely slow and it has 'living' character. Thus the polymerisation of styrene and either butadiene or isoprene can be conducted sequentially to form segregated blocks along a single chain. First, styrene is polymerised, followed by polymerisation of a diene, such as butadiene or isoprene, and then by polymerisation of styrene again for the final end group. If a saturated product is desired, the polymer is hydrogenated prior to precipitation.

In the Shell process, a difunctional coupling agent is used to link together two living diblocks of styrene-butadiene or styrene-isoprene. In this two-stage process, the styrene monomer polymerises first to form the end block and then the diene monomer is added to form the centre block. The diblocks are then coupled to yield SIS or SBS. In the process pioneered by Phillips and practiced by its licensees, multiblock radial SBS or SIS copolymers are produced through the use of multifunctional coupling agents such as $SiCl_4$, divinylbenzene or PCl_3.

3.7.1.3 Properties

The styrene block polymers consists of the styrene-butadiene-styrene, styrene-isoprene-styrene types as well as their hydrogenated versions. These polymers, unusually, have exceptional elasticity and recovery from deformation without vulcanisation. In normal use they have the thermal properties of the elastomeric mid section. Thus the butadiene copolymers have a lower T_g but are thermally less stable than their hydrogenated counterparts. Hydrogenation of the block polymers is very selective since the styrene is unaffected.

3.7.1.4 Uses

Adhesives and sealants are now the largest end use area with about 40% of the worldwide volume being used here. Asphalt modifiers are now the fastest-growth end use and are the second-largest application. Use of polymer modifiers is also showing strong growth and is the third largest end use. Footwear, once the largest application area, has significantly diminished in importance. List prices for the diene copolymers are about $1.75/kg while the hydrogenated polymers were approximately $1.10 to $1.76/kg higher.

3.7.2 Thermoplastic polyurethanes (TPU)

3.7.2.1 Producers

The wordwide capacity for TPU is estimated to be about 215 kilotonnes. Within the USA, BFGoodrich has 9% of the worldwide capacity, followed by Dow (7%), BASF

(6%), Miles (6%) and Morton Thiokol (6%). In Europe the principal manufacturers are BFGoodrich (7%), Bayer (6%). The principal Japanese manufacturers are Nippon (3%), Sumitome (3%) and Takeda (3%). These production numbers do not include about 20 smaller manufacturers, nor do not reflect a large amount of TPU made by condensation of the prepolymers by users, e.g., foams.

3.7.2.2 Processing

TPUs are made by the condensation of the oligomers of the soft block with the hard block. The condensation is conducted in the melt. During the condensation the isocyanate groups react with the hydroxy groups to form the urethane linkage.

3.7.2.3 Structure

The soft block of TPU consists of oligomers of polyesters or polyethers (see Figure 3.14). The polyesters are copolymers of adipic acid with either ethylene glycol, butane 1,4-diol or hexane 1,6-diol. The most important polyethers are poly(oxypropylene) glycol and poly(oxytetramethylene) glycol. The hard segment of TPU contains polyisocyanates derived from 4,4´-diphenylmethane diisocyanate or 1,5-naphthalene diisocyanate. Chain extenders such as dihydroxy compounds are used to increase the molecular weight.

3.7.2.4 Properties

TPUs were the first materials to combine rubber and thermoplastic characteristics. The hardness and the T_g increase with increasing amounts of the hard segment. The useful temperature range is about –40 °C to 80 °C. Within this range the TPU exhibit

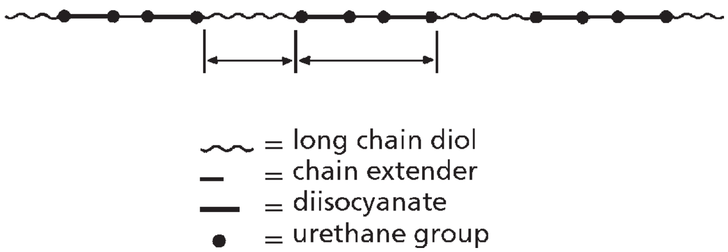


Figure 3.14 Structure of TPU

elongation greater than 800% with almost instantaneous recovery to original dimensions. Due to the large amount of polar substitution in their backbone the TPUs are resistant to organic solvents.

3.7.2.5 Uses

TPUs form part of a larger polyurethanes business which include reaction injection mouldable pre-polymers, castable liquid systems, microcellular shoe soling and millable gums. In the US, TPUs constitute a small part (16%) of the total, though they are more significant in Europe (32%). TPU is used for hydraulic hoses, cable sheathing, belting, hydraulic seals, cattle tags, sports items, magnetic tape and fabric coatings as well as for adhesives.

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4 Thermoplastic Elastomers

S. K. De and P. Antony

4.1 Introduction

Thermoplastic elastomers (TPEs) are polymeric materials, which combine the processability of thermoplastics and the functional performance of vulcanised rubbers [1-5]. The unique combination of properties enables the processing of TPEs in conventional plastic equipment, such as injection moulders, blow moulders, sheet and profile extruders. Such behaviour of TPEs is assigned to their structures which contain both soft and elastic segments of high extensibility with low glass transition temperature (T_g) and hard segments of low extensibility with a high T_g and/or crystalline melting point (T_m). The hard segments are susceptible to association leading to physical crosslinking which disappear when heated above a certain temperature and reappear immediately on cooling. Figure 4.1 shows the phase structure of a TPE consisting of hard glassy domains and soft rubbery segments, which must be thermodynamically incompatible with each other.

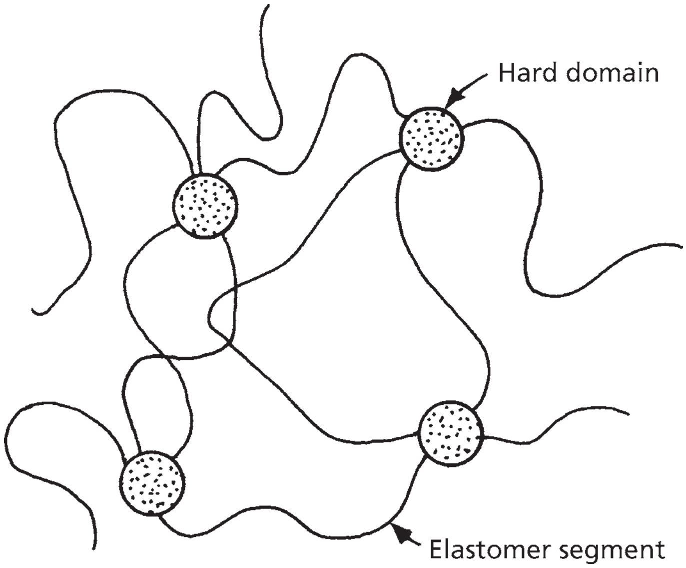


Figure 4.1 Phase structure of thermoplastic elastomers

The ratio of soft and hard segments determines the hardness and the modulus of elasticity. The chemical nature of the soft segments has an influence on elastic behaviour and low temperature flexibility, whilst the hard segments determine the heat resistance, the mechanical strength and the swelling behaviour. The main advantage of TPEs over conventional rubbers is that in TPEs, the transition from a processible melt to a solid rubber-like object is reversible and takes place on cooling. Conventional rubbers, on the other hand, must be vulcanised to get the useful properties and this is a slow irreversible process. Figure 4.2 shows the comparison of hardness of TPEs versus thermoplastics and elastomers and the relative cost of TPEs.

TPEs cover a broad hardness range from approximately 30 Shore A to 80 Shore D. The advantages in processing have resulted in significant growth of these materials, replacing both thermoplastics and vulcanised rubbers in many applications [6-8].

4.1.1 Thermoplastic elastomers versus thermoset rubbers

Thermoplastic elastomers have both advantages and limitations over conventional thermoset rubbers. The important practical advantages of TPEs include the following:

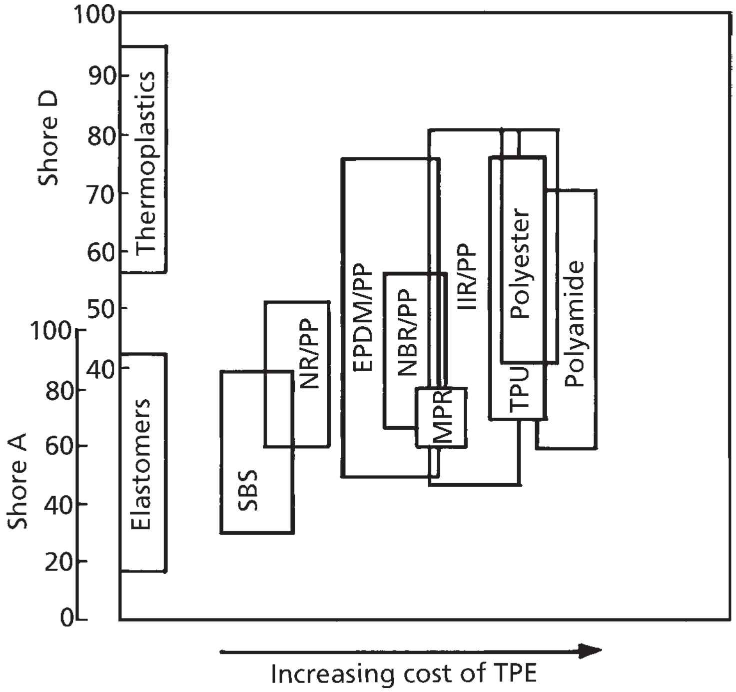


Figure 4.2 Comparison of hardness of TPEs versus elastomers and plastics and the relative increasing cost of TPEs

1. The ability of TPEs to become fluid on heating and then solidify on cooling gives manufacturers the ability to produce rubber-like articles using plastics processing equipment. Additionally, in some TPEs, a similar reversible transition from a solid to a fluid state can take place on addition and subsequent removal of a solvent. However, vulcanisation of rubbers is a thermosetting process, which is slow, irreversible and takes place on heating (see Figure 4.3).

2. There is little or no compounding or mixing required for TPEs. Most TPEs are fully compounded and ready for fabrication into finished components. Thermoset rubbers, on the other hand, require mixing of curatives, stabilisers, fillers, process aids, and other additives.

3. TPEs do not require vulcanisation. As shown in Figure 4.4, TPE processing consists of fewer steps as than thermoset rubber processing.

4. The scrap produced in the TPE process can be reprocessed. Scrap generated in thermoset rubber processing, however, has a limited reuse potential and the product cost is made greater by loss of material and disposal cost of the scrap.

5. Thermoplastic processing consumes less total energy due to more efficient processing and shorter cycle times.

The limitations of TPEs over thermoset rubbers include the following:

1. TPEs are relatively new materials destined to replace thermoset rubbers. However, the processing behaviour of these materials is unfamiliar to most of the thermoset rubber processors.

2. Thermoplastic processing equipment is different from thermoset rubber processing equipment. Therefore, capital investment is required for the thermoset rubber processor to produce TPE parts.

3. TPEs melt or soften at a specific temperature, above which they do not function as rubbers and a relatively brief exposure at or above that temperature will result in permanent deformation of TPEs. Brief exposure of thermoset rubbers to high temperature would probably not result in significant deformation.

4. Many TPEs require a drying step prior to processing into final products.

5. TPEs have higher tension and compression set than vulcanised rubbers (see Figure 4.5).

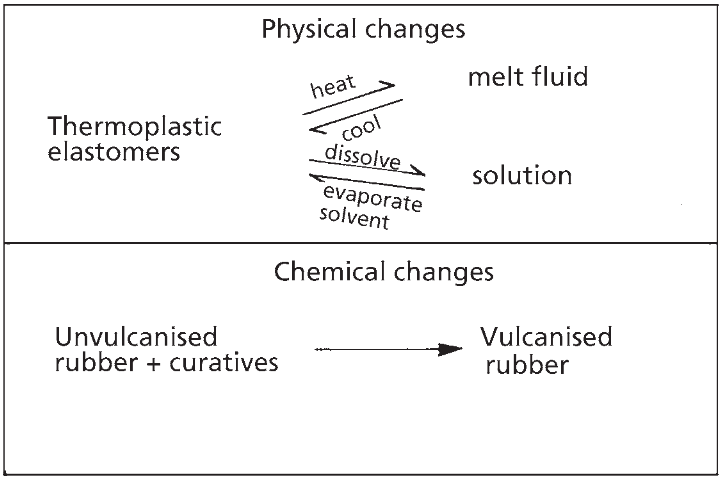


Figure 4.3 Irreversible and reversible changes

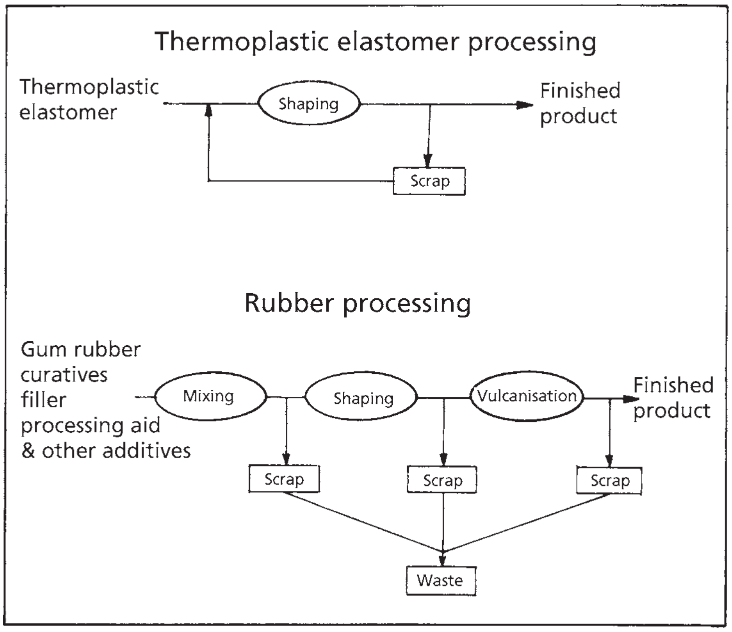


Figure 4.4 Thermoplastic elastomer processing versus rubber processing

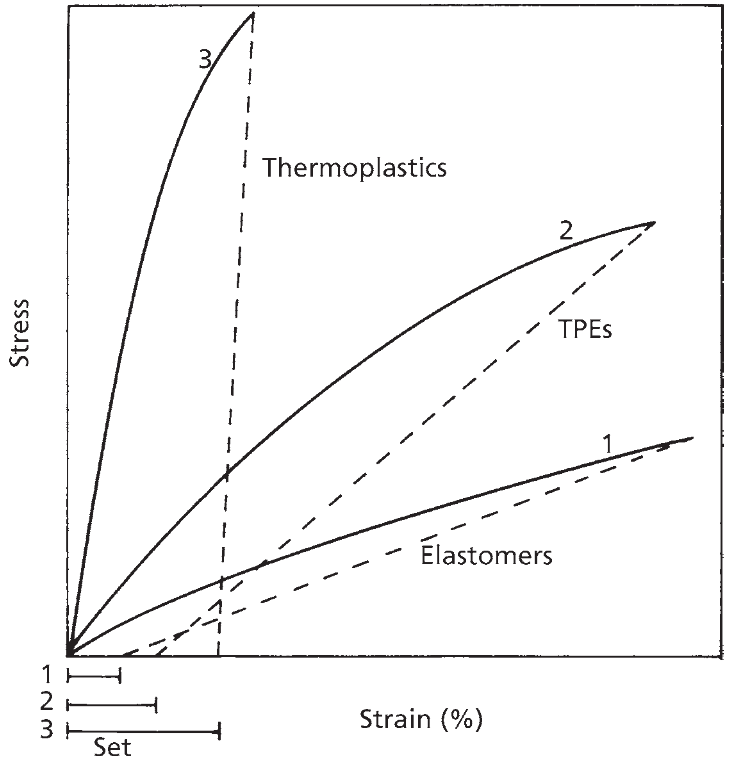


Figure 4.5 Stress-strain plots showing the set of elastomers, TPEs and thermoplastics

4.1.2 Types of thermoplastic elastomers

The main types of commercially available TPEs are listed in Tables 4.1 and 4.2. There are three major classes of thermoplastic elastomers :

a. Block copolymers

b. Dynamically vulcanised rubber/plastic blends

c. Ionic thermoplastic elastomers

Table 4.1 Different classes of commercially available thermoplastic elastomers based on block copolymers [3-7]

TPE Class	Hardness (Shore)	Examples (Trade name/ manufacturer)	Polymer segments or phase		Service temp limit (°C)	Note
			Soft	Hard		
Styrene grades SBS, SIS	30A to 85A	Kraton D/Shell Cariflex TR/Shell Solprene/Phillips	Polybutadiene or polyisoprene	Polystyrene	–70 to +70	General purpose
SEBS		Kraton G/Shell Dynaflex/GLS Multi-flex/Multibase Elexar/Teknor Apex	Ethylene-butylene copolymer	Polystyrene	–70 to +70	Improved ageing resistance
Polyurethanes	75A to 75D	Desmopan/Bayer Estane/Goodrich Pellethane/Dow Texin/Bayer	Polyether or amorphous polyesters	Polyisocyanate chain	–40 to +130	Hard, abrasion and oil resistant
Polyesters	85A to 75D	Arnitel/DSM Hytrel/DuPont Lomod/GE Ecdel/Eastman	Polyether or amorphous polyesters	Polyalkylene terephthalate	–50 to +150	Good low temperature flexibility, chemical resistance
Polyamides	60A to 70D	Pebax/Atochem Montac/Monsanto Grilamid/Emser Vestenamer/Huls	Polyether or amorphous polyesters	Polyamide	–40 to +170	Similar to polyurethanes, very good at low temperatures

Table 4.2 Different classes of commercially available thermoplastic vulcanisates based on rubber/thermoplastic blends [3-7]

TPVs Class	Hardness (Shore)	Examples (Trade name/ manufacturer)	Polymer segments or phase		Service temp limit (°C)	Note
			Soft	Hard		
EPDM/PP	55A to 75D	Santoprene/AES Uniprene/Teknor Apex Sarlink 3000 and 4000/DSM	Crosslinked EPDM	Polypropylene	–50 to +120	Ozone resistant, low density
NR/PP	60A to 50A	Vyram/AES	Crosslinked NR	Polypropylene	–50 to +100	Low cost
NBR/PP	65A to 55D	Geolast/Monsanto	Crosslinked NBR	Polypropylene	–40 to +120	Oil resistant
IIR/PP	45A to 80D	Trefsin/AES Sarlink 2000/DSM	Crosslinked IIR	Polypropylene	–50 to +120	Low permeability, high damping
Chlorinated polyolefin base	60A to 80A	Alcryn/DuPont	Ethylene interpolymer	Chlorinated polyolefin	–40 to + 120	Single phase, soft, and oil resistant

4.2 Block copolymers

The majority of thermoplastic elastomers are block copolymers consisting of a simple A-B-A structure, where A is a linear polymeric segment, which is hard at room temperature, but softens at higher temperature, and B is an elastomeric segment. The consequence of this type of structure is that the blocks are phase separated, quite unlike the corresponding random copolymers. At room temperature, domains of the block copolymers act as multifunctional junction points to produce a crosslinked elastomer network and show properties similar to those of conventional vulcanised rubbers. However, the crosslinks here are of physical nature rather than chemical and are thermolabile. Thus when the copolymer is heated, the hard domains soften and the network loses its strength, and when the heated block copolymer is cooled down, the domains reform and the original properties are regained. Similarly, such a block copolymer will be soluble in a suitable solvent but it will regain its original properties when the solvent is evaporated. A crosslinked elastomer shows only one glass transition and no melting peak, indicating a single phase structure, whereas in the case of a TPE two clear phase transitions are evident, i.e., the T_g of the elastic phase and a T_g of the hard phase or melting peak due to the crystalline phase (see Figure 4.6). The upper service temperature of a TPE is generally about 30 °C lower than the T_m.

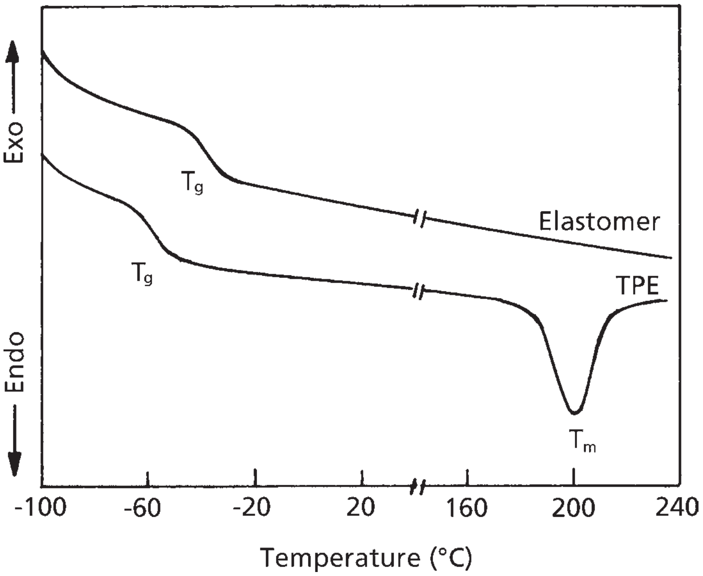


Figure 4.6 DSC curves of a crosslinked elastomer and a polyester TPE

The microphase separation of block copolymers can be understood from the thermodynamic principle. In block copolymers phase separation will occur when the free energy of mixing (ΔG) is positive. The free energy can be expressed as:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔH and ΔS are the enthalpy and entropy of mixing, respectively, and T is the absolute temperature. Thus the condition for domain formation is:

$$\Delta H > T\Delta S \tag{2}$$

The enthalpy is equal to the heat of mixing and is related to the Flory-Huggins interaction parameter (χ_{ab}), which in turn, is a function of the difference in solubility parameters between the block segments (that is, ($\delta_a - \delta_b$)) and the molecular weight (M_a) and density (ρ_a) of the 'a' segments.

$$\Delta H = f\ (\chi_{ab}) \tag{3}$$

$$\chi_{ab} = \frac{\left(\partial_a - \partial_b\right)^2 M_a}{\rho aRT} \tag{4}$$

Hydrocarbon polymers have a positive ΔH value due to the absence of strongly interacting groups and this will increase further if the structures of the two polymers are different. ΔS will always be positive and approaches zero for high molecular weight polymers. Therefore, the important parameters which govern the domain formation in block copolymers are the structural difference between the segments, high segmental molecular weight and low temperature.

4.2.1 Polystyrene/elastomer block copolymers

Most of the polystyrene/polydiene block (b) copolymers that are TPEs have structures such as poly(styrene-b-butadiene-b-styrene) and poly(styrene-b-isoprene-b-styrene), hereafter referred as S-B-S and S-I-S, respectively. The two phases, polystyrene and polydienes retain many of the properties of the respective homopolymers. Such block copolymers have two T_gs corresponding to the respective homopolymers, whereas the corresponding random copolymers have a single intermediate T_g, as shown in Figure 4.7. The higher storage modulus of S-B-S as compared to styrene-butadiene-rubber (SBR) is due to the presence of hard polystyrene blocks which act as reinforcing fillers, in addition

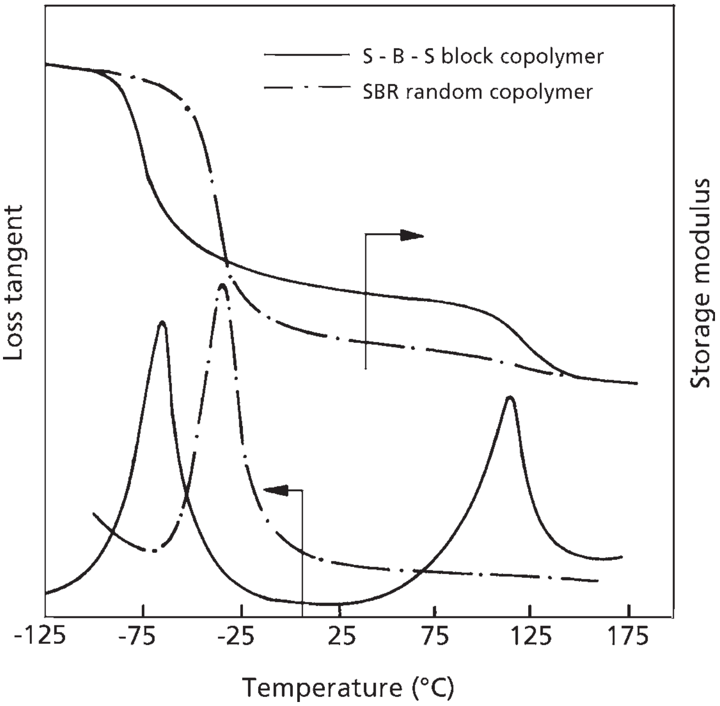


Figure 4.7 Plots of loss tangent and storage modulus versus temperature for S-B-S block copolymer and SBR random copolymer

to their role as physical crosslinks below their glass transition temperature. The polydiene segments are responsible for the low temperature flexibility above their glass transition temperature.

S-B-S and similar block copolymers are made by anionic polymerisation [1, 9]. The reaction is usually carried out in an inert hydrocarbon solvent such as cyclohexane or toluene and it is necessary to rigorously exclude oxygen, water or any other impurities. The preferred initiators are organolithiums.

During the initiation step, the initiator first reacts with one molecule of styrene monomer (S).

$$R^- Li^+ + S \rightarrow RS^- Li^+$$

During the propagation step, the product can continue polymerisation of the styrene.

$$RS^- Li^+ + n\,S \rightarrow R\,(S)_n S^- Li^+ \; (S^- Li^+)$$

If a diene (B) is added (after the styrene monomer has been exhausted), the end product denoted as $S^- Li^+$, can initiate further polymerisation:

$$S^- Li^+ + n\,B \rightarrow S\,(B)_{n-1}B^- Li^+ \;(S\text{-}B^- Li^+)$$

This reaction product, denoted as $S\text{-}B^- Li^+$, can also act as an initiator and if more styrene monomer is added (after the diene monomer has been exhausted), it will polymerise onto the living end of the polymer chain:

$$S\text{-}B^- Li^+ + n\,S \rightarrow S\text{-}B\text{-}(S)_{n-1}\,S^- Li^+ \;(S\text{-}B\text{-}S^- Li^+)$$

In the termination step either the product $S\text{-}B\text{-}S^- Li^+$ can be inactivated by the addition of a protonating species such as alcohol or a suitable coupling agent.

$$S\text{-}B\text{-}S^- Li^+ + ROH \rightarrow S\text{-}B\text{-}SH + ROLi$$

The relative ratio of the molecular weights of polystyrene (PS) blocks and those of the diene rubber segments determines the morphology of the material and affects the overall performance characteristics of the S-B-S or S-I-S material. Generally, the relative ratio is from 15:85 to 50:50 S:B or S:I. The polystyrene block typically will have a molecular weight of 4,000-40,000 and polydiene block will have a molecular weight of 20,000 to 150,000. The change in morphology of S-B-S or S-I-S block copolymer TPE with S:B or S:I ratio is shown in Figure 4.8. As the polystyrene content is increased, the morphology of the PS phase changes from spheres to cylinders, both dispersed in a continuous elastomeric phase. When the volume fractions of the elastomer and polystyrene phases are about equal, the two form alternating lamellae. With further increase in polystyrene content, a continuous PS phase is formed in which either cylinders or spheres of the elastomer are dispersed [9, 10]. At low levels of polystyrene content, the elastomer is

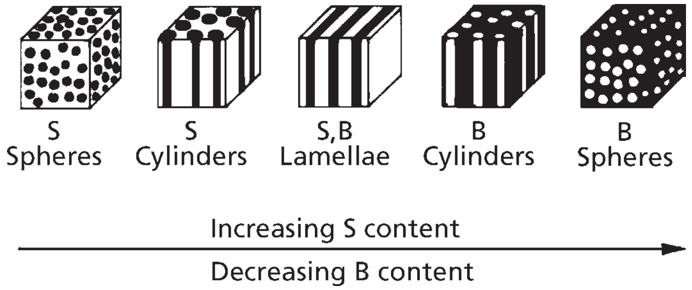
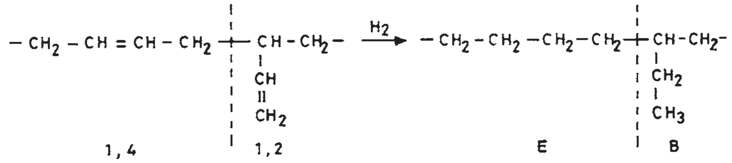


Figure 4.8 Changes in morphology of a S-B-S type block copolymer as a function of composition

continuous phase with the PS serving as hard connector for the flexible rubber segments and the resultant TPE is soft and rubbery with a relatively low tensile strength. However, at high polystyrene content an impact modified plastic results.

The hydrogenation of polybutadiene segments present in S-B-S and polyisoprene segments present in S-I-S gives ethylene-butylene copolymers (EB) and ethylene-propylene copolymers (EP), respectively. The resultant S-EB-S and S-EP-S block copolymers have outstanding ageing resistance.



The block copolymers typically have a tensile strength of about 30 MPa and elongation of up to 700%. These values are much higher than those obtained from unreinforced vulcanisates of SBR or polybutadiene. The apparent anomaly has been explained by two possible mechanisms. According to one mechanism, the hard domains act as reinforcing fillers and according to the second mechanism the increased tensile strength is ascribed to the slippage of the entangled chains [7].

It is important to note that the structure of the block copolymer is S-B-S or S-I-S and not B-S-B or I-S-I. The elastomeric component gives the material the characteristics of a rubber, but only when it is 'tied' on both ends to a stiff, non-flexible block like PS. The PS block behaves essentially as a chemical crosslink in a conventional thermoset rubber. The bonding between the PS segment and the elastomeric segment is through covalent bonding. The two phase structure occurs because of the microphase separation or incompatibility of the two segments.

Polystyrene is often used as a compounding ingredient for S-B-S block copolymers. It acts as a processing aid and makes the product stiffer. Oils and resins are used to soften or even tackify the polymer. Paraffinic and naphthenic oils are preferred and oils with high aromatic contents should be avoided, since they plasticise the PS domains. Crystalline polymers such as polyethylene, polypropylene, ethylene-vinyl acetate copolymer can be blended with styrenic block copolymers to form interpenetrating networks and technologically useful mixtures with improved solvent and ozone resistance. Large amounts of inert fillers such as powdered chalks, talcs and clays can also be added. They have only a small effect on physical properties but reduce cost. Typical property ranges for styrenic TPEs are shown in Table 4.3. The hardness ranges from 30 to 85 Shore A. Table 4.3 also shows some of the applications of compounded thermoplastic elastomers

Table 4.3 Properties of compounded styrenic block copolymers [7]

Product	Kraton D2109	Kraton D2705	Kraton G7720	Multi-Flex A 4001 LC	Multi-Flex A 8832	Dyna-flex D3202	Dynaflex GX-7722	Elexar 8431	Elexar 8614
Base polymer	S-B-S	S-EB-S	S-EB-S	S-EB-S	S-EB-S	S-B-S	S-EB-S	S-EB-S	S-EB-S
Application	Milk tubing and film	Medical	Automotive, general purpose	Automotive, low compression set	Automotive, sound barrier	General purpose	Automotive, low compression set	Wire and cable	Wire and cable fire retardant control
Properties: Hardness, Shore A or D	48A	55A	60A	40A	88A	50A	57A	64D	95A
Tensile strength, MPa	11.0	6.0	5.0	4.5	4.3	5.6	5.0	9.6	14.0
300% Modulus, MPa	2.0	2.8	2.5	3.1	1.4	4.3	2.5	3.6	9.7
Elongation at break, %	850	700	700	900	1400	400	700	650	500
Specific gravity	0.94	0.9	1.19	1.08	0.94	1.0	1.19	0.92	1.2

Reproduced with permission from G. Holden in Thermoplastic Elastomers – A Comprehensive Review, Eds., G. Holden, N. R. Legge, R. Quirk and H. E. Schroeder, Hanser Publishers, Munich, 1996, 583 based on styrenic block copolymers [7]. The other important applications of styrenic block copolymers include solvent-based and hot melt adhesives, sealants, coatings, hoses, asphalt modifiers and sporting goods.

4.2.2 Polyester/elastomer block copolymers

The polyester elastomers are multi-block copolymers which can be represented by the generalised formula (-A-B-)$_n$. Crystalline polyester segments form the high melting blocks (hard segments) and the amorphous polyether segments having a relatively low T_g form the rubbery soft segments. Copolymers based on alkylene terephthalate and alkylene glycol blocks are both hard thermoplastic as well as highly elastic. They are best known under the trade names Hytrel (DuPont) and Arnitel (DSM). The morphology of this thermoplastic copolyester resembles that of styrenic triblock copolymers. The hard and crystallizing chain segments are formed by butylene terephthalate segments consisting of 7 to 10 monomers (corresponding to segment molecular weights of around 1,700 to 2,500), and having a melting point of around 200 °C. The soft and flexible segments, on the other hand, consist of butylene glycol ether with 12 to 16 butylene ether monomer units, corresponding to segment molecular weights of about 1,000-1,400. At useful service temperatures, the polyester elastomers resist deformation because of the presence of a network of micro-crystallites formed by partial crystallisation of hard segments. The micro-crystallites function as physical crosslinks. At elevated temperatures the crystallites break down to yield a polymer melt, thus facilitating the thermoplastic processing.

The Hytrel copolyesters are synthesised by melt condensation polymerisation of dimethyl terephthalate, poly(oxytetramethylene) glycol and 1,4 butanediol in the presence of an ester interchange catalyst at 240 ° to 260 °C [2].

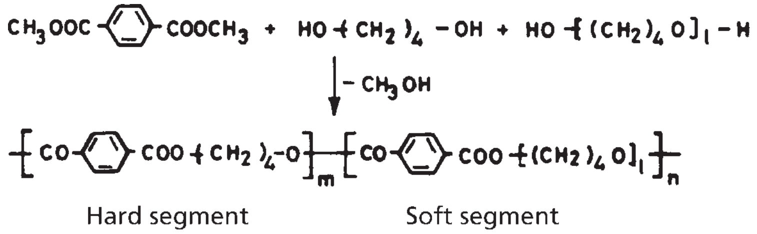


Table 4.4 shows the physical properties of polyester/elastomer block copolymers [7]. Thermoplastic copolyesters are growing in popularity for many applications because of their high mechanical strength, heat and chemical resistance, as well as their flexibility and resistance to flex fatigue. Copolyesters show good resistance to oils, aliphatic and

Table 4.4 Properties of polyester/elastomer block copolymers [7]

Product	Hytrel 4056	Hytrel 5526	Hytrel 6356	Hytrel 7246	Gaflex 547	Lomod B0100
Hardness, Shore A or D	92A	55D	62D	72D	47D	35D
Tensile Strength, MPa	26	40	41	46	32	17
100% Modulus, MPa	9.5	19	20[a]	25[a]	11	–
Elongation at break, %	550	500	420	350	750	685
Specific gravity	1.17	1.20	1.22	1.25	1.18	1.16

[a] *After yielding at lower elongation*
Gaflex is a trade name of GAF Materials Corporation
Lomod is a trade name of GE Plastics

aromatic hydrocarbons, alcohols, ketones, esters and hydraulic fluids. Thermoplastic copolyesters can be processed only on plastics processing equipment because of their high melting points. Thermoplastic copolyesters are in competition mainly with thermoplastic polyurethanes and polyether amides. The vast difference between the T_g of thermoplastic copolyesters (around -50 °C) and melting point (around 200 °C) provides a wide service temperature range.

The Hytrel polyesters have a unique combination of physical properties, which make these materials well suited for use in industrial, recreational, and chemical environments. These materials because of their service life and functionality, have been able to replace polyurethanes and nylons as well as some rubbers, PVC and other plastics in applications ranging from hydraulic hoses, tubings, seals, flexible couplings, fuel tanks, pipe clamps, gaskets, and wire and cable jacketing.

4.2.3 Polyamide/elastomer block copolymers

The chemical description of a polyamide elastomer is a multiblock copolymer of hard and soft segments connected by amide linkages. The hard segments are polyamides and the soft segments are either polyester or polyetherester. The important examples for thermoplastic polyamide elastomers are polyesteramides (PEA) and polyetheresteramides (PEEA). In PEA, the soft segments are derived from aliphatic polyesters, while PEEA has aliphatic polyethers linked to the hard amide segment by an ester group.

PEA and PEEA are synthesised by the condensation of the aromatic diisocyanate, 4,4′-diphenylmethane diisocyanate (MDI), with dicarboxylic acids and a carboxylic acid terminated polyester or polyether prepolymer. Two moles of carbon dioxide are lost for every mole of the diisocyanate consumed in the reaction. The homogeneous polymerisation is usually carried out at an elevated temperature in a polar solvent, which is non-reactive with isocyanates. The dicarboxylic acid serves as the hard segment chain extender and forms an amide hard segment with the MDI. The carboxylic acid terminated prepolymer, which can be either ester- or ether-based, forms the soft segment matrix for PEA or PEEA, respectively [11].

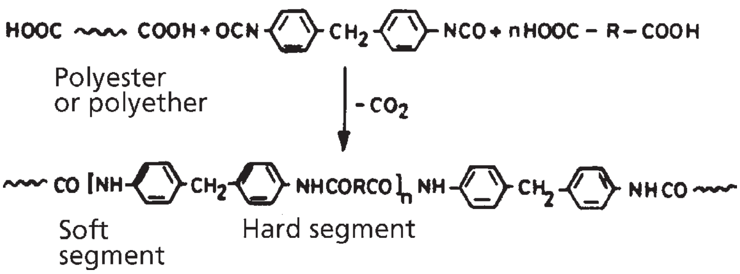


Table 4.5 shows the typical properties of some representative grades [7]. The initial moduli of the PEA and PEEA elastomers, which parallel the amide content, are much higher than for many other TPEs in the same hardness range, which is due to higher load bearing ability of the hard crystalline domains. The high temperature performance of a segmented elastomer is closely dependent upon the hard segment crystallinity and its melting point. It is also noteworthy that these materials retain useful tensile properties under high temperature conditions where most other TPEs could not even be tested.

The physical properties of PEA and PEEA are dependent upon parameters such as the chemical composition and molecular weight of the hard and soft segments. The hard segment controls the polymer melting point, and mechanical strength, while the soft segment controls the hydrolytic stability, chemical and solvent resistance, thermo-oxidative stability and low temperature flexibility.

Because of the higher service temperature and good thermal ageing and solvent resistance characteristics, the PEA and to some extent the PEEA thermoplastic elastomers are expected to be categorised in between the thermoplastic urethanes and silicone polymers. Application areas for this material include conveyor and drive belts, Nordic ski and soccer shoe soles, as well as key pads. Potential application in electrical areas include wire and cable jacketing for high temperature applications such as low voltage wiring in confined areas and in the vicinity of engines and motors.

Table 4.5 Typical properties of polyamide/elastomer block copolymers [7]

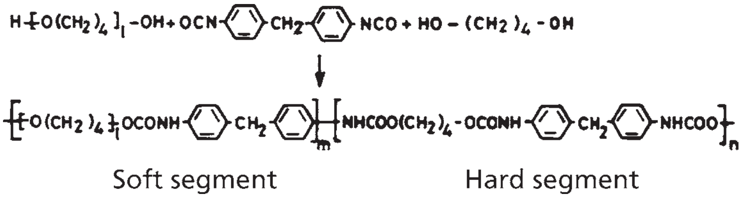
Product	Pebax 2533	Pebax 4033	Pebax 6333	Estamid 90A	Grilamid Ely 60
Hardness Shore A or D	75A	40D	63D	93A	62D
Tensile strength, MPa	29	33	49	27	36
100% Modulus, MPa	4.3	10	19	14	–
Elongation at break, %	350	620	680	320	300
Specific gravity	1.01	1.01	1.01	1.14	1.01

Adapted with permission from G. Holden in Thermoplastic Elastomers, 2nd edition, Eds., G. Holden, N. R. Legge, R. Quirk and H. E. Schroeder, Hanser Publishers, Munich, 1996, 593
Estamid is a trade name of Upjohn
Grilamid is a trade name of Emser

4.2.4 Polyurethane/elastomer block copolymers

Thermoplastic polyurethanes (TPUs) are made generally from long chain polyols with an average molecular weight of 600 to 4,000, chain extenders with a molecular weight of 60 to 400 and diisocyanates. Depending on the ratio of hard to soft segments, TPU can be formulated in different grades which range from soft flexible elastomeric materials to brittle and high modulus plastics. The flexible soft segment largely controls the low temperature properties, solvent resistance and weather resistance properties of TPU. The two types of flexible segments (polyols) are the hydroxyl terminated polyesters and the hydroxyl terminated polyethers. The typical hydroxyl terminated polyester is made from adipic acid and an excess of glycol such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol or mixtures of these diols. There are two classes of polyethers of technical importance, the poly(oxypropylene) glycols and the poly(oxytetramethylene) glycols. The hard segment is formed by addition of the chain extender to the diisocyanate. The most important diisocyanate is MDI. The other diisocyanates include hexamethylene diisocyanate (HDI), 4,4´-dicyclohexylmethane diisocyanate and 2,4 and 2,6-toluene diisocyanate (TDI). The choice of a chain extender and diisocyanate determines the characteristics of the hard segment and to a large extent the physical properties of TPU. The most important chain extenders for TPU are the linear glycols such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol and hydroquinone *bis*(2-hydroxyethyl) ether.

Polyurethanes are synthesised by two commercial methods, namely the prepolymer method (two step) process and the one shot process. The former involves preparation of a low molecular weight isocyanate-terminated prepolymer, followed by its chain extension to a high polymer. In the one shot process the diisocyanate, polyol and chain extender are mixed together at one time. The polymerisation by polyaddition reaction yields a high polymer with alternating soft and hard segments [3, 4]:



The TPU grades cover a wide range of hardness from 75 Shore A to 75 Shore D. The grades of lower hardness of up to about 85 Shore A compete with conventional elastomers, while the harder TPU grades (that is, above 55 Shore D) compete with thermoplastics. The grades between 40 to 55 Shore D close the gap between rubbers and thermoplastics. Depending on their chemical structures and hardness, the tensile strength of TPUs vary from 25 to 50 MPa. Table 4.6 shows typical physical properties of representative TPU grades. Figures 4.9 and 4.10 shows the stress-strain plots and dynamic mechanical behaviour, respectively, of Desmopan TPUs having three different hardnesses [12].

Table 4.6 Properties of polyurethane/elastomer block copolymers [4,7,12]

Product	Estane 58113	Estane 58880	Pellethane 2102-90A	Pellethane 2103-70A	Desmopan 385	Desmopan KA 8375
Type	Polyester	Polyether	Polycaprolactone	Polyether	Polyester	Polyether
Hardness Shore A or D	55D	80A	90A	70A	86A	93A
Tensile strength, MPa	35	24	48	24	40	40
100% Modulus, MPa	13	4.5	10.7	3.5	6.0	11.0
Elongation at break, %	500	600	500	700	450	380
Specific gravity	1.22	1.10	1.20	1.06	1.20	1.14

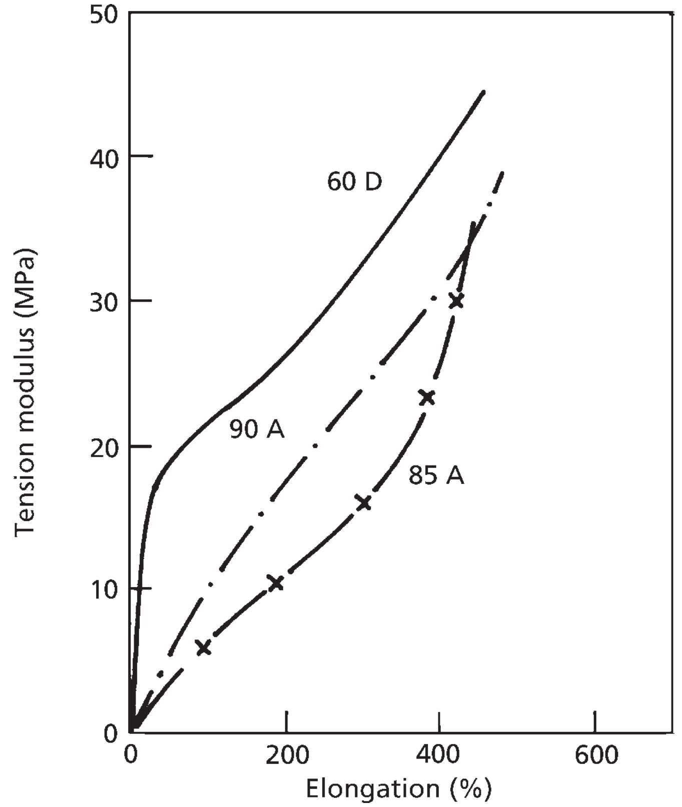


Figure 4.9 Tension modulus versus elongation at room temperature for Desmopan 460 (——), 790 (— . —), and 385 (— x —) TPU grades of hardness 60 shore D, 90 shore A and 85 shore A

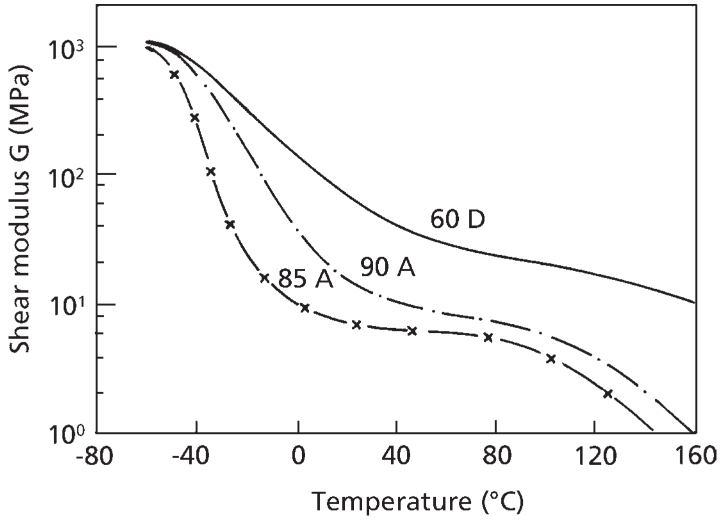


Figure 4.10 Shear modulus versus temperature for Desmopan 460 (——), 790 (— . —), and 385 (— x —) TPU grades of hardness 60 shore D, 90 shore A and 85 shore A

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A severe drop of the modulus occurs at elevated temperature for Desmopan 385. With increasing hardness, this drop becomes less pronounced, indicating the role of hard domains acting as physical crosslinks and as reinforcing fillers. All TPUs show a rubbery plateau over a reasonable temperature range. A second drop in modulus occurs when the temperature is increased to the hard-segment melting point. It is also apparent that the shear modulus of the TPUs increases with an increasing hardness (that is, with an increasing weight % of the hard segment content).

One of the main advantages of TPU is its high abrasion resistance. Therefore, polyurethanes (PU), especially ester- or ether-ester-PU are the materials of choice for shoe soles, and cable jacketing. At equivalent hardness, TPU has a much higher load bearing capacity than other conventional rubbers. The impact resistance of hard TPU parts is much greater than that of most plastics. Ester-TPU shows better abrasion and cut resistance, tensile and tear strength than ether-TPU. Ester-TPU also swells less in oil, grease and water than ether TPU. TPU can be used in pure water over a period of several years at room temperature without any significant drop in mechanical properties. However, at 70 °C a reduction in tensile strength of about 30% is seen after weeks or months. The hydrolytic stability of TPU is dependent on the structure of the polyol. Ester-TPU is less resistant than ether-TPU and can be protected by adding 1-2% by weight of sterically hindered aromatic carbodiimides. With increasing hardness, TPU becomes more hydrolytically stable. Dilute acids and bases attack TPUs at room temperature only moderately.

TPUs are also very resistant to ageing, weathering, oxygen and ozone as well as to oils, motor fuels, hydraulic fluids, and many other non-polar solvents such as hexane, heptane, etc. However, chlorinated hydrocarbons or aromatic solvents like toluene cause a very severe swelling of TPU. Ester types swell less than ether-types and hard PUs swell less than the soft ones. Polar solvents like tetrahydrofuran, methylethyl ketone or dimethylformamide are capable of partially or completely dissolving TPU. Soft ester-TPU can be attacked by microorganisms after long contact with moist earth. However, soft and hard ether-, ether-ester-TPU or hard ester-TPU are normally resistant to such attack.

TPUs can be extruded into films and sheets of different thickness. Films of TPU have outstanding properties regarding abrasion, flexibility, toughness, puncture and tear propagation resistance in combination with high elasticity. Many different types of hoses and tubes are made from TPUs. The high flexibility, toughness, oil resistance, good hydrolysis and microbe resistance and the high mechanical properties of ether-ester or ether-polyurethanes are an ideal combination for industrial hoses.

The polyurethane properties of good abrasion and cut resistance, permanent buckling strength and the high impact strength at low temperatures and flexibility are particularly useful for ski boots, shoe soles and heels. Exterior automotive body parts can be injection-moulded from pure TPU, TPU-polycarbonate blends and glass reinforced TPU. These materials find many applications in mechanical goods. Screens of TPU, with its high abrasion resistance, exhibit a longer lifetime in comparison to rubber and steel elements. In addition to this, TPUs have been recommended for different medical applications. TPUs are non-toxic and show a good compatibility to human skin. The good compatibility of ether-PU elastomers with human blood and tissues allows catheters and tubes to be made from TPU.

4.3 Dynamically vulcanised rubber/plastic blends

Thermoplastic elastomers can be prepared by blending a plastic with a rubber in desired compositions [3, 13-15]. However, the major problem in polymer blending is the lack of compatibility between the rubbery and the plastic phases [16-18]. Often therefore, different compatibilisers have been employed to improve the physical properties of a blend [19-21]. Rubber/plastic blends have become technologically useful as TPEs. The blends possess many of the properties of elastomers but they are processable like thermoplastics. Elastomeric alloys are blends of a rubber and a plastic in which the rubber phase has been dynamically vulcanised [22]. Dynamic vulcanisation is the process of vulcanising the rubber during its melt mixing with molten plastic which results in a fine dispersion of elastomer particles in the plastic matrix [23-26]. The dynamic vulcanisation of blends of ethylene-propylene-diene rubber (EPDM) with polypropylene (PP) has been described elsewhere [25, 26]. The resultant thermoplastic elastomers are commonly known as thermoplastic vulcanisates (TPVs). If enough of a thermoplastic resin is present in the molten state, the mixture does not lose processability as a result of vulcanisation. This is true even when the rubber is fully cured. This product which is elastomeric in nature and yet can be fabricated as thermoplastics, can be prepared, within a certain range of proportions of rubber and plastic. Decrease in particle size of the elastomer particles in the blend by dynamic vulcanisation causes dramatic improvements in the blend properties such as:

a. more reliable thermoplastic fabrication,

b. greater stability of phase morphology in the melt,

c. greater melt strength,

d. reduced permanent set,

e. improved ultimate mechanical properties,

f. improved fatigue resistance,

g. greater resistance to attack by fluids, and

h. improved high temperature performance [26].

4.3.1 EPDM/polyolefin

The most common example of a commercially available rubber/plastic blend is that of ethylene-propylene-diene terpolymer (EPDM) and polypropylene (PP). Similarly blends of polyethylene (PE) with EPDM and with ethylene-propylene rubber (EPM) have been reported [14, 27-29]. The rubber component may contain the usual ingredients found in vulcanised rubber formulations, such as curatives, fillers, extender oil and stabilisers. The partial or full vulcanisation of the elastomer phase is achieved by peroxides, resin or a sulphur/accelerator system. Most often, the plastic phase is a homopolymer such as isotactic PP, although copolymers of propylene with ethylene are used as well. The unvulcanised blends have poor set properties and poor hydrocarbon fluid resistance. To maintain good fabricability and a balance of rubber-like performance at room temperature, the morphology of these blends has to be one of a dispersed EPDM rubber in a continuous matrix of PP. Partial vulcanisation of the rubber phase results in a more stable morphology and extends the elastic range of the rubber. The important factors which determine the ultimate properties of EPDM/PP TPVs are the size of the dispersed elastomer particles, the degree of crosslinking of the rubber phase and the rubber to plastic ratio. Blends of EPDM and PP or PE show good elastomeric behaviour when the EPDM is well dispersed as small (approximately 10 μm or less) particles. The particle size of the dispersed particles in the dynamically vulcanised blends has pronounced effect on mechanical properties as reported by Coran and Patel [25].

4.3.2 NBR/polyolefin

An oil resistant thermoplastic elastomer can be prepared by blending a polyolefin resin with nitrile rubber (NBR) in the desired proportions. The large difference in surface energy between the two types of polymers, causes incompatibility between the two phases. However, use of compatibilisation techniques makes them technologically compatible. Coran and Patel observed that a dimethylol phenolic compound (such as a 'phenolic resin' curative, SP-1045, Schenectady International) can be used to technologically compatibilise a mixture of polyolefin and NBR [30]. The compatibilisation could be the result of the formation of a block copolymer. The formation of polymer-polymer grafts can be accomplished by a number of other chemical means, in addition to the use of dimethylol phenolic derivatives. If a part of PP in a NBR-PP composition is maleic modified, and if a part of the NBR is amine-terminated (that is ATBN), then a compatibilising amount of NBR-PP block copolymers is formed *in situ* during melt mixing as shown in Figure 4.11 [26, 30].

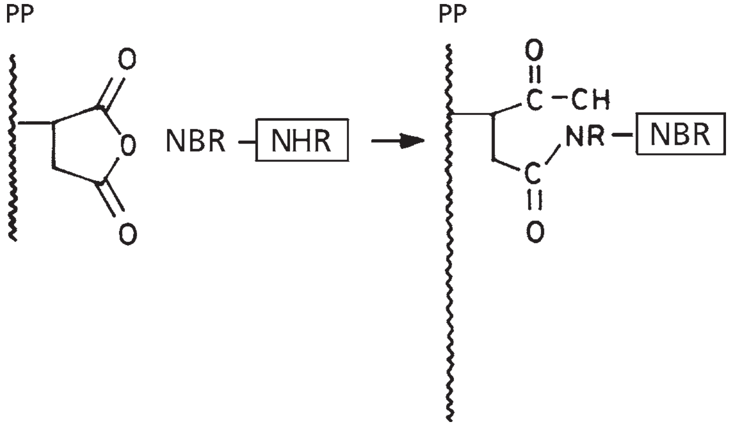

Figure 4.11 Schematic representation of formation of compatibilising block copolymer

Only a small amount of compatibilising block copolymer is needed to obtain a substantial improvement in the properties of a blend. Table 4.7 shows the effect of compatibilisers on the physical properties of NBR/PP blend. The NBR/PP blends are used for applications in which low swell is required in oils, fuels and other hydrocarbon media. Commercial NBR/PP blends range in hardness from 65 shore A to 55 shore D.

Table 4.7 Effect of compatibilisation and dynamic vulcanisation of properties of NBR/PP blends

	1	2	3	4	5	6
Recipe[a]:						
Polypropylene[b]	50	45	45	45	45	45
Maleic-modified PP	–	5	5	5	5	5
NBR[c]	50	50	46.88	37.5	25	–
NBR masterbatch	–	–	3.12	12.5	25	50
SP-1045[d]	3.75	3.75	3.75	3.75	3.75	3.75
$SnCl_2$-$2H_2O$	0.5	0.5	0.5	0.5	0.5	0.5
Properties:						
Tensile strength, MPa	8.8	12.0	15.2	25.5	25.7	26.7
Stress at 100% strain, MPa	–	12.0	12.0	12.3	12.5	12.9
Young's modulus, MPa	209	200	223	188	184	237
Ultimate elongation, %	19	110	290	440	430	540
Tension set, %	–	–	40	40	42	45
True stress at break, MPa	10	25	59	138	136	171
Breaking energy, mJ/m^3	1.2	11.0	34.6	64.1	61.7	86.5
Improvement in breaking energy due to compatibilisation, %	–	–	215	483	461	686

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[a] *Parts by weight*

[b] *Profax 6723*

[c] *90% wt., Hycar 1092-80, 10%wt., Hycar ATBN 1300x16*

[d] *Dimethylolphenolic vulcanising agent*

4.3.3 Natural rubber/polyolefin

Thermoplastic elastomers based on natural rubber (NR)/PP blends have been prepared by the Malaysian Rubber Producer's Research Association by blending NR with crystalline polyolefins such as PP [31, 32]. The blends are known as thermoplastic natural rubber (TPNR). Like EPDM/PP elastomeric alloys, the NR/PP blends are also prepared by dynamic vulcanisation [33-35]. The NR/PP elastomeric alloys with a low NR/PP ratio have a morphology with a continuous PP phase and a discontinuous (particulate) crosslinked NR phase, similar to the EPDM/PP elastomeric alloys. As the NR:PP ratio is increased, however, the morphology shifts progressively toward two interpenetrating continuous phases. The tensile stress-strain and set properties are comparable to those of the EPDM/PP and NBR/PP alloys. As expected, resistance to oil and other hydrocarbon media is inferior to NBR/PP alloys, but similar to EPDM/PP alloys. The useful temperature range of the NR/PP elastomeric alloys extends from a low temperature of approximately -50 °C to a high temperature of approximately 100 °C. In a variety of fluids, the NR/PP elastomeric alloys have been found only slightly inferior to the EPDM/PP elastomeric alloys. The NR/PP elastomeric alloys are inferior to EPDM/PP and NBR/PP elastomeric alloys in elevated temperature performance and resistance to environmental attack. However, there is a distinct niche for NR/PP elastomeric alloys in the elastomeric materials spectrum due to the low cost and abundant supply of natural rubber.

Dynamically vulcanised thermoplastic elastomeric NR/PE blends in some blend ratios (for example 70/30 NR/PE) have also been reported to function as TPEs [36-40]. Choudhury, Bhowmick and De have published a review on thermoplastic NR [41].

4.3.4 Butyl rubber/polyolefin

A series of thermoplastic elastomers called ET polymers (butyl rubber/PE blends prepared by the Allied Chemical Corporation) have been prepared by grafting isobutylene-isoprene rubber (IIR) onto PE [42]. The physical properties of blends of IIR with PE and PP have been reported elsewhere [43]. The IIR/PP system has a morphology of fine crosslinked rubber particles in a continuous PP matrix, which is very similar to the EPDM/PP blends. The useful service temperature range (–50° to 120 °C) of the IIR/PP elastomeric alloy is similar to that of the EPDM/PP elastomeric alloy [44]. The fluid resistance of the two blends is similar. The unique advantages of the IIR/PP elastomeric alloy are its low permeability to gases such as oxygen, nitrogen and water vapor, and high damping, which are comparable to thermoset butyl rubber. The low permeability of IIR/PP elastomeric alloy makes it a strong contender in applications such as bladders and stoppers.

The largest application area for polyolefin thermoplastic elastomers is presently in the automotive market. The excellent combination of properties, processability, wide service temperature range, low temperature flexibility, high temperature stiffness, resilience, and paintability have encouraged fast acceptance of these materials by the automotive industry. The major automotive market is in exterior body applications such as filler panels, bumper covers, fender extensions, flexible front and rear panels, corner panels, weather stripping and sight shields. Interior automotive parts made with olefinic thermoplastic elastomers include steering wheels, connector strips, seals, bushings, seat belt housings, horn pads, and flexible trim. Wire and cable applications provide the largest potential non-automotive market for thermoplastic elastomers. The polyolefin thermoplastic elastomers are used mainly as insulation and jacketing materials where environmental and heat resistance are needed. Other application areas of polyolefinic thermoplastic elastomers include belting, hoses, toys, household wares and shoe soles.

4.3.5 Melt processable rubber

All the elastomeric alloys discussed in Section 4.3 are phase separated systems. Another commercially important TPE based on polymer blends, Alcryn (DuPont), is an elastomeric alloy of chlorinated polyolefin and ethylene interpolymer in which the ethylene polymer component is partially crosslinked *in situ* [45, 46]. This forms a single phase system and often fillers, plasticisers and stabilisers have been incorporated to give a useful balance of properties over a wide range of temperatures. These soft and flexible single phase amorphous polymer systems show stress-strain curves identical to those of thermoset rubbers. It is because of these inherent rubbery characteristics they are called as melt processable rubber (MPR). The combination of resistance to heat, oils and weather make Alcryn blends suitable for use in many applications, including hose, tubing, wire and cable jacketing, automotive parts, seals and gaskets. Table 4.8 shows the physical properties of typical dynamically vulcanised commercially available rubber/thermoplastic blends.

Table 4.8 Properties of rubber/thermoplastic blends [4-7]

	MPR Alcryn	**IIR/PP Trefsin**	**EPDM/PP Santoprene**		**NBR/PP Geolast**	
	2070 NC	3201-60	201-73	203-40	701-80	701-87
Hardness Shore A or D	80A	60A	73A	40D	80A	87A
Tensile strength, MPa	11.0	4.6	8.4	19	11	14.2
100% Modulus, MPa	6.4	1.9	3.2	8.6	5.4	6.9
Elongation at break, %	285	355	375	600	310	380
Specific gravity	1.17	0.97	0.98	0.95	1.09	1.07

4.4 Ionic thermoplastic elastomers

The ionic elastomers and ionomeric polyblends are classified under TPEs because of the thermolabile nature of the ionic domains.

4.4.1 Ionic elastomers

An ionomer is a polymeric material containing a small amount (<15%) of ionic groups as pendant to the polymer chain. The presence of a low level of ionic groups has a dramatic influence on the polymer properties [47, 48]. Elastomeric ionomers have received special attention owing to their potential as thermoplastic elastomers. The thermolabile nature of the ionic domains present in the elastomeric ionomers enable them to be processed like a thermoplastic at elevated temperatures. Moreover, the ionic domains act as reinforcing fillers at ambient temperature contributing to the strength of the materials. MacKnight and Lundberg [49] have reviewed different types of elastomeric ionomers. The important ionic elastomers which behave as ionic thermoplastic elastomers are zinc salt of sulphonated EPDM rubber (Zn-SEPDM), zinc salt of maleated EPDM rubber (Zn-mEPDM) and zinc salt of carboxylated nitrile rubber (Zn-XNBR).

Zn-SEPDM containing a few metal sulphonate groups displays properties approaching those of vulcanised EPDM rubber. Because of the unique properties of Zn-SEPDM, it could be considered as a replacement for vulcanised EPDM rubber [50, 51]. When EPDM with high ethylene:propylene ratio (75:25) is used, Zn-SEPDM behaves as a thermoplastic elastomer. The polymer is partially crystalline due to a high ethylene content. The morphological structure of Zn-SEPDM is believed to be similar to that of conventional thermoplastic elastomers, i.e., a combination of hard domains and soft segments. While the hydrocarbon backbone chains form the soft segments, the hard domains may consist of both crystallites due to polyethylene blocks present in the EPDM and ionic aggregates due to metal sulphonate groups [52]. It is also found that this elastomeric ionomer can be reinforced by high abrasion furnace (HAF) carbon black and precipitated silica. Table 4.9 shows the comparison of the physical properties of EPDM and Zn-SEPDM and also the effects of HAF carbon black and precipitated silica on the properties of Zn-SEPDM. At room temperature, incorporation of filler causes a gradual increase in modulus and decrease in elongation at break, but tensile strength remains constant [53, 54]. The incorporation of fillers seems to strengthen the physical crosslinks arising out of the ionic aggregates. Zn-SEPDM exhibits high melt viscosity because of the presence of ionic crosslinks, which resist the melt flow. Therefore, an ionic plasticiser like zinc stearate is often used. Above the melting point of zinc stearate, it plasticises the ionic domains and thereby weakens the ionic network structure and enables the melt processing. At the same time, it acts as a reinforcing filler at ambient temperature and enhances the physical properties [55-56].

Table 4.9 Physical properties of ionic elastomer based on zinc salt of sulphonated EPDM rubber with 75% ethylene content at 25 °C [52-54]

Properties	EPDM[a]	ZnSEPDM[b]	ZnSEPDM + 20 phr HAF carbon black	ZnSEPDM + 20 phr silica
Hardness, Shore A	56	69	75	77
Modulus at 300% elongation, MPa	2.7	7.3	12.9	11.8
Tensile strength, MPa	11.0	23.0	22.5	21.7
Elongation at break, %	1036	691	494	520
Tension set at 200% elongation, %	46	35	32	33
Tear strength, kNm^{-1}	63	115	144	177
Abrasion loss, mm^3 h^{-1}	290	210	140	30

[a] *V-7000 (Exxon Research and Engineering Company, USA)*
[b] *TP-301 (Exxon Research and Engineering Company, USA)*

Table 4.10 Physical properties of ionic elastomer based on zinc salt of maleated EPDM rubber with 55% ethylene content at 25 °C [57-59]

Ingredients[a]	**1**	**2**	**3**	**4**	**5**
mEPDM[b]	100	100	100	100	100
ZnO	10	10	10	10	10
Stearic acid	1	1	1	1	1
Zinc stearate	–	20	30	30	30
HAF carbon black	–	–	–	20	–
Precipitated silica	–	–	–	–	20
Properties: Modulus at 300% elongation, MPa	2.2	2.8	2.9	3.6	3.6
Elongation at break, %	620	800	760	710	1340
Tensile strength, MPa	5.8	8.5	7.7	8.1	14.4
Tear strength, kN/m	37	40	41.8	51	44.9
Tension set at 100% extension, %	10	13	13	14	22
Hardness, Shore A	53	58	62	71	67

[a] *parts by weight*
[b] *maleated EPDM rubber; Royaltuf-465 (Uniroyal Chemical Co., USA)*

The ionic elastomer based on Zn-mEPDM also behaves as an ionic thermoplastic elastomer [57]. It shows a glass-rubber transition around –37 °C and a high temperature ionic transition above 50 °C, which in the presence of fillers, becomes prominent and is shifted to the higher temperature side (say, from 53 °C to 73 °C) [58, 59]. Table 4.10 shows the effect of zinc stearate and fillers like HAF carbon black and precipitated silica on the physical properties of Zn-mEPDM. As was observed in the case of Zn-SEPDM, the addition of fillers improves the physical properties of the ionic elastomer based on Zn-mEPDM [58, 59].

It is apparent from the Table 4.11 that Zn-XNBR behaves as an ionic thermoplastic elastomer. Incorporation of ZnO into XNBR increases the modulus, tensile strength, hardness and tear strength. Addition of HAF carbon black and precipitated silica causes further improvement in physical properties [60, 61]. Zinc stearate also plays a dual role as in the case of ionomers based on EPDM rubber [62]. Figure 4.12 shows the effect of carbon black loading on the dynamic mechanical properties of Zn-XNBR [60]. The existence of two phase structure in Zn-XNBR becomes more prominent in the presence of reinforcing HAF carbon black. Furthermore, as the filler loading increases, the high temperature transition peak height gradually increases along with broadening of the

Table 4.11 Physical properties of ionic elastomer based on zinc salt of carboxylated nitrile rubber at 25 °C [60-62]

Ingredients[a]	**1**	**2**	**3**	**4**	**5**
XNBR[b]	100	100	100	100	100
ZnO	12	12	12	12	12
Stearic acid	1	1	1	1	1
HAF carbon black	0	20	30	0	0
Zinc stearate	0	0	0	30	60
Properties: Modulus at 100% elongation, MPa	1.8	4.2	6.6	3.8	5.6
Modulus at 300% elongation, MPa	3.2	11.6	18.0	5.7	9.4
Tensile strength, MPa	33	31	28	29	26
Elongation at break, %	1150	1000	900	1050	950
Tear strength, kN/cm	32	45	48	58	62
Hardness, IRHD	56	70	75	72	88
Tension set at 100% elongation, %	9	11	11	15	16

[a] *parts by weight*
[b] *Krynac 7.50 (Bayer Polysar, France)*
IRHD: International Rubber Hardness Degrees

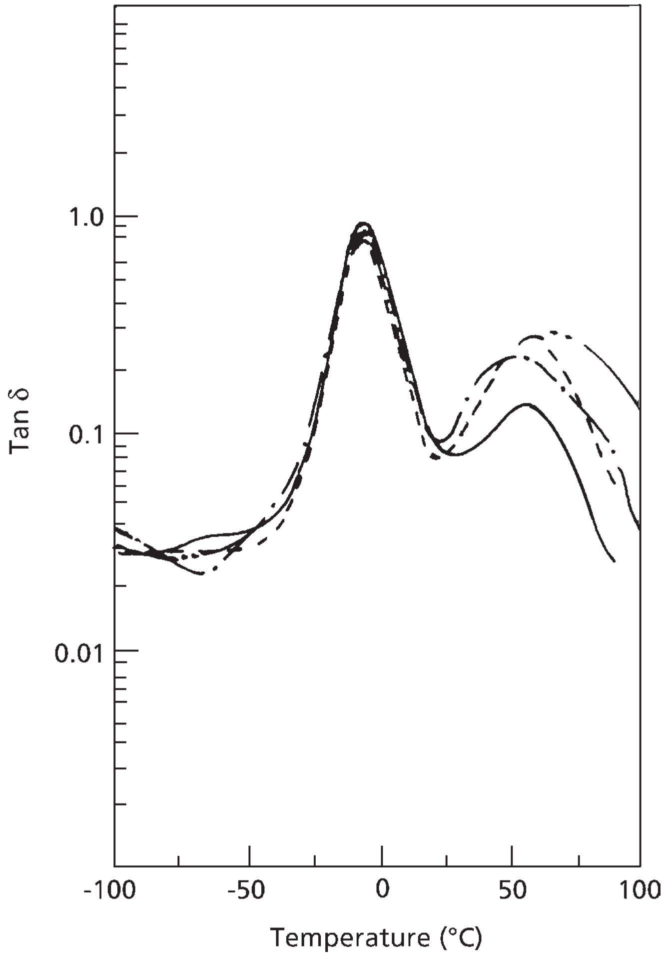

Figure 4.12 Plots of tan δ as a function of temperature for XNBR-ZnO system: effect of carbon black loading. 0 phr (———) ; 10 phr (— - —); 20 phr (- - - - -); and 30 phr (— - - —)

peak. Addition of the filler also causes a shift of the high temperature transition to higher temperature without shifting the T_g. On the basis of dynamic mechanical properties it has been proposed that the rubber-filler interactions in the case of silica and HAF carbon black filled ionic elastomers are of two types: a) the interaction between the filler particles and the non-ionic segments of the polymer backbone, which is similar to the interaction involving diene rubber and reinforcing fillers, as manifested in the lowering of tan δ at T_g, and b) the interaction between the ionic groups of the polymer and the polar sites (or silanol groups in the case of silica) present on the filler surface, which is manifested in an increase in tan δ at the high temperature transition region.

4.4.2 Ionomeric polyblends

A more general method of increasing compatibility is based on the incorporation of specific interacting groups into the polymers to be blended. Strong interactions between the blend components improve the interfacial adhesion and help in efficient stress transfer from one phase to the other phase. The potentially useful specific interactions range from strong ionic interactions to weak dispersive interactions. Hydrogen bonding is an important specific interaction which has been proposed for many miscible polymer systems [63]. Other types of specific interactions include proton transfer, charge transfer, transition metal complexation, acid-base, ion-dipole and ion-ion interactions [64].

Recently, De and co-workers have developed ionic thermoplastic elastomers from different ionomeric polyblends, wherein the compatibilisation between the rubbery and the plastic phases was achieved by using intermolecular ionic interactions which act as compatibilising agents [65-76]. The ionomeric polyblends exhibit synergism in physical properties. The synergistic effect in the blends of two ionomers is attributed to the enhanced compatibility caused by the interpenetrating networks arising out of the interaction of the ionic groups present in the two polymers. The ionomeric polyblends studied include blends of Zn-mEPDM, Zn-SEPDM and Zn-XNBR with different ionomeric plastics based on PE and PP (Table 4.12).

Tables 4.13 and 4.14 show the physical properties of typical ionomeric polyblends based on Zn-mEPDM and Zn-XNBR. Figure 4.13 shows the variation of physical properties of the representative blends with blend composition [67, 73]. It is interesting to note that the ionomeric polyblends exert synergism in tensile strength and tear strength in the sense that the observed experimental values are higher than those predicted by the additivity rule. The reason for the synergism in properties is believed to be due to the enhanced compatibility via formation of interfacial ionic interactions in the blends. Synergism in properties is reported to be observed in the case of compatible blends [64]. Expectedly, the modulus and tension set increase with an increase in plastic content in the blend.

The role of interfacial ionic aggregates acting as compatibilising agents in the polyblends is evident from the comparison of the physical properties of the ionomeric polyblends (that is, the polyblends in presence of ZnO and stearic acid) against the corresponding non-ionomeric polyblends (that is, the polyblends without ZnO and stearic acid). Figure 4.14 shows the typical stress-strain plots of the ionomeric polyblends and the corresponding non-ionomeric polyblends [68, 74].

As expected, ionomeric polyblends show higher physical properties than the corresponding non-ionomeric polyblends. The improved physical properties of the ionomeric polyblends

Table 4.12 List of ionomeric polyblends behaving as TPEs [65-76]

Ionic rubber	Ionic plastic	Blend ratios rubber/plastic (w/w)	Note
Zn-mEPDM	Zn-mHDPE	90/10, 80/20, 70/30, 60/40, 50/50.	Ozone and weather resistant; melt processable in the presence of zinc stearate.
Zn-mEPDM	Zn-PEA	90/10, 80/20, 70/30, 60/40, 50/50.	
Zn-mEPDM	Zn-EMA	90/10, 80/20, 70/30, 60/40, 50/50.	
Zn-mEPDM	Zn-mPP	90/10, 80/20, 70/30, 60/40.	
Zn-SEPDM	Zn-EMA	75/25, 50/50, 25/75.	
Zn-XNBR	Zn-mHDPE	90/10, 80/20, 70/30, 60/40.	Improved solvent and oil resistance, melt processable at low shear rates. Zinc stearate is not recommended as processing aid.
Zn-XNBR	Zn-EMA	90/10, 80/20, 70/30, 60/40, 50/50.	
Zn-XNBR	Zn-PEA	90/10, 80/20,	
Zn-XNBR	Zn-PPA	90/10, 80/20.	

Zn-HDPE: Zinc salt of maleated high density polyethylene
Zn-PEA: Zinc salt of poly(ethylene-co-acrylic acid)
ZN-EMA: Zinc salt of poly(ethylene-co-methacrylic acid)
Zn-mPP: Zinc salt of maleated polypropylene
Zn-PPA: Zinc salt of poly(propylene-co-acrylic acid)

are the result of formation of intermolecular ionic network structure, which decreases the interfacial energy and enhances the adhesion at the interface, thereby promoting the compatibility in the blend.

Figure 4.15 shows the plots of tan δ and log E′ versus temperature of the typical ionomeric polyblend and the corresponding non-ionomeric polyblend [73]. It is apparent that the value of tan δ at the T_g of the ionomeric polyblend is less than that of the corresponding non-ionomeric polyblend. This may be due to the stiffness arising out of the ionic interactions in the ionomeric polyblend. The ionomeric polyblend shows a distinct T_g around 68 °C, whereas the corresponding non-ionomeric polyblend does not exhibit any

Table 4.13 Physical properties of ionomeric polyblends based on maleated EPDM rubber at 25 °C [67-69]

Ingredients[a]	1	2	3	4	5	6
mEPDM[b]	70	60	70	60	70	60
mHDPE[c]	30	40	–	–	–	–
PEA[d]	–	–	30	40	–	–
mPP[e]	–	–	–	–	30	40
Stearic acid	1	1	1	1	1	1
ZnO	10	10	20	20	10	10
Properties:						
Modulus at 100% elongation, MPa	5.0	6.6	5.4	6.6	5.7	8.8
Modulus at 200% elongation, MPa	6.2	7.6	6.9	7.7	7.2	10.2
Tensile strength, MPa	8.5	10.1	10.9	12.3	9.8	11.9
Elongation at break, %	471	418	610	608	350	329
Tear strength, kNm^{-1}	62.1	76.1	72.6	83.7	67.8	87.1
Hardness, Shore A	78	80	77	84	80	90
Tension set at 100% elongation %	10	15	16	20	15	25
Percentage crystallinity, %	18	23	18	21	17	23

[a] *parts by weight*
[b] *Royaltuf-465 (Uniroyal Chemical Co., USA)*
[c] *Polybond-3009 (Uniroyal Chemical Co., USA)*
[d] *Polybond-1009 (Uniroyal Chemical Co., USA)*
[e] *Polybond-3150 (Uniroyal Chemical Co., USA)*

high temperature transition. It is also interesting to note that the ionomeric polyblend exhibits a higher modulus at all temperatures than the corresponding non-ionomeric polyblend, which is attributed to the reinforcing ability of the ionic aggregates.

Figure 4.16 shows the log-log plots of apparent viscosity versus shear rate of the 60/40 Zn-mEPDM/Zn-mHDPE ionomeric polyblend, the corresponding non-ionomeric polyblend and zinc stearate filled ionomeric polyblend. The apparent viscosity of the blends decreases with increasing shear rate, thus indicating the pseudoplastic behaviour

Table 4.14 Physical properties of ionomeric polyblends based on carboxylated nitrile rubber at 25 °C [73-76]

Ingredients[a]	**1**	**2**	**3**	**4**	**5**	**6**
XNBR[b]	70	60	70	60	–	–
XNBR[c]	–	–	–	–	80	80
mHDPE[d]	30	40	–	–	–	–
Zn-EMA[e]	–	–	30	40	–	–
PEA[f]	–	–	–	–	20	–
PPA[g]	–	–	–	–	–	20
Stearic acid	1	1	–	–	1	1
ZnO	12	12	12	12	20	10
Properties:						
Modulus at 200% elongation, MPa	10.9	13.0	12.5	16.7	10.8	12.4
Tensile strength, MPa	23.4	22.1	24.9	23.3	26.5	22.6
Elongation at break, %	550	517	494	318	555	400
Tear strength, kNm^{-1}	82.7	93.9	85.0	87.0	101.6	100.2
Hardness, Shore A	79	82	82	83	75	78
Tension set at 100% elongation, %	25	40	25	30	20	25
Percentage crystallinity, %	18	24	4	6	11	8

[a] *parts by weight*
[b] *Krynac X7.50 (Bayer Polysar, France)*
[c] *Grade X48/1 (Goodyear Rubber and Tyre Co., USA)*
[d] *Polybond-3009 (Uniroyal Chemical Co., USA)*
[e] *Surlyn (E.I. Du Pont Neumors, USA)*
[f] *Polybond-1009 (Uniroyal Chemical Co., USA)*
[g] *Polybond-1002 (Uniroyal Chemical Co., USA)*

of the blends. The higher melt viscosity of the ionomeric polyblend as compared to the corresponding non-ionomeric polyblend is due to the occurrence of strong ionic network structure in the ionomeric polyblend, which resists the melt flow. The incorporation of zinc stearate causes a drastic reduction in the melt viscosity of the ionomeric polyblends. Zinc stearate acts as an ionic plasticiser above its melting point, and hence, reduces the melt viscosity of the ionomer either by solvation or by shear induced exchange reaction between zinc stearate and the metal carboxylate groups in the ionomer during melt flow

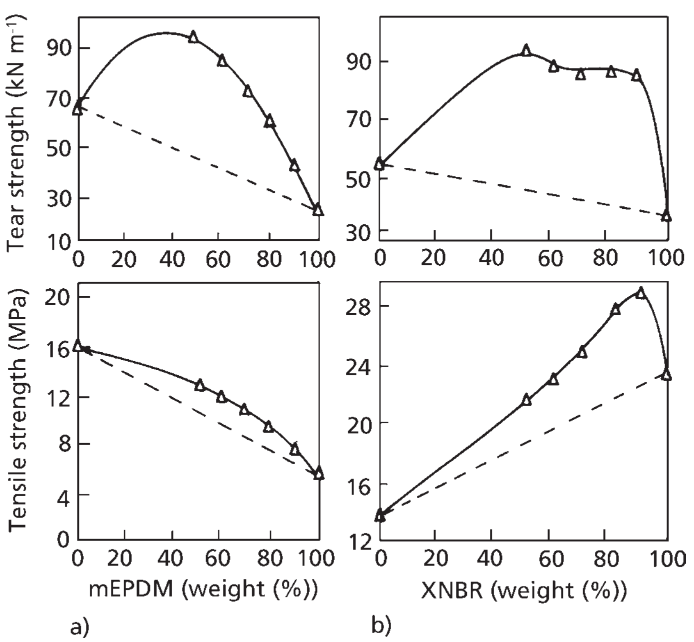

Figure 4.13 Variation of tensile strength and tear strength with blend composition in the ionomeric polyblends: a) Zn-mEPDM/Zn-PEA; and b) Zn-XNBR/Zn-EMA, Δ, observed values at 25 °C; ----, additivity line

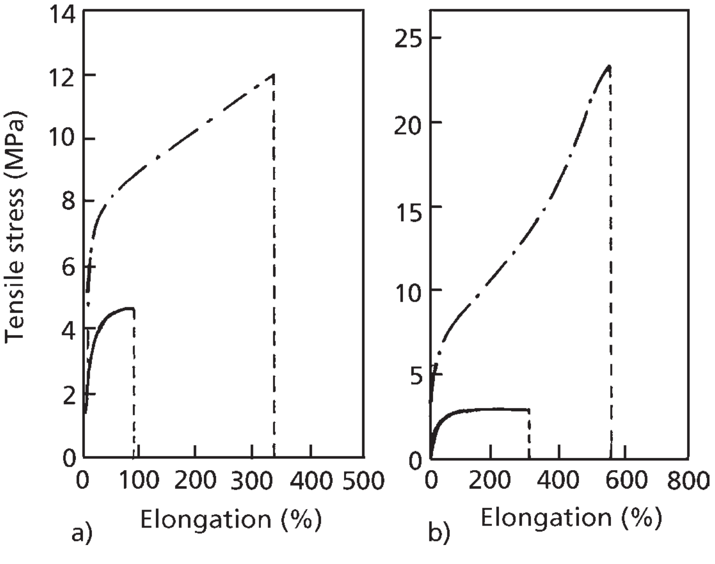

Figure 4.14 Stress-strain plots of a) 60/40 Zn-mEPDM/Zn-mPP (— · —) and 60/40 mEPDM/mPP (——) blends; and b) 70/30 Zn-XNBR/Zn-mHDPE (— · —) and 70/30 XNBR/mHDPE (——) blends

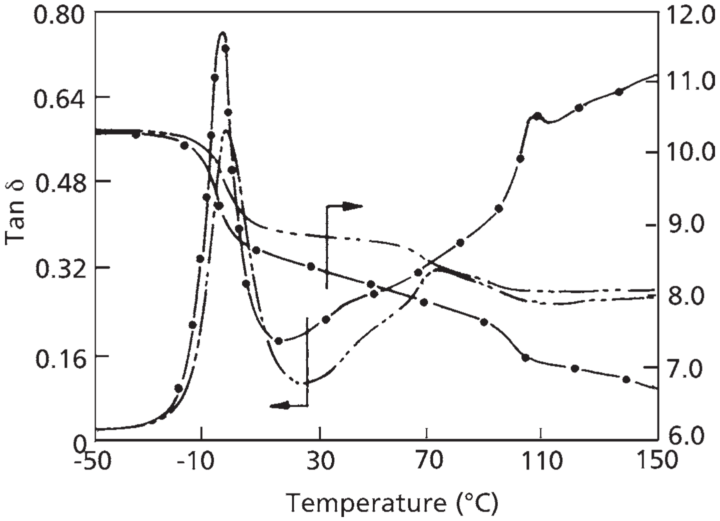

Figure 4.15 Plots of tan δ and log E′ versus temperature for 70/30 Zn-XNBR/Zn-EMA (— - - —) and 70/30 XNBR/EMA (—•—) blends

[57, 71, 72]. Studies on the variation of apparent viscosity and tensile strength of the extrudate of the ionomeric polyblends based on maleated EPDM rubber with the number of cycles of extrusion through the Monsanto processability tester reveal that the apparent viscosity of the blends and the tensile strength of the extrudates almost remain unchanged by repeated extrusions, indicating the thermoplastic nature of the blend [68, 71, 72].

A schematic representation of the biphasic structure of a representative ionomeric polyblend is shown in Figure 4.17 [67,68]. The phase structure is similar to that of conventional thermoplastic elastomers, consisting of hard domains and soft rubbery segments. However, the hard domains in the ionomeric polyblends consist of crystalline domains due to PE or PP blocks and the ionic domains due to zinc carboxylate salts.

Ionomers typically exhibit high melt viscosities and superior tensile properties than those of the corresponding non-ionic polymers. The high melt viscosities enable extrusion and blow moulding. Since ionomers contain polar salt groups, they adhere better to most polar surfaces than do polyolefins. In addition, toughness, oil resistance and abrasion resistance are characteristics of ionomers. The thermoplastic nature of the elastomeric ionomers allows them to be processed in conventional moulding machines. They can also be used as heat seal layers in co-extrusions. Sulphonated EPDM ionomers have properties that match flexible vinyls and some urethanes. Thus they could replace flexible

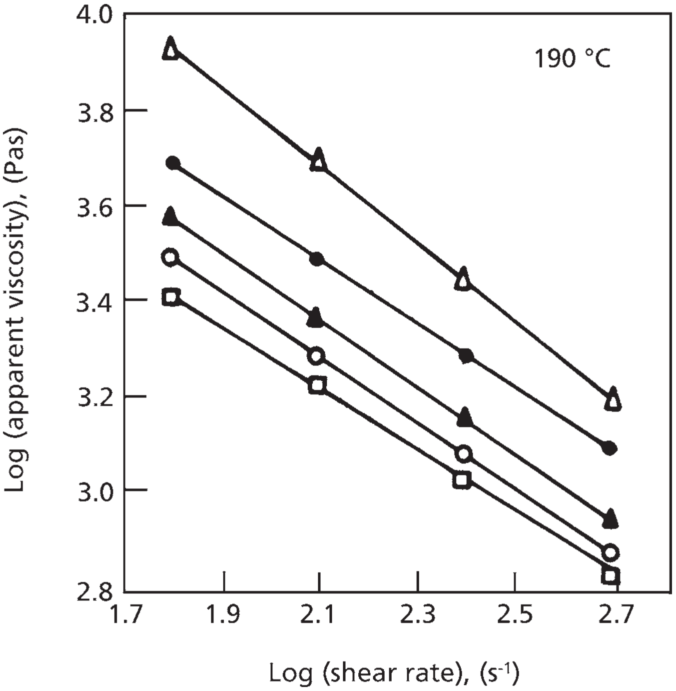

Figure 4.16 Log-log plots of apparent viscosity versus shear rates of 60/40 Zn-mEPDM/Zn-mHDPE blend containing 0 (△), 10 (•), 20 (▲), 30 (o) parts per 100 parts of polymer by weight of zinc stearate and 60/40 mEPDM/mHDPE non-ionomeric blend (❑) (a). The processability studies of the blends were carried out by using a Monsanto processability tester at 190 °C. The capillary length to diameter ratio (L/D) was 30

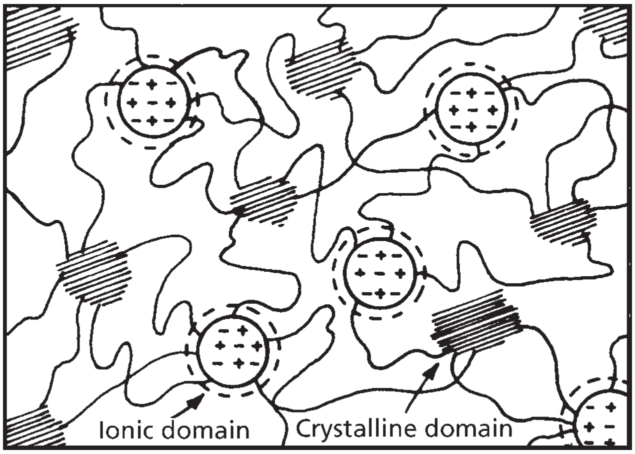

Figure 4.17 Schematic representation of the biphasic structure of a representative ionomeric polyblend

plastics and vulcanised rubbers in many applications. They can be compounded with fillers, rubber processing oils and selected polymers into a variety of elastomeric materials. The important applications include adhesives, impact modifiers and garden hoses.

Conclusions

TPEs are phase separated systems in which one phase is thermoplastic and hard, while the other phase is elastomeric and soft. The hard phase gives the strength and its thermolabile nature enables the processing of TPEs at elevated temperature like thermoplastics. Because of the rapid and easy processing of TPEs the cost of final product can be made less, even though their raw material prices are relatively high compared to those of conventional elastomers. The hard phase/soft phase ratio determines the performance of a TPE. As the proportion of the hard phase increases, TPEs lose their elastomeric character and at a high proportion of the hard phase, they behave like high impact thermoplastics. The applications of TPEs are numerous and varied dependent upon their chemical structure. The soft TPEs have found many applications as replacements for vulcanised rubbers. These include adhesives, sealant, polymer modification and asphalt blending. The harder products based on polyurethanes and polyamides usually have much better resistance to oils and solvents and also to compression set. TPEs have proven themselves in meeting the wide range of demanding engineering requirements for automotive applications.

The new polymerisation techniques can be used to polymerize wide rage of monomers which allow the preparation of many new block, segmented, functionalised, and branched polymers for use as TPEs. Another area of significant effort will be to improve the chemical, oil and temperature resistance of existing TPEs by blending with other polymers. Thermoplastic vulcanisates (TPVs) based on blends of polyolefins are an important family of engineering materials. Their importance arises from a combination of rubbery properties along with their thermoplastic nature in contrast to thermoset elastomers. TPVs consist of a finely dispersed chemically crosslinked elastomer phase in a melt processable thermoplastic matrix.

TPEs will continue to replace vulcanised rubbers in many applications because of their fast processing, cost advantages and design flexibility. Thermoplastic elastomeric nature of the elastomeric ionomers is due to the thermolabile nature of the ionic domains, which enable them to be processed at elevated temperatures like thermoplastics. Lately research interest has been directed towards the development of ionic TPEs by blending an ionic thermoplastic with an elastomeric ionomer, wherein the compatibility between the plastic and the rubbery phases has been achieved through intermolecular ionic interactions.

Figure References

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5 Fillers

H. Mouri

5.1 Preface

Fillers are used in rubbers and plastics for various purposes. In fact, reinforcing fillers, when added to an elastomer, can provide a composite product with very high strength. Reinforcing fillers are particularly important for synthetic rubbers, where the unfilled gum compound virtually has no practical application because of its very low strength as compared to the strength of an unfilled natural rubber. Carbon black has become the most important filler in the rubber industry since its discovery as an active filler by Mote in England in1904. Historically, the use of carbon black dates back to ancient China, when soot was used in inks and paint. Soot is a product of incomplete combustion of any organic substance, which is basically how carbon black is produced today. Of course, sophisticated ways to manufacture carbon black in mass production have been developed over the years, and modern methods produce carbon blacks with various tailored structures to satisfy specific application needs. The production of carbon black today exceeds 650 million tons per year (see Table 5.1). Silica, calcium carbonate, and clay are second to carbon black as far as overall consumption is concerned.

The type of filler in a specific application must be selected carefully, depending on the requirements of its end use. Carbon black is used as a reinforcing filler in a variety of rubber products including industrial applications such as conveyer belts, dock fenders, tank tracks and roofing materials, and consumer products such as footwear, automobile tyres, inner tubes hoses or shock absorbers. The application of non-black fillers, especially the use of precipitated silicas in passenger tyre treads, is growing.

The purpose of this chapter is to give a guide to carbon black surface and particle structure, grade classification, and reinforcement and influence on physical properties when added to rubber. Some insight into non-black fillers is also given.

5.2 Manufacture of carbon black

Since the structure of carbon black is largely determined by the way it is produced, some information on carbon black manufacturing will be given at the beginning.

Table 5.1 Carbon black worldwide production (thousand tons)

	1997	1998	1999	% worldwide in 1999
USA	1,600	1,655	1,720	25.4
Japan	740	690	690	10.2
China	400	470	450	6.6
Korea	415	430	430	6.3
CIS	300	350	400	5.9
India	250	250	270	4.0
Germany	250	240	260	3.8
France	250	255	250	3.7
Brazil	205	215	215	3.2
Canada	170	165	190	2.8
Italy	180	190	185	2.7
Thailand	165	180	180	2.7
UK	145	160	180	2.7
Netherlands	125	135	140	2.1
Mexico	122	120	120	1.8
Taiwan	105	105	105	1.5
Spain	90	95	100	1.5
Egypt	N/A	N/A	90	1.3
Australia	75	75	N/A	-
Other Countries	877	766	801	11.8
Total	**6,464**	**6,546**	**6,776**	**100.0**

Source: CTC International

The lampblack process, patented by Hancock in 1830, is the oldest known method to make carbon black. In this process, highly aromatic oil is burned in cast-iron open pans to yield carbon black with a relatively large particle diameter. Channel black is produced by burning natural gas with a supply of air insufficient for complete combustion, followed by collection of the carbon black on a cool metal surface in contact with the flame. The hot product has free access to air which leads to oxidation of the surface. The oxygen groups give an acidic character to channel blacks that usually retards the cure rate of rubber compounds. At present, the production of channel black is very limited.

Today, most of the reinforcing blacks are manufactured by the oil furnace process, introduced in 1943 (see Figures 5.1 and 5.2). Complete combustion of natural gas generates a very hot zone in the furnace. An aromatic hydrocarbon feedstock, continuously fed into the hot zone as a mist without air, is thermally cracked in less than a microsecond to obtain carbon black nuclei. The reactions by which the aromatic feedstock is converted to elemental carbon black are complex and not fully understood. The combustion of feedstock produces individual carbon particles that are still in a liquid state. They collide in the gas stream and stick together, forming random, grape-like clusters or aggregates. Quenching determines the final aggregate configuration. Bag filters separate carbon black from the combustion gas to yield a fluffy black with a bulk density of about 30 kg/m^3. The pelletising process increases the bulk density to 300–500 kg/m^3 for ease of handling, economical transportation and safety. Blacks with various structures can be obtained in a furnace process through the combination of operating conditions in the plant such as feedstock flow rate, gas rate, air rate, and quench position. Furnace blacks have low oxygen content and their surface is neutral, and does not retard cure rate like channel blacks.

Other processes include the thermal black process, where carbon black is made in a batch process by thermal decomposition of natural gas in contact with a hot refractory surface in the absence of oxygen. Acetylene black is a conductive black formed when acetylene gas is decomposed in an exothermic reaction. Once the reaction is initiated, the process runs continuously due to its exothermic reaction.

Practically all blacks used by the rubber industry today are supplied in a pellet form for handling reasons. Mouri and Kawaguchi [1] reported that pellet hardness could affect carbon black dispersion in rubber. Pellets that are too soft tend to break up during shipping and handling, creating fines that are difficult to disperse. Pellets that are too hard will not break up during mixing causing a dispersion problem. The recommended pellet hardness was in the range of 5 to 20 g for pellet sizes of 1 mm or less, and 15 to 30 g for larger pellet sizes. Variation in the size of pellets may also relate to the level of dispersion and to the ease of handling.

5.3 Surface and particle structure of carbon black

Carbon black primary particles have an onion-like paracrystalline structure. The bent and fractured crystallites consist of parallel, graphitic layer planes. The carbon black

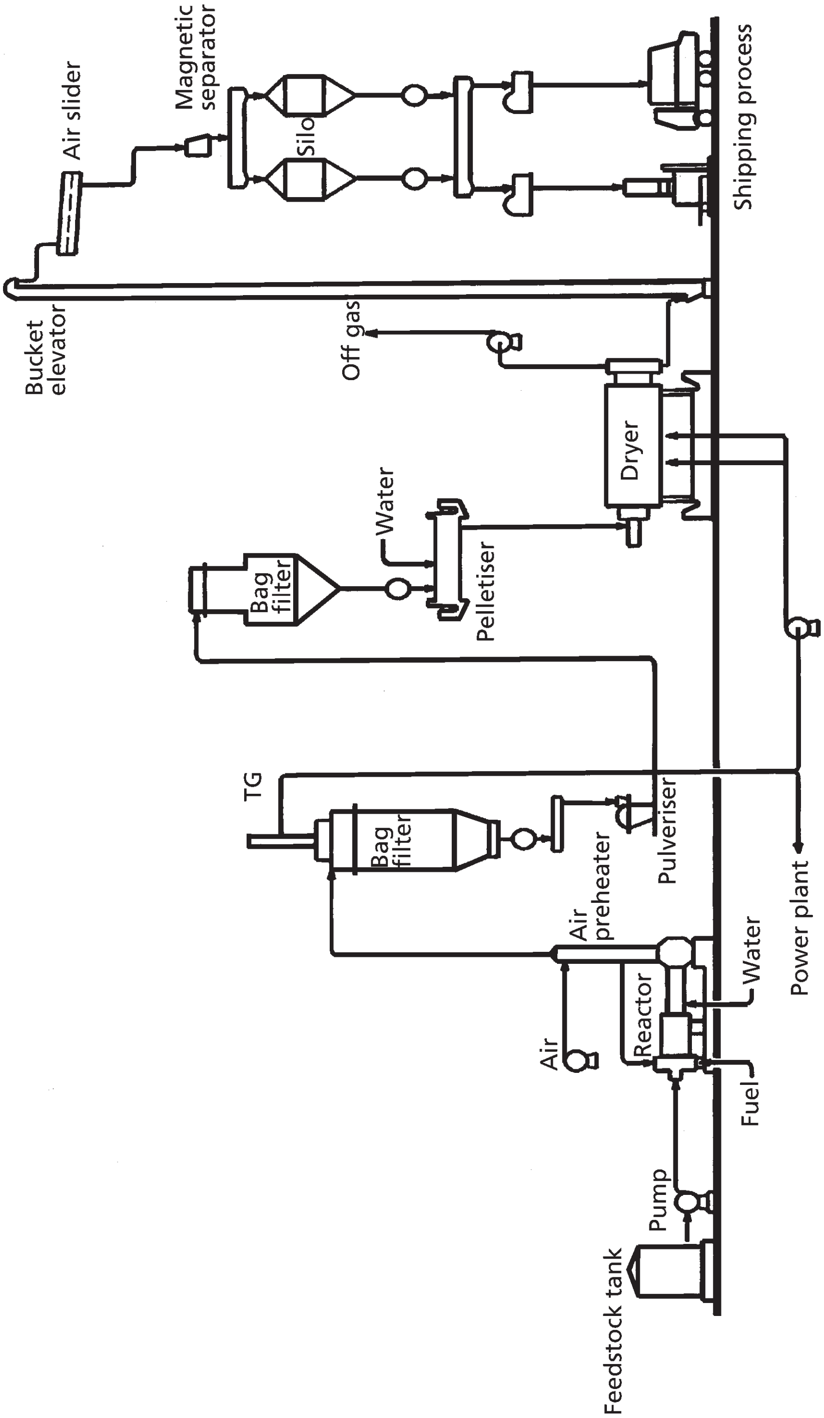

Figure 5.1 Illustration of a furnace black plant

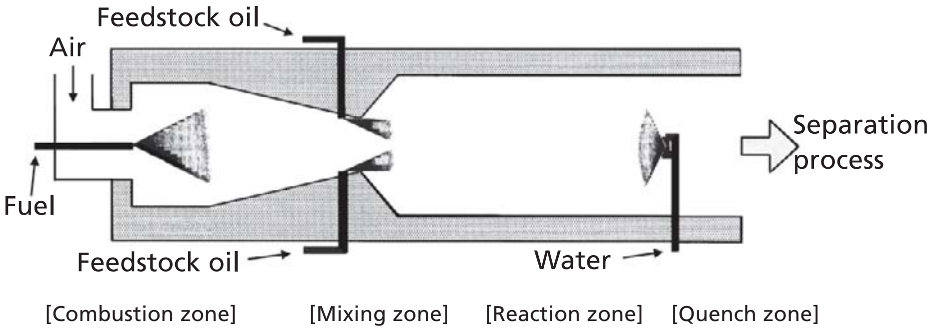

Figure 5.2 Schematic representation of a furnace black reactor

surface has functional groups that can react with rubber molecules. A comprehensive summary of carbon black microstructure can be found in publications by Donnet and others [2, 3]. X-ray diffraction studies indicate that carbon blacks are composed of small crystallites made up of parallel graphitic layers with a spacing of approximately 0.35 nm. The structure is intermediate between graphite and an amorphous material. A transmission electron microscope (TEM) image of carbon black microstructure at very high magnification is shown in Figure 5.3. L_c represents the average stacking height of the layers and L_a represents average length of the layer plane. L_c for typical furnace blacks is in the range of 1.0–1.2 nm, and increases with increasing particle size. A higher L_c value indicates a tendency towards increased crystalline development which provides increased

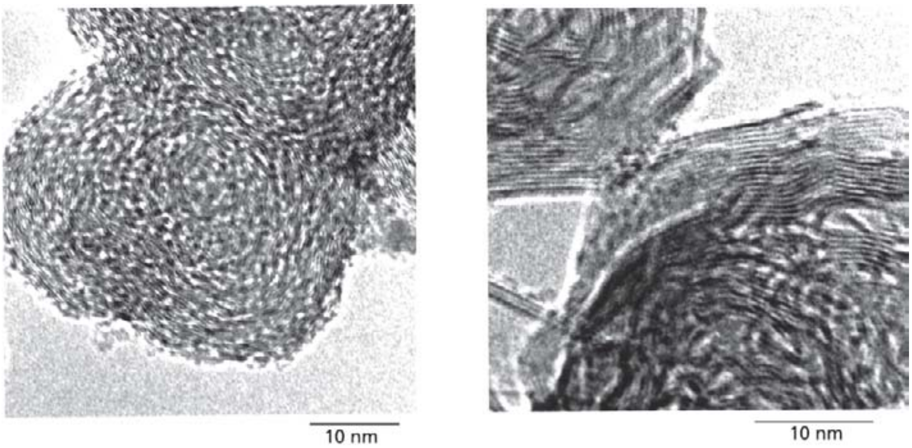

Figure 5.3 Transmission electron micrograph image of carbon black microstructure. Left: N660, right: acetylene black

Table 5.2 Surface groups on some rubber grade carbon blacks

Carbon black grade	Surface group (Meq/g)					Surface area m^2/g	Total groups	Non -H groups	Total groups per 100 m^2	Non -H groups per 100 m^2
	-OH	=O	$-CO_2H$	$-CO_2-$	-H					
S300	0.88	0.48	0.07	0.28	5.25	110	6.96	1.71	4.77	1.55
N110	0.59	0.01	0.03	0.17	1.50	135	2.30	0.80	1.70	0.59
N220	0.61	0.03	0.01	0.12	1.70	122	2.47	0.77	2.03	0.63
N330	0.55	0.00	0.01	0.17	1.94	76	2.67	0.73	3.51	0.96
N440	0.31	0.02	0.03	0.07	3.50	45	3.93	0.43	8.73	0.96
N770	0.18	0.02	0.01	0.05	3.79	23	4.05	0.26	17.6	1.13
N990	0.1	0.01	0.00	0.02	3.82	7	3.95	0.13	56.4	1.86

Taken from Medalia and Rivin [4]

thermal and electrical conductivities. L_a is less sensitive to particle size and is 1.5–1.6 nm for typical furnace blacks. A higher L_a value indicates increased crystalline development.

Although carbon blacks are mainly composed of carbon, they also contain small amounts of chemically combined hydrogen and oxygen functional groups. It has been found that the functional groups are primarily concentrated at the edges of the graphitic crystallites and at the surface of the particle. Medalia and Rivin [4] reviewed the functional groups present on carbon black surfaces. Surface functionality includes carboxyl, phenol, quinone, lactone and hydrogen groups (see Table 5.2). Among the functional groups, quinone functionality is thought to react with unsaturated polymers. Functional groups are controlled by the manufacturer through furnace temperature, fuel type, fuel flow rate, nozzle spray pattern, residence time, quench position and feedstock flow rate. No standard procedure to estimate the degree of surface activity is currently available. The functional groups play a major role in carbon black interaction with polymers. Physico-chemical adsorption of polymer on the carbon black surface results in partial immobilisation of the polymer chains. The polymer layer with restricted mobility surrounding the carbon black particle is gauged by the bound rubber measurement. Bound rubber is the insoluble polymer, when uncured rubber compound is placed in a good, common solvent such as benzene. A portion of the bound rubber, nearest the carbon black surface, is believed to behave like a glass. Polymer mobility increases with distance from the carbon black surface. The overall reduction in polymer mobility associated with bound rubber gives a broad relaxation behaviour to the rubber compound. Bound rubber actually consists of physical adsorption of polymer chain as well as chemical adsorption, and it is generally accepted that physical adsorption is of greater importance for rubber reinforcement than chemical adsorption. Only a fraction of the bound rubber actually participates in the chemical adsorption and the majority consists of loops and dangling chains [5]. When a bound rubber experiment is carried out at an elevated temperature around 100 °C, a drastic decrease in bound rubber level is observed. This would be an indication of physical adsorption being dominant, because it is unlikely that chemical bonding can break down at this temperature range. In another experiment (results shown in Figure 5.4), where the sample extracted with solvent was stirred at different stirring rates, clearly demonstrated that bound rubber is primarily a physical adsorption because chemical adsorption is not likely to break down upon such stirring. It is said that large polymer molecules are preferentially attached onto the filler surface.

The oxygen content from functional groups on the carbon black surface, gives a lower pH that could significantly retard cure rate when mixed into a rubber compound. However, alkalinity of the water, used in quenching and beading of furnace blacks, offsets the effect of the oxygen groups, giving accelerated cure. Other materials found on carbon black are small amounts of sulphur, ash, and moisture. At the time of manufacture, the moisture content is under 0.5 percent. Upon storage, moisture can be absorbed to a level of perhaps 1 percent for coarse blacks and up to about 3 percent for the finer blacks.

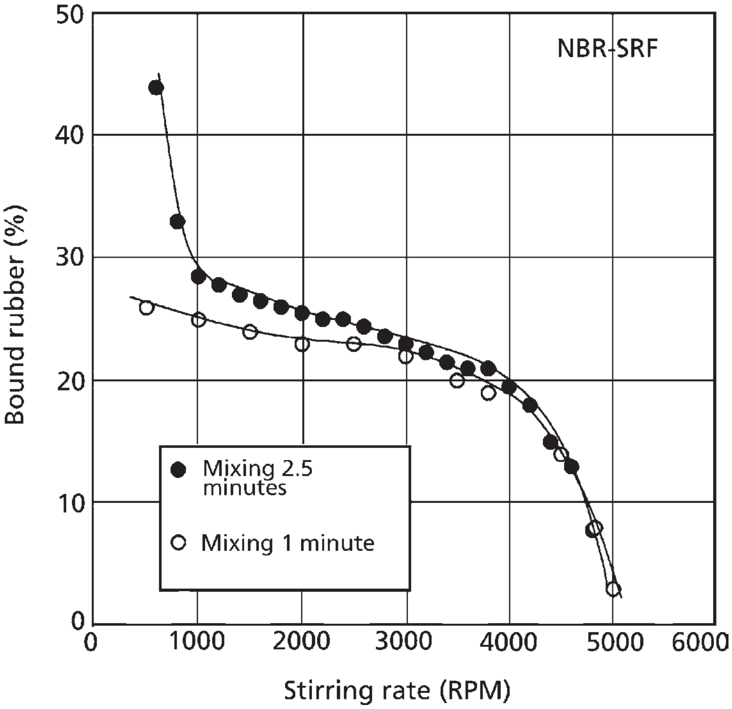

Figure 5.4 Effect of stirring rate on bound rubber [6]

5.4 Carbon black aggregate structure

The two characteristics of carbon black aggregates primarily responsible for its performance when compounded into rubber are particle size and structure. The electron micrograph of carbon black shown in Figure 5.5 indicates that aggregates, the smallest dispersible unit of carbon black, are made up of spherical nodules or domains of carbon that are fused together into a structure that superficially resemble grapes in a bunch. For convenience, the spherical nodules are referred to as particles, but they are not individual particles. High resolution TEM shows that the nodules share graphitic layer planes toward their outer radii. The true individual carbon black particle is thus the aggregate. Bond strength between individual nodules is quite strong, but can be broken appreciably when subjected to high shear force in the rubber mixing operation. Structure refers to the number of nodules in an aggregate, and the aggregate's irregularity of shape. A low structure black has an average of 30 particles or nodules per aggregate, whereas a high structure black may average up to more than 200 particles per aggregate. The primary structure is the single aggregate. A secondary structure is the agglomerate, which is clusters of physically bound and entangled aggregates, held together by binder used in the beading process and possibly by van der Waals forces as well. Agglomerates appear as undispersed carbon black in rubber mixes.

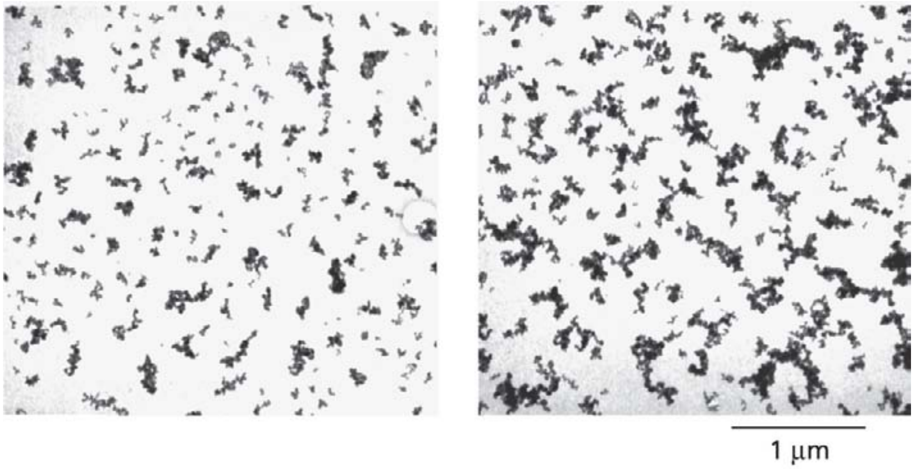

Figure 5.5 Transmission electron micrograph image of carbon black macrostructure. Left: N110, right: N121

Various ways to characterise carbon black geometry have been proposed. First, the most direct method to determine carbon black size is direct observation by TEM (see Figure 5.5). In practice, this is an extremely tedious and labourious way to determine carbon black size. Thus, specific surface area is usually used as an indicator of spherical particle size, which can be estimated by gas adsorption. The Brunauer-Emmett-Taylor (BET) nitrogen adsorption method, recognised as nitrogen surface area (N_2SA) in the industry, is the most commonly used method for surface area determination. Alternately, carbon black surface area can be estimated by the adsorption of cetyltrimethyl ammonium bromide (CTAB). This is a better way to determine carbon black surface area when it comes to rubber applications. Due to its larger molecular size, CTAB adsorption does not include contributions from fine pores and hollows on the carbon black surface that will not participate in elastomer interaction. As is shown in Figure 5.6, the surface area calculated from average values of primary particle diameter, assuming a density of 1850 kg/m^3, is generally somewhat larger than the surface area derived from N_2SA adsorption. This is because primary particles are fused together to form a structured aggregate. In general, the smaller the difference between these two values, the smaller the contact area of primary particles within the aggregate suggesting that even aggregates could be susceptive to break if the contact area is small. Thus, another aspect of carbon black reinforcement is the breakdown of aggregates during rubber mixing. That is, aggregates can fracture and generate free radicals that readily react with polymer chains to increase bound rubber.

Structure is usually estimated by incrementally adding oil to dry carbon black in a small, laboratory mixer. When the void spaces between carbon black aggregates are filled, rotor

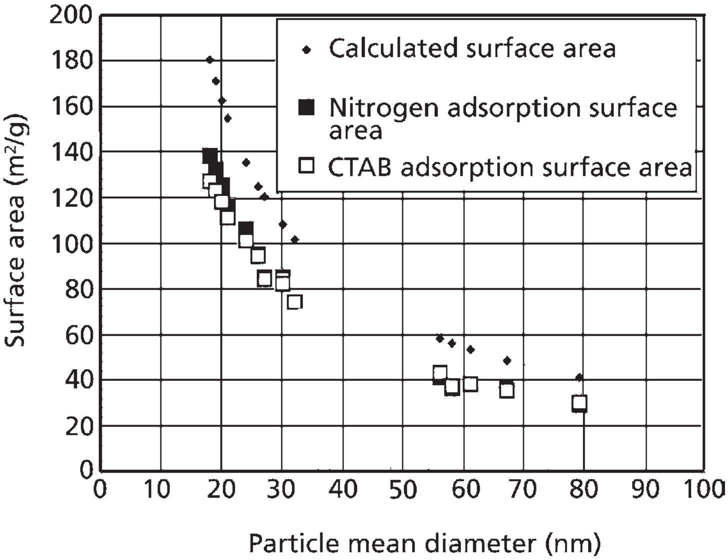

Figure 5.6 Comparison between calculated surface area based on mean particle size versus surface area derived from adsorption

torque rises dramatically. The volume of oil absorbed per gram of carbon black at the torque rise is a measure of structure. The structure test method is dibutylphthalate (DBP) absorption, which is the number of cubic centimetres of DBP absorbed by 100 g of carbon black under specified test conditions. Higher oil adsorption indicates more deviation from a sphere, because highly structured blacks will pack differently from spheres. Compressed DBP is DBP adsorption after first compressing the carbon black to break down aggregates to an extent comparable to aggregate breakdown encountered in the rubber and carbon black mixing process. The compressed DBP test is thus more indicative of the carbon black aggregate in rubber while unstrained DBP will be more indicative of the carbon black product itself. The tinting strength test is generally used as a rough indicator of carbon black aggregate average size, and is primarily useful as a routine control test. The degree of greyness of a mixture of carbon black with zinc oxide and a soybean oil epoxide provides the basis of tint strength determination. Unlike TEM, none of the adsorption methods provide information on the distribution of particle size or aggregate structure.

The disc centrifuge photo sedimentometry (DCPS) technique is probably the most commonly utilised method other than microscopy to determine carbon black aggregate size distribution. The aggregate size distribution is determined using Stoke's law modified for centrifugal sedimentation [7]. The concentration of aggregates in a certain size range is measured by the absorbance of a light beam as the aggregates settle by centrifugal force. The measured aggregate diameter is D_{st}, the equivalent Stoke's diameter. The breadth of the aggregate size distribution is termed ΔD_{st}.

The use of fractal dimension, D, has been used recently to quantify the irregularity of carbon black aggregates. The fractal geometry can vary depending on the model used. Gerspacher and O'Farrell [8] reported fractal dimensions for a wide range of carbon blacks using Equation (5.1),

$$P \propto A^{D/2} \tag{5.1}$$

where P is the perimeter of the aggregate, A is the projected area of the aggregate, and D is the perimeter fractal dimension. The fractal dimension lies between 1 and 2, where the larger value represents higher irregularity of the aggregate. There appears to be a general correlation between DBP adsorption and fractal dimension.

5.5 Classification of carbon black

Carbon black is classified in several ways. One way is to classify carbon black in accordance to their levels of abrasion resistance; super abrasion furnace (SAF), intermediate super abrasion furnace (ISAF), and high abrasion furnace (HAF). Extrusion rate is another way to classify carbon black, where fast extrusion furnace (FEF) and general-purpose furnace (GPF) are in that category. There are other classifications, but basically they all depend on their manufacturing process, structure and surface area. The American Society of Testing Material (ASTM) designated ASTM numbers for rubber grade carbon blacks. Typical grades are summarised in Table 5.3 according to ASTM D1765 [9]. The N series comprises normal curing furnace and thermal blacks. The S series is slow curing channel blacks and oxidised furnace blacks. The first digit of the three digit number, following the alphabet character, represents the particle size range, which increases as the number becomes higher. With respect to tyre applications, fine particle blacks in the 100 range to 200 range, SAF and ISAF, respectively, are mainly used in truck tyre tread stocks to maximise tread wear resistance. Passenger tyre treads primarily use blacks in the 300 range, which represents the HAF family, typically N339 or N343. Medium to coarse blacks such as N550 (FEF) are used in body skim stocks for better processability, and low structure black such as N326 is used in steel skim stocks to provide a fatigue resistant compound. Innerliner butyl rubber stocks may use N660 black (GPF) at high loading in order to achieve good impermeability with easy processing. A recent report [10] indicated that semi-reinforcing furnace black (SRF) would further improve innerliner impermeability.

Table 5.3 Carbon black properties (ASTM D1765-00a) [9]

ASTM classification	D6556 N_2SA adsorption m^2/g	D2414-00 DBP adsorption 10^{-5} m^3/kg	D3493-00 DBP no. compressed 10^{-5} m^3/kg	D1510-99 Iodine adsorption g/kg	D3265-00 Tint strength
N110	130	113	98	145	124
N115	143	113	96	160	123
N120	126	114	98	122	131
N121	124	132	109	121	121
N125	122	104	89	117	123
N134	145	127	102	142	132
N135	141	135	117	151	119
N220	115	114	100	121	115
N231	111	92	86	121	117
N234	120	125	103	120	124
N293	130	100	92	145	120
N299	103	124	105	108	113
N326	78	72	69	82	112
N330	79	102	88	82	103
N335	85	110	94	92	110
N339	92	120	101	90	110
N343	96	130	104	92	114
N347	85	124	100	90	105
N351	71	120	97	68	100
N356	91	154	112	92	115
N358	82	150	112	81	99
N375	93	114	97	90	115
N539	40	111	84	43	-
N550	41	121	86	43	-

Table 5.3 Continued

ASTM classification	D6556 N_2SA adsorption m^2/g	D2414-00 DBP adsorption 10^{-5} m^3/kg	D3493-00 DBP no. compressed 10^{-5} m^3/kg	D1510-99 Iodine adsorption g/kg	D3265-00 Tint strength
N582	80	180	114	100	-
N630	34	78	62	36	-
N642	39	64	62	36	-
N650	37	122	85	36	-
N660	35	90	75	35	-
N754	25	58	57	24	-
N762	28	65	60	27	-
N765	36	115	82	31	-
N772	31	65	58	30	-
N774	29	72	62	29	-
N787	30	80	74	30	-
N990	9	43	40	-	-
N991	9	35	38	-	-

5.6 Mixing of carbon black with rubber and carbon black dispersion

Carbon black and rubber are typically mixed in an internal mixer. The Banbury is a mixer often used in the rubber industry. Factors that can affect carbon black dispersion in an internal mixer are mixing pressure, mixing temperature, fill factor, mixing intensity (rotor speed, rotor shape, rotor gap) and mixing time. Black incorporation time is the second power peak of a mixing energy profile, which identifies the point of carbon black incorporation into rubber. Most of the bound rubber is formed before this second power peak. After black incorporation, power consumption starts to decrease due to polymer chain scission, while the black is further dispersed and the amount of bound rubber is further increased. Small particle size blacks are usually difficult to incorporate because of the narrow spacing between particles; this is discussed later in the chapter (see Section 5.9). High structure blacks contain more void volume to be penetrated by rubber and thus take longer to incorporate. But once incorporated, they disperse more easily than lower structure blacks. High structure black also encounters more break down of primary aggregates during mixing which creates fresh surfaces with free radicals leading to higher bound rubber content (see Figure 5.7). In general, bound rubber is a function of specific surface area (see Figure 5.8). It is interesting to note that, when bound rubber is normalised by the specific surface area, bound rubber per unit surface area increases with reduced surface area, indicating that lower surface area black absorbs more polymer.

Increased surface area or increased loading in a compound dictates an increase in viscosity, which in turn causes heat generation. The optimum maximum mixing temperature in the nonproductive masterbatch, to form sufficient bound rubber while preventing excess polymer breakdown, is in the range of 155 to 170 °C. One important point that a compounder has to consider is the re-flocculation of carbon black that occurs during storage between mixing and curing. Carbon black, once dispersed in rubber, may reform contacts among aggregates, because of attractive forces between the aggregates themselves. Proper storage conditions can thus lead to good control of cured rubber performance. Bohm and others [11, 12] demonstrated that the rate of flocculation was governed by the type and loading of the black, polymer molecular weight, mixing history and annealing temperature. Higher loadings of higher surface area blacks have higher tendency to re-flocculate.

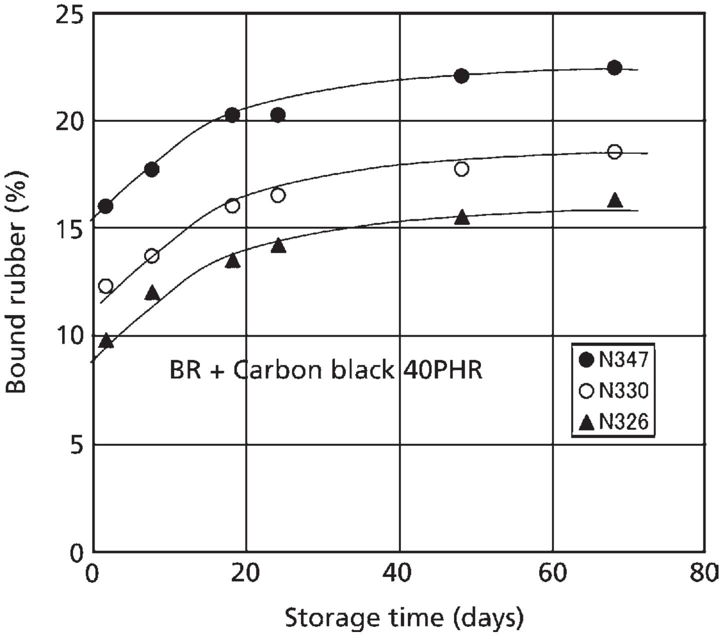

Figure 5.7 Effect of carbon black structure on bound rubber [13]

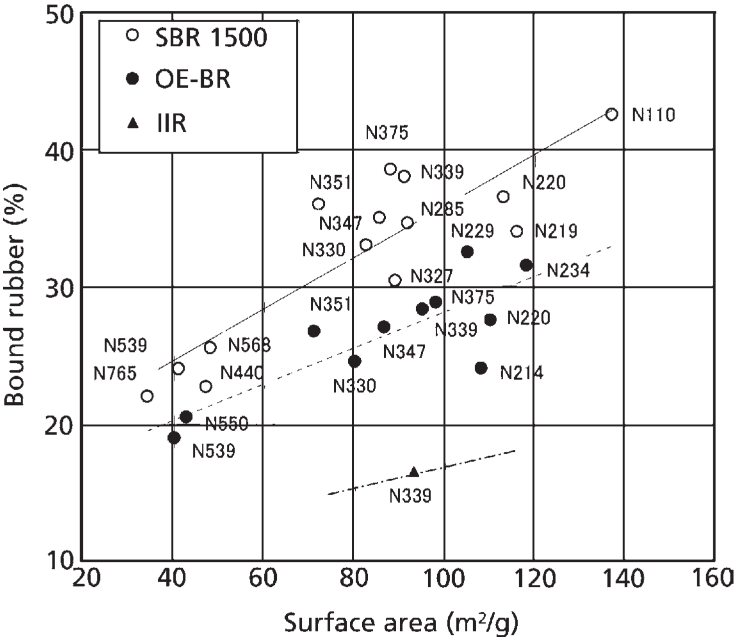

Figure 5.8 Effect of polymer and surface area of carbon black on bound rubber formation [14]

Good carbon black dispersion in rubber is an important factor to realise the full reinforcement potential of carbon black. Inadequate dispersion generally results in poor physical properties, or poor processing. For example, lower structure blacks are more difficult to disperse, because of the lower power generated throughout the mixing cycle, leading to premature rubber cracking during service. Thus, the goal is usually to obtain better dispersion, through a controlled mixing process. The mechanism of carbon black dispersion is discussed in detail by Kraus [15]. Carbon black dispersion can be considered as a reduction of carbon black agglomerate size. There are many methods to determine the degree of carbon black dispersion. For example, the original method for direct measurement of agglomerates in rubber is an optical method described in ASTM D2663-95a [16]. Another example is the DisperGrader [17], which is an optical test method that automatically evaluates the degree of dispersion in a quick manner, and excludes subjective human judgment. Characterisation of carbon black dispersion is summarised by Hess [18].

Examples of good/poor carbon black dispersion are shown in Figure 5.9. The degree of dispersion can be classified on a scale from 0 to 10 where 0 is the poorest dispersion and 10 is a perfect dispersion. Alternatively, carbon black dispersion can be expressed more functionally as the percentage of dispersed carbon black as agglomerates less than a given size, usually about 10 μm.

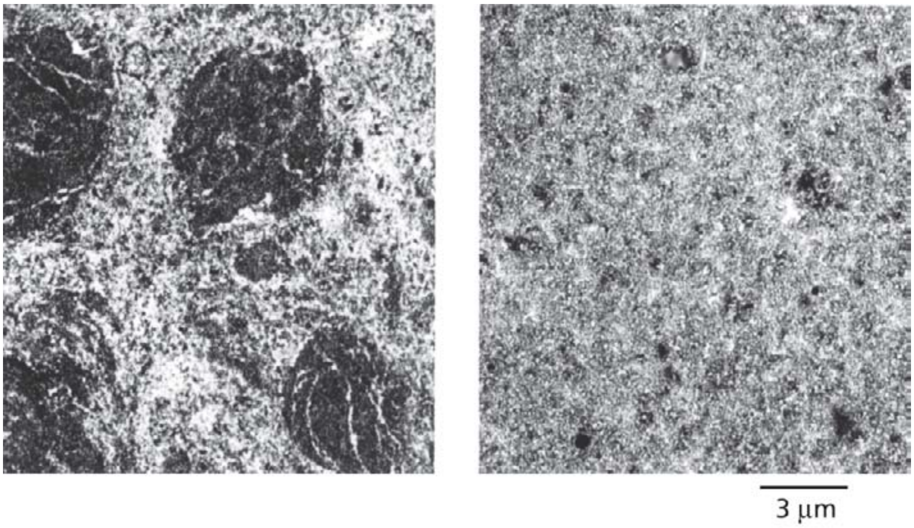

Figure 5.9 Comparison of poor carbon black dispersion (left) and good carbon black dispersion (right) (x 3,000)

Takeshita and others [19] attempted to improve carbon black dispersion by carbon black modification in which the carbon black was treated with various compounds in plasma at low temperature.

The distribution of carbon black in individual phases of polymer blends has been studied by Hess and others [20], Mouri and Tonosaki [21] and others. In general, carbon black will preferentially reside within the higher solubility parameter phase in a polymer blend. Using natural rubber (NR) and EPDM blend as an example, where NR is the higher solubility parameter phase and will accommodate carbon black preferentially. In this case, even if carbon black is first mixed with EPDM and then NR is added, one will find more carbon black in the NR phase. It is generally accepted that migration of carbon black takes place, perhaps, during the second mixing stage, when NR was added, or during resting. An example of carbon black distribution in a NR/BR blend is shown in Figure 5.10, where more carbon black can be seen in the BR phase.

5.7 Rheology of carbon black filled rubber

Reinforcement of carbon black filled rubber is discussed by many investigators [15, 22], in conjunction with the volume loading of carbon black. The viscosity of a suspension of spherical particles, η is given by the Guth-Gold equation (Equation 5.2),

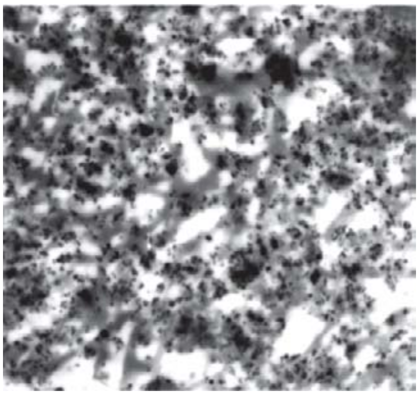

Figure 5.10 Carbon black distribution in NR/BR blend. NR/BR = 50/50, N220 = 20 phr, x 5,600

$$\eta = \eta_0(1 + 2.5\phi + 14.1\phi^2) \tag{5.2}$$

where η_0 is the unfilled viscosity, and ϕ is the volume loading of filler. When the volume loading ϕ is small, the third term becomes negligible and Equation 5.2 reduces to the Einstein viscosity law. Equation (5.2) is applicable up to medium thermal black (N990). However, when surface area is greater than about 10 m^2/g, the viscosity behaviour deviates significantly from Equation (5.2). This is because several complicated factors come into the picture. For example, aggregates are not spherical, agglomerates can cause highly non-Newtonian and thixotropic behaviour, and polymer is occluded in the interstices of the carbon black aggregates. In addition, polymer molecules are absorbed at the filler surface, causing a reduction of free rubber molecular weight, since large molecules are preferentially adsorbed. Further, at high loadings, there are attractive forces (van der Waals forces) between the aggregates themselves, which hinders their motion. In other words, many additional terms may be necessary in Equation (5.2) for accurate viscosity prediction. In general, higher surface area or higher structure provide higher compound viscosity. At the same time, the non-Newtonian behaviour of the compound will be pronounced; the rate of viscosity rise at low strain will be higher as compared to the rate of viscosity rise at high strain. In practice, flow characteristics of filled rubber can be expressed as a power law equation with an additional constant (Equation 5.3),

$$\tau_w = \eta\, \gamma^n + \tau_y \tag{5.3}$$

where τ_w is the shear force, η is the viscosity and γ is the shear rate and τ_y is a yield stress. The carbon black network will not allow the uncured rubber to flow until the stress exceeds the critical value, $\tau_{y,}$ where the network is destroyed. Note that both η and n will be a function of volume loading ϕ.

Extrusion behaviour is strongly affected by the morphology and loading of carbon black. Proper selection of carbon black may allow smooth extrusions with sharp edges, controlled die swell and increased throughput. Higher carbon black loading gives less extrusion shrinkage and less die swell, because increased loading diminishes the volume fraction of elastic rubber within the compound. However, increased loading has a penalty of significantly increased viscosity. The influence of the morphological characteristics of carbon black on the quality of extruded rubber hoses was reviewed by Monthey [23]. Building tack is also affected by carbon black morphology and loading, for example, a high loading of a high surface area black may produce a dry compound with poor tack.

5.8 Viscoelasticity of carbon black filled rubber

The properties of filled, or reinforced rubbers are time dependent, that is reinforced rubbers are viscoelastic materials. Viscoelastic properties are often measured by dynamic testing, where a filled rubber sample is subjected to a periodic, sinusoidal strain at constant frequency and at a controlled temperature. In tensile deformation, the storage modulus, E', is proportional to the stress component in phase with the strain, while the loss modulus, E'', is proportional to the stress component that is out of phase with the strain. The tangent of the phase angle, δ, between stress and strain is equal to E''/E'. Dynamic viscoelastic measurements will provide much insight into the rubber filler interaction when dynamic properties are measured as a function of increasing strain amplitude. Results of such an experiment are shown in Figure 5.11. The effect of carbon black on the storage modulus as a function of strain amplitude is large. At low strains, the three-dimensional secondary network of carbon black aggregates provides a high modulus, due almost entirely to the elastic forces between aggregates. As the amplitude of deformation is increased, the network undergoes breakdown. Consequently, E' decreases until an asymptote is reached at, conceptually, infinite strain, where the filler network is completely destroyed. The strain dependent viscoelastic behaviour of a filled compound is often referred to as the Payne effect, named after Payne in honour of his extensive work on the topic [24]. Network breakdown is partially reversible, and dynamic modulus can be recovered to some extent by resting the sample in an unstrained condition. This network breakdown and recovery process is said to play major role on tyre performance stability. The strain dependence of E' and E'' becomes more pronounced as the volume fraction of black increases. The magnitude of this effect and the volume fraction where it becomes important depends on the type of black. In the absence of carbon black, dynamic modulus of a rubber compound is not a function of strain. The Payne effect becomes more pronounced at low temperatures, but it is not fully understood why the Payne effect is temperature dependent.

According to Fujimaki and others [25], the Payne effect can be reduced by using a tin functionalised solution SBR. In his study, tin tetrachloride was added to an anionic

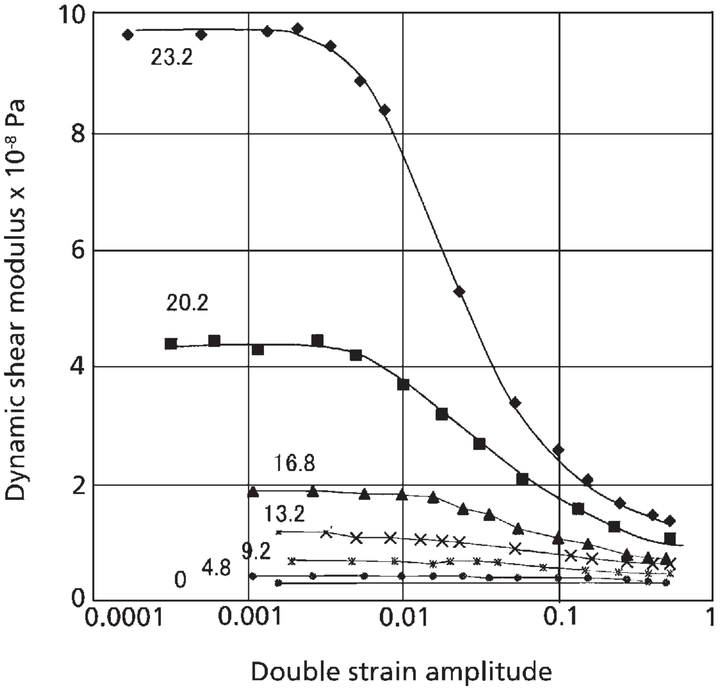

Figure 5.11 Variation of in-phase shear modulus for butyl rubber containing concentrations up to 23.2% volume HAF black [24]

polymerisation when the polymerisation was nearly complete. The living polymer chains were terminated with the tin tetrachloride, creating branched polymers with four arms. The tin coupling broke down upon mixing with carbon black and readily reacted with the carbon black surface to form chemically bound rubber. The chemically bound rubber reduced interaction between filler particles. Consequently, the carbon black network was substantially reduced, resulting in a lower Payne effect. This gave a lower loss tangent at moderate strain, which led to improved fuel economy in tyres.

The effect of filler volume loading, ϕ, on the storage modulus, E´, is given in the same form as Equation (5.2), based on the Guth-Gold equation.

$$E' = E'_0(1 + 2.5\phi + 14.1\phi^2) \qquad (5.4)$$

where E´ is storage modulus of the filled compound and E'_0 is the storage modulus of unfilled, or gum, compound.

Again, with a surface area larger than 10 m^2/g and at high loading above $\phi = 0.15$, the storage modulus significantly deviates from Equation (5.4) as is shown in Figure 5.12.

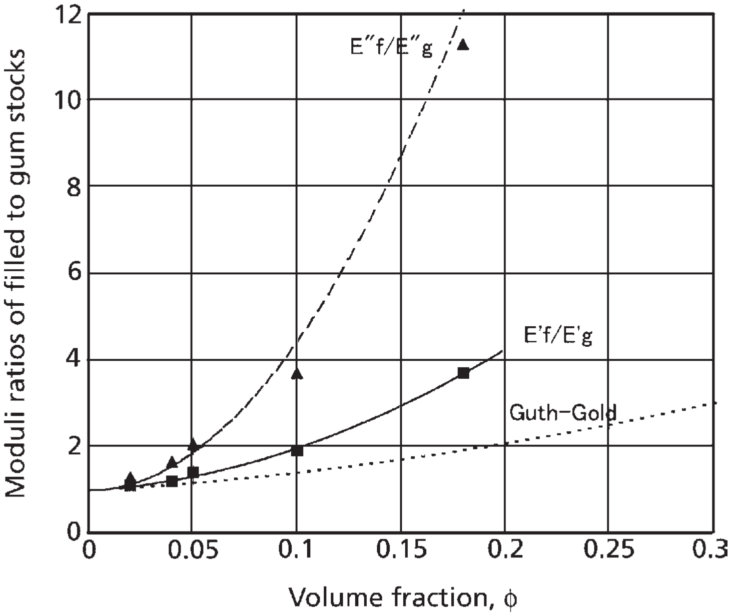

Figure 5.12 Effect of volume fraction of N220 on E″f/E″g and E′f/E′g ratios (10% strain 25 °C) [26]

The reason is the same as was discussed in Section 5.7. Ulmer and others [26] reported that the increase in loss modulus is much larger than the increase in storage modulus and deviates further from Equation (5.4) as shown in Figure 5.12 where the subscripts f and g denote the filled and unfilled gum compounds, respectively.

Medalia [22] postulated that the effective volume of an aggregate was greater than its actual solid volume, due to the rubber chains being occluded, and shielded from deformation by the carbon black aggregates. The DBP adsorption is used to calculate V, the effective volume fraction of the filler as shown in Equation (5.5).

$$V = \phi[(1 + 0.2139\text{DBP})/1.46] \tag{5.5}$$

If the volume fraction of the filler ϕ is replaced by V, the effective volume fraction of the filler, Equation (5.4) can be rewritten as Equation (5.6).

$$E' = E'_0(1 + 2.5V + 14.1V^2) \tag{5.6}$$

From equations (5.5) and (5.6), one can realise why a higher structure black provides higher modulus.

5.9 Physical properties of carbon black filled rubber

Physical properties responsible for the end application performance are basically viscoelastic and those measured by tensile stress-strain tests. Viscoelastic properties, or more specifically, dynamic properties, characterise mechanical behaviour at relatively small strains, from about 0.001 to 10%. Tensile stress-strain measurements characterise mechanical behaviour at strains larger than 100%. As already pointed out, the surface activity of the carbon black plays major role in reinforcing rubber. The extent of the interaction of the carbon black surface with elastomers depends on the random orientation of the graphitic layers on the surface of the carbon black. The more disorganised and the higher the energy of the carbon black surface, the higher the interaction level of the surface and the rubber molecules. Higher interaction usually results in higher strength, higher modulus at low strain and a less resilient material.

Regarding tyre applications, the most important contribution of carbon black to tyre performance is the tremendous improvement in tread wear resistance. The amount and type of carbon black play major roles in tread wear. Shieh and Funt [27] examined the effects of carbon black surface area, aggregate size distribution, aggregate complexity, surface activity and the dispersion of carbon black on wear resistance of tyre tread compounds. The surface area of carbon black is the most important parameter affecting tread wear. For a given carbon black loading, the wear resistance passes through a maximum with increased carbon black surface area level as shown in Figure 5.13. For a

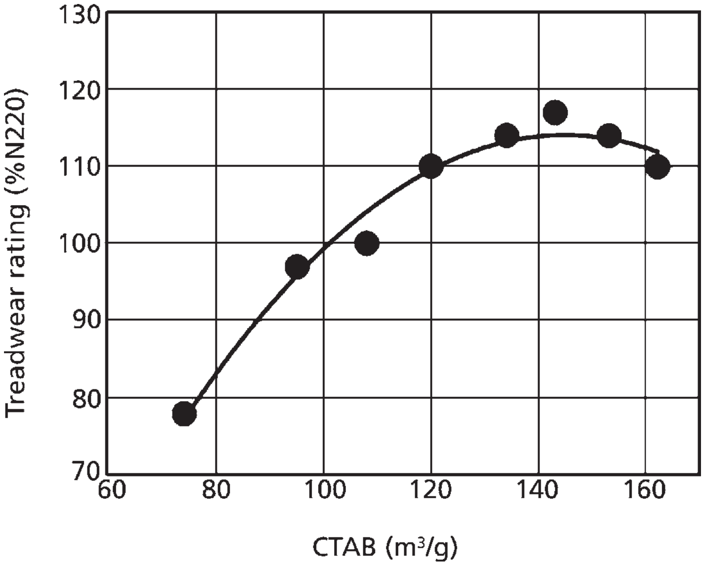

Figure 5.13 Tread wear versus surface area (SBR/BR = 65/35, black/oil = 65/35) [27]

given carbon black surface area, an optimum loading exists as shown in Figure 5.14. Three possible reasons are responsible for the existence of optimum surface area and optimum loading. First, higher surface area carbon black will create more heat during service, which may induce thermal degradation of the compound. Second, higher surface area blacks will be more difficult to disperse, especially at high loading. Third, higher surface area blacks will have a smaller particle to particle spacing. The nearest neighbour particle spacing, L, for a given volume fraction, ϕ, of carbon black can be estimated as

$$L = D/2\ (1.612/\phi^{1/3} - 2) \tag{5.7}$$

where D is the diameter of a sphere with volume equivalent to a single aggregate. D can be determined using Equation (5.8) [28],

$$D = 6000/(\rho S) \times \beta^{1.43} \tag{5.8}$$

where ρ is the density of the filler, S is the specific surface area (N_2SA), $\beta = V/\phi$, and V is the effective volume fraction of the filler estimated from Equation (5.5). Take an example of a typical tread compound containing styrene butadiene rubber (SBR) and an ISAF black with volume fraction $\phi = 0.30$. From Table 5.3, $N_2SA = 120$ and DBP = 125, thus

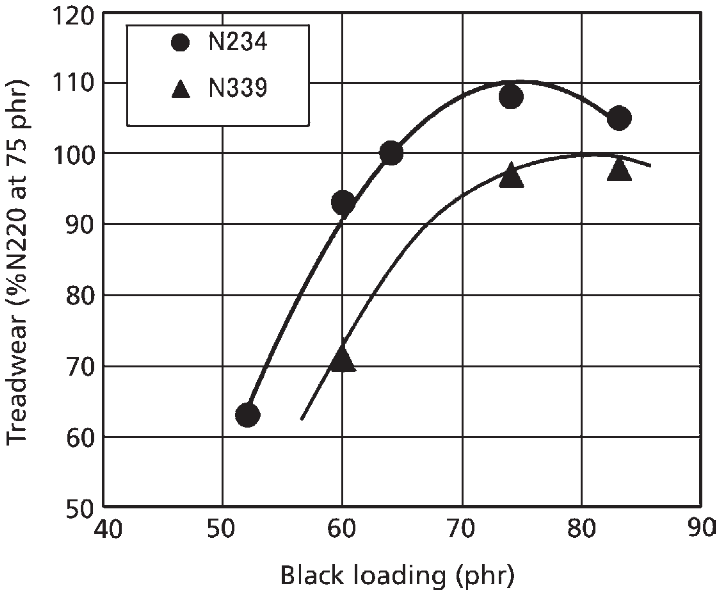

Figure 5.14 Tread wear versus black loading (SBR/BR = 65/35, oil varied to maintain equal hardness [27]

the apparent diameter of an ISAF aggregate will be D = 101 nm from Equation (5.8) assuming a density of 1850 kg/m^3. From Equation (5.7), the spacing between carbon black particles can be calculated as L = 21 nm. Meanwhile the radius of gyration of SBR can be calculated using Equation (5.9),

$$D_g/2 = 0.019\ M^{1/2} \tag{5.9}$$

where M is the molecular weight of the polymer and D_g is the polymer coil size. For molecular weight of 600,000, D_g is 28 nm. From Figure 5.15, one can realise that spacing (L) is smaller than the polymer coil size (D_g). In this situation, the polymer chain will not have enough room to change its configuration upon deformation or will be restricted from free motion due to the adjacent carbon black particle, causing higher local stress. Polymer chains will become more susceptible to break because of the higher stress. When the elastomer coil size D_g is greater than the particle-to-particle spacing, uniform dispersion will also be difficult to obtain. The reason behind the optimum loading and optimum surface area for tread wear resistance is mainly attributed to the third factor, spacing between particles. From this point of view, going to a very high surface area black does not necessarily result in improved wear resistance no matter how well the black is dispersed. Note that at ϕ>0.20, the spacing becomes small enough to show electrical percolation.

Tread wear and heat build up are the general trade off in truck tyre applications. Increased carbon black loading or the use of higher surface area black may improve tread wear but at the same time will result in high heat build up. High heat build up arises from the

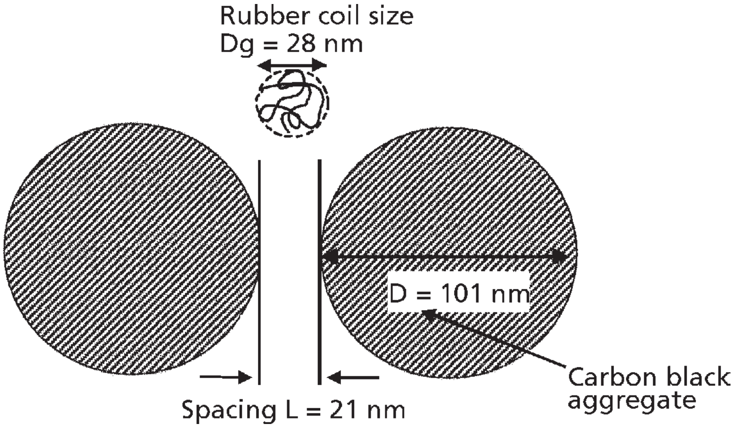

Figure 5.15 Spacing between carbon black particles in typical tread compound (ϕ = 0.30, D = 101 nm, ISAF black in SBR)

increased carbon network at high loadings, which gives high E′. Since the tread deformation is between conditions of constant load and constant energy [29], increasing storage modulus, E′, by increasing carbon black loading, should reduce energy loss (less heat build up). However, energy loss and heat build up will increase with higher carbon black loading, because, as mentioned earlier, increase in loss modulus is much greater than the increase in storage modulus. The overall goal is to achieve a new carbon black that can offer improved tread wear without increasing heat build up. Niedermeier and Freund [30] recently introduced a new carbon black family, nano-structure blacks, that improve tread wear without increasing heat build up. The main feature of the new black is its unusually rough surface, which provides enhanced interaction forces with the rubber matrix. Another factor that affects tread wear is the amount of bound rubber, as shown in Figure 5.16.

A carcass compound often uses N326, a low structure HAF black in order to achieve better fatigue resistance. The main reason why a low structure black shows better fatigue resistance is because carbon black aggregates show orientation in the direction of stretch as shown in Figure 5.17. The orientation becomes permanent as the strain cycle is repeated and the contrast between filled area and unfilled area becomes apparent. As a result, tear strength along the direction of orientation will approach the strength level of an unfilled rubber which is very low. Lower structure black has fewer propensities to show orientation because of the lower aspect ratio and thus results in better fatigue resistance.

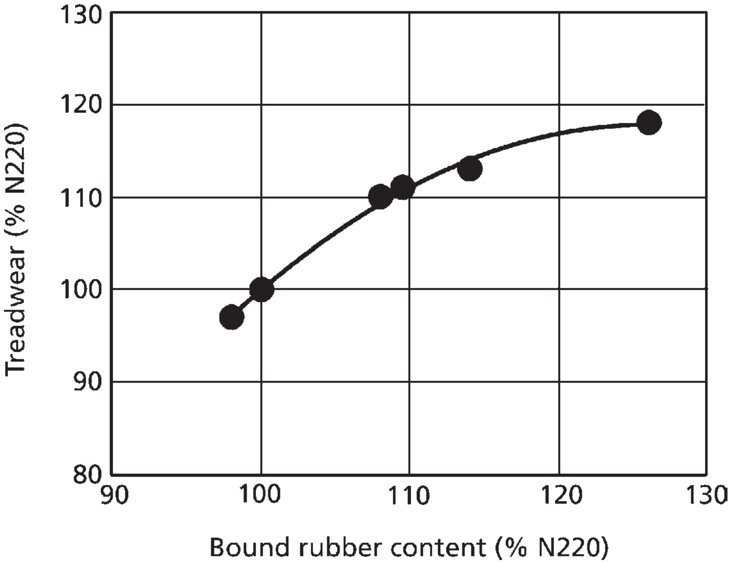

Figure 5.16 Tread wear versus bound rubber [27]

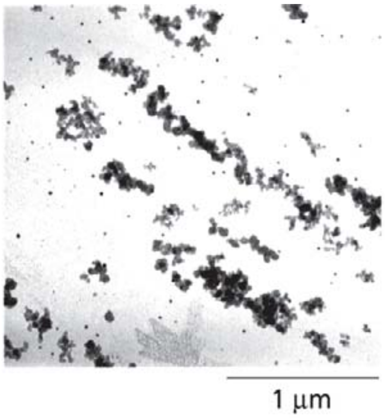

Figure 5.17 Orientation of carbon black. NR = 100, N121 = 10 phr, 100% elongation

Innerliner and inner tube compounds usually contain high carbon black loading to further enhance the impermeability of butyl rubber. In this case, a coarse black such as GPF is used in order to ease processing in tyre manufacturing plants.

5.10 Non-black fillers and applications

A wide variety of non-black fillers for rubber exist. Today, the principal non-black fillers are clays, precipitated silicas and calcium carbonates. Other major fillers include mica, talc, zinc oxide, magnesium carbonate, magnesium oxide, titanium oxide, barites and many others. Short fibres of aramid, carbon, glass, nylon or polyester, are also widely used in rubber compounds. It will be impossible to discuss all of these non-black fillers within a single chapter. Therefore, the discussion will describe some non-black fillers, and will also examine differences between reinforcing mechanisms of the non-black fillers and carbon black. Non-black fillers can be classified in three categories by their function in rubber. Non-black fillers of the first category are called reinforcing pigments. They include precipitated silica, fine particle size precipitated calcium carbonate, and perhaps hard clay with surface treatment. Note that they all have very fine particle size, less than 1 μm, especially to add high strength to synthetic rubbers. Non-black fillers of the second category are called diluents. In practice, they are used to reduce cost of the compound. Soft clay, ground calcium carbonate, talc and barytes fall into this category. They are all considered inert fillers and sometimes can be used at loadings as high as 200 phr, without significantly increasing the modulus of the compound. Usually this family of filler reduces compound die swell and provides sharp-edged extrudates and smooth calendering behaviour in the rubber manufacturing process. The third category of non-black filler consists of materials that add special traits to the compound, for example, colour, electrical conductivity, flame resistance, impermeability, or oil resistance characteristics. All of these traits depend on the particle size, structure, shape and surface chemistry of the filler when compounded into rubber. Table 5.4 lists chemical compositions of typical non-black fillers, with some fundamental characteristics. Waddel and Evans [31] made a comprehensive summary of non-black fillers used in tyre applications including black sidewalls, white sidewalls, wire coats, inner liners, carcass ply coats, and treads.

5.10.1 Calcium carbonate

Calcium carbonates may be considered as materials of two families. One is natural calcium carbonate, a ground limestone, used as diluents to reduce compound cost. The particle diameter is relatively large, ranging from 1 to 5 μm, and bulk density is low. Ground calcium carbonates generally mix easily into rubber. Good dispersion is obtained even at very high loadings, up to 200 phr, without significant increases in compound viscosity. Although ground calcium carbonates reduce cost, the magnitude of the practically important volume cost reduction is limited because of the high specific gravity. The other family is precipitated calcium carbonate. Limestone is burned in a kiln driving off carbon dioxide gas and leaving calcium oxide. The carbon dioxide gas is transferred to a calcium oxide suspension to form calcium carbonate again. The resulting carbonates are filtered, dried, ground and separated by size. The particle size of precipitated calcium carbonate

Table 5.4 Characterisation of mineral fillers

	Chemical composition	Particle diameter (nm)	Density (kg/m^3)	Surface area (m^2/g)
Carbon black	C	17–26	1850	85–130
Silica	SiO_2	15–25	2360	150–380
Aluminum trihydrate	$Al(OH)_3$	600–2,500	2420	1.3–8.0
Clay	$Al_2O_3.2SiO_2.2H_2O$	300–1,500	2500–2650	4–60
Aluminum oxide	Al_2O_3	400–2,300	3880–3990	5–85
Calcium carbonate	$CaCO_3$	40–3,000	2590–2700	2–31
Talc	$3MgO.4SiO_2.H_2O$	200–8,000	2580–2830	1–40
Mica	$Al_2O_3.2SiO_2.2H_2O$	3,000	2600–3000	29

is below 0.1 μm, thus the small particles are reinforcing in rubber compounds. Coating agents such as fatty acids or lignin are used to prevent secondary flocculation. Without coating, they tend to stick to the walls of the internal mixer and become difficult to disperse in rubber. Silane modification of precipitated calcium carbonate can further increase tensile strength of the compound but not to the level achieved with a high surface area carbon black.

5.10.2 Clay

Clay is hydrated aluminum silicate produced by decomposition of alumina-silica minerals such as kaolin. The finer grade is called hard clay, where more than 80% of the particles are smaller than 2 μm. Hard clay is reinforcing and provides high modulus and good wear resistance, but the properties are inferior to those obtained with a furnace carbon black. Silane treatment of clay gives additional reinforcement with better permanent set and lower heat build up. Soft clay on the other hand is merely a cost reducer. More than 20% of soft clay particles are greater than 5 μm in size, and the reinforcing effect is much less than that of a hard clay. Rubber compounds can take clay loading as high as 300 phr. Both types tend to retard cure, because they have an acidic pH of around 5 and absorb cure accelerators. Accordingly, cure rate must be adjusted, when using clay, by the use of ethylene glycol or triethanolamine for example. Calcined clay is kaolin treated at 600 to 800 °C to remove bound water. Calcined clay imparts electrical insulation resistance to rubber. Clay is in a way an environmental friendly filler because of the very low energy required to produce the material, as compared to other major fillers (see Table 5.5) [32].

Table 5.5 Filler energy requirements

Filler	Energy, MJ/kg
Carbon black (ISAF)	90–110
Medium thermal black	140
Precipitated silica	70
Precipitated silicate	17
Calcined clay	14
Silanised and grafted clays	4
Air floated clays	<0.5
Ground $CaCO_3$	<0.5

Source: Dannenberg [32]

5.10.3 Silica

Precipitated silica is the highest reinforcing non-black filler and is closest to carbon black in compound properties. The formation of precipitated silica [33] is a chemical reaction of sodium silicate (water glass), and sulphuric acid. By products of the reaction are sodium sulphate, which must be washed out, and water. The chemical reaction is an equilibrium reaction which can be influenced by process parameters such as pH, temperature and concentration. The most important properties: surface area, structure, and silanol group density, are controlled in the precipitation process. Figure 5.18 is a transmission electron micrograph of precipitated silica. It is surprising, in spite of the major difference in manufacturing methods, that the morphology of silica is similar to that of carbon black, except that silica fusion tends to be a little more extensive. Recent work [34, 35] indicates that highly dispersible silica can be obtained through optimum precipitation conditions of high pH value with a short drying time.

The largest commercial use of silica has been in treads for off the road, giant earthmover and loader tyres. The trend in the mining industry continues to be larger size dump trucks, with tyres that have rim diameters greater than 1.6 m. Silica is essential for maintaining a good balance of heat build up, wear resistance, and cut-chip resistance in this application, and the use of silica in this area will continue. Since the advent of silica compounds in passenger tyres in the early 1990s, consumption of silica has grown rapidly. Silica, as a principle filler in passenger tread compounds, gives higher wet traction and better rolling resistance, at a reasonable wear resistance level compared to carbon black. However silica

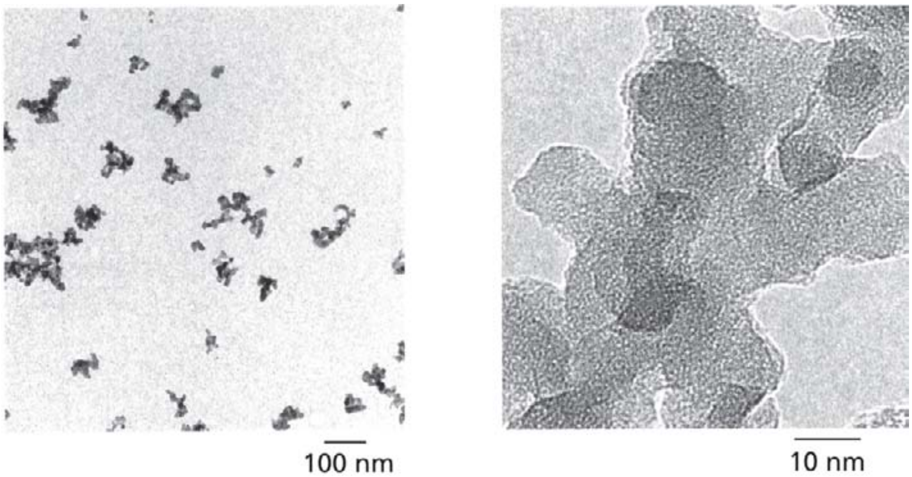

Figure 5.18 Transmission electron micrograph of silica

has significant penalties in raw material cost, process cost, and poor electrical conductivity. Compared to carbon black with a similar surface area and structure, silica gives lower polymer-filler interaction and tends to agglomerate, forming a filler network in the compound. The result is poor processability and unacceptable dynamic properties. However, the addition of silane coupling agents, for example, TESPT (bis(3-triethoxysilylpropyl-)tetra sulphide) to the compound markedly improves silica performance. The coupling agent lowers the filler to filler interaction by coating the polar surface, which inhibits polar interaction between silica particles. In addition, the mercapto functionality can participate in vulcanisation during the curing process of the rubber compound. In these ways, the dynamic properties become favourable, allowing application of silica in passenger tread compounds. Details on the silanisation reaction are reviewed by Luginsland and Hasse [36]. The silanisation reaction is a two-step process. Hydrolysis of ethoxysilyl group to yield ethanol takes place first. The second reaction is condensation of the hydrolysed silane with a silanol group on the silica surface, releasing water necessary for the preceding hydrolysis reaction. Figure 5.19 shows that the amount of ethanol evolved at 50 °C becomes constant at a moisture level above 5%, indicating that moisture content of silica must be higher than 5% to obtain a fast silanisation reaction.

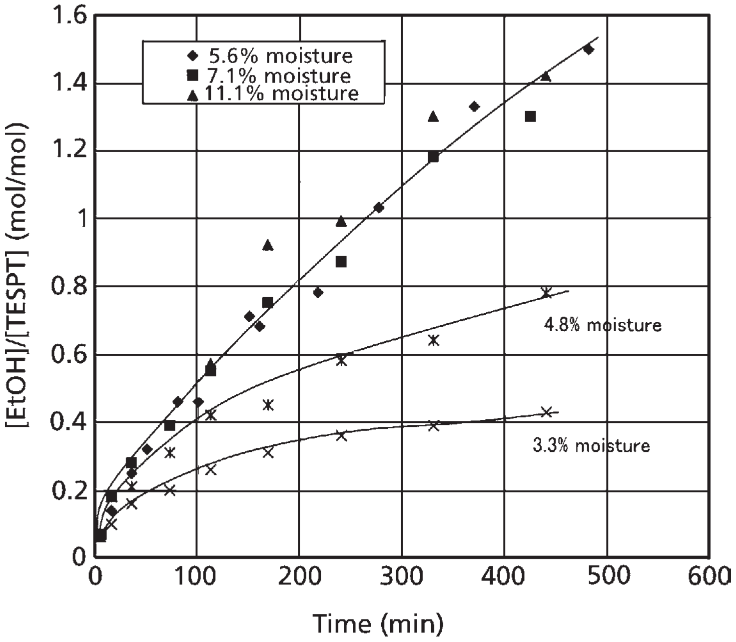

Figure 5.19 Reaction of silica with TESPT in decane; formation of ethanol versus reaction time at 50 ° C (8 phr TESPT) [36]

The use of precipitated silica as a reinforcing filler to improve rolling loss of tyres without other performance detriments, has been reported by several investigators [37, 38]. However, the mechanism for the good wet traction associated with silica remained an open question. According to Schuring and Futamura's deformation index analysis [29], wet traction reflects a constant strain process. Thus, energy loss and wet traction are proportional to loss modulus, E´´. As shown in Figure 5.20, a frequency sweep of loss modulus was constructed by shifting the temperature sweep result using the time-temperature superposition principle [39]. The silica filled compound shifted to a lower frequency than the carbon black loaded compound. It is believed that higher loss modulus at frequencies in the range of 10^5 to 10^6 Hz provides increased wet traction. It is apparent from Figure 5.20 that silica compounds have a much higher loss modulus than carbon black compounds in this frequency range. This may be the mechanism for improved wet traction of silica compounds compared to carbon black loaded compounds. The following discussion may give further understanding for the shift factor difference between different types of fillers.

Mouri and others [38, 40], and Wang and others [41] found that the time temperature superposition, based on the WLF equation [39], described in Equation (5.10), will be a function of the filler type.

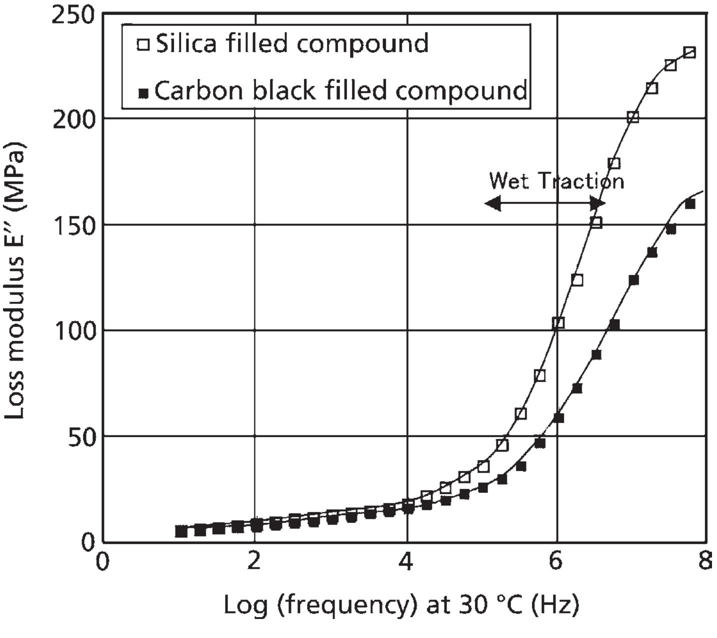

Figure 5.20 Loss modulus as a function of frequency for compounds loaded with different fillers [38]

$$\log a_T = -C_1\ (\ T - T_s) \ /\ (C_2 + T - T_s) \qquad (5.10)$$

C_1 and C_2 are experimental constants for the reference temperature T_s. As shown in Table 5.6, C_1 and C_2 deviate significantly from their values for unfilled rubber, when highly reinforcing filler is used at high loading. The carbon black compound had the largest values, followed by the silica compound, and finally by the unfilled gum rubber. An increase in the WLF constants appears to reflect reinforcement, since higher polymer-filler interaction, and increased immobile polymer bonded to the filler will result in less free volume. This indicates that the polymer chain in silica compounds may be more mobile than the polymer chain in carbon black compounds. At temperatures, typically greater than 100 °C above the glass transition temperature, the WLF equation does not apply to the frequency-temperature shift. Instead, the shift factor has been proposed to follow an Arrhenius type temperature dependence [41], as shown in Equation (5.11),

$$\log a_T = A + E_a/RT \qquad (5.11)$$

where a_T is the shift factor, A is a constant, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. Wang [41] reported that the activation energy, E_a, was also a function of the filler type, and reflected the degree of reinforcement as was seen in C_1 and C_2 obtained from the WLF equation. Since the viscoelastic modulus was measured at strains where the particle network provides a large contribution to the modulus, E´ and E´´, an alternative or additional explanation for the differences in effect

Table 5.6 Calculated WLF constants as a function of T_g for SBR [38]

	Styrene = 23.5%		Styrene = 35%		Styrene = 45%	
	T_g $^{(1)}$ = –0 °C		T_g $^{(1)}$ = –28 °C		T_g $^{(1)}$ = –13 °C	
Constants at 18 °C	C_1^0	C_2^0	C_1^0	C_2^0	C_1^0	C_2^0
Unloaded compound	7.1	126	7.8	115	8.6	104
Silica loaded	15.8	156	23.1	194	29.7	196
Carbon black loaded	23.2	176	28.5	194	36.7	244
Constants at T_g (1)	C_1^g	C_2^g	C_1^g	C_2^g	C_1^g	C_2^g
Unloaded compound	13.2	68	13	69	12.4	73
Silica loaded	25.2	98	30.3	148	35.3	165
Carbon black loaded	34.6	118	37.4	148	42	213

(1): Inflection point of G ´ temperature sweep

produced by silica and carbon black may relate to the frequency shift with temperature of the particle network instead of the polymer itself.

The advent of silica tread in passenger tyre treads triggered extensive work on non-black fillers other than silica. Wang and Mahmud [41, 42] modified carbon black using a unique co-fuming technology to yield carbon-silica dual phase filler. The filler contains 3 to 7% silica primarily residing at the surface of carbon black. This enables carbon black to perform similarly to silica, with the help of a silane-coupling agent. Work by Mouri and Akutagawa [40] suggested that aluminum trihydrate could improve vehicle fuel economy and provide good wet traction, without other performance detriments. Corvasce and others [43] found that a rubber composition containing a starch/plasticiser composite can significantly improve rolling resistance, with equal to better wet traction and wear resistance than a carbon black loaded compound.

One of the surprising and excellent aspects of carbon black, lacking in silica, is the carbon black's inhibition of cure reversion upon compound ageing. Reversion inhibition is attributed to radicals on the carbon black surface. The carbon black radicals can quench polymer free radicals or peroxy radicals, generated by polymer scission during oxidative ageing of the compound. Silica lacks this aspect, and additional amounts of antioxidant such as *N*-(1,3-dimethyl-butyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD) are necessary to prevent compound reversion. Another compounding precaution with silica is to increase the accelerator level to adjust for the adsorptive nature of silica. Regarding the ingredient addition sequence, when mixing silica compounds, zinc oxide should not be added prior to the coupling agent addition. Zinc oxide can readily react with silanol groups present on the silica surface and inhibit the silanisation reaction.

5.11 Summary

The rubber compounder must select the right type of filler and its optimum loading, as well as consider other factors mentioned in the chapter, in order to arrive at the best balance in compound quality. Optimum quality can only be achieved through careful observation of the product's field performance, determination of the proper testing methods, and knowledge of rubber physics. As a final note, the optimum carbon black grade for a particular application in one market, may not be satisfactory for the application in another market, since end use conditions can vary widely around the globe. The essence of the compounding, in an age of global market, is an understanding of end use conditions in each local market, so that filler type and loading can be tailored to meet local requirements. For more detailed information on carbon black, see the comprehensive review by Donnet [3].

Acknowledgements

The author would like to thank J. D. Ulmer and H. Yamada for useful comments and review.

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6 Rubber Additives - Compounding Ingredients

R. N. Datta and F. A. A. Ingham

Introduction

The basic properties of rubber products are highly dependent on the elastomer(s) used in their manufacture. However, these properties can be modified favourably through the appropriate choice of compounding ingredients. Some are added to facilitate or accelerate crosslinking, others improve processability and others to improve the properties of the finished rubber product. Excluding mineral-based fillers these compounding ingredients can be classified as follows: vulcanising agents, vulcanisation accelerators, activators of vulcanisation, retarders and inhibitors of vulcanisation, antidegradants, antireversion agents, plasticisers and softeners, and miscellaneous ingredients. Each class will be dealt with in turn in the following sections.

6.1 Vulcanising agents

Materials that are able to form crosslinks between polymer chains may be generally classified as vulcanising agents. Listed below, and described in some detail, are the curing agents in common use together with a category of less frequently used materials.

6.1.1 Sulphur

Elemental sulphur is the most widely used vulcanisation agent in the rubber industry and is effective in elastomers containing some degree of unsaturation. Ground sulphur is most widely used, often referred to as rhombic sulphur or rubber makers' sulphur. The molecular structure of rhombic sulphur comprises an eight membered ring and is crystalline in nature. It has a melting point of 115 °C and is soluble to a limited degree in elastomers; for example, around 1% w/w in natural rubber at room temperature, increasing to a level of the order of 7% at 100 °C. The relatively low solubility of sulphur in rubber at ambient temperature is the cause of so-called 'sulphur bloom'. It appears as an off-white powdery coating on the surface of the uncured compound due to migration from the bulk compound when the limit of solubility is exceeded. If present in excess it has an unfavourable effect on the building tack of green components. Sulphur bloom can also occur in vulcanisates but here the disadvantage is largely cosmetic.

Sulphur bloom can be prevented by substituting rubber makers' sulphur with so called insoluble sulphur. This is a crystalline, polymeric form of sulphur [1] and is insoluble in solvents and elastomers. It should be processed at temperatures not exceeding 110 °C, preferably 105 °C, in order to prevent excessive conversion into the rhombic form. During vulcanisation it is converted into rhombic sulphur allowing the vulcanisation process to proceed as normal. The following advantages are claimed with regard to the use of insoluble sulphur [1, 2]:

- elimination of sulphur bloom,
- prevention of sulphur migration between green components during storage,
- reduced bin-scorch during the storage of green compounds.

6.1.2 Sulphur donors

The term 'sulphur donor' is a common designation for organic disulphides and higher sulphides that are capable of providing active sulphur during the vulcanisation process thereby generating sulphidic crosslinks. Sulphur donors can be categorised into those that are applied as a direct substitute for free sulphur, with no major change in vulcanisation characteristics, and those that act simultaneously as vulcanisation accelerators (see Section 6.2). Products of the first type are, for example, dithiomorpholine (DTDM) and caprolactam disulphide (CLD). Examples of the second category of sulphur donors are 2-morpholinodithiobenzothiazole(MBSS), dipentamethylenethiuram-tetrasulphide (DPTT), *N*-oxydiethylene-*N′*-oxydiethylene thiocarbamyl sulphenamide (OTOS), tetramethylthiuram disulphide (TMTD) and its analogues. The chemical structures of these sulphur donors are shown in Figure 6.1.

With the demand for *N*-nitrosamine free sulphur donors, tetrabenzylthiuram disulphide (TBzTD; Figure 6.2) has been introduced. The prime function of TBzTD is as a secondary accelerator but at higher loading it can also function as a sulphur donor [3].

Some additional materials are available that are capable of acting as sulphur donors; for example, alkyl phenol polysulphide [4], bis(3-triethoxy silyl propyl) tetrasulphide [5] (TESPT), and dialkyl dithiophosphate polysulphide [6].

6.1.3 Peroxides

Crosslinking with peroxides has been known since 1915 when Ostromyslenski disclosed that natural rubber could be transformed into a crosslinked state with dibenzoyl peroxide [7]. However, there was little interest in peroxide crosslinking until the development of fully saturated ethylenepropylene copolymers in the early 1970s.

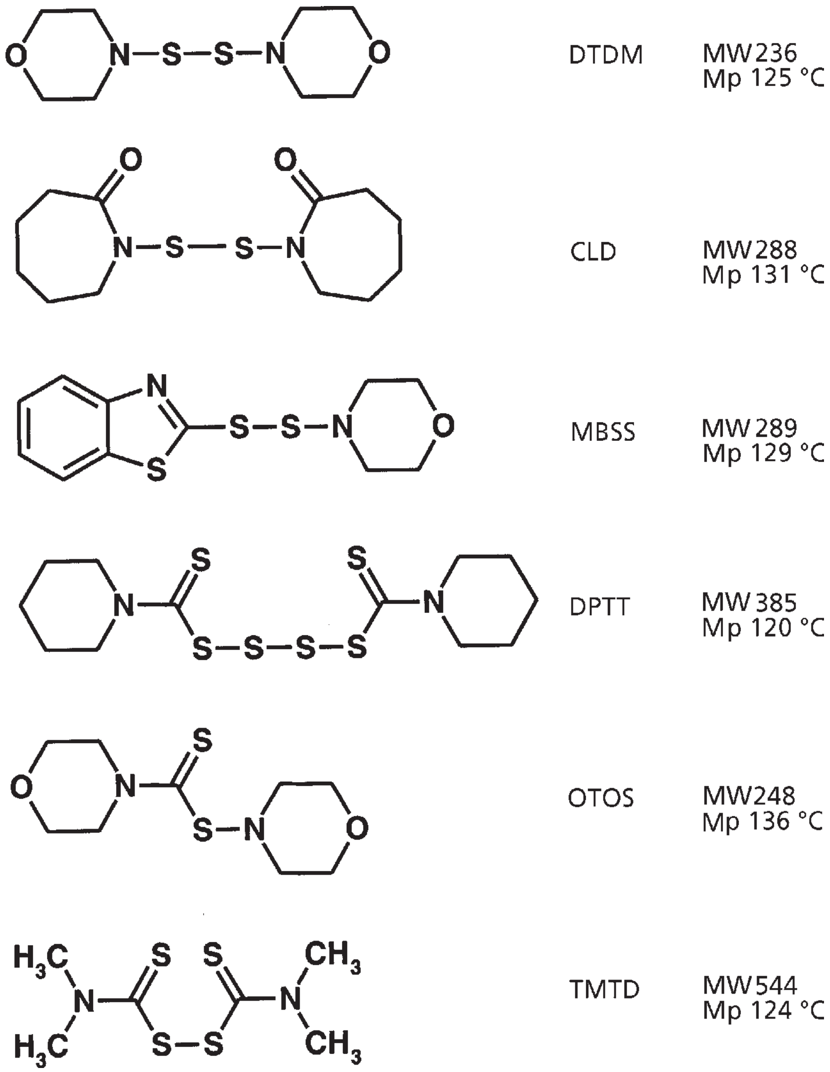


Figure 6.1 Structures of sulphur donors

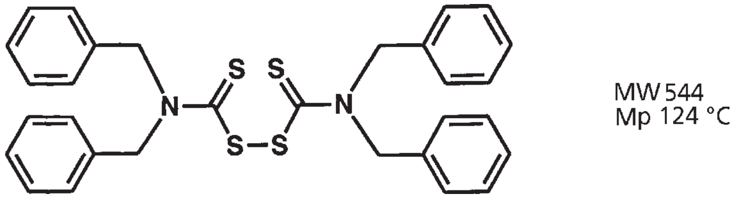


Figure 6.2 Structure of TBzTD

The use of peroxides for the crosslinking of elastomers is limited to those that are stable during storage, safe to handle during processing but, on the other hand, decompose sufficiently fast at cure temperatures. In order to meet these requirements peroxides containing tertiary carbon atoms are most suitable [8], whilst peroxy groups bonded to primary and secondary carbon atoms are less stable. Organic peroxides that are suitable for crosslinking elastomers are shown in Figure 6.3.

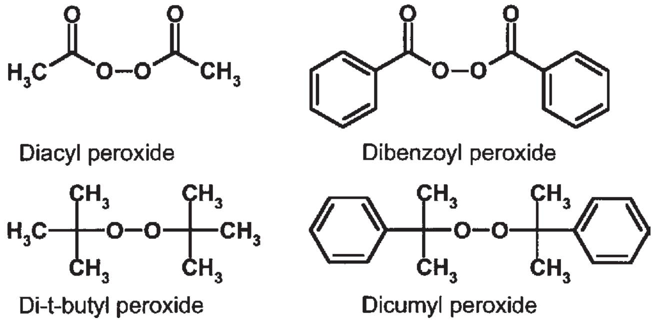


Figure 6.3 Structures of peroxides

In addition to the symmetrical peroxides, asymmetrical peroxides are also in use, as for example *tert*-butyl perbenzoate, *tert*-butylcumyl peroxide and some polymeric peroxides [9].

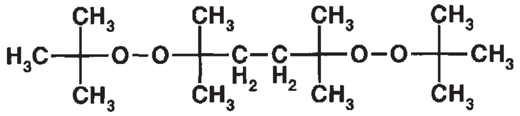
A further limitation with regard to the suitability of peroxides concerns the efficiency of crosslinking. Higher efficiencies are observed for those peroxides that form one of the following radicals during homolytic decomposition [10] (see Figure 6.4).

The thermal stability of peroxides can be expressed in terms of their half-life ($t_{1/2}$). Half-life values can be estimated in solution utilising the technique of differential thermal analysis. These values, or more precisely the temperatures at which their half-life is equivalent, provide an indication of practical vulcanisation temperatures [11] (see Table 6.1).

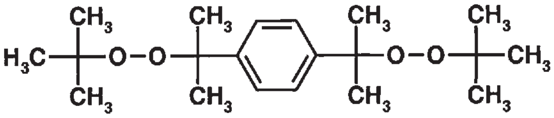
There are a number of advantages, associated with the peroxide vulcanisation of elastomers:

- scorch free storage of compounds,
- possibility to apply high vulcanisation temperatures without reversion,
- simple compound formulation,
- low compression set even at high cure temperatures,

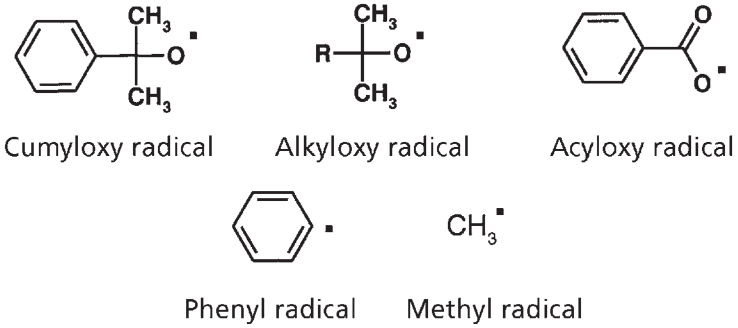
Peroxides containing more than one peroxy group are also suitable, for example:



2,5-Bis(*tert*-butylperoxy)-2,5 dimethyl hexane



1,4-Bis(*tert*-butylperoxy isopropyl) benzene



Cumyloxy radical Alkyloxy radical Acyloxy radical

Phenyl radical Methyl radical

Figure 6.4 Radicals formed during the homolytic cleavage of peroxides that are most effective in producing crosslinks

- good electrical properties of vulcanisates,
- good high temperature vulcanisate stability,
- no discoloration of compounds.

There are, however, some drawbacks compared to sulphur vulcanisation:

- limited compounding flexibility due to the reaction of peroxides with other compounding ingredients; for example with antioxidants, plasticisers and resins,
- sensitivity of vulcanisation reactions to oxygen,

Table 6.1 Typical crosslinking temperatures of crosslinking peroxides based on their half-life

Class	Example	Temp. °C $T_{1/2}$ = 6 min	Typical crosslinking temperature °C
Dialkyl peroxide	2,5-Bis(tert-butylperoxy) 2,5-Dimethyl-3-hexyne	173	180
	2,5-Bis(tert-butylperoxy) 2,5-Dimethyl hexane	159	180
Alkyl-aralkyl peroxide	Bis(tert-butylperoxy Isopropyl) benzene	160	180
	Tert-butylcumyl peroxide	160	180
Diaralkyl peroxide	Dicumyl peroxide	155	170
Peroxy ketals	Butyl 4,4-bis (tert-butyl peroxy) valerate	143	160
	1,1-Bis(tert-butyl peroxy) 3,3,5-Trimethyl cyclohexane	129	150
Peroxy ester	Tert-butylperoxy benzoate	146	140

- lack of flexibility in regulating scorch and optimum cure time,
- inferior tensile, tear and flex properties,
- inferior abrasion resistance,
- frequently disturbing odours of peroxide decomposition products,
- generally higher cost.

6.1.4 Urethane crosslinking

A novel process of vulcanising olefin elastomers with sulphur was developed in the UK by the Malaysian Rubber Producers Research Association (MRPRA) [12]. The materials are sold under the trade name of Novor, the most popular grade being Novor 924. The term 'Urethane' was applied to these materials because of their analogy with regular urethane compounds, Novor 924 being an adduct of a substituted nitrosophenol and toluene isocyanate. It is a dustless, free flowing powder containing 75% active ingredients and 25% naphthenic oil. References have been made to its use in natural rubber (NR), SBR and polychloroprene (CR) based compounds [13, 14].

Despite a great deal of early interest in urethane based crosslinking agents their use in the industry has found limited application. There are several reasons for this: they are expensive, they exhibit little scorch resistance and the materials possess limited storage stability, absorbing moisture under humid conditions.

6.1.5 Metal oxides

Vulcanisation of CR rubber is often carried out with a combination of zinc and magnesium oxides. Lead oxides can also be used particularly to obtain vulcanisates with low water absorption. Polysulphide rubbers (Thiokol) and chlorosulphonated polyethylene (Hypalon) are also vulcanised using metal oxides.

6.1.6 Other vulcanising agents

Quinone dioxime is used for the vulcanisation of butyl rubber. The presence of an oxidising agent in the vulcanising system is necessary to convert the dioxime into p-nitrosobenzene, the actual vulcanising agent. Lead oxide (Pb_3O_4; 5–10 phr) or 2,2´-dithiobis(benzothiazole) (MBTS; 4 phr) can be used.

Diamines with blocked amino groups, e.g., hexamethylene diaminocarbamate, ethylene diaminocarbamate and dicinnamylidinehexamethylenediamine, are used to vulcanise fluoroelastomers.

6.2 Vulcanisation accelerators

The reaction of rubber with sulphur is slow even at high temperatures. Natural rubber containing only sulphur would require around 4 hours at 140 °C to fully vulcanise. It is not surprising then that for the past 150 years efforts have been made to speed up the vulcanisation process.

The first such cure acceleration was accomplished by adding metal oxides to the compound, such as those of lead, calcium and magnesium. The improvement was rather limited however and it was not until Oenslager [15] discovered organic accelerators in 1906 that significant improvements in the rate of vulcanisation were feasible [16]. Aniline was the first of such organic accelerators but owing to its toxicity was soon replaced by the reaction product of aniline and carbon disulphide [17]. This followed with the introduction of *N*,*N*´-

Diphenylguanidine [18] which, although still in use, is slow by today's standards and is rarely used alone but in combination with other accelerators.

A significant step forward was the discovery of 2-mercaptobenzothiazole (MBT) in 1921 [19]. Following the discovery of MBT, the disulphide, MBTS, was found to provide greater scorch (premature vulcanisation generally due to excessive heat history) safety at higher temperatures. A further important step was the discovery of sulphenamide type accelerators. They represent the products of the oxidative condensation of thiazoles with an amine. The application of these more effective accelerators has allowed, in general, a reduction of compound sulphur levels in addition to increased rates of vulcanisation. This more efficient use of sulphur has led to improved vulcanisate properties.

Triazine-based accelerators have been introduced that provide even higher crosslinking efficiency. However, they have not established themselves as an important class of accelerators possibly due to an unfavourable price versus performance.

There are a wide variety of accelerators available to the compounder. These include accelerator blends of which there are well over 100. In order to rationalise this extensive range of materials it is useful to classify them in terms of their generic chemical designation listed below:

Sulphenamides
Thiazoles
Guanidines
Thiurams
Dithocarbamates
Dithiophosphates
Miscellaneous

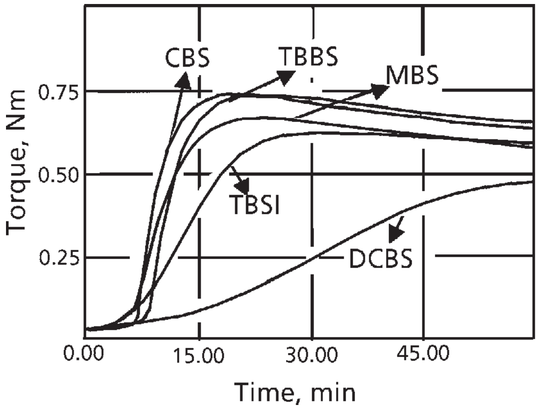
Some specific chemical structures belonging to each class are shown in Sections 6.2.1 to 6.2.7.

6.2.1 Sulphenamides

A significant step forward with regard to the development of accelerators occurred in the 1930s when Zaucker and Bagemann found that sulphenamides provided a delayed action to the vulcanisation process [20]. Today there are a number of commercially available suphenamide-based accelerators differing in amine moiety, thereby providing control over scorch time and cure rate. The more basic the attached amine, the shorter is the scorch time and the higher is the cure rate. Perhaps the most widely applied sulphenamide is *N*-cyclohexyl-2-benzothiazolesulphenamide (CBS) due to a good balance between scorch safety and cure rate. If greater scorch safety is required the sulphenamide of choice should be *N-tert*-butyl-2-benzothiazolesulphenamide (TBBS) or 2-(4-morpholinothio)benzothiazole (MBS). TBBS not only provides greater scorch delay than CBS but also produces a vulcanisate of higher modulus, permitting greater economy of use at equal modulus [21].

The processing safety afforded by the commonly used sulphenamides increases in the order MBS, CBS, TBBS, whilst rate of vulcanisation decreases in the same order. Typical cure characteristics of these sulphenamides are shown in Figure 6.5.

Sulphenamides are the preferred accelerators for steelcord skim stocks where long scorch times are required to ensure adequate build up of the interfacial copper sulphide layer on the surface of the brass coated steelcord prior to the onset of vulcanisation. In this way, the



Compound recipe	phr
NR	100.0
Zinc oxide	5.0
Stearic acid	2.0
Sulphenamide	0.6
Sulphur	2.5

Figure 6.5 Cure characteristics at 150 °C

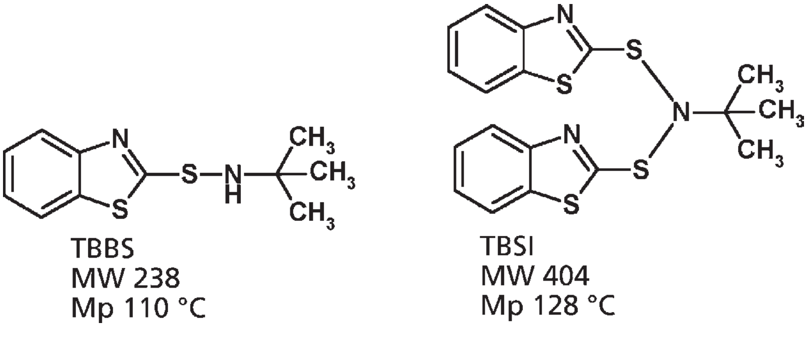


Figure 6.6 Structures of TBBS and TBSI

adhesion between compound and steelcord is achieved. Relatively low cure rates are also preferred in this application, thus TBBS is often the choice rather than CBS. Whilst MBS exhibits the slowest cure rate and the longest scorch time, this accelerator is now out of favour in the tyre industry due to toxicological concerns related to nitrosamine formation.

TBBS has been modified, by addition of a second benzothiazole group, to produce the corresponding sulphenimide (TBSI). Their chemical structures are shown in Figure 6.6. TBSI exhibits long scorch delay in addition to a slow cure rate and as such is used increasingly in steelcord skim stocks. An additional benefit is its increased resistance to hydrolysis compared to the sulphenamides, a noteworthy consideration when used in high temperature, high humidity conditions.

Sulphenamides can be activated by the addition of a secondary accelerator, for example diphenyl guanidine (DPG) or TMTD. This results in an increase in crosslinking efficiency of the cure system, but also a decrease in processing safety (see Table 6.2).

Although as yet unavailable commercially, excellent processing safety combined with a high cure rate and high crosslinking efficiency can be achieved by the use of a bis(sulphenamide) and pyrimidine sulphenamide [22] (Figure 6.7).

Table 6.2 Effect of secondary accelerators on the vulcanisation characteristics of CBS

Ingredients	Formulation		
	1	2	3
CBS Sulphur DPG TMTD	0.6 2.3 0 0	0.6 2.3 0.2 0	0.6 2.3 0 0.2
Mooney scorch, t5, min @ 121 °C	28	24	19
Rheometer at 150 °C			
Scorch time, ts2, min	3.9	3.0	2.7
Optimum cure time, t90, min	10.7	8.5	5.1
Cure 150 °C /t90			
M100, MPa	2.6	2.9	3.6
Tensile, MPa	24.9	23.6	25.1
Elongation, %	530	510	440

Formulation (in phr): NR, 80; BR, 20; N-375, 55; ZnO, 4; Stearic acid, 2; Aromatic oil, 8; N-(1,3-dimethylbutyl)-N´-phenyl-p-phenylenediamine (6PPD), 2
M100: Modulus at 100%

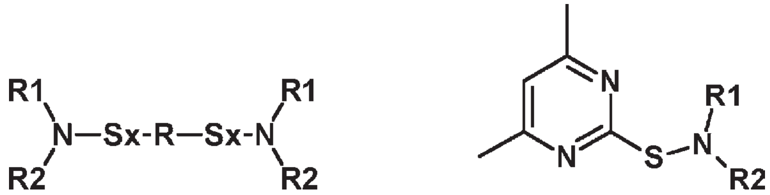


Figure 6.7 Structures of bis(sulphenamide) and pyrimidine sulphenamide

A thiocarbamyl sulphenamide, OTOS, derived from the hypothetical dialkyldithiocarbamic acid provides processing safety comparable to the typical sulphenamides. In addition it exhibits a high cure rate approaching that of an ultra accelerator [23]. The general structure of thiocarbamyl sulphenamide is shown in Figure 6.8.

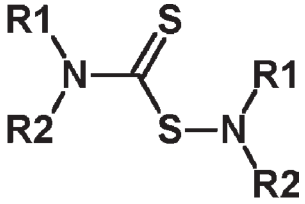
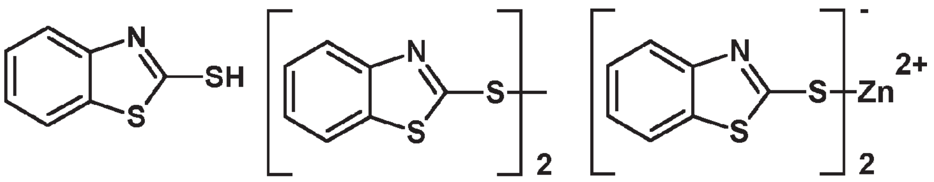


Figure 6.8 General structure of thiocarbamyl sulphenamide

6.2.2 Thiazoles

Thiazoles are by far the most commonly applied accelerators. The most important accelerator of the group, MBT, was introduced in 1930 and its subsequent impact on the rubber industry has been remarkable. Later came its disulphide, MBTS, and the zinc salt, zinc-2-mercaptobenzothiazole (ZMBT). The zinc salt is rarely used in dry compounding but is commonly used in the natural rubber latex industry, particularly in the manufacture of elastic thread. The chemical structures of MBT, MBTS and ZMBT are shown in Figure 6.9.



MBT
MW 167
Mp 121 °C

MBTS
MW 322
Mp 167 °C

ZMBT
MW 398
Mp > 200 °C

Figure 6.9 Chemical structures of MBT, MBTS and ZMBT

MBT provides a medium vulcanisation rate giving relatively low modulus vulcanisates, both in NR and synthetic elastomers. It has a tendency, mainly in NR, to scorch during the processing and storage of the green compound. Scorch safety can be increased by partial replacement of MBT with its disulphide, MBTS. In natural rubber, MBT acts as a peptising agent at elevated temperatures. It is common practice to use a secondary accelerator, a so-called booster or kicker, in combination with MBT. With DPG, for example, a rapid vulcanisation rate with considerable increase in modulus can be achieved. MBT can be boosted with thiuram disulphides or dithiocarbamates to provide shorter cure times, but at the expense of scorch safety.

MBTS gives vulcanisates of relatively low modulus as does MBT. It does, however, provide increased processing safety. It can be activated in a similar manner to MBT. ZMBT too gives vulcanisates of low modulus, but it is used mainly in latex applications. In terms of its activity and tendency to scorch it can be classified between MBT and MBTS.

6.2.3 Guanidines

The two main guanidine accelerators are DPG and di-*o*-tolyl guanidine (DOTG). Their chemical structures are shown in Figure 6.10.

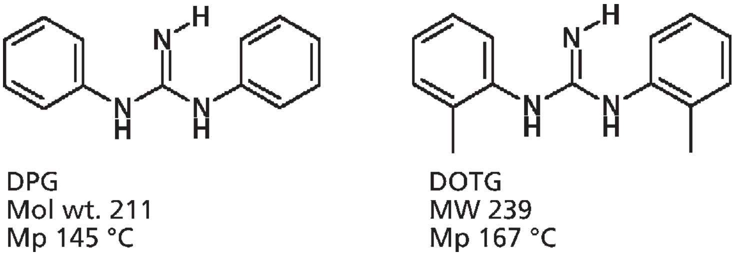


Figure 6.10 Chemical structures of DPG and DOTG

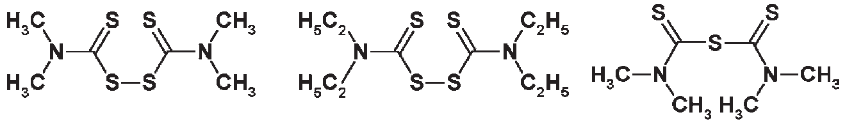
The guanidines are slow with regard to rate of vulcanisation but relatively safe accelerators in terms of processing. They are rarely used as primary accelerators due to their slow cure rates, although this can be put to good use in the cure of large sectioned articles. Their main use is as a secondary accelerator in thiazole or sulphenamide accelerated NR or SBR compounds.

DPG is also used in speciality rubbers such as CR and polysulphide rubber where it acts as a peptiser [24].

In silica containing compounds DPG is employed as a so-called cure activator. In reality its role is to adsorb preferentially onto the acidic silica surface thereby preventing the deactivation of the cure system. In addition, DPG facilitates the compatibilisation of the silica/elastomer mix thus improving dispersion and processability.

6.2.4 Thiurams

The major members of this class are tetramethyl thiuram disulphide (TMTD), tetraethyl thiuram disulphide (TETD) and tetramethyl thiuram monosulphide (TMTM), the former being the most widely used. Their chemical structures are shown in Figure 6.11.



TMTD
MW 240
Mp 140 °C

TETD
MW 297
Mp 65 °C

TMTM
MW 208
Mp 105 °C

Figure 6.11 Chemical structures of TMTD, TETD and TMTM

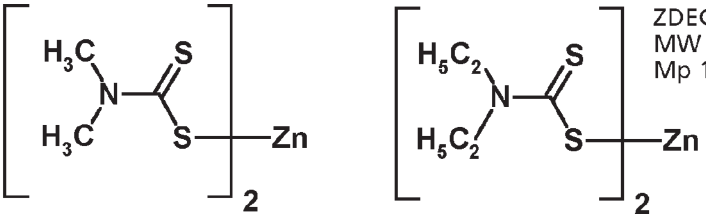
They give a rapid rate of vulcanisation but are seldom used as primary accelerators. The disulphides are able to function as sulphur donors, being used in curing systems containing low or no elemental sulphur. The monosulphide, however, cannot function in this role but does have the advantage of providing increased processing safety.

Thiuram accelerators have a broad range of applications from dipped latex goods, vulcanised at low temperatures, to articles produced by press or injection moulding with very short vulcanisation times. They are also applied in the manufacture of profiles by continuous vulcanisation and in the manufacture of butyl rubber-based tyre tubes.

6.2.5 Dithiocarbamates

The metal and amine salts of dithiocarbamic acids provide a class of accelerators often termed ultra accelerators due to the rapid cure rates that they impart. Popular members of this class are zinc dimethyl dithiocarbamate (ZDMC) and zinc diethyl dithiocarbamate (ZDEC), Figure 6.12. Salts of bismuth, cadmium, copper, lead, selenium and tellurium are also available.

ZDMC
MW 305
Mp 245 °C

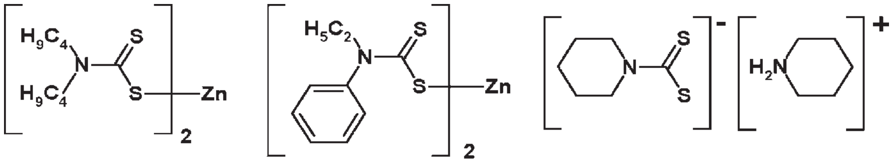


ZDEC
MW 362
Mp 175 °C

Figure 6.12 Chemical structures of ZDMC and ZDEC

Dithiocarbamates are considered as medium modulus accelerators but active at temperatures even as low as 100 °C. As a result, they are often employed in the manufacture of latex dipped goods. Another major application area is in the manufacture of EPDM based profiles often in conjunction with thiazoles or sulphenamides.

Other dithiocarbamates that are commercially available are zinc dibutyl dithiocarbamate (ZDBC), zinc ethyl phenyl dithiocarbamate (ZEPC) and piperidinium *N*-pentamethylene dithiocarbamate (PPDC). Their chemical structures are shown in Figure 6.13.



ZDBC
MW 474
Mp 104 °C

ZEPC
MW 410
Mp > 200 °C

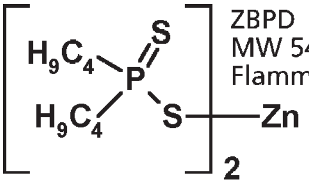
PPDC
MW 246
Mp > 165 °C

Figure 6.13 Chemical structures of ZDBC, ZEPC and PPDC

ZDBC, ZEPC and PPDC are mainly used for vulcanisation of lattices and as non-staining stabilisers of unvulcanised rubber solutions.

6.2.6 Dithiophosphates

Phosphorus-based compounds represent a second group of rapid curing accelerators, the dithiophosphates. Their structure resembles that of dithiocarbamates, the most widely used being zinc dibutyl dithiophosphate (ZBPD; Figure 6.14).



ZBPD
MW 547
Flammability point 195 °C

Figure 6.14 Chemical structure of ZBPD

They are used mainly as components of vulcanisation systems for EPDM. In combination with thiazoles, good processing safety and a relatively fast cure rate can be achieved.

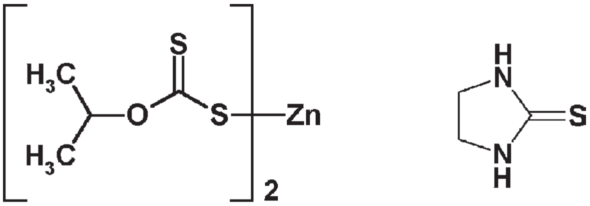
ZBPD can also be applied in the sulphur vulcanisation of diene elastomers. A partial replacement of elemental sulphur in conventional vulcanisation systems improves resistance to ageing and reversion whilst maintaining a good level of mechanical properties. Dithiophosphates are non-staining and can be used at relatively high levels, up to 2 phr, with no detrimental effects from blooming. They can be boosted with thiazoles, thiurams and dithiocarbamates.

6.2.7 Miscellaneous

In addition to the six classes described in Sections 6.2.1–6.2.6, there are further examples which are discussed here.

Accelerators based on xanthate and thiourea structures are commercially available. The former are mainly applied in latex applications to avoid copper staining whereas thioureas are used as boosters in combination with MBT.

The most widely used materials are zinc isopropyl xanthate (ZIX) and ethylene thiourea (ETU), Figure 6.15.



ZIX
MW 335
Mp > 160 °C

ETU
MW 102
Mp 195 °C

Figure 6.15 Chemical structures of ZIX and ETU

The use of thioureas is diminishing due to toxicological concerns.

6.2.8 N-Nitrosamines and accelerators

There is growing concern with regard to the presence of *N*-nitrosamines in rubber articles. One source stems from the decomposition products of certain accelerators. The concern centres on the suspected carcinogenic nature of these materials [25, 26].

Nitrosamines that are considered unsafe derive from accelerators containing secondary amines. Currently the most commonly used accelerators that fall into this category are listed in Figure 6.16.

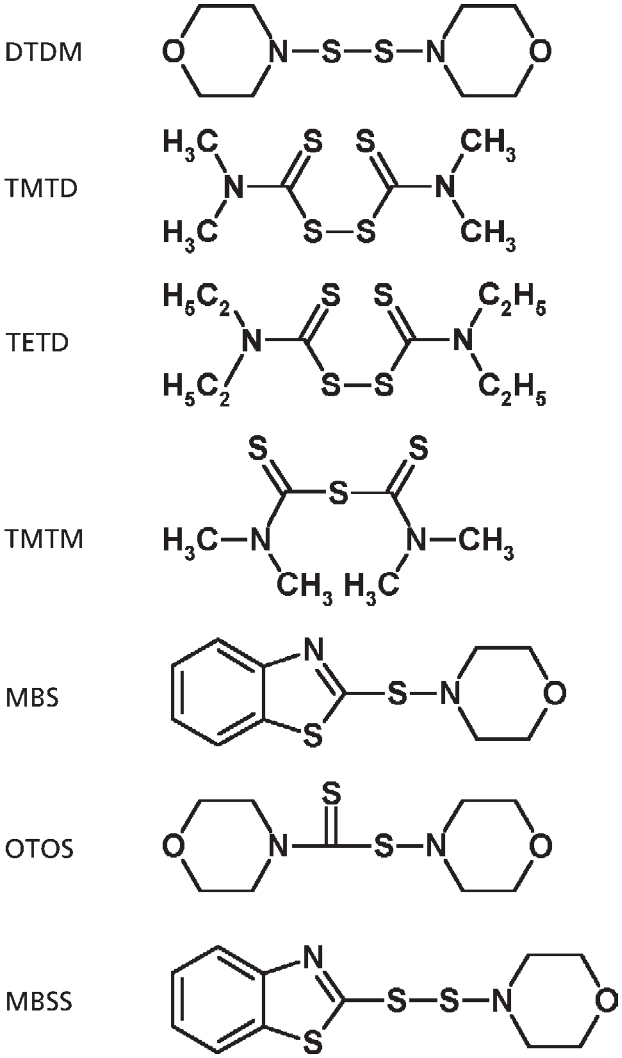


Figure 6.16 Accelerators that give rise to suspected unsafe nitrosamines

Due to the suspected carcinogenicity of some nitrosamines, rubber chemical manufacturers have been active in developing alternative accelerators that provide equivalent cure characteristics whilst safe with regard to nitrosamine formation. The alternatives that are gaining in commercial importance are TBSI, TBzTD and CLD.

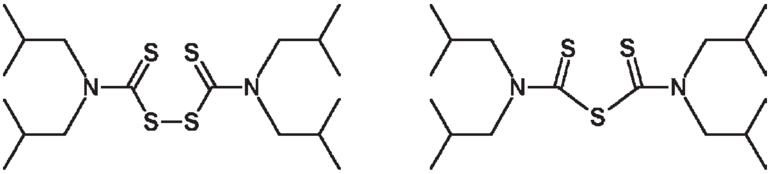
TBSI, see Figure 6.6, provides an improvement in reversion resistance compared to the corresponding sulphenamide and also possesses excellent storage stability; sulphenamides are susceptible to hydrolysis, a significant problem in high temperature, high humidity environments. TBSI is often employed as an alternative to MOR [27, 28], particularly in steelcord skim stocks.

TBzTD, see Figure 6.2, is capable of producing nitrosamines, but nitrosamines that are judged non-carcinogenic [29]. With minor compound changes it can replace TMTD.

TBzTD should be used at higher levels compared to TMTD to allow for its higher MW. In addition, an increase in sulphur level is recommended [30].

CLD (see Figure 6.1), has been introduced as a potential replacement for DTDM. This product does not generate nitrosamines.

Recently thiuram derivatives of diisobutyl amine, tetraisobutylthiuram disulphide (TiBTD) and tetraisobutylthiuram monosulphide (TiBTM), have been introduced [31] as potential substitutes for TMTD and TMTM, respectively, (see Figure 6.17). *N*-nitroso diisobutyl amine, although considered carcinogenic, is reported to be safer than the nitrosamines derived from TMTD and TMTM.



TiBTD
MW 408
Mp 71 °C

TiBTM
MW 376
Mp 62 °C

Figure 6.17 Chemical structures of TiBTD and TiBTM

6.3 Activators of vulcanisation

These are used both in sulphur as well as in peroxide vulcanisation. In the latter, they are more commonly referred to as co-agents. The effect of activators is to increase the crosslinking efficiency of the vulcanisation system.

Zinc oxide is the most commonly used activator in both sulphur and sulphur donor vulcanisation. In addition to zinc oxide, magnesium oxide is often employed in the vulcanisation of CR. Lead oxide is an effective activator for sulphur vulcanisation but it is expensive and toxic, therefore seldom used.

As an activator of vulcanisation, zinc oxide requires the presence of fatty acids, thereby converting the zinc into a rubber soluble form. Stearic acid is the most commonly used fatty acid but can be replaced by lauric acid. The latter, being more soluble in elastomers, provides more bloom resistance. Oleic acid is not recommended as it negatively affects the ageing properties of the vulcanisate. Fatty acids also provide enhanced compound processing characteristics together with improved dispersion of fillers and chemicals.

6.4 Retarders and inhibitors of vulcanisation

Vulcanisation retarders and inhibitors have been used in rubber compounds for many years as a means of increasing processing safety. A vulcanisation retarder increases scorch time, thereby improving processing safety, but also slows down the rate of vulcanisation. This reduced rate of vulcanisation, however, is often an undesirable effect. True vulcanisation inhibitors, on the other hand, increase scorch safety whilst having no adverse effect on the rate of vulcanisation.

Substances that fall into the first category are acidic in nature, for example benzoic acid, salicylic acid and phthalic anhydride. They prolong scorch time in thiazole accelerated compounds but their effect in sulphenamide accelerated stocks is poor [32]. *N*-chlorosuccinimide, nitroparaffins, sulphenic acid and sulphonic acid derivatives have been described as retarders [33] but appear to have little practical significance.

N-nitrosodiphenylamine (NDPA) has a positive effect on the processing safety of compounds accelerated with sulphenamides [34]. It prolongs the induction period with regard to the onset of cure but does not reduce the rate of vulcanisation. As such it can be classified as a vulcanisation inhibitor. However, it is no longer in use because of toxicological concerns.

The major and most effective representative of the class of vulcanisation inhibitors is *N*-(cyclohexylthio)phthalimide (CTP), (see Figure 6.18), often termed pre-vulcanisation inhibitor (PVI). It is effective with a wide range of polymers, accelerators and other compounding ingredients. It neither affects vulcanisate properties nor causes staining or porosity. Although most effective in sulphenamide accelerated stocks, it is also used with both MBT and MBTS. There is a linearity about its response that allows the dosage necessary to give a certain scorch resistance to be readily determined. In most applications 0.1–0.3 phr is used. The scorch resistance increases proportionally with the dosage and an addition of 0.1 phr causes a considerable improvement (see Table 6.3). Furthermore the addition of PVI permits processing at elevated temperatures, thereby increasing productivity.

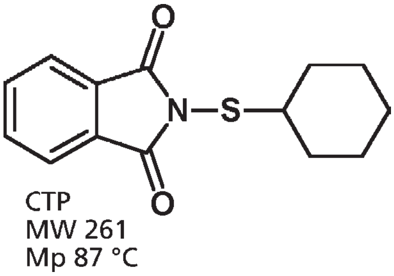


Figure 6.18 Chemical structure of CTP

Although normally added during the mixing stage, PVI can also be added to compounds during processing that are in danger of vulcanising prematurely. In doing so additional processing safety is introduced.

PVI is not effective in thiuram accelerated stocks or resin and metal oxide curing systems. In butyl-based compounds dosages should be adjusted upward from the range given, perhaps up to 1 phr.

Additional products are commercially available but not as effective in terms of providing scorch resistance. Examples are *N*-isopropylthio-*N*-cyclohexyl-2-benzothiazolyl sulphonamide and *N*,*N´*,*N´´*–tri(thioizopropyl)-*N*,*N´*,*N´´*–triphenyl phosphorotriamide.

6.5 Antidegradants

Elastomer-based products suffer irreversible changes to their required design properties during service. These changes, brought about by a number of agents such as oxygen,

Table 6.3 Effect of CTP on Mooney scorch time

	Formulation			
Ingredients	**1**	**2**	**3**	**4**
MBS	0.65			
Sulphur	1.75			
PVI CTP	-	0.1	0.2	0.4
Mooney scorch, t5, min @ 121 °C	42	60	74	99
Formulation (in phr): NR, 75; BR, 25; N-220, 45; ZnO, 3; Stearic acid, 2				

ozone, heat, light and mechanical deformation, are collectively referred to as ageing. In addition to a loss in mechanical properties, changes in surface aspect can occur that, whilst perhaps not damaging with regard to performance, impair appearance. In order to combat these detrimental changes additives, often collectively referred to as antidegradants, are employed. Typical loading levels are of the order of 1–4 phr.

Antidegradants can be conveniently categorised into antioxidants and antiozonants. However, this is not an unambiguous division since these materials often impart additional benefits in addition to their primary function. A multitude of antidegradants are commercially available and no attempt will be made here to describe the entire range but only those of major importance. An abundance of literature exists to which the reader can refer [35-41].

6.5.1 Antioxidants

Antioxidants are often further referred to as 'staining' and 'non-staining', designations associated with the effect of these materials on the staining characteristics of the compound to which they are added.

6.5.1.1 Phenolics

The most important group of non-staining antioxidants is based on phenol. Whilst not as powerful as some staining antioxidants, phenolics are nevertheless an important class of antidegradants due indeed to their non-staining and non-discolouring nature. Appropriately they are applied in white and coloured vulcanisates. This group includes monophenols, bisphenols, thiobisphenols, polyphenols and hydroquinone derivatives. 2,6-di-*t*-butyl-*p*-cresol, frequently referred to as BHT (see Figure 6.19), is the most widely used phenolic antioxidant. It is also representative of the basic, generic building block of all phenolic antioxidants.

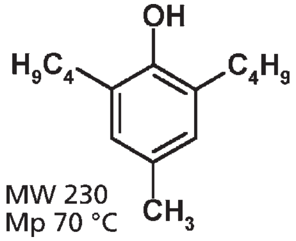
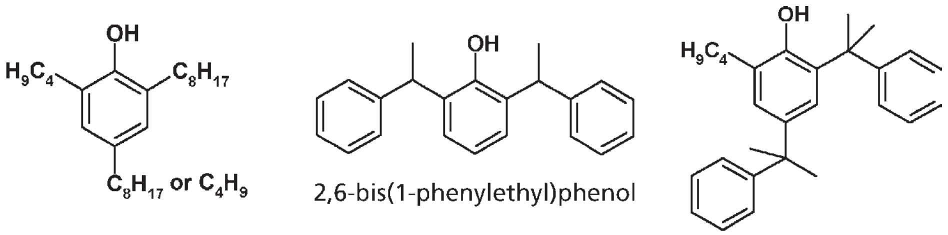


Figure 6.19 Structure of BHT

In Figure 6.20, additional examples based on the monophenolic BHT structure are shown.

The higher MW bisphenolic antioxidants, see Figure 6.21, offer reduced volatility and increased activity but at a price premium compared to the monophenolics.

Polyphenolic antioxidants offer still further resistance to volatility during processing and service; an example is shown in Figure 6.22.



2,6-bis(1-phenylethyl)phenol

mixture
2-t-butyl-4,6-dioctyl phenol
2,4-di-t-butyl-6-octyl phenol

2-t-butyl-4,6-bis(1-methyl-1-phenylethyl)phenol

Figure 6.20 Some examples of monophenolic antioxidants

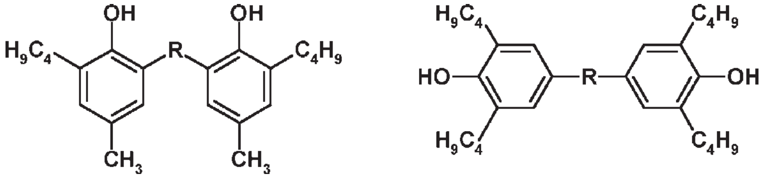


Figure 6.21 Examples of bisphenolic antioxidants

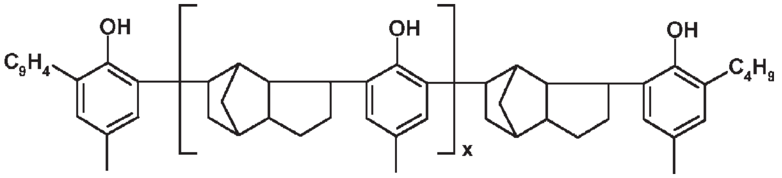


Figure 6.22 A polyphenolic antioxidant

Hydroquinone derivatives based on the structure shown in Figure 6.23 also offer non-staining performance. An additional major use is in the polymer manufacturing industry as a MW modifier [42].

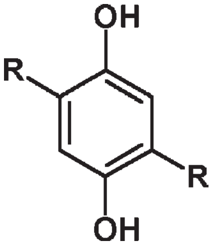


Figure 6.23 Hydroquinone derivatives

6.5.1.2 Phosphites

Phosphites are the second major class of non-staining antioxidants. The most commonly used material of this class is tris(nonylphenyl)phosphite, (TNP; see Figure 6.24). However, it suffers from a tendency to hydrolyse during prolonged contact with moisture and it is destroyed during vulcanisation. Nevertheless, its exceptional non-tinting property has made it the industry's standard non-staining SBR stabiliser. TNP is ideally suited to the emulsion polymerisation process because of its liquid physical form.

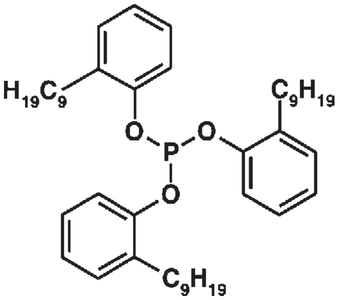


Figure 6.24 Tris(nonylphenyl)phosphite

6.5.1.3 Thioesters

A third category of antioxidants comprises thioesters with essentially two classes of materials: the bis-(alkylthiopropionate)diesters (BTPDE) and the alkylthiodipropionate esters (TDPE). Typical structures are shown in Figure 6.25.

As for phosphite-based antioxidants, they are destroyed during vulcanisation and thus find little use in the rubber industry. They are used primarily for the stabilisation of polyolefins.

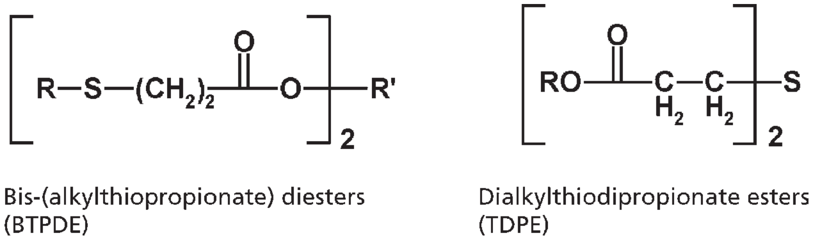


Figure 6.25 Chemical structures of BTPDE and TDPE

6.5.1.4 Amines

Historically, amine-based antioxidants were the first really effective rubber antioxidants. The materials can be categorised as: naphthylamines, diphenyl amine derivatives, dihydroquinolines and paraphenylenediamines (see also Section 6.5.2).

The naphthylamines, phenyl-β-naphthylamine (PBNA) and its companion phenyl-$\propto$-naphthylamine (PANA), whilst extremely effective antioxidants have now almost disappeared due to toxicological concerns [43].

Structures of the four types are shown in Figure 6.26.

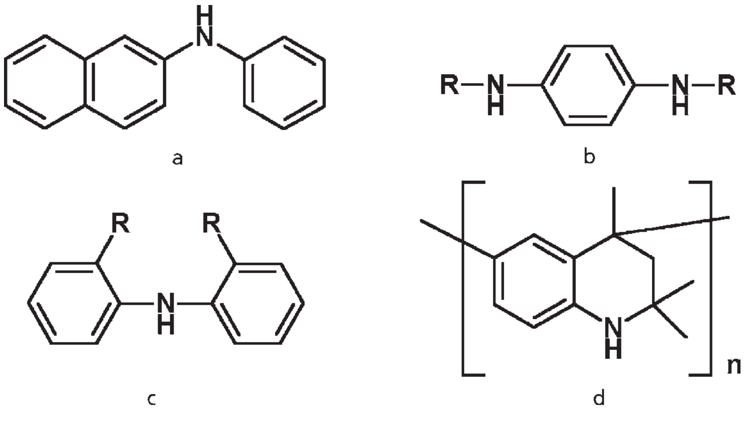


Figure 6.26 Amine-based antioxidants: a) Phenyl-$\propto$-naphthylamine b) diphenyl amine c) *p*-phenylenediamine and d) dihydroquinoline

6.5.1.5 Bound antioxidants

In 1972, The Malaysian Rubber Producers Research Association reported that quinonediimines could provide bound antioxidant activity [44], the antioxidant becoming attached to the elastomer during vulcanisation. This prevents the antidegradant from being extracted during service of the rubber article thereby providing long term protection. At the time the materials were not commercialised but recently one such product has been introduced, *N*-1,3-dimethyl butyl-*N′*-phenyl-*p*-quinone diimine (QDI), Figure 6.27. In addition to providing long term antioxidant protection it can also serve as a peptiser, a vulcanisation retarder and can enhance polymer-filler interaction [45].

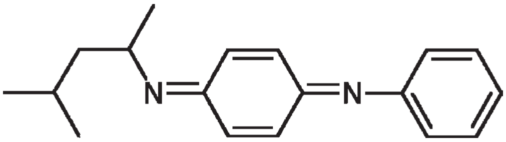
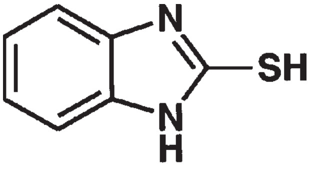


Figure 6.27 Structure of *N*-1,3-dimethyl butyl-*N′*-phenyl-*p*-quinone diimine (QDI)

6.5.1.6 Miscellaneous

In addition to the several classes described above there are other materials that can act as antioxidants. The zinc and nickel salts of the dithiocarbamates are two such materials. They are sometimes applied [46] in CR, chlorosulphonated-polyethylene (CSM), polyepichlorohydrin (CO), the copolymer of epichlorohydrin and ethylene oxide (ECO) and EPDM based compounds. The zinc salt of MBT is also reported to act as an antioxidant in latex applications.

2-Mercaptobenzimidazole (MBI) and its zinc salt are efficient antioxidants for both natural and synthetic rubbers, providing protection against oxidation, high temperatures and surface crazing. It does not protect against fatigue and ozone. The structure of MBI is shown in Figure 6.28.



MW 150
Mp 290 °C

Figure 6.28 Structure of MBI

6.5.2 Antiozonants

Under deformation vulcanisates that are susceptible to ozone attack have a critical elongation below which cracks will not form. This varies with the type of rubber and compounding ingredients, but it is usually in the range of 5–10% for diene rubbers. Above this critical elongation cracks do appear, becoming progressively more numerous as a function of time. The incorporation of antiozonants in the compound, however, provides a marked improvement in the resistance to ozone attack. They function by migrating from the bulk of the vulcanisate to the surface where they react preferentially with the ozone thereby safeguarding the integrity of the component.

The most widely used antiozonants are the substituted *para*-phenylenediamines. They not only offer protection against ozone but also function as antioxidants and as outstanding antiflex agents. Nickel dithiocarbamates are also active as antiozonants but they are of minor importance in terms of usage [47].

6.5.2.1 Para-phenylenediamines

Para-phenylenediamines, the most widely used class of antidegradant, provide protection against oxygen, ozone, metal ions and flex fatigue. One major drawback, however, is that they are discolouring and staining. They can be conveniently grouped into three categories based on the chemical nature of substituents (see Figure 6.29): diaryl-*p*-phenylenediamines, dialkyl-*p*-pheylenediamines and alkyl-aryl-*p*-phenylenediamines.

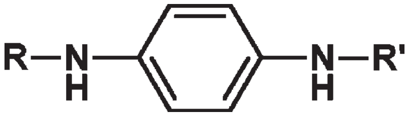


Figure 6.29 General structure of *para*-phenylenediamines

a) Diaryl-p-phenylenediamines

The diaryl-*p*-phenylenediamines are the least reactive of the *p*-phenylene diamines towards ozone but they possess relatively low volatility and provide long protection. Due to their basicity they have an activating effect on sulphur cure systems. The most widely used diaryl derivative is the diphenyl, Figure 6.30.

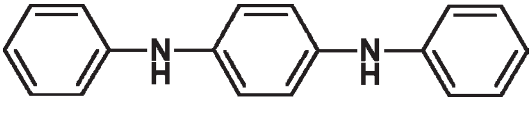


Figure 6.30 *N*, *N*´-diphenyl-*p*-phenylenediamine

b) Dialkyl-p-phenylenediamines

The most common member of this group incorporates branched C_7 substituents (see Figure 6.31). The dialkyls provide superior ozone resistance but do not offer the same degree of protection against oxygen as other *p*-phenylenediamines. They are more volatile than the diaryls and hence do not provide such long-term protection. As for other *p*-phenylenediamines they also provide flex crack resistance and protect against metal ion catalysed degradation.

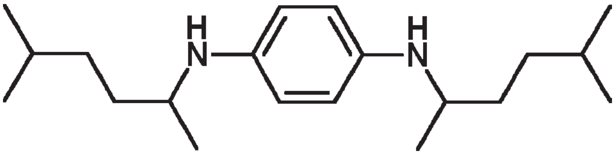


Figure 6.31 *N*,*N*´–bis-1,4-dimethyl pentyl-*p*-phenylene diamine (77PD)

c) Alkyl-Aryl-p-phenylenediamines

The alkyl-aryl-*p*-phenylenediamines offer the best all round antidegradant protection. They are not as reactive as the dialkyls but are not as volatile, thus provide longer protection. The most widely used antiozanant in this group is the product bearing a phenyl and a branched C_6 alkyl group, 6PPD, Figure 6.32. The isopropyl analogue, IPPD, is also commonly used but is gradually being replaced by 6PPD; IPPD is more readily leached from vulcanisates during service.

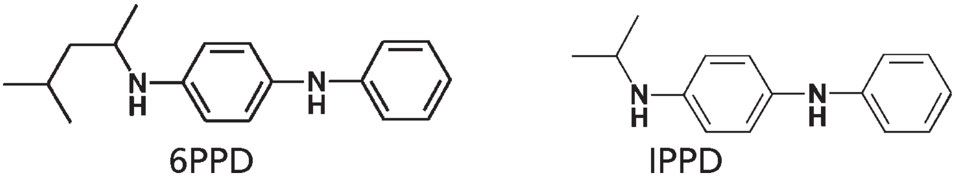


Figure 6.32 Chemical structures of 6PPD and IPPD

6.5.2.2 Triazine derivative

(*N*-1,4-dimethylpentyl-*p*-phenylenediamino)-1,3,5-triazine, although an active antiozonant is not used extensively in the rubber industry due to its limited solubility in synthetic rubbers and its high cost. It functions also as an antioxidant and is non-staining. The structure is shown in Figure 6.33.

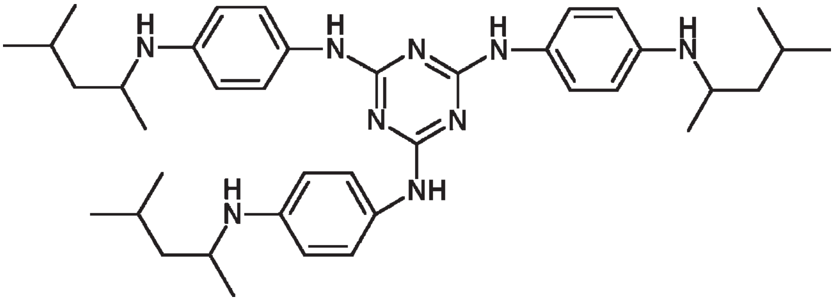


Figure 6.33 Chemical structure of (*N*-1,4-dimethylpentyl-*p*-phenylenediamino)-1,3,5-triazine

6.5.2.3 Waxes

Waxes provide protection from ozone by blooming to the surface of the rubber component. However, unlike the *p*-phenylenediamines they offer only physical protection. This is a result of the formation of a thin film of wax at the surface acting as a barrier toward ozone attack of the elastomer. If, however, the film is ruptured, for example on flexing of the component, the ozone resistance is lost. Waxes therefore are effective with regard to static ozone protection only and do not provide protection under dynamic conditions.

The migration rate of the wax is important in providing optimum static ozone protection. Often a blend of paraffin and microcrystalline waxes are used in order to provide protection over a wide range of temperature.

6.6 Antireversion agents

Reversion of sulphur-based crosslinks and the consequent loss in vulcanisate properties presents a major challenge to the rubber compounder. A number of additives are available that, in one way or another, provide some protection against reversion.

6.6.1 Zinc carboxylates

A blend of aliphatic and aromatic zinc carboxylic acid salts is commercially available that provides reversion resistance by promoting the formation of sulphidic crosslinks of lower sulphur rank. The general structure of the material is shown in Figure 6.34. Its mechanism of action is due to increased solubility in the rubber matrix compared to the zinc salt of stearic acid [48]. The latter is normally generated *in situ* as a result of the reaction between zinc oxide and stearic acid.

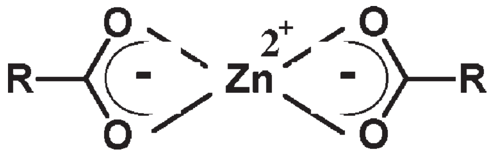


Figure 6.34 Zinc carboxylate

The data shown in Table 6.4 clearly demonstrate the effect of the material on crosslink network structure [49].

6.6.2 Thiophosphoryl derivatives

Thiophosphoryl derivatives such as ZBPD (see Figure 6.35) provide improvement in reversion resistance when added to a sulphenamide cure system [50]. Again, reversion resistance is a result of the formation of a crosslink network containing a higher proportion of monosulphidic crosslinks. Data listed in Table 6.5 demonstrate the effect for a ZBPD based compound [49].

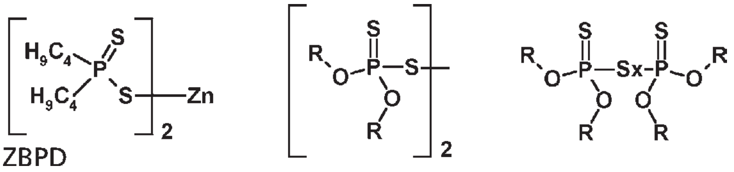


Figure 6.35 Chemical structures of thiophosphoryl derivatives

Table 6.4 Effect of zinc carboxylate on network structure

Compounds	A	B
Stearic acid, phr Zinc soap, phr	2 0	0 2
Cure temperature, °C Cure time, min	150 13	150 13
Crosslink density % Polysulphide % Disulphide % Monosulphide	5.10 50 15 35	5.24 40 12 48

Crosslink density expressed in g mol/g rubber hydrocarbon x 10^5
Formulation (in phr): NR, 100; N-375, 45; Zinc oxide, 5; Peptiser, 0.3; Microcrystalline wax, 1.4; CTP, 0.5; 2,2,4-trimethyl-1,2-dihydroquinoline, polymerised (TMQ), 1.5; 6PPD, 1.2, TBBS, 1.4 and Sulphur,1.4

Table 6.5 Effect of ZBPD on network structure

Compounds	C	D
TBBS, phr	0.6	0.2
Sulphur, phr	2.5	2.5
ZBPD, phr	-	0.75
Cure temperature, °C	144	144
Cure time, min	23	13
Crosslink density	4.80	4.70
% Polysulphide	72	39
% Disulphide	10	17
% Monosulphide	18	44

Crosslink density expressed in gmole/g rubber hydrocarbon x 10^5
Formulation (in phr): NR, 100; N-330, 50; Naphthenic oil, 5; Zinc oxide, 5; Stearic acid, 2; 6PPD, 2.0

6.6.3 Silane coupling agents

Silane coupling agents possess multifunctional activity. Their major role is, as the name implies, as a coupling agent between silica filler and elastomer. This action provides significant improvements in the physical properties of vulcanisates [51]. The most widely used material, bis-(3-triethoxysilylpropyl)-tetrasulphide TESPT is shown in Figure 6.36. It also functions, however, as a sulphur donor, providing an ‘equilibrium cure system’ [52]. Its mechanism of action is associated also with the formation of crosslinks of lower sulphur rank.

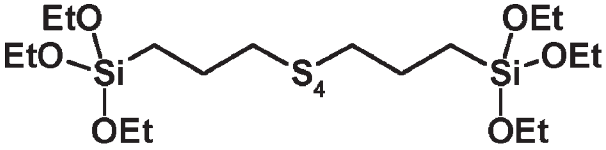


Figure 6.36 Chemical structure of TESPT

The effect of TESPT on the network structure of a NR based compound is shown in Table 6.6 [49].

6.6.4 Sulphenimide accelerator

A commercially available sulphenimide accelerator, TBSI (see Figure 6.6), provides a long scorch delay together with a slow cure rate [53]. Its effect on network structure is

Table 6.6 Effect of TESPT on network structure

Stocks	E	F
TESPT, phr	0	3
Cure temperature, °C	150	150
Cure time, min	6	11
Crosslink density	4.90	5.34
% Polysulphide	50	44
% Disulphide	15	12
% Monosulphide	35	44

Crosslink density expressed in g mole/g rubber hydrocarbon x 10^5
Formulation (in phr): NR, 100; N-220, 40; Silica, 20; Zinc oxide, 5; Stearic acid, 2; aromatic oil, 3; Resin Coumaron, 3; MC wax, 1.0; TMQ, 1.5; 6PPD, 2.5; CBS, 1.4; DPG, 2; Sulphur, 1.4

once again to shift the distribution of crosslink type towards lower sulphur rank thus enhancing reversion resistance.

Its effect on network structure of a NR based compound is shown in Table 6.7 [49].

6.6.5 Hexamethylene-1,6-bis thiosulphate disodium dihydrate (Duralink HTS)

Duralink HTS (see Figure 6.37), is a material that functions during vulcanisation by forming hybrid crosslinks composed of hexamethylene and sulphidic moieties [54, 55].

Table 6.7 Effect of TBSI on network structure

Compounds	G	H
TBBS, phr	0.6	0
TBSI, phr	0	0.6
Sulphur, phr	2.5	2.5
Cure temperature °C	150	150
Cure time, min	16	19
Crosslink density	4.90	4.85
% Polysulphide	70	57
% Disulphide	16	12
% Monosulphide	14	30

Crosslink density expressed in g mole/g rubber hydrocarbon x 10^5
Formulation (in phr): NR, 100; N-339, 55; Zinc oxide, 5; Stearic acid, 2; Aromatic oil, 3; MC Wax, 1; 6PPD, 2; TMQ, 1.0

Figure 6.37 Structure of hexamethylene-1,6-bis thiosulphate disodium dihydrate

The presence of these hybrid crosslinks increases the reversion resistance of the network and is particularly beneficial in maintaining flex/fatigue resistance.

6.6.6 1,3-Bis(citraconimidomethyl)benzene (BCI-MX; Perkalink 900)

The most recently introduced antirevesion agent, 1,3-bis(citraconimidomethyl)benzene (Perkalink 900; Figure 6.38), functions by a crosslink compensation mechanism [56-62]. It compensates for the loss of polysulphidic crosslinks during the process of reversion with crosslinks based essentially on a carbon-carbon structure. The material reacts at the onset of reversion and can be added to existing compounds with no further change in formulation. Its effect on the network structure of a NR based compound is shown in Table 6.8.

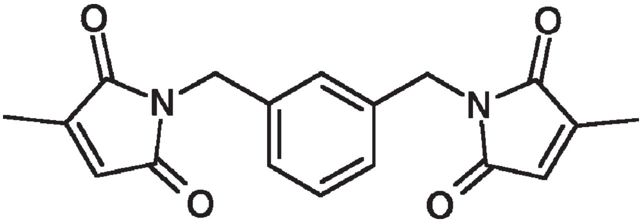


Figure 6.38 Structure of BCI-MX

Table 6.8 Effect of 1,3-*bis*(citraconimidomethyl)benzene on network structure

Compounds	I		J	
BCI-MX, phr	0		1	
Cure time, min, at 150 °C	t90	60	t90	60
Crosslink density	4.95	3.56	5.11	4.99
Polysulphide	3.96	2.16	4.04	2.29
Disulphide	0.84	0.36	0.90	0.42
Monosulphide	0.15	1.06	0.17	1.06
Carbon-Carbon	0.00	0.00	0.00	1.22

Crosslink density expressed in g mole/g rubber hydrocarbon x 10^5
Formulation (in phr): NR, 100; N-330, 50; Zinc oxide, 5; Stearic acid, 2.0; Aromatic oil, 3; CBS, 0.6; Sulphur, 2.3

6.7 Plasticisers and softeners

Plasticisers and softeners are relatively non-volatile organic materials that when added to compounds will improve their workability during processing, modify green and cured compound properties and reduce cost. They are materials coming from a number of sources and may be conveniently classified according to their origin. The main groups discussed in Section 6.7.1 are petroleum products, coal tar products, pine products, synthetic softeners, and other products.

6.7.1 Petroleum products

6.7.1.1 Petroleum waxes

About 90% of all waxes used for commercial purposes are recovered from petroleum. Petroleum waxes are generally classified into three principle types: paraffinic, microcrystalline and petrolatum. Paraffin wax is a solid, colourless substance composed of alkanes up to 30 carbon atoms in length with a low level of branching. As a consequence of the regular structure, paraffin wax crystallises relatively easily into large plates or needles.

Microcrystalline paraffin wax differs from paraffin wax in having a higher MW and, therefore, a higher softening temperature. The molecular structure is more branched resulting in a microcrystalline material.

Petrolactum is a semi-solid substance, substantially a mixture of a high MW hydrocarbon, ceresine and oils.

6.7.1.2 Mineral oils

Mineral oils are the most frequently used plasticisers for both natural and synthetic rubbers. They are high boiling fractions obtained in refining crude oil.

The oils are comprised mainly of ring structures: unsaturated (aromatics), saturated (naphthenes) and ring structures possessing saturated side chains (paraffins). They are classified accordingly as aromatic, naphthenic and paraffinic depending on the predominant structure of the oil.

The choice of oil depends largely on the compatibility with the elastomer. As a general rule paraffinic oils are best used with low polarity polymers whilst aromatics are more suited to the more polar polymers. Table 6.9 lists oil suitability with the more common elastomers [63].

Table 6.9 Oil suitability

Polymer	Paraffinic	Naphthenic	Aromatic
Natural rubber	Excellent	Fair	Fair
SBR	Fair	Good	Excellent
Butyl	Excellent	Good	Poor
Polybutadiene	Fair	Good	Excellent
Neoprene	Poor	Good	Excellent
Nitrile	Poor	Fair	Excellent
EPDM	Excellent	Good	Good

6.7.2 Coal tar products

Softeners belonging to this group are products of various consistency: oils, soft and hard resins and pitches. From the chemical point of view they comprise a rich mixture of components: non-aromatic, aromatic and polar hydrocarbons including sulphur, nitrogen and oxygen containing compounds.

6.7.2.1 Coumarone resin

The fraction of coal tar distilling in the 160–200 °C range contains, after elimination of phenol, cresol and pyridine, mainly coumarone and indene. Under the effect of 2–5% sulphuric acid, polymerisation takes place producing a copolymer referred to as coumarone resin. According to the degree of polymerisation a variety of products can be obtained, from viscous liquids to hard brittle resins with softening point of 100 °C and higher. Their colour depends on the degree of preliminary refinement of the coumarone-indene fraction, varying from colourless to dark brown. Both solid and liquid resins are used in the rubber industry.

6.7.3 Pine products

Colophony (rosin) is present in the resin flowing from cut pine trees (primarily *Pinus palustris*). It is added to rubber compounds to impart tack, soften the compound and to improve flow. Pine rosin is a solid, yellow-dark brown resin with softening point around 70 °C. It is acidic in nature due to its main component, abietic acid, and its isomer, pimaric acid. As a result of its acidic character it retards vulcanisation. In addition to its softening action it aids in the dispersion of carbon black and provides some age resistance to compounds.

6.7.4 Synthetic softeners

There is a broad variety of ester plasticisers possessing widely different properties. The group comprises esters of polycarboxylic acids such as adipic, phosphoric, phthalic, sebacic and higher aliphatic alcohols or phenols such as butanol, cresols, cyclohexanol and octanol. Dibutyl phthalate, di-2-ethylhexyl phthalate, di-2-ethylhexyl sebacate and tricresyl phosphate are commonly used. Esters are relatively high priced and are used to provide low temperature flexibility to the more polar rubbers such as chloroprene, nitrile and acrylate elastomers.

Ether type plasticisers include dibenzyl ether, polyethers and polyether-thioethers.

6.7.5 Other products

Vegetable oils and fats are occasionally used in rubber compounding. These include unsaturated oils such as linseed, rapeseed and sunflower oils. They are mostly used in chloroprene to obtain low temperature flexibility, tear resistance and antiozonant protection. The use of these plasticisers, however, should be avoided in hot and humid areas of the world due to their tendency to promote fungal growth. Allied to the vegetable oils are the vulcanised vegetable oils such as factice. If the oil is vulcanised with sulphur, the product is dark and is termed 'brown factice'. If sulphur monochloride is used as the vulcanisation agent the product is light coloured and is referred to as 'white factice'. The addition of 5 to 20 phr of factice to a compound improves processibility.

Fatty acid derivatives such as stearic, palmitic, oleic or linoleic acid act as effective processing agents. In this respect the most commonly used processing additive is stearic acid, used primarily however for cure activation. Technical grade stearic acid is a mixture of approximately equal amounts of stearic acid (C_{18}) and palmitic acid (C_{16}) together with a small amount of oleic acid (unsaturated C_{18}).

Zinc salts of unsaturated fatty acids are also available and are commonly used to improve compound processability and as compatibilising agents for compounds based on polymer blends.

6.8 Miscellaneous ingredients

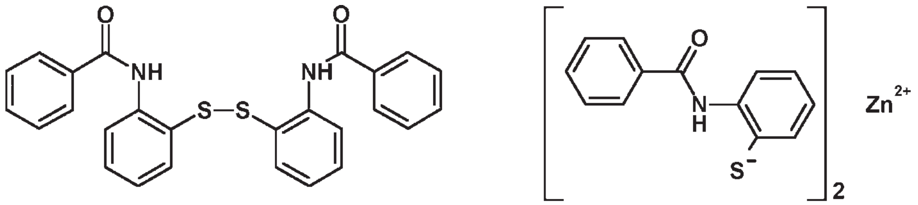
A number of additional compounding materials, although not as widely used as those mentioned previously, warrant a brief review. These include: peptising agents, blowing agents, bonding agents and pigments.

6.8.1 Peptising agents

Peptising agents are substances that act as chain terminating agents during the mastication of rubber. They may also act as pro-oxidants during the mastication process. This significantly reduces the time necessary to lower the viscosity of the rubber to a workable level, which in turn brings savings in mixing time and energy.

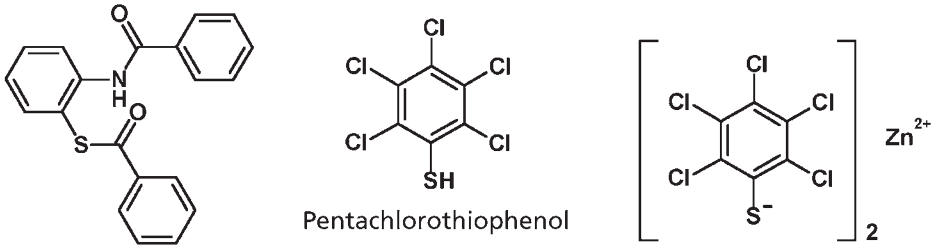
Although numerous materials are known to possess chemical peptising activity, in practice the choice is limited due to additional considerations such as health and safety, effect on vulcanisation characteristics and price. Consequently only a limited number of substances are commercially available. These are indicated in Figure 6.39.

Recently a multifunctional additive has been introduced which possesses chemical peptising activity in NR-based compounds. In addition it acts both as an antiozanant and a bound antidegradant following reaction during mixing and vulcanisation [64]. The material is a quinonediimine, *N*-1,3-dimethyl butyl-*N*′-phenyl-*p*-quinonediimine, and is described in Section 6.5.1.5.



Bis(2-benzamidophenyl) disulphide

Zinc-2-benzamidothiophenolate



Pentachlorothiophenol

N-S-Dibenzoyl-2-aminothiophenol

Zinc pentachlorothiophenolate

Figure 6.39 Commercially available peptising agents

6.8.2 Blowing agents

Blowing agents are used in the manufacture of sponge rubber. Sodium bicarbonate, the first commercially used blowing agent, reacts with stearic acid to produce carbon dioxide at vulcanisation temperatures. A disadvantage of using sodium bicarbonate is that residual soap is left in the final product.

The commonly used blowing agents now rely on the formation of nitrogen as the effective expansion agent resulting from thermal decomposition at vulcanising temperatures. Blowing agents of this class are: *p*-toluenesulphonylsemicarbizide, azodicarbonamide, diazoaminobenzene, *N*,*N*´-dinitrosopentamethylenetetramine and *p*-*p*´-oxy bis(benzenesulphonylhydrazide).

Although the latter has been marketed widely, it has the disadvantage of having low decomposition temperatures and an unpleasant fish odour.

6.8.3 Bonding agents

Most large volume rubber products are bonded composites: tyres, hoses and belts, for example. During their manufacture bonding agents added to the compound may be required in order to increase the bond strength between the different components. A complicating feature of composite bonding is the variety of metals and fabrics to which the rubber compound must be bonded. The metals, usually plated with zinc, brass or aluminium, are used in the form of metal plate or wire. Textiles used in the manufacture of composites include cotton, nylon, polyester, rayon, aramid and glass.

The integrity of steelcord rubber composites is of great concern in the radial tyre manufacturing industry. Often, in order to ensure increased adhesion retention, bonding agents are employed as adjuncts to the compound formulation. Bonding agents commonly employed are cobalt-based salts such as naphthenate or stearate. Proprietary materials are also available based on cobalt and boron complexes.

For adhesion of rubber compounds to synthetic fibres such as polyester or nylon it is common practice not only to treat the surface of the fibre with a two component resin system, such as resorcinol together with a methylene donor, but also to include such a system in the compound itself. Resorcinol together with hexamethylenetetramine or hexamethoxymethylmelamine is commonly employed.

6.8.4 Pigments

Although most rubber compounds are black, coloured rubber compounds are frequently required to add appeal to consumer items such as sports shoes, household gloves, rubber toys, bathing caps, etc., (see also Chapter 13). In addition colour coding is often a necessity in products such as hoses and cables. Clearly pigments are required to impart the desired colour.

Pigments can be classified as inorganic or organic. Comparing the two, inorganic pigments are often dull and in some cases too opaque to impart the desired richness of shade. They are insoluble and thus cannot bloom. Organic pigments generally give brighter shades but are more sensitive to heat and other chemicals. On long-term exposure to sunlight they can fade badly. Above all they are relatively expensive.

Some commonly used inorganic and organic pigments are shown in Table 6.10.

Table 6.10 Commonly used pigments

Colour	Organic/Inorganic	Pigment
Green	Inorganic	Chromium oxide
Blue	Inorganic	Cobalt blue, ultramarine (iron blue)
Brown	Inorganic	Iron oxides
Yellow	Inorganic	Cadmium sulphide, lead chromate, iron oxide
Red	Inorganic	Iron oxide, cadmium sulphide selenide
Red	Organic	Red pyrazoline
Yellow	Organic	Diarylide
Orange	Organic	Diasnisidine
Blue/Green	Organic	Phthalocyanine

6.9 Concluding remarks

Rubber additives play an important role in achieving the performance requirements of rubber articles. Furthermore, these performance requirements are becoming more and more demanding due to the ever-increasing severity of service conditions, health and safety concerns and quality expectations.

Today, more and more additives are available to the rubber compounder allowing him to meet these requirements. Whilst many of these rubber additives have been commercially available for years, others have become available relatively recently. Antireversion agents constitute a class of such materials, once again emphasizing the need to meet more demanding service conditions. Health and safety issues, as for example that concerning the generation of *N*-nitrosamines, have also lead to the introduction of new rubber additives.

Rubber additives, however, paint only part of the picture with regard to the manufacture of rubber articles; polymers and fillers are equally important in meeting performance requirements. In addition, compound mixing and processing play a vital role in achieving final vulcanisate properties. These are the subject of other chapters in this publication.

Acknowledgements

The authors wish to thank the many contributors of the information contained within this chapter. Special thanks are due to Dr. A. G. Talma and Dr. J. P. Baaij for their assistance and valuable suggestions in preparation of the manuscript.

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7 Rubber Mixing

P. K. Freakley

7.1 Introduction

Rubber mixing, linked with filler reinforcement, has been the subject of many investigations and developments. That the field is still the focus of research, controversy and innovation is a measure of its complexity and importance. Rubber compound behaviour is influenced profoundly by the treatment received in the mixing process, affecting the productivity of downstream operations and the service performance of end products. In this chapter, the physics and, to a limited extent, the chemistry of mixing will be outlined, followed by a review of practical mixing equipment - its design, operation and control. Before moving on to the technical aspects of mixing, it is worth summarising some of the recent history of rubber mixing and the industrial context of current mixing technology.

In addition to mixing system productivity, improving the properties of the mixed compound, the repeatability of the operation and process cleanliness have influenced the design of modern mixing systems and continue to act as powerful drivers for development. The majority of mixing systems now used by the rubber industry have been shaped by several key factors:

- the supply of rubber in 20–30 kg bales,
- ability to change quickly from one compound to another with minimal cross-contamination,
- limitations on rubber compound temperature.

Supply of rubber in bale form has dictated that primary rubber mixers are large batch operated machines, capable of being fed with entire bales. Equipment throughout the mixing system is scaled to the batch size of the primary mixer, dictating that it too is of large size. While there are undoubted economies of scale in the operation of large mixing systems, the capital cost of new plant is very high and it cannot be accommodated in standard industrial buildings. Manufacturing flexibility and the ability to respond quickly to change is low.

The continuing use of bale rubber and batch mixers by the rubber industry is, for the most part, pragmatic. However, the plastics industry made the transition from batch to continuous mixing over a decade ago and it is interesting to examine why the rubber industry did not. A main reason can be found in differences in feedstock behaviour. Thermoplastic granules are hard and non-adhesive at ambient temperatures, well suited to standard powder handling and blending methods. In contrast rubber granules deform under the forces encountered in transport and storage and tend to be self-adhesive. There have been several attempts to produce rubber in granular form, as an essential precursor for continuous mixing. A notable effort was made during the 1970s but it became clear that the materials technology was not sufficiently advanced to enable it to succeed. Rubber compound properties were affected by the partitioning agents used to prevent inter-particle adhesion and production was dependent on mechanical granulation of bales. There is now rekindled interest, with an increasing number of rubbers becoming available in granular form direct from the polymerisation process.

The difficulty of controlling rubber compound temperature during mixing has also influenced the retention of batch processes. Limiting temperature rise is important for the efficiency of mixing and for minimising the progress of the chemical reactions, which lead to crosslinking, but the very high viscosity of rubber compounds results in large amounts of heat being generated during mixing. The severity of the temperature control problem increases as mixer size is increased due to the deteriorating ratio of cooling surface area to rubber compound volume and it also increases as mixer speed is increased, limiting productivity. The introduction of materials at ambient temperature into a batch mixer and the cooling of the mixer which occurs between cycles, both have a substantial effect on rubber compound temperature, additional to that of the cooling system during the mixing cycle.

Modern cooling systems and mixer designs have done much to improve temperature control and reduce the importance of the additional cooling, enabling mixer productivity to be improved. Continuous mixers, which do not have the benefit of the additional cooling, have also been shown to be capable of accomplishing complete mixing without excessive rubber compound temperatures. While rubber compound temperature remains as one of the key factors, which limit mixer productivity, it no longer dictates the choice of a batch mixer.

7.2 Mechanisms of mixing

7.2.1 Viscosity reduction

Reduction of rubber viscosity is not itself a mixing mechanism but it is often a necessary precursor to mixing and it always accompanies mixing. The main causes of viscosity reduction are:

- temperature increase,
- flow induced molecular dis-entanglement,
- chain scission (mastication).

The dependence of rubber viscosity on temperature is adequately described by an Arrhenius-like equation

$$\eta = \eta_0 e^{-\left(\frac{\Delta E}{RT_0} - \frac{\Delta E}{RT}\right)} \tag{1}$$

where η is viscosity, T is temperature, η_o is viscosity at reference temperature T_o, ΔE is the activation energy of flow and R is the universal gas constant. The sensitivity of rubber viscosity to changes in temperature depends strongly on the separation of the process temperature from the glass transition temperature T_g. Hence the viscosity of styrene-butadiene rubber, with a T_g of –60 °C is less sensitive to changes of temperature in the processing region than a 40% acrylonitrile-butadiene rubber with a T_g of –22 °C.

Flow induced dis-entanglement of rubber molecules is a primary source of the substantial reduction of viscosity, which occurs as strain rate is increased. However, the effect is not instantaneous and a step increase in strain rate will cause a substantial stress overshoot, which will decay to the steady state flow value as the amount of dis-entanglement appropriate to the new strain rate is reached. In contrast, a step decrease of strain rate will cause a stress undershoot. Both are viscoelastic effects and the former can be exploited to improve the intensity and efficiency of rubber mixing.

Both temperature and flow induced changes in viscosity are reversible but chain scission brings about a permanent change. All rubbers undergo chain scission during processing although attention has focussed on natural rubber for a number of reasons; it is the most susceptible of all the commercially available rubbers to scission, it requires viscosity reduction to render it processable and, for some time, it was the only rubber available for study. A minimum rate of chain scission has been found in the region of 100 °C, below this temperature the rate increases due to mechanical chain scission while above the increase is due to oxidative chain scission [1]. Chemical peptisers increase the scission rate in the oxidative region while the so-called physical peptisers (lubricants) reduce viscosity without scission [2, 3].

7.2.2 Incorporation

The term incorporation is used rather loosely to describe the transition of a rubber compound from separate ingredients to a cohesive and substantially incompressible mass capable of undergoing viscous flow. When only rubber and particulate materials are involved the transition is normally accomplished in three overlapping stages [4, 5]:

- encapsulation,
- subdivision,
- immobilisation.

In batch rubber mixing processes the encapsulation is achieved by the free-surface folding flows that occur between the rotors of an internal mixer or, less often now, between the rolls of a two-roll mill. In continuous processes, where a particulate preblend is used, encapsulation can be accomplished by applying shear and pressure, causing the rubber granules to coalesce around the particulate materials. After encapsulation a rubber compound is capable of undergoing flow, although it is friable and grossly heterogeneous.

Subdivision is the first step towards achieving uniformity of composition in a rubber compound at the microscopic level. Subdivision acts on encapsulated particulate masses, utilising shear and elongational flows in the rubber to pull them apart and then surround them. During subdivision the scale of separation of the particulate materials - the distance between adjacent masses - is reduced substantially, as is the size of the masses. At the end of subdivision the typical particulate unit is the pellet or agglomerate.

Immobilisation refers to the entrapment of rubber within pellets or agglomerates [6]. Reinforcing fillers, carbon blacks and silicas, have substantial internal void volume, typically twice the volume of the solid material. During encapsulation and subdivision the air in the voids is displaced progressively by rubber, which is then shielded from further flow by the rigid filler. During incorporation the density of a rubber compound rises progressively until it reaches its solid density, at which point incorporation can be considered to be complete. Although there is substantial cleavage of pellets and agglomerates during incorporation, the amount of filler reduced to the primary aggregate or particle level during incorporation appears to be minimal, thus there is little or no reduction of the internal void volume available for immobilisation of rubber. The effect of reducing the amount of rubber available for flow is profound. Viscosity at the end of incorporation can be more than three times that calculated from the filler loading in the rubber compound formulation [6].

Many rubber compounds include substantial volumes of oils or plasticisers. Efficient incorporation of these liquid additives can only be accomplished by absorbing them onto the particulate filler prior to encapsulation in the rubber, dictating that they are added early in the mixing cycle. The mobility of oils and plasticisers allows them to enter the internal void volume of filler pellets and agglomerates more quickly than the rubber molecules. In addition to reducing the void volume available for immobilisation of rubber and thus limiting the increase in viscosity, oils and plasticisers reduce overall incorporation time. It is not yet clear if this reduction is simply due to the reduced amount of void volume to be filled with rubber or if oils and plasticisers also have a significant lubricant or surfactant effect, easing the entry of rubber molecules into the internal void volume of the filler. Work with dispersing agents, which are added in small amounts into rubber compounds and which exert their main effect on incorporation, suggests the latter mode of action is also important.

7.2.3 Dispersion

The transition from incorporation to the dispersion phase of mixing is defined by a maximum in viscosity, when the internal voids of the filler are completely occupied by rubber, oil or plasticiser, giving the rubber compound its solid density. Dispersion is then the process of breaking the filler agglomerates into their component primary aggregates or particles. At the start of the dispersion stage the high viscosity and the incompressibility of the rubber compound enable high stresses to be generated by both shear and elongation flows. Also, the large size of the agglomerates makes them very susceptible to fracture, enabling dispersion to proceed rapidly. Unfortunately, this process creates conditions in which dispersion becomes progressively more difficult. Agglomerate fracture releases immobilised rubber, which has the effect of reducing viscosity and thus reduces the stress available for further agglomerate fracture. Concurrently, the decreased size of the agglomerates raises the critical stress level needed for fracture. In practical mixing processes complete dispersion is rarely achieved and a small fraction of undispersed filler persists into the final product.

7.2.4 Distribution

In Section 7.2.2 subdivision was identified as the first step towards achieving uniformity of composition in a rubber compound at the microscopic level. Distributive mixing takes over from subdivision and completes the process. It is convenient to separate distribution processes into two types, macro- and micro-. Macro-distribution is the gross homogenisation of the rubber compound, acting over large distances. It is particularly important when batch weighing and feeding is used, when a minor additive may initially be concentrated in a small region of the mixer. Adequate distribution of the minor components of a rubber compound, such as the crosslinking additives and anti-degradants, is much more difficult to achieve than that of the major components, such as fillers and determines the macro-distributive mixing capability required of a mixer. In contrast, micro-distribution is concerned with separation of filler agglomerate fragments after fracture during dispersive mixing and, as the name suggests, has only to operate over small distances.

Macro-distribution is accomplished by two mechanisms - laminar shear mixing and exponential mixing. The progress of each can be described by reduction of the scale of segregation between two components of a rubber compound. In laminar shear mixing, shown in Figure 7.1, the shear strain must double to achieve a halving of the scale of segregation, whereas Figure 7.2 shows that halving of the scale of segregation is achieved by each sub-division and re-combination.

Situations in which laminar shear mixing is dominant usually occur when the mixing zone is substantially filled and involve closed streamline flows. The efficiency of large-scale homogenisation is poor unless measures are taken to force exchange of material between streamlines. Disruption of closed streamlines and introduction of sub-division mixing can usually be accomplished by the creation of free surface flows; for this reason most practical mixers are operated in a partially filled condition.

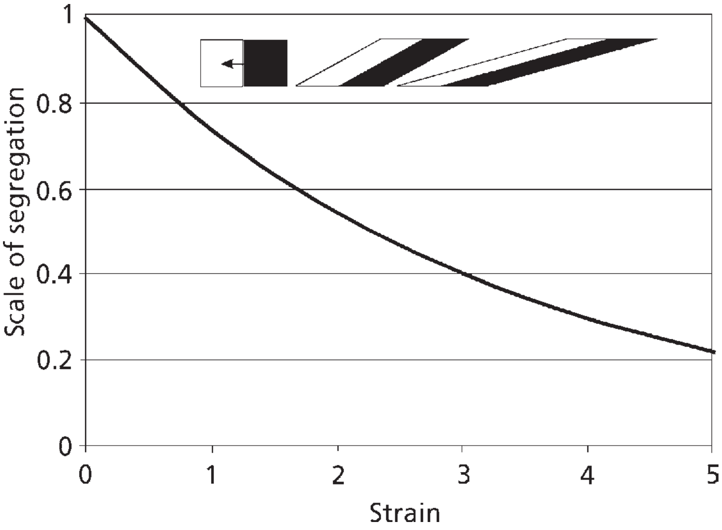

Figure 7.1 Laminar shear mixing

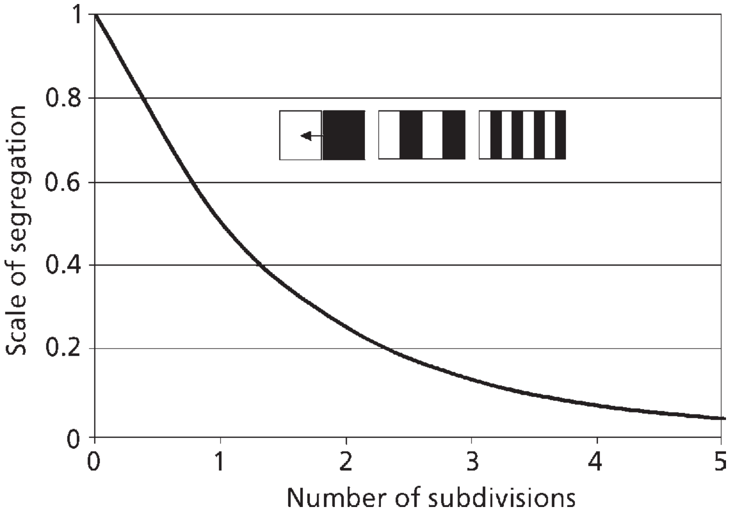

Figure 7.2 Subdivision or exponential mixing

7.3 Rheology of mixing

7.3.1 Flow behaviour of rubber compounds

The flow behaviour of all rubber compounds is strongly non-Newtonian, viscosity decreases rapidly as strain rate is increased. It is also viscoelastic, thixotropic and temperature dependent. All these aspects of the complex flow behaviour of rubber compounds are important in practical rubber processes.

For most purposes, steady-state viscous shear flow of rubber compounds can be described by the power law model:

$$\tau = K\dot{\gamma}^{n} \tag{2}$$

where τ is shear stress, K is the consistency constant (equal to the viscosity at a shear rate of 1 s^{-1} and approximately proportional to Mooney viscosity), $\dot{\gamma}$ is the shear rate and n is the power-law index. The power-law index is a measure of deviation from simple Newtonian behaviour and is a valuable indicator of behaviour in high rate processes. Values of n for most rubber compounds are in the range 0.1 to 0.3. If two rubber compounds have similar values of K but different values of n, their Mooney viscosities will be similar but their behaviour in extrusion or injection moulding will be substantially different. This can be seen by considering the apparent viscosity η_a:

$$\eta_a = \tau / \dot{\gamma} \tag{3}$$

and substituting for τ in Equation 2:

$$\eta_a = K \dot{\gamma}^{\,n-1} \tag{4}$$

The temperature dependence of the apparent viscosity of rubber compounds is described adequately by Equation 1, although the dependence diminishes significantly as shear rate is increased.

Modelling the viscoelasticity of rubber compounds is difficult and has not been satisfactorily resolved. In addition to the mathematical difficulties, the rheometry and subsequent analysis needed to evaluate the parameters of useful viscoelastic models requires careful and time-consuming work. While a close acquaintance with viscoelastic models is only required by those involved in detailed mathematical simulation of processes, practical measurements of viscoelastic behaviour are an essential part of 'fingerprinting' the flow behaviour of rubber compounds. Stress relaxation following steady-state flow in a rotational rheometer or viscometer provides a simple and robust measurement and many Mooney viscometers now include this function. Stress relaxation is normally plotted on ln(τ) versus time axes. In very general terms, rapid relaxation denotes trouble-free processing and batch-to-batch changes in the relaxation behaviour of a rubber compound will usually indicate changes in extrudate dimensions.

Thixotropy in rubber compounds is associated with rubber–filler and filler–filler networks. They are disrupted rapidly by flow and have a slow reformation rate, so only affect processing behaviour in specific instances. These include dimensional stability of uncured rubber compound in storage (yield stress), high stresses on first introduction into a process and inhibition of recovery after extrusion or calandering. In testing they can exert a substantial influence on stress relaxation measurements and on flow measurements at low strain rates, when partial reformation of the networks occurs.

7.3.2 Measurement of state-of-mix

State-of-mix is a 'catch-all' expression which encompasses the extent to which the filler agglomerates have been broken down into single particles or primary aggregates (fused groups of particles), how the remaining agglomerates are distributed throughout the rubber matrix and the general uniformity of the composition of the rubber compound.

The latter includes the dispersion and distribution of the cure system and anti-degradant additives. It is also possible to separate filler dispersion into macro and micro [7, 8]. Macro-dispersion is defined as the extent to which the filler agglomerates have been broken down whereas micro dispersion is less well defined but is associated with fracture of aggregates.

State-of-mix can be measured directly, by microscopic examination of filler dispersion or indirectly, by measurement of some property known to be directly correlated with filler dispersion. In most cases the main concern is the development of the mixing-dependent properties needed in downstream processes and in the final product. These can be divided into two main categories - bulk properties, such as viscosity and modulus, which are substantially dependent on the average filler dispersion and fracture properties, which are much more sensitive to local variations in dispersion. In the latter case, a small number of large agglomerates can cause a substantial reduction of fracture property levels (tear, fatigue), even in cases where the average filler dispersion is ‘good’.

The primary indirect methods of dispersion assessment are surface texture, electrical conductivity and microwave heating measurements [7]. The first one is limited to the macro range but provides some information on the distribution of dispersion, whereas the latter two are sensitive to changes in macro- and micro-dispersion but only provide a measure of average dispersion level. The texture of a cut surface is related to filler dispersion due to the local irregularities caused by cutting through agglomerates. This fact has been used in several measuring devices, utilising direct surface roughness measurements and light scattering. The main disadvantage of these techniques is the strong influence of rubber compound composition on results, limiting their application to comparisons within single formulations. Direct current conductivity measurements have been used for many years in rubber research but the problems of variable contact resistance have inhibited their routine use. This disadvantage was overcome by changing to alternating current and a commercial instrument, the Tangent Electroscanner (Tangent Ltd, Eire), has been developed. Work with this instrument has revealed that control of the test atmosphere (temperature and humidity) is important for reproducibility and that test samples should be allowed to rest for several hours after cutting. The use of microwave heating as a measure of dispersion is more recent than electrical conductivity and is derived from observed behaviour in microwave continuous vulcanisation systems. As filler dispersion is improved the rate of sample temperature rise under conditions of controlled microwave energy decreases. This principle is used in the Dielecmeter (Sairem, France) [7].

Direct dispersion measurement methods are important for process development, problem solving and research. All the available methods give information on the distribution of filler agglomerate size, either qualitatively or quantitatively. Quantitative methods usually require the cutting of a very thin sample (<2 μm) for transmission electron microscopy

(TEM). Both light and electron microscopy can be used. The former is limited by the maximum available magnification to characterisation of macro-dispersion but the latter can give some information about micro-dispersion. However, sample preparation for TEM is substantially more difficult than for optical microscopy and is generally only used for research purposes.

Quantitative analysis of dispersion by transmitted light microscopy, to give a percentage dispersion, is well established and computer-aided image analysis has replaced the tedious manual determination of the area of undispersed agglomerates. Progress has recently been made with determination of percentage dispersion using reflected light microscopy of a cut rubber surface, thus completely avoiding the difficult step of preparing a thin specimen [9].

7.3.3 Dependence of flow behaviour on state-of-mix

In Section 7.2 the immobilisation of rubber in the internal void spaces of the filler during incorporation was described, followed by its release during dispersive mixing. The immobilised rubber behaves as part of the filler, causing changes in dispersion level to have an effect similar to changes in filler loading. In this section the effects on viscosity and extrudate swell will be explored [6, 10].

A measure of the internal void volume of a filler agglomerate is provided by the dibutyl phthalate absorption (DBPA) test for carbon black structure. The volume fraction a of rubber, which an agglomerate can immobilise, is given by:

$$\alpha = \text{DBPA}/[\text{DBPA} + (100/\rho_f)] \tag{5}$$

where ρ_f is the density of the filler. For N330 carbon black the value of α is 0.647, indicating that the amount of rubber immobilised is almost twice that of the carbon black in the agglomerate. Since the filler dispersion controls the effective filler loading, it is useful to calculate an effective filler volume fraction (EFVF):

$$\text{EFVF} = (\phi_a . \alpha) + \phi_t \tag{6}$$

where ϕ_a is the area fraction of agglomerates (numerically equal to the volume fraction), determined by one of the optical microscopy methods mentioned in the previous section and ϕ_t is the true volume fraction of filler, calculated from the rubber compound formulation.

One of the better-known models for describing the effect of filler loading on viscosity is the Guth-Gold equation. If the EFVF is used, rather than the true value of filler loading, the Guth-Gold equation gives impressive accuracy over a wide range of fillers and loadings:

$$\eta_c = \eta_g\{1 + 2.5(\text{EFVF}) + k_1(\text{EFVF})^2\} \qquad (7)$$

where η_c is the viscosity of the compound, η_g is the viscosity of the gum rubber and k_1 is a constant that can take values between 7.35 and 14.1, depending on the assumed packing of the filler particles [6]. The accuracy is also dependent on determining an appropriate value for η_g. If the rubber is susceptible to mastication, treatment under similar mixing conditions as the compound is necessary prior to viscosity measurement. In addition, since filler is non-deformable, the rubber in a filled compound will experience a higher strain rate than the gum rubber, under similar test conditions. This effect has been named strain rate amplification and the appropriate strain rate for testing the gum rubber is given by:

$$\dot{\gamma}_g = \dot{\gamma}_c/(1 - \text{EFVF}) \qquad (8)$$

In principle, the Guth-Gold equation is also valid for describing the effect of state-of-mix on elastic modulus of vulcanisates, although in practice the effects of crosslinking and, at low strains, rubber–filler and filler–filler networks, obscure this simple relationship. Only in the case of elastic recovery of unvulcanised rubber compounds following a flow process can the relationship be used with any degree of success. The rubber–filler and filler–filler networks are disrupted by flow and the majority of recovery occurs prior to their reformation after cessation of flow. Extrudate swell is produced by elastic recovery following flow and a good correlation is found between extrudate swell and the modulus of the unvulcanised rubber compound, measured after conditioning at large strain to disrupt the filler networks, as shown in Figure 7.3.

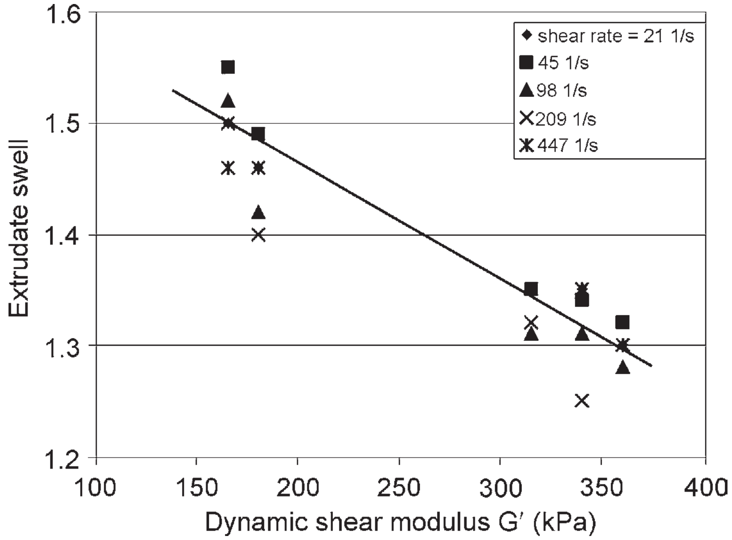

Figure 7.3 Relationship of extrudate swell with the in-phase or elastic component of dynamic shear modulus of an uncured, carbon black filled SBR compound [10]

7.3.4 Kinetics of dispersive mixing

As noted in Section 7.2.3, the extent of fracture of a filler agglomerate depends on the available stress intensity and the size of the agglomerate. Moderate stresses will fracture large agglomerates into several smaller agglomerates whereas high stresses appear to be capable of completely disrupting an agglomerate into its component primary aggregates or particles.

Further consideration of the fracture process suggests that complete disruption is not instantaneous but cyclic, requiring flow following each fracture event to separate and encapsulate agglomerate fragments and allow stress to be re-applied to cause a subsequent fracture event, continuing until disruption is complete or the available stress is insufficient for further fracture. Given that stress and flow are necessary for agglomerate fracture, power density (MW/m^3), is a useful single quantity to define mixing intensity.

Dispersive mixing can be described by first order kinetics [11]. A plot of ln (volume fraction of agglomerates) versus mixing time produces a linear relationship, which can be defined as the dispersion rate. Figure 7.4 shows that the dispersion rate of a simple compound of SBR + 30 phr (by weight) N330 carbon black is strongly dependent on power density. The relationship of power density and dispersion rate can be utilised in two ways. The results in Figure 7.4 were obtained from a capillary rheometer experiment, in which the entire rubber compound was subjected to the power density given. Such results can be used in association with numerical modelling for mixer design. Alternatively, for comparison between existing mixers and for optimisation studies, the dependence of dispersion rate on average power density, defined as the power demand of the mixer motor divided by the batch volume, provides a useful indicator of performance.

In practical mixers, there are regions of high power density, in which the dispersive mixing is accomplished and regions of low power density for distributive mixing. The proper balance and interaction of these regions is crucial for the mixer to be able to produce a high output of rubber compound with acceptably low levels of undispersed agglomerates and uniform composition. Figure 7.5 shows a conceptual operation model of a mixer, in which agglomerates passing through the high power density regions are completely disrupted [12]. The progress of mixing is characterised by a diminishing number of large agglomerates, those yet to pass through a region of high power density. The rate of dispersive mixing is therefore controlled by the efficiency with which agglomerates are guided towards the regions of high power density by the distributive mixing zones. In contrast, if disruption is not completed in a single pass through a region of high power density, the progress of mixing will be characterised by the creation of a large number of small agglomerates, followed by their progressive disappearance as they undergo further passes. Again, the rate of dispersive mixing is controlled by the guidance from the distributive zones. Although two or more passes to achieve complete disruption appear less efficient than one pass, the effect on rate of dispersion will also depend on the flow rate through the high power density regions.

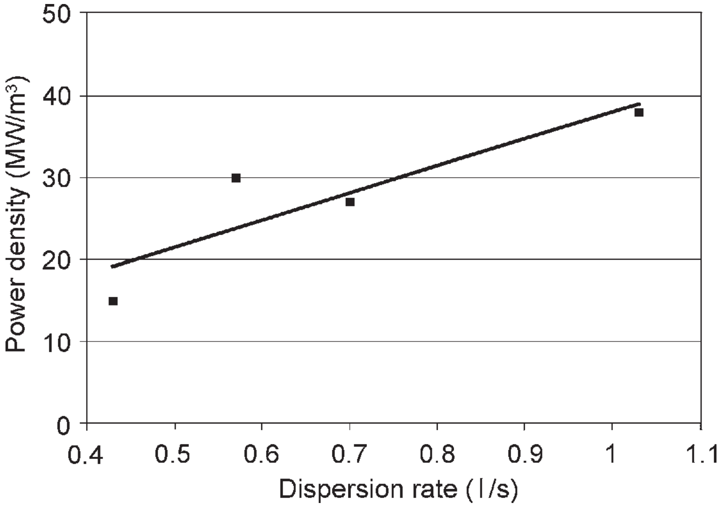

Figure 7.4 Dependence of rate of carbon black dispersion on mixing power density for an SBR compound [11]

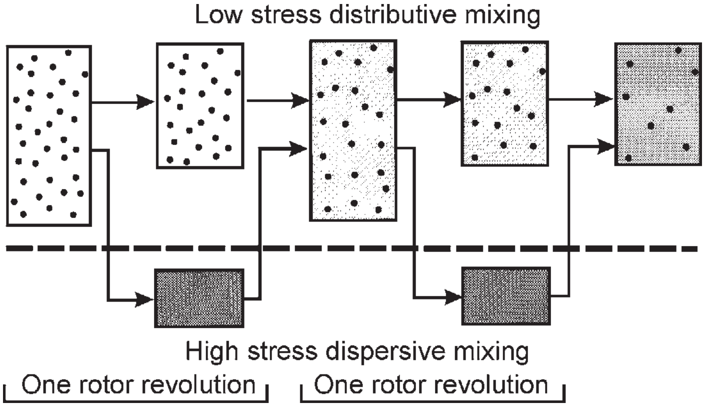

Figure 7.5 A conceptual model of the interaction between the dispersive and distributive mixing functions of an internal mixer [12]

7.3.5 Mixing of blend compounds

Blend compounds are used widely to achieve combinations of properties not available from compounds based on a single rubber. All rubber blend compounds are immiscible at the molecular level and produce a phase morphology during mixing, usually at the micron level. The mixing of compatible rubbers, those with similar solubility parameters, does not normally present problems if their flow behaviour is also similar. In such cases a fine textured morphology is achieved quickly and the rate of filler dispersion remains as the controlling characteristic of the mixing process [13]. In contrast, mixing of compounds with incompatible and rheologically dissimilar rubbers presents substantial difficulties but may be necessary to achieve desired property combinations.

Differences in both flow behaviour and solubility parameter influence the location of fillers and other additives during incorporation. The rubber with the lower viscosity will undergo more flow and consequently be able to encapsulate more filler [14]. This preferential incorporation will continue until filler loading in the initially lower viscosity rubber raises it to a viscosity similar to that of the other rubber. Strain rates in the incorporation zones of most mixers are low, so the traditional Mooney viscosity is a reasonable guide to incorporation behaviour. The preferential incorporation due to flow behaviour can be modified or reversed by differences of the affinities of the rubbers for the fillers and other additives. Carbon black, with its substantially non-polar surface, will incorporate preferentially into non-polar elastomers, such as NR and SBR, whereas silica and mineral fillers will favour polar elastomers. Coatings on fillers and additives are used to improve incorporation behaviour and to overcome problems of compatibility.

If the measures available to improve the one-step mixing of blend compounds are inadequate, separate mixing of each rubber with a proportion of the compound ingredients, followed by blending of the sub-compounds thus formed, must be used. Provided a moderate level of filler dispersion is achieved in each sub-compound, transfer between phases does not occur [14]. In contrast, great care must be taken with selection of the crosslinking system to avoid migration between phases, both in mixing and subsequent processes [15].

7.4 Heat history

The heat history of a rubber compound is defined by its temperature-time profile during processing; from mixing, through storage and into shaping operations and, eventually, curing.

This section will be concerned only with heat history during mixing, where it is one of the determining factors in process selection and operation. Mixing operations are heat history or temperature limited in several ways:

- the power density available for dispersive mixing diminishes as rubber temperature increases,
- the oxidative degradation of some rubbers is considerable at high mixing temperatures,
- there are maximum permissible heat histories for crosslinking precursor reactions (scorch time reduction),
- a specific heat history is required for silane coupling agent reaction.

While the effect of rubber temperature on power density is direct and immediate, the other factors identified above involve chemical reactions, the progress of which depends on accumulated heat history. Both oxidative degradation and crosslinking precursor reactions can be described by the Arrhenius-type equation for first order reactions. Equation 9 is written for the relationship between scorch time t at temperature T and scorch time t_0 at reference temperature T_0:

$$t_T = t_{T_0} e^{-\left(\frac{\Delta E}{RT_0} - \frac{\Delta E}{RT}\right)} \quad (9)$$

where ΔE is the activation energy (derived from scorch tests at a series of temperatures) and R is the universal gas constant. If the heat history is divided into a series of time steps, as shown in Figure 7.6, the average temperature in each step can be inserted into Equation 9 to obtain a time at the selected reference temperature. Summing these times together gives the scorch time reduction due to the applied heat history:

$$t_{sum} = \sum_{i=1}^{n} t_1 + t_2 + t_3 \ldots + t_n \quad (10)$$

The above procedure can be applied to determine if it is possible to design an efficient single-stage mixing procedure or if the energy intensive dispersive mixing should be carried out in a first stage and the curatives added in a second, gentler, stage.

7.5 Batch mixing methods and systems

7.5.1 Two-roll mills

A schematic of a two-roll mill in Figure 7.7 shows the three main zones of the machine: (1) the nip region between the rolls, where the rubber is subjected to high power densities, (2) the rolling bank above the nip, which acts as a reservoir to feed the nip and also provides encapsulating flows for filler incorporation and (3) the band, returning the

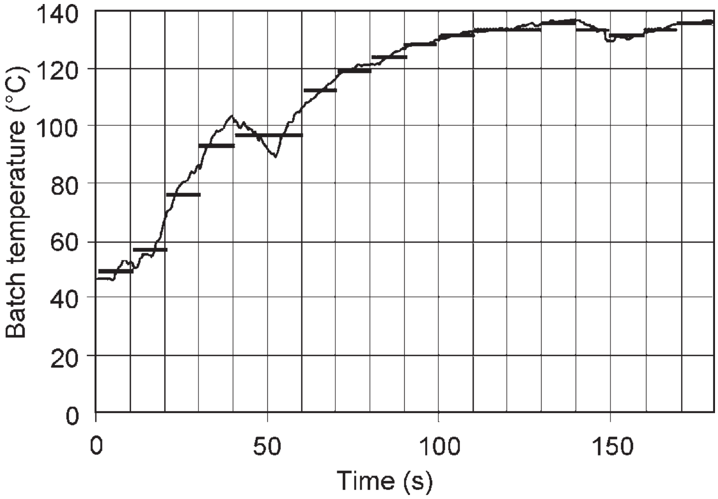

Figure 7.6 A typical batch temperature versus mixing time profile divided into time steps for determination of its effect on scorch time reduction

rubber from the nip to the rolling bank and both cooling it and allowing it to relax in transit. The rolls are normally run at different speeds, with a ratio (the fraction ratio) normally in the region of 1:1.1. This ratio controls the flow pattern in the rolling bank so that all the material is directed through the nip. Running mill rolls at even speeds tends to cause closed recirculation of the rubber compound, preventing a portion of the batch from it from reaching the nip. The localised region of high power density and the large cooling surface of the mill roll give the two-roll mill an inherent low temperature of operation in comparison with other mixing processes. Water is circulated through the hollow roll casting to remove heat or, for more efficient cooling and precise temperature control, rolls with peripheral drilled water channels are used. The high water flow rate and the proximity of the drilled channels to the roll surface provide good heat transfer.

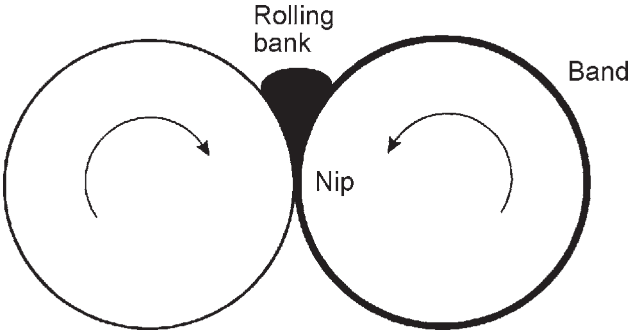

Figure 7.7 Schematic of a two-roll mill

The two-roll mill is used as a complete mixing system for laboratory and low volume production but has otherwise been largely superseded by other devices for this application due to the long time needed for filler incorporation and to the dust hazard thus created. Its main use is as a second stage-mixing device, for adding curatives and for completing dispersive mixing. In both these applications, the characteristic low operation temperature is an advantage.

In its basic form the two-roll mill is entirely dependent on operator intervention for successful operation. The distributive mixing in the axial direction is very poor unless material is moved physically across the mill roll. The operator accomplishes this by cutting and folding, which also has the effect of improving the circumferential distributive mixing. A degree of automation is provided by stock blenders, shown in Figure 7.8, relieving the operator of a strenuous task and bringing a degree of consistency to the milling operation. Schemes for automatic or semi-automatic loading and unloading of two-roll mills are also used widely, varying in form according to the application and the handling characteristics of the rubber compound.

The behaviour of a rubber compound on a two-roll mill depends on its flow characteristics and on the selected milling conditions [16]. ‘Good’ behaviour comprises (1) consistent banding round the working (front) roll during loading, (2) an active rolling bank, with little or no stagnation and (3) a band that does not sag and remains in full contact with the mill roll.

Maintaining an active rolling bank is largely a matter of not overloading the two-roll mill. Table 7.1 gives typical capacities for a range of machine sizes. Consistent banding round the front roll depends on roll temperature and nip setting. As temperature is increased or nip reduced, there will be a tendency of the rubber to band preferentially

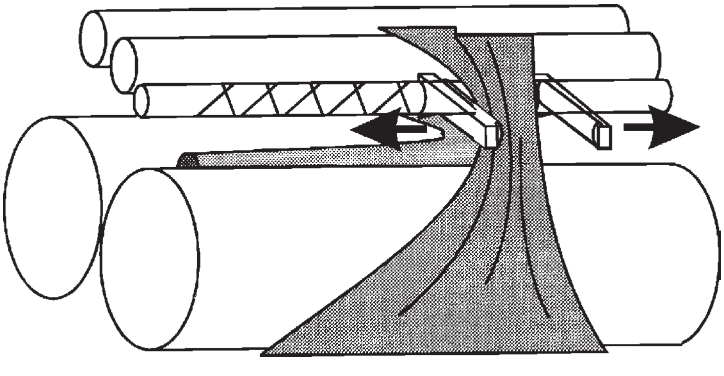

Figure 7.8 A two-roll mill fitted with a stock blender

Table 7.1 Typical two-roll mill sizes and capacities

Roll length (m)	Roll diameter (m)	Mix capacity (kg)	
		Minimum	Maximum
0.75	0.35	9	13.5
1.1	0.40	13.5	23
1.2	0.45	20	32
1.5	0.55	34	57
1.8	0.60	57	91
2.1	0.65	68	114
2.1	0.70	80	136

around the back roll, the combinations of nip setting and temperature depending on the rubber compound being milled. This effect is sufficiently powerful that reducing the nip after a band has been formed can cause a transition to the back roll. Sagging (or bagging) occurs when recovery, characterised by longitudinal shrinkage and thickening of the band after passing through the nip, is inadequate. The recovery is a viscoelastic response and is thus rate and temperature sensitive. Rubbers with a narrow molecular weight distribution (MWD) generally suffer from sagging to a greater extent than those with a broad MWD due to their narrow relaxation spectrum. An increase in roll temperature, a decrease in roll speed and increase in nip all help to reduce or eliminate sagging.

7.5.2 Internal mixers – design and performance

The batch operated internal mixer is the primary mixing device used throughout the rubber industry. Its dominance can be assigned to a number of factors but foremost among them is its ability to accept rubber in bale form and its versatility. Most internal mixers are general-purpose machines, able to mix a very wide range of rubber compounds without any change to the machine geometry being needed.

There are two primary internal mixers designs - intermeshing rotor and tangential (non-intermeshing) rotor - and many variations on these two themes. Figures 7.9 and 7.10 show cross-sections of examples of these two designs. The main features of both designs are the two contra-rotating rotors; the ram, which is raised to permit feeding and lowered and pressurised to hold the rubber compound in the active mixing region; the drop door, designed for rapid discharge of the batch; and the channels in the chamber walls, the

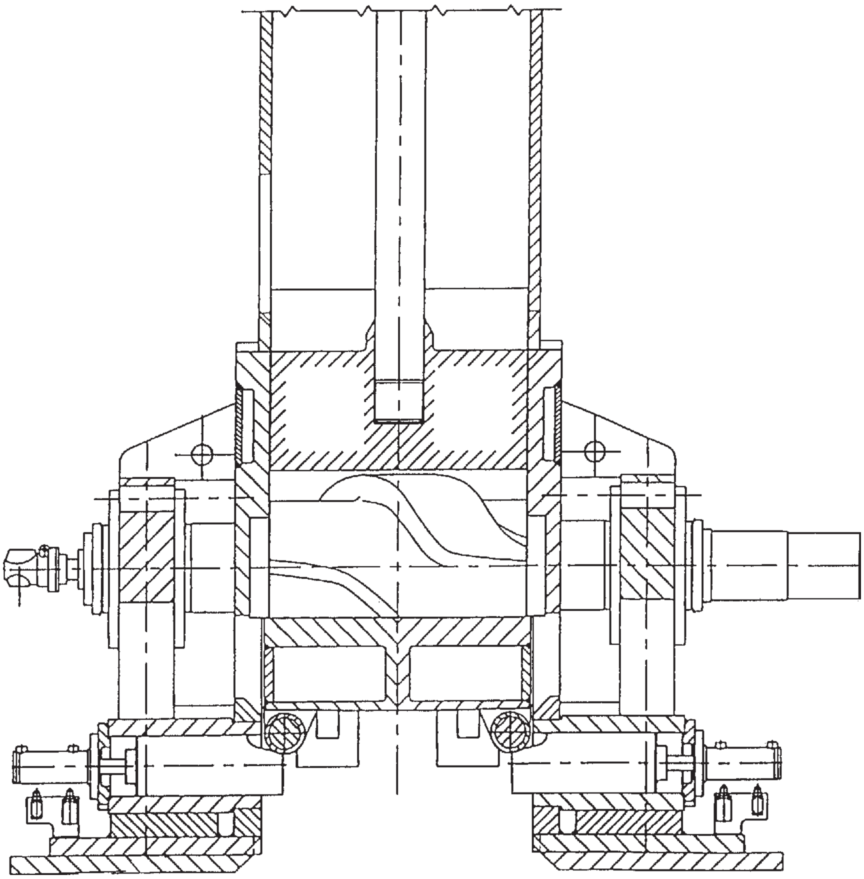

Figure 7.9 Cross-section of an intermeshing rotor internal mixer

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rotors, the drop door and (sometimes) the ram for circulation of cooling water. The wide range of designs for both intermeshing and tangential rotors, some of which combine features of both types, makes it difficult to identify unique characteristics for each. Four aspects will be considered here: incorporation, dispersive mixing, distributive mixing and heat transfer.

The feeding characteristics of an internal mixer can be taken to be part of its incorporation behaviour, in association with encapsulation of filler by the rubber and the subsequent immobilisation of rubber within the filler agglomerates. There is little published work on incorporation efficiency but the tangential design is noted for its rapid feeding and filler encapsulation, attributed to the large ingestion zone between the rotors. However,

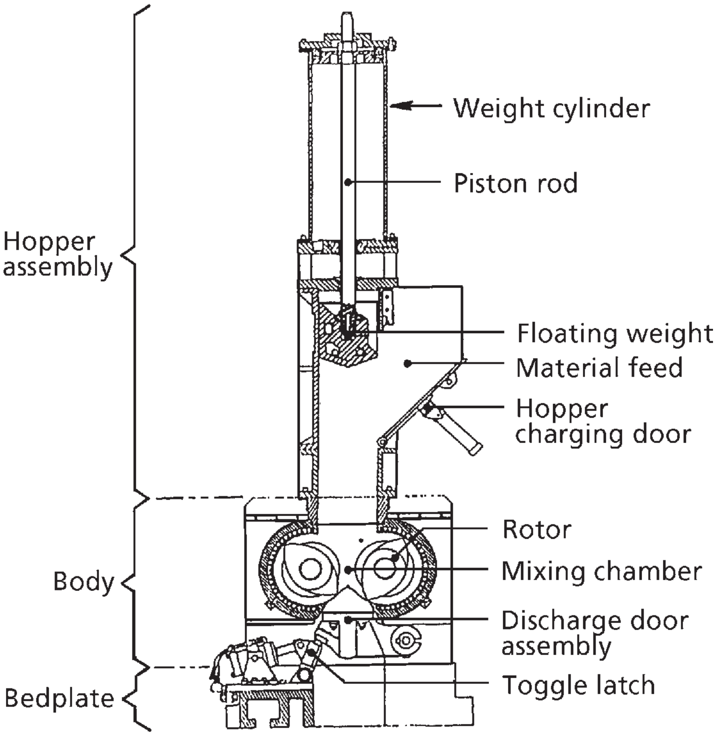

Figure 7.10 Cross-section of a tangential rotor internal mixer

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rapid feeding is also dependent on the rate at which material can be removed from the ingestion zone by the action of the rotors and the feeding performance of the intermeshing rotor design, with its much smaller ingestion zone, is attributed to this latter factor. The Pomini company of Italy have designed their variable intermeshing clearance (VIC) machine to improve the overall incorporation behaviour of the intermeshing rotor mixer. It is designed to allow the rotors to be moved apart prior to the start of mixing, to increase the size of the incorporation zone and to then be moved back to their most efficient operating positions for the remainder of the cycle. Results to date suggest that the VIC mixer also has benefits for optimisation of dispersive mixing [17].

The dispersive mixing region of the tangential rotor design comprises the convergent flow zone in the approach to the rotor tip and the zone of small clearance between the rotor tip and the chamber wall. In the conventional tangential design the rotor tip is narrow, giving a short flow path and low residence time but a high flow rate. The approach angle of the convergent flow zone is steeper in intermeshing designs based on the Cooke patent [18] and the flow path though the region of small clearance is much longer, giving more complete filler agglomerate disruption in a single pass. However, the geometry of the approach zone tends to promote a strong elastic response in the rubber, which prevents it from entering the small clearance zone in the early stages of the mixing cycle. To compensate for this delay, the intermeshing design has a region of small clearance between the rotors in which high stresses are generated and dispersive mixing occurs. In the original design concept this region was seen as being the main location of dispersive mixing, analogous to the two-roll mill but subsequent work has shown the interaction of rotor and chamber wall is more important. In both intermeshing and tangential designs the mixing characteristics can be varied over a wide range by adjusting the approach angle, the tip clearance and the tip width. For example, Carter Bros. (Rochdale) Ltd., of the UK have produced a tangential rotor design with a tip width substantially broader than that of the conventional machine and Krupp of Germany have decreased the angle of the approach zone in their intermeshing rotor design.

In addition to homogenisation of the rubber compound, the distributive mixing action is also required to guide material into the dispersion zones, as noted in Section 7.3.4. The design of intermeshing rotors enables them to act in a manner analogous to an extruder screw, pumping material axially but encouraging 'leakage flow' into the small clearances between the chamber wall and the rotor for dispersive mixing [19]. As each rotor pumps in the opposite direction, there is a positive circulation, with forced exchange of material between the rotors at each end of the mixing chamber, as shown in Figure 7.11.

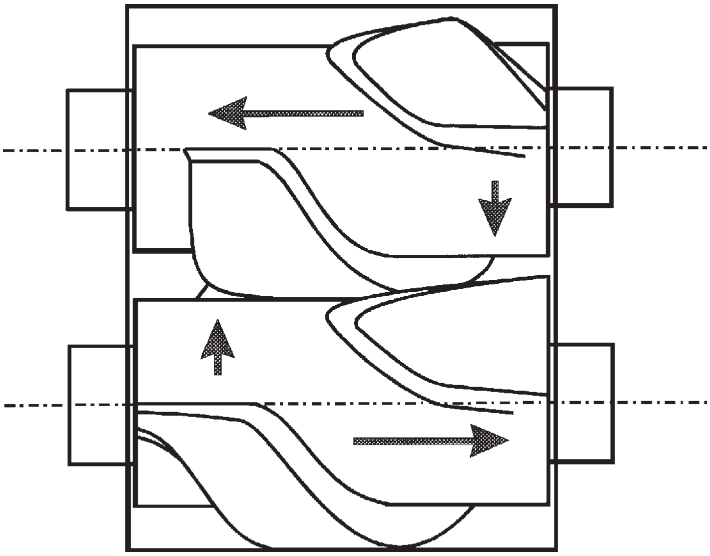

Figure 7.11 Intermeshing internal mixer rotors, showing the primary re-circulation flow paths

The pumping action of the rotors ensures good exchange of material between the extremities of the mixing chamber but local homogenisation is accomplished mainly by the coalescence of circumferential flows from each rotor in the region under the ram and subsequent division of the flow between the rotors over the apex of the drop door. The helix angles of tangential rotors are set to pump material from the ends of the chamber towards the centre. Both two wing and four wing designs are used and in each design a long wing on one rotor interacts with a short wing on the other, to create an axial circulation for exchange between the extremities of the mixing chamber. There is also a cascade effect, in which the flow around the end of the long rotor is delivered into the dispersive zone of the short wing on each rotor and vice versa [20]. As with the intermeshing design, local distributive mixing is accomplished by the coalescence of circumferential flows from each rotor in the region under the ram and subsequent division of the flow between the rotors over the apex of the drop door. The weaker flow interaction between the rotors of a conventional tangential rotor mixer and the less positive long-range circulation result in a lower distributive mixing efficiency than intermeshing designs. Rotor designs for improved distributive mixing have been produced by several companies, including the Farrel Corporation (ST rotors) and Carter Bros. (Rochdale) Ltd. (Turbo-Swirl rotors). Both these designs include lengthening the long rotor and shortening the short rotor, to produce a near-unidirectional circulation analogous to that of the intermeshing designs, as shown in Figure 7.12.

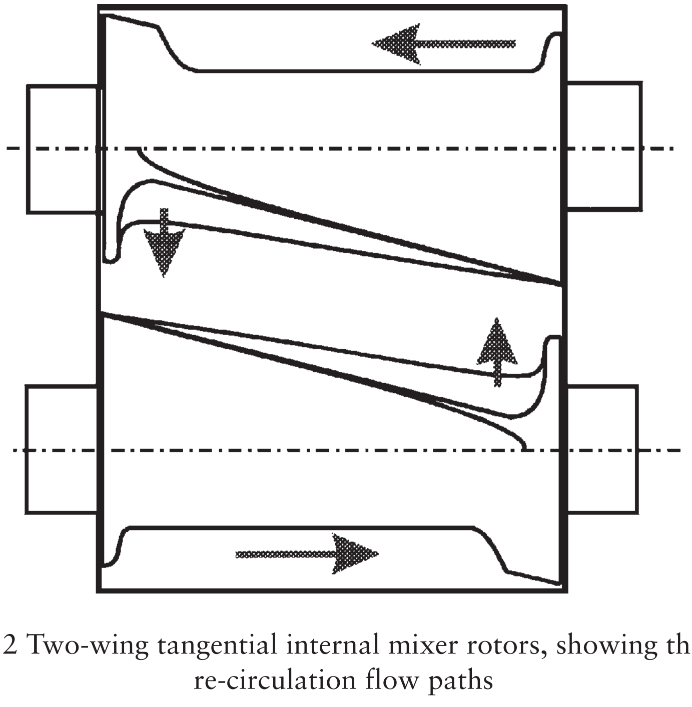

Figure 7.12 Two-wing tangential internal mixer rotors, showing the primary re-circulation flow paths

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In addition, Farrel introduced synchronous rotor speeds, replacing the differential speeds used traditionally with conventional tangential rotor mixers, to ensure that the interaction of the wings on the two rotors remain at the optimum configuration for distributive mixing. This measure has subsequently been adopted by other tangential rotor mixer manufacturers.

Control of batch temperature is a vital ingredient of mixing efficiency, as described in Section 7.4. In general, the main concern is to reduce the rate of temperature rise, which depends on several factors: (1) the area of the cooling surfaces accessible to the batch, (2) the rate of replacement of all parts of the batch at the cooling surfaces and (3) the rate at which heat can be withdrawn from the rubber at the cooling surfaces, per unit area. The latter is independent of whether the mixer is of tangential or intermeshing type and is determined by the proximity of the water channels to the rubber, the number of channels, the water flow rate and the water temperature. From Figures 7.9 and 7.10 it can be seen that the intermeshing rotor mixer has a surface area advantage over the tangential type and, given an equivalent heat extraction per unit area, can be expected to extract more heat from the rubber compound. However, conduction through rubber is very slow and heat transfer is dominated by the physical movement of the rubber compound to the cooling surfaces, termed forced convection. This, in turn, is controlled by the distributive mixing action. The combination of high surface area and high distributive mixing efficiency gives the intermeshing rotor mixer a substantial advantage in terms of cooling efficiency in comparison with the tangential type.

7.5.3 Internal mixers – operation

A key attribute of all internal mixers is their ability to mix a very wide range of rubber compounds without any changes to the mixing geometry being needed. This versatility is due to the extent to which the mixing treatment can be manipulated by adjusting the available operation variables. Those available within the mixing cycle include: (1) mixing time, (2) rotor speed, (3) fill factor, (4) ram pressure and (5) circulating water temperature. Although the range of variables available provide versatility, their number makes optimisation of mixing procedure a complex matter, particularly as all the variables interact with each other to some extent.

Mixing time is usually considered to be the dominant mixing variable because of its direct link with the progress of mixing, though consideration of the dynamics of mixing suggests it is the number of rotor revolutions, which determine flow through the regions of high power density and thus determine the progress of dispersive mixing. If properties are plotted as a function of the number of rotor revolutions (speed x time) for a range of rotor speeds, as shown in Figure 7.13, they fall into a band, the width of which is

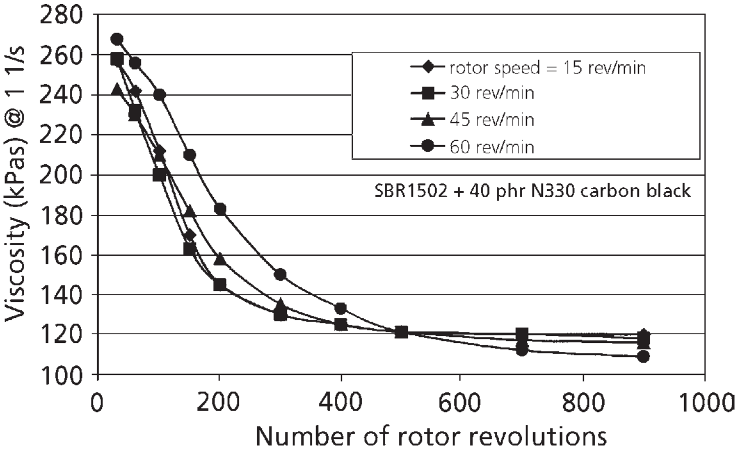

Figure 7.13 Dependence of the viscosity of a carbon black filled SBR compound on the number of rotor revolutions and on rotor speed

determined by the effect of rotor speed on the measured properties. This relationship presents an opportunity to raise rotor speed and decrease mixing time, until further gains are prevented by increasing batch temperature.

The relationship between properties and rotor revolutions will be influenced by other variables, notably fill factor and ram pressure, both of which interact with rotor speed.

Fill factor is defined as the proportion of the mixing chamber filled with rubber compound (at the fully mixed density) and is normally in the range 0.6 to 0.9, depending on rubber compound composition and mixer type. The efficiency of distributive mixing, heat transfer and flows through the regions of high power density are critically dependent on there being free volume in the mixing chamber, although there is usually a broad range of fill factors in which successful mixing can be accomplished [21]. This is shown in Figure 7.14, where the distribution of 300% tensile modulus (M_{300}) for samples taken at random from batches mixed at different fill factors in a conventional tangential rotor mixer is given. As fill factor is increased, the up-thrust on the ram (see Figures 7.9 and 7.10) is increased and, if fill factor is too high or ram pressure inadequate, a region of stagnation is created in the throat of the mixer. This may persist during the whole mixing cycle but moderate overloading will delay the entry of material into the region of active mixing at the beginning of the mixing cycle. Increasing ram pressure will reduce delay and stagnation and allow fill factor to be increased, theoretically up to the limit set by the free volume needed in the mixing chamber for efficient distributive mixing and heat transfer flows. Practical fill factors are limited by the effect of rubber compound elasticity and rotor speed on the up-thrust tending to displace the ram into regions of stagnation.

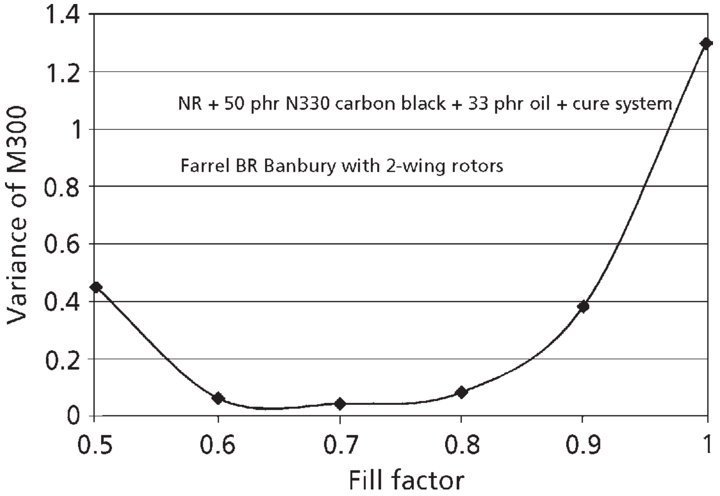

Figure 7.14 Dependence of the in-batch variation of 300% tensile modulus (M_{300}) of a NR compound on fill factor [21]

As described in Section 7.4, heat history has a substantial effect on mixing, requiring stable circulating water temperature and flow rates for consistent mixed compound properties. The choice of water temperature is usually a compromise between conflicting requirements. While a low water temperature will delay batch temperature rise and improve the efficiency of dispersive mixing, a moderately elevated temperature will accelerate incorporation. The latter is due in part to the increase in adhesion between the rubber and the surfaces of the rotors and chamber wall as temperature is increased and in part to the accelerated rise in rubber temperature reducing its elasticity, enabling it to flow more readily to encapsulate and 'wet out' the filler. In general, water temperatures in the range 20–70 °C are used in combination with high water flow rates to induce turbulence and achieve a high heat transfer rate from the modest temperature differential between the rubber compound and the water.

7.5.4 Mixing sequences

Choice of the sequence of feeding an internal mixer depends strongly on the formulation of the rubber compound but it is a sound principle to minimise the number of additions, as the efficiency of mixing drops substantially while the ram is raised for feeding. A number of factors guide the choice of sequence:

- some rubbers will not incorporate fillers effectively until their elasticity has been reduced by shearing and an increase in temperature,

- large volumes of oil or plasticiser need to be absorbed onto free filler, to avoid lubrication of rotors and chamber wall and loss of the rubber – metal adhesion needed for efficient mixing,

- very large filler loadings may have to be fed in two stages, to avoid immobilising so much of the rubber in the filler during incorporation that there is insufficient free rubber to prevent the action of the rotors from breaking the batch into fragments,

- in single-stage mixing, curative additions usually have to be delayed until near the end of the cycle, to avoid accumulating an excessive heat history.

Conventional mixing is used when prior shearing and heating of the rubber is required and, in the case of single-stage mixing, involves separate additions for rubber, fillers and curatives. The minor additives which are not sensitive to heat history, such as zinc oxide, stearic acid and the anti-degradants are normally added with the rubber. Oils and plasticisers are usually injected directly into the mixing chamber while the ram is in its working position. When a large loading of filler is combined with a large volume of oil, as is the case for many EPDM compounds, an upside-down mixing cycle is useful. This is so named because the filler is added and the oil injected, to allow the latter to be absorbed on the former, before the rubber is added, achieving rapid incorporation and avoiding loss of rubber - metal adhesion. In some cases, with tractable synthetic rubbers such as emulsion SBR, it is possible to feed the rubber and filler and start the oil injection concurrently. This minimum feed time procedure is sometimes named 'dump' mixing.

Many variations on the main themes of conventional, upside-down and dump mixing are possible and their selection can be guided by consideration of how the mixing conditions for achieving each aspect of the required rubber compound characteristics can be created and combined. If conditions are incompatible, such as those for high power density dispersive mixing and for curative mixing, two-stage mixing must be considered. Similarly, if high power density dispersive mixing cannot be completed in a single cycle due to an excessive batch temperature, either a reduction of rotor speed and (perhaps) fill factor must be considered, or the creation of a second dispersive mixing stage (this is sometimes named a 're-mill' cycle).

Addition of curatives towards the end of a single-stage mixing cycle must be guided by the number of rotor revolutions needed for adequately uniform distribution in the batch. In some intermeshing rotor mixers this can be accomplished in as little as 12 revolutions but the figure is strongly dependent on the physical form of the curatives, their initial distribution due to the feeding method and on the specific design and of the mixer [22].

7.6 Batch-off extruders and festoon coolers

Large extruders, capable of accepting an internal mixer batch, are used as an alternative to the two-roll mill, particularly by the tyre industry. Similar machines are used both for first-stage dispersive mixing and for second-stage curative additions. In both applications efficient cooling of the rubber is important, initiated in the extruder and continued in a cooler. A typical system arrangement is shown in Figure 7.15.

The typical batch-off extruder is a single screw device. This design requires assistance in order to feed the large irregularly shaped batch of rubber discharged from the internal mixer and a reciprocating ram is used for the purpose. The use of a roller die enables sheet to be formed at a low extruder head pressure, helping the cooling of the rubber. Roller die speed must be matched to the supply of rubber in order to maintain process continuity and this is normally accomplished by linking it to extruder head pressure. If the mixer is stopped and the rubber supply interrupted, the roller die also stops and the sheet continuity is maintained.

As an alternative to the single-screw batch-off extruder, conical twin-screw machines have been introduced. As Figure 7.16 shows, these machines do not require a feed ram. The advantages claimed are superior cooling and reduced batch-to-batch contamination.

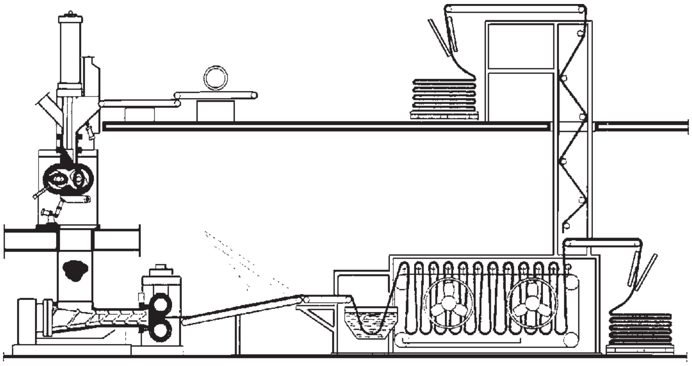

Figure 7.15 A schematic of a mixing installation, showing the batch-off system, including the dip tank for application of anti-tack solution, festoon cooler and sheet stacker

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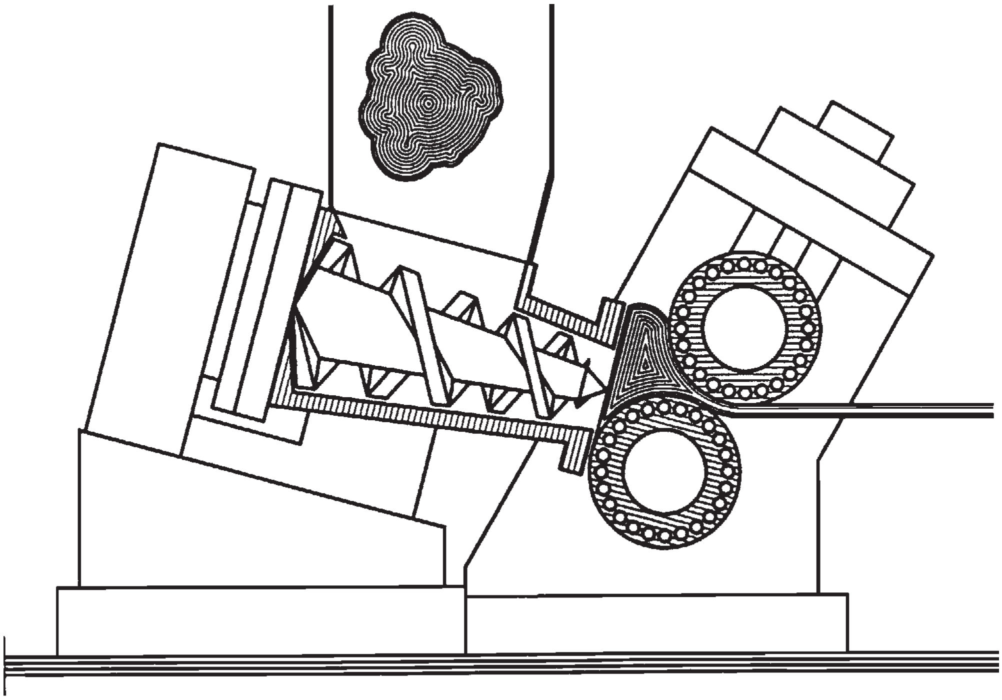

Figure 7.16 Cross-section of a conical, twin-screw batch-off extruder, showing a roller die

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Coolers have three main elements: (1) a dip bath to apply an anti-tack agent to the rubber sheet, (2) a forced air-cooling zone and (3) a batch-off system. Both suspension and solution anti-tack agents are available. The well-established main ingredient of the former is zinc stearate, although alternatives are now being offered due to the environmental problems associated with zinc. Solutions are based on soaps manufactured from fatty acids to cover the range of surface characteristics of rubber compounds. Both types of anti-tack agents are required to wet the rubber surface effectively and to form a stable coating. They also play an important role in cooling. In addition to the direct but brief cooling in the dip tank, the liquid film deposited increases the surface heat transfer coefficient of the rubber sheet and thus increases the efficiency of the forced air-cooling zone. Vaporisation of the liquid film also gives very effective cooling, exploiting the latent heat of vaporisation. Calculations for the length of the cooling zone and number of fans (air speed) for required end-point rubber temperature and line speed are based on well-established heat transfer relations. The basic bath-off system is the wig-wag sheet stacker (guides the rubber sheet back and forth as it descends onto a pallet to create a folded stack) shown in Figure 7.15 but the available level of capability and automation has improved substantially in recent years. The use of systems designed for strip production is increasing, incorporating weighing or exact portioning on a pallet or in a box [23].

7.7 Materials handling

This section is concerned with the delivery of materials to the internal mixer, handling of mixed rubber compound having been dealt with in Section 7.6. The materials handling system for batch rubber mixing is split into four distinct regions: (1) bale rubber, (2) bulk powders, (3) minor additives (predominantly powders and pellets) and (4) liquids. A schematic of a complete system is shown in Figure 7.17.

Virtually all bale rubber is delivered on standard pallets, requiring forklift truck handling until the pallet is broken down into batch lots. Wherever possible, mixer batches are sized so that whole bales can be used, enabling them to be transferred directly from the pallet to the mixer band scale. The use of manually operated hoists with suction heads has made this transfer a much safer task than hitherto.

The handling of bulk powders is an area of active and continuous improvement, driven by both performance and environmental criteria. Improvements in accuracy and stability have been made possible by advances in weighing hardware and in system intelligence. The rubber industry has also demanded a reduction in the damage to filler pellets caused by conveying and weighing. Fines generated by damage are considered to have a detrimental effect on mixing and hence on rubber compound behaviour. Pneumatic conveying is the primary method of moving fillers from the delivery point to bulk hopper storage and subsequently from storage to day bins (if used). It is also used for batch transfer, if the point of weighing is remote from the mixer. Improved transmitter designs for control of air velocities, pressures and the filling of the transfer pipe have reduced pellet damage substantially. The technique used for feeding material from the storage or day hopper to the weigh hopper is determined by its flow behaviour. Carbon black and other materials amenable to stable fluidisation can be moved by air slides, in which low pressure air is passed through a membrane into the transport channel. Virtual elimination of inter-particle friction means that conveying down low incline angles is possible [24]. More cohesive powders, which include most white fillers, require more positive feeding and screw conveyors are widely used. As an alternative to the positive pressure systems described above, vacuum methods are gaining in importance. The key element is a vacuum scale, which draws the fillers from the storage hopper or day bin. In addition to the environmental advantages of using a negative pressure system, vacuum scales provide improvements in accuracy and stability over conventional types.

Minor additives are usually weighed into polyethylene bags and charged into the internal mixer via the band scale. This approach is prescribed by the number of different minor additives, which makes direct feeding complicated and costly and by the requirement for a low loss method to give weight accuracy at the ±1% level needed for consistent mixed compound properties. Weighing systems are available at two main levels - automatic

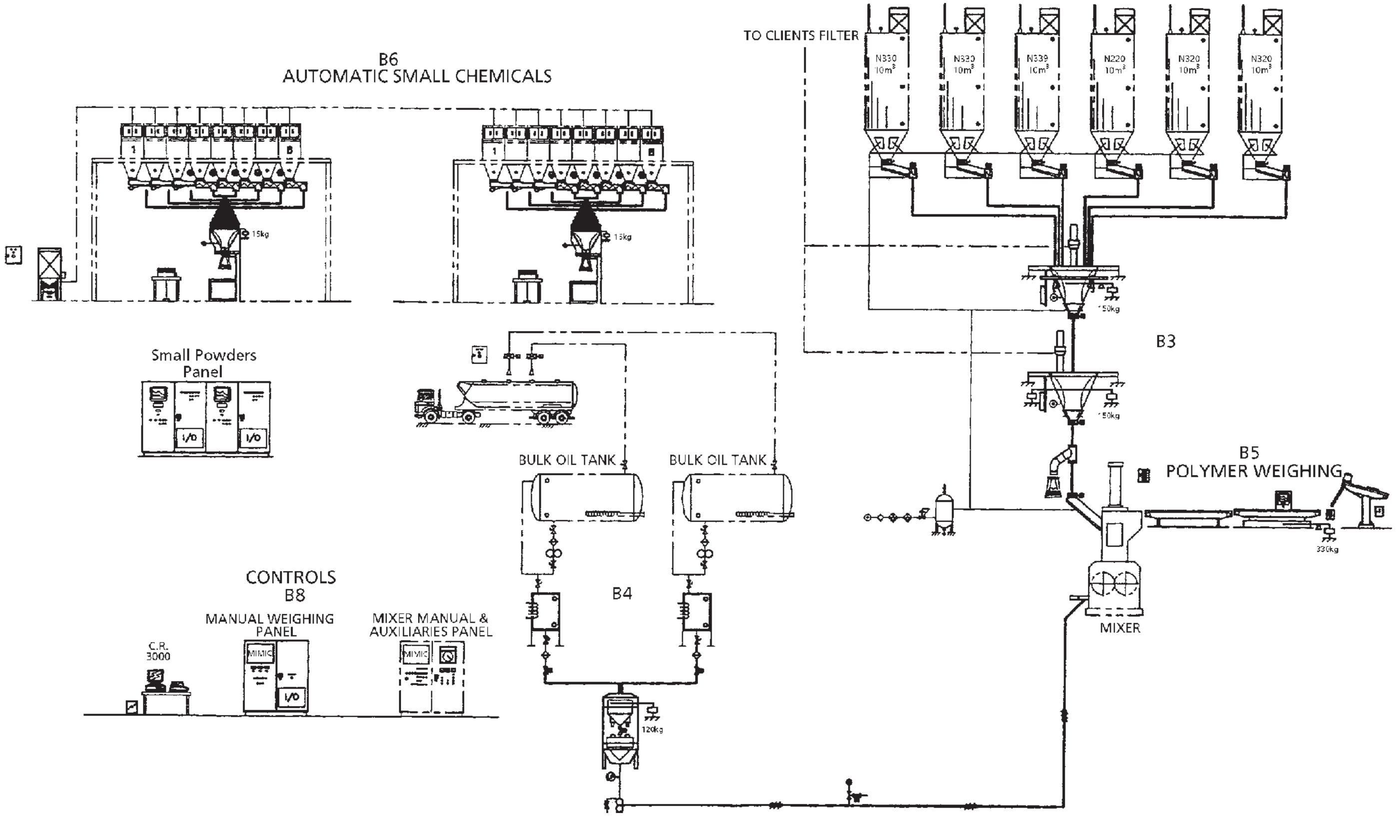

Figure 7.17 A complete materials handling, weighing and control scheme for a mixing installation

Reproduced with permission from Chronos Richardson Ltd and computer-aided manual weighing. In automatic systems screw feeders are used to transfer the additives from day bins or big bags to a scale. Sequential weighing of ingredients is carried out directly into a plastic bag and automatic sealing may be incorporated. In the typical computer-aided system the operator transfers the additives from scoop bins into a plastic bag placed on a carriage-based weigh station. A computer monitor identifies the additives required and the system will only move on when the correct weight of additive has been placed on the scale. The precise location of the moving carriage at each scoop bin enables effective dust extraction to be applied. Increasing understanding of the health implications of contact with minor additives has lead to substantial improvements in the weighing environment and it is possible that a move to completely enclosed systems will be necessary in the future.

Oil and plasticisers are amenable to conventional tank storage and piped transport methods, although heating of some of the more viscous process oils is essential to avoid high pressure and pipe losses. In most installations the amount of oil to be delivered to the mixer is determined by weighing, contrary to normal practice of metering liquids. A simple pump is then used to inject the weighed amount of oil directly into the internal mixer chamber, via a shut-off valve.

7.8 Instrumentation and control of mixing

During batch internal mixing a number of physical and chemical processes go on simultaneously, as described in earlier sections. The rates of all these processes depend on the stresses, flows and temperatures developed during mixing but to different extents. To complicate matters, mixing conditions are affected by the heat history developed in previous mixing cycles due to the thermal inertia of the massive metal components of the mixer and by the inherent properties of the materials being mixed. Consequently, the foundation of any mixer control strategy is to implement quality systems for material uniformity and to minimise the effect of thermal inertia. The latter is well known as 'the first batch effect' being most pronounced at start-up.

Mixer instrumentation has two main purposes, to provide the feedback signals for automatic control devices and to provide information for operator or supervisor action. Conventional measurements, which provide the most direct information on the progress of mixing, comprise batch temperature, drive power and ram position. The batch temperature is an indicator of the energy utilised in mixing but is subject to other influences. A low mixer temperature, as will occur during start-up or after a break in production, will depress the batch temperature. Input material temperatures will also exert a significant influence. However, batch temperature has a direct influence on the rate of the chemical processes, which occur during mixing. Accurate measurement is important but is not simple due to the conflict between design for detection of the rapidly changing rubber compound temperature and design to withstand the conditions in the mixing chamber. Practical temperature probes tend to have a high thermal mass and a long response time. Lag errors of 20 or 30 °C are not uncommon in short, intensive mixing cycles. Some progress has been made with algorithms for correction of the lag error but there is ample scope for further improvement [25].

Drive power provides a direct indication of the progress of mixing and is usually taken as the electrical power demand of the motor minus an allowance for efficiency and friction losses. The idealised power profile in Figure 7.18 shows the progress of a conventional single-stage mixing cycle, from the engagement and mastication of the rubber, to the incorporation and start of dispersion of the carbon black, to the oil addition and the depression of power while it is absorbed onto the available loose carbon black and finally to the curative addition, followed by discharge. In practice, power profiles are 'noisy' due to the effect of rotor position and the distribution of material in the mixing chamber on power demand. The integration of drive power with respect to mixing time provides a measure of the energy utilised in mixing and has a substantial smoothing effect on the power signal, enabling energy to be used as a reliable criterion for control actions [26].

Ram position also provides substantial information on the progress of mixing [27, 28] and can be monitored by conventional displacement transducers. Figure 7.19 shows an idealised ram position profile for the mixing cycle used to illustrate the power profile in Figure 7.18, characteristic of tangential rotor mixers. At the start of the mixing cycle, the rubber engages progressively with the rotors, allowing the ram to descend as the amount

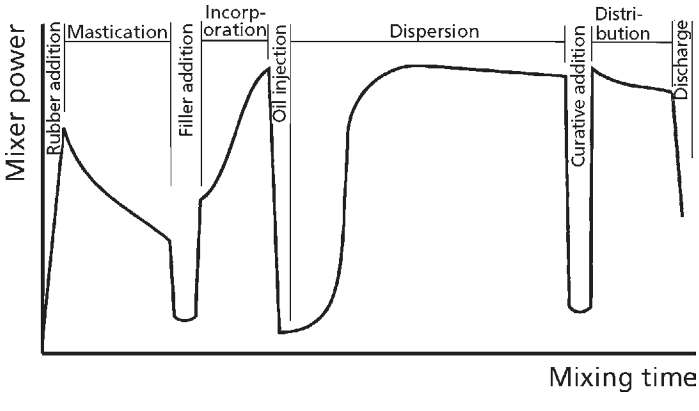

Figure 7.18 An idealised internal mixer power profile for a conventional, single-stage mixing cycle

of rubber in the throat of the mixer diminishes. When the rubber is fully engaged the ram displacement will be negligible, as the mixer is under-loaded at this stage in the cycle. After adding the carbon black the ram descent will again be restricted by the material in the throat of the mixer and displacement provides a good indication of the progress of incorporation. Oil injection is normally carried out under ram pressure and the effect of position depends strongly on the rubber compound formulation. In the example shown there is a 'flat spot' in the power profile in Figure 7.18, attributed to loss of effective mixing due to oil lubrication. At the end of incorporation the ram should be in its final position, showing a cyclic motion with the rotor speed frequency and the lowest point of the oscillation at the zero displacement mark. This behaviour shows that the mixer is optimally loaded and that there is no stagnant material in the throat of the mixer to cause in-batch variation. Clearly, ram position is very useful in determining fill factor. The characteristics of a typical ram position profile for an intermeshing rotor mixer are somewhat different. The proximity of the rotors to each other results in active flows the throat region and effective interchange of material between the throat and the rotors. Clearly, excessive material in the throat region will result in stagnation and, as a working guide, a correct fill factor will result in the ram reaching the zero displacement mark in the final 10% of the mixing cycle.

The conventional criteria for mixer control actions are mixing time, batch temperature and mixing energy [26]. Mixing time is entirely 'open-loop' in that there is no compensatory action for variation of material input or mixer temperature. Both batch temperature and mixing energy are influenced strongly by the progress of mixing and provide some closed-loop control, shortening or extending the mixing time in response to changes in material input and mixer temperature. Mixing to target temperatures gives better control of the chemistry of mixing (cure behaviour) than target energy but the latter is preferable when control of the physics of mixing (filler dispersion) is paramount.

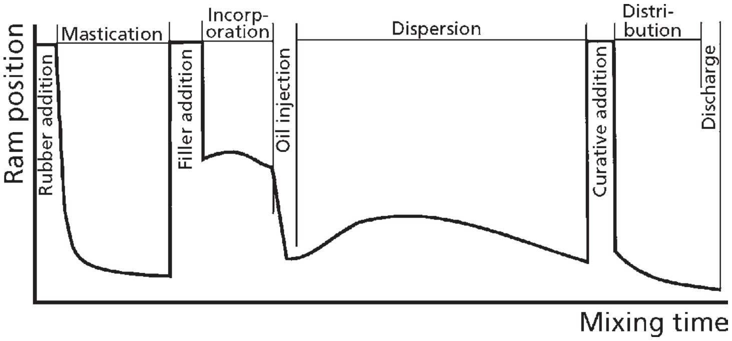

Figure 7.19 An idealised internal mixer ram position profile for a conventional, single-stage mixing cycle

Neither target temperature nor energy take any account of the temperature or power profile by which the target is reached, so actions, which give consistent profiles, such as control of material, input, initial mixer temperature and cooling, are important. A number of strategies have been developed to link control more closely with state of mix and provide improved closed-loop control. Direct control of temperature and energy profiles via rotor speed is used to reduce the effect of uncontrolled variables on the route to target values. More sophisticated methods treat the mixer as a large viscometer, using rotor torque, corrected for batch temperature, as an indicator of state of mix [29].

None of the methods provide an ideal answer to the problem of control due to the complexity of the physical and chemical processes occurring during mixing. Modern control systems enable the user to explore a wide range of control options and choose the one, which is most appropriate to the specific operation.

7.9 Continuous mixing

7.9.1 Continuous mixing versus batch mixing

Continuous mixing offers a number of potential advantages over batch mixing, including inherently stable and consistent operation, cleanliness and reduced capital and operation costs. These advantages have been realised in the thermoplastics compounding industry, where continuous compounding is now the dominant method but the growth of continuous mixing in the rubber industry has been inhibited by a number of factors. Those which defeated attempts to introduce continuous mixing in the 1960's included: (1) lack of availability of granular rubber in a consistently free-flowing form and at a cost comparable with that of bale rubber, (2) the segregation of particulate pre-blends during transport and feeding to the continuous mixer and (3) the inability of most continuous mixers then available to accommodate the wide range of compounds used by rubber companies, without time-consuming changes to mixing geometry. Although much remains to be done before continuous mixing challenges the dominance of batch mixing, the increasing availability of granular rubber from the major material suppliers and the resurgence of industry interest in continuous mixing justified an examination of the current state-of-the-art.

7.9.2 Powder weighing, blending and handling

Delivery of the ingredients to the continuous mixer in the proportions required in the final rubber compound is a key requirement of continuous mixing. Reduction of the scale of segregation of ingredients at the feed entry to a continuous mixer enables a proportional reduction of the amount of energy intensive distributive mixing. While this can be accomplished by continuous metering of all the separate ingredients, the number of feeders needed and the difficulties of rapid change from one formulation to another usually render this approach impractical. A normal approach to overcome these problems is batch blending of particulate ingredients prior to feeding to the continuous mixer. Most continuous mixers require a metered feed but if a uniform and consistent blend of all the ingredients can be achieved, only one metering device is required. In addition, conventional batch weighing methods used throughout the rubber industry can be utilised to deliver ingredients to the blender.

Despite the convenience and economy of batch blending prior to continuous mixing, there are several potential problems, which must be addressed. Segregation, effectively un-blending, occurs during flow of blends comprising particles with differing densities, sizes and shapes [30]. Segregation of such blends will occur during conveying and during flow into and out of hoppers. It will also occur in simple drum or tumble blenders. The segregation problem during blending can be overcome by moving to more vigorous devices but the action of these on filler pellets, particularly carbon black, must be considered. Agglomeration of carbon black into ‘super pellets’ several centimetres across has been observed in trough and orbital screw blenders while pellet attrition in blenders with high speed impellers may cause unacceptably high fines levels. In all three types of blender coating of carbon black onto metal surfaces can occur, building up substantial layers.

The severity and solution of the problems of segregation and of filler agglomeration/attrition will be specific to individual mixing systems and application. However, there are some general guidelines, which can be applied. The tendency to segregation is normally reduced if the rubber granule size is reduced, ideally to less than 1 mm [31]. It can be further reduced by minimisation of transport and storage between the blender and continuous mixer. Taken to a logical conclusion, direct coupling of a batch blender to a continuous mixing system via a metering device will minimise the opportunities for segregation. In such a system two blenders would be needed for alternate filling and feeding. As an alternative, sub-blends of ingredients with little tendency to segregate can be prepared separately and brought together by metered feeding into the continuous mixer entry point.

7.9.3 Continuous mixing – principles

Continuous mixers are required to perform four main functions: (1) compaction, (2) distributive mixing, (3) dispersive mixing and (4) micro-distributive mixing. Compaction is approximately equivalent to incorporation in batch mixing. It comprises reduction of the voids between blend particles and penetration of rubber into filler agglomerates, until the compound has a density close to that of the solid material. Compaction enables high stresses to be developed in the rubber compound and is an essential precursor to dispersive mixing.

Distributive mixing is needed to eliminate variations of composition due to imperfect blending or subsequent segregation. In this respect, it is also referred to as 'back mixing'. It also causes flow and smearing of the rubber particles, reducing the scale of segregation between ingredients further than is possible with blending. As with batch mixing, the efficiency of dispersive mixing is largely controlled by stress intensity. In contrast, dispersive mixing does not have to be combined with large-scale distributive mixing, substantial uniformity of composition having been achieved by this stage of the process. The term micro-distribution is used to describe homogenisation of rubber compound microstructure at the agglomerate and primary aggregate level, following agglomerate fracture.

The output rate of continuous mixers is dominated by limits on the temperature of the rubber compound. There are ample opportunities to design for lower specific mixing energy than is possible with batch mixing but this is offset to some extent by the continuous heat generation.

As with batch mixers, the cooling arrangements are crucial to performance.

7.9.4 Continuous mixers - examples

The machines described here are those, which have been demonstrated to be capable of converting a particulate feedstock to a finished rubber compound and include the Farrel Continuous Mixer (FCM), the Farrel MVX and the co-rotating twin-screw compounder.

Variants of the FCM are now produced by a number of machinery manufacturers and there are a number of companies, which manufacture twin-screw compounders. Both these machines are used widely for thermoplastics compounding and exploration of the latter for rubber compounding is a recent development.

The FCM design is derived from the tangential rotor internal mixer, as can be seen from Figure 7.20. It is operated in a partially full condition, as with internal mixers, to gain efficient distributive mixing and forced convection heat transfer. The amount of filling and residence time is controlled by separate adjustment of the feed rate and the output rate. In most machines the setting of a discharge door controls the output but a more precise control can be obtained by using a gear pump [32, 33]. Combined with rotor speed, these variables enable the mixing treatment to be varied over a wide range, limited

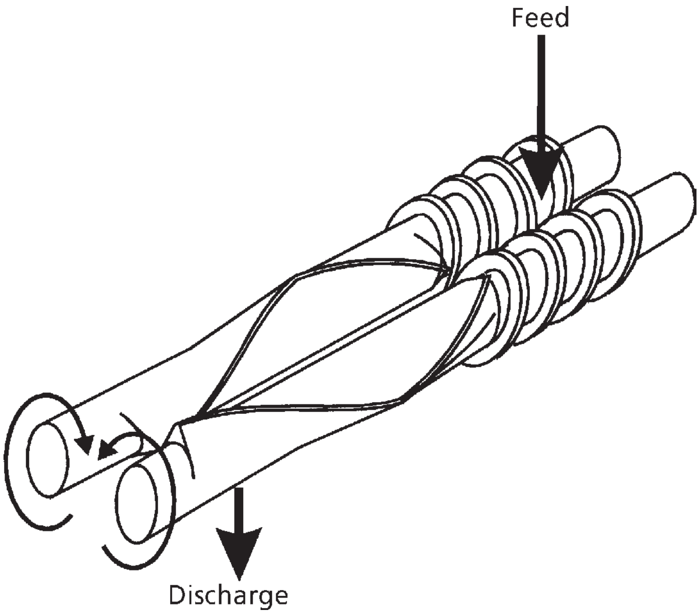

Figure 7.20 A typical screw and rotor arrangement for a Farrel Continuous Mixer

primarily by the temperature rise in the rubber compound. In contrast to internal mixer cycles the residence time is short, in the order of tens of seconds. Size 4 FCMs, with an output in the range 150 to 300 kg/h, have been used for a limited application in single pass mixing of rubber compound for general rubber products. Larger FCMs, typically the size 9 with an output in the range 1800 to 4500 kg/h, have been used for applications in the tyre industry, which depend on an internal mixer being used for the primary mixing stage [34].

The Farrel MVX, developed at Farrel-Bridge in the UK, is designed for single pass mixing and shaping of a wide range of rubber compounds. The initials MVX stand for mix-vent-extrude. As with the FCM, it is intended to be operated in a partially filled condition but the non-conveying rotor design demands force-feeding. Figure 7.21 shows a reciprocating ram, which pushes the particulate feedstock into the mixing zone and displaces material previously delivered along the rotors towards the exit. The close-coupled extruder controls removal of material from the mixing zone. The MVX has been shown to be capable of single-pass mixing of high-reinforced compounds without the generation of excessive rubber temperatures, suggesting that it is substantially more energy-efficient than the FCM [34]. Part of this advantage can be attributed to design for cooling but it is clear that reduction of energy input brought about by eliminating any ‘back mixing’ capability from the rotors (zero helix angle) makes a significant contribution.

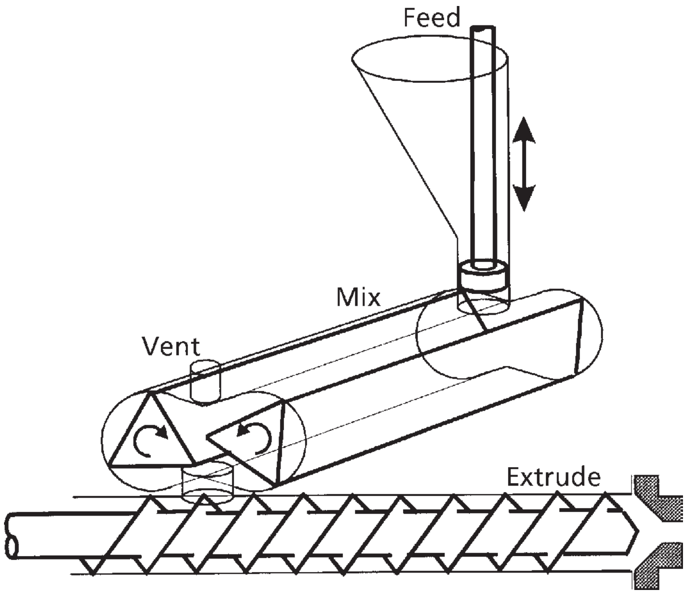

Figure 7.21 A schematic layout of the Farrel MVX (mix-vent-extrude) continuous mixer

In contrast, the positive and negative helix angles of the FCM rotors give substantial back mixing. In practical terms, variations in feedstock composition delivered into the MVX by the reciprocating ram will appear as variations in the mixed compound. Accurate control of feedstock composition is essential for consistent results.

Co-rotating, modular, twin screw compounders are produced by a number of machinery manufacturers, including Krupp, Berstorff, APV and Farrel. The main design features are interchangeable barrel and screw sections, as shown in Figure 7.22. These enable the machine configuration to be changed to accommodate a very wide range of compounds and mixing requirements. Screw configurations for rubber compounding normally comprise kneading blocks for dispersive and mixing separated by long conveying elements in which cooling is accomplished. Additionally, Berstorff use toothed discs for distributive mixing and Farrel have introduced a combined distributive and dispersive mixing section with a geometry derived from the FCM. Figure 7.22 shows a sequential addition configuration for single-pass mixing. High temperatures, typically 180 °C, are generated by the kneading blocks following the carbon black addition and the subsequent oil addition and conveying sections are used for cooling to achieve a viable temperature for the curative addition. The interest in these machines for rubber compounds has been brought about by improvements, which include increases in maximum torque levels and in the permissible free volume (fill factor) [35]. The former is required to accommodate the high viscosities of rubber compounds while the latter is important for efficient cooling. Berstorff have reported successful single-pass mixing of a 90 ML(1+4) EPDM compound, with an output rate of 500–600 kg/h and an exit temperature of 130–135 °C from a machine with a 90 mm screw diameter. It is mentioned that chilled cooling water circulation was necessary to achieve this result [35].

7.10 Acknowledgements

Staff in a number of companies provided information and diagrams vital for the practical processing content of this chapter and their help is gratefully acknowledged. The companies included Carter Bros Ltd, Chronos Richardson Ltd, Farrel-Shaw Ltd, Pomini-Techint SpA, Stephenson Process Chemicals Ltd and VMI EPE Holland BV.

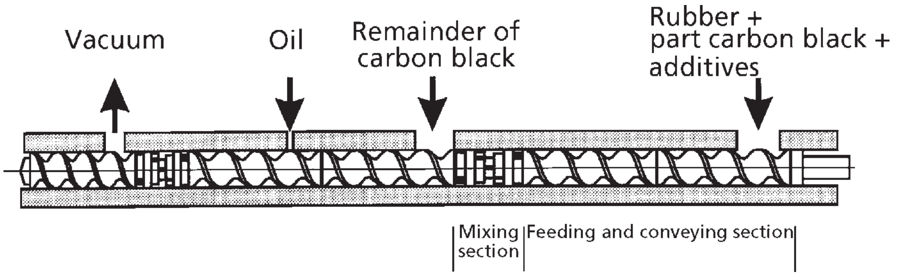

Figure 7.22 A modular twin-screw compounder configured for an EPDM rubber compound

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8

Durability of Engineering Products

R. Campion

8.1 Introduction

General design principles for rubber in engineering are discussed in Chapter 9 in this book. An extra aspect which increasingly needs consideration at the design stage is the durability of the rubber component, whether it be wholly elastomeric or of a composite nature. For dynamic applications, one basic form of assessing durability involves measurement of the rubber fatigue life. As shown in Chapter 9, this can be achieved by following a fracture mechanics approach, where a characteristic tearing energy versus crack growth rate log/log plot, obtained from simple geometry test pieces, describes the fracture behaviour of a particular rubber at one temperature: a numerical approach is then possible to apply this measurement to more complicated component geometries functioning dynamically in their applications, to give predictions of where and by how much actual cracks will grow in the components in service. Alternatively, an empirical approach, whereby the actual rubber component is machine-tested to failure, can be more applicable to some situations.

However, fatigue life is not the most critical parameter in assessing durability for some rubber components in service. Stress relaxation or creep behaviour might dominate, and effects of fluids (liquids or gases) will probably be of equal importance in applications where a rubber performs a containment role, for example. The intent of the present chapter is to examine the factors involved in fluid-related phenomena which can degrade rubber, basing the study mainly (although not absolutely) around a group of rubber components which depend on fluid resistance (and other factors) to function correctly – that is, seals, hoses and cables. Some case studies or appropriate diagnostic model tests will also be described.

In terms of fluid resistance at severe conditions, nowhere is there a greater need for durable elastomers (the rubbery class of polymers) than in oil and gas production. This is, annually, a multi-billion dollar business worldwide, involving much hardware (oil rigs, drilling rigs and ships, well and wellhead equipment, plus numerous ancillaries). From a materials viewpoint, the vast bulk used is metallic but, at the scale involved, the quantity of polymeric material employed is still significant - and the *role* of rubbers in the harsh environments associated with gas/oil extraction is critical if acceptable service lives are to be achieved by the various components. For example, long-lasting packing seals are essential to handling high-pressure crude oil at the very onset of production, right at the bottom of the oil well – see Figure 8.1. Numerous rubber types in components of all shapes and sizes are employed, often in locations where their replacement is essentially impossible when the well is on stream.

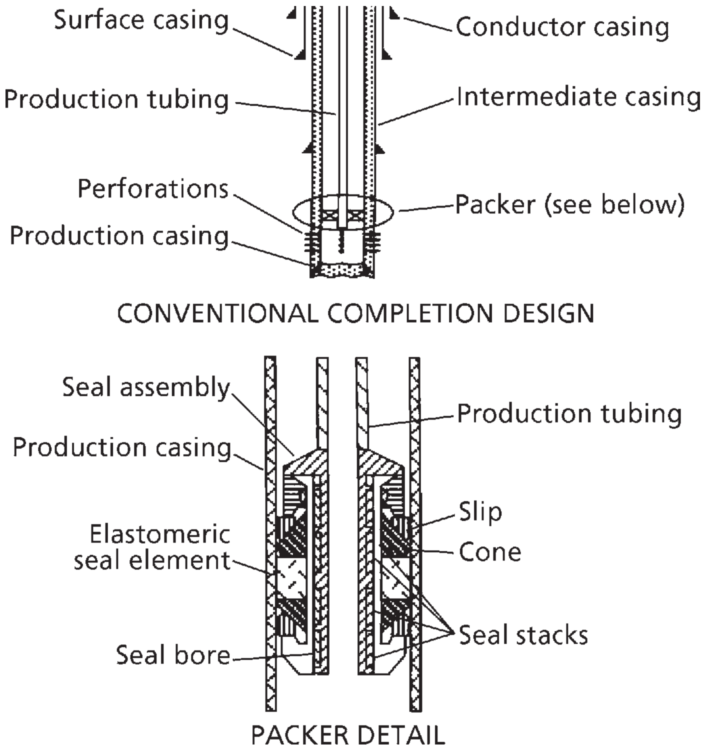

Figure 8.1 Traditional down hole well bore completion with close-up of packer seal assembly [21]

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Turning to other uses of rubbers during oil/gas production, multi-layered rubber/metal bonded laminates ('flex elements') are used to support the massive loads and accommodate the significant motions associated with tension leg oil platforms; 'flex joints', essentially of similar construction but with a hollow central core, perform a similar role in making connections along the pipeline whilst maintaining the flow of fluid. Rubber-based hoses or flexible pipes (the latter term being preferred for sub sea situations or when linking a sub sea location with the oil rig, etc) are used to transport oil (crude and refined) and gas, and related chemicals. Cables enable operational signals to be transmitted to working units such as valves. Elastomeric seals are employed throughout the whole system to keep fluids where they should be. The materials for these applications frequently need to resist different fluid types, and extremes of temperature and pressure – the correct selection of rubber type is of paramount importance.

To provide a background for examining the durability aspects of these classes of rubber component, some general manufacturing and design comments are given in Section 8.2.

8.2 Outline design factors of seals, hoses and cables

8.2.1 Seals

Elastomeric seals are often 100% rubber in constituency, but on occasions can be reinforced by bonded-on fabric, or can possess similarly attached spring metal pieces for energisation purposes when sealing. Normal moulding/curing techniques are employed during their manufacture, depending on size, detail of section profile, and preference of individual seal manufacturing companies. Extrusion might be used for small-section seals at the preparation stage, with multi-cavity compression moulding/curing to follow. Whichever technique is used by different organisations, the aim is the same – the production of flaw-free consistent products to as great an extent as possible, but also as rapidly as possible for sound commercial reasons. Small diameter seals are frequently cured for a few minutes only at temperatures of 180 °C or more.

For a seal to function correctly, it normally operates between two or three adjacent (but in themselves not leak proof where they join) rigid surfaces ('the housing') to form a complete boundary separating two different fluids or pressures. Two seal operation modes are shown conceptually in Figure 8.2. The left-hand sketch shows a rubber O-ring section: pressurised fluid acting from the left pushes the seal against the housing surface on the right, resulting in lateral seal deformation. This movement causes interference sealing if other nearby steel surfaces are contacted. In the right-hand sketch, the analogous situation is shown for the operation of a lip seal.

Seals range in size from the very large to the very small and, from the normal geometries of such arrangements, are nearly always circular (although some exceptions exist, e.g., gaskets for factory air conditioning trunking). It is not the intent in this chapter to discuss sealing mechanisms in detail, or describe the various profiles of seal section that have been developed over the years to accommodate a wide variety of applications; these seal design considerations have already been detailed – see, for example, Figures 8.3 and 8.4, and References 1 and 2.

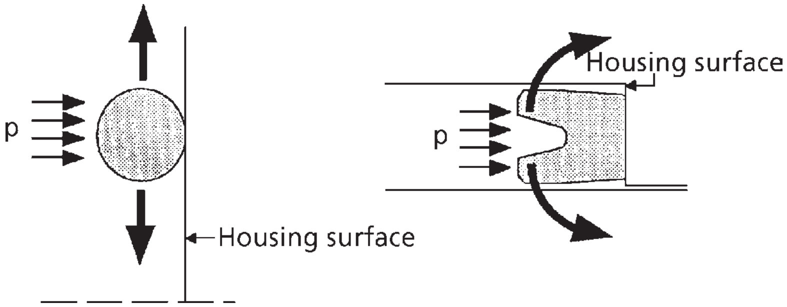

Figure 8.2 Two conceptual modes of operation of rubber seals [2]

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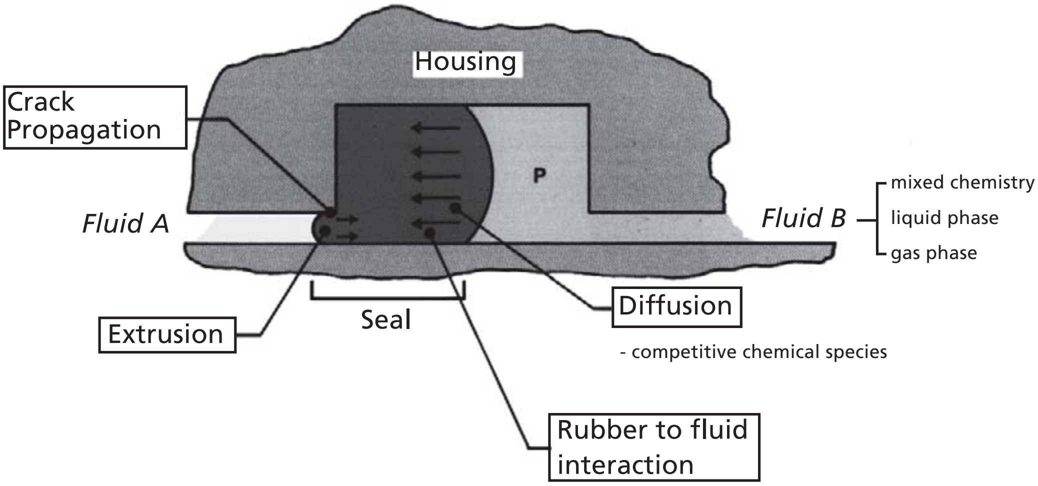

Figure 8.3 General arrangement for O-ring sealing

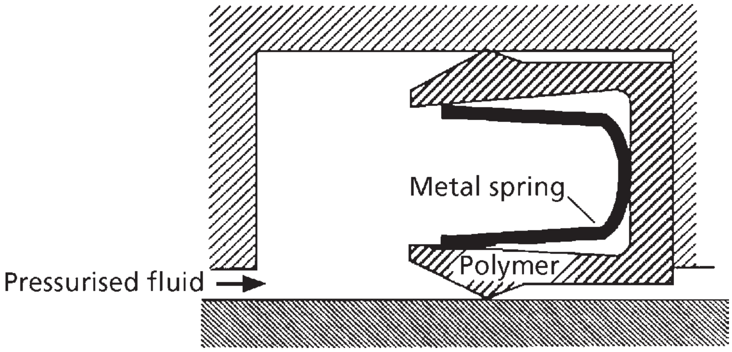

Figure 8.4 Lip seal operated by a mechanical spring, for use when the rubber is not very elastic or more commonly for a thermoplastic [2]

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It is more relevant to discuss how failure might happen. Fluid leakage (Figure 8.5) occurs if the sealing force against the housing ceases for any reason or if a crack is initiated: in that case, a hydrostatic fluid flow will commence.

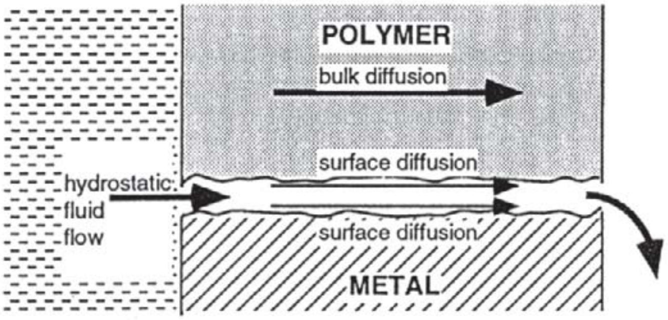

Figure 8.5 Three modes of fluid passage past a rubber seal

Another form of fluid transport across a seal is due to permeation, in which the step involving fluid dissolved within the rubber bulk is diffusion (see Section 8.3.3.2): in work involving equipment described in Section 8.6.1.1 and other high pressure gas permeation testing equipment (see Section 8.3.3.2), permeation rate is shown to be only approximately 1% of the leakage rate [3]. Figure 8.5 also indicates a possible 'surface diffusion' rate – probably negligible compared with the bulk diffusion on a surface area basis (and because extra time will be necessary to pressurise each of the numerous microscopic surface cavities between rubber and metal before the fluid continues by dissolving again back into the surface layer).

To illustrate the basic premise running throughout all seal designs – that the sealing force must be maintained throughout a seal's life – the sealing mode for an O-ring arrangement is used as an example (see Figure 8.3). In this case, a pre-compression is applied to the seal (by bolting the assembly together, due to the choice of housing dimensions) before the pressurised fluid is introduced. For an O-ring assembly, it turns out that, although the pressurised fluid brings about the deformation indicated in Figure 8.3, the actual sealing force is initially dominated by this pre-compression. Hence, for durability, in the first place, if the fluid is temporarily removed, this force should not diminish to zero by stress relaxation or thermal shrinkage, or the like. In the second place, cracks should not form, e.g., due to explosive decompression (Section 8.3.3.3) or to excessive extrusion (see Figure 8.6). Finally, as discussed later, these properties should not be affected deleteriously by interactions between the seal's rubber and the fluid being contained, and these interactions in themselves should not cause excessive amounts of other forms of rubber deterioration.

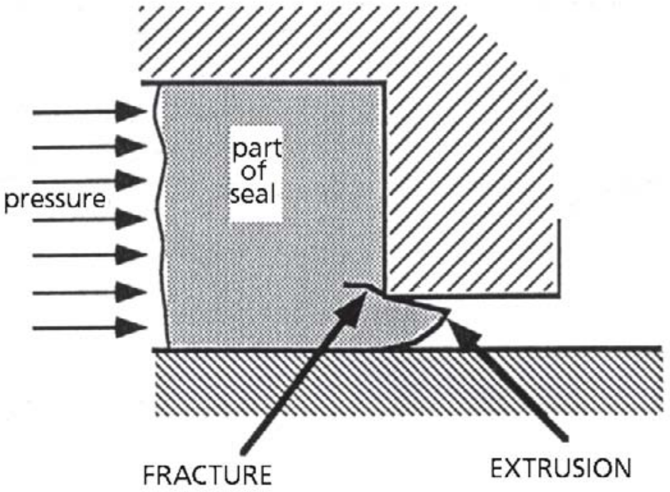

Figure 8.6 Extrusion of a seal leading to cracking [2]

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8.2.2 Hoses

Hoses are essentially reinforced rubber-based tubes used for transporting fluids, often at high pressures, and perhaps at elevated temperatures. They vary in size from the small and short, e.g., brake hoses, to the very large and long, e.g., floating hoses and flexible pipes for use offshore in oil production. In principle, all hoses follow a similar design pattern in that an unbroken inner tubular liner contains the fluid being transported, a series of contacting concentric reinforcing layers are then successively positioned outside the liner, on the outside a suitable cover is located, and suitable end-fittings are securely attached. In practice, the fine detail of these various components varies considerably, according to specific requirements.

Important parameters for the hose design include:

1. The lining material should resist the fluid across the service temperature range of the application.

2. The design must accommodate the fluid pressure specified plus an acceptable safety margin.

3. The cover should withstand any external fluids, buffeting, impacts, etc, envisaged for the application.

4. Points 1 to 3 should be maintained throughout all dynamic motions associated with the application.

5. Points 1 to 4 should be maintained despite any material ageing which might occur throughout the specified service life.

6. The design of end-fittings and their attachment to the main hose is of paramount importance.

Other requirements then arise implicitly from the above:

a. The number of reinforcing layers, and their detail, is strongly dependent on liner inner diameter.

b. Rubbers for resisting fluids well are not the best for cover compounds, lacking in mechanical property magnitudes. Hence the rubber layers in which the reinforcing wires, cords, braids or fabrics are embedded need to bridge sequentially the compatibility gap between cover and liner, all layers bonding together during cure.

For small hoses, the reinforcing layers often comprise braided wire filaments; for large hoses, the reinforcing layers will depend on thick wires/cords to withstand the pressure, but fabric based on thinner wires (perhaps 'rubberised' – calendered into a thin rubber sheet) can be necessary for use as the layer inside the thick wires, to share the loads and bridge the gaps between these wires. Attachment to the end-fittings can also utilise these wires – see Figure 8.7, which shows a short end-fitting axial section from a typical offshore oil transportation hose; the various hose layers are clearly visible, as are some geometrical features involved with clamping to the end-fitting.

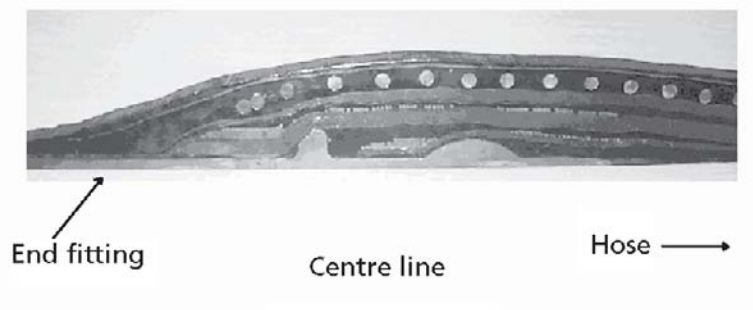

Figure 8.7 An axial section of an offshore hose end fitting

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Figure 8.8 Offshore hose used typically for loading/offloading tankers, and for dredging

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Figure 8.8 shows floating hoses (not too dissimilar in structure to the above) in operation at moderate pressures. In all cases, an important feature is the retention of dimensional stability when the hose is pressurised by the fluid being transported; this is achieved during manufacture by applying the reinforcing cords at their neutral braid angle (at approximately 54° to the axis when one complete spiral of cord is projected on to a flat surface) [4].

Manufacturing processes vary according to the size of hose being constructed [4]. Extrusion is often the preferred procedure for the liner, to give an unbroken tube in which to contain the fluid; however, for lower pressure service, other techniques can be applied. For large hoses, the building-up of the construction is performed on extended lathes, successive rubber layers being applied interdispersed with the reinforcing wires, etc. At certain points in the hose, small pieces of 'infill' rubber compound are accurately located to prevent rubber flow in an unwanted direction during the early stages of curing. Various consolidation procedures are applied at intervals. For small hoses, end-fittings are swaged on to the hose. Curing is often performed in autoclaves. Manufacturing of hoses, or at least large diameter ones, is a combination of highly technical fabrication performed mechanically and manual input following strict procedures.

Initial durability issues of hoses are covered by validation tests for bursting pressure and fatigue. Regarding property deterioration with service, the general principles discussed below apply, e.g., for chemical ageing. Stress relaxation will probably only be a concern near clamped/crimped wires at the end fitting. Gas permeation could lead to problems if certain gases permeating from the transported oil, (e.g., a $H_2S/CO_2/H_2$ mixture which can emanate from crude oil), reach metal reinforcements, to corrode them: designed vents can diminish this problem. The related problem of explosive decompression (see Section 8.3.3.3) needs to be avoided, by selection of a suitable explosive decompression-resistant formulation, as should disbondment of the liner, which can occur for similar reasons to those causing explosive decompression.

8.2.3 Cables

The technology of cables covers the full range of materials, from gases to solids, and employing metallics and non-metallics. Design aspects and descriptions for the many possible variations, and the properties involved – most of these being associated with electrical transmission – are included in references 5 to 7. Rubbers are considered mainly in their role as insulators and according to their temperature resistance; manufacturing factors are not included, but these are outlined in another publication, which focuses generally on rubber manufacturing technology [8]. Selection of rubbers used is greatly influenced by temperature resistance, with an important factor being the dielectric loss angle – if high, this increases heat build-up. EPM/EPDM rubbers are rated to 90 °C maximum continuous operating temperature [5, 8], butyl rubber to 85 °C [5], and silicone to 150 °C [5, 8]: however, special reinforcement braided layers may be required with the silicone rubber. Many factors of design and application are considered when selecting rubbers. In addition, the choice of some additives may require care, especially the effect of carbon black filler and its structure on the electrical conductivity of the rubber.

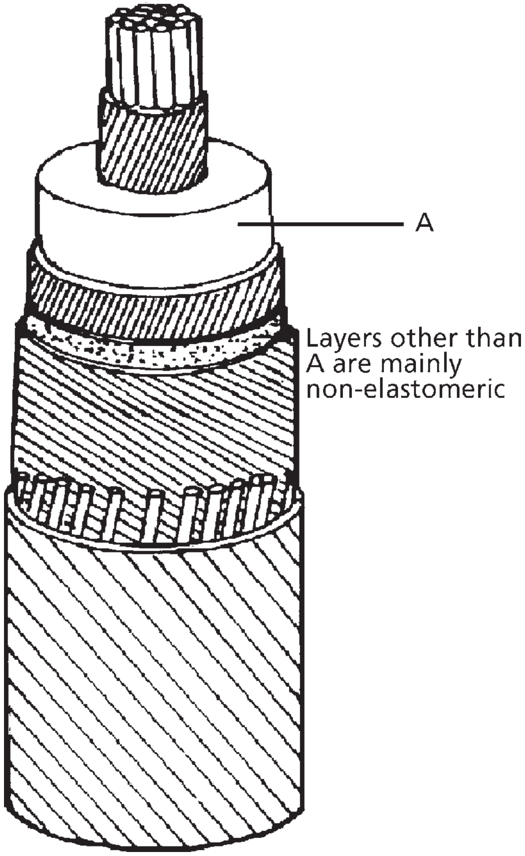

Figure 8.9 Schematic view of location of rubber layer (A) in a typical cable

Cables using rubbers as insulation and cover sheaths can be typified by the schematic drawing in Figure 8.9; here, a thick continuous layer of rubber (A) is shown as an extruded insulation. The extrusion processes require specialist techniques and equipment. Continuous vulcanisation extrusion with a curing tube attached to the extruder head die face is used to obtain the very long lengths of cable required for service applications which will link units located great distances apart. Three types of continuous vulcanisation extrusion are horizontal, catenary and vertical: the first of these methods is only used for cables with relatively small core diameters, as gravity otherwise causes the cable to touch the curing tube. The fine-scale details of the curing tube are considerable to obtain successfully extruded cured cables [8].

For a cable to function correctly, it should be able to withstand any fluids (including air) it contacts, just as applies for any other rubber components exposed to fluids in service. However, cables are also required to maintain electrical insulation throughout their lifetime; effects of electrical voltages (especially high ones) are clearly a primary consideration. Some applications require cables to function dynamically and so, once again, a fatigue aspect can apply.

8.3 Durability aspects

Different rubbers do not respond in the same way to factors such as applied stresses or strains, oscillations, or various fluid environments. Hence, for any application, the most suitable rubber, which will function as required for the lifetime of the service, needs to be selected – the rubber must be durable in its service environment. In practice, it is likely that some deterioration still occurs during the service, but at a rate slow enough to make the use of the component feasible. Hence, at the development stage, attempts are made to quantify the degree of durability in some way; appropriate methods are employed to make some sort of life assessment with regard to the component in the particular service.

It is intended herein to examine briefly examples from different component types from a life assessment viewpoint. To lead to this, it is useful to discuss factors involved when rubbers deteriorate in different situations and environments, and to define relevant key properties. In addition, as the term 'life assessment' implies that the material will ultimately fail, modes and definitions of possible failure require some comment. However, it may not always be possible to predict the time to ultimate failure, but instead the applied scientist or engineer might foretell from accelerated test observations a service time after which a key property will still be at an acceptable level.

Before enlarging on these points, it can be helpful to remind ourselves of the structural nature of the material under investigation.

8.3.1 The structural nature of rubbers

The elastomeric properties and fluid resistance of rubbers depend on the nature of their molecular structure. At normal temperatures, kinetic energy causes random motion amongst the closely packed entwined long molecular chains of rubbers, with chain portions and segments moving relatively rapidly and (for uncured material) whole molecules moving much more slowly. In addition, the application of forces to the rubber bulk will cause similar motions, but to a greater extent and in a more concerted fashion. The chemical crosslinks in cured rubber resist these wholesale motions (and impart elasticity). An obvious consequence of this structure is that a significant amount (perhaps in the order of 10%) of free space ('free volume') exists in an ever-changing pattern between the molecules, giving rise to the desirable flexible properties of rubbers. However, free volume also provides the physical means of entry of environmental fluids, and allows stress relaxation or creep – all less desirable occurrences with regard to the service life of rubbers.

8.3.2 General mechanical properties

To quantify material deterioration, clearly, changes in magnitude of relevant properties need to be measured; properties such as hardness, tensile strength (with associated moduli at various elongations, and elongation at break), tear strength, compression set and density, established in the rubber industry for many years [9, 10] are discussed in Chapter 10. But are these enough in themselves? It is perhaps a truism that the best method of assessing the service performance of an elastomeric article is to test the article itself but, for prediction purposes, model tests on the article which simulate its *modus operandi* and the likely service conditions provide the best means of making meaningful assessments of likely performance. However, these tests are often difficult to develop, time-consuming and costly to run. Hence relevant mechanical property tests can be employed to perform useful screening assessments to reduce the amount of subsequent testing using product-orientated tests. When applied to samples previously aged in hostile environments, data from these tests can contribute to life prediction techniques, especially if design of a product is made using a particular mechanical property, e.g., stiffness (modulus), to set limits.

8.3.3 Properties for long-term performance

8.3.3.1 Stress relaxation

If a rubber is held at constant deformation, the stress required to maintain the deformation decreases with time: this phenomenon is stress relaxation [11, 12], which can be expressed simply as loss in stress, divided by initial stress (often expressed as a percentage of the initial stress). The rate of stress relaxation will be the above quantity divided by time, or some function of time. Physical stress relaxation is proportional to log time. Any chemical changes to the rubber, e.g., oxidation-induced, can also change relaxation rate, but now proportionally to linear time. For an unpressurised elastomeric seal, if the sealing stress becomes zero, then the ability to seal may have finished (although in static systems any adhesion between seal and metal housing might allow sealing to continue for a while even then).

Stress relaxation is closely related to creep – that is the increase in deformation, which occurs when a rubber is held at constant stress. Another deformation term, 'extrusion', is also used in oilfield sealing and pipeline circles – not as a manufacturing term, but applying when high pressure fluid forces seal rubber into gaps in adjacent rigid support surfaces (see Figure 8.6, which also illustrates how a crack might then be initiated).

8.3.3.2 General effects of fluid environments

Although no rubber is completely immune to chemical and/or physico-chemical effects arising from contact with fluids, some rubbers provide considerable resistance. Organic liquids can weaken rubbers by physico-chemical means only (causing swelling), whereas corrosive liquids such as acids, alkalis, etc, attack rubber chemically. Different rubbers withstand such attacks to different extents. A highly swollen rubber is probably too weak to be of practical use, and chemical attack can cause further deterioration. In either case, weakening will be progressive. Excessive gas permeation might preclude a rubber for use as a hose liner, for instance. Rubber selection therefore needs to take into account the service fluid composition; general lists exist for many rubbers and other polymers showing levels of resistance to chemical attack by a variety of fluids [13, 14].

Fluid absorption by a rubber involves two physico-chemical processes. Gases and liquids dissolve into rubber surfaces (adsorb) and penetrate further by diffusion. The likelihood of a particular rubber absorbing large quantities of a low-viscosity liquid depends on thermodynamic considerations. A drive exists for a liquid and a rubber to mix if a negative free energy change (governed by enthalpic and entropic considerations) will take place during the mixing. Enthalpic considerations are largely influenced by solubility parameter, δ values, for liquid and rubber, where δ^2 in each case is the cohesive energy density – a measure of the energy of attractions between molecules. For instance, if δ values for a rubber and a low-viscosity solvent are within approximately 4.1 to 6.15 $\text{MPa}^{1/2}$ of each other, considerable swelling can occur. If the liquid is a moderately viscous oil, then this maximum swell reduces somewhat. Other 'structural' factors (crosslink density, T_g – associated with free volume, Section 8.3.1 – and filler content) can also diminish degree of swell by affecting the entropic contribution to the free energy equation.

Other factors may also apply. If water-swellable particulate fillers etc are present in a rubber, water absorption can increase, even when δ considerations indicate that the base rubber will not absorb water [13]. This might not happen until high temperatures are reached [15].

Regarding rate processes, to determine the diffusion coefficient, D, for a sheet sample of rubber immersed in liquid, simple weighing is used, whereas for gas exposures, permeation experiments are most suitable.

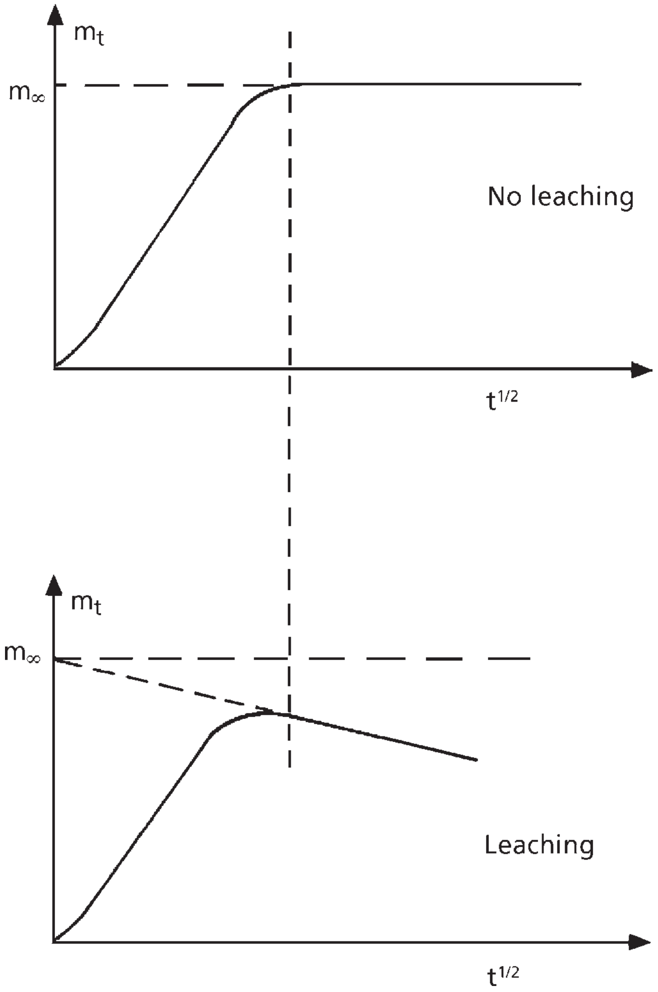

Figure 8.10 Schematic view of liquid absorption plots, with and without leaching. Conceptual plots of mass uptake m_t versus root time, showing equilibrium mass uptake m_∞ and possible leaching effects

- *Liquid diffusion*

The solution of Fick's Second Law of Diffusion [16, 17] for absorption measurements on sheet test pieces with appropriate boundary conditions to give an average value of D conveniently utilises:

$$0.5 = (2/h') (D_{av}t_{av}/\pi)^{1/2} \tag{1}$$

where 2h´ is thickness and t_{av} is the time for an increase in the rubber's mass of 50% of the final equilibrium value – see the schematic representation in Figure 8.10, upper plot. If the liquid causes a soluble species to leach out of the rubber with time, a plot such as the lower one in Figure 8.10 is obtained. Back-extrapolation will then show the true equilibrium mass uptake value but, to create a properly-corrected curve to obtain an accurate D_{av} value, a series of weighings is necessary on replicate test pieces exposed for different times, each test piece then being dried and re-weighed; the difference of each dried mass with the appropriate original unexposed mass leads to a plot of leached amount versus (root) time, which can be used to correct the original plot.

From the form of this equation, it can also be seen that resistance to swelling increases as the square of component thickness.

- *Gas permeation (especially at high pressures in sealing duties)*

Gas permeation relates to the molecular transport of gas right through a rubber membrane or other component. For certain sealing geometries, external constraints might effectively prevent gas-escape on the low-pressure side. Nevertheless, the stages in the ensuing gas absorption can be regarded as gas permeation without the final evaporation step; the processes involved are otherwise the same. Hence, gas permeation measurements can be employed to quantify solubility aspects in the rubber at required high pressure and (if appropriate) elevated temperature conditions.

In permeation [16, 17], gas first instantaneously adsorbs according to Henry's Law – concentration is proportional to applied pressure, the proportionality term being the solubility coefficient, s – and diffuses according to Fick's Laws – D (see above) again applying. From these expressions, for a membrane the equation for steady state permeation is derived:

$$(q/t) = QA.\Delta P/h \tag{2}$$

where q is the volume at STP of diffusing gas in time t, Q is the permeation coefficient (and equal to the product of D and s), h and A are sample thickness and area, and

$\Delta P = P_1 - P_2$ where P_1 and P_2 are the high and low pressures, respectively. Hence gas permeation is very dependent on applied gas pressure. This equation also applies to liquids with P referring to vapour pressure but, because vapour pressure is not very dependent on applied liquid pressure, permeation rate here is essentially pressure-independent.

Many examples of methods of measuring permeation rates have been described (summarised by Lomax [18 and 19 or 20]). For high-pressure gas permeation, equipment has been developed by MERL [21, 22], measurements being possible up to 103 MPa and 200 °C. Data have been acquired [23] to show, for instance, how similar permeation coefficients might result from either high-diffusion/low-concentration or high-concentration/low-diffusion systems. The same equipment, with an *in situ* thickness gauge, has indicated material changes, which can accompany the application of high-pressure gas to rubbers. Compaction (densification) initially occurs, followed for some chemically compatible rubber/high pressure-gas systems by swelling due to matrix-diffusant interactions, even at 103 MPa on occasions [21, 22, 24]. Both effects reduce Q.

- *Temperature effects*

Arrhenius-type plots (see later) apply to permeation, diffusion and solubility coefficients for both liquids and gases in elastomers [17].

8.3.3.3 Explosive decompression (a specific fracturing phenomenon when high pressure gas pressure is rapidly removed from around a rubber)

When pressurised gas is being sealed by elastomeric components, the possibility of failure by explosive decompression [23, 25, 26] should always be considered. With this failure mode, rapid loss of pressure causes blistering, splitting and/or swelling of the rubber. If the ruptures so induced in the components of a seal-stack cause a removal of its sealing ability, loss of production or safety can result, with considerable consequences in financial terms at least.

There are two main factors in explosive decompression:

1. Initial absorption of a sufficient quantity of gas at high pressure – quantified by high-pressure gas permeation tests.
2. Growth and rupture associated with flaws after rapid decompression from this pressure, involving material mechanical properties.

To resist firstly the growth of very small bubbles and secondly the eventual onset of fracturing, both modulus and tearing energy (or tear strength) must be maximized in practical elastomer formulations which bid to overcome explosive decompression when sealing. Those who develop recipes for rubber compounds know the difficulties in optimising both of these properties at the same state of cure. The general approach is the use of high molecular mass polymer, high loadings of small particle-size reinforcing filler and high levels of cross-linking – to align partially with theory above by optimising modulus. In one particular approach for hydrogenated acrylonitrile-butadiene rubber (HNBR), an attempt has been made to obtain good levels of both modulus and tear strength, by developing a 'biphasic single component elastomer' (BPSCE) [27] type with significantly advanced resistance to explosive decompression.

Constraints afforded by the surrounding walls, etc, of seal grooves or housings, perhaps with additional, stiffer, thermoplastic back-up rigs, assist resistance to explosive decompression.

8.3.3.4 Thermal effects

If a seal is subjected to temperature cycling during service, dimensional changes can lead to leakage, especially if sub-T_g temperatures are met. Compression set can be associated with such failures, and stress relaxation behaviour can be complex (see Section 8.6.3.1).

8.3.3.5 Chemical ageing (accelerated by application of stress)

Two basic forms of chemical ageing exist for rubbers – continuation of cure at elevated temperatures due to unstable cure systems, and exposure to hostile fluids (the latter occurring initially at the rubber surface, subsequently depending on diffusion to access the bulk unless surface cracking provides a more rapid route). For many situations, the fluid is air, with oxygen being the active species, and the process is merely termed 'thermal ageing'. As noted in Section 8.3.3.2, general lists exist showing the levels of resistance of various rubbers to different fluids, e.g., for air [13], and for other fluids [14].

In the oilfield industry, hostile fluids can include hydrogen sulphide (produced in some wells) and various amines and amides used as corrosion inhibitors, etc. The former can attack unsaturated sealing rubbers such as nitriles, so that use of hydrogenated nitrile rubbers and fluoroelastomers can be beneficial here. Some FKMs are prone to attack by amines at high temperatures, a process accelerated by application of stress (presumably the increase in stored energy also increasing chemical potential). A consequence of this attack can be surface cracking, the process then being an instance of environmental stress cracking (ESC); another example of this in the rubber industry is ozone cracking (which is now controlled well by use of suitable antidegradant additives).

8.3.3.6 Fatigue life

Approaches used regarding fatigue life are already outlined early in the Introduction, and the topic is discussed more fully in Chapter 9. However, it must be remembered that ageing effects can alter fatigue performance – tests should be conducted on appropriately aged samples as well as on unaged ones.

8.3.3.7 Electrical breakdown

Cables in service are clearly at risk of potential damage from the very high voltages to which they are subjected. A form of breakdown which EPDMs (and, indeed, other polymers such as crosslinked polyethylene) can exhibit is termed 'water treeing'; it occurs [5] when the cable is exposed to water in some form whilst its core is transmitting electricity. Some absorption takes place, although this may be against the thermal gradient induced by the electrical transmission – effects of the electric field may account for this. When sufficient water is present in the rubber to allow discharge, fine interlinked erosion channels are formed, taking the general form of trees.

Water trees increase in length with frequency and voltage of the electrical waveform, and time. Underlying mechanisms are manifold and not well understood; factors involved are thought [5] to include polymer morphology, internal stresses, material purity, ionic concentration of the water, ion penetration and polymer oxidation, all of which could affect the rate of water propagation through the rubber and thus, presumably, the ease of electrical discharge to the locality of the water.

In the absence of water trees, cables possess a limiting AC or DC current so-called 'breakdown stress', describing the maximum voltage that they can be safely associated with. The presence of water trees reduces the level of breakdown stresses, significantly on occasions.

8.4 Definitions of failure

Causes of rubber failure can be manifold, depending on application. Some are gradual and insidious, others can be more abrupt and unexpected. The most appropriate failure mode for a service should be identified beforehand; a decision is then required on what will constitute final failure. Possible modes include:

- Increase or decrease in stiffness (or modulus) to values outside design limits, e.g., for hoses, seals, automotive engine mounts etc, building mounts, bridge bearings, flex elements.
- Occurrence of surface cracks due to
  - initiation, perhaps affecting the stiffness factors in the item above
  - dynamic growth of service cracks to unacceptable limits, e.g., for flex elements, flex joints, cables, engine mounts and other under bonnet applications, drive shaft seals.
- Loss of sealing stress-by-stress relaxation (seals, end-fittings for hoses).
- Extrusion/creep of seal/hose lining into gap in surrounding supporting structure when transporting pressurised fuel.
- Weakening by excessive swelling when transporting or containing fluid (and effects on factors above).
- Electrically induced degradation (cables).
- General degradation (hoses, seals, mounts in extremely hostile fluids and/or at high temperatures).
- Excessive build-up of gas (oilfield) due to:
  - leakage (from factors above or from contraction due to temperature decrease)
  - permeation (inadequate design of seals, more likely a problem in high pressure flexible pipes).
- Formation of cracks/blisters in bulk, e.g., from explosive decompression, for oilfield seals, flex joints or due to thermal contractions within highly constrained bulky rubber articles.

8.5 Life assessment

The confidence held in any life assessment method will be influenced by the most likely type of failure mode involved, i.e., by whether failure occurs gradually and in a well-ordered way, or whether it occurs abruptly. For some applications, design criteria are used to set limits, the criteria being based on a property which will change with time for whatever reason: for these, residual life becomes zero after such a service period that one or the other limit is reached. Service life assessment from accelerated testing is ideally based on anticipating when this stage is reached. Some procedures are mentioned below but, before applying these approaches, the warning is necessary that such predictions assume no other failure mechanism becomes dominant instead. For instance, a rubber seal may be expected to have a 10 year life from a prediction based on stress relaxation and stiffness changes, but if it unexpectedly exposed to an explosive decompression situation, it could fail immediately: a risk assessment might be necessary on the likelihood of another failure type occurring. All factors must be considered and, if possible, the determining one identified.

At constant temperature, if laboratory testing can be performed for the full service life, then the response of a critical property, e.g., modulus, stiffness, for a rubber to, for instance, exposure to a particular fluid can be checked in full before the service application is started. However, in reality, frequently it is not possible to test to the full service duration at service temperature. Hence accelerated tests are required, using time alone (Section 8.6.1.1) or by other means instead.

The behaviour of properties such as stress relaxation, which follow well-established rules and involve (for the basic physical contribution) the logarithm of time, can be extrapolated with confidence to much beyond testing times - care only being required that the relative contributions of physical and chemical stress relaxation have been properly resolved. In addition, extrapolation of other properties is possible if a clear pattern is established for the property level (or its logarithm) against time, but sometimes-competing reactions cause some confusion in these patterns. This possibility exists because increase in temperature causes increase in reaction rates, so that a means of conducting laboratory testing at temperatures well above service temperature (provided no transition or degradation temperature is surpassed), thus shortening test time, provides the required accelerated testing (see Section 8.5.1).

8.5.1 Predictions

It has become an empirically established practice over recent years to apply the Arrhenius equation, derived from physical chemistry, to property changes. The equation has been applied to two general areas:

a. Chemical ageing effects on a mechanical property, where rate $k = A_o \exp(-E_a/RT)$

   where E_a is activation energy,

   R the gas constant,

T temperature (K),

A_o is a frequency factor.

b. Permeation, diffusion, solubility coefficients (linked by Q = D.s, see Section 8.3.3.2, so that all follow the Arrhenius type of relationship [17]); hence $C = C_o \exp(-E_a/RT)$, where the coefficient C = Q, D or S as appropriate and C_o is a proportionality constant.

The E_a/RT term is a statistically derived term, associated with the amount of reaction occurring (measured as concentrations) for (a), and to the probability governing the number of big enough holes (between molecules as they continually move kinetically) capable of accepting diffusing molecules of another species for (b).

For both chemical and diffusion-related situations, the expected linearity (gradient E_a/R) of plots of log k or log D against 1/T has been frequently observed. According to the 'statistical network theory' for elastomers [28], at any one temperature applied stress is directly proportional to crosslink density (XLD) plus another minor factor. Hence changes in stress on samples after ageing should reflect changes in XLD (a concentration), so that reaction rate k can be applied to any changes in a stress-related property, modulus, stiffness, etc., measured after ageing. Figure 8.11 shows schematically the sequence of mechanical property changes that might occur at three temperatures when a rubber is aged in a fluid: a relevant feature applying to each plot, e.g., maximum property level, or – beyond this – the point where property level again matches its original unaged value, is selected so that, at any of the temperatures, reciprocal time to that feature defines the rate.

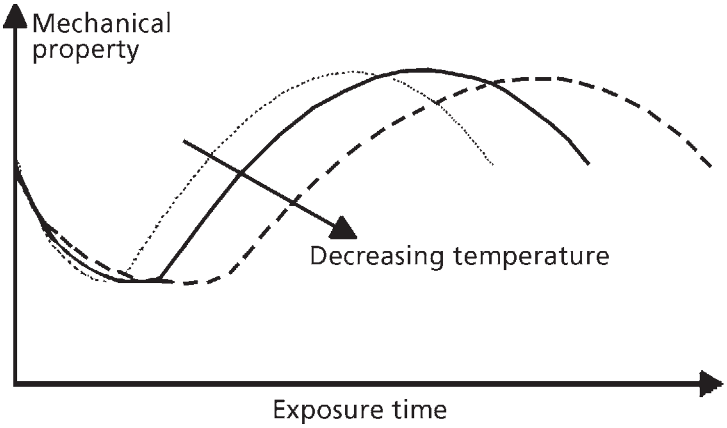

Figure 8.11 Effect of fluid exposures on property levels versus time, at three temperatures

Repeating this for the other temperatures, with a minimum of three but preferably (many) more, the Arrhenius plot is developed. Figure 8.12 is a schematic of how this might work, and how an extrapolation to service temperature could be carried out, based on actual time data for the property to reach its maximum.

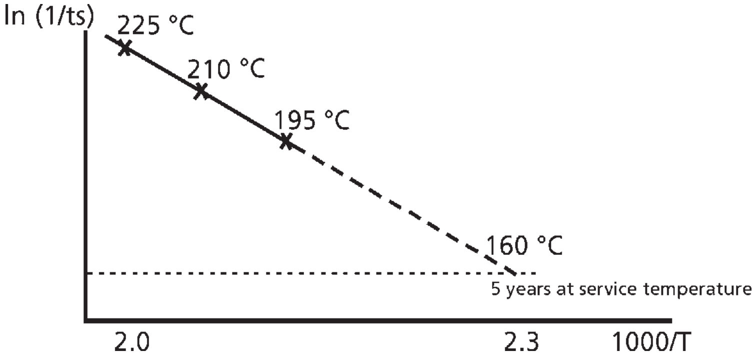

Figure 8.12 Extrapolation to service temperature using an Arrhenius plot

If other properties (tensile strength, tear strength) are dominated by stiffness aspects, they could also be treated in this way: however, if flaws dominate the measured value, clearly they will not be governed by stiffness factors so that the Arrhenius approach may not then apply.

Sometimes in these tests there is insufficient time at the lower exposure temperatures to reach the specified stiffness change. By making a significant number of measurements at shorter times, it may be possible to extrapolate the property/time plot until the specified stiffness change is reached, to give a predicted time which can then be used in an Arrhenius plot. Strictly, applying the stiffness-for-concentration argument to chemical kinetic equations, it is most appropriate to plot the logarithm of the property, rather than the actual property magnitude, against time when making the initial extrapolation; practically this makes little difference.

A key factor in making predictions on this basis is the confidence established on the gradients measured for the plots. Ideally, a significant number of ageing tests is required; however, this is frequently not possible, due to predictions being required in a short period of time for commercial reasons, etc. With a limited number of test data, approaches can be:

a. Establish the tolerance limits statistically, and then predict on a worst-case basis

b. Determine the underlying mechanism of degradation, and whether a suitable chemical analytical tool can follow this mechanism accurately (providing many data), to give a reliable E_a value. Then apply this E_a value to the few mechanical data obtained to make the extrapolation to service temperature.

Some workers apply more empirical approaches to making predictions from these types of plots, for those cases where linearity is not achieved. One way is to attempt to curve-fit statistically. For two-reaction systems, a method is to decide which portion of the plot is dominated by which reaction, effectively divide the plot accordingly, and treat each part as applying solely to its dominant reaction. It could be argued that, when taking purely empirical approaches, direct plots of rate of property change versus temperature would suffice as a basis for making extrapolations to service temperatures.

8.5.2 Permeation/diffusion etc at high pressures/different temperatures

Arrhenius-type plots of permeation, diffusion and solubility can be in the form of series of bands rather then a line, as both time and high pressure can cause values to decrease (by causing physical compaction of the polymer to occur, *cf* Section 8.3.3.2). This has been verified for rubbers at high gas pressures.

8.5.3 Factors which can override predictions

Attempts to predict when failure will occur due to other factors such as swelling require extra investigations, e.g., (loss of) stiffness might be used to quantify the swelling meaningfully, but less predictable factors such as extrusion might also intervene. Validation testing is required in such a case. Predicting the onset of explosive decompression damage can be even more difficult – with this property, care has to be taken not to ‘over-accelerate’ the effects. The usual approach is to design service-realistic housings for holding the seals during testing, and then to perform multicycle tests at somewhat higher pressures and temperatures than used in service to accelerate matters reasonably. Comparative tests made on this basis can then determine the best materials for the same application.

In addition, crack growth fatigue behaviour may have become altered during ageing, producing changes which may override other factors.

8.6 Case studies – components and models

The methodology appropriate to different applications will be governed by details of their service requirements. Some examples of different prediction approaches are given below.

8.6.1 Predictions by time alone

8.6.1.1 Reduction of cycle times

HPHT seal stacks for deep oil wells

An example of how time aspects alone can be used under realistic simulation conditions to allow prediction and partial verification of some rubber components follows. A high pressure-high temperature (HPHT) dynamic test facility for rubber chevron seals has been developed and constructed at MERL (Shepherd and others) [29], to provide the means of testing seal stacks under the very severe conditions which apply in the deepest oil wells.

In practice, a number of these seal stacks positioned together in a continuous line inside a polished bore in the production tube prevent escape of the HPHT fluids being produced; any escaping fluid would eventually reach the atmosphere. The situation is dynamic because thermal contractions/expansions of the tubing, or pressure fluctuations, can mean that the seals move considerable distances, with some reciprocations, inside the bore during their service life.

To simulate this action, the test rig comprises a full scale polished bore pressure vessel and a centrally-located reciprocating mandrel with two seal stack locations containing the high pressure zone between them. The test procedures set out to test the seal stacks

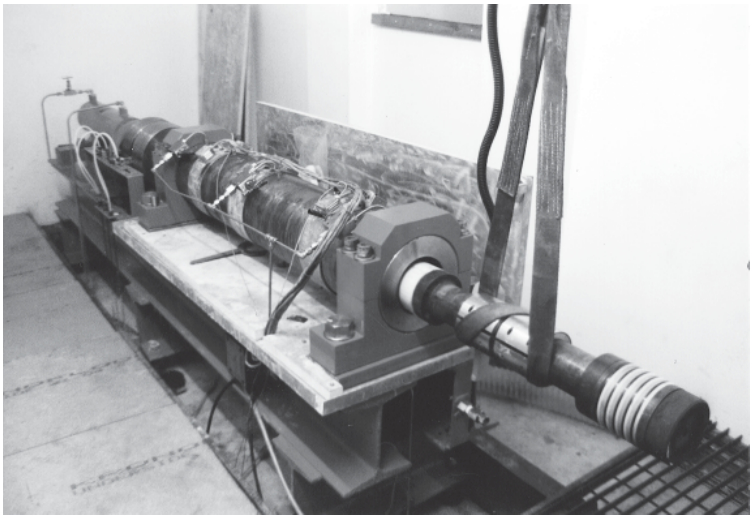

Figure 8.13 The HPHT dynamic seal stack testing facility at MERL

to the full operating conditions in terms of temperature, pressure and distance travelled. Test pressure is applied to one side of the seals only, any leakage being measured (as pressure-increase for gas or volume collected at the end of test for liquid) from the other side in a sealed volume, which starts at atmospheric, or a reduced, pressure. Figure 8.13 shows a general view of the main test vessel, which has operating limits of 250 °C and 100 MPa. The test rig is able to monitor continuous real-time behaviour of seals under a range of gas/liquid test fluids including hydrogen sulphide mixtures and with either absolute or differential pressures. Hence, the delay, which exists in service between expansion/contraction events, means that continuous real time laboratory testing at a reasonable testing cycle rate provides an acceleration over the service situation. Replicates of actual seals for use in service can be tested for leakage at the actual HPHT conditions whilst moving for the actual distance they will be forced to move in service. In addition, the tested seals can be examined fully afterwards. Some typical results are shown in Figures 8.14 and 8.15; in both cases, the test has been ended after 6,300 cycles, which represented a total seal movement equivalent to that estimated for service.

In Figure 8.14, absolute pressure was applied to the seal stack – in Figure 8.15, the pressure applied was a differential one. In both cases, the lower pressure did not increase at all during the test, showing that no leakage had occurred during this service related test.

The procedure described above represents a verification from a mechanical viewpoint alone, and leakage rates past the rubber seals can be used for predictive purposes. However, if any chemical ageing is involved, because in service this will obviously occur during static as well as dynamic periods, i.e., over the full service period, a

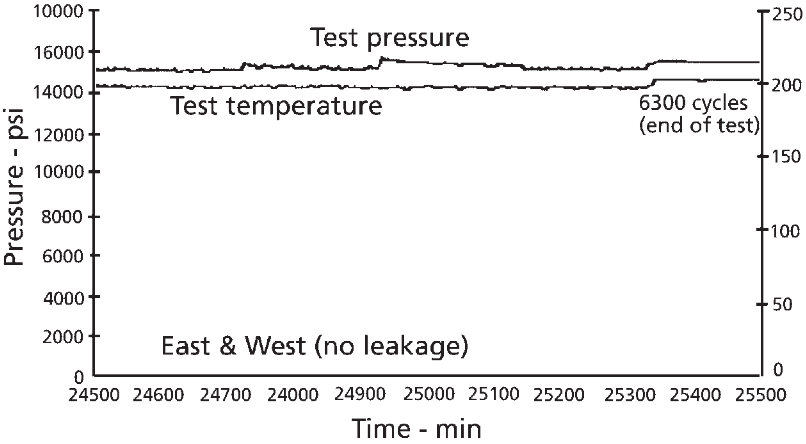

Figure 8.14 HPHT dynamic seal stack data, absolute pressure across seal

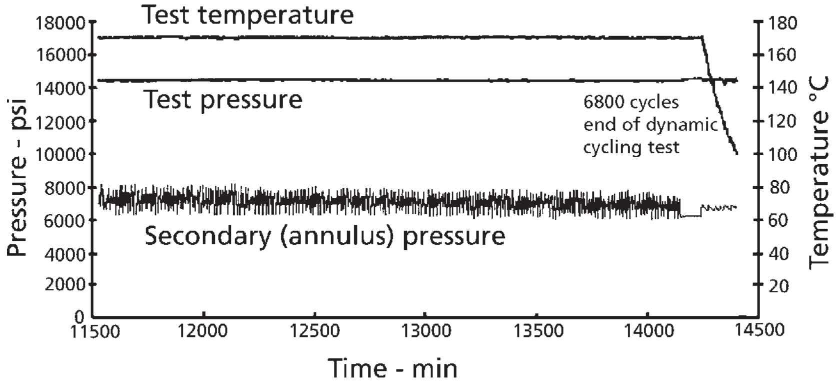

Figure 8.15 As Figure 8.14, but differential pressure across seal

means of accelerating the chemistry (compare Sections 8.5.1 and 8.6.3.2) would be necessary for the laboratory testing

Seals for air conditioning systems and fuel lines

Recently, push fit couplings have been developed for the fluid circuits of automobile air conditioning systems which are simpler to assemble. The couplings rely on elastomeric seals to contain the refrigerant. The long-term performance of these seals is therefore very important. Sealing force may be lost due to stress relaxation and set (physical and chemical ageing). With the passage of time, refrigerant will be absorbed and will permeate through the seal. The compatibility of the refrigerant and rate of diffusion through the rubber are important properties. In service the couplings will be subjected to heat and pressure cycles, and vibration, which may also lead to leakage.

An accelerated ageing test has been developed by Harrison [30] that includes the effect of vehicle vibration and thermal cycles using a novel test rig, which allows 12 couplings to be tested simultaneously. There is continuous monitoring of the amount of gas that leaks past the coupling seals. A test sequence has been developed which includes periods at high temperature followed by periods at sub zero temperatures. In most cases leakage occurs during the cooling cycle, when the seals are most vulnerable. This enables the performance of different coupling designs and sealing materials to be compared in the test laboratory.

Proposed chlorofluorocarbon (CFC) and hydrofluorocarbon (HFC) replacement refrigerant gases are likely to be less efficient which means that the climate control systems will be working harder, putting the seals in the system under increased strain. This underlines the importance of life assessment tests and accelerated tests, which will permit, say 10 years service conditions to be compressed into a few months. In addition, some proposed refrigerant gases are absorbed so readily by certain rubber types, that the pressure cycling due to normal operation of the climate control system may cause seal rupture due to explosive decompression. Ongoing tests will lead to selection of the most suitable rubbers for this application.

8.6.1.2 Creep

- *Building mount*

Creep is the increase in deformation, which occurs when a material is held at constant stress. At constant temperature, physical creep is *proportional* to log time. Any chemical changes to the rubber, e.g., oxidation-induced, can also change creep rate, but now proportionally to linear time. These characteristics lead to the possibility of making simple but reasonably accurate predictions for the static operational performance of some load-bearing elastomer components not subjected to significant temperature variations. As an example, a detailed case study has been made by Derham of a set of building mounts in operation over a period of 15 years [31]. Albany Court, a building in London, is supported by 13 bearings of a suitable load-bearing capacity. A main concern during construction was that creep in the rubber should be neither excessive nor variable, since this could cause uneven settlement and structural damage to the building. An extensive set of laboratory tests was performed to establish the creep rates for the type of rubber compound selected for use. The physical creep rate A was measured as 6.6 + 1.2% per decade and the chemical creep rate B was 0.47 + 0.2% per year. Using these laboratory values, calculations were performed for the full-scale building mount, which led to the estimate that creep in the rubber bearings would be not more than 6 mm after 100 years' service – an acceptable conclusion for the specified requirements.

Following construction, detailed on-site measurements of creep were made at regular intervals for up to 15 years. The results of these measurements within reasonable statistical limits have been in good agreement with the predictions from the laboratory experiments, and consistent with the prediction that creep would be less than 6 mm after 100 years' service. All the measurements taken were averages from readings on seven different bearings and all have been corrected for small seasonal fluctuations in temperature. The general condition of the rubber in all these bearings still appears to be excellent, and no replacement has proved necessary. There is thus good evidence that creep in rubber over long periods of time can be correctly predicted from short-term laboratory tests.

8.6.2 Effects of fluid environments

8.6.2.1 Liquids

As discussed in Section 8.3.3.2, no rubber is completely immune to physico-chemical effects arising from contact with fluids, causing swelling. However, on occasions the swelling is contained, and some can even be beneficial.

- *O-ring seal in housing*

On occasions, rubber seals are constrained in their housings to such an extent that they are unable to swell in a liquid to any great extent, even if the two possess similar δ values and the seals would have swollen excessively if left free in that liquid. Derham [32] has developed a stress relaxometer designed specifically to measure for an O-ring the outward force applying to the housing surface as a consequence. The basic arrangement is shown schematically in Figure 8.16; in reality, the whole is mounted in a rigid steel multi-column structure, temperature is controlled to a fine degree, and stresses are measured on a strain gauge system.

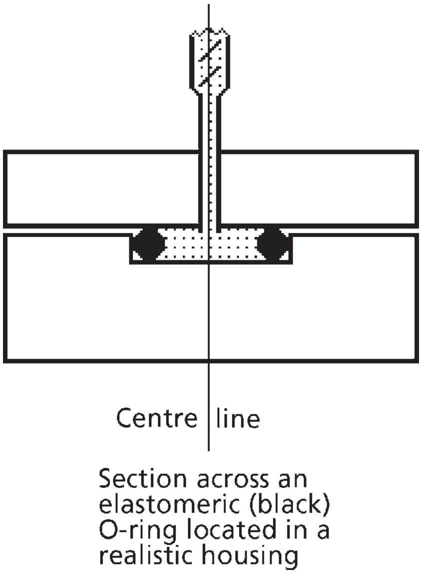

Figure 8.16 Arrangement for realistic stress relaxation testing in a liquid environment

Stress relaxation is the decrease in stress, which occurs if a rubber is held at constant deformation. As with the related phenomenon creep, at constant temperature physical stress relaxation is proportional to log time, and chemical stress relaxation to actual time. In one test [32] at 23 °C, the liquid was a 90/10 vol/vol mixture of *iso*-octane and toluene, so that effects were only physical in nature. The results obtained are shown in Figure 8.17. After the expected log/linear slope for the initial dry period, the addition of the solvent caused a doubling of the stress; the scale of this increase has been discussed [32].

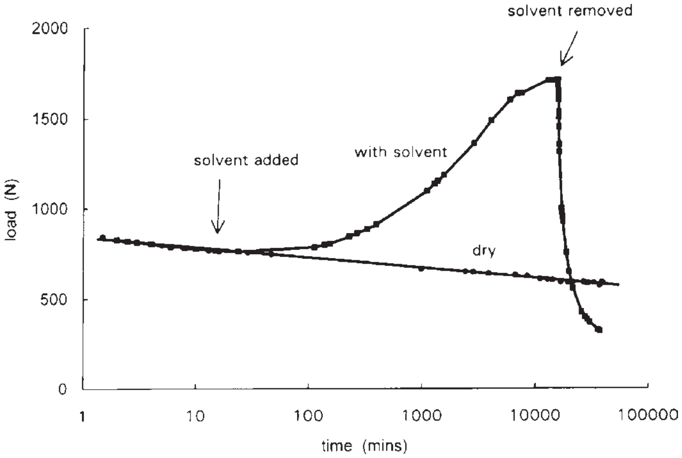

Figure 8.17 Effect of constrained liquid absorption on stress relaxation

Interestingly, removal of the solvent with a syringe plus air-drying reversed the phenomenon even more rapidly. In practice, the swelling effect can be used to combat relaxation and maintain sealing, but predictions are likely to be empirical, and difficult. Moreover, excessive liquid absorption will weaken the rubber, and might lead to extrusion through the gap being sealed if high liquid pressures are being employed.

Figure 8.18 Pressure hoses (and assembly items)

- *Multi-layered hoses*

The inner liner of a multi-layered hose carrying liquids protects the outer, load-carrying, layers, but the protection is on a kinetic, not permanent, basis. For a hose of the type shown in Figure 8.18, the liner was chloroprene rubber (CR) and the cover natural rubber (NR). In tests on samples of these rubbers, at 100 °C and 35 MPa, using the MERL high pressure permeation equipment, in 24 hours oil passed through the CR (which did not swell) into the NR, to swell the latter excessively (Figure 8.19). The reason is due to the chemical potential involved.

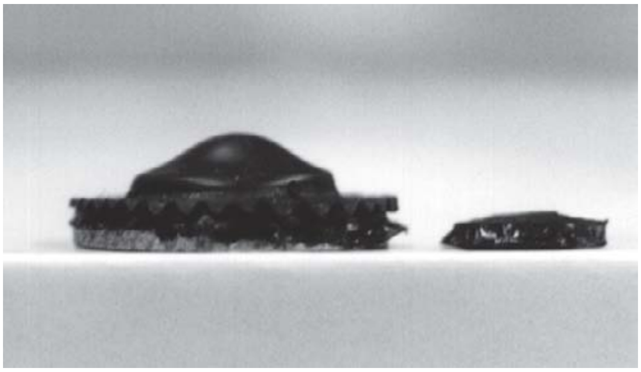

Figure 8.19 Samples after high pressure oil permeation testing – NR (left) and CR; oil contact via CR only

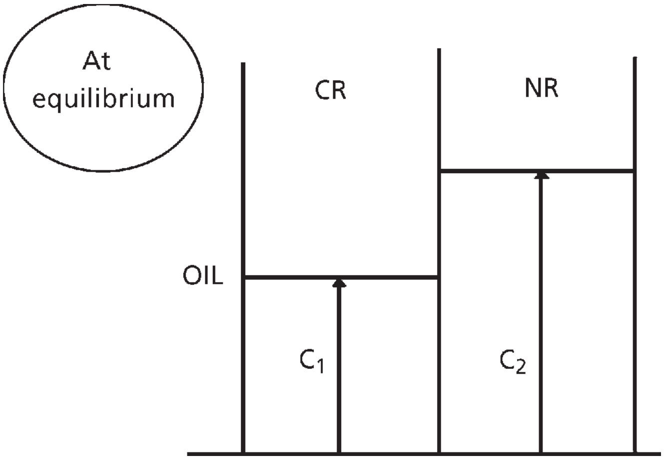

Figure 8.20 Schematic view of equilibrium concentrations of oil in NR and CR

Considering the schematic situation shown in Figure 8.20 to help explain the observations above, the two columns represent Sections of CR and NR sheets in contact; if the interface between the rubbers consists of a thin impermeable membrane, and the whole is immersed as a unit into test oil, the rubbers will absorb independently of each other, and the concentrations absorbed at equilibrium will be as shown, i.e., C_2 (NR) > C_1 (CR). At this condition, the chemical potential of the oil is at the same level whether the oil is outside the rubbers or within either of them – there is a balance of chemical potential across the whole system. This chemical potential level, and hence these concentrations, will be achieved whenever equilibrium is reached, whatever the absorption route employed by the oil. For new samples, if the impermeable membrane is removed so that direct contact is now made between the two rubbers, and the oil is now made to contact the left hand (CR) surface only, we have the hose situation – oil can only reach the NR via the CR; nevertheless, when equilibrium is achieved, the same values C_1 and C_2 will again apply. However, the kinetics for the two situations discussed will be very different, the former route being much the faster. Hence rubbers for hose liners are chosen which will not allow the oil (or appropriate liquid) to permeate into the cover to any significant degree during the anticipated service life of the hose (a more oil-resistant rubber such as NBR (nitrile) might well be selected): the thickness of liner and the rubber layers between liner and cover will also be a factor here. To quantify how much might be allowed into the cover, clearly, amounts corresponding to leakage right through the cover are completely unacceptable; a more realistic definition would be made around the extent of weakening due to absorbed liquid that can be tolerated by the cover in its application.

8.6.3 Effects of temperature on predictions

8.6.3.1 Transient effects of temperature on sealing force

- *Elastomer seals*

A compressed elastomeric seal will lose sealing force when the temperature is reduced due to thermal contraction and thermodynamic effects [32]. Many seals have to accept changes in temperature during service. Taking the example of a simple rubber O-ring seal, two factors reduce the sealing force when the temperature is lowered. The first is due to thermal contraction of the seal, and the second is a thermodynamic effect whereby theoretically the stress in a strained rubber is a direct function of absolute temperature. From the moment of its installation, a compressed seal is also losing sealing force due to stress relaxation; hence it is easy to appreciate that a further reduction in sealing force due to a decrease in temperature may lead to leakage.

Derham has analysed the situation as follows. The coefficient of linear thermal expansion (or contraction) is typically 2 x 10^{-4} K^{-1} for a rubber, whereas the equivalent coefficient for steel (the usual housing material) is 1.2 x 10^{-5} K^{-1}. This means that an elastomeric seal will contract several times more than it's housing when the temperature is lowered. Because the stress distribution in an O-ring is complex, i.e., the stress versus strain curve is non-linear; it is not straightforward to calculate the reduction in sealing force, which will accompany thermal contraction. The best possible theoretical calculation will underestimate the reduction in force, which actually occurs. The tests carried out to give this conclusion are detailed elsewhere [32], and are only given in outline here.

In order to eliminate complications from physical stress relaxation effects, which have their highest rate in the early stages after compression of a seal, some temperature cycling tests were carried out using the arrangement shown in Figure 8.16, but with no liquid. These were performed on FKM seals, which had already been compressed for at least two months at 80 °C, the testing stage illustrated at the left hand side of Figure 8.21 for one such test. The O-ring here was then subjected to temperature cycling between 80 °C and ambient (23 °C) with in-situ sealing force measurement.

Taking account of both thermal contraction and the thermodynamic effect, it was calculated that the sealing force should theoretically fall by 27% when the temperature was reduced and, of course, rise by 27% when the temperature was again raised. The change in sealing force measured experimentally (see Figure 8.21) was essentially reversible as expected, but was 50% – nearly double that predicted theoretically.

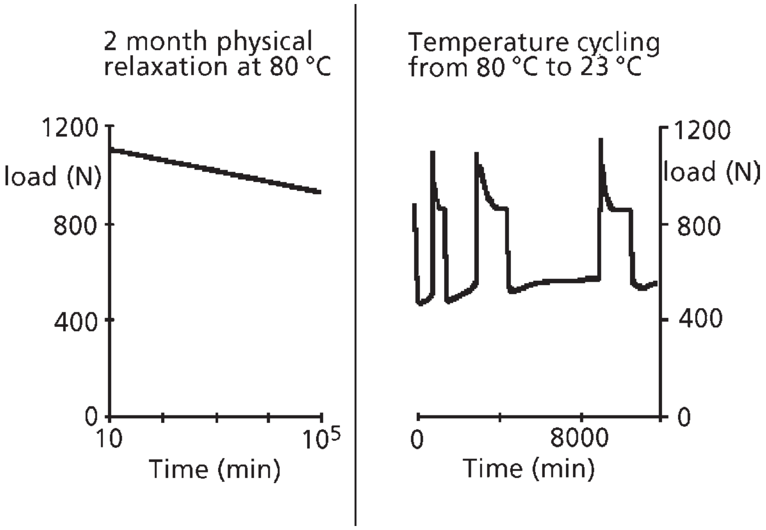

Figure 8.21 Temperature-induced changes in stress relaxation rate

The explanation for why the actual decrease in sealing force is so much greater than that predicted theoretically is believed to be associated with compression set [32], in that a rubber O-ring which has suffered compression set will have a stiffer stress/strain characteristic than a new O-ring. Therefore a small change in strain, brought about by contraction due to a temperature drop, will have a proportionately larger effect on the stress in an O-ring, which has been compressed for some time than it will have on an otherwise identical new O-ring. In effect, the 'shape factor' of the seal has increased due to compression set.

Clearly, in the absence thus far of adequate theory to form the basis of prediction of sealing force retention with time when variable temperatures are involved, a considerable safety factor must be applied, for instance, by applying a high initial force. Potential problems with this approach could be the initiation of surface cracks at some stage due to the high energies formed at any bulging surfaces, and the possibility of increased fluid absorption due to the stresses involved (see below).

8.6.3.2 Chemical ageing

TFE/TFP seals

Figure 8.11, already used in Section 8.5.1 to describe the Arrhenius approach for chemical ageing, shows schematically the sequence of mechanical property changes that occurred at three temperatures when elastomeric copolymers of tetrofluoroethylene and tetrafluoropropylene (TFE/TFP) replicate seals were aged in a service-realistic hostile fluid. Figure 8.12 is a schematic of how an extrapolation to service temperature was carried out.

8.6.3.3 Stress accelerated ageing

Some FKMs are prone to attack by amines at high temperatures, a process accelerated by application of stress (presumably the increase in stored energy also increasing chemical potential). In an examination of this effect [15], competing processes of degradation due to hot water (via the metal oxide additives) and crosslinking (via dehydrofluorination) were involved. Tensile modulus measurements on test pieces previously aged (some stressed, some unstressed) in aqueous amine solution at three temperatures for various times were made; at each temperature, rates of modulus decrease were then obtained, which were in turn plotted against temperature – see Figure 8.22. The added strain increased rate for the chemical crosslinking reaction rather than the (probably physico-chemical) degradation process.

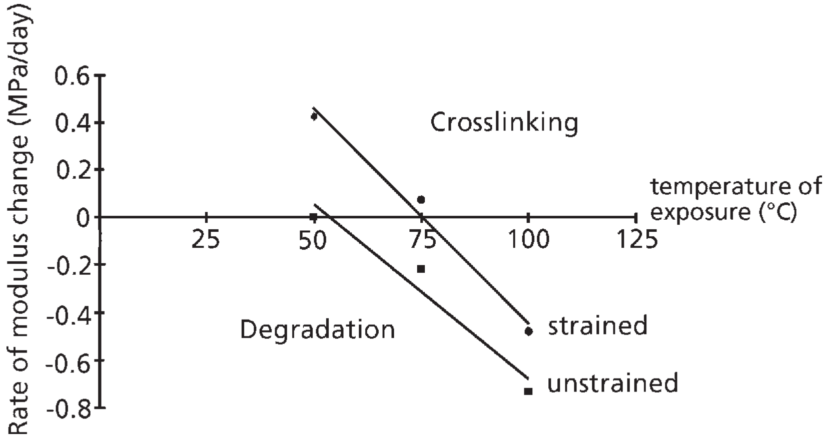

Figure 8.22 FKM: effect of stress on ageing mechanism balance

Conclusion

Although many deterioration processes exist by which the durability of rubber components can be limited, an even wider range of rubbers is available. For most applications, one or more types of rubber exist to meet requirements of durability, especially if associated with correct design for the service. However, careful testing and application of life assessment methods are necessary to be confident that required service lifetimes would be met.

Acknowledgements

The author thanks MERL colleagues Messrs C. J. Derham, G. J. Morgan, R. Shepherd and C. Harrison, and Dr A. Stevenson, who have contributed significantly to the development and validation of some methods discussed herein.

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9

Engineering with Elastomers

A. Stevenson

9.1 Introduction

Elastomers have been used as engineering materials since the 1850s. Natural rubber was used in energy absorbing rings in rail buffers from 1850 and as load bearing pads supporting a railway viaduct constructed in 1890 in Melbourne, Australia. The use of elastomeric components often accompanies greater sophistication in engineering design and enables compliance and flexibility to be introduced in a controlled and generally failsafe manner. For example the trend towards longer bridge spans and closer tolerance designs has increased the need for reliable and maintenance free bridge bearings. Elastomeric bridge bearings have now become the preferred solution in many parts of the world. The earthquake protection of buildings has been implemented using a compliant foundation system with elastomeric bearings isolating both the building and its contents from seismic disturbances. Offshore oil platform design has evolved from rigid towers of steel and concrete to compliant structures which are more suitable for deep water production. Compliant structures rely on elastomeric flexible joints as an intrinsic part of the structural design. Elastomers in sealing systems are essential to oil and gas pipe and valve systems. The ride comfort and safety of modern automobiles, trucks and buses depend on suspension systems which often use a large number of rubber components of complex design. Modern aircraft, helicopters and the space shuttle all use elastomer based components in key locations where the consequences of failure would be catastrophic.

This chapter reviews the basic principles for engineering design with elastomeric materials.

What makes elastomers unique materials for engineering purposes? They combine a very low Young's modulus with a bulk modulus which is about two thousand times greater and with an ability to deform elastically by several hundred percent before failure. Large deformations occur because of a long chain molecular structure which forms a network able to respond to deformation by changes in chain configuration instead of the stretching of molecular bonds (as occurs in a normal rigid solid). Rubber is thus highly extensible under modes of deformation which do not constrain it hydrostatically, but much less so when hydrostatic compression is involved since this causes direct straining of the molecular bonds. It is therefore possible to design a component with no moving parts but very different stiffnesses in different directions.

Raw rubber would in most cases be relatively unstable and tend to flow under the action of a force at room temperature. For engineering applications therefore it is crosslinked (or vulcanised). This process involves mixing with a chemical, e.g., sulphur, able to promote crosslinking between the molecular chains under the action of heat and pressure. Rubber components are thus normally manufactured by means of a cure process in a metal mould. The resulting material can be stable over a wide range of temperatures, generally within the limits -60 to +200 °C, although some special purpose elastomers can function outside this range. The Young's modulus of vulcanised rubber is usually between about 1 and 10 MPa. Tensile strength is normally between 10 and 50 MPa, with elongations up to 1000% possible, without rupture. Most types of rubber used for engineering applications incorporate carbon black filler when the maximum elongation at break is usually less than 500%. Fillers may be 'reinforcing' and improve tear strength, abrasion resistance and tensile strength of the cured rubber as well as increasing the elastic modulus. This is usually accompanied by an increase in hysteresis and creep. The finer grades of carbon black are particularly effective reinforcing fillers. Fillers can also be 'inert' and have little effect on strength with only moderate effect on modulus, hysteresis or creep. 'Soft' fillers can also be used as in oil extension, which reduces the amount of rubber required while having a slight weakening effect and increasing hysteresis.

9.2 Design equations – static force/deflection behaviour

Most rubber engineering components incorporate rubber bonded to one or more layers of metal for reinforcing or fixing purposes. This prevents slippage at load bearing surfaces and ensures reliable load/deflection characteristics. The standard design equations assume no slip at load carrying surfaces. Although the equations presented are not exact, they should give reasonable approximations in most cases. An accuracy at the initial design stage of 15% is normally adequate as manufacturing tolerances can preclude greater precision. Shear modulus is used as the basis of the design equations in this chapter and is inherently more accurate and reliable than hardness or tensile modulus.

9.2.1 Shear

When a shear force is applied to a flat bonded rubber layer, the principal effect is simple shear deformation. This is shown in the upper part of Figure 9.1.

Shear stiffness is given by:

$$K_1 = F/x = GA/t$$

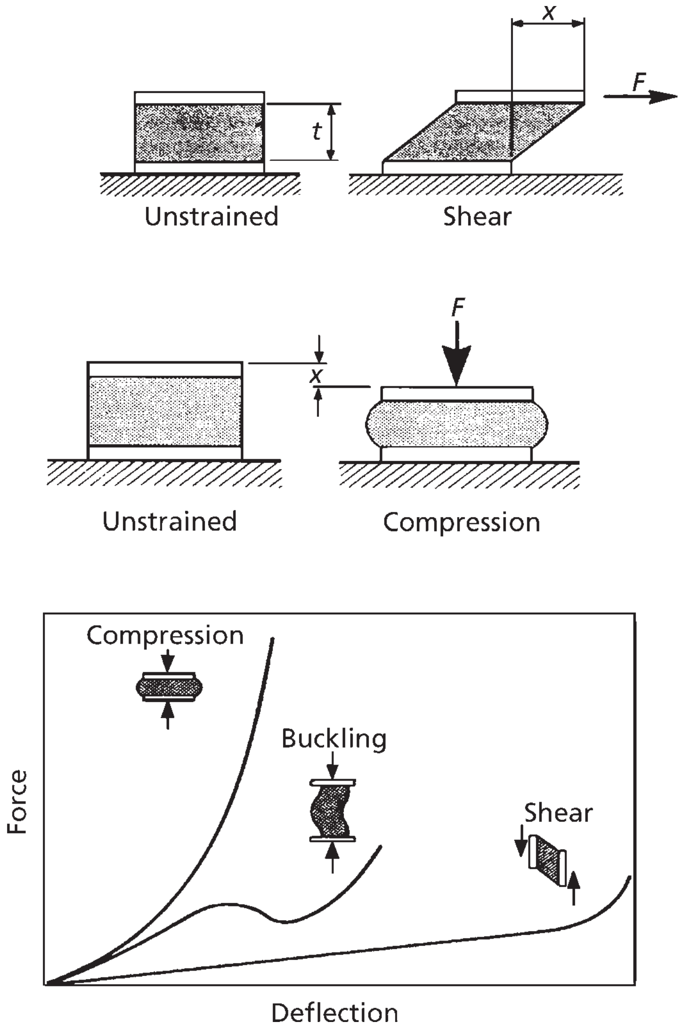


Figure 9.1 Shear and compression modes of deformation

where A is the loaded area and t is the rubber layer thickness;

F is the applied force and x is shear deflection;

Shear stress, $q = F/A$; Shear strain, $e_s = x/t$.

For a laminated unit with *n* rubber layers separated by bonded rigid plates, this becomes:

$K_1 = GA/nt$

The incorporation of intermediate metal plates into a block of rubber does not affect the shear stiffness, which depends not on shape, but only on the total rubber thickness, nt.

The shear mode of deformation is the most linear of all of the modes of deformation and is usually used as the basis for engineering calculations. The lower part of Figure 9.1 shows typical force/deflection behaviour in shear. The shear modulus, G in this region, is approximately one-third of the Young's modulus, E, the value expected from classical elasticity theory.

9.2.1.1 Hardness

Hardness is widely used as a quality control test in the rubber industry but is not generally reliable as a means of determining force-deflection behaviour for engineering components. Readings are usually quoted either in International Rubber Hardness Degrees (IRHD) or on the Shore Durometer A scale, which are approximately the same. The scales are non-linear in both cases, reading from 1 to 100. Hardness measurements are subject to considerable uncertainty of at least ± 1.5 degrees and often ± 5 degrees in practice. Hardness cannot be used directly in design calculations and relates only approximately to shear modulus.

9.2.1.2 Second order couples

When a shear force is applied to a flat laminated bearing, the shear force reactions will generate a couple which tends to rotate any intermediate bonded metal plates. If a normal (compressive) force also acts then there is an additional couple due to its now being off-centre. For each intermediate plate, the horizontal component of shear force is balanced by an equal and opposite reaction from the rubber. Since force is transmitted uniformly within each individual layer, the horizontal component of shear force will be equal through all of the layers. If all intermediate plates are of equal area, then equal forces will lead to equal stresses, and if each rubber layer is of equal modulus, this will lead to equal shear strains. There will also be a contribution to elastomer strain from the tilting of the intermediate plates. If, however, the tilting stiffness of each layer is high enough, then this contribution will be small. The resultant couple on the centre plate(s) will also be balanced at equilibrium. Such considerations determine the stability criteria for laminated bearings as these twisting couples can be sufficient to cause the whole bearing to become unstable.

9.2.2 Compression

9.2.2.1 Shape factor

The stiffness of rubber in compression depends on the shape factor, S defined by:

S = Loaded Area/Force Free Area;

For a circular block of thickness t, $S = r/2t$

Uniaxal compression of a rubber layer whose loaded areas are constrained laterally, e.g., by bonding, produces a mixture of hydrostatic compression (at sufficiently high shape factors) towards the centre and shear strain distributions which increase towards the free edges. This causes the rubber to bulge at the force free areas as shown in Figure 9.1. It has been shown [1] that to a first approximation there is a parabolic distribution of shear strains which are at a maximum at the bond edge of the force free region. From this the following dependence of compression modulus on shape factor can be derived [1]:

$$E_C = G(3 + CS^2)$$

where G is the small strain shear modulus of the rubber and C is a geometrical factor which depends on shape. Two extreme values for C are, for a plane circular disc, $C = 6$ and for a long thin strip or annulus, $C = 4$. This equation provides a good approximation for E_1 for shape factors above about 0.5 and below about 10.

For most modes of deformation and low shape factors rubber may be considered effectively incompressible. Its Poisson's ratio is generally considered to be about 0.499. For high shape factors, e.g., above 10, the effect of bulk compression needs to be included. This may be done by considering the strain in the elastomer arising from changes in molecular configuration and the strain arising from bulk compression to occur in parallel.

Thus the total compression modulus is given by:

$$E_t = (1/E_c + 1/B)^{-1}$$

where B is the bulk modulus of the rubber.

As the shape factor increases, the total compression modulus E_t, increases towards the bulk modulus of the material. This effect of shape factor is illustrated by Figure 9.2 which shows data for a series of natural rubber engineering vulcanisates with increasing carbon black contents (with a hardness range of 35-75 IRHD).

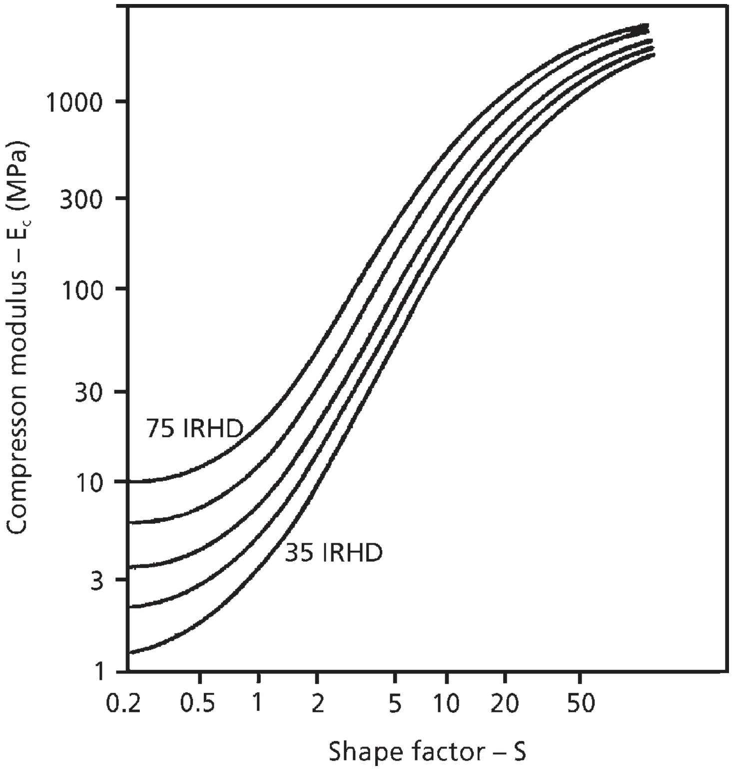


Figure 9.2 Effect of shape factor on compression modulus

It is difficult to determine accurate independent values for the bulk modulus, B of rubber. Typical values of B are 1500–3000 MPa, whereas the shear modulus will usually be between 0.5 MPa and 10 MPa [2, 3]. Further discussion and design equations for combinations of shear and compression as well as torsional bushes may be found in references [2, 3].

The introduction of intermediate rigid reinforcing layers into a rubber block has a very strong effect in increasing the overall stiffness of the unit, by dividing the block into layers, each of increased shape factor.

9.2.3 Curved bearings

Curved section reinforcements are used in a number of more sophisticated laminated engineering components such as helicopter mounts and flexelements for tension leg platforms. When a curved bearing is deformed, as shown in Figure 9.3, it will in general

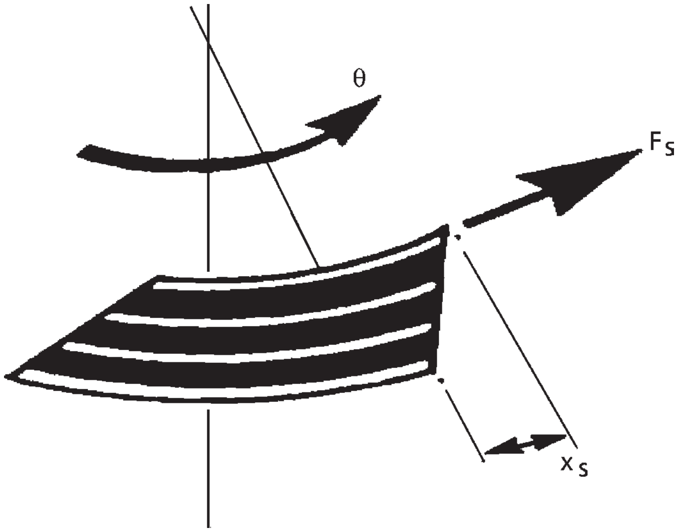


Figure 9.3 Deformation of curved laminated bearings

experience a distribution of shear and compressive reactions under the action of a force in a given direction.

To a first approximation the curved segments may be considered as a series of flat elements inclined at different angles. The above equations may then be applied, integrating between the angular constraints if necessary. The rotation of such a unit may be considered in terms of the tangential shear strains set up in the elastomer. When a shear force is applied to a flat laminated bearing, shear force reactions will generate a couple which will tend to rotate the intermediate rigid plates. For a laminated bearing constructed from segments of spherical shells, the situation is more complex, but the same principles apply. If the outer shell is fixed and the inner shell is rotated by means of a shaft attached to its centre, then a torque is applied to the unit which must, at equilibrium, be balanced by an equal and opposite reaction torque composed of contributions from each of the layers. At each layer, there will be both a tangential shear force and also a couple made up from the reacting forces. These internal couples need to be considered when considering the balancing of couples through the stack of layers, and will tend to twist the metal plates into non-concentric positions. The resultant force constitutes the reaction to an externally applied force, such as a horizontal force, applied remotely to a centrally located shaft.

9.2.4 Non-linearity

The foregoing equations only calculate the stiffness of a component for moderate strains. Force/deflection curves in compression are markedly non-linear and other means may be needed to calculate behaviour. There have been several attempts to calculate the non-linear behaviour of rubber solids in compression. There is no universally successful or generally approved method.

A hyperelastic model that has been found to be successful [4, 5] is as follows:

$$W = \frac{a}{b}[1-e^{-b(I_1-3)}]+C_{10}(I_1-3)+C_{20}(I_1-3)^2+C_{30}(I_1-3)^3$$

where W is the stored energy density, I_1 is the strain invariant $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$ of the three principal extension ratios, C_{10}, C_{20}, C_{30} are the Rivlin polynomial coefficients and a and b are materials constants.

This form of elasticity model is based on the assumption that for practical purposes $\delta W/\delta I_2 = 0$ as discussed in [5]. This is generally a reasonable assumption and enables simple shear tests to provide the necessary force/deflection data from which the coefficients of the elasticity model may be derived.

The calculation of non-linearity can be made on the basis of the first cycle behaviour and then these may be corrected for stress softening using appropriate stress softening equations [6].

In addition, several empirical attempts have been made to use polynomial fits to the shape of the load-deformation curve, using more or less arbitrary numerical constants as fitting parameters. These are of limited predictive power, but can be very useful to interpolate or extrapolate force/deflection curves within a given category of component.

9.2.5 Instability

Instability is considered by calculating the critical force at which a stack of n layers will just buckle in an unstable manner due to second order tilting moments. Gent [7] gives the following expression for the critical buckling load F_c of a laminated rubber column, of height h restrained at both ends:

$$F_c/T'(1+F_c/K') = \pi^2/ h^2$$

Where, T′ is the tilting stiffness for unit length of a single column unit, comprising a rubber layer and a rigid separating plate and K′ is the shear stiffness of a column unit. This has been applied to develop equations for use in earthquake protection mounts for buildings as described in reference [3].

9.3 Design principles - dynamic properties

Some engineering applications require elastomeric components to have precise dynamic behaviour for antivibration or energy absorbing applications. Although the force/deflection behaviour of rubber is nonlinear over large strain ranges, over small strain amplitudes normally associated with vibrations, approximations to linearity can be effective and components can be successfully designed with reproducible dynamic performance. In some cases the consequences of non-linearity can be exploited in novel ways to enhance the performance of rubber components. Dynamic properties of elastomers are usually determined using double shear test pieces.

9.3.1 Theoretical background

A mass supported by a spring and viscous damper combined in parallel, is commonly used to represent a single degree of freedom system for modelling vibration isolation. The dynamic stiffness can then be expressed in complex form as:

$$K^* = K + jC\omega$$

where K^* is the vector sum of an elastic (in phase) component K and a viscous (out of phase) damping component $C\omega$.

This approach has been widely used. In fact both C and K vary with frequency, which limits the value of the idealised simple ‘spring and dashpot’ model. A more general approach is to represent the complex stiffness (spring rate) as:

$$K^* = K_1 + jK_2$$

In polar form, this is represented by a dynamic stiffness of magnitude $|K^*|$ and a phase angle θ, with:

$$|K^*|^2 = K^2_1 + K^2_2 \text{ and } \theta = \tan^{-1}(K_2/K_1)$$

The dynamic properties of rubber are usually characterised in simple shear, where the dynamic shear modulus *G** and phase angle θ are measured, and:

$$K^* = G^* A/t$$

This assumes an underlying linear and sinusoidal behaviour.

9.3.2 Transmissibility

Transmissibility T is a measure of the amplification or attenuation of vibration from one point in the system (input) to another (response). Assuming equilibrium, transmissibility may be derived from the basic differential equation:

$$(K^* - \omega^2 M)x^*_0 = K^* x_i$$

where x_i and x^*_0 are the displacements at the input and response points respectively, the former being real and the latter complex. This leads to the following general expression for transmissibility as a function of circular frequency:

$$T = \left|\frac{x_0^*}{x_i}\right| = \frac{\left[K_2^2 + K_1^2 - \omega^2 M K_1^2 + \omega^4 M^2 K_2^2\right]^{/2}}{\left(K_1 - \omega^2 M\right)^2 + K_2^2}$$

This equation allows transmissibility of a system to be calculated provided the real and complex parts of the dynamic spring rate are known at the relevant frequency, temperature and strain amplitude. Transmissibility (T) is normally characterised in logarithmic units of dB. At very low frequencies, the transmissibility tends to unity in each case.

The natural frequency, nf, is determined by the stiffness, K, for a given preload, or mass M applied to the spring:

$$nf = {}^1\!/_2\, \pi.\ (K/M)^{1/2}$$

An increase in stiffness will increase the natural frequency nf.

9.3.3 Effect of elastomer type and temperature

Different types of unfilled rubber have different degrees of damping and also different degrees of sensitivity to frequency, as shown in the upper part of Figure 9.4 for various unfilled elastomers at 23 °C:

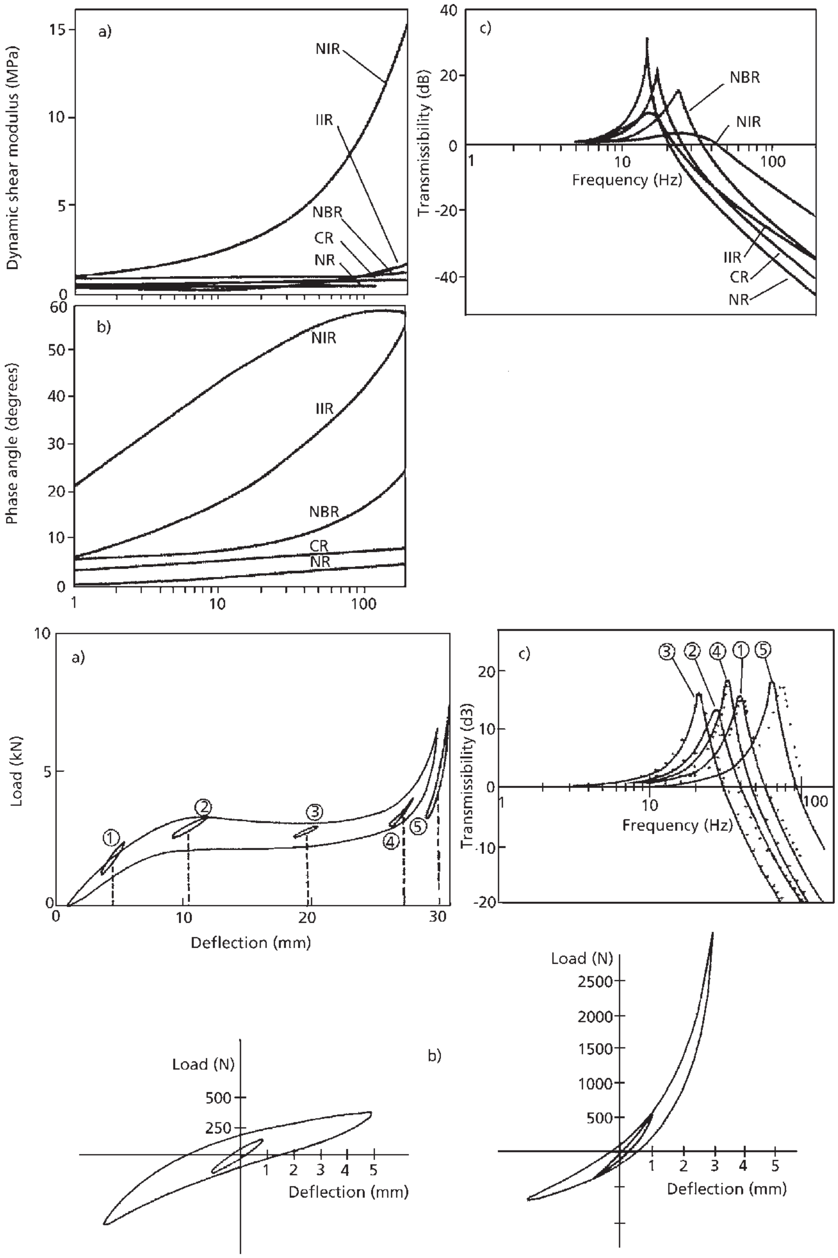


Figure 9.4 Dynamic mechanical properties

Natural rubber (NR)
Polychloroprene (CR)
Nitrile rubber (NBR)
Butyl rubber (IIR)
Nitrile isoprene copolymer (NIR)

For each are shown: a) Dynamic shear modulus, b) Phase angle, c) Transmissibility, T, as function of frequency in Hz. The strain amplitude was 10% shear strain in all cases.

NR is very low damping and neither phase angle nor dynamic stiffness varies substantially with frequency over the range 1 to 200 Hz. NIR on the other hand is a much higher damping material even at low frequencies and moreover both its dynamic stiffness and phase angle increase very substantially between 1 and 200 Hz. The data for phase angle and dynamic stiffness were combined with the aid of the equation for T to present a series of transmissibility curves. This enables the overall effect in a spring mass system to be seen more clearly, and this is probably the most useful format for engineering design. The highest damping of these elastomers, NIR, shows the lowest resonant peak but also the poorest isolation at high frequencies. This illustrates the general principle that isolation is generally more effective than damping above the natural frequancy of the system. Higher damping polymers inhibit the effect of resonance more successfully whenever there are input vibrations at resonance. However, they are less successful at isolating the system from input vibrations at frequencies significantly above the natural frequency. In selecting a material for a specific design, the optimum will depend on the range of input vibrations of greatest concern. High damping polymers also usually show high creep rates and greater sensitivity to temperature. A rise in temperature in NIR from 23 °C to 50 °C is sufficient to increase the height of the peak transmissibility at resonance by 10 dB.

9.3.4 Effect of non-linearity

The lower half of Figure 9.4 illustrates the effect of overall non-linearity on transmissibility. The shape of non-linear hysteresis loops is shown in the lower two figures. Decreasing the mass (or preload) or increasing the spring stiffness, e.g., from points 3 to 5, shifts these curves to higher frequencies. There can be significant advantages from non-linear systems. An automotive mount where the vehicle weight is such that deflection is normally at point 3, for example, will have much better isolation than one at point 2 and will also offer a rising rate to overload conditions, e.g., point 5. Several patents exploiting this principle have been obtained but it has not yet been widely adopted.

9.3.5 Effect of fillers and strain amplitude

The addition of carbon black filler to rubber increases both the dynamic modulus and the phase angle (and hence damping) and these properties also become amplitude dependent. The magnitude of these effects depends on the type and quantity of carbon black. The resulting effects on transmissibility are discussed by Stevenson [2, 3]. At low strain amplitudes, the dynamic stiffness is unexpectedly high, and the phase angle low, resulting in higher natural frequency and higher peak transmissibility than at lower amplitudes. This effect is important in the design of antivibration mounts that experience a range of input vibrations, such as automotive suspensions. A mount designed on the basis of materials test data at a strain of 10% shear leads to the expectation of an attenuation of 15 dB at an input frequency of 75 Hz. In fact, vibrations of 0.2% amplitude at this frequency will be *amplified* by almost 20 dB.

Further detail on dynamic properties of rubber may be found in References [8] and [9].

9.4 Fatigue of elastomers for engineering components

The fatigue of elastomers has been successfully characterised in terms of the concept of tearing energy, which is a fracture mechanics approach. Tearing energy is the same as the strain energy release rate, or fracture energy, defined for metals and plastics. In some ways the use of a fracture mechanics approach for rubbers is simpler than it is for metals or plastics as there are no plastic zone effects and the complications from plane strain versus plane stress cases do not arise. This renders the approach more directly applicable to fatigue life determinations of practical rubber engineering components to which it has been applied with considerable success. This enables the resistance to fracture or fatigue to be characterised as a fundamental geometry-independent characteristic of any particular type of rubber. Once this property is determined, then, in principle, the fatigue and fracture resistance of a component of any geometry can be calculated. This approach is normally discussed for rubber in terms of the tearing energy, (T), which is defined as the energy required to cause unit area of new crack growth, i.e.

$$T = \left(\frac{\delta U}{\delta A} \right)_l$$

where U is the stored elastic energy; A is the area of new crack growth and *l* denotes that the partial differentiation is with respect to constant deformation, i.e., no work done by the applied load.

9.4.1 Material behaviour

The relation between tearing energy and crack growth rate is a material characteristic, independent of component geometry. This relation differs for different rubbers, but once it has been derived, crack growth rate can be estimated. These relations follow a characteristic form.

At very low tearing energies, only chemical failure mechanisms occur, and these proceed at an extremely low rate (0.1 mm/year). The minimum value for T below which no mechanical fatigue crack growth can occur is referred to as T_o, the threshold tearing energy. The value of this varies for different rubbers between 0.05 and 0.1 kJ/m^2 and may be understood in terms of the molecular structure of the rubber.

As the tearing energy increases above T_o, the crack growth rate increases in accord with at least two different power law relations, depending on the value of T. At high enough values of T, failure will occur from a single cycle, and so dc/dN increases asymptotically towards T_c, the critical tearing energy. Consideration of the shape of the T versus dc/dN curve immediately suggests the basis for good fatigue resistant design, namely to ensure that the maximum tearing energies of a component in service are in a stable region well away from the asymptote to T_c where even approximate predictions of crack growth rate become very difficult.

Different elastomers have different shapes of tearing energy curve and the curves may cross. Figure 9.5 shows typical results for three typical engineering elastomers: NR, CR and NBR. Which material provides the longest fatigue life depends on which portion of the dc/dN curve predominates for the life of the component. For very large numbers of very low amplitude cycles CR will show less crack growth than NBR and NBR less than NR. There is a central region where the fatigue resistance of all three rubbers is very similar and at high tearing energies NR will show more resistance than the others. It should be remembered that results may differ widely for different compounds of the same polymer type so that the above results are only illustrative.

9.4.2 Calculation of tearing energies for different geometry components

Difficulties can arise from the problem of calculating tearing energy for different geometry engineering components. Initial work in this field provided analytical solutions for different cases involving thin rubber strips. Subsequent solutions were for bonded rubber layers in simple shear and uniaxial compression. This enables approximate tearing energy to be estimated for many engineering components based on these geometries.

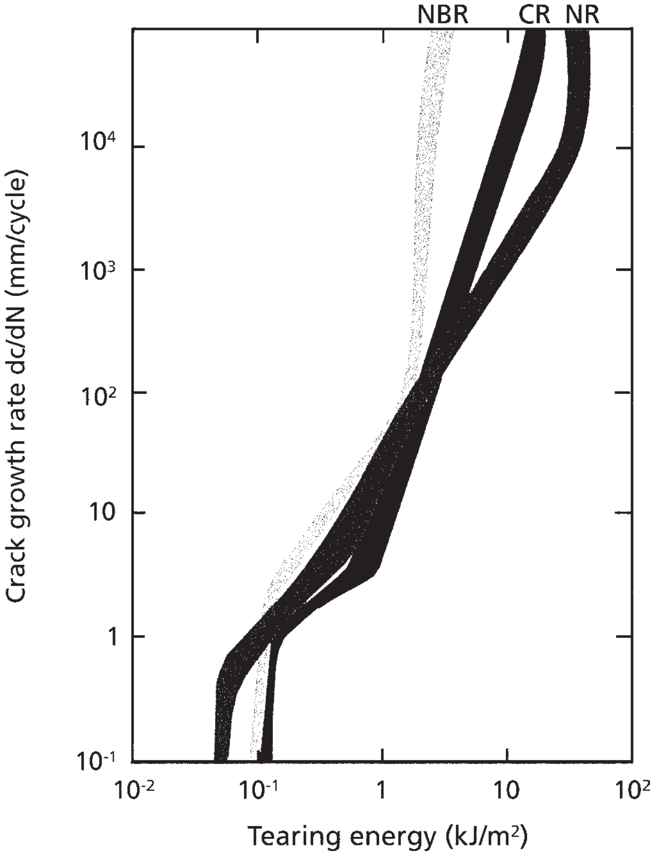


Figure 9.5 Tearing energy plots for three engineering elastomers showing crossovers

The expressions for tearing energy in particular cases consist of an expression for the uniform (or average) stored energy density in the rubber layer(s), W, and for the appropriate multiplicative geometrical factor, which depends on the locus of crack growth and may contain explicit dependence on crack length, as in the case of simple extension

For uniaxial compression: T= 0.5 Wt;

For simple shear: T = 0.4 Wt (short cracks);

For simple extension: T = 2 k Wc.

Where W is the uniform (or average) stored energy density in the rubber layer.

In shear and in compression, the tearing energy is not simply a direct function of crack length. This means that the growth of a fatigue crack will not accelerate, as in simple extension, where the direct dependence on c causes T to increase as the crack grows. This is the reason why rubber is less frequently used in tension than in compression or shear. In many cases in compression, the strains are small enough for *W* to be given approximately by the linear expression:

$$W = {}^{1}/_{2}\varepsilon^{2}E$$

The success of this approach for dynamic fatigue crack growths in shear, compression and tension is illustrated by Figure 9.6, which shows the results of tests performed

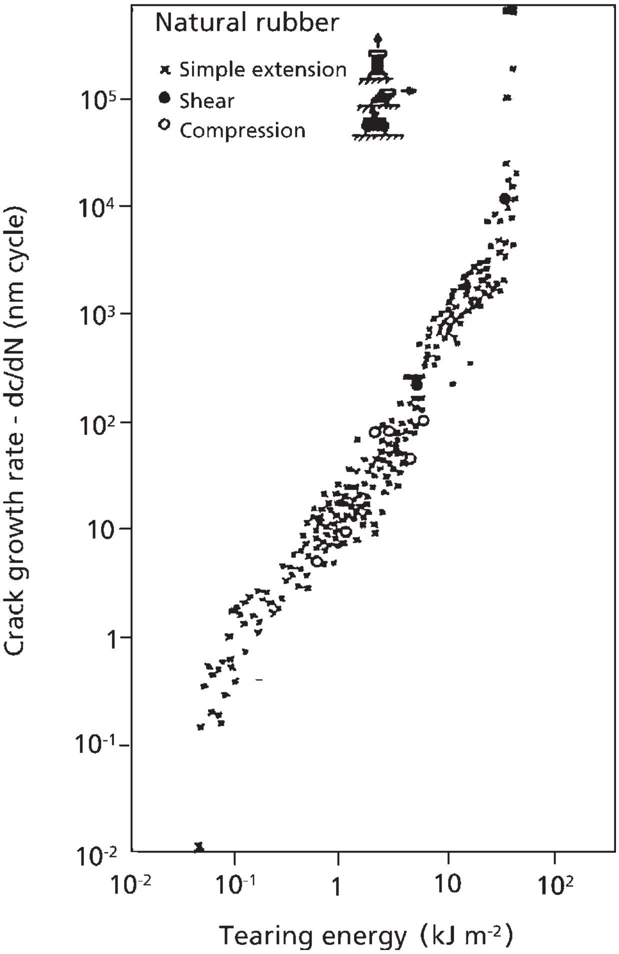


Figure 9.6 Comparison of fatigue in simple extension, shear and compression

with an engineering NR vulcanisate fatigued at a frequency of 2 Hz in shear, compression and simple extension. Although the data show scatter, as is usual, within the accuracy of the experiments at a given calculated tearing energy the crack growth rates were the same for each geometry. This means that if the tearing energy can be calculated, fatigue lives in shear or compression may be determined by reference to dc/dN curves obtained on strip testpieces in simple extension. The large number of data points shown for the latter case reflects the ease of obtaining accurate measurements of crack growth rate with this geometry.

The factors considered so far indicate how crack growth rates may be calculated for rubber components subjected to known loads or motions. To apply this to a component, a load/motion spectrum needs to be determined, either from past experience of similar applications or from engineering analysis. This spectrum can then be converted to a spectrum of tearing energies by the methods discussed, and thus the cumulative crack growth calculated. To interpret this in terms of component life requires life to be defined in terms of crack growth. For any component, this definition requires some analysis of the effect that a crack will have on its performance.

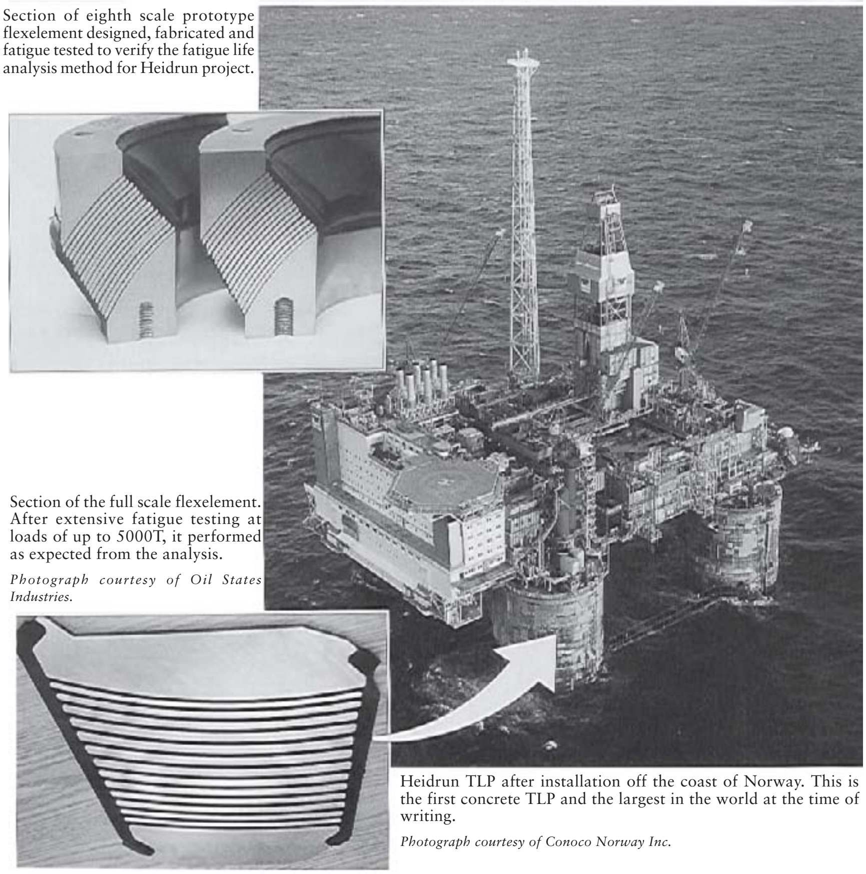
An example of a critical engineering component for which this approach was used by the author is shown in Figure 9.7. The safety case for the flexelements shown was made on the basis of fracture machanics calculations. A significant safety margin over and above the required 50 year design life was shown and verified by means of specially designed full scale fatigue tests. The elastomeric flexelements are designed to support a mass up to 5,000 tonnes and shear deformations in excess of 150%. This has now been in service for more than 6 years without problems.

The calculations for such components require also non-zero minimum fatigue data such as those shown in Figure 9.8 [10].

This approach has been successfully applied to the fatigue life analysis of rail car mounts, to automotive suspension mounts and to seals. The effect of internal fracture caused by explosive decompression of absorbed gases has been determined at 130 °C and 155 °C. The elastomer is weaker at the higher temperature and so shows more failure. As the dissolved gas comes out of solution a small bubble may grow to an internal tear if the fracture criterion is exceeded. For more detailed information [11].

9.4.3 Finite element analysis

Increasing use is being made of finite element analysis (FEA) to aid the design of rubber engineering components. Compared with FEA of other engineering materials there are



Section of eighth scale prototype flexelement designed, fabricated and fatigue tested to verify the fatigue life analysis method for Heidrun project.

Section of the full scale flexelement. After extensive fatigue testing at loads of up to 5000T, it performed as expected from the analysis.

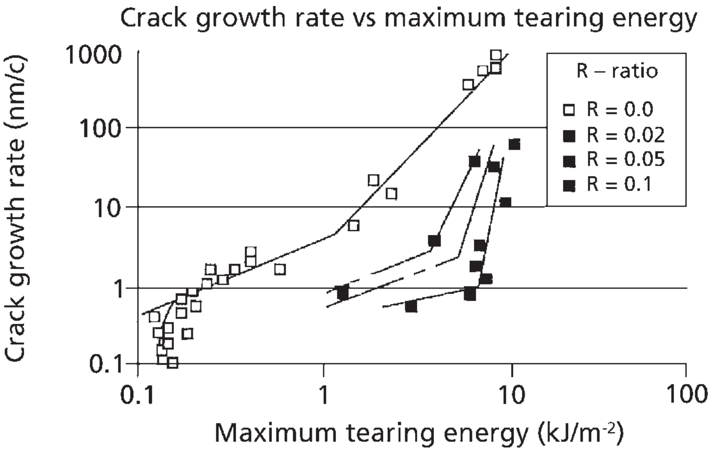
Photograph courtesy of Oil States Industries.

Heidrun TLP after installation off the coast of Norway. This is the first concrete TLP and the largest in the world at the time of writing.

Photograph courtesy of Conoco Norway Inc.

Figure 9.7 Comparison of fatigue in simple extension, shear and compression

three problems with this for elastomers i) the occurrence of large deformations, ii) near incompressibility of the materials and iii) nonlinear force/deflection behaviour. There is no generally accepted, validated non-linear elasticity model for elastomers. The reader is advised to check carefully the validity of the elasticity model before relying on finite element results. However the approach described in Section 9.2.4 has been found to be successful in a variety of cases for different component geometries and different elastomers [4].



Typical fatigue test data for an elastomer. The contours for R>O apply to applications with non-zero minimum loads and are most pronounced for strain crystallising materials.

Figure 9.8 Fatigue behaviour under non-relaxing conditions

The recent surge in development of computer power has improved the feasibility of realistic computations taking into account both material non-linearity and geometric non-linearity. An industry-wide consortium, Mechanics Software, Inc., formed in 1992 has sponsored the development of a new code, FLEXPAC, designed also to compute fatigue crack growth rates in elastomeric components. The approach is to compute values for tearing energy by means of energy differences per unit area of crack insertion. This enables tearing energy values to be recalculated as a function of crack depth. The results for tearing energy obtained from FLEXPAC indicate that the crack may slow down beyond a certain depth. This result was not apparent from analytical fracture mechanics solutions. Laboratory testing is being done to validate such calculations but this approach offers considerable hope for the future that fatigue life calculations may become eventually a relatively routine part of the design process.

9.5 Environmental factors

The life and performance of a rubber component can also be strongly influenced by its service environment, which can cause changes in stiffness and other engineering properties.

These changes may be classified into a) reversible physical changes, e.g., low temperature crystallisation, b) irreversible physical changes, e.g., permanent set, swelling in some fluids and c) chemical changes, e.g., oxidation, thermal degradation.

9.5.1 The effect of low temperatures

At very low temperatures, all rubbers undergo a rapid transition to the glassy state becoming brittle and stiffening by factors of about 1,000. In this state they clearly cannot function in any engineering application. The temperature at which this state occurs differs widely for different rubbers, depending mainly on the molecular structure of the polymer and varies from -100 °C for silicone rubber to values above zero for some fluoroelastomers.

There can be significant changes in mechanical properties even at temperatures 20 °C or more above the actual transition to a glassy state due to low temperature crystallisation. Stiffness may increase and the material will show much greater hysteresis, creep, stress relaxation and set. CR and NR are the principal types of crystallising rubber, crystallising at maximum rate at -25 and -10 °C, respectively; in fact the good strength and fatigue resistance that CR and NR possess derive largely from their ability to strain crystallise locally at a crack tip even at working temperatures. Whereas glass transition is almost instantaneous, crystallisation proceeds more slowly and may take several months to reach equilibrium. Its most important effect for engineering applications is gradually to increase the rubber modulus by factors between 1 and 100 depending on compound type. In addition to the choice of elastomer, choice of the most appropriate vulcanisation system is also important. NR possesses greater resistance to low temperature crystallisation than CR, although in both cases the low temperature behaviour is very strongly influenced by the vulcanisation system.

It has been shown that [12, 13] if low temperatures occur when the elastomer is deformed then the rate of crystallisation will be accelerated by an amount that can be calculated from the strain of the deformation. There is an interrelationship between strain induced crystallisation and low temperature crystallisation.

There can be substantial effects in some types of polychloroprene and NR even after prolonged exposure to temperatures as moderate as +3 °C and this effect should be considered carefully when designing structural bearings for cold climates.

9.5.2 Durability

There is evidence that rubber can survive very long periods in service at ambient temperatures up to at least 30 °C without any serious deterioration at all. Data obtained in 1983 from rubber bearings used for gun recoil testing equipment by the UK Ministry of Defence from 1953 consisting of thick blocks of black filled vulcanised natural rubber bonded to thin steel outer plates show only about 10% increase in stiffness over the 30 year life of the bearings. A range of polychloroprenes and fluoroelastomers have been characterised in 14 year trials of longevity at an outdoor weathering site in Panama [14]. NR and CR bridge bearings have now been in continual service since 1957 with no need for maintenance or replacement. The effect of 42 years sea water immersion on NR in a tyre has been studied [15]. It was found that the amount of water absorbed after this time was less than 5% and also there were no adverse effects on the rubber strength. In another study, it was shown that after 100 years in air, vulcanised NR pads had only deteriorated in a skin region of depth no more than 2 mm. Beneath this depth the skin offered protection from further oxygen ingress and ageing.

9.5.3 Rubber/metal bonds

Most rubber engineering components use rubber layers bonded to metallic end plates, thus the testing and durability of these bonds is frequently of crucial importance.

Rubber-metal bonds are generally stronger in dry conditions than the rubber itself so that when failure does occur, e.g., on a pull to failure test, it occurs through the rubber (often denoted as 100%R) for a good bond. The occurrence of dry rubber/metal bond failure usually indicates a manufacturing process error. Prolonged exposure to water can however cause bond failure. Only 'hot formed bonds' produced during the vulcanisation of the rubber will be at all durable in water; cold bonded systems, e.g., with epoxy resins or cyanoacrylates, lead both to weaker initial bonds and to more rapid deterioration in the presence of moisture.

There are a number of tests for rubber/metal bond strength but the most effective are probably the double shear test and the peel test. Fracture mechanics solutions exist for both testpiece geometries, so that interfacial bond strength can be measured in fundamental terms and the fatigue life of the adhesive bond analysed for cohesive failure of the rubber itself. The double shear testpiece has advantages where it is desired to maintain a constant shear strain on the adhesive joint during an environmental exposure test, e.g., to simulate specific mechanical (or electrochemical) aspects of service conditions. For general characterisations of bond strength and durability, however, the peel test is usually more convenient. This can also be adapted for site application of samples, e.g., of pipe linings or coatings, as a QC check.

For the peel testpiece:

$$\text{Peel energy, } P = F/\omega[\lambda - \cos\phi]l - Wt$$

where, W is the strain energy density in the peeled leg, ϕ is the peel angle, λ is the extension ratio, t is the unstrained rubber layer thickness, w is the width of the peel strip and F is the peel force.

It has been found that bond failure in wet conditions is not necessarily accelerated by elevated temperatures and other environmental factors can be more important [16]. In particular if there is contact between metals in different places in the galvanic series, the rate of bond failure of elastomers bonded to one of the metals can be greatly accelerated. The degree of salinity and the degree of oxygenation are also important factors.

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10

Testing

R. Brown

10.1 Introduction

10.1.1 General

The physical testing of rubber is now a mature technology, methods for all physical parameters have been developed and have been subjected to a process of refinement. These methods have been standardised at national and international level, in most cases for many years. There is still some divergence, especially in detail, between national standards but many countries now align their standards with those of the International Standards Organisation (ISO). Hence, in this chapter ISO methods will be considered. The process of refinement and development continues, so amendments and additions still occur quite frequently and it is necessary to check for the latest editions of standard methods.

Although there are standard methods for just about every property, the great majority were developed primarily for quality control purposes. It is important to appreciate different classes of test based on the purpose of the results. One classification is to distinguish between Fundamental tests, Apparent tests and Functional tests. A fundamental test would produce results which can be expressed independently of test conditions whilst an apparent test yields results under arbitrary conditions which cannot easily be related to other conditions. A functional test is one measured under the mechanical conditions of service, usually on the complete product. It follows that fundamental tests are highly desirable to generate design data, an apparent test is well suited to quality control and a functional test is often the best approach to demonstrating fitness for purpose.

The greatest criticism of the standard methods available is that the great majority are apparent in nature and do not yield fundamental properties, which limits their value for generating design data. However, to maximise the comparability of data, these procedures should be adhered to in routine work as no purpose is served by ‘reinventing the wheel’. The usefulness of the standard methods can often be extended by making tests as a function of conditions such as temperature, test speed, etc.

Inevitably, the restraints on space in covering testing in one chapter means that the methods will be dealt with relatively briefly. For greater detail reference is made to *Physical Testing of Rubber* [1].

10.1.2 Test piece preparation

Other than for work on complete products, test pieces must be produced before the test can be carried out. In most tests the result will be dependent on test piece geometry, which is why test piece shape and size are carefully defined in standards. Standard test pieces are normally produced by cutting moulded sheets, although some, such as compression set buttons, can be moulded direct. To obtain test pieces from products will generally involve cutting and/or buffing.

Where laboratory prepared compounds and moulding takes place it is sensible to have standardised procedures to reduce as far as possible the sources of variability. Such procedures are contained in ISO 2393 [2] which covers both mills and internal mixers together with procedures for compression moulding. The British standard is now identical but previously differed in several respects including a wider range of moulds. At best this standard can be considered as a basis for producing reproducible test pieces but is far from comprehensive. Clearly, many tests are made on factory mixed material and it will often be desirable to mould test pieces, simulating production conditions.

Stamping test pieces from sheet is covered in ISO 4661 Part 1 [3]. This seemingly simple operation can easily produce significant errors if cutting dies are not carefully maintained to be dimensionally correct, very sharp and free from nicks or unevenness in the cutting edge. The standard does not deal with dimensions which are specified in the individual test method standards. A variety of presses can be used to perform the stamping operation and experience indicates that the type is not critical.

Rotary cutters can be used to produce disks or rings from thin sheet and are essential above about 4 mm to prevent distortion. Cutting is made much easier and effective if a lubricant such as weak detergent solution is used. Cylindrical test pieces such as compression set buttons are preferably moulded.

To obtain test pieces from finished products may additionally require cutting from a large block and reduction of thickness or removal of irregularities. The best approach to obtaining sheets from a thick product is to use slitting machines as used in the leather industry. These are expensive but can produce excellent results. Buffing away large amounts is likely to cause excessive heat build up and be tedious but is very suitable for removing surface irregularities. It will be appreciated that in both cases removal of the moulded surface is likely to affect results. A careful and detailed study of slitting and buffing has been made by James and Guilder [4].

10.1.3 Conditioning

It is a simple fact that results obtained are dependent on the atmospheric conditions prevailing when the test is carried out and on the prior history of the material. Consequently, to produce comparable results it is essential that storage and conditioning are controlled within suitable limits. The period before testing is conveniently divided into storage and conditioning where conditioning refers specifically to the process of bringing the test pieces to the required conditions of temperature and sometimes humidity immediately before testing and storage refers to the period before this back to the time of forming.

There is some difficulty in specifying the storage times and conditions for products when the date of manufacture is unknown but a creditable attempt is made in standard wording used in ISO 471 [5]:

'For all test purposes the minimum time between vulcanisation and testing shall be 16 h. For non-product tests, the maximum time between vulcanisation and testing shall be 4 weeks and for evaluations intended to be comparable the tests should, as far as possible, be after the same time interval. For product tests, whenever possible, the time between vulcanisation and testing should not exceed 3 months. In other cases, tests shall be made within 2 months of the date of receipt of the product by the customer'.

Regardless of the time of storage, it is necessary that the rubber is not subjected during this period to high temperatures or other conditions likely to cause deterioration including UV light, ozone and other chemicals. The actual temperature and humidity during storage are not critical as conditioning takes place afterwards, but sensible limits would be between 10 and 30 °C and below 80% relative humidity. In addition, different rubbers must be separated such that there is no migration of constituents. Special attention needs to be given when the surface condition of the test piece is important, for example ozone or paint staining tests.

ISO 471 [5] specifically covers temperatures and humidities for conditioning and testing rubber test pieces and is referenced in all test method standards. The standard temperature is either 23 °C or 27 °C and if control of humidity is also needed the standard conditions are 23 °C and 50% relative humidity or 27 °C and 65% humidity. The higher temperature is intended for use in tropical countries. Where neither temperature nor humidity need be controlled the prevailing ambient temperature and humidity can be used. Attention is drawn to the atmosphere 20 °C and 65% relative humidity used for textiles, which may be used if necessary where the product is a composite of textile and rubber. A list of preferred sub-normal and elevated temperatures is also given, which would be used when testing was carried out at other than the normal ambient temperatures. The normal tolerances are ±2 °C for temperature and ±5% for relative humidity; however, provision is made for closer tolerances if required.

When both temperature and humidity are controlled the standard conditioning time is a minimum of 16 h and where temperature only is controlled at 23 °C or 27 °C, a minimum of 3 h. At the sub-normal and elevated temperatures, it is simply specified that the time should be sufficient for the test piece to reach equilibrium with the environment. Tables of times to reach equilibrium can be found in ISO 3383 [6]. Generally, three hours in air is more than sufficient to reach equilibrium at the normal temperatures of 23 °C and 27 °C whatever the test piece geometry. Usually rather shorter times would be used at the sub-normal or elevated temperatures and it is important to note that, whilst a minimum time is required, an excessive time at an elevated temperature may cause significant ageing before test.

It is generally assumed that humidity is not important in most rubber tests and hence conditioning in an atmosphere with control of temperature only is usually specified. Control of humidity is considered necessary in certain cases, however, e.g., testing latex rubber and electrical tests. In many instances the 16 h minimum conditioning period will not be sufficient for equilibrium to have been reached, especially with relatively thick test pieces. Hence, all that this conditioning can hope to achieve is to bring test pieces having similar dimensions into more nearly comparable states than they would otherwise be. To reach complete moisture equilibrium would in many cases take several days and for thicker test pieces probably weeks.

Inevitably there are certain special cases found in test method standards including after accelerated ageing tests, after exposure to liquids, where there has been buffing or cutting and after mechanical conditioning.

The object of conditioning is to bring the test piece as nearly as possible into equilibrium with a standard atmosphere and it is reasonable that the test atmosphere should be identical with the conditioning atmosphere. ISO 471 [5] states that this should be the case unless otherwise specified but includes a note to the effect that test pieces conditioned in one atmosphere may be tested in a less rigorous atmosphere in cases where the changes do not affect the results. Most testing is carried out in one of the normal standard atmospheres but ISO 471 [5] gives a list of preferred sub-normal and elevated temperatures.

The stress-strain curve of filled rubbers is altered by deformation so that to measure properties in the equilibrium condition mechanical conditioning in the form of repeated stressing can be carried out. This is rarely specified other than in dynamic tests where it is automatically applied.

10.1.4 Density

Density is important in cost considerations, is often used as a basic control test against gross errors in compounding and is needed in conjunction with such properties as abrasion resistance. It is usually measured relative to the density of water by weighing in air and water and standard procedures are given in ISO 2781 [7]. Greater accuracy can be achieved if required by using a density column as standardised for plastics in ISO 1183 [8].

10.1.5 Dimensions

Dimensions are a critical factor in most physical tests and because the dimensional measurements reflect directly on the accuracy of the result it is necessary to give them careful attention.

Standard procedures have evolved and are given in ISO 4648 [9]. The most important considerations are to use an instrument that has the required accuracy (not the same as its discrimination) and to distinguish between contact and non-contact methods. The latter is important because in any contact method the relatively soft rubber is deformed. As examples, the thickness of a dumbbell is measured with a dial gauge or equivalent with a defined foot pressure whilst the length of the nick in a tear test piece needs a travelling or projection microscope. The width of dumbbells is usually taken from the width of the cutting die.

Extensometry is a particular type of dimensional measurement which figures highly in such tests as tension or compression stress strain. Method of measurement and the accuracy needed is largely dependent on the particular test method and requirements are specified in the relevant standard.

The dispersion of compounding ingredients, particularly carbon black, in the rubber can have a large effect on physical properties and a measure of dispersion is a way of judging the efficiency of mixing. The usual dimensional approach involves examining a cut or torn surface under a microscope and comparing to standard photographs. Methods, including the use of a split field microscope procedure, have only recently been standardised in ISO 11345 [10].

10.2 Processability tests

10.2.1 Introduction

How the rubber compound processes is of great importance to the producer of rubber products as it will be reflected in his throughput and reject rates. The somewhat vague term 'processability' is taken to mean all aspects of material behaviour which contribute to producing a satisfactory compound and forming it into a satisfactory product. Processability testing has received enormous attention both to develop tests which realistically predict processing behaviour and to make quality control more efficient. Nevertheless, some widely used tests have been in existence for many years. The two principal properties to be measured are viscoelastic flow behaviour and curing characteristics.

The mixing procedures referenced in Section 10.1.2 are relevant to preparation for processability tests but additionally simple procedures for homogenising a sample by milling are given in ISO 1796 [11].

10.2.2 Viscoelastic flow behaviour

Viscosity is the resistance to plastic flow, the inverse of plasticity which is ease of deformation. However, plasticity results are sometimes confusingly given in stiffness units. Viscosity is shear rate dependent and the relationship is generally not linear so that the behaviour cannot be represented by a single measurement. Also, unvulcanised rubbers are not totally viscous but have an elastic component of deformation. The most commonly used geometries for processability tests are shown diagrammatically in Figure 10.1.

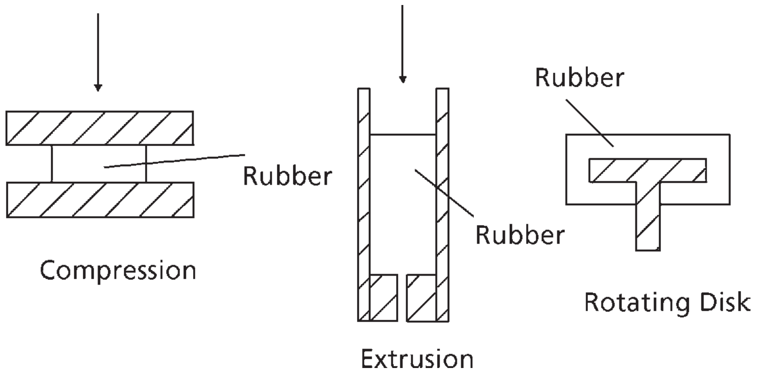

Figure 10.1 Types of viscosity test, compression plastimeter, extrusion rheometer, rotation plastimeter

Compression plastimeters are the earliest form of processability test but only operate at shear rates below most processing operations and also have the disadvantages of not breaking down structure effects in filled materials and the shear rate is not uniform through the test piece. The parallel plate plasticity test is standardised in ISO 7323 [12] and the rapid plasticity test in ISO 2007 [13], the latter having several advantages including a higher shear rate.

ISO 2930 [14], the plasticity retention index test, is used to assess the oxidative effects of storage of natural rubber and consists of measuring compression plasticity before and after oven ageing.

A compression plastimeter can be used to determine recovery after compression and hence obtain a measure of both the elastic and the plastic components of deformation. Alternatively, the relaxation of stress can be measured but neither approach has found widespread use.

A rotation plastimeter allows shearing at a constant rate for prolonged times to overcome thixotropic effects but shear rate is restricted by slippage and heat build up problems. The Mooney instrument, ISO 289 [15, 16, 17], has been a universal standard for decades and is used by many synthetic rubber manufacturers as the prime measure of processing behaviour. Particular conditions are specified for different polymer types. The Delta Mooney, ISO 289-3 [18], is an extension of the Mooney test which is used specifically for characterising non-pigmented oil extended emulsion SBR. The Mooney test can be used to measure the onset of cure or scorch but the rotating action prohibits testing through the curing process (ISO 289-2) [17]. At least one modern version of the Mooney apparatus is capable of measuring stress relaxation by monitoring the decay of torque after the rotor is stopped. The slope of a plot of torque against log time indicates the relative proportions of elastic and viscous components.

The Mooney test is restricted to an average shear rate of about 1 s^{-1} and for higher shear rates a capillary rheometer is used. Rubber is extruded through a die and the rate can readily be varied. An advanced form of rheometer such as the Monsanto Processability Tester can additionally measure die swell. There is an ASTM standard, D5099 [19] but not as yet an ISO method. Small instrumented extruders as described in ASTM D2230 [20] can also be used to simulate production and give an indication of extrudability. Miniature internal mixers or torque rheometers are intended to simulate production to measure mixing behaviour but are relatively little used for rubbers. The oscillating disc and rotorless types of curemeter as described below also measure viscosity before the onset of, as well as during, cure.

10.2.3 Curing characteristics

Curing characteristics are measured with oscillating rheometers which allow the monitoring of stiffness changes as cure progresses. The most popular instrument for many years was the oscillating disc curemeter which is standardised in ISO 3417 [21]. Increasingly, rotorless curemeters in which one platen oscillates are now being used as they have several advantages, in particular far better heat transfer characteristics. ISO 6502 [22] is a guide rather than a definitive standard which reflects the various forms of apparatus commercially available. The principle of the two geometries is illustrated in Figure 10.2. An advanced form of rotorless curemeter is marketed as the Rubber Process Analyser which allows tests over ranges of strains, frequencies and temperatures and is capable of measuring the viscous and elastic components of dynamic behaviour.

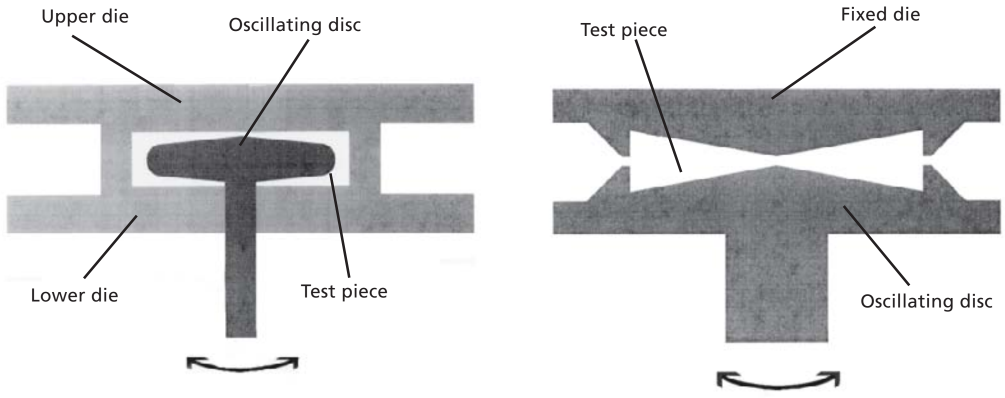

Figure 10.2 Curemeter types, oscillation disk and oscillating die

10.2.4 Other tests

Tack is the ability of two pieces of rubber to stick when pressed together and is important in articles built up from separate pieces of rubber, such as tyres. A large number of instruments have been developed for measuring tack but few have found widespread use and interest is too narrow to merit international standardisation. Tests consist essentially of pressing two pieces of rubber together and measuring the force needed to separate them. Green strength is the strength of unvulcanised compound and a tensile method is given in ISO 9026 [23].

10.3 Mechanical properties

10.3.1 Introduction

Mechanical properties can broadly be defined as those involving stiffness and strength which are clearly important in most applications. The distinction can be made between short term or quasi static measurements (the usual stress strain methods) and both dynamic measurements and time dependent properties such as creep and stress relaxation. Also considered here, are the durability properties of abrasion resistance and fatigue.

In most cases the methods used have changed little for many years but there have been refinements and very considerable advances in instrumentation. Very significantly, almost all the methods are 'apparent' and the results cannot easily be related to other test conditions.

10.3.2 Hardness

Hardness is a quick and simple way of obtaining a measure of the modulus of a rubber by determining its resistance to a rigid indentor to which is applied a force. Despite its arbitrary nature and having relatively low discrimination it has remained popular for many decades and appears in almost all specifications. There are essentially two types of test, dead load in which the indenting force is applied by a mass and durometers which can be hand held and apply the force by means of a spring. The former are generally more accurate with better reproducibility.

The international method for dead load hardness is ISO 48 [24] which also includes a very useful micro method that can be used on thin test pieces. The indentor is a ball, 2.5 mm diameter for the normal test and 0.395 mm diameter for the micro test. The result is expressed in International rubber hardness degrees (IRHD). The most common durometers give Shore A hardness which is quite close to the IRHD scale. A Shore D scale is used for very hard materials and there are other Shore scales for very soft materials. The Shore indentor is a truncated cone which is more prone to damage than a ball. At least one manufacturer makes a hemispherical-headed durometer which reads in IRHD. Both types of durometer are standardised in ISO 7619 [25].

Hardness can be related to Young's modulus but this is not normally considered in routine use. An interesting consideration of the relationship is given by Yeoh [26] and Hawley [27] whilst the errors in hardness tests are examined by Brown and Soekarnein [28].

10.3.3 Tensile stress-strain properties

The ability of rubber to stretch several times its original length is one of its chief characteristics but it should be noted that at least as many rubber products are used in compression or shear as are used in tension. Nevertheless, tensile stress-strain is the second most common test (after hardness) and the strength properties are used as a general guide to quality.

The standard test given in ISO 37 [29] is arbitrary, the result being dependent on test piece geometry and speed. Dumbbell test pieces are generally used with four sizes being specified, although there is also provision for rings. A typical stress-strain curve is shown in Figure 10.3. The properties measured are tensile strength, elongation at break and stress at a given elongation (rubber technologist's modulus).

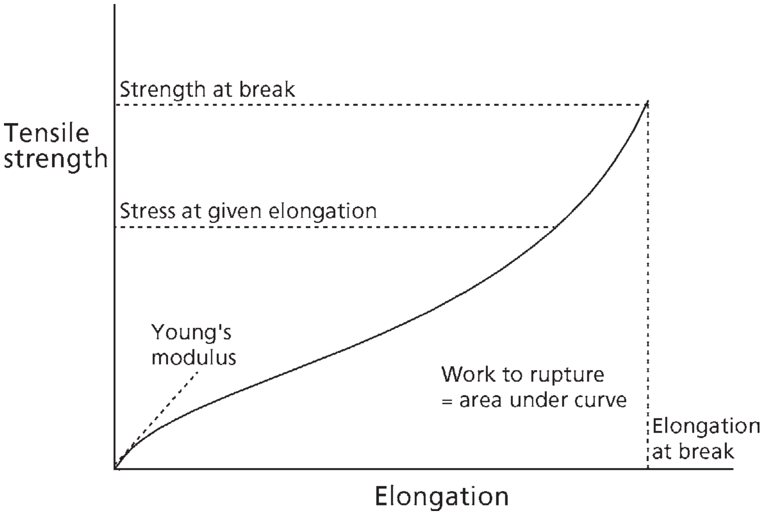

Figure 10.3 Typical tensile stress-strain curve

Tensile tests are carried out on a machine comprised of grips to hold the test piece, means of separating the grips at constant rate of traverse, a load cell to measure force and an extensometer to measure elongation. Tensile machines are often 'universal' and can also be used for tear and adhesion tests and stress-strain characteristics in compression and shear. Specification of the apparatus is given in ISO 5893 [30]. Although the test has changed relatively little, there have been great advances in apparatus with most machines being computer controlled and laser and video extensometers to make non-contact measurement of elongation.

Biaxial extension has more engineering significance than uniaxial but, largely because the apparatus is more complicated, measurements are rarely made in industrial laboratories and there is no international standard.

10.3.4 Compression stress-strain

Despite the number of products which are stressed in compression, the international standard method ISO 7743 [31] was relatively late in being developed. It uses cylindrical test pieces which are compressed at 10 mm per minute to give the moduli at 10% and 20% strain. The test piece height is significantly smaller than the compressed area so there is no question of buckling.

The ratio of height to area is important together with whether or not the test piece is lubricated. In theory, there are two limiting conditions under which a test piece can be compressed: either with perfect slippage between the test piece and compressing members of the apparatus or with complete absence of slip. If there were perfect slippage, every element of the test piece would be subjected to the stress and strain and a cylindrical test piece would remain a true cylinder without barrelling. Under these conditions the stress and strain are approximately related by:

$$\frac{F}{A} = G\left(\lambda^{-2} - \lambda\right) = \frac{E}{3}\left(\lambda^{-2} - \lambda\right) \qquad (10.1)$$

Where F = compression force, A = initial cross-sectional area, E = Young's modulus, G = shear modulus and λ = ratio of compressed height to initial height.

If there is complete absence of slippage, stress and strain are not uniform throughout the test piece and barrelling takes place on compression. The relation between stress and strain is then very dependent on the shape factor of the test piece. The stress strain relationship can then be expressed using an effective modulus E_c:

$$E_c = E(A + BS^n) \qquad (10.2)$$

Where B is a constant and S is the shape factor defined as the ratio of the loaded cross-sectional area to the force free area (Figure 10.4).

The most common situation, both in practice and in experiment, is for the rubber to be bonded to metal plates or held between surfaces which effectively eliminate slip. In this situation the effect of shape factor means that the thinner the rubber the stiffer it appears and this property is much exploited in the design of rubber mounts and bearings.

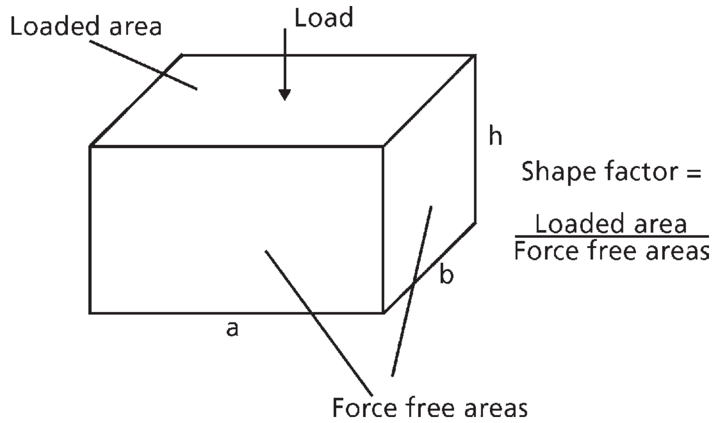

Figure 10.4 Definition of shape factor – loaded area/force-free area

When the shape factor becomes very high such that E_c approaches the bulk modulus K, the effective modulus is less than expected due to appreciable bulk compression and can be estimated from:

$$\frac{E_c}{1+\frac{E_c}{K}} \qquad (10.3)$$

10.3.5 Shear stress-strain

Shear is also more important for engineering applications than tension but even less shear testing than compression testing is carried out in most laboratories. Testing in shear is no more difficult than testing in tension except for the fact that the test piece has to be first bonded to rigid members through which the strain is applied.

In ISO 1827 [32] what is known as a quadruple block test piece is used which has four rubber pads bonded to rigid members as shown in Figure 10.5 and is very stable under load. The rubber is either bonded to metal supports during vulcanisation or moulded blocks are attached with a high modulus adhesive. The test piece is strained at 5 mm per minute and the modulus taken at 25% strain. The stress-strain curve in simple shear is linear up to relatively large strains but the aspect ratio of the rubber blocks must not be too large or there will be appreciable bending in addition to shear.

In principle, shear modulus could be measured by straining in torsion but it is not common to use this mode of deformation except in certain low temperature tests. A close approximation to pure shear can also be achieved in rubbers by stretching a strip with length much greater than width in the direction normal to its length.

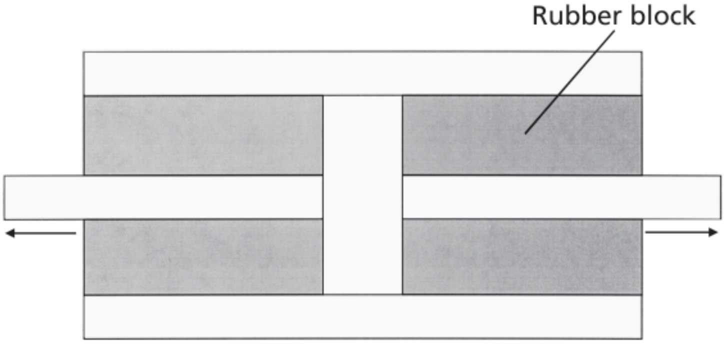

Figure 10.5 Quadruple shear test piece

10.3.6 Tear tests

In a tear test, the geometry of the test piece is arranged so that the force is concentrated on a deliberately introduced flaw or sharp discontinuity. Because tearing can occur in a wide range of products and is also involved in abrasion and fatigue processes, it is not surprising that a considerable number of tear tests have been devised. Some of the geometries used are arbitrary and the measured tear strength is then difficult to directly correlate with service performance. However, with certain geometries it is possible to apply a fracture mechanics approach and derive the energy of tearing which is a basic material characteristic independent of geometry. Although the concept and importance of tearing energy has been long established, the standard methods still do not make use of it but report only the arbitrary tearing force.

A distinction can be made between the force required to initiate a tear and the force to propagate it. Standard tests generally measure the maximum force and hence make no such distinction but most also start with an artificially introduced cut which can be considered the initiation. Once a tear has started it can be argued that the product has failed but in most circumstances it is the growth of small flaws or cuts which is important to service life.

ISO 34 [33] has five methods based on the test pieces shown in Figure 10.6. The crescent test piece is the most popular whilst the angle test piece without a nick is the only one not to use a pre-cut flaw. The Delft test piece is used when only small amounts of material are available. With the trouser test piece, tearing energy can be deduced and it also allows the force as a function of tear length to be monitored. When working with tearing force, it is found that for many materials the ranking is the same whichever method is used and this also correlates with tensile strength. Hence, it has been argued that a measure of tearing force (as opposed to tearing energy) is unnecessary [34].

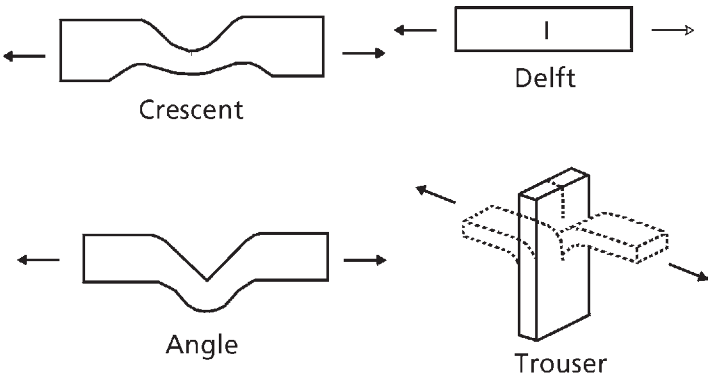

Figure 10.6 Tear test piece

A useful summary account of the development of the concept of tearing energy and its application to the understanding of failure of rubbers has been given by Thomas [35].

The tearing energy for the trouser test piece is given by:

$$T = \frac{2\lambda F}{t} - wW \tag{10.4}$$

where T = tearing energy, λ = extension ratio in legs of test piece, F = measured force, w = width of test piece, t = thickness, and W = strain energy density.

W can be obtained by extending a test piece without a nick and plotting a stress-strain curve, W being derived from the area under the stress-strain curve up to the extension ratio under the conditions described in Equation (10.4).

If the legs of the test piece are sufficiently stiff so that extension is negligible λ = 1 and W is zero and the relationship (Equation 10.4) reduces to:

$$T = \frac{2F}{t} \tag{10.5}$$

This approximation has generally been found adequate for most purposes, even without reinforcing the legs of the test piece to prevent extension.

Tearing energy is actually not a unique material property as it depends on the cut geometry. Very sharp cuts require relatively little energy to propagate them.

10.3.7 Dynamic stress-strain

In a dynamic test the rubber is subjected to cyclic stress or strain. There are basically two classes of dynamic motion: free vibration in which the test piece is set into motion and the amplitude is allowed to decay through damping, and forced vibration in which the oscillation is maintained by external input of energy. Rebound resilience is a particular case where a single half cycle is applied. Forced vibration can further be divided into tests at and tests away from resonance.

The significance of dynamic tests is that both the elastic and viscous components of material behaviour are considered, which is important in a number of applications including springs and dampers. Dynamic properties are less often measured than they should be, mostly because of the apparatus cost, but the growing availability of dynamic mechanical analysers is significantly improving the situation.

ISO 4664 [36] is a guide to dynamic testing which gives definitions and the basic theory of the response of rubber to cyclic stress and strain. Recommendations are given for the test pieces, mode of deformation, test conditions and procedures.

Forced vibration away from resonance using a sinusoidal wave form in shear or compression is generally preferred for obtaining engineering data. Servohydraulic machines are most commonly used but these can be large and very expensive. They can cope with a range of strains and used to test whole products.

The term dynamic mechanical thermal analyser is generally taken to refer to modest sized, bench mounted test machines which allow the measurement of dynamic properties over a range of frequency and of temperature and which are automated/computerised to a various degrees. The terms can cover free vibration apparatus as well as forced vibration and there is a variety of analysers on the market, representing different geometries and control systems. They generally use small test pieces and are especially efficient at characterising materials as functions of temperature and frequency to give comparative results. Perhaps their greatest importance has been in encouraging a much increased amount of dynamic testing because of the efficiency and relatively low cost. There is, of course, no fine distinction as to whether an apparatus is a dynamic analyser and the so-called analysers vary considerably in their capability.

ISO 4664 [36] was published as a guide because the variety of machines on the market made standardisation of analysers extremely difficult. The previous edition dealt only with the larger forced vibration machines which are relatively little used. The most widely used free vibration apparatus is the torsion pendulum and there is a separate standard, ISO 4663 [37] for this. There are moves now in ISO to create separate standards for both small and large forced vibration machines but opinion varies as to whether this is worthwhile.

Rebound resilience is a very basic form of dynamic test in which the strain is applied by impacting the test piece with an indentor which is free to rebound after the impact. Rebound resilience is defined as the ratio of the energy of the indentor after impact to its energy before impact expressed as a percentage and hence, in the case where the indentor falls under gravity, is equal to the ratio of rebound height to the drop height, which is the measure used in most instruments.

Resilience is not an arbitrary parameter but is approximately related to the loss tangent. Despite being such a crude measure of a dynamic property, it is an attractive test, especially for quality control purposes, because of its simplicity and the fact that the apparatus required is inexpensive. The two basic forms of resilience apparatus are a ball falling under gravity and an indentor attached to a swinging pendulum; but the latter is the more common.

ISO 4662 [38], is not based on any particular pendulum design but on giving limits for various parameters including the so-called apparent strain energy density. The values specified correspond to those for the well-known Lüpke pendulum and also to a modified version of the Schob pendulum, these being the most commonly used instruments. Other penduli, for example, the Dunlop tripsometer, will give different results.

10.3.8 Creep, stress relaxation and set

The stress-strain behaviour considered in previous sections is that at short times. Creep, relaxation and set are the effects of longer term application of stress or strain. Creep is the measurement of the increase of strain with time under constant force; stress relaxation is the measurement of change of stress with time under constant strain, and set is the measurement of recovery after the removal of an applied stress or strain. It is important to appreciate that there are two distinct causes for the phenomena of creep, relaxation and set: the first is physical and the second is chemical. The physical effect is due to rubbers being viscoelastic and the response to a stress or strain is not instantaneous but develops with time. The chemical effect is due to ageing processes. In practice, it is often rather difficult to distinguish between the two causes but, generally, physical effects are dominant at short times and low temperatures and the chemical effects are more apparent at longer times and higher temperatures.

Creep is measured relatively infrequently except for applications, such as bridge bearings, where it is very important. The principle is simple enough, a constant force is applied and the resultant change in deformation with time monitored. In practice, careful design of apparatus is necessary to ensure accurate measurements. ISO 8013 [38] has procedures for shear and compression. In compression tests, set buttons (see compression set) are used and in shear tests a double sandwich test piece is used.

Stress relaxation is particularly important in sealing applications and is a measure of sealing force. The wider appreciation of its importance in this respect has encouraged greater use in recent years. ISO 3384 [39] covers relaxation in compression, which is the most useful mode. The usual practice is to have a number of jigs to hold test pieces at constant strain which are placed at intervals under a measuring head. The measuring head accurately detects a small over-compression when the force can be measured (see Figure 10.7). Compression set buttons or small rings are used. Rings reflect the seals connection and allow the maximum surface area to be exposed when the test is conducted in the presence of a liquid.

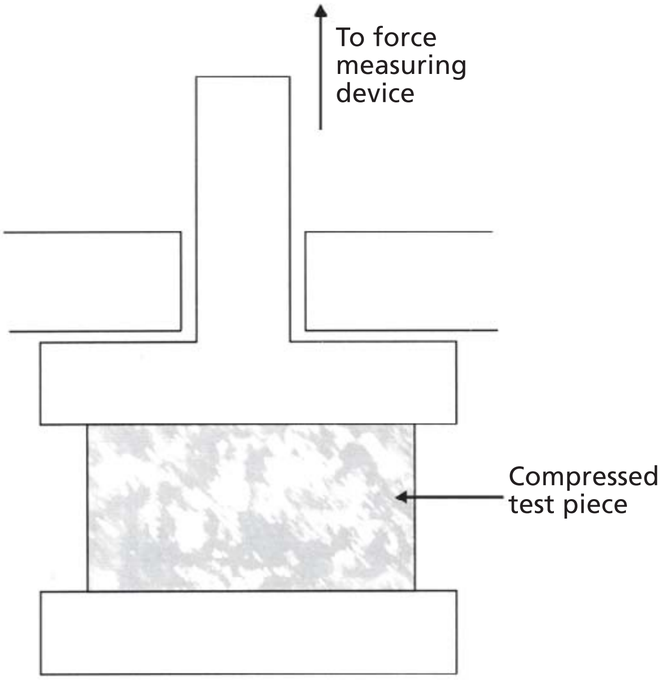

Figure 10.7 Principle of stress relaxation in compression jig. Force exerted by test piece is measured when the top platen and jig body are just separated by a small additional compression

Traditionally, much more attention was paid to set than relaxation, largely because of the relatively simple apparatus required. Either compression or tension set is a convenient quality control test which can be used to give an indication of state of cure. The principle of a compression set measurement is shown in Figure 10.8. Compression set also appears to be important with respect to sealing efficiency but in most applications it is the force exerted by the seal rather than the amount it would recover if released that matters, and set does not always correlate well with relaxation.

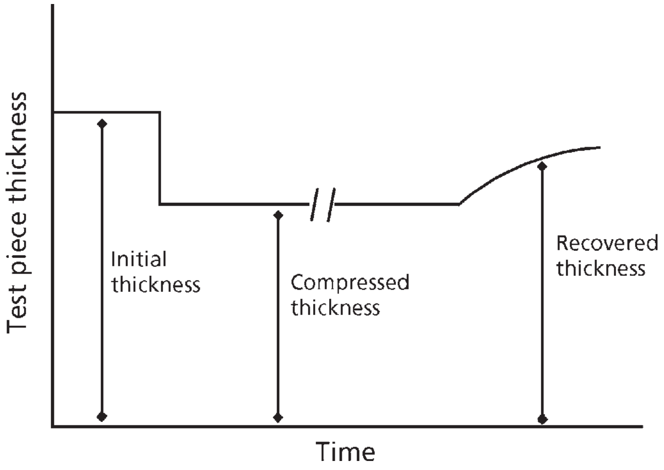

Figure 10.8 Illustration of compression set

The standard method in compression is given in ISO 815 [40] and for tension in ISO 2285 [41]. In compression, the test pieces are held under constant strain and lubricated to approximate to perfect slippage. The tension standard has the more usual constant strain method but the latest draft revision also has a very simple constant load method which includes measurement of extension and creep. This is currently in ISO 12244 [42]. Compression set at constant stress used to be standardised and is relevant to such applications as flooring. The procedures use an arbitrary recovery time of 30 minutes but there are choices as to whether the recovery is at room temperature or the test temperature and whether cooling takes place before or after release of strain.

10.3.9 Fatigue

Fatigue of rubbers is taken to cover the effects of repeated application of a stress or strain. Two quite distinct types of test are used, those where the aim is to induce and propagate cracks without significantly raising the temperature and those where the prime purpose is to cause heating of the test piece through the stressing action. The former is generally referred to as flex cracking or cut growth tests and the latter as heat build up.

There have been a variety of flex cracking tests which strain the test piece by bending it in somewhat arbitrary geometries. The most widely used is the De Mattia method which has survived in ISO 132 [43]. The test piece is a strip with a moulded groove which is repeatedly bent into a loop. The maximum strain is not accurately controlled and, perhaps more importantly, the minimum strain is only nominally zero. There are two procedures, crack initiation and crack growth, the essential difference being that for crack growth the test piece is pierced with a specified tool before being fatigued. Crack growth was previously in a separate standard.

A more scientific approach is to strain test pieces in tension when both maximum and minimum strains are better controlled (and can be varied) and it is possible to apply the concept of tearing energy. This approach is standardised in ISO 6943 [44] which uses either strip or ring test pieces. The number of cycles to complete failure is noted and if this is plotted against strain there is generally a fatigue limit below which fatigue life is very long (see Figure 10.9).

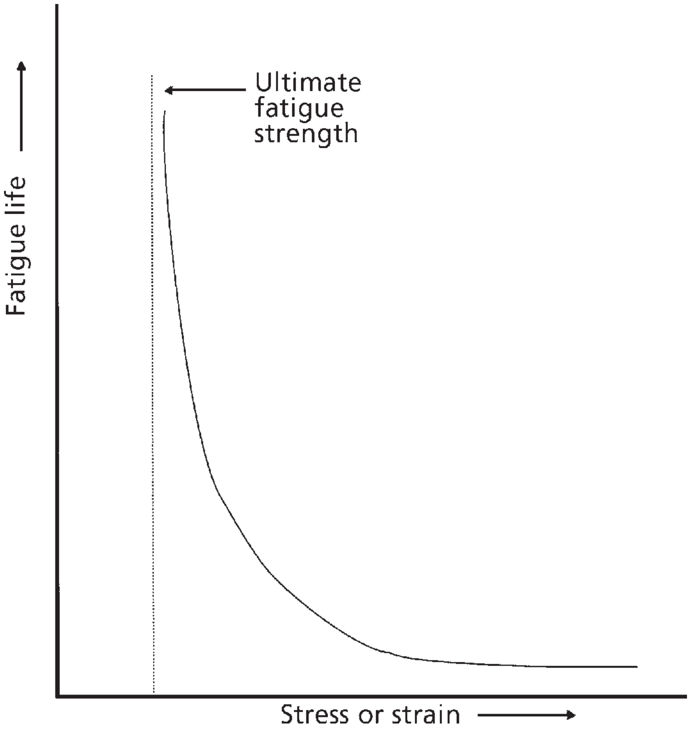

Figure 10.9 Relationship between fatigue life and stress or strain amplitude

Tests to induce heat build up use bulky test pieces and operate in compression, shear or a combination of these. Various apparatus and geometries have been used which are more or less arbitrary. The so-called compression and rotary flexometers are standardised in ISO 4666 [45]. The temperature rise is the main parameter measured.

In many circumstances, the best approach to investigating fatigue performance is to make tests on the complete product using a servo controlled universal testing machine or a specially designed test rig.

10.3.10 Abrasion

Laboratory abrasion tests are notorious for being difficult to correlate the results with service performance. The problem stems from there being more than one wear process, usually classified as:

Abrasive wear – caused by hard asperities cutting the rubber

Fatigue wear – caused by particles of rubber being detached as a result of dynamic stressing on a localised scale

Adhesive wear – the transfer of particles of rubber to another surface as a result of adhesive forces between the two surfaces

The conditions in service are usually complex with more than one mechanism involved – although one may predominate. Even a comparison between rubbers may be invalid if the predominant wear process in the test is different to that in service. It is clearly essential to match the service conditions in the laboratory test, but in many cases this is extremely difficult.

There are several factors involved in the design of an abrasion test and the number of permutations of these is very large, resulting in a considerable number of apparatus having been used. The abradant can be a solid or a loose powder or a combination. Solid abradants include paper, cloth, wheels and metal knives. Of the many geometries which can be used to rub the test piece and abradant together, two factors in particular can be noted. Firstly, the degree of slip which is 100% in linear reciprocation but can be varied with, for example, two wheels inclined to each other. Secondly, the test piece may be totally and always in contact with the abradant which can generate considerable heat or may successively visit different areas of the abradant.

In ISO only one method is currently standardised which is the DIN abrader in ISO 4649 [46]. In this apparatus the test piece traverses across a revolving drum around which is wrapped a sheet of abradant. It is essentially a quality control method. The British standard, BS 903 Part A9 [47], still retains four types of machine, the ISO method, DuPont, Akron and Taber. The DuPont uses a disk of abrasive paper which rotates whilst two test pieces are pressed against it. The only advantage of this apparatus is that the load can be constant torque. The Akron has the two wheel geometry which allows variable slip and a loose powder can be introduced. The Taber or rotary platform machine has two abrasive wheels running off centre on a disk test piece. It is probably the most versatile abrasion apparatus on which the abradant is readily changed, the force varied and powder or liquid introduced between the surfaces.

There is now a move in ISO to produce a guide to abrasion testing which will explain the significance of the various factors and advise on selection of tests for given applications. To fully characterise a material, even for one application, requires tests under a range of conditions. A very sophisticated apparatus is available which does this [48] and associated software uses the results from a number of conditions to give abrasion as a function of energy and speed. Tyre tread wear can be estimated via a simulation programme. The apparatus also performs friction tests.

Particularly because of the difficulty of maintaining a reproducible abradant, it is common practice to refer abrasion results to those obtained at the same time on a 'standard' rubber. The assumption then has to be made that the rubber is reproducible. The test rubber and the standard can be directly compared to produce an abrasion resistance index or the standard can be used to normalise the abradant.

10.4 Other physical properties

10.4.1 Introduction

The subjects considered in this section are friction, electrical properties, thermal properties, permeability and staining. Optical properties very rarely apply to rubbers. Most of the mechanical properties are relevant to a wide range of applications whereas all but a few of the physical properties considered here are only of importance for particular products. Where a physical property is relevant it can be the most critical factor in performance of the product.

Most of the tests used to measure the properties dealt within this section yield fundamental values, independent of test piece geometry and test conditions. Also, many of the methods have greater similarity to the methods used for other materials than the mechanical tests, which reflects the need to cater for the unique mechanical properties of rubbers.

10.4.2 Friction

There are a surprising number of products for which friction is important. Too little friction may be a problem in, for example, flooring and too much in the case of shaft seals. Relatively crude measures of friction can be easily obtained with inclined planes and simple towed sleds but accurate and complete characterisation of a material requires very well designed apparatus and is time consuming. One difficulty is that friction is sensitive to just about all experimental factors, including temperature, velocity and stiffness of the apparatus. Further, it can change significantly with quite small variations in the surface conditions of texture and contaminants. The limited value of measurements made on simple apparatus and at one set of conditions is not always appreciated. It is only very recently that comprehensive procedures for rubbers have been standardised as ISO 15113 [49]. This is based on plane on plane geometry and requires a well engineered towed sled type of apparatus.

10.4.3 Electrical properties

Electrical properties are of interest not only in electrical and electronic components, but also in any product where electricity could be a hazard, including static build up. When considering properties to be measured and the test methods, a distinction can be made between materials which are conducting or semi-conducting (antistatic) and those which are insulating, although there is a grey region at the higher end of semi-conducting and the lower end of insulating.

The main tests on insulating materials are resistance or resistivity (conductivity), power factor, permittivity, electric strength and tracking resistance. For conducting and antistatic materials only resistivity and surface charge are useful because such materials would not be used in situations requiring low dielectric loss or high electric strength. With insulating materials a distinction can be made between surface and volume resistivity as the surface is often more conductive than the bulk, but with conducting materials such distinction is not sensible.

The only ISO standard for electrical tests specifically for non-conducting rubbers is ISO 2951 [50], and this is heavily based on the general method IEC 167 [51]. It uses sheet, tube or rod test pieces with conducting paint electrodes but is more generally useful to measure resistance between points on a product. Resistivity is measured with a three electrode system on disk test pieces and the international test method is IEC 93 [52]. Resistance of antistatic and conducting rubber products is covered by ISO 2878 [53], which uses a commercial insulation tester. ISO 1853 [54] for resistivity of antistatic and conducting rubbers specifies a four electrode system designed to eliminate contact resistance. An alternative approach is to minimise the contact resistance by bonding to brass electrodes or, less efficiently, by using metal foil on wet colloidal graphite. All three methods are given in BS 2044 [55].

There are international standards for insulating materials in general covering electric strength (IEC 243) [56], tracking resistance (IEC 112) [57] and power factor and permittivity (IEC 250) [58]. Electrostatic properties are of considerable importance, not least because of the potential hazards of static charge. The general principles and a compendium of methods can be found in BS 7506 [59, 60].

10.4.4 Thermal properties

10.4.4.1 Thermal transport

The thermal properties are conductivity, diffusivity and specific heat. Other properties are sometimes included under this title but thermal expansion, transition points, low temperature properties and heat ageing are more properly the effect of temperature (see Section 10.5). Thermal analysis in most of its various forms is also a study of the effect of temperature rather than measurements concerning the transport of heat.

The first, and obvious, area of interest in thermal properties is for applications involving thermal insulation. However, the polymer type most frequently involved is foams rather than rubbers. Thermal transport properties, particularly diffusivity, are also most important in the prediction of processing behaviour where heat is involved, often for quite short times, and the rate at which heat is transferred can be critical.

Thermal properties have received considerable attention in recent times due to the need for data to predict processing and cure behaviour. Nevertheless, there are no international standard methods for rubbers and thermal measurements are considered specialised and performed in few laboratories. The methods are in principle the same as for other materials but there are particular factors because of the low conductivity and the difficulties inherent at processing temperatures, which place restrictions on the design of apparatus.

A detailed account of thermal transport measurements can be found in *Handbook of Polymer Test Methods* [61]. For conductivity, procedures are given in BS 874 [62] for the classic steady state methods, notably the guarded hotplate, and for transient methods. Several different approaches have been developed for measuring thermal diffusivity but are not standardised. Specific heat is nowadays most commonly measured by differential scanning calorimetry (DSC). Where heat is transferred across the boundary between two materials a surface heat transfer coefficient can be defined which is generally treated as an empirical factor.

10.4.4.2 Thermal analysis

Thermal analysis has been one of the largest growth areas in testing in recent times. It is basically the study of one or more properties of a material as a function of temperature and hence a thermal analyser is an apparatus which allows the automatic monitoring of the chosen property with temperature change. In principle any property can be measured and a great many have been, including dynamic mechanical thermal analysis (DMTA), thermogravimetry (to measure weight changes) and thermodilatometry (to measure dimensional change).

It becomes clear that, although thermal analysis is often treated as one subject, the information gained and the uses to which it is put are very varied. The rapid growth and widespread adoption of thermal analysis techniques arises from the value of temperature/property relationships being exploited once advances in instrumentation made the measurements rapid and convenient. Where appropriate, particular techniques are mentioned in the relevant section, for example DMTA in 10.3.7 and thermodilatometry in 10.5.1.2.

For thermal properties, the techniques of interest are differential thermal analysis (DTA) and its variant (DSC). In these techniques heat losses to the surrounding medium are allowed but assumed to be dependent on temperature only. The heat input and temperature rise for the material under test are compared with those for a standard material which does not have a transition or melting temperature within the temperature range under investigation. In DTA, the test piece and standard piece are heated simultaneously under the same conditions and the difference in temperature between the two is monitored whereas, in DSC, the difference in heat input to maintain both test pieces at the same temperature is recorded.

There have been many papers describing applications of thermal analysis to polymers but the classic reference is *Thermal Characterisation of Polymeric Materials* edited by Turi [63].

10.4.5 Permeability

For applications where rubbers are used as barriers to liquids and gases, for example protective clothing, tyres and balloons, the permeability will be a prime consideration in the selection of materials. However, in most cases the known level of performance is sufficient and consequently measurements are made relatively infrequently.

Permeability measurement becomes increasingly difficult and time consuming as the rate of permeation decreases. The basic methods are based on direct measurement of the amount of substance permeated using weight, volume or pressure change but at the lower permeation levels these techniques reach their limit of sensitivity and become very time consuming and experimentally difficult. More sensitive and/or rapid methods using more sophisticated detection systems were then developed for quality control in particular industries or to enable very low permeation rates to be measured, particularly with low pressure differentials. However, these are not commonly used for rubbers and have been ignored by standards committees.

If required, there is a general method for water vapour permeability based on weight gain by a desiccant in ISO 2528 [53]. A method specifically for transmission of volatile liquids through rubber is given in ISO 6179 [64] where the test piece forms the lid of a container holding the test fluid and weight loss is measured.

In the standard methods for gas permeability a pressure differential is set up across the test piece and the amount of gas permeating measured from either the change in volume or change in pressure on the downstream side. Both constant pressure and constant volume procedures are now found in the same standard, ISO 2782 [65]. Most measurements are made at constant volume using more modern pressure transducers in place of the apparatus shown in the standard.

10.4.6 Staining

Additives such as antioxidants can cause staining of any surface which comes in contact with or near to the rubber material and the problem is greatest with such consumer products as cars and kitchen appliances. The compounder has to achieve adequate environmental resistance without an unacceptable degree of staining, none would be ideal but in practice some staining may have to be tolerated. To ensure that levels are acceptable, tests to produce and measure staining are often included in specifications.

Staining can occur by direct contact, on the area surrounding contact and by water which has leached constituents from the polymer compound. The staining can also be intensified by heat and light and one or both of these is usually included in the test procedure. There had been confusion over terms used to describe the cause of staining until ISO 3865 [66] was published which gives definitions as well as the test procedures.

10.5 Environmental resistance

10.5.1 Effect of temperature

10.5.1.1 Introduction

The effects of temperature can be separated into short term and long term effects. As a generality, short term effects are physical and reversible whereas long term effects are dominated by chemical change and are not reversible. The long term chemical changes are usually referred to as the results of ageing.

In principle, any property could be used to monitor the short term effect of temperature but some are more sensitive and/or more convenient to use than others. Because all physical properties are temperature sensitive, to fully characterise a material the properties of interest should be measured over a range of temperatures relevant to the application. The same principle applies to monitoring the effects of ageing but in practice the simpler mechanical tests are usually chosen because of cost considerations, regardless of whether they are the most sensitive or the most relevant.

10.5.1.2 Thermal expansion

Thermal expansion is a particular case of the short term effects of temperature. Relatively crude measurements are made averaged over a wide temperature span as mould shrinkage (which is largely caused by thermal contraction) by measuring the length of a moulded bar relative to the mould dimension. Linear expansion can similarly be measured with a bar supported on rollers in a glass sided bath and using a cathetometer (instrument measuring small vertical distances with great accuracy). For more precise measurements a dilatometer to measure volume expansion or thermal mechanical analysis (TMA) is required. TMA can be used to obtain results in three directions and yield volume expansion.

10.5.1.3 Glass transition temperature

Rubbers show a second order transition when they change from the rubbery to the glassy state at low temperatures known as the glass transition temperature (T_g). The transition is marked by a large change in modulus but other physical properties change by various degrees, so that potentially a number of different tests could be used to detect the transition temperature. Because of the interdependence of temperature and frequency, the transition temperature measured will depend on the speed of the test, so that change in density would give a lower figure than change in rebound resilience. In practice, T_g is usually measured by thermal analysis methods, DSC or DMTA.

10.5.1.4 Low temperature tests

As mentioned above, any physical test could be used to monitor the change in behaviour at sub-ambient temperatures but, largely for convenience, a number of specific low temperature tests have been adopted. These measure different aspects of low temperature behaviour:

Rate of recovery (set and retraction)
Change in stiffness
Brittleness point

Compression set is an obvious way to measure recovery but monitoring the recovery at the test temperature is a little tricky. A particular form of recovery test for low temperature use has been developed as the temperature retraction test which operates in tension and is standardised in ISO 2921 [67].

Stiffness is best measured by DMTA but the standard method in ISO 1432 [68] uses the Gehman apparatus which operates in torsion, a mode very rarely used at ambient temperatures. Using a torsion wire makes for a relatively simple but not very sophisticated apparatus.

Brittleness temperature simply indicates when the rubber is so stiff that it is well past the point at which it is adequate for its job. The impact procedure is standardised in ISO 812 [69].

Some rubbers stiffen over a period of time at low temperatures by partial crystallisation. Most of the low temperature tests indicate that the test piece can be ‘aged’ at a low temperature to measure crystallisation but the use of hardness has been standardised in ISO 3387 [70]. This has the advantage that it can be used with unvulcanised materials. There is also a form of compression set test standardised (ISO 6471) [71] but is probably very little used.

10.5.1.5 Heat ageing

Heat ageing is the effect of elevated temperatures on rubbers for prolonged times and is carried out for two distinct purposes:

(i) To measure changes at the (elevated) service temperature.

(ii) As accelerated tests to estimate the change over much longer times at normal ambient temperature.

In practice, most tests are carried out as essentially a quality control measure with no attempt to numerically relate the result to lower temperature service life.

The standard procedure is ISO 188 [15] which specifies an air oven and an oxygen bomb method, although the latter is very little used. Test pieces are exposed for a given period at a given temperature and then tested in comparison to unaged test pieces for whatever physical properties have been selected. Hardness and tensile stress-strain properties are by far the most common properties specified. It is now appreciated that the air flow and velocity in the oven affects results and ovens fully complying with the standard should be used.

If an attempt is to be made to predict ageing at lower temperatures it is necessary to carry out ageing tests at a series of temperatures and for a number of times at each temperature. ISO 11346 [72] gives the procedure for extrapolating the results using the Arrhenius relation (see Equation 10.6). From the plots of property against time, measures of the reaction rates are taken which may be the times to a given level of deterioration (see Figure 10.10). The logarithm of reaction rate is then plotted against the reciprocal of absolute temperature which should yield a straight line (see Figure 10.11).

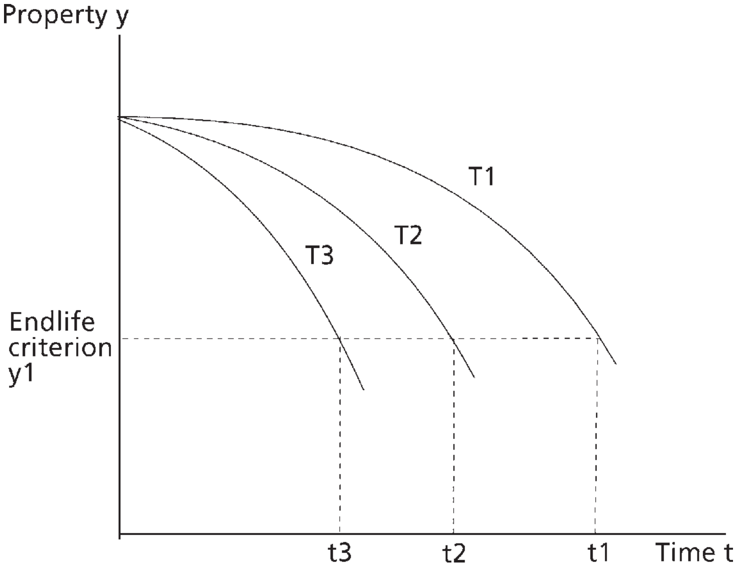

Figure 10.10 Property as a function of ageing time at three temperatures

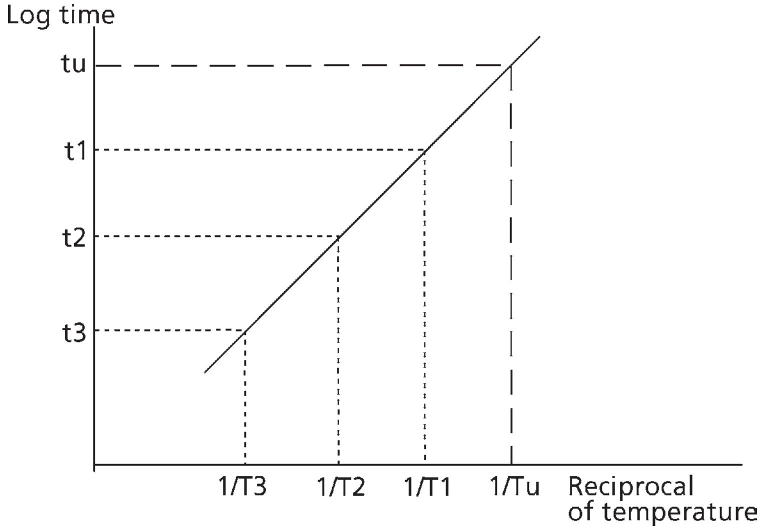

Figure 10.11 Arrhenius plot of ageing data

$$K(T) = A \exp(-E/RT) \tag{10.6}$$

hence

$$\ln K(T) = -E/RT + C \tag{10.7}$$

where K(T) is the reaction rate, E is the reaction energy, R is the gas constant, T is absolute temperature and C is a constant.

An alternative approach, which is included in a revision of the standard, is to apply the Williams Landel and Ferry (WLF) time-temperature transform

$$\log(a_T) = \frac{-c_1(T - T_0)}{c_2 + T - T_0} \tag{10.8}$$

where a_T = shift factor, c_1 and c_2 are constants, and T_0 = reference temperature. The shift factors to align the plots at different temperatures with the plot for the chosen reference temperature are determined and then these are fitted to the WLF equation to find the constants. The equation can then be used to predict the response at service temperatures (see Figures 10.12 and 10.13). This technique has the advantage that no particular measure of the reaction rate has to be chosen nor any form assumed for the change of parameter with time, but can only be used if the curves at different temperatures are of the same form.

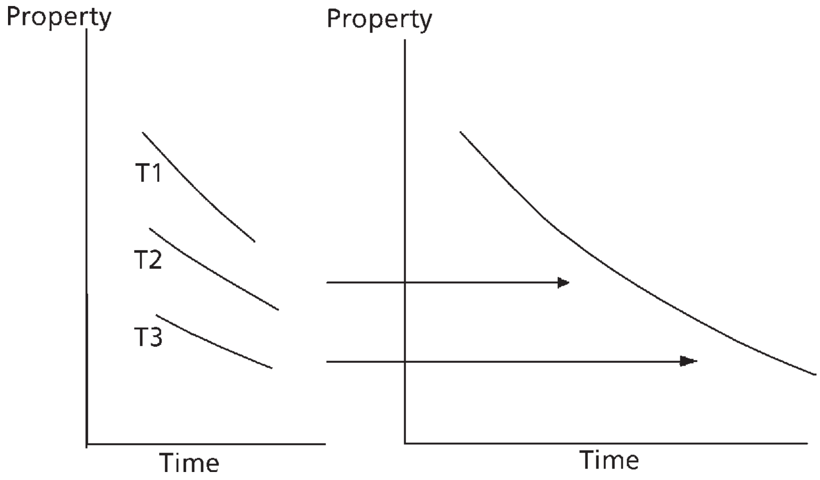

Figure 10.12 Construction of master curve by time shift

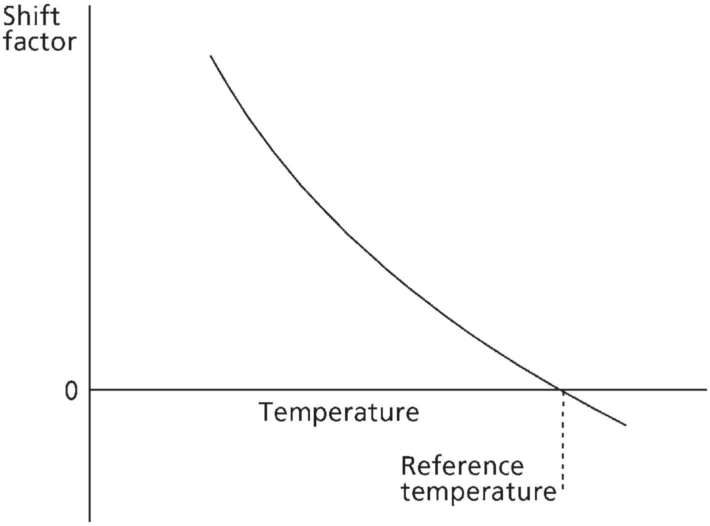

Figure 10.13 WLF relationship

Stress relaxation in tension is potentially a very elegant way of monitoring ageing as it can be related to network changes. It also has the advantages of using the same test pieces at different ageing times which reduces variability and can be less time consuming than more conventional tests. The measurement consists basically of monitoring the stress in a sample whilst subjecting it to an ageing procedure, usually accelerated. There are two variants of the technique: continuous relaxation in which the sample is held stretched throughout the test and intermittent relaxation in which the sample is stretched only periodically for short times to enable measurements to be made.

Under suitable conditions when viscous flow is not dominant, it has been proposed that the reactions within the rubber network may be related to stress changes. The decay of stress in continuous relaxation measurements provides a measure of the degradative reactions in the network whilst intermittent relaxation measures the net effect of both degradative and crosslinking reactions. In the continuous measurement any new networks formed are considered to be in equilibrium with the main network and do not impose any new stress.

There is now an international standard, ISO 6914 [73], which covers both the continuous and intermittent procedures plus a simplified intermittent method where the stress measurement is made at standard laboratory temperature. The term stress relaxation is not adopted in this standard on the basis that increases in stress as occur with intermittent tests cannot be called relaxation.

One problem with ageing tests is that the degradation is limited by diffusion of oxygen into the test piece so that, particularly in accelerated tests, there will be a degradation gradient through the thickness. This has to be considered when relating the results from thin test pieces to thick products or if using thick test pieces. Test pieces need to be less than 1 mm thick to completely avoid the problem.

10.5.2 Effect of liquids

Exposure to liquids is often called a swelling test because the effect generally measured is the change in volume due to absorption of liquid. The procedure is essentially an ageing test with the test piece exposed in the liquid instead of air. Standard procedures are given in ISO 1817 [74] which includes a one sided exposure variant.

Volume change is usually measured by weighing in air and water. Exposure is normally for a single time but it is important to know whether the test piece has reached equilibrium absorption (see Figure 10.14). Chemical change can take place in addition to swelling (or extraction) and measuring change in other properties is desirable. Tensile stress-strain and hardness are most commonly specified.

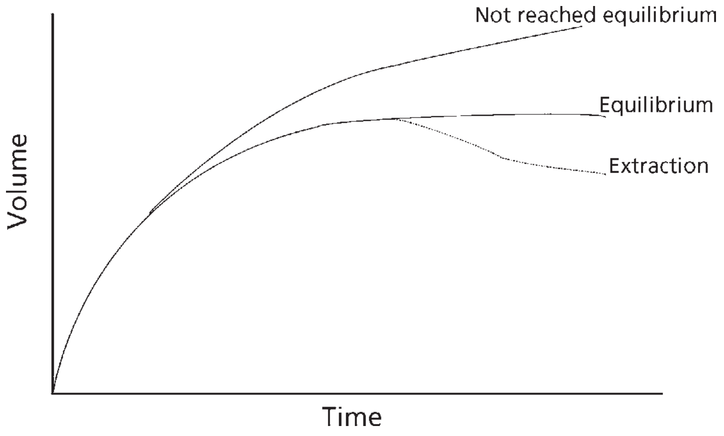

Figure 10.14 Curves of volume change against time

Standard fluids are often used to aid comparability of results, mostly oils and fuels, and these are given in ISO 1817 [74]. The particular case of water absorption is covered in BS 903 Part A18 [47] which uses small particles of the rubber to give a large surface area and overcome the very slow rate of absorption.

In addition to volume change being a good measure of the general resistance of a rubber to a liquid, the degree of swelling can be related to the degree of cure.

10.5.3 Effect of gases

With the notable exceptions of air and ozone, there are relatively few applications involving gases. Where the effect of a gas is important the same principles as for liquids could be applied but the experimental problems are much greater. A phenomenon where high pressures are involved is explosive decompression which is due to absorbed gas causing rupture when the pressure is released rather than any chemical effect. This can cause serious problems in, for example, high pressure hoses.

Ozone is a very important special case. Even very small amounts of ozone in the atmosphere of less than 1 part per 100 million cause cracking in susceptible compounds under tensile strain. The procedure is to expose strained test pieces in a cabinet containing an ozone atmosphere and examining for visible cracks after a given time. Procedures are given in ISO 1431, Part 1 [75] or the usual static exposure, Part 2 [76] for dynamic exposure and Part 3 [77] for the measurement of concentration.

Most tests involve a single strain, ozone concentration and exposure time and are used as a quality control measure. A fuller evaluation is made by exposing at several strains and finding the time to the first appearance of cracks. In many cases a threshold strain is found below which no cracks are formed for very long times.

10.5.4 Weathering

With plastics, exposure to natural or accelerated weathering is often carried out with emphasis on the effect of UV light. With black rubbers the effect of UV is rather less important than heat and ozone, and weathering tests are much less common. Procedures are standardised in ISO 4665 [78] which are heavily based on the plastics equivalents. In natural weathering, one difference is that rubbers need to be strained to find the effect of ozone, whilst in accelerated tests ozone is eliminated. The same principles as for ageing tests apply in respect of the properties chosen to monitor degradation.

10.5.5 Biological attack

Biological attack is relatively rare and generally restricted to particular applications such as water pipe seals or specific problems in tropical countries. There are no general standard test methods although procedures are specified for pipe seals. Such exposure to micro-organisms is generally carried out in specialist laboratories.

10.5.6 Fire resistance

Although most rubbers burn, testing for fire resistance has received far less attention than the flammability of plastics, probably reflecting the differences in high volume and high risk applications. The result is that there are no international test methods specifically for rubbers but the tests and principles used for plastics can be readily applied. The main distinctions are between small and large scale tests and between the various aspects of fire which can be evaluated. Small scale tests are essentially for quality control and cover such factors as ease of ignition and rate of burning. Large scale tests are necessary to evaluate performance in real fire situations and are not usually specific to one type of material.

10.5.7 Radiation

Radiation is taken here to mean *gamma* rays, electrons, neutrons, etc., and is clearly only of importance in nuclear applications or perhaps where radiation is used to induce crosslinking. There is an IEC publication (IEC 544) [79] which is a guide to determining the effects of ionising radiation on insulating materials and ASTM E1027 [80] is a recommended practice for exposure of polymeric materials to various types of radiation. Although the exposure requires a specialised facility, the methods used to monitor changes are the same as for other ageing tests.

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11 Trends in Tyre Technology

D. M. Dryden, J. R. Luchini and G. B. Ouyang

11.1 Introduction

The pace of innovation and change within the tyre industry has been more rapid and volatile in the last half of the 1990s than during anytime since radialisation swept through the North American tyre market in the early 1970s. Advances in tyre materials, tyre constructions and tyre manufacturing technology have led to new types of products and the development of new market segments. Tyre manufacturing technology has progressed in parallel with tyre construction technology so that tyres are now designed not only to meet specific performance targets, but also to enable improved ‘manufacturability’, i.e., more efficient, lower cost and more uniform production. Continual improvements in computer microprocessor speed and memory capacity now permit many types of computer simulations of tyre performance to be run on the tyre engineer’s desktop workstation that previously required more expensive mainframe or supercomputers. The expanding implementation of microprocessor technology in on-board automotive systems, along with advances in sensor technology and improved control algorithms, are enabling the integration of the automobile’s active suspension components and braking control systems with sensor information regarding the vehicle’s attitude and the tyre’s deformation and slip rate, leading to the development of the so-called ‘smart tyre’. These simultaneous technology developments are leading not only to the development of tyres with an unprecedented balance of advanced tyre performance characteristics, increased durability and improved uniformity, but are also contributing to shorter product development cycles and faster ‘speed-to-market’.

Many sources of information are available regarding the historical developments of the pneumatic tyre, and the evolution of tyre technology, constructions, materials and rubber compounds [1, 2, 3]. This chapter will focus primarily on recent developments in tyre technology.

11.1.1 Tyre basics

Since its invention by Robert William Thomson in 1845 and John Boyd Dunlop in 1888, the pneumatic tyre has undergone many evolutionary changes in response to the ever-increasing demands of modern transportation. Yet there are two features that are likely to remain unchanged, at least for the near future: the use of pressurised air to support the load, and the use of rubber in the tread to provide traction. The air cushion not only improves ride comfort, but also helps spread the load onto a larger contact area with less stress concentration. As a result, the pneumatic tyre is capable of operating successfully on a variety of surfaces, from highway to unpaved terrain, and even on soft sand beaches. Moreover, the modern vehicle owes its great manoeuvrability to the use of rubber in the tread and its capacity to provide a dry tractive ratio, i.e., longitudinal shear divided by the contact pressure, greater than one.

A pneumatic tyre is a toroidal structure with a typical cross-sectional geometry as shown in Figure 11.1. The major components are the tread, belts, carcass plies, innerliner, bead, chafer,

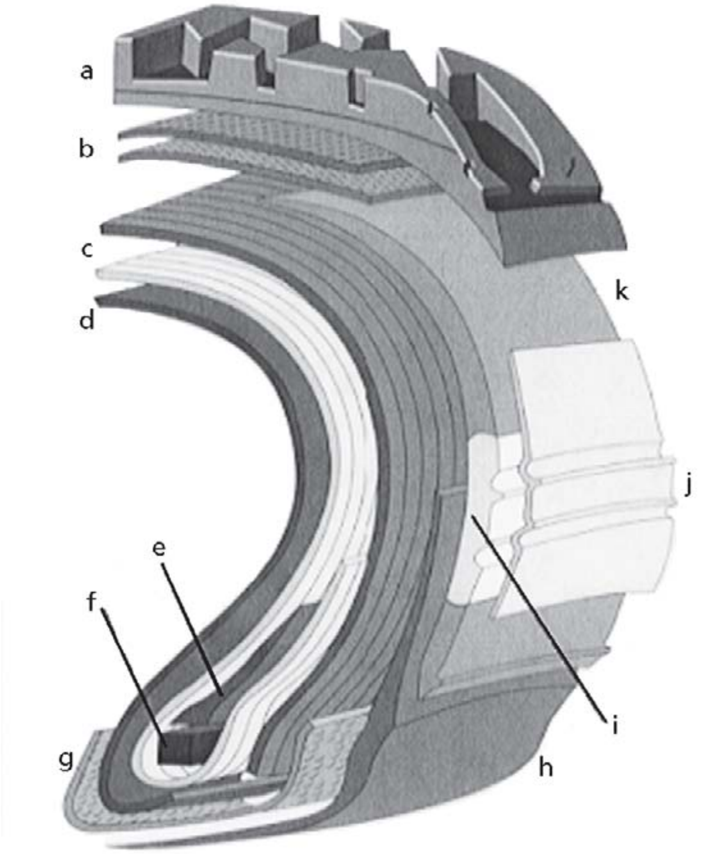


Figure 11.1 Typical radial passenger tyre construction with a) tread, b) steel belts, c) carcass plies, d) inner liner, e) apex, f) bead, g) chafer, h) rim cushion, i) white sidewall, j) veneer coverstrip and k) black sidewall

apex or bead filler, and sidewalls. Some tyres also include a white sidewall component with a protective black coverstrip.

11.1.1.1 Tread/cap

The tread or cap is the part of the tyre that contacts the road. Though it serves to protect the tyre casing from cuts and punctures, its major role is to provide wear resistance and the traction that is critically important for generating the forces required for vehicle manoeuvring. Ideally, a tyre should provide good traction in all kinds of weather and road conditions, including wet and dry, hot and cold, snow and ice, etc. In reality, however, a tyre's tread compound is often formulated to emphasise some capabilities over others based on the tyre's intended application. For off-the-road tyres, cut and chip resistance is an important requirement. The pattern moulded into the tread serves mainly for improving road grip in rain or snow, though it plays an aesthetic role as well. On the other hand, tread patterns are also a major source of the excitations that contribute to ride vibrations and tyre noise.

11.1.1.2 Belts and overwrap/belt cap

Tyre belts, located between the tread and carcass plies, are today typically made of two cross plies of steel cord, though fibreglass belts were also popular in the 1970s and early 1980s. Though the introduction of belts in the 'crossply belted' construction of the late 1960s improved the performance of the crossply tyre, the use of belts in radial tyres is essential because the radial carcass is simply too weak in the circumferential direction. The belt reinforcement provides a solid foundation for the tread, and substantially eliminates the interfacial slippage between the tyre and road during mild operations such as free rolling. Without proper belt reinforcement, a crossply tyre casing will deform during road contact in such a way that the tread elements are forced to slip even during free rolling. This is the main reason for the better than threefold increase in treadwear mileage demonstrated by a radial tyre as compared to its crossply tyre counterpart. A belted radial tyre also provides better handling characteristics because the slippage is only moderate during normal cornering operations, resulting in more efficient lateral force generation. A zero degree (circumferential) nylon overwrap or cap is sometimes added above the steel belts to limit their growth due to centrifugal force and thus improve the tyre's durability under high speeds. It also suppresses the formation of standing waves at high speeds.

11.1.1.3 Carcass

The carcass is made of rubberised fabric, such as rayon, polyester, nylon or steel cords. It is useful to consider this layer as a membrane or tensile structure whose surface tension, due to the load of the tyre, is carried mainly by the cords attached on both ends to the tyre's beads. The shape of this membrane is controlled by the cord angle and can be calculated using the membrane theory [4]. For a crossply tyre, the cord angle could be ±30°, and can be varied to change the tyre's profile. For example, increasing the cord angle will make the tyre cross-section flatter with a lower aspect ratio. For a radial tyre, the cord angle is around 90°; i.e., in the radial direction. A radial carcass, since it does not pantograph (the change in angles of the parallelograms formed by the wires of the steel belts as observed perpendicular to the plane of the steel belts), is considerably more flexible than that of a crossply tyre. This is one of the reasons that radial tyres generally demonstrate lower rolling resistance. On the other hand, a radial carcass is intrinsically weaker for torque transfer, such as required during braking or driving operations. Its lateral stiffness is also less.

11.1.1.4 Innerliner

The innerliner is the innermost layer of a tyre body, typically made of a low permeability rubber such as halobutyl rubber, to slow the tyre's loss of air pressure due to diffusion. The innerliner is also important for reducing the diffusion of oxygen into the tyre body, particularly in the belt area. Oxidative degradation of rubber is a major cause for long term durability problems.

11.1.1.5 Bead and chafer

The bead is a hoop typically made of bronze-coated high tensile steel multi-strand wires or cables. It is usually coated with rubber and is sometimes wrapped with fabric to protect the adjacent carcass plies. The pair of bead rings provides the anchors for the carcass cords and supports the cord tension. For a tubeless tyre the beads also make the seal, through a tight interference fit against the wheel rim flange, that contains the internal air pressure. Forces generated in the tyre/road contact are transmitted through the bead/rim contact to the vehicle. The chafer is an abrasion resistant rubber, sometimes reinforced with fabric, to protect the tyre's lower sidewall from chafing against the rim flange.

11.1.1.6 Apex/bead filler

The apex or bead filler is a component with a triangular cross-section that fills the void between the carcass ply and its turn-up around the bead. It serves to strengthen the area above the bead to improve rim chafing. In the more flexible radial tyre carcass, a larger bead apex is often used to stiffen the lower sidewall, thus enhancing both the lateral and the torsional stiffness of the tyre casing.

11.1.1.7 Sidewall

The sidewalls serve to protect the carcass. The sidewall compound requires good flex life and resistance against weathering, including ozone cracking. The sidewall on the outboard side of the tyre is sometimes slightly thicker for more protection against abrasion with road curbs.

11.2 New tyre materials

11.2.1 Rubbers

In most tyre compounds, the rubber or elastomer, is (by weight) the largest single ingredient in the formulation. It is the 'binder' into which the remainder of the compound's ingredients are dispersed. Elastomers demonstrate a unique set of materials properties, including viscoelastic characteristics and the ability to undergo extreme deformations. The modern pneumatic tyre would be impossible without the use of elastomers.

Solution polymerised styrene butadiene rubber (S-SBR) is gradually replacing emulsion polymerised SBR (E-SBR), particularly in original equipment (OE) passenger tyres, due to the tremendous pressure to reduce rolling resistance in this market. This is mainly due to the ability within the solution polymerisation process to control the microstructure of the polymer so that its hysteresis characteristics are such that both rolling resistance and wet traction can be improved at the same time [5]. Tin-coupled S-SBR has also been introduced for low rolling resistance tread applications.

Another rubber introduced in the 1990s for tyre applications is brominated isobutylene-co-*para*-methylstyrene (BIMS) [6]. This elastomer imparts resistance to attack by oxygen and ozone without the use of chemical antioxidants and antiozonants and has been promoted for use in i) innerliner due to its superior heat and flex resistance, ii) sidewall for better ozone cracking resistance and no staining, and iii) in tread for better wear, wet traction and rolling resistance [7, 8].

Masterbatches of natural rubber and carbon black produced by jet mixing of the rubber latex with carbon black slurry has shown excellent macro- and micro-dispersions. This material offers the potential for reducing processing time, i.e., mixing cycles, particularly for the more difficult to mix carbon blacks with higher surface area and lower structure. The most probable performance advantages resulting from this material are slower cut growth and lower heat build up [9].

11.2.2 Fillers

The most significant development in tyre materials in recent years has been the replacement of carbon black with precipitated silica in many tread compounds. While the partial replacement of carbon black with silica has been attempted for many years [10, 11], the complete replacement of carbon black with silica has only been accomplished in production tyres since the mid-1990s. An example of this strategy, as patented by Michelin in the early 1990s [12, 13, 14], has been reported to provide a 20% reduction in rolling resistance, an 8% improvement in snow traction, a 5% improvement in wet traction, and equal treadlife (abrasion resistance) and noise [15]. Michelin's patented approach utilises a highly dispersible precipitated silica in combination with a high vinyl S-SBR and a silane coupling agent. Hysteresis, as determined by measuring tan δ at 60 °C, reportedly can be reduced by 50%. It has been pointed out that in Europe, where gasoline prices are high, the savings in fuel over the lifetime of a passenger tyre could be more than the cost of a new tyre. Lower fuel consumption is also expected to have an impact on air quality in dense urban environments due to reduced pollutant emission.

The substantial reduction of hysteresis by silica is achieved not by preventing slippage at the rubber-filler interface, but rather by increasing the distance between the filler network junctions. It has been suggested that at small strains, the tan δ is inversely proportional to the average junction width in the filler network [16]. The key factors for controlling the micro-dispersion are the relative strength of the filler-filler interaction versus the filler-polymer interaction, the mixing temperature and duration, and the molecular weight of the polymer that fills in between the filler network junctions. The superior micro-dispersion of silica is realised by using a silane coupling agent, e.g., bis(3-triethoxysilylpropyl)tetrasulphide (TESPT). This coupling agent makes the filler surface more compatible with the non-polar S-SBR, resulting in better wetting and micro-dispersion. An extended heat treatment, at about 160 °C, is required to graft the coupling agent onto the silica surface. Interestingly, the macro-dispersion of silica is generally not as good as that of carbon black. This is probably due to the strong hydrogen bonding force from the silanols on the filler surface. Hard agglomerates may be formed under high pressure in the mixer before some silica pellets have a chance to interact with the coupling agent and the rubber. Poor macro-dispersion is relatively unimportant for treadwear, but is detrimental to flex life and resistance to cut growth. Various processing aids, as well as modified mixing procedures, have been introduced to improve mix quality

[17]. In general, silica reinforced tread compounds are much more expensive than those with carbon black in regard to both materials and processing costs. Nevertheless, the marketplace, particularly for OE passenger tyres in Europe, appears to be willing to accept the added cost for the extra performance.

Among the carbon black manufacturers' responses to the silica challenge are two new products worth noting. Cabot's carbon-silica *dual phase* filler (CSDPF), is made by co-fuming in a furnace reactor [18]. Recent inverse gas chromatography (IGC) studies have revealed that the carbon black phase has stronger filler-polymer interaction than conventional carbon black [19]. Less coupling agent is needed because silica occupies only part of the filler's total surface area. It has been shown that with proper mixing, CSDPF can match the dynamic properties of silica. The main difference is found in stress softening, where the ranking follows the order of silica > CSDPF > carbon black [20].

The second product is Degussa's 'inversion' carbon black, which is reported to have a rougher surface, and thus higher surface energy, leading to stronger mechanical and physicochemical interactions with the polymer. Compared with conventional carbon blacks with similar surface area and structure, inversion carbon blacks have shown about 20-23% reduction of 60° tan δ in a NR tread formulation, and 10–15% in an S-SBR/BR tread formulation [21].

11.2.3 Fabrics and steel wires

In recent years, the tyre industry has evaluated several new reinforcement materials for carcass, belts and beads, however, the price pressure in the tyre market over the last decade has made it difficult to demonstrate performance advantages sufficient to justify the increased cost of these new materials. Some of these materials have in fact made it beyond the experimental stage and into limited use in production tyres, but none has yet made a significant presence in the market.

11.2.3.1 Carcass applications

Two textile products have received some attention: poly(ethylene naphthalate) (PEN) and poly(olefin ketone) (POK). Both of these materials are potential replacements for polyester (PET polyethylene terephthalate) or rayon for use in carcass ply. The tyre maker's goal for a new carcass material is high strength and thermal stability at a low cost. The material properties of these two materials have been demonstrated, but as yet both are costly and available only in limited supply.

In 1998, Goodyear introduced the use of thin-gauge high-tensile steel wire [22] in the carcass ply of radial passenger tyres [23]. Though steel wire has been used for many years in the carcass of radial medium duty (RMD) truck and bus tyres, and in some radial light truck (RLT) tyres, this attempt to implement similar technology in passenger tyres, while demonstrating that the ultra-high tensile strength properties of this steel cord can meet the performance requirements, has been at the expense of adding considerable weight to the tyre.

11.2.3.2 Belt applications

Several steel cord manufacturers have developed new wire constructions for this application. One area of interest for the tyre manufacturer is improving the penetration of rubber between the cable filaments to help prevent belt corrosion from punctures encountered in service. A common strategy for achieving improved rubber penetration is to change the cross section of the belt wire. One technique that has been introduced is to pre-form or 'crimp' the filaments in one or more axes to keep the cable construction more open. Bekaert's 'B-tru' and TrefilArbed's 'A-tru' wires employ this strategy. Another strategy proposed for improving rubber penetration into twisted steel belt cord is the use of an oval or ellipsoid helical shape rather than the typical round shape of the steel cord cross-section [24].

Ultra-high tensile steel wire has also been evaluated for use in steel belts. Because high-tensile wire can be drawn to a smaller diameter, the strength requirements of the belt ply can be met at a lower overall ply gauge.

11.2.3.3 Bead applications

Steel has conventionally been the material of choice for tyre beads, however aramid has been evaluated as a bead material in some specialty tyres. Aramid beads are capable of providing the required strength, and at a significantly reduced weight relative to steel beads.

11.3 Tyre manufacturing technology

11.3.1 Process optimisation and design robustness

Variation, wherever it occurs in the overall tyre manufacturing process, is generally an obstacle in the tyre manufacturer's continuing efforts to improve a broad range of critical tyre performance characteristics and durability. Accounting methods have been developed to determine the effects of this variation on manufacturing costs (COPQ – Cost of Poor Quality).

Examples of variation that can contribute to the cost of poor quality include:

- Variation in tyre component dimensions during component preparation.
- Variation in component placement within the tyre during the tyre building operation.
- Variation in material composition and properties originating in the rubber compound mixing operation and/or in the production of raw materials.

Efforts to combat potential sources of 'special' or 'non-random' variation include a variety of quality system components such as statistical process control (SPC) techniques, system capability studies, and failure mode and effects analysis (FMEA). These systems are invaluable for helping to identify steps within the tyre manufacturing process where improvements in process control, manufacturing methods, and equipment operation can lead to measurable improvements in product quality and tyre uniformity. Concurrently, tyre design optimisation methods, which include a variety of design of experiments (DOE) methodologies, can lead not only to a set of 'optimum' design parameters, i.e., a combination of component gauges, component placement and rubber compound and material properties that lead to an 'optimum' balance of tyre performance characteristics, but also to 'robust' tyre designs that are inherently stable and resistant to the effects of normal or random manufacturing variation.

11.3.2 Design for manufacturability

11.3.2.1 Tyre design for manufacturability

For most of the history of the tyre industry, tyre engineers, tyre designers and tyre materials engineers have struggled with the problems of developing tyre constructions, tyre designs, tyre materials and rubber formulations, that in combination met or exceeded a list of specific tyre performance characteristics and durability targets within a pre-determined cost envelope. Existing tyre manufacturing processes and capabilities were often viewed as constraints that inhibited the use of novel tyre constructions and the introduction of new tyre materials. The idea of 'Design for Manufacturability' was typically understood to mean developing tyre constructions and materials that 'fit' within the constraints of existing manufacturing capabilities (due to the high capital costs of replacing tyre manufacturing equipment). Examples of this type of 'Design for Manufacturing' strategies include:

- Increasing rubber compound 'green strength' to improve the dimensional stability of uncured tyre components.
- Reducing the number of tyre components that must be assembled.
- Designing the arrangement and placement of specific tyre components so that they can be 'pre-assembled' in a continuous production process prior to final green tyre assembly at the tyre building machine.

11.3.2.2 Concurrent tyre and manufacturing system design

Beginning in the early 1980s, and progressing throughout the 1990s, a great deal of effort within the tyre industry has been focused on true 'design for manufacturability' in which many aspects of the tyre's construction, and materials, are designed with the primary objective of achieving an efficient, uniform, and low-cost manufacturing process rather than to achieve specific tyre performance targets. Concurrently, the whole tyre manufacturing process was also re-examined, and in many ways completely redesigned by some manufacturers, in order to achieve the sought after improvements in tyre production costs and efficiency, i.e., lower capital costs, lower energy costs, lower labour costs and more flexibility in switching production between different types of tyres.

Though much of this development in tyre manufacturing technology is proprietary and is closely guarded by each tyre manufacturer, some information about these developments has been made public and many articles on this topic have appeared in the trade press in recent years. In addition, much information about these advances can be gleaned from an examination of the patents that have been filed and awarded to various tyre manufacturers and producers of tyre manufacturing equipment. In the past 20 years, dozens of patents have been awarded in the US and in Europe to each of the major tyre companies for entirely new tyre constructions, new methods for manufacturing various tyre components including belts, carcass plies, and beads, new tyre materials, new mixing and extrusion techniques, new curing technologies, and new tyre building equipment including building drums, component applicators, and ever more automated tyre building machines. Many of these patents have been related to the work of Eric Holroyd and Colin Holroyd [25, 26, 27, 28, 29, 30], two inventors who have been active in developing new tyre manufacturing processes and tyre manufacturing equipment and who have worked with several major tyre companies in these areas. They later formed their own company, Holroyd Associates Ltd, which in turn also holds a share in 3 Seas Group Ltd

[31]. Both companies are involved in the distribution of tyre manufacturing technology [32]. Further insight into these new tyre manufacturing technologies can be gained through a careful analysis of tyres that have been manufactured with these new processes.

11.3.2.3 Michelin's C3M manufacturing process

The most publicised of these new manufacturing technologies is the 'C3M' process implemented by Michelin. C3M has been identified as an acronym for 'Continuous Cold Compounding by Michelin' [33]. Michelin began producing tyres with this method starting in 1991 [34], and by 1999, had built at least eight tyre plants utilizing this technology in France, Sweden, the United States and Brazil [35]. While early announcements about the C3M process indicated that Michelin projected that by the year 2000, 30 to 40 percent of its passenger tyre production would be converted to this new process, by 1998 it was reported that Michelin was producing only about 3 million tyres annually (or between 1 or 2 percent of its production) using the C3M method. More recent estimates indicate that Michelin may eventually expand the use of C3M up to only about 30 percent of its production. The C3M process, originally developed to produce only passenger tyres, is reportedly also being modified to produce truck tyres as well [36].

The reported advantages of the 3CM process include:

- A 60% savings in the energy requirement. Electricity is the only required energy source. No steam generation is needed [34].

- A 90% reduction in work area. Francois Michelin is quoted as saying 'that the entire C3M machine could fit in his dining room' [36].

- An 85% reduction in overall manufacturing time [37].

- The highly automated process results in a significant reduction in the required labor force. Michelin's Reno, NV plant is reported to produce 1 million tyres annually with a labour force of 130 workers and technicians [36].

- A highly uniform product. The very precise component placement enabled by the C3M system has reportedly been essential to the manufacture of some new lines of Michelin and BFGoodrich brand tyres featuring coloured tread stripes [38].

The coventional tyre manufacturing process begins with an initial stage in which the various rubber compounds are mixed, followed by several different types of component preparation operations such as the extrusion of tread, sidewalls, and apex; the calendering of cord reinforced sheets such as steel belts, polyester carcass plies, rayon overwraps and innerliner plies; and then the assembly of these components on a tyre building machines prior to vulcanisation of the tyre in a steam or nitrogen heated curing press. Though details of this process vary between tyre manufactures, differing in regard to such things as the level of component pre-assembly and the degree of automation at various steps in the process (especially in the tyre building operation), the overall process is typically characterised by a series of multiple parallel, yet discrete, sub-processes.

Based on an examination of the relative patents, and information that has been made public, the C3M process integrates the rubber mixing, component preparation, tyre building and curing processes into a unified manufacturing cell [31]. Unlike the typical tyre plant in which all of the rubber compound mixing stages are completed in a separate mixing operation and the final batches of the compounds transported to various extruders and calenders for subsequent tyre component preparation, in the 'tyre manufacturing cell' process, rubber compound mixing is integrated within each tyre manufacturing cell using a continuous mixing process employing a special mixing extruder that operates at much lower temperatures than either conventional mixing extruders or Banbury type mixers [39]. One variation of the system could be to keep the initial steps of rubber compound mixing within a separate mixing facility and only completing the final stage of mixing within the manufacturing cell. The final rubber compounds are then extruded, at the tyre building machine in a manner similar to the 'Orbitread' process [40] that has been used for retreading, onto the green tyre to form the various tyre components. This process creates jagged component junctions due to the thin strips of extruded rubber that can be observed in a section cut from a C3M tyre.

Another distinct difference of the Michelin C3M process is that the green tyre is built on a metal torus based on the shape of the inside surface (innerliner) of the final cured tyre rather than on the collapsible metal drum that is part of most conventional tyre building machines [41]. The imprint of the segments of this torus is obvious when the otherwise smooth innerliner of a C3M tyre is examined [42]. In contrast to the conventional tyre curing process in which the exterior of the tyre is moulded against a steel or aluminium mould mounted in a curing press between two steam heated platens in order to impart the tyre's tread pattern and sidewall lettering, and in which the interior of the tyre is moulded by a rubber curing bladder inflated by either pressurised hot water, steam or heated nitrogen gas; the C3M process cures the tyre by electrically heating both the metal building torus and the outer tyre mould, thereby eliminating the costly tyre curing bladder and the attendant issues of bladder life (requiring frequent bladder replacement due to mechanical fatigue) and steam generation. This metal torus not only eliminates the 'shaping' step in which the diameter of the drum shaped green tyre is stretched to the tyre's final diameter, but it also eliminates the costly tyre curing bladder and the attendant issues of bladder life and steam generation. Instead, the metal torus is electrically heated, and along with the outer tyre mould, is utilised for vulcanising the tyre.

Another novel technology employed by the C3M process is the elimination of the conventional calendering of carcass plies and its replacement by ‘weaving’ the tyre’s carcass directly on the toroidal building ‘drum’ just described and as illustrated in Figure 11.2 [43]. Both variations of this technology, one of which involves looping the strands of the carcass ply around each bead, and the second technique that ‘clamps’ or ‘anchors’ the ends of the carcass strands between layers of the bead bundle as shown in Figure 11.3, result in the elimination of the carcass ply ‘turn-up’ and any potential for ‘turn-up’ separation as an eventual mode of tyre failure [44]. Concurrent with this innovation in carcass ply production has been the adoption of novel tyre beads including the use of several nested strands of ‘kidney bead’ or ‘concave’ shaped wire, or alternately, the use of wire cable constructions similar to those used in wire for steel tyre belts.

Some questions about the C3M cell manufacturing process have been raised:

- Incompatibility of the C3M process with conventional tyre manufacturing equipment? The initial capital costs are relatively high because the C3M equipment cannot be

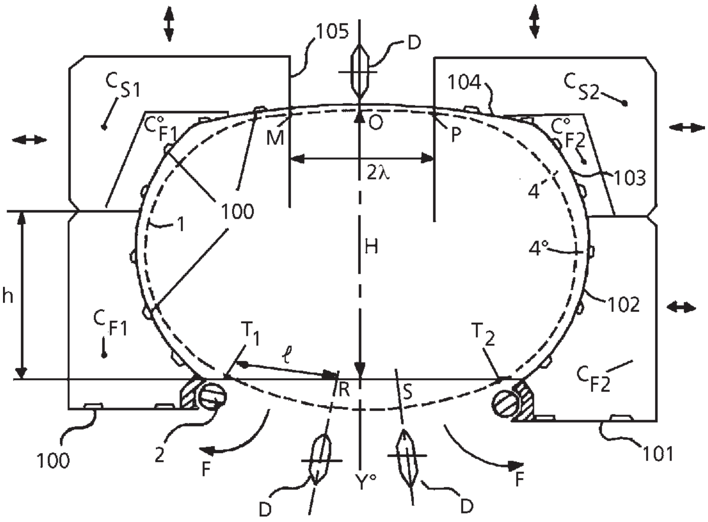


Figure 11.2 Diagram from US Patent 5,700,339 [41] of an apparatus for producing a tyre carcass by winding a cord around an ‘annular building core’

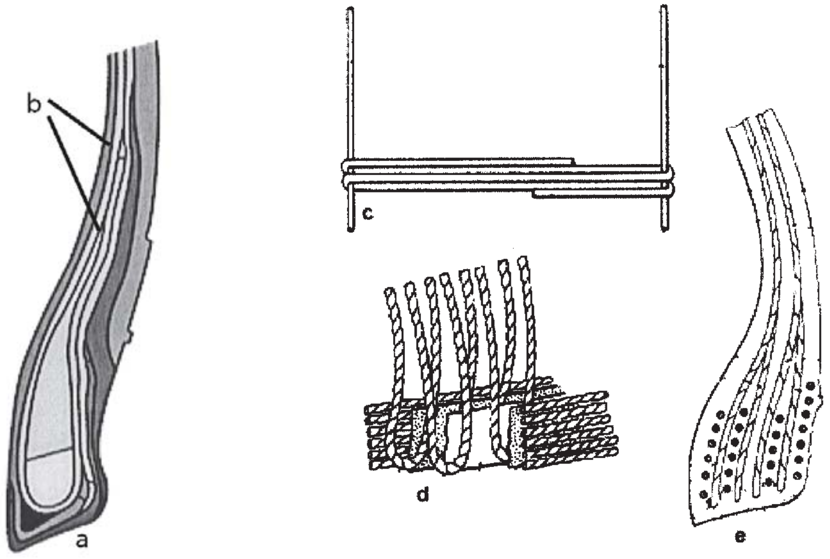


Figure 11.3 a) Conventional 2-ply carcass construction with ply turn-ups, b) in lower sidewall, c) schematic of single cord ply construction from US Patent 4,967,821 [43], and two embodiments, d) and e) of 'anchored carcass' from US Patent 5,660,656 [44]

added incrementally to existing tyre plant equipment. Completely new equipment, and typically a complete new tyre plant, are required.

- Reliability of the machinery? Since all of the sub-processes have been integrated into a unified cell, any mechanical malfunction in one part of the equipment could shutdown the entire unit.
- Flexibility of the process. The toroid building core, like the external tyre mould, can be used for only one rim width and diameter.
- Effect on labour? The implementation of C3M technology is thought to be somewhat related to recent layoffs in Michelin's European factories [45, 46].

11.3.2.4 Manufacturing technologies at other tyre companies

Goodyear announced their IMPACT (Integrated Manufacturing Precision-Assembled Cellular Technology) process in 1998 [47] and like Michelin, have been very active in obtaining patents related to this technology [48]. Like Michelin, Goodyear makes similar, though less dramatic, claims regarding the benefits of their new manufacturing technology: a 15% reduction in material costs; a 35% reduction in labour costs, 20% reduction in curing time, and reductions in floor space, in-process inventory and energy costs. One advantage claimed over the C3M process is that Goodyear's technology is somewhat compatible with conventional tyre manufacturing and it is being introduced gradually in all Goodyear factories [35].

In 1997, Continental AG announced its plan to implement a large-scale modular manufacturing process it labelled Modular Manufacturing Process (MMP) that entails building casing 'platforms' at one tyre plant that are then partially vulcanised before being shipped to a different tyre plant at another site for final assembly, curing and finishing [49]. The MMP technology is reported to have taken three years to develop and is designed to make Continental's manufacturing system more flexible by accommodating small runs (as few as 100 tyres) with quick delivery to customers. In contrast to Michelin's C3M technology, MMP is said to utilise Continental's present manufacturing capacity while minimizing workforce reductions.

Pirelli introduced its 'Flexi' system that, like Continental's MMP process, can produce small runs with as few as 100 tyres [35]. Sumitomo has stated that it too has developed a manufacturing system similar in some aspects to Michelin's C3M process. On the other hand, Bridgestone revealed very little about their 'Tochigi' tyre manufacturing process [35] until 1999 when it opened a new passenger and light truck tyre plant in South Carolina that it claimed was built around its Automated Continuous Tyre Assembly System (ACTAS). This system, which is reported to use 22 highly automated tyre building machines to feed 150-160 curing presses, appears to be more like Goodyear's IMPACT system than Michelin's C3M technology. Bridgestone claims that at full capacity, the new tyre plant will achieve an average of 31 tyres per day per employee [50].

11.4 Tyre performance

11.4.1 Rolling resistance

Modern computational methods and testing methods, offer the opportunity to model tyre rolling resistance analytically as well as experimentally and obtain similar results. The choice between methods is dependent on the desired results and the availability of computer equipment and testing hardware. Recent advances in tyre mechanics and computer technology combined with good test protocols have made it relatively simple to accurately model both the equilibrium and transient rolling resistance of a tyre.

11.4.1.1 Definitions

The term 'Tyre Rolling Resistance' is used and defined in several different ways within the technical literature. In some of these definitions the losses due to aerodynamics are included in the tyre rolling resistance, while others include only the energy losses that appear in the tyre's structure as heat.

Rolling Resistance Force The 'rolling resistance force is the negative component of longitudinal force resulting from energy losses due to deformations of the rolling tyre' [51]. This rolling resistance is a force vector applied through a tyre. This definition works for a vehicle with its tyres rolling straight ahead on a flat surface, but it becomes ambiguous when the tyres are rolled on a curved surface or rolled in a curved trajectory.

Free Rolling Resistance The free rolling resistance is 'the scalar sum of all contact forces tangent to the test surface and parallel to the wheel plane of the tyre' [52]. In this definition, rolling resistance on either a flat or a curved surface is a 'scalar' quantity, which has the units of a force. This definition was intended for use with a 'free rolling' tyre and it becomes ambiguous when the tyre is rolled in a curved trajectory or when it has applied (braking or driving) torque.

Tyre Rolling Loss Tyre rolling loss is computed as the loss of energy per unit of distance travelled. This most general definition of tyre rolling resistance is based on energy rather than forces [53]. This definition is consistent with the preceding definitions and is very useful in the analytical modeling of tyre rolling resistance.

Tyre Rolling Resistance For the remainder of this chapter, tyre rolling resistance is defined as the energy loss due to cycling tyre materials within the tyre structure, per unit distance traveled. This provides for the same measurement units as a force vector, although it is a scalar quantity based on energy.

11.4.1.2 Rolling resistance measurement

Several methods exist for the measurement of tyre rolling resistance, however, these methods give somewhat different results and must not be used interchangeably. Some methods focus on force measurements rather than energy losses, or include aerodynamics or other non-tyre effects. Experimental measurement of tyre rolling resistance is typically done on a cylindrical test drum. The method of SAE J-1269 specifies a 67.23 inch (1.7 m) diameter test drum with an approximation formula for estimating the value on a flat road surface. The method of ISO 8767, which is being harmonised with ISO 9948 and ISO 3327, provide a method for estimating the value on other test drums in the range of 1.5 m to 3 m.

The SAE Test Method J-1269 [54] provides a standardised way to test tyres at different laboratories and arrive at consistent conclusions. The Information Report SAE J-1270 is a companion to J-1269 and provides an explanation of the various parameters, tolerances, and effects so that the data from the testing may be interpreted appropriately. The rationales for specific measurement and control accuracy for ambient temperature, tyre load, and inflation pressure are explained in terms of their effects on the measured value of tyre rolling resistance [52].

Methods developed for testing tyre rolling resistance using highway vehicles have been used in both the tyre and vehicle manufacturing industries in demonstrations of the role of tyre rolling resistance in reducing fuel consumption. These methods generate primarily qualitative results because over-the-road testing is less sensitive to tyre features than laboratory testing. Experiments that define the role of individual tyre components and variables have been conducted in the laboratory, with most of them using the SAE test method J-1269.

11.4.1.3 Rolling resistance computation

Only recently has computational modelling of tyres as discussed in Section 11.5.2 been able to replace some of the need for measurement of prototype tyres. Recently however, tyre modelling procedures have reached a point where it is possible to make reasonably accurate predictions of the rolling loss of a tyre solely from knowledge of the basic materials and construction. As a tyre rolls in use, every component is loaded to some level and then unloaded to a base level. Due to the hysteretic nature of the materials, the total applied energy is not recovered. The amount of energy loss is a function of the material, the details of the strain cycle, and the ambient conditions including temperature and nominal strain. The total loss in rolling a tyre is the integral of the loss energy of each portion of the tyre.

One general problem in the computer modelling of tyre rolling loss is the adequacy of the material models, and the data needed to parameterise the models, for finite element analysis (FEA) computations. Often simplified models, which have been developed with laboratory data, are presumed to represent conditions seen in the tyre during service. This can lead to computed results that do not match experimental results since the three dimensional, non-sinusoidal, stress-strain cycle in the tyre can have 1.5–2.5 times greater energy loss than a uniaxial sinusoidal laboratory test.

Assuming an appropriate material property model for both the computation of the stress state and the hysteretic losses, tyre rolling resistance may be obtained by a finite element analysis [55, 56, 57]. The stress and strain, which are complex multiaxial tensors, can be integrated through a rolling cycle and the energy loss obtained. The importance of the proper definition for rolling resistance is noted in these analytical computations of the amount of energy used to roll the tyre. This energy computation is scaled per unit distance travelled and the tyre rolling resistance is thus reported in units of force (work/distance). The heat flowing out of the tyre is the same as the material mechanical hysteresis. Therefore, the energy per cycle can be used for thermal analyses and the resulting material temperatures used to update the model results. A 'hybrid' thermomechanical model can thus be used for any steady state or transient conditions [58].

Note again the importance of the proper definition for rolling resistance when comparing analytical computations and experiments. When the tyre is not in equilibrium, the instantaneous measurement of rolling resistance force would include the effects of inertia and heat storage. The energy based definition of tyre rolling resistance would not include these effects.

11.4.1.4 General relationships for tyre rolling resistance

Many aspects of selecting, maintaining, and retreading tyres for good fuel efficiency are common knowledge today. In addition, tyre rolling resistance can be incrementally reduced with small changes to materials, construction, or shape. However, it has been shown repeatedly in practice that large changes, or combinations of changes, in the main engineering variables can put the tyre into a new 'design space' in which predictions from previous studies are totally inaccurate. Therefore, published reports of changes in tyre rolling resistance, such as those listed in Table 11.1, must be considered as individual, small perturbations from an existing tyre design or operating condition and should not be perceived as general design rules.

11.4.2 Treadwear

One of the major attributes of the radial belted tyre is its more than three fold improvement in treadwear compared to a similarly sized crossply tyre. This is achieved primarily by reducing interfacial slippage between the tyre and road through strong belt reinforcement [64]. Slippage happens only intermittently during more severe operations, such as cornering, braking or driving. A crossply tyre, on the other hand, without belt reinforcement will pantograph in the road contact region and will be forced to slip even during mild free rolling. This conclusion is supported by the observation that the footprint of a rolling crossply tyre is narrower at the middle than at either the entrance or the exit.

Table 11.1 General relationships for tyre rolling resistance

General Statement	Caveat
Lower load reduces rolling resistance	For a single tyre at the same operating inflation pressure. (Pressure increases due to temperature at operating conditions)
Higher inflation pressure reduces rolling resistance	For a single tyre at the same operating load
Radial construction has lower rolling resistance than crossply construction	The effects of basic tyre construction (radial or crossply) show overall advantages in rolling resistance and in fuel economy for the radial ply over the cross ply construction when the tyres are nominally the same size and application with different materials as well as different constructions. It is possible to build a crossply tyre with less rolling resistance than a similar radial through use of unique materials or modification of operation conditions
Laboratory testing shows an improvement in rolling resistance Over the road testing shows no improvement in rolling resistance	The percent change in laboratory measurements and in the fuel economy (on a track test) are not the same. Road test data is also less sensitive than laboratory testing [59]
Tyre carcass construction improves rolling resistance	Based on comparison with a given construction and set of compounds. The results may not apply to other brands or for other sizes of tyre [60]
Change in tyre geometry (size) and the operating conditions show only moderate changes in efficiency	Limiting experiments to standard tyre design parameters, increased tyre inflation pressure can compensate for the effect of increased load on the tyre [61]
Tyres of a specific size improves rolling resistance	Based on a specific type of service and may not apply to the same tyres used in another application. For example ‘super single’ tyres have about twice the rolling resistance of a typical tyre carrying half of the total load
More uniform wheels, or better matched dual wheels, improve rolling resistance.	This may be due to the dual tyres working against each other or extra stress cycles due to bouncing contact with the road
New material improves rolling resistance by {x}%	Based on the use of the material in a specific tyre construction or specific size tyre

Table 11.1 General relationships for tyre rolling resistance (continued)

General Statement	Caveat
The {tread/belt/bead/etc.} is responsible for {x}% of tyre rolling resistance	Based on changes or removal of that component, which also changes the general stress cycle
Worn tyres (reduced tread depth) have improved rolling resistance	Artificially removed tread can change the tyre shape and contact stress, confounding the effect of material loss. Changes are not uniform. The effect of tread depth has also been confounded with the effects of moulding, tread compounding strategy, construction strategy, compound ageing, and number of cycles on the tyre carcass. Bosik [62] showed that half-tread tyres had lower rolling resistance than the new tyres but fully worn tyres had about the same rolling resistance as the half tread tyres
Retreaded tyres are equivalent to new tyres	Characteristics in combination confound the effects, such that it may not be clear if a radial or crossply construction is superior. For tyres with identical tread compounds it was found that retreaded truck tyres could exhibit rolling resistance equivalent to new truck tyres [63]

It can also be shown that a radial tyre runs cooler in both the sidewall and tread because of less shear and slippage. Another interesting consequence of belt reinforcement is the virtual elimination of the well known Schalamach ridge pattern [65] in the texture of the radial tyre's worn tread surface. This type of ridge wear pattern is attributable to *continuous slip*, under which the surface of the tread rubber becomes considerably hotter. In a continuous slip laboratory abrasion test (such as the Lambourne type) [66], the average distance between the ridges has been found to increase linearly with an increase in slip ratio.

In a study of wear particles collected from treadwear road tests, particles were found to have a sausage shape with a diameter in the range of 2 to 100+ μm, and an average of about 20 μm [67]. If one assumes i) a wear rate of 0.75 mm per 10,000 km, and ii) the smallest discrete wear particle to be 2 μm in size, then it would take more than 25 km of travelling distance before one particle is removed from a particular point on the tread surface. It is therefore reasonable to say that normal treadwear is a fatigue failure process involving thousands of cycles of road contact with various levels of stresses and slippage. Only when the tread skin becomes too weak to withstand the shear and slip, will a roll-formation process finally set in to remove the degraded rubber.

The thickness of this degraded skin layer is controlled mainly by the coarseness of the road surface, contact pressure, tread compound modulus and its heat transfer characteristics. Normally, it can be anywhere from 2 to 100+ μm as reflected by the size of the wear particles. The key in treadwear improvement from a material design perspective is to slow the degradation and maintain the strength of the skin rubber. Proper selection of rubbers, fillers and anti-degradants are important considerations. Fillers with higher surface area, higher structure and increased filler-rubber interaction are known to improve treadwear. Temperature is a strong factor affecting the rate of oxidative degradation. A cooler running tyre can improve treadwear by slowing the degradation component of the treadwear process.

11.4.2.1 Irregular wear

In an ideal situation, the tyre would wear slowly, but also uniformly. Uneven or irregular wear is undesirable and easily recognizable from the tyre noise and vibrations that result. The deterioration of ride and handling can become so annoying that the tyres may become unacceptable even if the total wear rate is low. Irregular wear is often caused by, and used as a diagnostic tool for, problems in a vehicle's suspension system, such as misalignment, excessive toe [51] or camber, soft spring and/or shock absorber, etc. Some types of irregular wear, however, can be attributable to the tyre itself.

Irregular wear in non-driven all-season passenger type tyres has in the past been a common problem in North America. Many of these tyres, generally with block tread element designs intended for better snow and wet traction, developed heel-and-toe wear on non-driven positions even when they were used primarily for highway driving with less frequent stop-and-go traffic and less cornering than in city driving. On a front-wheel-drive vehicle, for example, it is the rear tyres that would develop irregular wear. Though the front (driven) tyres might wear faster, in general their wear pattern would be quite even. Both the front and rear wheels undergo cornering and braking, therefore they are not the culprits. The main difference is that, except during cornering or braking, the front tyres are operated under driving torque almost all the time, while the rear tyres are free rolling with no torque load. Therefore, it would be useful to examine the differences between the free rolling and the driving modes. Figures 11.4a and 11.4b depict the contact pressure and longitudinal shear behaviour of an ungrooved radial tyre at the tread surface, respectively.

Under free rolling conditions, the contact pressure is skew-symmetric along the contact length. When a driving or braking force is applied, moment balance will require some shift of the contact pressure. Part of the moment balance can be provided by the vertical load through a slight shift of the centre of the footprint. More interesting is the longitudinal

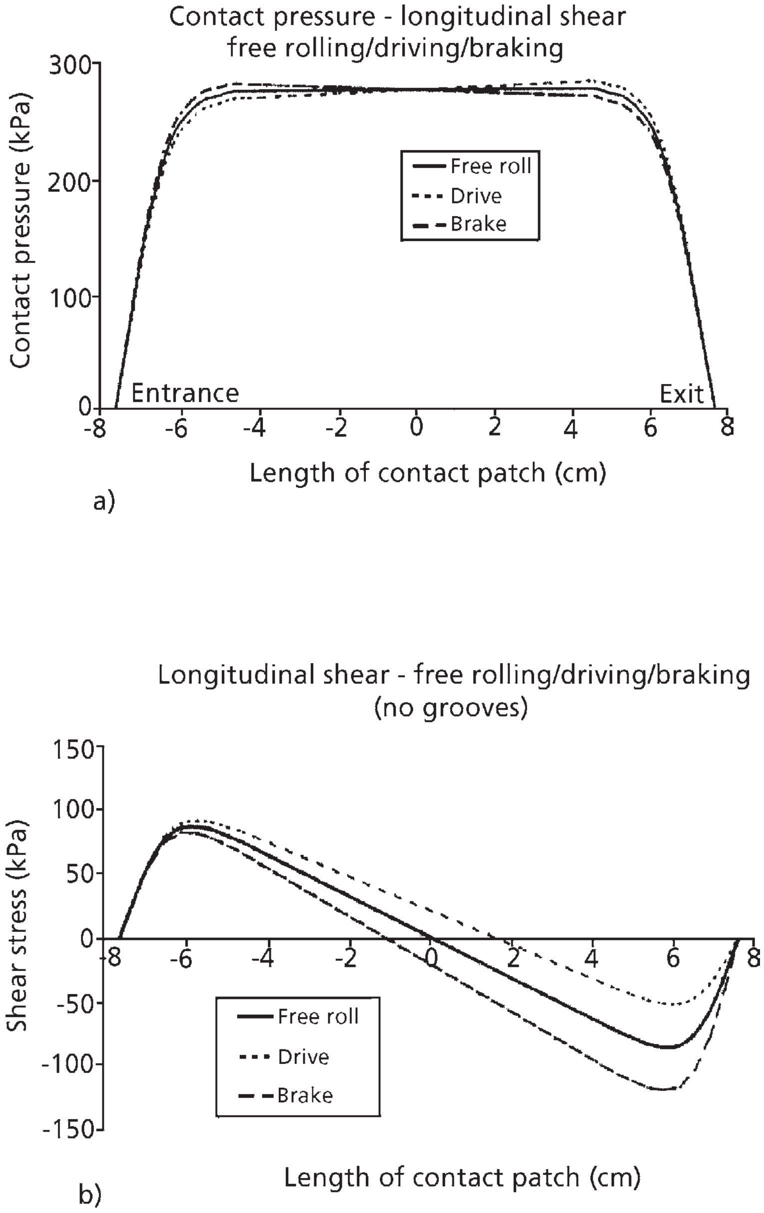


Figure 11.4a and 11.4b Illustrate contact pressure and shear stress within the contact patch in relation to the length of the contact patch for a free rolling, driven or braking tyre

shear, which during free rolling will increase first and then decrease in an anti-symmetric fashion. The area under the negative shear should be slightly larger than that of the positive shear, and correspond to the magnitude of the rolling resistance. As a driving torque is applied, the shear stress will increase more or less linearly along the contact length as shown in the figure. The magnitude of the shear stress cycle, as determined by the maximum and the minimum stresses, would be *reduced* when compared to that of the free rolling mode. On the other hand, when a braking torque of equal magnitude is applied, the shear stress cycle will get larger. One can therefore conclude that, within normal driving severity and at equal vertical loading, the rate of shear stress cycle induced tread surface degradation should follow this order:

Braking > Free Rolling > Driving.

This result suggests that a non-driven tyre could have worse wear due to more degradation in the tread skin than a slightly driven tyre.

To better understand heel-and-toe wear, we further consider the behaviour of a block tread element on a *free rolling* tyre with no side slip. The leading edge of a tread element, i.e., the *heel* that makes road contact first as the element rolls into the footprint, will have a compression induced shear pointing into the forward direction. The trailing edge or the toe, on the other hand, will have an induced shear pointing in the braking direction. The contact pressure on the edges will be lower than that of the centre, depending on the shape factor of the tread element. The heel has a 'bite' at the entrance, namely, an increase of contact pressure in part to make up for the loss in the groove area. The toe will have a corresponding reduction of contact pressure. At the exit from the footprint, the 'bite', or 'snap', will move to the trailing edge of the element. Additional shift of the contact pressure between heel and toe is due to the shear deformation of the tread element. The combined effect of having grooves cut to form individual tread elements is shown in Figures 11.5a and 11.5b. Comparing the tractive ratio, it is interesting to see that near the exit the toe is much worse than the heel in terms of likelihood to develop the slippage.

Actual slippage will not take place until either the skin rubber degrades or, during more severe operations, the local friction coefficient drops below the magnitude of the tractive ratio. From Figure 11.5a, it is not difficult to see that under a moderate driving torque, the shear stress near the exit will increase and get closer to zero for both the heel and the toe. Indeed, when examining the surface of a tyre after a driving torque was applied, scratch marks in the tread from the road surface were found to be light and even from heel to toe. After braking, however, these scratch marks were found to be quite uneven, i.e., become denser and longer toward the trailing edge. The irregular wear of non-driven all-season tyres appears to be a combined result of more severe degradation and of the heel-and-toe differences in the free rolling tyre as compared to one slightly driven.

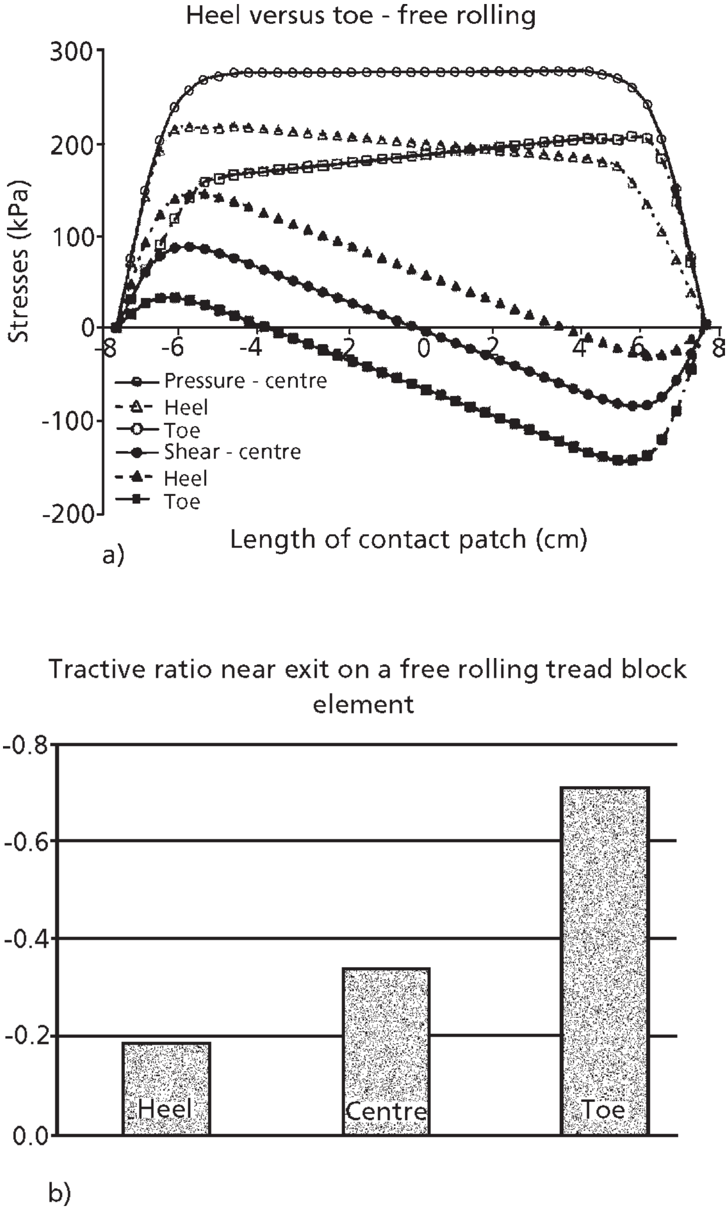


Figure 11.5a and 11.5b Illustrate the relative contact pressure and tractive ratio for the heel, centre and toe of a free rolling tread element

As the toe wear develops, a vicious cycle will begin, because the tractive ratio near the toe can only get worse as the local contact pressure becomes lower due to the uneven wear. Since there is no self-correcting mechanism, the only way to overcome this problem is by reversing the direction of rotation. This forms the basis for the generally recommended cross rotation pattern for radial passenger tyres.

Since the unevenness between heel and toe is intrinsic to a tread block element's rolling process, one cannot eliminate it. However, there are a few measures that can be taken to minimise the problem. From the material property consideration, one should use a compound whose wear rate sensitivity to the slip ratio is low. The wear rate, W, is known to follow the relationship, $W \propto S^N$, where S is the slip ratio and $N \approx 2+$. The frictional energy dissipation should be proportional to the square of S if the frictional force is proportional to the slip ratio. However, the power index, N, can be as large as 3 or higher for some compounds. The wear rate's departure from quadratic relationship usually can be attributed to the compound's lack of resistance to thermal-chemical degradation. One should also consider the shape factor of the tread element including the selection of kerfs (width of a groove) so that the compression-induced shear stress and tread element stability are optimised to avoid excessive and uneven slippage.

11.4.2.2 Rolling radius and irregular wear

A third factor that is important for irregular wear is the uneven rolling radii for different tread rows. It is not difficult to see that when two tread rows of different rolling radii are forced to travel the same distance, the small one will be running in continuous braking mode, and the large one in driving mode. The tread row with smaller radius will develop irregular wear, such as heel-and-toe. This is analogous to mis-matching sizes in a dual truck tyre assembly, where the smaller tyre is known to develop irregular wear very quickly.

To help understand what controls the individual rolling radius, it is useful to use the 'point definition' of the rolling radius of a straight running tyre as depicted in Figure 11.6. The point definition not only allows the investigation of differences between tread rows, it could also be applied to compare any two points on a tread surface. Let us follow a particular point on the tread that enters and leaves the road contact at A. The other end of the contact length is labelled as B. During this time, the centre of the tyre will move from O to O′, with a distance ΔL, and the tyre will rotate by an angle Δθ. The rolling radius for this point can be defined as

$$R = \Delta L / \Delta\theta \quad = \ (X_O - X_{O'}) / (\theta_B - \theta_A)$$

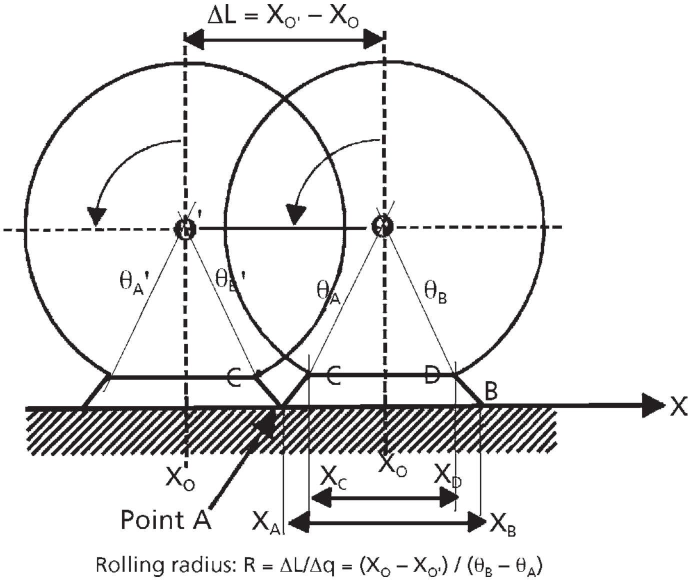


Figure 11.6 Point definition of the rolling radius

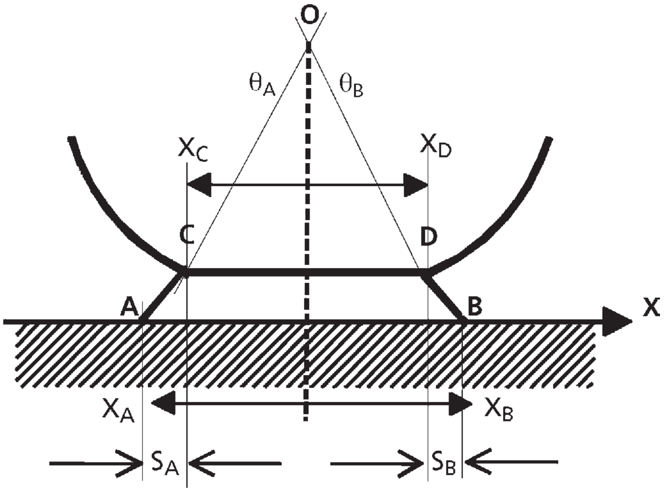
where θ_A and θ_B are, respectively, the angular coordinates of the entrance and exit points in the rotating tyre's reference coordinate system *before* being deformed. If there is no slippage, then $(X_O - X_{O'}) = (X_B - X_A)$, and the rolling radius can be rewritten as

$$R = \Delta L/\Delta\theta \; = (X_B - X_A)/(\theta_B - \theta_A),$$

where X_A and X_B are the coordinates of the beginning and the end of the footprint contact. The flattened circle represents the belt, where points C and D have the same angular coordinates as θ_A and θ_B, respectively. The length of $\underline{CD}$, $(X_D - X_C)$, is the deformed belt length that supports the tread in the road contact. Since $(\theta_B - \theta_A)$ is determined mainly by the load and the inflation pressure and remains basically unchanged with the applied torque, the rolling radius is controlled by contact length, $(X_B - X_A)$, which can be broken into three components as shown in Figure 11.7:

$$(X_B - X_A) = (X_D - X_C) + S_A + S_B,$$

where S_A and S_B can be thought of as the 'strides' at the two ends of the footprint contact. The strides can vary, particularly the rear one, according to the mode of operation. It can be shown that the rolling radius should increase for braking, and decrease for driving



Rolling radius: $R = \Delta L/\Delta\theta = (X_B - X_A)/(\theta_B - \theta_A)$
Strides: S_A and S_B
Contact length: $(X_B - X_A) = (X_D - X_C) + S_A + S_B$

Figure 11.7 Rolling radius and strides

mode. To be more complete in this 'point definition', we should mention that positive and negative slip lengths can be added, at point B, to modify ΔL for more severe braking and driving, respectively.

For each tread row, the supporting belt foundation will deform differently as the double-curvature crown flattens in the road contact. The effective contact belt length, $(X_D - X_C)$, is determined by the double-curvatured belt composite characteristics as it flattens. Usually, as a result of the crown curvature, the shoulder rows would have smaller rolling radii. They tend to be run in a slightly braking mode during free rolling, because they are forced to travel with a larger rolling radius. It is interesting to point out that sometimes the first inside rows, e.g., the second and fourth rows in a five-row tread pattern design, could have even smaller rolling radii. This could be a result of weak belt combined with the lifting from bending in the buttress area during the sidewall deflection. The reduced contact pressure in these rows would change the belt and tread element deformations as they are entering the footprint in such a way that the 'strides' are reduced, resulting in smaller rolling radii. A well-designed tyre should have minimum differences in rolling radii for all the tread rows. Major factors for controlling rolling radius are the length of the deformed belt foundation, undertread, tread element geometry including groove and sipe design, and contact conditions, such as the pressure distribution, etc.

11.4.3 Ride and handling

In handling, tyre tractive forces are generated by deforming the tread rubber with proper contact pressure to hold the road, and shear forces to move the vehicle. The bulk modulus of the tread should be high to generate forces efficiently, yet the tread skin rubber ought to be soft for proper engagement with the road surface texture and thus provide the grip. Designing a compound to satisfy these seemingly contradictory requirements is an interesting challenge to the tyre material engineer.

For high performance tyres, the trend is toward lower aspect ratio. In other words, for a given diameter and load requirement, a wider tread and a larger diameter rim are preferred. The reason for increasing the tread width is mainly for reducing the road contact length. Since the footprint area is constant for a given load and inflation pressure, a wider tread means shorter footprint. During normal braking, cornering and severe acceleration, the magnitude of the shear stress increases along the contact length. For a given slip ratio or slip angle, shorter road contact length gives lower *peak* in the shear stress, thus better road grip for more efficient tractive force generation. The benefit of using a larger rim is two-fold: i) it offers room for a larger, thus more efficient brake, ii) it shortens the sidewall to help increase the tyre casing's torsional stiffness, which is important for driving and braking operations.

In cornering, high lateral stiffness can help shorten the distance that a tyre needs to travel before rolling into the full development of the side force. Therefore, it is common to add a hard apex in the lower sidewall for improving handling response. A hard apex can help increase the torsional as well as the lateral stiffness. Another important consideration is in the sidewall carcass contour. It can be shown by a simple membrane theory analysis that the lateral stiffness can be effectively raised by adjusting the height and the radius of curvature for the widest point on the sidewall's radial carcass contour.

Low aspect ratio tyres are better for handling, but a short sidewall reduces the air volume for cushioning, and thus ride comfort is generally poorer. A short footprint can also result in a large percentage loss of contact area available for traction in rain. Wet traction can be affected because the footprint needs a certain length in the front for squeezing out road surface water. Moreover, a wide tread can also have more difficulty pushing water out laterally, simply because the water has a longer distance to travel. However, this problem can be substantially alleviated by proper footprint shape and tread pattern design. Larger voids, particularly near the centre of the footprint, can help reduce the amount of water that needs to be removed out of the footprint area. Aggressive grooves following the direction of natural water flow, e.g., diagonal or arrow shaped grooves pointing into the footprint contact, have also been employed successfully. Since this kind of tread pattern would perform poorly when the direction of rotation is reversed, uni-directional tyres have been introduced for some high performance applications.

Asymmetric tread patterns with heavier outside shoulders have also been used in high performance tyres. These designs are in response to the fact that during cornering, a lateral load transfer, i.e., shift of contact pressure distribution, is required for balancing the overturning moment created by the side forces. When the load transfers within a footprint, and between the left and the right tyres, are combined, it is always the outside shoulders that will carry more loads from either left or right turns. Strengthening the outside shoulder with larger and stronger tread patterns is helpful.

As a result of the sidewall lateral deformation, the centre of the footprint contact will move to create another overturning torque from the vertical load. Higher lateral stiffness is desirable for reducing this second component of the overturning moment. The road contact area responds by not only shifting the contact pressure distribution, but also distorting the shape of the footprint. The side that faces the lateral force will develop longer contact length while the other side shortens. Excessive pressure transfer and extra long contact length are both undesirable for wear and traction.

A wider tread is more efficient in generating the counterbalancing moment, therefore, it will have less pressure increment at the shoulders. In footprint design, an elliptical shape is preferred over the so-called 'M' or 'W' shape shown in Figure 11.8. Long contact lengths at the two shoulders characterise the latter. The camber operation considered in terms of footprint contact is a method for reducing the distortion and uneven pressure distribution. It can be valuable for more efficient cornering force generation.

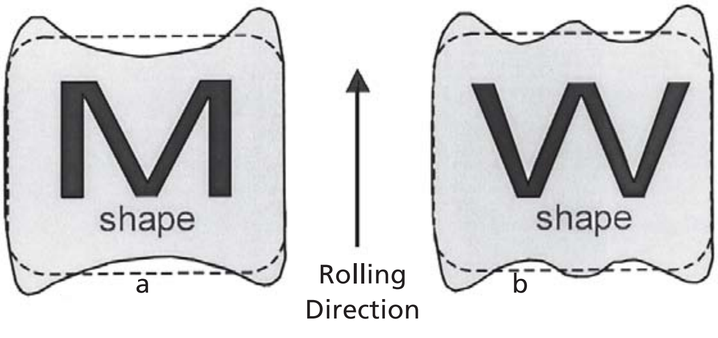


Figure 11.8 Illustration of so-called a) 'M' and b) 'W' shaped footprints. An elliptical shape (dotted line) is generally preferred

Uniformity is important for better ride simply because of the need to minimise the excitations in vibration. Tread patterns can create noise and vibration, but are necessary for traction in wet or snow. A low speed uniformity tester can measure uniformity in the tyre geometry. A high-speed test is necessary for determining the inertial effect of mass distribution non-uniformity.

As a transmitter of excitation from road contact to a vehicle, the tyre body's natural frequency and its damping are the fundamental parameters affecting performance. The torsional vibrational characteristics of a tyre are of particular interest for the transmission of the fore-and-aft force variations. The suspension system has a shock absorber to effectively absorb most of the vibrations in the vertical direction. For fore-and-aft vibrations, it is more practical to tune the tyre so that its natural frequency is far away from that of the suspension system. Reinforcing the lower sidewall with hard apex can help increase the resonance frequency through higher torsional stiffness. The added rubber can also help damping and reducing the transmissivity.

11.4.4 Wet/snow/ice traction

Tyre traction is a momentum transfer process. Energy loss in the tyre should be very small when compared to the kinetic energy of the vehicle mass. When the road grip is good, there should be no slippage at the tyre/road interface. Traction is obtained through mechanical interlock at the microscopic level between the rubber and the road surface texture. During slippage, traction comes from a series of stick-slips. Momentum transfer is effective during 'stick' and vanishes during 'slip'. In the time integral of the transmitted force, apparently long 'sticks' together with short 'slips' is desirable for more effective momentum transfer. The role of compound hysteresis is believed to be mainly in lengthening the 'sticks', and quickly re-engaging with the next interlock, as the 'teeth' made on the previously deformed surface rubber still partially remain due to slow relaxation. Indeed, hysteresis at near 0 °C has been used by various investigators to study wet traction with some success [68].

A second important factor in the stick-slip model of traction is the peak force that can be developed before slip. The degree of mechanical interlock is controlled by the coarseness of the road surface texture, the contact pressure and softness of the rubber. Combined with the skin rubber's strength and the degree of interfacial lubrication, the peak retaining force could be determined. The importance of *softness* and *hysteresis* in wet skid has been verified by results from the British Pendulum Skid Tester, showing loss compliance to be the key factor [69]. However, road tests indicate that it is the loss modulus that correlates better with tyre wet traction results [70]. From the previous discussion on tractive force generation in a tread element, the importance of *bulk modulus* is explained.

Apparently, property requirements on a tread rubber in the surface and the bulk are *not* the same. Understanding the character of each laboratory test and applying them properly is essential for successful product development. Among the recently commercialised laboratory tests, Grosch's angle abrader is noteworthy for its wet traction prediction capability [71]. It can measure the cornering coefficient at different speeds for a solid rubber sample wheel against a grindstone wheel with water lubrication. This test design allows evaluation of both the bulk and surface tread rubber properties in a more realistic simulation of the traction process. Using different water temperatures and applying a WLF (Willaims Landel Ferry) shift factor a_T, Grosch was able to construct a master curve for the side force coefficient, similar to his earlier work in demonstrating the viscoelastic nature of rubber friction [72]. Considering both the sliding speed and the wet surface rubber temperature, Grosch uses different portions of the master curve for prediction and has found good correlation with road tests in both locked wheel and antilock braking system (abs) wet braking performance [71]. Of particular interest is that Grosch's data suggest silica to be substantially better than carbon black in abs wet braking, and slightly inferior in the locked wheel situation. A possible explanation could be made by considering i) that the portion of the master curve used for abs prediction is the same part that reflects more of the 'deformation' contribution, according to an earlier report by Grosch [72], and ii) the silica compound's 'skin' may be softer, thus having more deformation. As mentioned earlier, silica has shown more stress softening [20], which could be attributable to breaking up of the filler's secondary network. A worn surface may become softened from damages similar to, but perhaps more severe than those from stress softening. One proposed explanation for the observation that silica-filled tread compounds provide poorer tread life on wet roads than tread compounds filled solely with carbon black is that the water from the wet road surface softens a thin skin of rubber tread, only a few microns deep, through hydrolysis of the secondary silica network. Silica's poor dry traction under severe slippage is mainly due to its poor thermal conductivity. However, with the advent of abs, this weakness is substantially accommodated. With relatively mild slippage, silica's advantage can be fully exploited in both wet abs braking and wet handling operations.

Hydrodynamic lubrication is an integral part of wet traction. Its consideration should be made at two levels. First, at the footprint, a tread pattern with proper groove depth and footprint shape for better water drainage is most important. The speed dependence of wet traction follows the square root of the speed of the tyre [73].

$$\mu = \mu_0\left[1 - \sqrt{v / v_c}\right]$$

where μ_0 is the wet traction coefficient at near zero speed, and v_c the critical speed for hydroplaning. The expression inside the parenthesis represents the speed dependency of water removal and the fraction of available footprint contact area for traction [73]. Second, a formula similar to the one above also holds for wet rubber friction at the individual tread element level, where the ability to squeeze out the water is controlled mainly by the coarseness of both the road surface and the tread surface. Porosity in the road surface is helpful in providing more channels for water drainage. It is interesting to note that the wet traction coefficient μ_0 at near zero speed is usually about 50-60% of its dry traction counterpart, e.g., a drop from 1.2 to 0.6. This suggests that given all the time needed to push the water away from the interface, rubber is capable of maintaining about one half of the effective contact. This is probably attributable to the rubber's chain mobility in bypassing the remaining water molecules and maintaining some mechanical interlock with the road surface texture at the sub-micron level. Only a few molecular layers of water would be sufficient to lubricate the interface substantially, if a rigid material were to replace the tread rubber.

For ice traction, the problem comes mainly from two areas: i) loss of the road surface coarseness from coverage by ice, and ii) melting of ice from contact pressure and forming a thin water film. Sand and salt are usually applied to the icy surface to take care of the first problem. To help break or remove the water film, sipes, or a tread compound with micro-porosity, have been used. For snow traction, large block tread elements with wide grooves can provide more 'bite'. To keep the tread grooves clean, the tread rubber should have sufficient elasticity at low temperatures so that the 'snap' at the exit of road contact can loosen and help throw away the packed snow effectively.

11.4.5 'Run-flat' safety tyres

11.4.5.1 First generation run-flat technology

Though they have yet to make a significant impact in either the automotive OE or replacement tyre markets, one of the most notable tyre innovations of the 1990s has been the concept of the 'run-flat' or 'safety' tyre. More than 30 US Patents have been awarded to various tyre companies since 1990 related to 'run-flat' or 'safety tyre' capability. Unlike puncture sealants that are 'self-repairing' and limit the loss of inflation pressure due to punctures, the run-flat tyre concept offers the capability of operating without inflation pressure, at least for a limited duration at a specified speed, thus eliminating the requirement for a spare tyre.

Bridgestone began producing the Expedia S-01 as early as 1992, but the first OE placement was the Goodyear Eagle GS-C EMT on the 1994 Chevrolet Corvette. Both of these tyre lines were confined to very low aspect ratios (40 series) with short sidewalls that contained stiff rubber inserts between the carcass plies as illustrated in Figure 11.9. Though both the Bridgestone and Goodyear tyres could be mounted on industry standard rims, they both had the drawback of requiring the use of an expensive low-pressure warning device. In 1995, Michelin entered the run-flat market with the MXV4-ZP 60 series tyre line with sizes that fit several popular auto platforms, but which required the use of a special SH-M tyre rim with a taller hump in the flange area. It too required the use of a low-pressure warning device [74, 75].

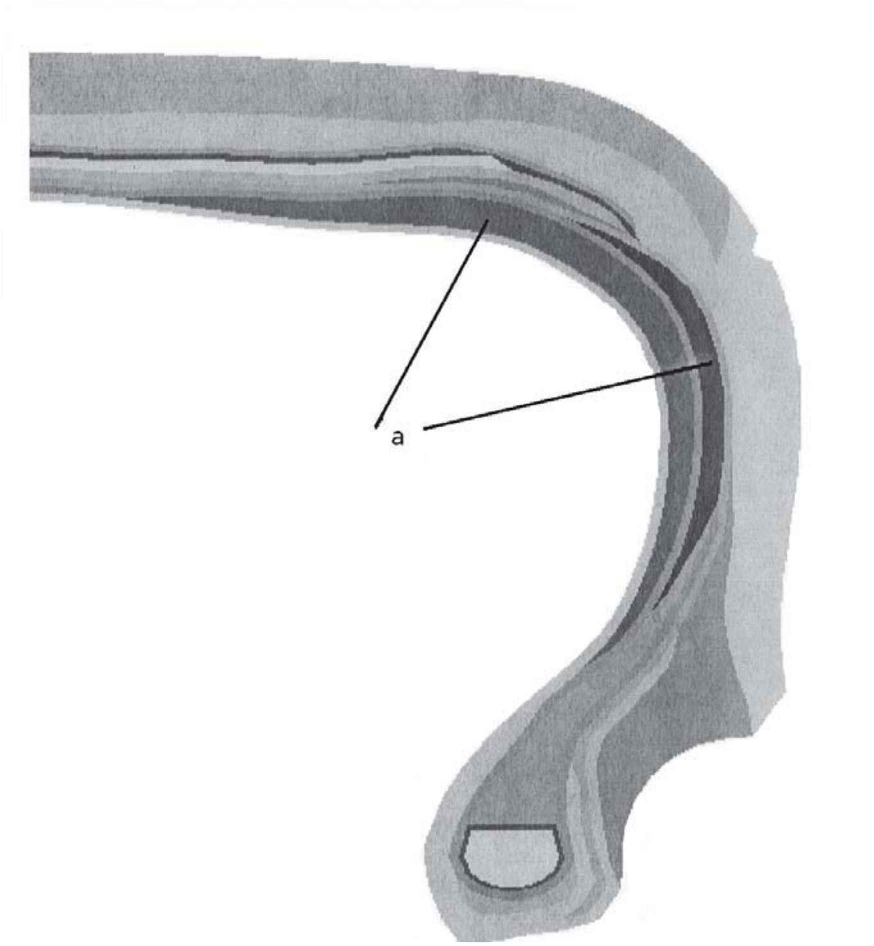


Figure 11.9 Typical 'conventional' run-flat tyre construction with sidewall stiffening inserts a) and heavy gauge sidewall components

The typical run-flat capability of these 'first generation' run-flat products at zero inflation pressure generally included:

- Operating distance limited to about 81-162 kilometers.
- Operating speed limited to no greater than 89 kilometers per hour.
- Handling characteristics as good as a 'normal' tyre under 'normal' inflation.
- Replacement of the tyre (no repairs permitted) after operating at zero pressure.
- Relatively poor fuel economy due to the tyre's heavy construction and high hysteresis rubber inserts.

Because of these limitations, combined with the high cost of the mandatory low-pressure warning system and the relatively low occurrence of flat tyres, sales of these early run-flat products never reached a significant portion of the market during the 1990s [76, 77].

11.4.5.2 New run-flat concepts

In the mid-1980s, Continental developed the ContiTireSystem (CTS), a radical tyre concept eliminating the conventional tyre bead and apex construction with an 'inverted rim'. Instead of the typical wire bead, the lower sidewall rubber of the tyre was clamped and bonded directly to a special wheel rim. In the 1990s, this concept was again employed in Continental's IWS (Integrated Wheel System), and still later in their ContiWheelSystem (CWS) in which it was combined with a supporting shelf built into the special wheel rim that provided run-flat capability while the rim clamping/bonding system kept the tyre on the rim [78]. Though providing a larger diameter wheel with the same tyre diameter leaves room for larger brakes and additional wheel and tyre sensors, the use of a non-standard wheel is a drawback for the adoption of this concept in either the OE or replacement tyre market.

Continental has introduced another concept, which provides the advantages of a 'safety tyre' but compatible with a standard wheel rim. The ContiSafetyRing (CSR) is a multi-piece, reusable, lightweight (3.2 kg) steel ring insert that is mounted inside a conventional tyre on a standard wheel rim. In profile, the CSR has a corrugated shape with rounded humps that supports the tyre if inflation pressure is lost. Unlike most 'run-flat' tyres, no low-pressure warning device is required with the CRS because vibration and noise is increased sufficiently to alert the driver if pressure has been lost.

In addition to the 'conventional' MXV4-ZP run-flat tyre, Michelin has also developed a new run-flat concept similar in some ways to Continental's CWS. Like the CWS, the Michelin PAX (formerly called PAV based on the French acronym for 'tyre anchored vertically'), utilises a larger diameter non-standard wheel rim with a supporting shelf insert as seen in Figure 11.10 [79]. Introduced in March 1997 the PAX concept is claimed to offer superior run-flat capability (up to 200 km at 88 kph), improved ride, and lower rolling resistance versus conventional run-flat tyres. Though Renault agreed early on to offer the PAX in small volumes on a production car model, the OE automotive market has been slow in accepting the PAX concept, not only because of its non-standard wheel

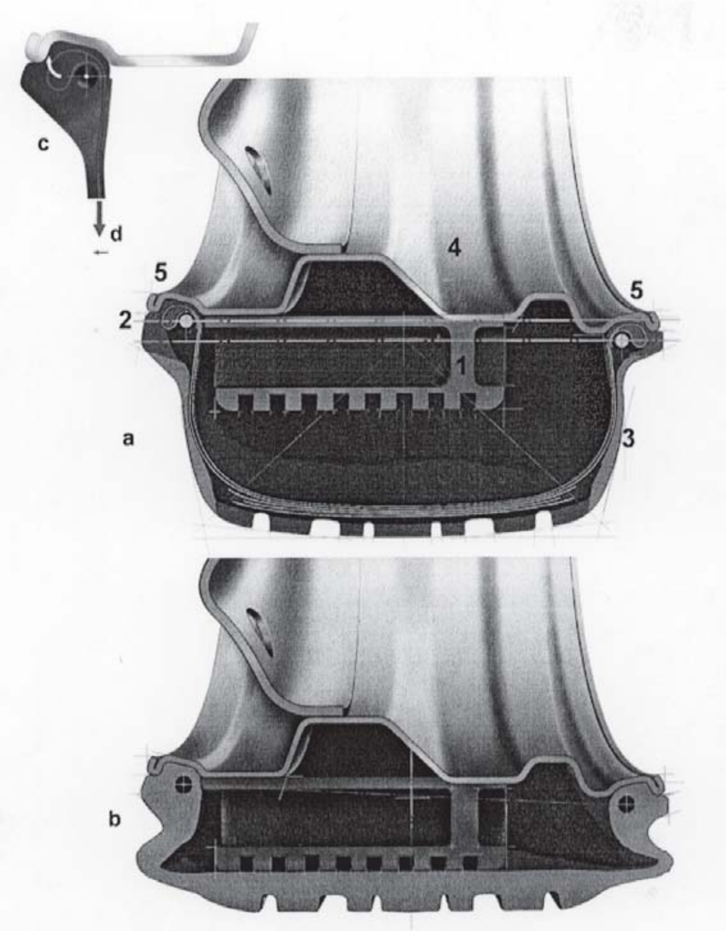


Figure 11.10 Michelin PAX System shown a) inflated and b) at zero pressure, illustrating 1) the flexible support ring, 2) mechanical locking mechanism, 3) shorter sidewalls, 4) one-piece wheel and 5) different anchoring diameters on the inside and outside of the wheel. Inset c) shows detail of the mechanical locking system. Any force d) on the casing increases the force against the wheel flange as the bead rotates

Reproduced with permission from Michelin North America (which requires a complete new system for sizing both tyres and wheel rims), but also because of the weight penalty. A set of four PAX tyres weighs 12% more than five (four plus a spare) conventional tyres. However, General Motors have produced PAX concept tyres in three sizes on its Cadillac Evoq and Oldsmobile Recon concept cars.

11.4.6 'Intelligent' or 'smart' tyres

The original application for the term 'smart' tyre was aimed at tyres with imbedded chips that can report real time pressure and temperature data, along with an identity code for each individual tyre, as well as the potential to store a history of this type of data for periodic retrieval. Goodyear has developed an experimental version of an aircraft tyre with these capabilities for the Joint Strike Fighter [80], though the most immediate market for this technology is in the trucking industry in which each rig typically rides on 18 tyres and for which the cost of tyres is a significant portion of overall operating costs.

Most recently, however, the technology behind the term 'smart' tyre has been expanded to include automobile, truck or motorcycle tyres that provide information directly to the vehicle's on-board microprocessors, becoming an integral part of the vehicle's control systems. Continental has developed the Side Wall Torsion (SWT) sensor system that utilises a tyre sidewall impregnated with magnetised powder. The sidewall of this 'intelligent' tyre incorporates magnetic markers, such as radial stripes of alternating magnetic poles, that are detected by a pair of sensors mounted on the wheel's suspension system. A similar system has also been developed by Freudenberg [81]. The signals from the pair of sensors, which monitor the upper and lower sidewall respectively, provide information (such as time difference between the signals) that can be analysed to determine how the tyre is reacting at any given moment. This information about the tyre's movements and deformations can be fed directly to on-board systems such as abs and electronic stability programmes (ESP). An essential part of this technology is the development of the algorithms for analysing these complex signals.

11.5 Advancement of tyre technology with computers

11.5.1 Computer aided engineering

Computer Aided Engineering (CAE) is a term used for a variety of engineering analysis and software tools which will be dealt with in the following sections. Of these, the technology that is typically of greatest interest to the rubber technologist working on tyres is tyre structural modelling using FEA.

11.5.1.1 Computer aided manufacture (CAM)

Though some robotic manufacturing systems have been purported to be in use in the tyre industry, a more common application for CAM is in the manufacture of metal tyre moulds. The use of CAM for metal machining is well documented elsewhere. One of the most important aspects for the effective use of CAM, however, is the integration between the CAM initialisation and a CAD system used for creating the mould drawings.

11.5.1.2 Computer aided design (CAD)

CAD systems are used in a variety of engineering and manufacturing operations. These systems speed the process of creating and modifying the drawings of the tyre profile and tread pattern. Linking CAD systems with CAM systems enables automation of tyre mould manufacturing.

11.5.1.3 Computational fluid dynamics (CFD)

The tread pattern affects how a tyre wears and provides traction in a variety of environmental conditions. CFD is used for hydroplaning (aquaplaning) analysis. In this type of analysis, the deformable tyre structure and tread pattern are made to move over, or through, a standing body of water. The analysis may also be applied to materials such as mud or snow, but the properties of these media are not well documented for input to a general purpose mathematical model. The technology in this field is being actively researched and commercial software is continually being improved.

11.5.1.4 Vehicle dynamics analysis (VDA)

The dimensions and structural response of a tyre affect how it performs when used on a vehicle. VDA programmes are used to examine the behaviour of a vehicle with tyres. The primary objective of such an analysis is to understand the vehicle motion as it might be affected by a change in tyre performance parameters. Tyre performance modelling includes vehicle handling simulations as well as structural dynamics and vibrational response of the vehicle system. The typical VDA uses simplified models of the tyre behaviour and typically does not have a sophisticated geometric representation of the tyre shape or structure.

11.5.1.5 Finite element analysis (FEA)

The CAD programs for using a computer system to describe tyre profiles and tread patterns presume that the desired shapes are known to the designer. However, in order to utilise shape and construction changes in the tyre to meet various performance criteria, a structural analysis program is required. The current technology for structural analysis is FEA in which the overall structure is mathematically represented by small volumetric elements with simplified geometry and material properties.

The complex geometric shape of the tyre, typically produced with CAD software, is provided to another computer programme, which creates a model of the internal structure in a step called 'pre-processing'. This model is then analysed by another programme, the FEA 'solver' programme itself, which performs the mathematical computations of the physical relationships represented by the tyre during use. Finally, a computer programme extracts and displays information about the performance of the tyre that was represented by the mathematical model in a step called 'post-processing'.

11.5.1.6 Integration of CAE systems

There are many commercially available programmes for performing the various steps in this structural analysis. Some programmes provide a complete analysis system and others specialise in only a portion of the system. Figure 11.11 illustrates the relationships among the CAE computer programs, and how they would typically be integrated. There will typically be people operating the software at each step, but many commercial and custom programmes provide methods for automating the transition between programmes for routine operations.

11.5.2 Computational modelling of tyres

Historically there have been many forms of mathematical models of tyres [4, 82, 83]. Some phenomenological models, such as a shell model [84, 85], a 'string' model [86, 87], or a multi-component composite model [88, 89] have provided a good insight on the way tyres carry load and respond to vibratory inputs. Other thermal models, often using the Finite Difference Method have provided ways to predict the operating temperature of a tyre or curing thermodynamics.

The current method of choice for modelling tyres is FEA. It has been many years since the first publication of a thermoviscoelastic tyre model using FEA [90, 91, 92, 93, 94,]. It is now well recognised that mechanical and thermal models of tyres developed using this method are excellent predictors of the quasi-static internal stress state of a tyre [55, 95]. However, computational resources have only recently become available to allow this technique to be used routinely in tyre design.

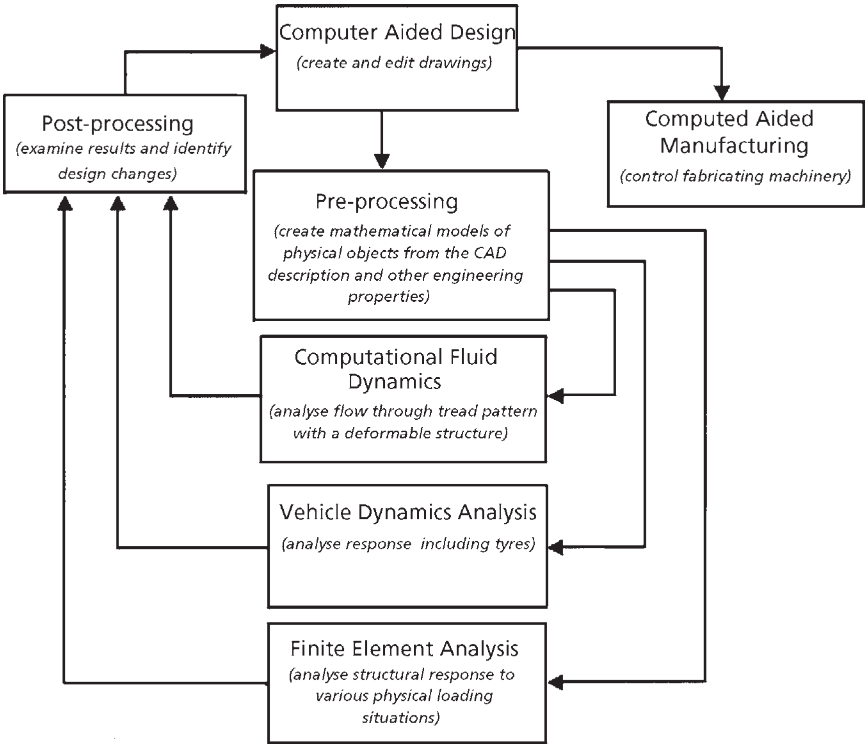


Figure 11.11 Diagram showing the relationships between different CAE (Computer Aided Engineering) programmes and their potential integration

Use of FEA has illustrated both the non-sinusoidal nature of the stress-strain cycle as well as the three-dimensional nature of the stress and strain tensors throughout the tyre structure. Thermal models for tyres, based on FEA models, can predict temperatures during curing. With an appropriate hysteretic model of the materials, the analyses can also predict tyre operating temperatures [96].

11.5.2.1 Modelling a complex structure

One of the major obstacles in structural analysis of tyres was shared by many other engineering structures: the shape and material distribution did not permit a solution from a closed form analytical technique. The FEA methodology overcame this obstacle by permitting the structure to be subdivided into small elements for which the analytical techniques would apply. The concatenation of the solutions for the small elements was mathematically shown to converge to the theoretically correct answer as the number of elements approaches infinity.

Initial use of the FEA technique was done without the digital computer. However, the analytical difficulties were exchanged for tedious accounting for the individual elements. In order to take advantage of computational resources specialised geometric approaches, using 'Jacobian' matrices to transform among coordinate systems were developed.

There are a number of different coordinate systems used within a given FEA computer programme. There is a global coordinate system associated with the structure, and various local coordinate systems associated with each element, with the materials, and with the loading axes. Figure 11.12 illustrates a tyre with a typical global coordinate system. One representative element from that tyre is shown with its own elemental coordinate system. The RCT (Radial – Circumferential – Thickness) system is useful for the performing tyre stress analysis. The RCT system provides a locally orthogonal, curvilinear, coordinate system that remains oriented with the materials in each element so that related elements may be identified around the tyre circumference.

11.5.2.2 Material response model

A Material Response Model is needed to predict internal stresses from the strains. The most common such material response model is linear elasticity represented by a material

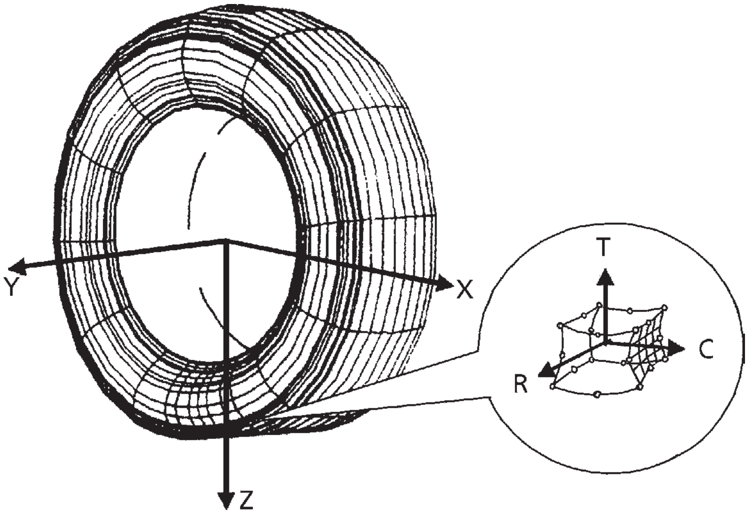


Figure 11.12 Global X, Y, Z and Local R, C, T (radial – circumferential – thickness) FEA Co-ordinate Systems

modulus. Viscoelastic, hyperelastic, and other nonlinear material models may also be available for use with the computation of tyre stress-strain behaviour. The model chosen for the material response determines the specifics of the required inputs for the available FEA computations, as well as creating limitations on how the outputs from the model may be interpreted.

A Material Response Model is also required to obtain tyre thermal response from temperature inputs, and for the computation of mechanical hysteresis or rolling resistance. The key to the accurate predictions from a computational model of the tyre is the mathematical representation of the material in a form that can be used by the computational model. Current research in this area has provided various material models that are functions of strain, stress, temperature, frequency, and history.

Ideally, laboratory testing of the tyre materials would provide values for parameters that can be used with the three-dimensional stress-strain cycle computed by a model. Many published works focus on representing tyre materials for a specific set of loading cases. While such work provides helpful insight for specific cases, it does not provide the material parameters that are needed for a general model of the tyre behaviour.

The selection of the parameters to be obtained and the conditions of measurement, as well as the details of the laboratory test, can substantially affect the results of a computational model. Unwarranted extrapolation from limited test data has been the cause of many questionable predictions from otherwise accurate computer models.

11.5.2.3 Mechanical response computation

The FEA method is ideally applied to the computations of tyre structural response. The selection of an adequate three-dimensional theory for the material response is key to obtaining an accurate solution in a reasonable time.

When an appropriate material response model is used, the computation of the mechanical response of the tyre structure can be very accurate. Many FEA practitioners have studied the relationship between stress analysis models and tyre behaviours. A detailed dynamic analysis of the tyre, using complex material response models, such as non-linear viscoelastic theory, often results in an unreasonable time for computing the tyre response. Therefore, sometimes a mechanical response is approximated from experimental parameters combined with FEA, such as the estimation of tyre rolling resistance using a ‘loss parameter’ for each material [97].

Knowledge of the type of response required helps in the selection of the appropriate material response model. For example, the effect of temperature enters the FEA model as a factor in the material properties. As the revised temperature (from a thermal analysis model) increases, the stress strain response of the material changes. This effect is not required if the prediction is only for quasistatic or fully dynamic response.

11.5.2.4 Thermodynamic considerations

The geometric and material representations of the tyre from a Finite Element model provide a good way of initiating a thermal analysis. Any thermal analysis will require appropriate properties for the materials, which can be input to the model through an FEA preprocessing system. Specification of the energy inputs and ambient thermal conditions can also be done with the preprocessing system.

For tyre curing analysis, the computation of the tyre temperature as a function of time is a result of the heat energy input, ambient temperatures, and the thermal boundary conditions. This type of analysis contains many significant mathematical considerations within the various computer programs. While the external appearance of the results and their application may be different, usually the thermal results do not contain significant technical differences.

For tyre heat buildup analysis, the energy input is from the mechanical hysteresis (tyre rolling loss) but there are some additional considerations. First, the appropriate heat transfer coefficients must be used in the modelling process based on the tyre velocity. A second effect is that of the temperature on the material stiffness and hysteresis.

The heat transfer coefficient includes the velocity and geometry dependence of heat transfer to the surroundings. A power law relationship is commonly observed between fluid velocity and the heat transfer coefficient. Several authors have reported that the power law relationship is valid for tyres [98, 99, 100, 101]. However, the large variation among published coefficients for tyre heat transfer illustrates the difficulty of obtaining precise heat transfer coefficients for a specific tyre. The computation of the steady state heat generation rate of a tyre uses only the loss generated by the materials and does not require the use of heat transfer coefficients for the tyre. A tyre's operating temperature should not be used to compute the material hysteresis because it is uncommon to have published values of heat transfer coefficients available for the tyre size under consideration. Where published values of heat transfer coefficients are available they may be used to estimate a tyre's temperature from computed energy losses for comparison with experimental results [58].

11.5.2.5 Hybrid modelling of tyres

There are several potential approaches to combining computational models of tyres. There is some research being reported on 'total physics' models that combine multiple sets of physical equations at a low level within a single computer programme.

A more practical approach at this time is the creation of hybrid models, which combine results from different computer programmes at a high level. Typical examples are the combination of results from programmes for structural analysis and thermal analysis (noted earlier), for structural analysis and fluid dynamics [102], or for structural analysis and vehicle dynamics.

11.5.2.6 Virtual tyre development

The last two decades of the 20th century have seen major improvements in the availability of computing power for FEA and in the capabilities of commercial FEA code. Computer processor speed has continued to increase as the cost has fallen. While the microprocessor of a typical desktop PC has jumped from 10MHz to 500+MHz during this period, the cost per millions of instructions per second (MIPS) has dropped from US$225 in 1991 to only US$2 in 1997. Continental Tyre has reported a 20-fold improvement in FEM efficiency in the past 10 years due to improvements in computer hardware and more efficient software code [103]. Goodyear has signed several cooperative agreements with Sandia Labs to develop new computational modelling tools for tyre mechanics and materials [104].

This increase in computer power on the desktop now permits many types of computer simulations of tyre performance to be run routinely by the tyre engineer. He can evaluate the predicted effect of various tyre design and material changes using a 'virtual tyre' before he ever builds the first prototype for actual testing. This capability is enabling tyre manufacturers to reduce their new product development cycles from years to months [105].

Acknowledgements

The authors would like to express their appreciation to William Jones, Keith Sansalone, and Marla Kelly for their contributions.

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12

Automotive Rubbers

J-M. Jaillet

Since the discovery of vulcanisation, rubber has invaded our life and occupies a significant place in the industrial world. The tyre sector alone consumes more than one-half of world rubber production. This particular automotive application is dealt with in the chapter by Dryden (Chapter 11). Rubber is used in various mechanical devices, including joints, elastic connections, tubes and pipes, membranes, anti-vibration devices, sound insulation for aeronautical applications, in medical applications and of course in the automotive industry.

Natural rubber is the basis of the materials used in many of their applications, but two major phenomena propelled a quest for alternative 'rubbers':

- the natural rubber shortage during the First World War, and
- the appearance of quite specific needs during the Second World War that required the development of specialised rubbers adapted for more demanding functions. This development of new rubbers came with the advent of the petrochemical industry.

From the end of the Second World War, new rubbers were developed in order to meet the increasingly constraining demands of industry. From the automotive point of view, the pressure for change accelerated recently. Car manufacturers must not only satisfy legitimate consumer demand but also the constraints of market forces and legislation.

Today the customers require a vehicle:

- that is at low cost,
- with improved and guaranteed safety,
- that has a minimal fuel consumption,
- that is comfortable,
- that respects the environment.

The constraints of the market are primarily economic whereas the legislative side intervenes primarily on the level of the safety, e.g., able to withstand shocks at 56 km/h, and the environment (Euro 2000 standards, for example)

The consequences of these requirements are:

- an increase in the temperatures under the engine cowling,
- an increase in the diversity of the fluids and pressures in the complete fuel line,
- an improvement in the acoustics and anti-vibration performance,
- better impermeability and sealing of the lines and connections,
- the most attractive appearance with least deterioration due to weathering,
- a need for lightweight products but with the same cost and performance.

These conditions are present in combined form (several constraints at the same time). The rubbers, used in the manufacture of various components or functions of the car, must allow for these conditions. The rubbers are used primarily for their physical properties (flexibility, elasticity, and ability to deform) as well as their chemical characteristics.

The main automotive functions of rubber are:

- the transport of fluids (water, air and petrol in particular),
- as seals,
- mechanical transmission,
- suspension and fixings,
- mechanical protection, insulation.

Rubbers can be classified into three major families:

i) Rubbers of general use which are found essentially in the manufacture of tyres. These are rubbers possessing good mechanical characteristics but which generally have the disadvantage of poor ageing characteristics and a sensitivity to hydrocarbon oils.

Natural rubber (NR), butadiene rubber (BR) and styrene butadiene rubber (SBR) will be mainly considered here.

ii) Speciality rubbers that have been developed to show very good fuel and ageing resistance are nitrile-butadiene copolymer (NBR), ethylene-propylene-diene terpolymer (EPDM), chloroprene (CR).

iii) Highly specialised rubbers, which include rubbers having one (or more) exceptional properties that are reserved for very specific applications in cases where it is not possible to use materials of the previous families. The silicones should be mentioned for the stability of their mechanical properties in very wide temperature ranges; fluororubbers for their resistance to hot oils and for their good impermeability to petrol; hydrogenated NBR (HNBR) for their high temperature resistance as compared to NBR, for example.

There is a fourth family of rubbers, the thermoplastic elastomers that show great promise for use in the automotive industry. These materials include a rubbery phase and a plastic phase and they are obtained either by physical mixtures between a rubber and a plastic or by copolymerisation techniques (see also Chapter 4).

Today this apparent distribution of the roles of rubbers in the car is partially called into question. Indeed, there is strong competition between the various types of materials that it is possible to use. The criteria which condition the choice of a material are the strong pressure generated by the need to reduce costs, the permanent concern to innovate, and the will to limit the fuel consumption of the vehicle by reducing its weight. Concerning the use of rubbers, one can note two complementary phenomena that are:

- a new distribution of the applications in the rubber family,
- a new technical strategy in certain fields to the detriment of rubber and to the advantage of other materials such as the plastics and the thermoplastics rubbers.

This chapter is divided into three major parts and these various subjects will be discussed.

In the first part the selection process of a car manufacturer to find rubber for a given application is discussed. The Renault selection process is taken to be representative of all manufacturers and is used to illustrate this point. After defining rubber from the point of view of the car manufacturer, the share of rubber in the automobile sector and the constraints to which it must answer will be analysed in detail.

Finally in the last part, the future of rubber in the automobile sector will be discussed.

12.1 Rubber selection

To determine which rubber can be used for which application a series of steps must be applied in order to ensure maximum functionality.

These steps are based on the following stages:

- determination of the environmental conditions,
- the choice of material when the conditions are defined, and
- the validation of this choice.

12.1.1 Determination of the environmental conditions

This stage is the most significant one. Besides the continuing search for the most economic solutions, if the environmental conditions are poorly evaluated this will produce risks of bad quality or an overvaluation of the function. Not only does the manufacturer lose out but so does the customer. The conditions under which rubbers work are very variable.

What are the environmental conditions that affect the choice of rubber for a particular application? The three main factors, in order of importance, are thermal conditions, chemical conditions and mechanical constraints.

12.1.1.1 Thermal conditions

The first factor is that of temperature. This can generally vary between 80 °C and 200 °C depending on the application:

- A car body can reach a maximum temperature of 80 °C when the vehicle is parked in summer.
- In the engine parts, three zones can be defined:

  - a zone at 80 °C in front of the engine

  - a zone at 120 °C to 140 °C close to the driving block.

  - a zone at a temperature higher than 150 °C (approximately 200 °C) for compressor engine pipes for example.

Depending on the application considered it is advisable to define the thermal conditions precisely. In certain cases it is necessary to know them very precisely by also taking into account the possibility of peaks of temperatures (in the case of the very high temperatures in particular).

The capacity of a rubber to function effectively in a given thermal environment is evaluated by comparing the mechanical properties before and after ageing. Car manufacturers generally define the duration of ageing in the schedule of conditions. These periods can vary from 168 hours, (i.e., one week), to 1000 hours. The definition of duration period also depends on the rubbers being tested. Indeed in certain cases, the evolution of the properties is very fast and stabilisation is complete at the end of a few hours.

12.1.1.2 Chemical environment

The chemical environment also conditions the choice of material as well as the temperature. Studies on the chemical environment resistance involve the compatibility of rubbers against the various fluids with which they come in contact. Ozone resistance is also included in these studies. In a car the main fluids present are petrol, the liquid in the coolant circuit (water and glycol), the engine oil and gearbox lubricant (which are different), air (generally charged with oil vapour, and petrol amongst other things), and the liquid of the windscreen washers. To qualify the rubber to function in a chemical environment, it is necessary to age this rubber in the environment concerned and compare the test results before and after ageing. The extent of swelling of a material in a fluid helps us understand the chemical resistance of a rubber in a given environment. One generally uses a reference fluid for the purpose. However, some fluids that are used in automobiles have alternatives that may differ significantly in their chemical make-up and it is advisable to test such alternatives in addition to the fluid reference. Petrol illustrates this perfectly. A reference petrol is used to evaluate the behaviour of a material in petrol but it is advisable to study the fluid resistance in the presence of methanol, ethanol or methyl tertiary butyl ether (MTBE) and even methyl ether from oil seed rape oil in order to take into account the presence of other chemicals. This point will be illustrated, when fuel lines and the constraints associated with a rubber are discussed (see Section 12.3.3).

12.1.1.3 Mechanical requirements

This deals with the resistance to vibration, to sealing properties, acoustics, and to the damping ratio. The qualities of rubber are essential, but the design of the part is also significant and can, in certain cases, correct a weakness of a selected rubber. Conversely, a rubber having good characteristics may lead to bad results if the design of the part is badly adapted.

There are different constraints, like the facility of assembly in factory, the integration of functions, the weight and the life span for example but which are not as restricting as those previously developed. A non technical factor, but very significant, which also contributes to the selection of material is its cost.

Once these conditions are known, a shortlist of rubbers that fulfil the main requirements is made. We must then pass to the second stage of selection, that of the choice of material.

12.1.2 Choice of rubber

Certain manufacturers such as Renault do not specify that a certain rubber be used but leave the choice to the initiative of the parts supplier. This choice will have to respect the requirements previously mentioned and defined by the manufacturer, who validates the choice of the parts supplier. In the case of Renault, for example, this validation results in the parts supplier signing the plan of the part and this signature is necessary before the tools for the part can be made. This choice is generally made with the help of databases of behaviour of materials or on the basis of experiment (renewal of solutions, evolution of solution). Once this choice is carried out, its validation still remains. It constitutes the third stage of this rational process.

12.1.3 Validation of the choice of rubber

After the first selection of various candidate rubbers based on materials tests, it is necessary to carry out tests on the parts. The tests are not totally functional tests (but are carried out in the laboratory and not on the vehicle). They aim to check the functionality of the part. The last stage is of course the final validation on the vehicle.

As an example, let us see which are the stages necessary to determine material adapted to an application like an o-ring in an air intake manifold.

12.1.4 Example: Manifold seals

The environmental conditions have been identified. The component is in a constant thermal environment at about 110 °C and in the presence of air charged with oil and petrol.

12.1.4.1 Selection of materials

The choice of materials falls between the NBR family or the HNBR family. The primary difference is the superior temperature resistance of HNBR. The acceptable higher temperature limit of NBR is 110 °C; the motive to use NBR compared to HNBR is an economic one. There is a ratio from 1 to 10 between the prices of these two rubbers in favour of the NBR.

To validate the choice of the NBR, a rubber sample is aged for a given time (each car manufacturer has its own requirements) at the operating temperature. In the present case, the operating temperature was chosen (100 °C) and the characteristics of the rubber before and after ageing were compared. The principal characteristics, which are compared, are the variations of hardness, the compression set, the breaking strength and the tensile strength. It will be checked that the reduction in key properties does not exceed a certain percentage (this minimum percentage of loss forms part of the schedule of conditions by the providers). This stage is not systematic. Indeed, each manufacturer has databases of materials data so as to free itself from the materials tests. In the present case, the NBR is being used at its higher limits, and it is probable that it will be necessary to carry out these tests to validate a special NBR formulation.

Once this stage is carried out, the function must be validated and for that purpose pressure tests must be carried out.

12.1.4.2 Parts testing

The first check must be that the sealing function is satisfied. A distribution frame equipped with joints is subjected to a certain air pressure and the seal is checked in a water tank (water bubbles appear if the seal is not gas tight). This test is carried out in the initial state and after thermal ageing of the part in order to check that the sealing is maintained during the life of the vehicle. This validation in the laboratory, which makes it possible to make a first check without engaging large test facilities, will be supplemented by tests on vehicles or on the engine alone. To this stage, the dynamic conditions are added. Now that the material choice has been discussed, the measurement of rubber characteristics will be considered.

12.2 Identification and characterisation of rubber

As shown previously it is necessary to characterise a rubber in order to make sure that it will be able to support the conditions to which it will be subjected. First of all, a rubber will be defined from a car manufacturer's point of view, then, the mechanical characteristics used for a rubber will be considered.

12.2.1 Rubber identification

Until now we have talked about rubber whereas it would be more accurate to speak about a rubber mixture. Indeed, 'a rubber compound' contains many ingredients that are mixed together and then vulcanised. For a car manufacturer, it is rarely possible to know the whole list of the ingredients constituting a reference compound, whereas it would be the case for example, for plastics. Technically it is not possible without heavy investment in characterisation equipment. Besides the provider does not wish to reveal what is regarded as a trade secret. Thus, the evaluation will be limited to the percentage and the type of gum used, EPDM, NBR, etc., the percentage of reinforcement charges and the percentage of plasticiser (mineral loads being deduced).

Thermal gravimetric analysis of a mixture reveals the proportions of the main components of the mixture. But information on a mixture is very general and a change of component cannot be detected.

A rubber is then defined as, for example, a mixture of 30% of gum EPDM, 30% of reinforcement charges, 10% of plasticiser and 30% of mineral charges. This information, associated with measured physical properties allows a sufficient follow-up quality to guarantee a good service of the function. These physical properties are the mechanical characteristics of the rubber compound.

The measured physical properties and the reasons for choosing them are considered in Section 12.2.2.

12.2.2 Rubber characterisation

The mechanical characteristics are influenced mainly by the type of polymer, the type and amount of (reinforcing) filler, the type and amount of plasticiser as well as the degree of vulcanisation. Of all these parameters, only the quantitative parameters are controllable by the manufacturer; the qualitative parameters (such as the volatile products) are not identifiable once the mixture has vulcanised. Let us consider in detail what the mechanical characteristics are available to choose a material in an automobile application.

In the continuation of this section functional criteria are discussed next. By a functional criterion we mean a criterion that has a direct impact on the functionality of the part. A non-functional criterion will be a criterion which characterises the material but which does not intervene directly on the functionality of the part.

12.2.2.1 Hardness (Shore or IRHD)

Hardness is a functional property which allows evaluation of the elasticity of the rubber and its capacity for energy absorption. Criteria based on hardness are significant for applications of sealing, absorption or ease of assembly for example.

12.2.2.2 Ultimate tensile stress

This is a non-functional property, which is in particular revealing of the quality of the material. Indeed in the car, it is rare to use rubbers near their tensile limit.

Moreover rubber most commonly works in compression, not in tension. Some rubbers work in tension such as, for example, the suspension supports or the pipes under pressure but in these cases, the material is far from the breaking stress. In fact the breaking strength is regarded as a criterion of homogeneity of the mixture, a standard quality. Rubbers in these applications have values ranging between 10 MPa for silicone to 30 MPa for NR or NBR and indeed a little more for HNBR.

12.2.2.3 Extensibility

This is used mainly for comparison between materials. It is not the basis of a functional criterion. This property must be considered like the breaking strength. The materials used have values ranging between 200% and 700%.

12.2.2.4 Tear resistance

This is a functional property. This entity is important in applications within assemblies (parts assembled under constraints, sharp angles). For example a silicone joint will be provided to minimise risks during assembly in the factory or in complex assemblies. The materials used have values ranging between 300 kN/m and 3 MN/m. Some applications require a value of, say, 1.5 MN/m (on an un-notched test piece) which demands quite a high quality rubber.

12.2.2.5 Remaining deformation after compression (compression set)

This is a means of checking that the material is well vulcanised when this measurement is carried out at a hot temperature (the material finishes vulcanisation in a crushed state and remains deformed once the force is removed). It is also the basis of a criterion of functionality because it intervenes in the evaluation of the quality of sealing and the quality of a connection with a collar for example. The compression set depends mainly on the nature of the gum, the loads, and the degree of vulcanisation. Generally a good compression set turns around 30%.

In certain applications, i.e., bumpers and engines, the compression set is close to 15%.

12.2.2.6 Stress resistance

Cyclic loading tests come in many forms and are not universal in application. They can indicate the quality of the rubber after ageing. The area enclosed in the stress-strain hysteresis loop formed during cyclic loading gives the energy dissipation. This appears in the form of heat, and may cause the material to overheat during service. This is known as thermal fatigue. If it does not occur, components may fail under cyclic loading as the result of cyclic crack growth, the process normally associated with fatigue failure in metals. The choice of NR, for applications in tyres or in the engine suspension, for example, is justified amongst other things because its fatigue characteristics are good.

12.2.2.7 Summary

The choice of a material for an application requires a good knowledge of the operating conditions. It is necessary to determine the conditions of ageing of the rubber selected and thus to evaluate its capacity to fulfil the function. As the result of comprehensive experimentation we have at our disposal qualitative databases, which enable a first evaluation of rubbers to be made prior to detailed directed validation procedures.

12.3 Rubber applications in the car

The applications of rubber in the car will now be considered. This section will be divided into three parts:

- A survey of the rubber content in the car.
- For each application, the constraints, and which rubbers are finally adopted.

- Some examples of constraints directly related to the function, and the constraints induced by indirect factors.

To begin with, let us consider the distribution of rubber in automobiles.

12.3.1 Rubber in the car

To illustrate the link between the world of rubber and that of the car we note that the automobile sector accounts for 70% of the applications of vulcanised rubbers. The following figures will show in a more detailed way the situation of rubber in the automotive industry. These figures result from a survey made by Renault on its own models. It will thus be advisable to consider these figures as defining a tendency and not as universal.

Table 12.1 shows the distribution of the principal families of materials used in a recent Renault model (a Clio II marketed in 1998). These figures are from an analysis of a vehicle with a standard level of equipment.

The distribution of rubbers by major function in the automobile sector except in tyres is roughly as follows (function tyre not taken into account):

Distribution by weight of the principal rubber applications:

Body sealing: approximately, 60%
Frame parts: approximately, 15%
Engine parts: approximately, 20%
Wiring and gear boxes: approximately, 5%

Table 12.1 Distribution by weight of the various families of material on model Clio II

Material	Weight kg	Proportion %
Plastics	91.2	9.5
Rubbers (without tyres)	20.8	2.2
Tyres	24	2.5
Putty and adhesives	8.5	0.9
Textiles	11.48	1.2

It is immediately seen that the sealing function represents more than half of the weight of the rubbers used. The following sectors are the frame parts (supports, pipes) and the engine (pipes, sealing).

In Figure 12.1 the evolution of the use of rubber since approximately 1976 is illustrated and shows the relative constancy of the volume of rubber used in the car.

However, use of all rubbers did not change in the same way as shown in the Table 12.2. It shows in a detailed way, the evolution of the consumption of various rubbers between Clio I (marketed in 1989) and Clio II (marketed in 1998).

NR is not taken into account in this evaluation. It has a strong presence in the manufacture of the tyres and in the suspensions of engines. It is not anticipated that NR will be replaced by other rubbers in these functions in the foreseeable future.

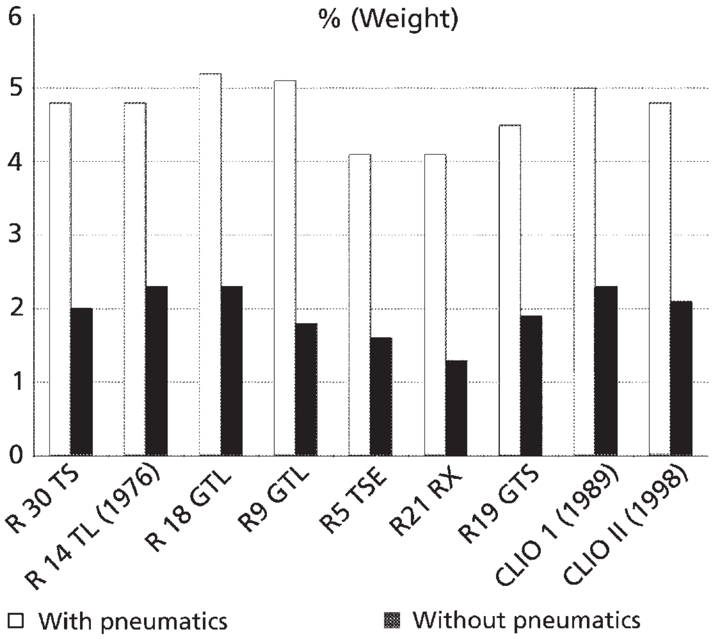

Figure 12.1 Example of rubber consumption of the last models of Renault segment I

Table 12.2 Evolution of rubber families by family between two car models

Type of rubber	Clio I (1989) kg	Clio II (1998) kg	Development
CSM	0.09	0.61	↑
EPDM	12.10	14.18	↑
NBR	0.08	0.38	↑
HNBR	0.07	0.2	↑
TPE	0.3	0.79	↑
ECO	< 0.01	< 0.01	=
MVQ	0.6	0.6	=
FPM	0.15	0.15	=
SBR	0.07	< 0.01	↓
CR	0.7	< 0.01	↓
NBR/PVC	0.8	< 0.01	↓
↑ : *increase* ↓: *decrease*			

12.3.2 Applications where rubber is present

In this section more precise ways of using different parts made of rubber are shown together with the requirements associated with these functions. The constraints indicated in Table 12.3 vary according to the model of car for which the function is used. The technical data in Table 12.3 gives an overview of the constraints seen in the vehicle by the use of rubber.

Summary

It is thus seen, that the constraints are multiple and this is why it is necessary to have a significant range of candidate rubbers. This is possible thanks to the use of various rubbers which are adapted to the various functions.

Table 12.3 Overview of rubber applications: Constraints and requirements

Fuel lines	
Fluid	Various fuels. Examples of variable parameters are the percentage of aromatics (influencing the swelling of rubbers amongst other things) and the alcoholic strength
	vapour
Temperature	Fluid temperature is between 40 °C and 80 °C; that of the environment is near to 125 °C in the driving compartment
Pressures	Feeding 0.35 MPa Return 0.05 MPa
Particularities	Request good impermeability, fire evaluation
Candidate rubbers	NBR/PVC, FPM
Oil lines	
Fluid	Engine oil
	Vapour
Temperature	130 °C approximately for oil: the environmental temperature is 140 °C with peaks at 160 °C
Pressures	Feeding 1 MPa
Particularities	Vibration, movement of engine
Candidate rubbers	Structured multi-materials reinforced with base EAM, FPM, CSM, CM
Air duct	
Fluid	Air charged with oils, petrol
Temperature	Between 80 °C and higher than 150 °C depending on the engine configuration
Pressures	Feeding specificity
Particularities	Movement of engine, vibration, acoustic
Candidate rubbers	CR, EAM, MVQ (depending on the temperature required)
Cooling line	
Fluid	Cooling liquid (water mixture/glycol)
Temperature	The fluid between 40 °C and 80 °C, environmental up to 120 °C
Pressures	0.22 MPa specificity
Particularities	Movement of engine
Candidate rubbers	EPDM

Table 12.3 Continued

Timing belt	
Temperature	Around 100 °C and peak at 120 °C
Environment	Presence of oil
Particularities	Must resist high tensions of installation; durability must be large
Jointed sealing (example of covers cylinder head)	
Fluid	Oil temperature: 140 °C for example
Tightening	80 to 100 N
Candidate rubbers	ACM, AEM, FPM, MVQ
Transmission bellows	
Fluid	Lubricant which can be heated near 150 °C
Particularities	Tightening, gritting, constraints related to misalignment
Candidate rubbers	CR
Driving supports	
Temperature	Between 80 °C and 110 °C
Particularities	Movements, vibrations, acoustics
Candidate rubbers	NR
Elastic supports	
Liquids	Behaviour with some liquids according to placement in the engine zone
Temperature	Between 80 °C and 100 °C
Candidate rubbers	NR, EPDM, CR
Electric insulation	
Temperature	Towards 120 °C and higher
Particularities	High voltage, flexibility, sealing (well of spark plug), fire resistance
Candidate rubbers	EPDM, CSM, MVQ
Fixing straps	
Temperature	Around 80 °C depending on placement
Particularities	Behaviour in tension
Candidate rubbers	EPDM

CM: chlorinated polyethylene

One of the most complicated conditions, which are most difficult to counter, is that of chemical compatibility. In the previous illustrations, this compatibility is associated with a single fluid. This is, unfortunately, not always the case. The example of petrol perfectly illustrates this. Moreover certain constraints known as secondary, because induced by secondary factors, are not quoted. This is what we will try to illustrate in Section 12.3.3.

12.3.3 Chemical constraints

First of all, in this section is a discussion about why it is necessary to use different petrols and we will also illustrate what is meant by secondary constraints.

12.3.3.1 Petroleum

The evolution of the technology of materials used for fuel lines illustrates perfectly well the need to adapt to which rubbers are subjected. This section will not deal with the change of the temperatures related to new technologies of injection because it is easy in this case to understand why a rubber identified as working at 60 °C will not work at 100 °C, for example (in the case of the diesel direct injection). The diversity of the petrol beyond the simple existing difference between the fuel and the petrol will be considered. Diversity is related to the addition of alcohol in the petrol. By alcohol we mean methanol (CH_3OH) and ethanol (C_2H_5OH). Alcohol is found, in petrol, in particular for the following reasons:

- The recognised qualities of alcohol are amongst others, protection against white frost and, mixed with fuel, to increase the octane level of the mixture. It is also possible to reduce the lead level contained in the petrol while maintaining a sufficiently high octane number (environmental aspect).

- Agricultural policies in certain countries like Brazil where the ethanol content can reach 30% of the composition of the petrol. The ethanol is the result of the fermentation of agricultural products like manioc, cane sugar waste, and sugar beet waste.

As an example, the addition of methanol will be considered, its influence on the properties of rubbers discussed. The proportion of methanol in petrol varies between 0% and 20%. The upper level is related to the fact that it is the maximum acceptable level so as to require no modifications of the engine. The solvent capacity of alcohol, and more particularly of methanol leads to a swelling of rubbers and to a loss of certain properties. From a theoretical point of view, swelling is explained through solubility parameters. Swelling is at a maximum when the solubility parameters of the fluid and polymer are equal.

For complex fluids (gasoline with alcohol type) the solubility of the fluid will be a function of the solubility of the basic components. One can have in the presence of alcohol the following phenomena:

- Plasticisation by the solvents (swelling and variation of the physical properties).
- Phenomena of diffusion and permeability.
- Plasticiser extraction, (stabilising and auxiliary), which can affect the ageing properties.
- Tensile cracking.

Figure 12.2 shows the influence of methanol on the characteristics of various rubbers that can be used in the lines with fuel.

This information is given as an indication, as the swelling is different for each rubber from a rubber family (function of vulcanisation, mix design). Though, one can notice:

- The influence of methanol on swelling and the fact that swelling is at a maximum in the case of a petrol comprising approximately 20% methanol. An effect of synergy is observed between the gasoline and alcohol. In the case of the NBR it is related to solubility and the difference in solubility parameters led, in theory, to a saturation approaching 30%.

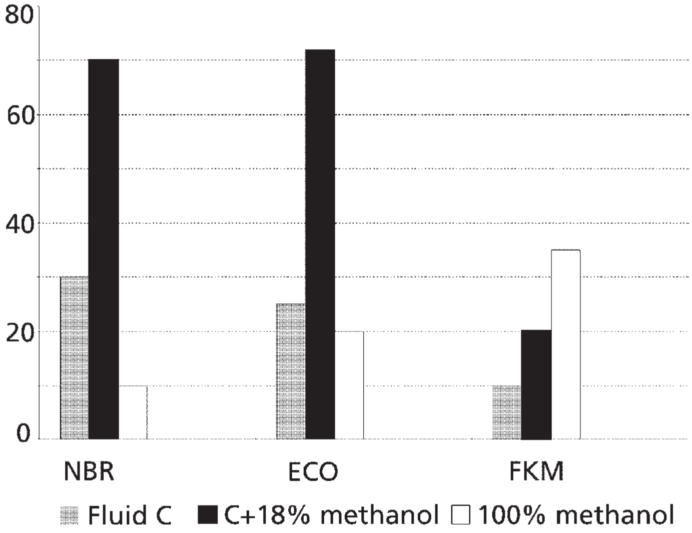

Figure 12.2 Influence of methanol on the swelling of materials. y-axis swelling %

- The behaviour of the FKM is atypical. It has a maximum swelling in 100% methanol.

Through various experiments which have been carried out, a maximum swelling appears for a proportion of methanol between 15 and 20% in the petrol. This proportion is commonly allowed and it is one of the reasons why petroleum with 15% methanol is used as a reference fluid.

In addition to the principal constraints, rubber may be subjected to secondary constraints. In Section 12.3.3.2 two examples of these constraints are presented.

12.3.3.2 Secondary constraints

New requirements relating to characteristics of materials can appear without external change constraints. The secondary constraints are, for example, the technical choice of neighbouring parts that contribute to the total function.

Peroxidised gasoline

The requirement of good behaviour in peroxidised petrol dates back to 1970 at Renault. It follows incidents with American vehicles where pipes used for petrol broke. The origin of these incidents was explained by a chemical attack of the rubber by peroxides formed in the petrol. The formation of these peroxides was intensified by repeated contact with the copper collector of the engine of the pump (secondary cause). Copper played a catalytic role in the formation of peroxides from the olefinic hydrocarbons that are always present in the petrol. Then decomposition of these hydroperoxides lead to the formation of free radicals, like $R—O—O^{\bullet}—$ starting a chemical degradation of certain rubbers in two ways:

- By continuing the crosslinking of the chains, which leads to a kind of ebonitisation of the rubber which makes them fragile to mechanical shocks (case of NBR mixtures).
- By leading to chain scission in certain rubbers (phenomenon of reversion) resulting in a very marked degradation of the mechanical properties, e.g., for epichlorohydric mixtures.

In both cases there are significant risks of embrittlement of the pipe, as noted on the American vehicles in the middle of the 1970s.

Table 12.4 shows the behaviour of some rubbers after an exposure of 72 hours at 40 °C, to the peroxidised petrol. The fluid is a standard petrol, 50% toluene, 50% iso-octane containing 3% of liquid petroleum olefin (LPO).

Table 12.4 Behaviour of certain rubbers in the presence of peroxidised petrol

Property	FKM	ECO	NBR	NBR/PVC
Variation of tensile stress (%)	- 10	- 70	- 65	- 40
Variation of tensile modulus (%)	- 4.5	-70	- 68	- 35
Swelling (%)	+ 9	+ 40	+ 25	+ 22
Swelling in fuel C (%)	+ 9	+30	+20	-

Results obtained using petrol-containing LPO are compared with those obtained using petrol without LPO in Table 12.4.

It is noted that the mixtures with ECO are sensitive to the peroxidised petrol whereas a mixture with FPM is not so sensitive to this same petrol.

Summary

To date, any rubber, under consideration for an application on the fuel system, must be evaluated in the presence of peroxidised petrol.

Another example to illustrate secondary constraints is the problem of the consumption of the corrosion inhibitors, and is presented in Section 12.3.3.3.

12.3.3.3 Consumption of the corrosion inhibitors contained in the cooling liquid

Tests on certain vehicles highlighted problems of corrosion of radiators made out of copper. This corrosion is due to the disappearance of the corrosion inhibitors tolyltriazole (TTZ). In this case the secondary cause is the formulation of the copper radiators. An experiment about the evolution of TTZ (corrosion inhibitor of copper) was undertaken at Renault. The results are shown in Table 12.5.

Pipes 1 and 2 are vulcanised with sulphur while pipe 3 is vulcanised with peroxide. Pipes 1 and 2 have different formulations. They are all EPDM.

The pipes vulcanised with sulphur consume much more of the TTZ than the pipes vulcanised with peroxide. The explanation could come from the zinc oxides that are used in the formulations vulcanised with sulphur as an activator. Indeed these products are mixed with the TTZ and prevent them from filling their role.

Summary

Although that does not call the use of the EPDM for the cooling pipes into question, a requirement of the consumption of the corrosion inhibitors, related to the technological choice of the radiators, can influence the choice of the type of vulcanisation used. Indeed vulcanisation by peroxide does not require the use of oxides which then eliminates any excessive cause of consumption of TTZ. Through the two examples described, we wanted to show that in addition to the functional constraints, the choice of a material could be conditioned by secondary constraints induced by the architecture or by the technological choice of surrounding functions.

All the constraints, which have been detailed, have an impact on the functionality. There is another type of constraint, which, although not having a direct impact on the functionality, is significant. They are the constraints of appearance. The example given in Section 12.3.4 illustrates this type of constraint. It is about the appearance of the body seals.

12.3.4 Appearance of the body seals

Most rubber parts show surface defects of varying degrees, which are the consequence of phenomena such as 'irrisation', efflorescence or bleaching. The final result is a degradation of the appearance. Although this degradation does not have major consequences on the functionality, it has nevertheless the disadvantage of being perceived as a defect by the customer or a disagreement in particular in the case of the body sealing.

Figures 12.3a and 12.3b illustrate these remarks. Figure 12.3a presents the reference joint such as it can appear after extrusion. Figure 12.3b shows this same joint after being stored for a period in a wall cupboard hidden from the light.

Table 12.5 Table of comparison of the consumption of TTZ

Liquid provider	Pipe 1 % of consumption	Pipe 2 % of consumption	Pipe 3 % of consumption
1	59	—	22
2	62	54	25

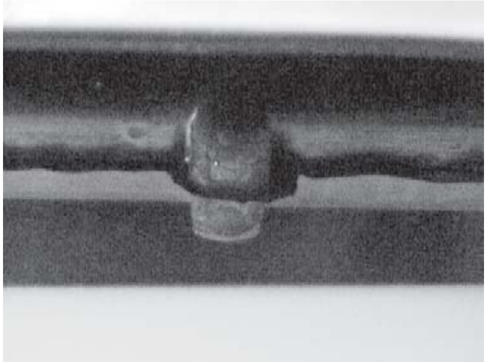

Figure 12.3a Reference sample

Figure 12.3b Ageing sample

Figure 12.3 Ageing behaviour of body seals

These phenomena are directly related to the formulation and the vulcanisation of rubber. The deterioration appearance is explained by the migration onto the surface of compounds, generally of low molecular weight. These compounds are either the residues of products which were not consumed during the vulcanisation phase (and are generally undesirable), or are additives included the products present for a quite precise reason like the improvement of friction, for example, and in this case cannot be regarded as undesirable.

The mechanisms responsible for these phenomena will not be discussed in detail here.

To solve this problem a manufacturer who controls neither vulcanisation, nor the formulation of the mixtures used must develop a suitable strategy. One of the first stages is to determine a method of accelerated ageing sufficiently correlated with the natural ageing and which will thus make it possible to reproduce these phenomena quickly.

Currently several testing methods for accelerated ageing are proposed. The details of these methods will not be presented here. Each one has advantages and disadvantages and from the analyses from specialists in these methods, it seems that no universal method is found yet. For information we will quote the method of ageing using a 'WeatherOmeter' (WOM), which seems to be in widespread use.

Once the testing method is defined, it remains to define a characteristic to measure the degree of ageing of a sample after conditioning it artificially or the naturally. One of the methods is the measurement of contrast, between a new part and a part which has been aged, with the method known as the grey scale, used in particular by French car manufacturers.

Knowing the means of making our sample age and the means of evaluating it, more requirements remain to be defined. For example at Renault, after 500 hours of WOM ageing, the sample must at least equal four on the grey scale.

Some evaluation of this type will be made on the reference sample for the agreement of conformity of the product, but other evaluations can be made on some samples regularly taken during the manufacture, in order to check that neither the formulation, nor the process of vulcanisation have changed.

The improvement of the appearance linked to the phenomena of irrisation or bleaching or efflorescence need a better understanding of the mechanisms related to these phenomena. This understanding falls within the competence of the equipment supplier but also of the manufacturer that is, in relation with the final customer, the guarantor of perceived quality.

12.4 The future of rubber in the automotive sector

One expects that certain components will always be made out of rubber since rubber confers essential characteristics. One thinks in particular of functions such as the driving supports and the tyres for which the dynamic characteristics of natural rubber, for example, are fully utilised. On the other hand, other fields currently reserved to rubber may sooner or later become the province of plastics or the thermoplastics rubbers. This swing, which we note in certain sectors like the fuel line, for example, is related to the increasingly strong constraints on the price, the recyclability, and the environmental requirements that are not necessarily to the advantage of rubbers.

In this section we will try to evaluate, function by function, the evolution to come, and the future of rubbers in these functions. Here again it is an analysis, based on our own experience in this field, which is quite personal. Thus it will be advisable to regard it as such.

12.4.1 The transport of fluids (water, air, petrol in particular)

What is the future of rubber in this kind of function? The following sections are intended to give some answers.

12.4.1.1 Fuel lines

The new requirements of the new Euro 2000 standards and the standards to come, Euro 2005, explain why the factor of good impermeability became a major criterion. The observed tendency is the replacement of rubbers by thermoplastics. The French car manufacturers joined the French Institute of Petrol (IFP) to develop a test to evaluate the current and future materials in terms of permeability and under various conditions of temperature, of fluids (fuels strongly modified with methanol, ethanol or MTBE). The results show very clearly that rubbers, which were generally used for the fuel lines, are not sufficiently impermeable for the requirements of Euro 2000. Some fluorinated rubbers give results close to the results obtained by some plastics but then the price criterion re-enters.

Figure 12.4 illustrates the permeability test.

Nitrogen circulates in a sealed enclosure inside of which is located the test sample. This sample is subjected to a circulation of fluid under varying temperature conditions. The hydrocarbon emissions are recovered by the circulation of nitrogen and are deposited on activated carbon. This method makes it possible to compare technical solutions, under various conditions of fluids and of temperature.

The results obtained are similar to those presented in Table 12.6.

The way taken is the multi-layer concept with the internal layer a thermoplastic in order to guarantee the requirements for impermeability and one or more other layers for the mechanical characteristics in particular. Multi-layer structures are becoming increasingly popular. Figures 12.5a and 12.5b illustrate the type of product that can be found on new vehicles nowadays.

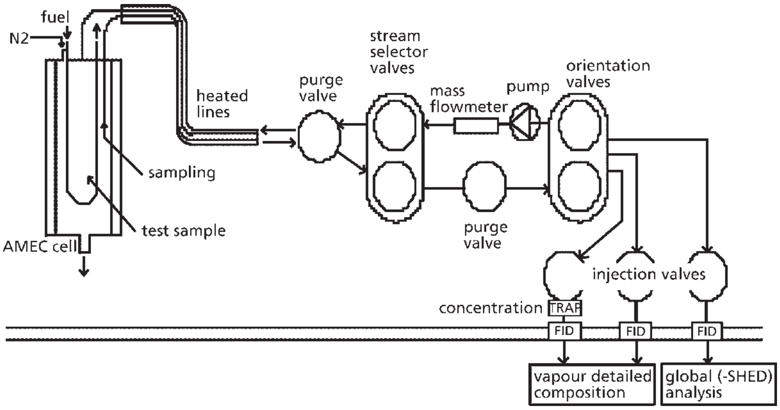

Figure 12.4 Illustration of the apparatus used for the permeability test

AMEC: Fuel emission measurement apparatus. –SHED: A cell with a flame ionisation detector for testing small parts of the vehicle

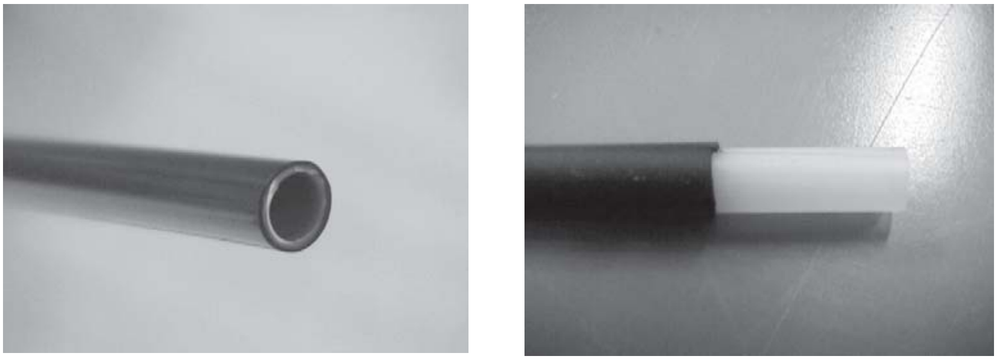

Figure 12.5a Design with PA6/PA12 Figure 12.5b Design with PA6/CSM

Figure 12.5 Examples of structure

12.4.1.2 Air ducts

One can consider using Renault cars as an example, in which until 1990 the air inlet pipes were practically all made out of rubber. Commonly CR and EAM were used. Thereafter, initially for technical reasons, there appeared some parts made from TPE; this was to solve acoustic problems for which the modulus of rubber was not sufficient (problem in depression). Thus in 1992, TPE first appeared in zones in which the thermal limit is close to approximately 120 °C. Later, to the technical interest came to be added the economic interest and with the TPE came the use of plastics. To date, on the Renault models in new series introduced since 1997 there exist few long rubber pipes. The latter were replaced by plastic pipes with, at the ends, rubber sleeves so necessary for movement in particular.

Figures 12.6a and 12.6b show some solutions to replace long rubber air ducts.

It is believed that the use of rubber in the air duct will be limited henceforth to specific functions to ensure, for example, engine movement. Conversely, one could also consider that this evolution may be opposed by difficulties in the development of the plastic solutions or by changes of environmental conditions which may render the plastic solutions unworkable. The strategy of replacing rubber by plastics for the air duct may be repelled by the evolution of improved rubbers. One thinks in particular of EPDM developed for improved resistance to oil (air charged oils) that could open up new opportunities.

Figure 12.6a PP for the rigid part PP/EPDM for the bellows

Figure 12.6b Plastic and rubber design

Figure 12.6 Air duct evolution

12.4.1.3 Coolant pipes

The function of these pipes could be compared with those of the air inlet. Currently it seems that substitutions of thermoplastic rubber for these pipes are not very advanced, in particular for large diameter pipes. Now it is clear that the advantages of thermoplastic, which is useful in the air inlet, can also be useful in the coolant circuit. This sector can be expected to evolve/move in the same way as that of the air inlet.

12.4.1.4 Other pipes

Some other examples of substitution of rubber by plastic can be quoted; for example the pipe for returning oil vapour or the pipe canisters. In both cases, we will note the appearance of polyamide 12 in place of the rubber pipes usually used.

12.4.2 Seals

12.4.2.1 Body seals

This is the major application of EPDM. Lately EPDM was put in competition with certain thermoplastic rubbers, PP/EPDM like styrene-ethylene-butylene-styrene (SEBS) or

Santoprene for example. One of the first applications of these thermoplastics was the interior joint of a door such as, for example, on the Mercedes Class A. The choice was made on this function because the geometry is simple (right form), and the environmental conditions are not too severe (application interior body). The interest is at the same time the weight saving, the price of the seal and the possibility of making coloured profiles. The two sections of sealing profile (see Figure 12.7) illustrate this reduction in weight and price through the reduction of the sections.

The idea of extending the application of the thermoplastic rubbers to other sealing functions is not easy but it is not impossible. In these cases problems of design and appearance can be encountered. If one part is made from rubber and another is made from TPE, then ageing behaviour can accentuate the differences.

Although today some applications are in thermoplastic rubber, the future in the short and medium term of the body sealing will still be by EPDM.

12.4.2.2 Mechanical seals

Today, the choice of rubber is the most economic solution thanks to the O-ring. Moreover, this solution perfectly fits the function. If there is no strategy of rupture, the future of rubber in the mechanical sealing will remain the solution of reference.

Figure 12.7a Solution rubber

Figure 12.7b Solution TPE

Figure 12.7 Comparison of profiles

12.4.3 Suspension/damping and fixings

The competition in this field does not occur between thermoplastics and rubbers, as rubbers are perfectly adapted to this function. The choice is between natural rubber and synthetic rubbers, since with the rise of the temperature, natural rubber can present some limits of use. There are studies on parts of CR suspensions or EPDM, which guarantee good behaviour at elevated temperature, but the requirements of behaviour in dynamics are still currently barriers to these applications.

This field is and will remain for a long time still the province of rubber.

12.4.4 Mechanical functions of transmission

To illustrate the substitution to rubber by another material, it is enough to consider about the bellows to transmissions and the replacement of CR by a polyether ester (PEE). Although the characteristics of fatigue behaviour favour rubber, the design of the part and the material characteristics made it possible to make this substitution. Indeed by decreasing the thickness of the part in particular on the level of the bellows, we decreased the amplitudes of movement by reducing the maximum distance from the neutral axis.

Figure 12.8 shows an example of bellows made from TPE and the difference between the two solutions in point of view of the design.

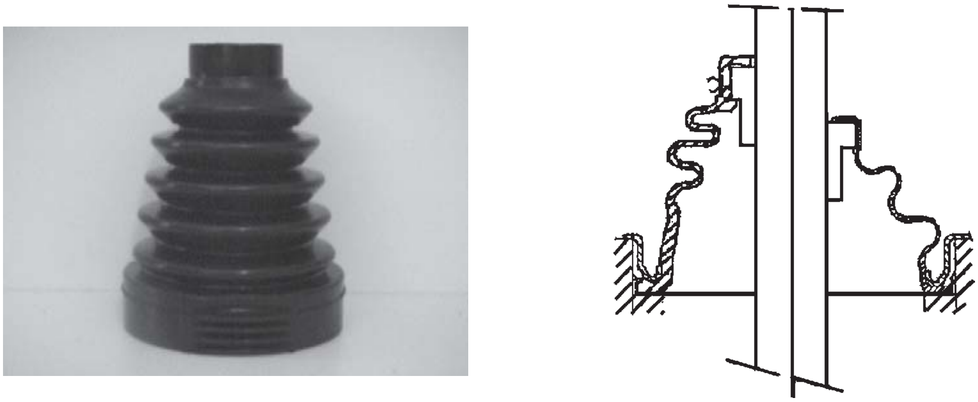

Figure 12.8a is an example of bellows made from PEE

Figure 12.8b shows the variation of thickness in the design conception between the rubber and the thermoplastic rubber solution

Figure 12.8

12.4.5 Timing belt

Rubber and HNBR in particular are still, for the moment, the materials of reference. The use of HNBR would tend to spread in particular to the American models still using the chain.

As can be seen, the economic pressure as well as the reduction of the weight (density of rubber 1,200 kg/m^3 and close to 1,000 kg/m^3 for the plastic) lead to a strong will to replace the rubber by thermoplastic or thermoplastic-rubber. On the other hand we note the enrichment of certain functions and the development of other functions, for example:

- the function of a double gasket, one for sealing, and one for noise disturbance,
- the development of the distribution belts and the generalisation of the HNBR.

12.5 Conclusions

In order to satisfy the new requirements imposed by the demands of customers, the legislation and market forces, it is necessary to seek the most outstanding concepts that fit best the delicate compromise between quality, cost, performance and weight. The material, which intervenes in the definition of the concept, is a major parameter mainly conditioning the final result. Two approaches are used to date in order to meet these new aims:

- A progressive optimisation of material. There is a continuing strategy of evolution and one will seek to improve a characteristic that becomes insufficient because of increased specification or expectation, to improve the processing of the parts; to reduce the cost; or to develop new characteristics. The evolution of materials for the timing belt perfectly illustrates this evolution. With each new development is imposed different and overall more severe requirements, and the rubber must to evolve to meet them. In the face of the problems of abrasion and increasingly raised temperature, CR was replaced by HNBR, and then by ACN.

The development of new ranks of EPDM for 'oil environment' also illustrates the type of answer that rubber can bring in order to fight replacement by other materials.

- A change of families of materials. We are, in this case, in a strategy of change. The example of the transmission bellows (although dated) illustrates this strategy. CR was replaced by a thermoplastic rubber (PEE) at the end of the 1980s at Renault before being generalised on all the range of vehicles in 1990. This change of family of material introduced the use of new processes of transformation and has been thanks to another definition of the parts of the vehicles and its design.

Although the rubber share in a car has been constant for a few years, one could nevertheless realise that the situation is not as inert as that. One can think that the share of very special rubbers will go in an increasing, in order to fit increasingly constraining requirements whereas the share of traditional rubbers will go on decreasing, because of competition with other types of materials. This phenomenon is already quite advanced.

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13 Rubber Compounding in Footwear

K. Ames

Introduction

The footwear industry has long assumed a secondary role in the rubber industry due in part, to the fact that footwear represents only 5% of worldwide rubber usage, as compared to 59% for tyres, Figure 13.1 [1]. It has also been due to the fact that cost, rather than performance, has historically been the driving force in the development of new compounds. Without clearly defined needs from shoe manufacturers, polymer research has focused on development of materials to meet the needs of the tyre and mechanical goods industries (low rolling resistance polymers for treads, low gas permeability polymers for inner tubes, hydrogenated polymers for severe service conditions) rather than footwear. The emergence of high performance athletic shoes over the past two decades has changed this. The performance requirements are much higher than before, necessitating the use of new polymers and fillers to meet these needs. The level of footwear compounding has increased dramatically. Polymer manufacturers as well as rubber chemicals suppliers are now working with shoe companies to develop new materials to specifically meet the demands of today's footwear.

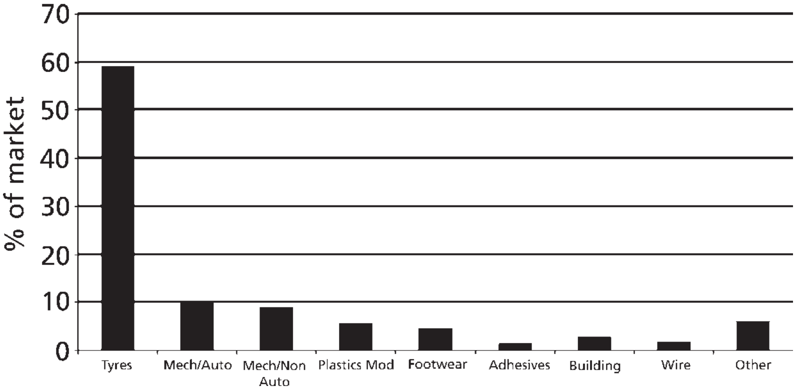

Figure 13.1 Rubber end use

In some ways, tyres and shoe outsoles have very similar requirements in terms of wear resistance and traction, and compounds to meet these needs can be very similar. However, there are differences in service conditions that can limit the use of certain materials. An example is long term durability; it is a selling point for both products. While tyres are able to make extensive use of carbon black to provide maximum durability, many outsoles must be non-marking for wooden floor and court use. This necessitates the use of silica as a filler, which can result in lower abrasion resistance than could be achieved with carbon black.

Tyres and footwear also need to have high traction properties; the difference is in the types and number of surfaces each comes in contact with. The average tyre is driven on a limited number of surfaces: concrete, asphalt, snow and ice. An athletic shoe (see Figure 13.2) may be used on concrete, asphalt, wooden courts with or without a polyurethane finish, rock, dirt, muddy trails, clay tennis courts, hard court tennis courts, rubberised running tracks, as well as snow and ice.

Today's footwear also has unique demands in terms of fashion; outsoles are often intricately designed combinations of multi-coloured and/or clear compounds that must bond together and still perform. Tyres are only beginning to use coloured rubber in the tread area, while this has been a mainstay of the shoe industry for years.

The key in developing any new compound is to prioritise the properties needed and to determine what polymers, fillers and additives will meet these requirements.

This chapter is divided by the type of footwear, such as safety shoes, high durability shoes, etc. The properties of key polymers, fillers and additives that meet the needs of

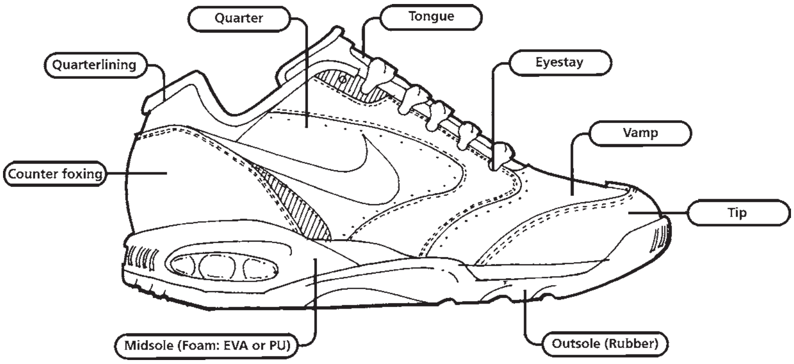

Figure 13.2 Schematic of a shoe
EVA: Ethylene-vinyl acetate PU: Polyurethane

these particular shoes are discussed. Formulae that may be considered typical for that type of application are given. They may be considered as a starting point, but additional work would be needed to develop and optimise a compound to meet specific needs.

While the title of this chapter is rubber in footwear, as we see in Figure 13.3, many other materials compete with rubber in the footwear market, such as thermoplastic elastomers (TPE), PU, and thermoplastics like polyvinyl chloride (PVC) [2]. These materials are discussed in terms of their properties and what disadvantages or benefits that they have compared to rubber.

13.1 Running shoes

Outsoles for running shoes need to provide good durability, good traction, and high energy return (rebound). As a person is running, the energy of the foot coming down and contacting the ground can either be returned to the shoe as energy to propel the runner forward, or dissipated as heat. For maximum performance, energy return (high rebound) is desirable. The polymers of choice for running outsoles are natural rubber (NR) and polybutadiene (BR); properly compounded both polymers can have rebound values greater than 90% [3]. Since one polymer can rarely meet all performance requirements, i.e., rebound, traction, durability, rubbers are usually used in blends to achieve the desired balance of physical properties. Prioritising these properties will determine the ratio of NR and BR, and whether other polymers such as styrene butadiene copolymer (SBR) need to be added as well.

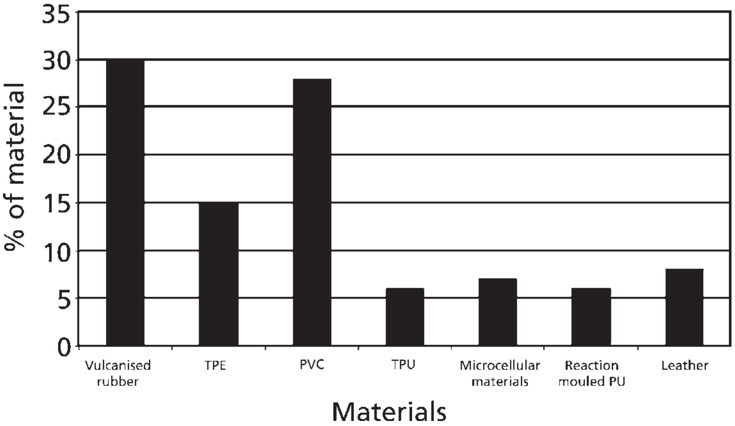

Figure 13.3 Worldwide use of outsole materials
TPU: Thermoplastic polyurethane

13.1.1 Polymers

13.1.1.1 Natural rubber

Natural rubber, *Hevea brasiliensis*, is approximately 96% *cis*-1,4 polyisoprene (see Figure 3.6), with proteins and lipids making up the remaining 4% [4]. The high linearity of chains results in the unique property of strain crystallisation. Due to its highly regular structure, it rapidly crystallises upon stretching, resulting in high tensile strength and tear resistance even in a pure gum or an unreinforced vulcanisate. It is used in many applications where high tear strength is needed. Natural rubber also has good resistance to flexing, fatigue, and heat generation, which makes it useful in an outsole compound that is flexed thousands of times per day. Abrasion resistance is high. Natural rubber is tough and nervy due to its high molecular weight (MW). Before blending with other polymers, it is often pre-masticated in an internal mixer (above 120 °C) or on the mill (below 80 °C) to 'break down' or lower the molecular weight of the chains [3]. Chemical peptisers such as pentachlorothophenol are used to lower the temperature needed and increase efficiency.

There are many grades of NR, from ribbed smoked sheets (RSS) which are made from coagulated field latex, to pale crepe which is made from a latex that has been preserved to prevent enzyme darkening, to technically specified (TSR) grades. These were first introduced by the Malaysian rubber industry [5], and are known as Standard Malaysian Rubbers (SMR) grades; there are standard rubber grades from Indonesia (SIR), Thailand (TTR) and Sri Lanka (SLR) as well [6]. These are NR grades which are cleaned and converted to a crumb, rather than a sheet rubber. They are further processed to achieve such properties as a constant viscosity (SMR-CV), a light colour (SMR-L) or specified grades of dirt and ash content (SMR 5, 10, 20 and 50). TSR grades have more consistent properties than conventional rubbers made from coagulated field latex. Table 13.1 lists the properties of SMR grades, in force since 1979, commonly used in footwear. A more detailed section on NR is found earlier in this book (Chapter 2).

Table 13.1 Standard Malaysian rubber grades

	SMR-L	SMR-5	SMR-10	SMR-20	SMR-50
Dirt retained, %	0.03	0.05	0.10	0.20	0.50
Ash content, %	0.50	0.60	0.75	1.00	1.50
Plasticity Retention Index	60	60	50	40	30

Synthetic polyisoprene (IR) was developed as an alternative to NR. It has the advantage of better control of molecular weight and better colour since there are no impurities; however it does not strain crystallise like natural rubber. This results in lower green strength (very important in tyre building), tensile properties, and aging properties [7]. IR has been, and can be, used in many but not all applications where NR is called for.

13.1.1.2 Polybutadiene

Polybutadiene can be polymerised to yield a large number of grades with different macrostructures and microstructures (*cis*, *trans*, vinyl, atactic, syndiotactic, isotactic) that have greatly varied properties. Commercially available grades include *cis*-1,4 and *trans*-1,4 isomers, as well as polymers with high levels of 1,2 (vinyl) addition into the polymer chain, see Figure 3.3 in Chapter 3.

Advances in catalysts allow control of the microstructure with great precision. The high *cis*-1,4 isomer (>90% *cis* addition) has a highly regular structure, and will strain crystallise when stretched over 200%. It has a very low T_g (–100 °C) which gives excellent low temperature properties. Like NR it has good flex and fatigue resistance, and is used in high flex applications. It also has outstanding abrasion resistance, but very poor wet traction [8, 9, 10]. In general, abrasion resistance is improved at the expense of wet traction. The introduction of vinyl groups into the backbone will improve wet traction, but reduce abrasion resistance [11]. For normal running compounds, high *cis* polymers are used; these are produced by cobalt, titanium or nickel Ziegler Natta catalysts. Common trade names include Taktene, Budene, Cariflex, Taipol, Ubepol, and Buna CB Bayer. The high vinyl polymer has found use in tyre treads where high traction and low rolling resistance are needed. The high *trans* polymer is a thermoplastic and is not used in footwear applications.

Most polybutadienes are resistant to breakdown, have poor mill banding properties, and give rough extrudates. Due to difficulties in mixing, BR is generally used in a blend with other diene elastomers such as NR or SBR. Blends with high levels of polybutadiene should be mixed in an internal mixer that generates high shear.

13.1.1.3 Styrene butadiene rubber

Styrene butadiene rubber is the most widely used synthetic rubber in the world. Developed as an alternative to natural rubber during the Second World War, it is now mainly used in tyre treads. A copolymer of styrene and butadiene monomers, styrene is generally present at 23.5%, although it may be polymerised at up to 40% for high performance and racing tyres. SBR can be produced by emulsion (E-SBR) or solution processes (S-SBR), while the emulsion grades can also be polymerised by the cold or hot process. Like BR, there are numerous grades with widely varying properties. Cold emulsion SBR has very good abrasion resistance and traction properties and is the polymer of choice for footwear. Emulsion polymers are made in oil extended grades, masterbatch versions with carbon black added, and grades with both oil and carbon black added. Rubber that is to be oil extended is polymerised to a much higher MW than non-oil extended grade. Higher molecular weight polymers have better tear, tensile, and abrasion resistance than lower MW polymers, but are more difficult to mix and process. The addition of oil allows it to be processed as if it were a lower MW grade. It also allows higher levels of carbon black to be added during compound mixing.

The process used to polymerise emulsion SBR does not allow for good control of MW, molecular weight distribution (MWD) or branching. This is acceptable for most applications, but not for the low rolling resistance requirements that came to dominate tyre tread development after the 1970s. Solution SBRs have much better control of molecular weight, MWD, and branching, which allow a better balance of rolling resistance, traction, and treadwear. Since rolling resistance is not a concern in footwear, the higher cost of solution SBR is generally not justified for use in outsoles [12, 13, 14, 15]. Some typical grades of SBR used in footwear are shown in Table 13.2. Common trade names include Solprene, Plioflex, Cariflex, Krylene HS, Polysar S, Humex, and Buna SL.

Emulsion SBR (E-SBR) has good abrasion resistance. It has higher traction properties than either NR or BR due to its more viscous nature. The tyre industry has developed good relationships between viscoelastic properties such as tan δ at 0 °C and wet traction [16]. While these relationships have not been determined for footwear, the same trends apply. A polymer that is highly viscous will have good traction properties, while a polymer that is very elastic will have better rebound properties.

Table 13.2 Styrene butadiene rubber grades

IISRP Number	% Bound styrene	Oil phr	Staining	Carbon black phr
1500	23.5	0	ST	0
1503	23.5	0	NST	0
1712	23.5	37.5	ST	0
1721	40.5	37.5	ST	0
1805	23.5	37.5	NST	75

ST: Staining
NST: Non-staining
IISRP: International Institute of Synthetic Rubber Producers
phr: parts per hundred rubber

E-SBR does not breakdown like NR during mixing, however SBR blends well with other polymers, and co-cures easily with them. It is considered a 'general purpose' polymer due to its good balance of properties which allow it to be used in a multitude of applications.

Compound composition is dependent on final property requirements. A compound that needs higher durability should have a higher level of BR. A higher level of E-SBR will provide higher wet traction. More NR will produce a compound with better tear resistance.

13.1.2 Fillers (see also Chapter 5)

13.1.2.1 Carbon black

Running outsoles need high durability. Since people generally run out-of-doors, compounds can be marking, making carbon black the filler of choice. Carbon black is produced by burning oil, natural gas or fuel in a reactor. Spherical particles are formed which collide and fuse with each other to form aggregates. The term structure is used to describe the degree of aggregation. Particle size is the mean diameter of the spherical particles that make up the aggregate and is measured using electron microscope micrographs. After further processing the aggregates come together to form agglomerates, also known as the secondary structure. Agglomerates can be broken, i.e., during mixing, while bonds between aggregates cannot be. Changing feed stock, reaction temperatures and other process conditions produces carbon blacks that range from highly reinforcing to inert.

Small particle size blacks are more reinforcing, providing better tensile, tear and abrasion properties. They are more difficult to mix into the compound.

Surface area is a measure of how much of the aggregate surface is available to interact with other chemicals. Small particle carbon blacks generally have high surface areas. It is measured by how much nitrogen (Brunauer-Emmett-Teller, BET method) [17], iodine (ASTM 1510 [18]) or CTAB (cetyl trimethylammonium bromide, ASTM D3765 [19]) is absorbed by the carbon black. Higher surface area increases tensile and modulus, tear, abrasion resistance and traction properties, while having a negative effect on rebound and flex resistance.

Structure is a measurement of the voids between aggregates, and corresponds to the spatial arrangement of the aggregates. It is measure by the absorption of a liquid, DBP (dibutyl phthalate) by the voids. Increasing structure results in an increase in modulus, hardness, and ease of mixing while reducing flex resistance.

Carbon blacks are classified according to ASTM D1765 [20] using a code consisting of a letter and three digit number. The letter indicates the cure rate: N for normal cure and

S for slow cure. The first digit indicates the particle size; a lower number indicates a smaller particle size. The last two digits are arbitrarily assigned. Blacks are still referred to by an old system based on particle size, and indirectly, abrasion or other properties such as SAF (super abrasion furnace), ISAF (intermediate super-abrasion furnace) or FEF (fast extrusion furnace). The ASTM designations are preferred. Table 13.3 lists the ASTM designation, particle size and surface area ranges for carbon blacks; Table 13.4 lists some common grades and the old nomenclature.

Table 13.3 ASTM first digit versus particle size

First digit	Particle size nm	Surface area m^3/g
0	1–10	>155
1	11–19	125–155
2	20–25	110–140
3	26–30	70–90
4	31–39	43–69
5	40–48	36–52
6	49–60	26–42
7	61–100	17–33
8	101–200	-
9	201–500	-

Table 13.4 Carbon black classification

ASTM designation	Old nomenclature
N110	SAF, super abrasion furnace
N220	ISAF, intermediate super abrasion furnace
N330	HAF, high abrasion furnace
N358	SPF, super processing furnace
N550	FEF, fast extrusion furnace
N660	GPF, general purpose furnace
N762	SRF, semi-reinforcing furnace
N990	MT, medium thermal

Reinforcing grades of carbon black such as N220 or N330 should be used to provide high abrasion resistance. N110 provides very high abrasion resistance, but is very difficult to process, and is used mainly in tyre treads. General purpose grades such as N550 or N660 will provide reasonable abrasion resistance at a lower cost [21, 22, 23].

13.1.2.2 Silica

There are two types of silica fillers: precipitated and fumed.

Fumed, pyrogenic or anhydrous silica is produced by treating silicone tetrachloride with hydrogen and oxygen at high temperatures. A fine particle size silica without any absorbed water is produced. The extra cost is justified only for silicone rubbers and transparent compounds.

Precipitated grades are produced by the controlled precipitation of sodium silicate with an acid. Process conditions can be varied to produce grades from semi- to highly-reinforcing. Silica grades are characterised in the same way as carbon black; by particle size, surface area (CTAB absorption) and structure (DBP absorption).

Silica particles have highly reactive hydroxyl groups on the surface that will react with accelerators to slow the cure rate of most compounds. Coating the particle surface with polyethylene glycol (PEG), diethylene glycol (DEG),or another polyol will reduce the number of sites for the accelerator to bond to [24, 25, 26, 27, 28].

Coupling agents are used with silicas to enhance reinforcement, abrasion resistance, and dynamic properties. Silane coupling agents have amino, mercapto, or polysulphidic linkages. Commonly used coupling agents are Degussa's Si69, and OSI's A1289 and A189 (mercaptopropyltrimethoxy silane).

13.1.2.3 Other white fillers

Other white fillers, range from inert fillers such as ground calcium carbonate to semi-reinforcing aluminium silicate.

Clays are naturally occurring aluminium silicates and are the most widely used non-black filler. They are low cost and provide low to moderate levels of reinforcement. Clays are dried, pulverised, and are separated by either a water or air process. Water washed clays have far fewer impurities such as mica or quartz. Both water washed and air floated clays are further classified as hard or soft, depending on the hardness levels produced in rubber. Clays can be calcined (bound water is removed) or modified with silane coupling agents to further improve reinforcement. Clays have a retarding effect on the cure rate and also need to be treated with diethylene glycol (DEG), PEG or other polyols.

Calcium carbonate can be produced naturally by grinding limestone, chalk or other naturally occurring sources or synthetically by precipitation. Ground calcium carbonate (GCC) is often used just as an extender, at levels up to 250 phr. The particle size and surface area of precipitated calcium carbonates (PCC) can be controlled well; PCC grades are semi-reinforcing. Calcium carbonates are basic in nature and do not affect compound cure rate [29].

Synthetic silicates such as aluminium silicates, sodium aluminium silicates, magnesium aluminium silicates, and calcium silicates are comparable to low structure, semi-reinforcing silicas. They provide similar properties at a lower cost. Table 13.5 gives a comparison of white fillers [26].

13.1.3 Pigments

13.1.3.1 Titanium dioxide

Titanium dioxide, TiO_2, is the most commonly used white pigment; it exists in two forms: rutile and anatase. In the naturally occurring forms, anatase TiO_2 is a blue-white colour, compared to the more yellow colour of the rutile grade. Modified rutile grades have the same blue-white colour but have 20–25% better colour coverage, and the compound has better mechanical properties after weathering [30, 31]. A blue-white colour is generally preferred for making a brighter white product.

Table 13.5 Non-black fillers

Material nature	**Reinforcing**
Silica	Reinforcing
Aluminosilicates	Semi to reinforcing
Treated clays	Semi-reinforcing
Precipitated $CaCO_3$	Semi-reinforcing
Clays	Diluent to semi-reinforcing
Ground $CaCO_3$	Diluent to degrading

13.1.3.2 Other pigments

Pigments can be organic or inorganic based. Many inorganic pigments are lead-based and have fallen out of use due to government regulations. Ultramarine blue is used in many white compounds as a tinting agent. Other commonly used inorganic pigments include iron oxide, chromium oxide green, and cadmium pigments.

Organic pigments provide a more attractive appearance, but are more expensive. Commonly used organic pigments include Permanent Red 2B, phthalocyanine blue, phthalocyanine green, carbazole violet and diarylide yellow [32].

13.1.4 Cure systems

13.1.4.1 Sulphur and accelerators

Rubber compounds based on diene rubbers are vulcanised using sulphur and accelerators; the choice of a cure system greatly affects the final properties of a compound. There are three classes of cure systems: conventional, efficient vulcanisation or EV, and semi-efficient vulcanisation or semi-EV. The amount of sulphur used affects the length of the sulphur cross-links.

Conventional systems use high levels of sulphur (2–3 phr) with 0.5–1.0 phr of accelerator, resulting in polysulphidic cross-links ($C\text{-}S_x\text{-}C$, where $x > 2$). Longer sulphur links allow more chain mobility. Tensile strength, elongation at break, dynamic damping and flex properties are improved with longer sulphur cross-links, while permanent set, aged properties, and thermal stability are worse.

Efficient cure systems may use very low levels of sulphur (0.2 phr) or sulphur donors, such as tetramethyl thiuram monosulphide (TMTM) at 2.5–3.5 phr, to form mono- and di-sulphidic cross-links (C-S-C, C-S-S-C). These shorter cross-links provide excellent heat stability, reversion stability and permanent set but poor flex properties. Cross-link length has little or no effect on abrasion resistance.

Semi-EV systems use low sulphur (0.5–1 phr) and higher accelerator (1.5–2.5 phr) levels to form disulphidic cross-links (C-S-S-C), which have good heat and reversion stability and permanent set resistance.

Peroxides can also be used to cross-link polymers resulting in carbon-carbon bonds (C-C). They must be used with polymers that have fully saturated backbones. Sulphur vulcanisation requires the presence of double bonds for curing reactions to occur. Advantages of peroxide cures, as compared to sulphur cures, include an absence of bloom, low compression set, good high temperature stability and a very controlled cross-link density. Disadvantages of using peroxides includes reaction with other compounding ingredients (such as antioxidants and antiozonants) instead of cross-linking, lower abrasion resistance, lower tensile strength and lower tear strength. Since shoes require high flex properties, conventional cure systems are often used.

A compound that is vulcanised only by sulphur will take hours to reach an acceptable state of cure. The addition of organic accelerators will reduce the cure time to a few minutes. Accelerators are divided into classes according to their chemical structure. The most commonly used in footwear are the thiazoles and thiurams. Thiazole accelerators are the most important class, accounting for approximately 80% of all accelerators used. They are further divided two subclasses; those based on mercapto-compounds and the benzothiazol sulphenamides. Mercapto-based accelerators are all based on 2-mercapto benzothiazole (MBT) and include dibenzothiazyl disulphide (MBTS) and zinc-2-mercaptobenzothiazole (ZMBT). These are good all purpose accelerators. Vulcanisation with MBT occurs quickly since only a hydrogen atom must be extracted to form the reactive moiety, while vulcanisation with MBTS is delayed, since it must first decompose into MBT fragments. Both provide good processing safety but a lower cross-link density than needed for the desired properties. For this reason, they are often used with a secondary accelerator such as a thiuram or dithiocarbamate. Secondary accelerators provide a synergistic effect; that is the cure rate or cross-link density achieved is more than just the sum of the individual accelerator's contributions.

Benzothiazyl sulphenamides are also based on 2-mercapto benzothiazole with an amine group bound to the mercapto sulphur. Accelerators in this group include *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS), *N*-*tert*-butyl-2-benzothiazyl sulphenamide (TBBS), 4-morpholinyl-2-benzothiazole disulphide (MBS), and *N*,*N*-dicyclohexyl-2-benzothiazyl sulphenamide (DCBS). These larger amine groups require more energy (higher temperatures) to decompose, providing more processing safety than the mercapto accelerators. This allows more time for the rubber to flow in the mould. The cure rate is rapid once it begins, and vulcanisates have a higher cross-link density than the mercapto accelerators resulting in good strength and elastic properties. Cure rate can also be enhanced by using thiurams and dithiocarbamates as secondary accelerators.

Thiurams such as tetramethylthiuram disulphide (TMTD) or TMTM can be used in all classes of cure systems: conventional, semi-EV and EV, making them among the most versatile of accelerators. They are commonly used as secondary accelerators, but can be used as primary accelerators or as sulphur donors. With sulphenamides, they provide an excellent balance of properties.

Dithiocarbamates are known as ultra accelerators, and include zinc dimethyldithiocarbamate (ZDMC), zinc diethyldithiocarbamate (ZDEC), zinc dibutyldithiocarbamate (ZDBC), zinc dibenzyldithiocarbamate (ZBEC), zinc pentamethylene dithiocarbamate (Z5MC), as well as those based on bismuth, cadmium, copper, lead, sodium and tellurium. The zinc grades are the most common in footwear. They were among the first organic accelerators discovered. They react so quickly that they cause scorch and processing problems and are used almost exclusively as secondary accelerators. They do provide good strength and elastic properties.

Other classes of accelerators that are occasionally used in footwear include the guanidines: diphenylguanidine (DPG), di-*o*-tolylguanidine (DOTG) and the thioureas: *N*,*N*′-ethylenethiourea (ETU) and *N*,*N*′-diethylthiourea (DETU). Retarders such as cyclohexylthiophthalimide (CTP), salicylic acid (SCS) and benzoic acid (BES) are used to provide more processing safety. Acidic materials will retard curing; accelerators are all basic materials.

Sulphur has a very limited solubility in rubber; it can bloom to the surface of rubber during storage. Insoluble sulphur is used to prevent bloom; it is often used in masterbatch form for better dispersion. Over time it will convert to its soluble form; storage temperatures should be as low as possible to delay this reaction [33, 34, 35, 36, 37].

In a 100% NR compound, 2–3 phr of sulphur with lower levels (0.2–1.0 phr) of a primary thiazole accelerator are needed to achieve an acceptable state of cure.

Polybutadiene requires less sulphur to cure than NR, about 1.6–1.9 phr. Thiazoles are also the best primary accelerator. Thiurams such as TMTD or TMTM are the best secondary accelerators; TMTD is more reactive than TMTM. For added scorch safety in hot production countries in Asia or South America, TMTM should be used.

In an NR/BR blend, 1.6–1.9 phr of sulphur is used with a sulphenamide accelerators. Blends with E-SBR will also use less sulphur than NR by itself.

13.1.4.2 Activators

Zinc or other metals oxide are used as cure activators usually at the 3–5 phr level. Fatty acids, usually stearic acid at 1–2 phr, are also used to increase the rate of cure. Stearic acid is often added to prevent mill sticking as well.

13.1.5 Plasticisers, processing aids and oils

Plasticisers are used to improve the processing, filler dispersion, tackiness, and physical properties of rubbers, especially synthetic rubbers since they are often more difficult to process than NR. Plasticisers may be mineral oils, natural products such as vegetable oils, fatty acids and rosins (pine tar) or synthetic plasticisers such as esters (phthalic esters, sebasic esters, etc).

Commonly used mineral oils are paraffinic, naphthenic and aromatic. Table 13.6 shows a comparison of oils in terms of compatibility with certain polymers. Paraffinic oils are the lightest in colour, while aromatic oils can be dark and quite staining. All of these oils are compatible with NR, BR and SBR. Aromatic oils are often used in compounds with high traction requirements; naphthenic or paraffinic can be used for all other applications.

Cumarone-indene resins are used as tackifiers for natural rubber and many synthetic rubbers. They are often used at 1–5 phr levels. Tackifiers are often necessary for synthetic rubbers since they are less tacky than NR [38, 39, 40, 41].

13.1.6 Antidegradants

Due to the high level of unsaturation in the backbone, diene rubbers such as NR, BR and SBR are attacked by ozone and oxygen and require the use of strong antioxidants and antiozonants. If the compound is carbon black filled and is not in contact with light coloured rubber, *p*-phenylinediamine based antiozonants can be used; these are strongly discolouring but provide the best protection from ozone and fatigue. If the compound is white or light coloured, non-staining materials such as phenols and waxes must be used [42, 43, 44].

13.1.7 Typical formulae

Table 13.7 shows some typical running outsoles based on blends of NR/BR and SBR.

Table 13.6 Mineral oils/polymer compatibility

	NR	BR	SBR	NBR	CR	EPDM	IIR
Paraffinic	+	+	+	-	-	+	+
Naphthenic	+	+	+	o	o	+	o
Aromatic	+	+	+	+	+	o	-

\+ *compatible*
\- *not compatible*
o *somewhat compatible*
EPDM: Ethylene-propylene-diene terpolymer
IIR: butyl rubber
NBR: nitrile rubber

Table 13.7 Rubber formulae for running outsoles – NR/BR based

	High rebound phr	High traction phr	High abrasion phr	General phr
Natural rubber	50	40	40	25
Polybutadiene	50	-	60	25
SBR	-	60	-	50
Carbon black (HAF or ISAF)	40–50	40–50	40–50	40–50
Process oil	10	-	10	10
Aromatic oil	-	10	-	-
Zinc oxide	3	3	3	3
Stearic acid	1	1	1	1
Antioxidant	1	1	1	1
Sulphur	1.8	1.9	1.8	1.9
TBBS	0.8	0.8	0.8	0.8
TMTM	0.1	0.1	0.1	0.1

13.1.8 Methods of manufacture

Outsoles are commonly made by compression moulding a preform of one or more rubbers in a mould that is cured in a hydraulic press under high temperature and pressure. Presses may be heated by hot oil, steam or electricity. During the cure cycle moulds are usually 'bumped,' the press is opened to allow air to escape.

Outsoles can also be produced by injection moulding, although the number of different colours or different rubbers is limited to two in a single moulding operation at the present time. The design is also more limited than in compression moulding. Injection systems often have a shorter cure time than compression moulded pieces.

13.2 Safety shoes

Safety shoes provide protection against severe work conditions and chemical contact.

13.2.1 Nitrile rubber-based compounds

Chemical resistant outsoles are often based on polyacrylonitrile butadiene rubber (nitrile rubber or NBR). Nitrile rubber is a copolymer of butadiene and acrylonitrile (ACN) with the level of ACN varying from 15–50%. The presence of acrylonitrile provides resistance to oil (petroleum hydrocarbons, mineral oils, greases, vegetable oils, animal fats) and fuel (Fuel B - 70:30 mixture of isocyanate and toluene, and Fuel C - 50:50 mixture of isocyanate and toluene), while the butadiene provides abrasion resistance and low temperature flexibility. The grade of NBR used is determined by the final properties required. Table 13.8 lists typical physical properties, and the effect that increasing acrylonitrile content has on them. Some typical trade names include Chemigum, Europrene N, Krynac, and Nipol.

Increasing the ACN content also increases the polarity and thermoplastic nature of the polymer. Nitrile rubber is not compatible with non-polar polymers such as NR, BR, SBR or EPDM. Small amounts of these rubbers are sometimes added to improve properties such as ozone resistance, processing or compound cost. The rubbers do not co-mix and two separate phases exist. Nitrile will easily mix with polar materials such as PVC.

Table 13.8 Effect of acrylonitrile on NBR properties

Physical properties	Effect of increasing ACN level
Oil resistance	+
Fuel resistance	+
Hardness (at room temperature)	+
Hardness (at 75 °C)	o
Tensile strength	+
Gas impermeability	+
Compatibility with polar materials	+
Abrasion resistance	+
Rebound resilience	-
Low temperature flexibility	-
Compression set	-

\+ *Property is improved with increasing acrylonitrile*
o *Property is unaffected by increasing acrylonitrile*
\- *Property is reduced with increasing acrylonitrile*

13.2.1.1 Fillers

Compounding nitrile rubber is very similar to compounding NR or SBR. Nitrile rubber does not strain crystallise and is not self-reinforcing. Carbon black or silica can be used as reinforcing fillers; silica based vulcanisates can be compounded to have tensile and hardness properties very similar to black filled compounds. Medium reinforcing carbon blacks such as N-550 may be preferred for better processing, especially in high ACN grades; although all grades can be used. N-220 and N-330 provide good abrasion resistance. Clays, talc, whiting and other semi-reinforcing fillers can be used, with the typical reduction in final properties.

13.2.1.2 Plasticisers, processing aids and oils

Non-polar plasticisers such as paraffinic or naphthenic oils have a limited compatibility with the polar nitrile rubber. Aromatic oils and ester based materials, i.e., esters from alkylsulphonic acids, as well as phthalates, are used as plasticisers and generally increase resilience (rebound) and low temperature flexibility. Plasticisers will reduce mechanical properties at higher loadings. Polar compounds such as xylene formaldehyde resins, wool fat, Koresin (Struktol), and coumarone resins are used as processing aids to improve calendering and extrusion quality; tack is also improved. Factices (sulphur cross-linked triglycerides such as rapeseed oil) are used in compounds with high levels of plasticisers to provide dimensional stability.

13.2.1.3 Cure systems

Zinc oxide and stearic acid are used for cure activation at the same levels for NR and SBR; 3–5 phr of zinc oxide and 1–2 phr of stearic acid.

Antidegradants are needed as nitrile is attacked by both oxygen and ozone; non-staining phenolics should be used in white or light coloured compounds as well as waxes.

For general footwear applications, nitrile is vulcanised with sulphur, from 0.75–2 phr, with sulphenamide or thiazole primary accelerators (1–2 phr) and thiuram secondary accelerators (0.05–0.2 phr). For injection moulding, a semi-EV type cure is used, with thiurams as the primary accelerator (TMTD). In compounds that need excellent compression set, higher levels of TMTD (1–3 phr) are used as the primary accelerator which may reduce the flex properties. Nitrile polymers can be vulcanised using peroxides, if needed.

13.2.1.4 Typical formulae

Table 13.9 lists typical compounds with oil and fuel resistance and other various properties.

13.2.1.5 Mixing

Nitrile rubber compounds can be mixed either on a mill or in an internal mixer. Processing is similar to SBR, with a few differences. Sulphur is difficult to disperse in nitrile rubber; either a sulphur masterbatch should be used, or sulphur should be added much earlier in the mix cycle to improve dispersion. In an internal mixer, filler and sulphur (powder form) should be added together, early in the mixing cycle. Plasticisers and other ingredients should be added next. Nitrile rubber does not breakdown as easily as NR, quickly generating high

Table 13.9 Safety outsoles - oil/fuel resistant

	Marking phr	Non-marking phr	Low compression set phr	Injection phr
NBR (high ACN level)	100	100	100	100
Carbon black (SAF, HAF, FEF)	40–50			
Silica		40–50	40–50	40–50
Coupling agent	3–4	3–4	3–4	3–4
Dibutyl phthalate	10	10	10	10
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Antioxidant	1	1	1	1
Sulphur	1.5	1.5	1.5	0.8
CBS			2	
TMTD				3
TBBS				2
Retarder				1
MBTS	1.5	1.5		
TMTM	0.1	0.1		

temperatures in the mixer. This necessitates keeping the mixing cycle short to avoid scorch problems. If a sulphur masterbatch is used, is can be added on the finishing mill, along with the accelerators. Because nitrile rubber does not break down and mixing cycles are short, this will result in a compound with higher final plasticity. If this causes processing problems, lower Mooney polymers or a mill mixing cycle may be necessary.

On the mill, NBR should be passed through a tight nip with cooling water on to facilitate polymer breakdown while keeping temperatures down. After several passes, it is allowed to band with a wider nip. Plasticisers and resins are added first. If phenolics are added, they can cause sticking; stearic acid should be added at this time. Ingredients that are difficult to disperse are added next: sulphur, small particle size carbon black, silica, other fillers, and zinc oxide. The fillers should be added in small amounts, and should be fully dispersed before cutting the sheet. Softeners and waxes are added after the fillers are well dispersed. Accelerators and sulphur masterbatch should be added last [45, 46, 47, 48, 49].

13.2.2 Poly(vinyl chloride)/nitrile blends

PVC is a thermoplastic material that is one of the most commonly used outsole materials; it is discussed later in Section 13.11. It has excellent resistance to oils, fats, and chemicals, but it has other drawbacks such as poor cold temperature flexibility and lower durability which limit its use. Blends of PVC with nitrile rubber (particularly powdered nitrile) can be used in safety and work shoes to provide chemical resistance above that of nitrile rubber on its own. Recent grades have been developed for shoes that see extremely severe conditions such as those found in abattoirs and poultry, meat, and fish processing facilities (oils, fats, blood, animal by-products) while still providing good wear resistance, flexibility and skid resistance [50]. In these blends, the powdered nitrile acts as a plasticiser for the PVC, providing a more rubber-like feel to the outsole.

13.2.2.1 Typical formulas

Formulations for these types of applications are shown in Table 13.10.

13.2.2.2 Mixing

Mixing takes place in two stages. In the first stage, all of the dry ingredients, except for the powdered nitrile rubber are added to the mixer and blending begins at a high speed. When a temperature of approximately 70 °C is reached, the mixing speed is reduced and the liquid ingredients are added. High speed mixing is resumed until a temperature of

Table 13.10 Safety outsoles - PVC/nitrile blends

	PVC/NBR blend phr	PVC/NBR (more rubber-like) phr
PVC	100	100
Powdered nitrile	20	30
Diisononyl phthalate (DINP)	80	95
BaCd stabiliser	3	3
Organic phosphite	1	1
Epoxidised soya oil	5	5
Calcium stearate	1	1

80 °C is obtained. It is important to make sure that all of plasticiser is absorbed by the PVC. The powdered nitrile is added and the blend is discharged. It can be granulated in an extruder, then calendered, extruded or injection moulded. PVC/nitrile outsoles are usually injection moulded [51, 52].

13.2.3 Polychloroprene-based compounds

Polychloroprene (2-chloro-1,3, butadiene; CR) is another polymer that is used in safety shoes where resistance to oils and many chemicals is needed. It competes directly against nitrile in these applications, having some advantages and some disadvantages. Table 13.11 shows a comparison between the two polymers.

For applications where high chemical and oil resistance is required, nitrile is the polymer of choice. When medium resistance plus good weathering properties are needed, polychloroprene is a good choice.

There are three different classes of polychloroprene rubbers that are used in moulded goods: sulphur modified, mercaptan modified and precross-linked, with many grades within each class. There are also grades which are used for adhesives. Common trade names include Neoprene, Baypren, and Butaclor. The sulphur modified grades are polymerised with sulphur to control the MW. This limits their storage life, but allows them to be vulcanised without additional sulphur or accelerators through the use of metal oxides (zinc oxide, magnesium oxide or lead oxide) alone. They are fast curing,

Table 13.11 Comparison of resistance properties of nitrile and polychloroprene rubbers

Property	Nitrile rubber	Polychloroprene
Resistance to petrol	very good	good
Resistance to benzene	fair	low
Resistance to oil	very good	good
Resistance to acids	good	good
Resistance to alkalis	good	good
Resistance to alcohols	low	low
Resistance to chlorinated hydrocarbons	fair	low
Resistance to weathering/ozone	fair	very good
Flame resistance	none	very good

but offer processing safety. They also have the best flex resistance, tear strength and rebound properties of all polychloroprene grades, which makes them an excellent choice for dynamic applications. Unlike the other grades, they will break down during mixing and can also be softened by adding chemical peptisers.

The mercaptan modified grades are polymerised with mercaptans rather than sulphur, and have excellent long term storage life, as well as lower compression set properties since the length of sulphur cross-links can be controlled better when the sulphur and accelerators are added during mixing. They also have the best heat aging properties. These grades require organic accelerators for vulcanisation; ETU is the most common one used for neoprenes.

The precross-linked grades contain a highly cross-linked gel which acts as an internal processing aid. This gives a much smoother surface on extruded or calendered articles. They are similar to the mercaptan modified grades in other respects.

Many CR grades crystallise with time, resulting in a gradual increase in compound hardness and other properties. While crystallisation has been important in the development of polychloroprene-based adhesives, it is generally an undesirable property in finished products. Grades exist which have been modified to reduce crystallisation.

13.2.3.1 Fillers

CR, like NR, will strain crystallise (different from age crystallisation) when stretched; unfilled compounds are self-reinforcing. Lower level of fillers are needed as compared to SBR, butyl or other non-strain crystallising polymers. Semi-reinforcing fillers will provide a higher level of reinforcement than in other polymers. Carbon black, silica, clays, calcium carbonate and fine particle sized whitings are used in polychloroprene compounds. In many general purpose applications, less reinforcing grades of carbon black such as N990 provide adequate physical properties. Reinforcing silica or semi-reinforcing blacks such as N732 are used when high levels of properties are needed.

13.2.3.2 Plasticisers, processing aids and oils

Aromatic or naphthenic oils are used to plasticise CR rubbers, although aromatic oils can discolour light coloured articles. At high oil loadings, aromatic oils are preferred because both materials are polar. Paraffinic oils are compatible only in very small quantities.

13.2.3.3 Antidegradants

Even though CR has good resistance to oxygen and ozone attack, it still requires the addition of antidegradants.

13.2.3.4 Cure systems

When curing sulphur modified grades by metal oxides alone, a combination of 4 phr of magnesium oxide with 5 phr of zinc oxide is used. When curing mercaptan modified or precross-linked grades, metal oxides are too slow on their own. Sulphur, ETU and possibly a secondary accelerator such as MBT, TMTD, or DOTG (depending on the final property requirements) are used.

CR is mixed in standard rubber equipment following standard procedures. Mixing temperatures must be kept as low as possible to avoid scorching.

13.2.3.5 Mixing

In an internal mixer, the rubber is added first and allowed to mix alone to reverse any hardening due to crystallisation. If sulphur modified grades are used, they are allowed to mix longer to lower the viscosity. Magnesium oxide and antioxidants are added first followed by the reinforcing fillers and stearic acid. CR mixes best when shearing forces are kept as high as possible. Inert fillers and plasticisers are added at the end of the mixing cycle; the compound should be dumped before the temperature reaches 110 °C if black filled or 130 °C if silica filled. The compound should be sheeted off and cooled as quickly as possible. Accelerators may be added at the end of the Banbury mix cycle if the temperature is well controlled, or on the mill; mill rolls should be cooled. Zinc oxide, ETU and other accelerators are added, and the compound is quickly mixed again in order to keep compound temperatures low [53, 54, 55, 56].

13.2.3.6 Typical formulae

Table 13.12 lists some typical CR-based oil resistant formulae.

Table 13.12 Safety outsoles - polychloroprene based

	CR/SBR/BR blend	CR-based
CR - mercaptan modified grade	50	100
SBR	30	
BR	20	
Naphthenic oil	15	15
Stearic acid	2	0.5
Magnesium oxide	2	4
Zinc oxide	2	5
Silica	40–60	
Coupling agent	3–5	
DEG	1	
N732	-	40–60
Sulphur	2.5	
MBTS	1.5	
DOTG	1	
ETU		1

13.3 High durability compounds

High durability compounds have many uses; they can be used on work shoes, especially those used in severe work conditions, on heavy duty hiking boots, and for sports played on highly abrasive surfaces such as tennis or outdoor basketball. High abrasion can be achieved through the use of high wearing polymers, such as natural rubber, polybutadiene, or carboxylated nitrile rubber (XNBR), the use of highly reinforcing fillers such as carbon black and/or silica, and reinforcing resins such as high styrene resins.

13.3.1 Carboxylated nitrile based compounds

Carboxylated nitrile rubber is an excellent choice for work boots that must also have some chemical resistance. XNBR is made by polymerising a monomer with carboxylic acid groups (generally acrylic acid) with the acrylonitrile and butadiene. The acid groups are randomly distributed and are present at levels of 10% or less. These groups produce extra cross-links during the vulcanisation process which are responsible for improved physical properties as compared to a non-carboxylated nitrile rubber. The acid groups readily react with metal oxides, such as zinc oxide, resulting in ionic bridges. These cross-links are formed along with sulphur or peroxide cross-links. The carboxylated polymer has better abrasion resistance than standard nitrile polymers [47]. A test recipe based on 100 phr of NBR has a Pico abrasion index [48] of 73, while the same recipe based on 100 phr of XNBR has an index of 493 (a higher number is better). XNBR is chemically resistant, although care must be taken to avoid chemicals and solvents that readily attack acids. Abrasion resistance of compounds can further be improved by the addition of up to 25 phr of polybutadiene; above this level, abrasion improvement decreases. XNBR can also be blended with SBR, NR or NBR, but the only real benefit in these blends is cost reduction. In blends, increasing levels of XNBR results in higher modulus, tensile strength, and hardness; it is very easy to produce compounds with hardness in the Shore A 80–90 range. However, compression set is worse (higher) and harder compounds may have traction limitations.

13.3.1.1 Fillers

With the reactive acid groups, fillers that are diluted in regular nitrile rubbers (clay) can be semi-reinforcing in XNBR. Silica or carbon black should be used to achieve the highest level of abrasion resistance. Athletic shoes that are used on court surfaces must be non-marking.

13.3.1.2 Plasticisers, processing aids and oils

Plasticisers and other processing aids that are used in nitrile rubbers can also be used in XNBR.

13.3.1.3 Cure systems

Sulphur-based cure systems work well; zinc peroxides are used to produce mechanical goods with high heat resistance but lower tensile strength, tear resistance and flexibility. Zinc oxide coated with a metal phosphate or with zinc sulphide will improve scorch safety; regular grades of zinc oxide have a large reactive surface area which can cause scorch by reacting with the acrylic acid.

Mixing of XNBR compounds is similar to NBR, although XNBR will band easier on the mill, resulting in a faster mix cycle. Sulphur will also blend easier in XNBR than NBR. Semi-EV cures are common with carboxylated grades as well [46, 47, 49, 50].

13.3.1.4 Typical formulae

Table 13.13 lists some high abrasion compounds based on carboxylated nitrile rubber.

Table 13.13 High abrasion outsoles - XNBR based

	High abrasion	Non-marking
XNBR	75	100
Polybutadiene (high-*cis*)	25	
Carbon black (SAF, HAF, FEF)	40–50	
Silica		20–50
Coupling agent		3–4
Clay		0–30
Dibutyl phthalate	10	10
Zinc oxide	5	5
Stearic acid	1	1
Antioxidant	1	1
Sulphur	1.5	1.5
MBTS	1.5	1.5
TMTM	0.1	0.1

13.3.2 Blends with high styrene resins

Less expensive, high durability work boot soles or hiking outsoles may be based on NR or SBR reinforced with high styrene resins. This allows production of a stiff, high wearing compound while retaining most of the properties of the base polymer (high rebound). Of course, durability may be less than compounds based on higher abrasion resistance polymers [3, 45, 52, 58]. Table 13.14 lists some high styrene reinforced compounds.

13.3.3 Polybutadiene-based compounds

For sports played on highly abrasive surfaces, such as tennis and outdoor basketball, a compound based on polybutadiene, blended with NR or SBR to achieve the necessary combination of properties is often used. Both sports require very high abrasion resistance with high traction; the player must change directions quickly while sliding over rough surfaces. Equally importantly, the outsole must not mark the court surface. While carbon black would normally be the filler of choice for abrasion and traction, silica must be used in order to make a non-marking outsole.

Table 13.14 High abrasion outsoles - NR or SBR based

	NR-based	SBR-based
NR	100	
SBR		100
Hi styrene resin	20–30	20–30
Carbon black	60–80	60–80
Process oil	10	10
Zinc oxide	5	3
Stearic acid	1	1
Antioxidant	1	1
Sulphur	2.5	1.9
CBS	0.8	0.8
TMTM	0.3	0.1

13.3.3.1 Fillers - high temperature silica mixing

Recent developments in the tyre industry with high temperature mixing of silica can yield silica based compounds with properties equal to a black filled compound in terms of traction and durability. This may someday be used in footwear. The concept was first developed by Michelin [59]. SBR, BR, or any other conjugated diene rubber, silica (CTAB surface area of 160 m^2/g) and coupling agent (one of the commercially available grades such as Si69, or a multi-functional acid such as dithiodipropionic acid) are mixed in an internal mixer until the temperature of the compound is between 145 °C and 180 °C. It is mixed at this temperature for between 10 seconds and 20 minutes. It is suggested that the silane of the coupling agent forms a bond to the silica surface (possibly through hydrolysis) as well as the rubber reactive surface. The resulting compound has very low rolling resistance (very important in tyres), good wet traction, good snow traction, and abrasion resistance equal to a black filled rubber. While we are not concerned with rolling resistance, the other gains could be very useful in a non-marking outsole. These compounds have already been used on many original equipment car tyres, as well as bicycle tyres. Additional patents have focused on silica/carbon black blends [60, 61, 62]. The use in outsoles is limited only by the mixing equipment in the factory.

13.3.3.2 Typical formulae

Table 13.15 lists some high abrasion outsoles based on BR blends and high temperature mixing.

13.4 High traction compounds

The development of high traction compounds, based on polyisobutylene-isoprene (butyl, IIR) or halogenated polyisobutylene-isoprene rubbers (bromobutyl, BIIR or chlorobutyl, CIIR) is an example of service conditions limiting the use of a material in tyres, but allowing it in footwear. The average foot strike occurs at a frequency of 1 Hz while walking; a tyre travelling at 100 km/h contacts the road surface at a frequency of 30 Hz, resulting in much higher deformation and heat generation. This has limited the use of butyl-based tread compounds to race tyre applications only while butyl-based footwear compounds are used in a much wider range of applications.

13.4.1 Polyisobutylene-isoprene based compounds

Butyl rubber (IIR) is a copolymer of isobutylene with 1–3% of isoprene, produced by cationic polymerisation in methylene chloride with an $AlCl_3$ initiator at –100 °C. The isoprene monomer provides sites of unsaturation which allows sulphur vulcanisation to take place. The commercially available grades have Mooney viscosities (ML 1 + 4 at 100 °C) of between 40–80 and isoprene content, reported as mole % unsaturation (the number of moles of isoprene per 100 moles of isobutylene) in the range of 0.7–2.2%. Compared to other grades of elastomers, this is of extremely low unsaturation and is responsible for the unique properties of butyl rubbers. The low level of double bonds produces a polymer that is resistant to oxygen, ozone, moisture and chemical attack. It also has low gas permeability, good vibration damping properties, a high coefficient of friction, but a slower cure rate than other commonly used rubbers. In the commercially available grades, as the level of unsaturation increases from 0.7 to 2.2%, the vulcanisation rate also increases. However, the increased number of double bonds provides more sites for chemical and ozone attack, and other physical properties are also reduced. For footwear applications, it is the damping and friction properties that we are most interested in, and the higher rate of cure is more beneficial than chemical resistance. Typical grades to use, include Exxon 365 or Polysar 402. IIR does not covulcanise with other rubbers and it is difficult to bond it to other materials with adhesives. Halogenated versions containing bromine (bromobutyl) or chlorine (chlorobutyl) were developed to improve these properties and increase the cure rate. The halobutyl rubbers have better physical properties than their parent butyl polymer; in particular BIIR has better ozone resistance, lower gas permeability, and higher hysteresis. The properties of CIIR are between bromobutyl and butyl; both halogenated polymers are more expensive than IIR. Bromobutyl covulcanises better with other diene polymers than CIIR and is a better choice for shoe outsoles. Typical BIIR grades that are used in footwear are Exxon's Bromobutyl 2244 or Polysar's X2.

Butyl and the halobutyl polymers are highly viscous materials and they have very good damping properties. Energy put into the compound is dissipated mainly as heat, rather than being returned (rebound). The rate of response to energy input or deformation is also delayed. This explains the use of butyl rubber in climbing and high traction compounds. In a running shoe, as the shoe contacts the ground, energy from the foot is transferred into the midsole then the outsole. The rubber compound, generally a highly elastic material, deforms instantaneously, and most of the energy is returned to the midsole, then to the foot to propel the runner forward. For climbing, we are trying to propel ourselves up a steep surface that is often smooth, with only small irregularities on the surface. We do not want to have the rubber outsole of our shoe bounce off the rock surface when the foot is placed there, so we would not want to use a running compound with high rebound properties. For this application, we want a rubber compound that is highly viscous. When the shoe is placed on the rock surface, the energy that is absorbed is used to deform the polymer chains so that flow around the irregularities on the rock surface provides traction. In climbing this is called 'smearing'. The use of butyl-based compounds in climbing shoes has allowed the level of rock climbing to improve dramatically over the past two decades. A typical climbing outsole is based on 100% butyl or bromobutyl rubber.

13.4.2 Fillers

Carbon black is the preferred filler, with the level dictated by hardness and abrasion resistance requirements. HAF or ISAF grades provide high durability and tensile strength.

Silica can be used if high tear resistance or a non-marking compound is needed. It will retard the already slow cure rate by preferentially reacting with the curatives, as well as having a hardening effect; the cure system will need to be adjusted. The retarding effect can be reduced by the addition of DEG, PEG, or another polyol during mixing. They will react with hydroxyl groups on the silica particle, reducing the number of sites for the accelerators to bond to. Blends of carbon black and silica can be used.

Talc, clay and whiting can be used as extending fillers to reduce cost; however properties will be reduced as well.

13.4.3 Plasticisers, processing aids and oils

Aromatic oils are generally used in tyre applications where high traction is desired, but in butyl compounds they will cause poor aging resistance of the vulcanisate. Naphthenic and paraffinic oils are used as plasticisers, due to butyl's low solubility parameter. Struktol 40 MS is used as a processing aid for butyl or halobutyl compounds. In blends of BIIR with other diene rubbers, it assists in the co-mixing of the polymers. Hydrocarbon resins can be used as tackifiers. Coumarone-indene resins can be used at levels up to 10 phr to increase hardness without increasing tensile strength

13.4.4 Antidegradants

Antidegradants are often not necessary in IIR or BIIR compounds due to the low level of unsaturation as well as antioxidants added during polymerisation. If needed, amine-type antioxidants and antiozonants such as *p*-phenylene diamine will react with the polymer and should be added with the curatives rather than in the masterbatch stage. Phenol type antioxidants can also be used.

13.4.5 Cure systems

Butyl rubber is slow curing due to the low levels of unsaturation; sulphur and thiazoles, in combination with more active accelerators such as thiurams and dithiocarbamates are used to achieve reasonable cure rates. Zinc oxide (5 phr) is added to activate the accelerators and provide reversion resistance. Stearic acid is not required for vulcanisation in butyl compounds, but is often added as a processing aid.

There are two additional methods to cure butyl rubber. The first is a combination of ρ-benzoquinone dioxime and ρ-quinone dioxime (CDO or GMF) with PbO_2 or Pb_3O_4 and MBTS to give a high heat resistance compound. A sulphur vulcanised butyl compound will tend to soften during long term exposure to temperatures of 150–200 °C. The second method makes use of phenol formaldehyde resin and a halogen containing activator such as stannous chloride ($SnCl_2$) or neoprene. The heat resistance of this cure system is outstanding and is used for tyre curing bladders.

Bromobutyl is faster curing than butyl and can be readily cured using sulphur with thiurams and thiazoles. The resin and CDO options are also available, as are cures using zinc oxide with stearic acid alone, or with a sulphur-donor. Halobutyls can be cured with peroxides, while butyl will depolymerise in their presence [63, 64, 65, 66, 64].

13.4.6 Typical formulas

Tables 13.16 and 13.17 list marking and non-marking climbing outsole formulas based on both butyl and bromobutyl compounds. Table 13.16 lists bromobutyl based hiking compounds, while Table 13.17 has a non-marking high traction compound used on boat shoes, windsurfing booties, and other shoes used in water sports, based on a suggested formula by Polysar SA [45].

Compounds for hiking boots, water sports shoes, and other applications may use blends of bromobutyl with other diene polymers to optimise properties and reduce cost. If abrasion resistance is important, polybutadiene should be added. NR may be added to improve flex resistance. The vulcanisation system is modified to allow the polymers to covulcanise.

13.4.7 Mixing

Butyl rubber is easily contaminated by other diene rubbers such as polybutadiene or NR. Due to the high degree of unsaturation, these polymers will preferentially react with the curatives and the resulting butyl rubber will be undercured. All mixing equipment should be cleaned before mixing butyl rubber.

Butyl and bromobutyl rubbers do not break down upon mixing, so there is no need for a pre-mastication step. Mixing should be done in two stages, with the first stage containing all ingredients except for zinc oxide and accelerators.

Table 13.16 Climbing outsole - butyl based

	Marking	Non-marking
Butyl	100	100
Carbon black (HAF or ISAF)	50–70	-
Silica	-	40–60
Coupling agent	-	3–5
DEG or PEG	-	4-6
Stearic acid	1	1
Paraffinic oil	-	5
Aromatic oil	5	-
Zinc oxide	5	5
Sulphur	1.5	1.5
MBTS	1	1
TMTD	0.5	0.5

Table 13.17 Climbing outsole - bromobutyl based

	Marking	Non-marking
Bromobutyl	100	100
Carbon black (HAF or ISAF)	50–70	-
Silica	-	40–60
Coupling agent	-	3–5
DEG or PEG	-	4–6
Stearic acid	1	1
Paraffinic oil	-	5
Aromatic oil	5	-
Zinc oxide	5	5
Sulphur	1.5	1.5
MBTS	1	1
TMTD	0.5	0.5

Table 13.18 Hiking outsole - bromobutyl based

	High abrasion phr	Low cost phr	Water sports shoes phr
Bromobutyl	60	60	80
Polybutadiene	40		
NR		40	20
Silica			30
Calcium carbonate			40
Carbon black (HAF or ISAF)	50–70	50–70	
Paraffinic oil	5	5	10
Zinc oxide	3	3	3
Stearic acid			1
Sulphur	0.5	0.5	1.5
Titanium dioxide			10
MBTS	1.5	1.5	1
TMTD	0.25	0.25	0.5

First stage (Banbury)	0 min	Polymers, filler, retarder
	1.5 min	Process aids, plasticisers
	3.5 min	Dump at 120–140 °C to avoid scorching
Second stage (Banbury)	0 min	Masterbatch plus cure, ZnO
	2 min	Dump at 100 °C

If the curatives are added on the mill, the mill rolls should have a roll-speed ratio of 1.25:1, with a roll temperature of 40 °C on the slow roll and 55 °C on the fast roll.

13.5 Blown rubber compounds

Light weight and good cushioning are key properties for athletic as well as casual footwear. Since vulcanised rubber has a density of 1,100–1,200 kg/m^3, it represents one of the heaviest components of a shoe. In order to reduce weight, compounds have been developed that are microcellular; they have a density of 500–800 kg/m^3. This is accomplished by adding a blowing agent; a chemical that is stable at room temperature but which breaks apart and releases gas at its decomposition temperature. The resulting foamed rubber has a density of less than 1,000 kg/m^3, and a more cushioned feel or ride [68, 69, 70, 71, 72, 73, 74].

13.5.1 Classifications of foams

The classifications of blown rubber are open cell (sponge foam), closed cell (may have open and closed cells present), and microcellular (small closed cells with thin cell walls). These classifications depend both on the blowing agent used, and the method of moulding during expansion.

13.5.1.1 Open celled foams

Sponge rubbers use inorganic blowing agents such as sodium bicarbonate ($NaHCO_3$) which releases carbon dioxide (CO_2). Carbon dioxide has a high level of permeability in most rubbers. The blowing process must be nearly complete before vulcanisation begins so that no gas is trapped within the sponge. This produces an open or interconnecting cell structure. For many articles, the expansion is pressureless, that is there are no physical constraints (such as a closed mould) controlling the foam expansion. This type of foamed rubber is not used in high performance outsoles, due to poor durability. It is used in slippers and very low cost/low performance shoes. The rubber can be foamed by itself in a mould, or a solid rubber skin can be applied to improve wear resistance. A thin calendered sheet of rubber is placed in the mould first, followed by the sponge compound. It expands first to partially or just barely fill the mould (resulting in an open cell structure), then vulcanisation begins so that it bonds to the calendered rubber. Foamed parts made in this manner are adequate for the low performance applications involved [52].

13.5.1.2 Closed and microcellular foams

Azodicarbonamide (ADC), hydrazides and nitroso-based blowing agents are used to produce closed and microcellular cell structures. They release nitrogen, which has lower permeability in rubber than carbon dioxide, resulting in non-interconnecting cells which will have much better wear resistance than an open cell foam. ADC decomposes at approximately 205 °C and gas generation begins in the rubber compound at approximately 140 °C. Hydrazides (benzenesulphohydrazide, BSH, and benzene-1,3-disulphohydrazide) will start to decompose at 95–100 °C, while nitroso compounds (dinitrosopentamethylene tetramine, DNPT) begin to break apart at 205 °C, although gas liberation begins at 120–125 °C. Sometimes activators are used which lower the decomposition temperatures by 20–30 °C. These include zinc oxide, zinc salts, and glycols. The choice of blowing agent is dependent on final properties needed. All three can be used to produce hard and soft microcellular outsoles. Table 13.19 gives a comparison of common blowing agents.

Even with a closed structure, durability will be lower than a compound with no blowing agent added. The trade-off between light weight and abrasion resistance is dictated by the end use, and can be controlled by the level of blowing agent added. The moulding process to produce closed or microcellular rubber is much different from that used to produce an open cell structure. An excess of rubber is placed in the mould (3–5%) so that the mould is completely filled. Blowing and vulcanisation take place at the same time; the mould is under pressure, and the nitrogen gas remains dissolved in the rubber. The mould is opened before curing is complete, and the part expands due to the high pressure of the trapped gas in the cells. The part must be vulcanised sufficiently so that the cells do not rupture when the mould is opened. If the curing cycle is lengthened, more cross-links will develop, and the amount of expansion will be reduced. Shorter cure times will result in a larger expansion ratio and finished parts will be larger and have a lower density. It is necessary to post cure microcellular rubbers to complete the vulcanisation cycle and to stabilise the part size.

Table 13.19 Blowing agent comparison

	ADC	BSH	DNPT	$NaHCO_3$
Slipper outsoles	-	++	o	+
Athletic (soft) microcellular rubber	++	++	++	-
Hard microcellular rubber	++	++	++	-
Pore size	Very fine	Very fine	Very fine	Visible

+ *good*
++ *very good*
- *not recommended*
o *possible*

13.5.2 Rubber-based compounds

Starting compounds for blown applications can be the same as non-blown compounds; the only difference is the addition of blowing agents. For casual and dress shoes, compounds with high levels of styrene resin are often used for good cosmetic definition. For athletic footwear, compounds based on NR, BR, SBR, CR and other diene rubbers can be used. Foamed neoprene is commonly used in wetsuits and it is also sometimes used in shoe midsoles [45].

13.5.2.1 Typical formulae

Table 13.20 lists some typical blown rubber outsole formulae.

13.5.3 Ethylene vinyl acetate rubber-based compounds

In the past decade, outsoles based on microcellular ethylene vinyl acetate rubber (EVM) have been developed. Ethylene vinyl acetate rubber is used both as a thermoplastic (packaging, adhesives) and as a thermoset cross-linked by peroxides (midsoles, outsoles).

Table 13.20 Blown rubber outsoles

	High abrasion	General
Natural rubber	40	25
SBR		75
BR	60	
Silica		20–30
Calcium carbonate		20
Carbon black	40–50	
Naphthenic oil	5	5
Coumarone indene resin	10	10
Sulphur	2	2
MBTS	1.5	1.5
ACD	3.5	3.5

Midsoles based on blown EVM rubber have been used in footwear in two forms. The first type of midsole is one that has been die cut out of sheets of blown EVM; these have only adequate cushioning properties. The second type of midsole is produced by compression moulding of a die cut foam to produce a midsole with outstanding cushioning properties.

Outsoles have been developed based only on EVM (with densities as low as 300 kg/m^3) or in blends with other diene rubbers such as SBR, NR, and BIIR to improve the range of properties. Outsoles can be produced by compression or injection moulding. Compression and injection moulding of EVM compounds operates on the same principle as moulding microcellular rubber, the mould is filled with a slight excess of compound so that it is completely filled. Blowing and vulcanisation take place at the same time, with the evolved gas dissolved in the compound. The mould is opened before vulcanisation is complete, and the part expands. Common trade names include Elvax and Levapren.

13.5.3.1 Compounding ingredients

Standard fillers are used in EVM compounds; carbon black (reinforcing, semi-reinforcing and inert grades), fumed silica, aluminium silicates, clays, talcs, zinc borate, and magnesium carbonate. Plasticisers are generally not needed, although low levels of paraffinic oils can be used. Stearic acid is usually added to prevent sticking on mills and to improve mixing and dispersion of fillers. Zinc oxide can be added to improve age resistance, but it does not have an activating function as in sulphur cured thermosets. EVM polymers are cured using peroxides; dicumyl peroxide (DCP) is the most commonly used.

13.5.3.2 Blowing agents

ADC blowing agents which have been modified for use in EVM rubber are commonly used [72].

13.5.3.3 Cure systems

EVM rubbers have saturated backbones and cannot be cross-linked with sulphur systems. When mixing EVM rubbers with other diene rubbers, the use of a peroxide is necessary to get co-curing between the polymers to produce the best combination of properties. If the compound is predominantly diene-based, the cure system can remain sulphur-based; the EVM will act as a polymeric plasticiser in the compound [45, 75, 76, 77, 78].

13.5.3.4 Typical formulae

Table 13.21 lists several EVM-based microcellular outsole compounds.

13.5.3.5 Mixing

EVM-based polymers can be mixed in internal mixers, as well as on the open mill. Equipment must be very clean because chemical residue can affect the peroxide cure. The polymer is added to the internal mixer first. Stearic acid and fillers are added next for good dispersion. The peroxide curing agent and blowing agent are added at the very end of the mix cycle to avoid premature reaction. On the mill, the order of addition is the same so that the stearic acid reduces sticking on the rolls. Zinc stearate can also be added to reduce sticking.

Compounds that are injection moulded are generally purchased in a precompounded pellet that requires no additional mixing.

Table 13.21 EVM-based outsoles

	Formula 1 phr	Formula 2 phr
EVM	75	80
BR	25	
BIIR		20
Silica		35
Calcium carbonate	50	
Zinc oxide	2	3
DCP	1	
Sulphur		2
MBTS	1.5	
ACD	3.5–5	3.5–5

13.6 Clear compounds

Fashion and cosmetics are one area where the footwear industry differs greatly from the tyre industry. While performance is what has driven the development of new compounds and materials for shoes, fashion is often what drives the purchase. Transparent and translucent rubber compounds are used to create unique design features in outsoles. They allow features on the midsole (using sublimation printed or screenprinted designs) as well as cushioning mechanisms to be clearly seen.

13.6.1 Ethylene propylene diene monomer rubber-based compounds

EPDM rubber is used when clarity is most important. EPDM can be cured to a 'water white' (transparent) colour, while other polymers may give a slightly yellow tint or only be translucent rather than transparent. EPDM is difficult to bond to other polymers, which has limited its use. Traction properties are not as good as other rubbers [75].

13.6.2 Diene rubber blends

Clear or translucent compounds can be made using synthetic natural rubber (IR), BR, SBR and other synthetic polymers. The starting materials must be very clean and white or light coloured, which eliminates most grades of NR, as well as oil extended SBRs. Millable polyurethane gums can also be used [79]. The base polymer will determine if the rubber is transparent or merely translucent.

13.6.2.1 Fillers/ingredients for transparency

There are several other compounding changes that must be made in order to produce a clear compound. First is the filler. Precipitated silica, which is used in other white or light coloured footwear compounds, has approximately 4–7% water bonded onto the surface of the silica particle [25]. The water causes a cloudy appearance in the finished product. Drying precipitated silica is not practical; even under harsh drying conditions, a monolayer of water remains. Fumed silica is produced in the vapour phase from silicon tetrachloride and contains no water on the particle. It must be used in all applications where transparency is needed. Transparent zinc oxide is used in place of normal zinc oxide as well. The use of oils should be kept to a minimum because most oils are discolouring; paraffinic oil should be used if needed. Finally, clear compounds are peroxide rather than sulphur cured. Dicumyl peroxide is one of the most commonly used peroxides [80, 81].

Clear or translucent rubber compounds with good durability and traction can be developed by first blending the polymers to achieve those properties, then using the fillers and cure system to achieve a clear compound. The final properties may not be equal to a sulphur-cured version of the same composition as peroxide cure systems give poorer abrasion resistance and lower tensile and tear properties. Clear tinted compounds can be made by adding small amounts of an appropriate pigment.

13.6.2.2 Mixing

The mixing process is as important as the choice of raw materials. Equipment must be as clean as possible to avoid contamination and discolouration. If enough clear rubber is mixed, there should be a mixer and mill dedicated strictly for clear rubber production. They should be as far removed as possible from equipment used to mix carbon black filled compounds. Seals on the equipment need to be checked frequently, as leaking oil can discolour the compound. If dedicating a mixer is not possible, then 'clean out' batches of rubber need to be used to remove all traces of materials that could stain the rubber or interfere with the peroxide cure system.

Millable polyurethane gum rubbers, described in Section 13.10 can also be used for clear outsoles.

When blending clear rubber with solid coloured rubbers, it is important that the cure systems are the same, or the rubbers will debond; sulphur and peroxide systems do not co-cure together.

13.7 Court compounds

Court sports such as basketball, squash, volleyball, racquetball and handball, require shoes that have good traction properties on wood surfaces that have often been treated with a polyurethane coating. The second most important property is for the compound to be non-marking and non-streaking. Gum compounds based on NR crepe have been used successfully for many years, see Table 13.22. Blends of NR, BR, and SBR are also a good starting point. Bromobutyl rubber, while providing high traction, has a tendency to abrade when subjected to high shear stresses. A non-marking compound based on BIIR could still leave rubber residue on the floor, which is not considered acceptable. One compound may not be suitable for all applications, as the action of each sport is different. Fillers such as silica, calcium carbonate, or clay are used. If the shoe is worn strictly indoors, then calcium carbonate, clay, or blends with silica are acceptable as the court surface is not rough and durability is not as critical. For shoes that are worn both in and outdoors, or for 'game' only shoes, then silica should be used to provide the best traction and durability. Outsoles can be coloured by adding a few phr of pigment; the addition of too much pigment (above 10 phr) can result in marking of the court surface. Non-marking black compounds can be produced by limiting the amount of carbon black to 2–3 phr. The use of clear compounds is also acceptable for court shoes, however the fumed silica has a tendency attract dust even more than precipitated silica causing the outsole to become slippery during play. Basketball players are known to wipe the bottom of their soles off often during a game to remove dust; the addition of antistatic agents can reduce this problem. Blown outsoles can also be used on court surfaces [58].

13.8 Autoclave shoes

Autoclave curing of rubber uses saturated steam as the curing medium in a closed, sealed container. Autoclave curing of a rubber outsole takes considerably longer than compression moulding in a heated mould and press, but less time than hot air curing. Footwear, hose and cable can be cured this way.

Table 13.22 Court outsoles

	NR-based phr	SBR/NR-based phr
NR (pale crepe)	100	40
SBR	-	60
Calcium carbonate	60–80	60–80
Silica	20–30	20–30
Coupling agent		
Process oil	10	10
Zinc oxide	5	3
Stearic acid	1	1
Antioxidant	1	1
Sulphur	2.5	1.9
CBS	0.8	0.8
TMTM	0.3	0.1

Shoes with canvas uppers are the most common type of footwear cured in an autoclave; canvas is not adversely affected by steam, while other upper materials (leather, synthetic leather) may be. Autoclave curing is generally used on casual or low cost/low performance athletic shoes.

13.8.1 Shoe production

While the canvas upper is still on the last (foot form), a rubber outsole is cemented to the bottom edge using appropriate adhesives and is pressed on in a bottom press to ensure contact between the rubber and canvas. Adhesives used on the upper must not yellow under the steam and temperature conditions present in the autoclave. The outsole is often based on crepe or gum rubber, and is produced by calendering and using a die to cut out the correct shape. Additional polymers may be added for specific properties; SBR may be added for higher traction on a basketball shoe. Since these are lower cost shoes, clays or calcium carbonates are often used as fillers. Silica is used if higher abrasion resistance is needed. Compounds may be pigmented or may remain gum coloured.

Depending on the type of shoe, additional rubber components may be added, including toe caps, toe guards, foxing, and other decorative pieces. The toe guard and cap are added to provide additional wear resistance in high wear areas. The extra durability is due to the fact that there is additional rubber present, rather than to the high abrasion resistance of the compounds. For cost savings these compounds are filled with diluent fillers rather than semi-reinforcing fillers. Foxing is a gum rubber strip that is wrapped around the bottom of the shoe to provide additional strength between the outsole and the upper. It is also known as a sole guard. All of these additional pieces are produced by calendering or extrusion. The foxing compound can be calendered onto a fabric to provide additional reinforcement. The completed shoes are placed in racks in the autoclave and are cured at 120–130 °C for 50–90 minutes at a pressure of 140–350 kPa [82, 83].

13.8.1.1 Typical formulas

Typical outsole and component formulae, based on suggestions by Rider [82], are shown in Table 13.23.

13.9 Thermoplastic elastomers (see also Chapter 4)

Thermoplastic elastomers (TPE) combine the ease of processing and recyclability of plastics with the performance of thermoset rubbers. TPE's unique properties are due to their backbone

Table 13.23 Autoclave outsoles

	General phr	Higher traction phr	Higher abrasion phr	Foxing phr
Natural rubber	80	40	80	80
SBR	20	60	20	20
Silica			40	-
Coupling agent			4	-
Clay	100	-		
Calcium carbonate	-	100		
Whiting	40	40	-	100
Process oil	10	10	10	10
Wax	1	1	1	1
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Antioxidant	1	1	1	1
Sulphur	2.5	2	2.5	2.5
MBTS	1.5	0.75	1.5	1.5
DPG	0.75	1.5	0.75	0.75

structure which consists of hard and soft segments. Cross-linking does not occur due to a chemical reaction but because of intermolecular (physical) forces such as hydrogen bonding or van der Waals forces, between the hard segments of the polymer chains (Figure 13.4). There are two basic types of TPEs: block copolymers and polymer alloys. Both consist of hard and soft segments, with the attractive forces occurring between the hard segments. In the block copolymer both types of segments are located in the same molecule. In an alloy, a soft, elastic material is dispersed in a harder thermoplastic phase [84, 85, 86, 87, 88].

13.9.1 Classes of TPE

Block copolymer TPEs include styrenic block copolymers, thermoplastic urethanes, thermoplastic copolyesters and thermoplastic polyamides. Alloys consist of rubber-polyolefin blends, thermoplastic vulcanisates (TPV) and melt processible rubbers (MPR).

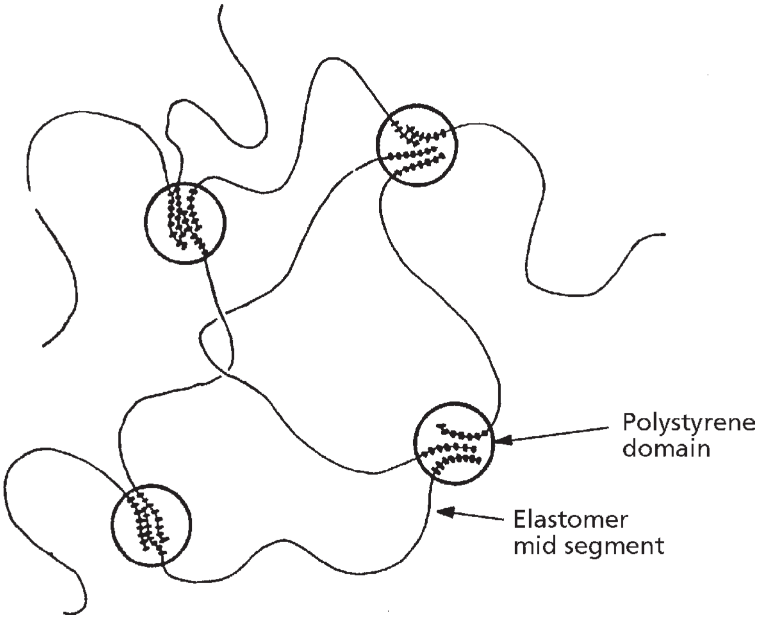

Figure 13.4 Structure of thermoplastic elastomers

Reproduced with kind permission from Handbook of Thermoplastic Elastomers, 2nd Edition, Eds., B. M. Walker and C. P. Rader, 1988, Figure 2.1. © Kluwer Academic Publishers, 1988

In an alloy, the rubber particles can be cross-linked, which considerably increases the physical properties of the blend; these are termed thermoplastic vulcanisates.

Thermoplastic elastomers have found many uses in footwear applications. The advantages and disadvantages of TPE compared with thermoset rubbers [84, 86] are:

Advantages

- Thermoplastic elastomers are generally sold as fully formulated materials; there is no need to mix or formulate new compounds.
- Fewer processing steps with shorter cycle times. There is no need to mix, calender, die cut, or otherwise process unfinished parts as there is with thermoset rubbers. Parts are injected on standard plastics machinery with cycle times generally being seconds rather than minutes.
- With fewer steps, there is less scrap. What is generated can be recycled back in with virgin material to produce acceptable parts.

- Energy costs per cycle are reduced. Steam or oil heating of banks of compression moulding presses is eliminated.

- Parts and shapes that cannot be made by compression moulding can be made by injection moulding.

- Physical properties are acceptable for most footwear applications.

- Better quality control of parts.

Disadvantages

- High temperature properties are inferior. Because the cross-links are physical rather than chemical, TPE will melt when subjected to high temperatures. This limits their use to casual shoes rather than high performance athletic footwear.

- New equipment is required. While plastics manufacturers would already have this equipment, companies that are currently compression moulding outsoles would require new equipment, which could involve a considerable investment.

- Processes are quite different from what thermoset moulders are used to. There will be a learning curve to get the processes optimised.

- Material handling is quite different, including the need to dry the raw material.

- Poor oil and chemical resistance for work and safety shoes.

- High mould costs for low volume production runs.

13.9.2 Styrenic TPE

Styrenic block copolymers are the most commonly used in footwear, over 70% of the TPE used in footwear outsoles are styrene-based [89]. Footwear is one of the major markets as one-third to one-half of all styrenics produced are used in footwear [2, 89]. Styrene may be copolymerised with isoprene (styrene-isoprene-styrene, SIS), butadiene (styrene-butadiene-styrene, SBS), ethylene/butylene (styrene-ethylene/butylene-styrene, SEBS) or ethylene/propylene (styrene-ethylene/propylene-styrene, SEPS). At room temperature, the styrene phase of the copolymer is hard but becomes fluid at elevated temperatures. Generally polymers are thermodynamically incompatible with other polymers and will separate into different phases. This occurs in the block copolymers;

the phases will separate, even within one molecule. The styrenic groups will form separate domains which act as physical cross-links. At room temperature, a three-dimensional network is established; it resembles a vulcanised rubber network. Upon heating the physical cross-links are broken, allowing the polymer to flow. The domains are re-established upon cooling. Unlike thermoset networks, the cross-linking process in TPE is reversible and can be repeated; this allows TPE to be processed as a plastic. It also allows scrap to be recycled back into the compound. Styrenics are the least expensive of the TPE, but they also provide the lowest performance. They do have good flex fatigue resistance, good low temperature properties (down to –70 °C), and can be formulated from 30 Shore A hardness to 55 Shore D. Kraton and Cariflex are two of the mostly commonly used materials in footwear. One of the problems with styrenics is that they will deform and/or melt under high temperatures since the cross-links are not permanent. Upper use temperatures are in the range of 90–100 °C, although the styrene blocks will begin to soften at 70–80 °C. In athletic shoes, temperatures can easily exceed this, especially in tennis or basketball (high temperatures generated in sliding) or running (high frequency of the foot striking the ground). This limits their use to casual shoes, low end canvas athletic footwear, and injection moulded unitsoles. Given the tonnage used yearly, this is still a considerable market [89, 90, 91].

13.9.3 Thermoplastic polyurethanes

Thermoplastic urethanes (TPU) are the next largest class of TPE used in footwear, and can cover a wide range of hardnesses, from 70 Shore A to 75 Shore D. They are also block copolymers with urethane linkages in the backbone. Hard segments are mainly isocyanate-based with short diol sections. The soft segments are longer chain diols. TPU are more expensive than styrenics, but they offer higher performance including better abrasion resistance (best of all TPE) and high flexibility over a wide temperature range [86]. High hardness grades (40–70 Shore D) are often used as outsoles on shoes used in athletics (track and field) and football (soccer), where high abrasion resistance and high stiffness properties are needed. Traction is supplied through the use of cleats on the outsole. They are also used extensively in ski and inline skate boot shells, with a usable temperature range of –60 °C to 130 °C. Softer, more flexible grades have been injected into a web pattern which are used as traction elements on high end running shoes. Commonly used materials include Pellethane, Estane, Desmopan, and Elastolan [92, 93].

13.9.4 Copolyester TPEs

Copolyesters are block copolymers with the hard (poly-1,4-butenediol terephthate) and soft (polyalkylene ether terephthalate) segments connected by ester and ether linkages.

They have high strength and high flexibility properties, with hardness in the range of 35–70 Shore D. Automotive applications are the most common for copolyesters (Hytrel, Arnitel and Lomod are common trade names), although they have found some use in footwear, where specific needs for flexibility, toughness, and high modulus can offset their higher cost [94].

13.9.5 Polyether polyamide TPE

Polyether polyamide TPE are also copolymers. They provide the highest overall performance of TPE and are also the most expensive. Upper use temperatures are much higher than other TPE (up to 170 °C) with good fatigue resistance, tear strength, and resistance to oil and chemicals. Abrasion resistance is second only to TPU. Hardness ranges from 75 Shore A to 65 Shore D and they can be formulated to give rubberlike properties and feel. Applications are generally in automotive and mechanical goods, although they are used in footwear where their outstanding properties are needed [95].

13.9.6 Thermoplastic polyolefins

Themoplastic polyolefinic elastomers (TPO) are mechanical blends of a thermoplastic (hard phase) such as polypropylene (PP) or polyethylene (PE) mechanically mixed with an unvulcanised rubber such as EPDM, NR or NBR acting as the soft phase. Blends can range from the hard phase being the continuous phase (an elasticised thermoplastic) to the soft phase being continuous (an elastomer reinforced by a plastic). Physical properties are a combination of the properties of both polymers. The best properties are achieved when the discontinuous phase is finely dispersed. TPO are generally used in automotive applications and have not been incorporated in footwear [96].

13.9.7 Elastomeric alloys

Elastomeric alloys are blends of elastomers and thermoplastics that have been processed so that the final properties are superior to a simple blend of the materials (TPO might be considered a simple blend) [97, 98, 99].

13.9.7.1 Thermoplastic vulcanisates

Thermoplastic vulcanisates are one class of elastomeric alloys and are produced by dynamically curing an elastomer such as EPDM with a plastic such as PP. Santoprene (originally Monsanto, now AES) was the first TPV produced. PP is the continuous phase, and properties improve as the size of the EPDM particles decreases, and as it is more finely dispersed in the mix. Physical properties are superior to styrenic TPE, including abrasion resistance. TPV are used in a variety of products (such as handles) where tactile properties are important. The service temperature of TPV is also higher than the styrenics, up to 135 °C.

13.9.7.2 Melt processible rubbers

Melt processible rubbers are proprietary blends of a chlorinated polyolefin, acrylic ester and an ethylene-vinyl acetate copolymer. It is commercially known as Alcryn. It has rubberlike properties and good to excellent resistance to oils (ASTM #1 - paraffinic, and ASTM #3 - aromatic), gasoline/alcohol mixtures, gasoline, diesel and jet fuels, and reference Fuels A, B, and C. Polar fuels will attack MPR.

13.10 Polyurethane elastomers

Polyurethanes, in the form of TPU, polyurethane elastomers, millable urethanes and cast urethanes are all used in outsole and other sportswear applications.

Polyurethanes are probably the most versatile chemical group used in footwear, with products that are solid, microcellular, cellular, thermoset, thermoplastic, flexible, rubber-like and rigid. Hardnesses can range from the low end of the 000 (foam) scale to the high end of the Shore D scale. In shoes, they are used as foams, adhesives, coatings, paints and inks, and outsoles [100, 101, 102, 103].

Polyurethanes are formed by the reaction of an isocyanate with a polyol to form a urethane linkage, the Figure in Chapter 4.2.4, shows the structure. Along the backbone of the polymer, there are rigid, hard sections and flexible, soft sections. In thermoplastic polyurethanes, physical cross-links occur between the hard segments of the urethane backbone. The functionality of both the isocyanate and polyol in a TPU is two; linear chains are formed. In a thermoset urethane, such as a foam, one of the components has a functionality greater than two and a three-dimensional network is formed [101]. Chemical cross-linking agents can also be used to form the network.

13.10.1 Isocyanates

There are two isocyanates that are used in approximately 95% of all urethane systems; diphenylmethyl diisocyanate (MDI) and 2,4 or 2,6-tolylene diisocyanate (TDI). Both are aromatic-based and will yellow upon exposure to light. Aliphatic diisocyanates such as methylene *bis* (4-cyclohexylisocyanate) (H_{12} MDI) are available which will not yellow, but which are often more expensive [101, 102].

13.10.2 Polyols

The polyol backbone is either a hydroxyl terminated polyether or a hydroxyl terminated polyester, depending on the final properties need. Polyethers are by far the most common polyols for most applications; however polyester polyols are more common in footwear applications [101]. They provide a good combination of properties including higher tear and abrasion resistance at a lower specific gravity than polyether systems.

13.10.3 Polyurethane elastomers

Polyurethane rubber (PUR) elastomers are used as outsoles on work, safety and athletic shoes, including hiking boots. They account for approximately 6% of all material used in outsoles [104]. As the name suggests, they have rubber-like qualities including feel and performance. The density of the unit sole is in the range of 500–1,000 kg/m^3, providing a weight saving compared to rubber. Abrasion resistance is approximately the same as rubber up to 70–80 °C, but is inferior to rubber at higher temperatures [105]. Rubber is considered superior to urethanes in terms of traction, especially on wet or icy surfaces. Systems can be compounded to improve traction as many PUR outsoles are used on hiking boots, which are often used in wet and slippery conditions. Recent work has been done on the addition of chemically treated rubber particles to PU systems to improve wet traction [106].

A drawback to the use of polyesters is the fact that they are attacked by water and microbes. Hydrolytic stabilisers can be added, but these increase the cost. Polyether systems are an alternative; they generally provide better hydrolytic stability and are easier to use in injection machines due to their lower viscosity. Recent work in polyether systems has been to lessen or overcome the deficiencies as compared to polyesters [51, 107, 109]. The choice of using PUR over vulcanised rubber depends on properties needed (weight, abrasion, traction) as well as available equipment.

13.10.4 Production methods

Outsoles and finished shoes can be produced by several methods. A unit sole (single density outsole) is manufactured by the low pressure mixing of a liquid isocyanate and polyol which are dispensed into a mould. Water is added to the system as a blowing agent. Machines can be high shear injection machines manufactured by companies such as DESMA, CIC, and Isotherm or low shear open pour machines made by companies such as Gusbi, BGM, or Korea Automation. A recent survey shows that unit soles account for 56% of all PU soles produced [101, 103].

Dual colour, density or hardness soles can be easily produced on an injection machine, where one material is shot into the mould, with a second material shot in a few seconds later. Unit or dual density outsoles are produced separately, then bonded onto a shoe upper. Direct moulding involves pouring the PU directly onto the upper. This eliminates the need for adhesives.

13.10.5 Millable polyurethane gums

For factories which are used to processing thermoset rubbers, a second choice is available: millable polyurethane gum rubbers. These are materials that can be mixed, milled, and cured like a standard rubber compound. These systems contain chain extenders with olefinic unsaturations to provide sites for sulphur to react with [79]. There are many millable grades available and Table 13.24 shows some common grades that have been used in footwear (produced by TSE Industries).

Millable gums can be blended with standard thermoset rubbers such as high *cis*-BR, NR and SBR. Polyether-1 has been used in hard, high abrasion heels for women's dress shoes, as well as tennis and running outsoles. Pure PUR gums can also be co-cured with standard rubbers to form multi-colour outsoles. The cure rates of both compounds must be coordinated so that adhesion/curing between the two compounds will take place. A blend compound may need to be used to promote adhesion; it bridges the properties of two

Table 13.24 Millable polyurethane rubber for footwear

Polyol	Isocyanate	Cure	Use
Polyether-1	TDI	Sulphur	High abrasion
Polyether-2	Aliphatic	Peroxide	Clear outsoles
Polyether-3	H_{12} MDI	Peroxide	Clear outsoles
Polyester	MDI	Peroxide	Low cost transparent soles

dissimilar compounds (especially hardness and cure rate) by being an intermediary between the two main compounds.

13.10.5.1 Typical formulae – solid compounds

Typical solid millable polyurethane gum formulas are shown in Table 13.25.

Millable PUR gums have been used to make transparent outsoles using a peroxide cure system. Fumed silica must be used in all applications where transparency is needed. The polyether used in the clear compounds is based on poly(tetramethylene ether glycol); this polyol is also used in many clear cast formulations.

Table 13.25 Millable polyurethane rubber for footwear

	Tennis/running	Blend
Polyether-1	100	50
NR	-	15
BR	-	20
SBR	-	15
Zinc stearate	0.5	0.25
Stearic acid	0.5	0.75
Silica	40	42.5
ZnO	-	2.5
Oil	-	2.5
Wax	3	0.5
TP95 plasticiser	8	4
MBTS	4	3
MBT	4	2
TMTD	-	0.1
TMTM	-	0.1
Thanecure accelerator	2	1
Sulphur	2	2

TP95: di(butoxy-ethyoxy-ethyl) adipate

13.10.5.2 Typical formulae - transparent compounds

Table 13.26 shows some typical clear PUR gum rubber formulations.

While PUR provide good abrasion, flex and cosmetic properties, wet traction and cost are drawbacks. Work is ongoing to improve these properties.

13.10.6 Cast polyurethane elastomers

Cast polyurethane elastomers (CPU) are made by mixing and pouring raw materials into moulds and curing. Since clarity and a smooth surface are often critical properties for cast parts, there must be no gas bubbles formed during production; degassing of the raw materials is necessary. Cast polymers are used to produce rolls, castor wheels, and inline skate wheels. Many cast systems are designed to have optimised properties at 80+ Shore A hardness, which is harder than most outsole applications. Use in outsoles is possible if the correct hardness range can be achieved.

13.11 Poly(vinyl chloride)

PVC is second only to vulcanised rubber in the number of outsoles produced. PVC is a true thermoplastic that can be rigid or flexible. It can be combined with thermoset rubbers or polyurethane elastomers to give a wide range of final properties. PVC has excellent resistance to alkalis, water, inorganic acids and oxygen and ozone attack with fairly

Table 13.26 Clear millable polyurethane rubber

	Formula #1	Formula #2
Polyether-2	100	-
Polyether-3	-	100
Stearic acid	0.5	0.25
Fumed silica	20	20
Silane coupling agent	0.5	0.25
Coagent	6	3
Ultramarine blue	0.003	0.003
Peroxide	0.5	0.5

good physical properties, but poor cold flex and wear resistance properties. Ease of processing and low cost has led to its increasing share of the footwear market. It is a good choice for casual or waterproof shoes and boots, but does not have the traction or durability needed for high performance footwear [52, 53, 110].

13.11.1 PVC compounding

13.11.1.1 Plasticisers, processing aids and oils

PVC requires the addition of plasticisers to make a flexible material that is suitable for footwear applications. The mixture of a PVC resin with a plasticiser is known as a plastisol. The most common plasticiser is dioctyl phthalate (DOP), a phthalate ester. Other phthalate esters (butyl, diisodecyl), epoxidised oils (soybean, linseed), and polymeric esters of glycols and sebacates are also used as plasticisers. Many of these materials are not totally compatible with PVC, and will eventually begin to leech out. Powdered nitrile rubber can also be added as a plasticiser to improve impact resistance and give a more rubber like feel to the final product.

13.11.1.2 Fillers

Calcium carbonate is the most commonly used filler for PVC; it is semi-reinforcing in the resin. Clays, silica and silicates are also used. Glass fibres, graphite and asbestos are reinforcing but are not commonly used in footwear.

13.11.1.3 Thermal stabilisers

PVCs also require the addition of thermal stabilisers to keep the polymer from discolouring or dehydrochlorinating at processing temperatures above 100 °C. Organic metal salts, phosphite esters, calcium stearate, organo-tin compounds and epoxidised soybean oil are examples of stabilisers.

13.11.1.4 Blowing agents

Blowing agents can also be used to produce a sponge rubber with a density less than one.

13.11.2 Production methods

13.11.2.1 Injection moulding

Since PVC is a true thermoplastic, no cross-linking agents are needed. There are several common methods to produce shoes with PVC outsoles. The first involves directly injecting the compounded PVC plastisol onto a lasted upper which has been heated to approximately 100 °C. The compound is injected and the cooled on the last for 60–70 seconds before removing. Uppers can include leather, textiles, and synthetic leathers.

13.11.2.2 Slush moulding

Slush moulding involves pouring a PVC plastisol into a mould and pouring out the excess to get a skin of the proper thickness. The mould is then heated up to 190 °C to cause the plastisol to gel and fuse. Moulds can be spun or vibrated to eliminate bubbles. The moulds are cooled and the finished shoe is removed. Wellington and gum boots are made by this process, an advantage of which is the ability to produce a boot with no seams.

The two pour method, where one compound is poured in and fused, followed by a second allows the production of shoes with different PVC compounds in the outsole and upper.

13.11.3 Typical formulas

Table 13.27 lists some typical PVC based formulae.

Table 13.27 PVC outsoles

	General	Blown
PVC resin	100	100
Powdered nitrile	15	-
DOP	75	75
Phosphite	0.75	-
Calcium carbonate	12	10
BaCd stabiliser	2	1.9
Zinc stearate	0.2	0.1
Stearic acid	0.5	0.1
ACD	-	1

13.12 Summary

The footwear industry has progressed over the last two decades from an industry driven mainly by cost to one where performance requirements are the most important factor in new compound development. As this trend continues, footwear will begin to drive new material developments, rather than just follow other industries.

Acknowledgements

The author would like to thank all of my colleagues who offered suggestions and assistance, especially Dr. Colleen McMahon of AES and Dr. Walter H. Waddell of Exxon Corporation. A special thanks to my parents, who made this possible.

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14 Rubber in Construction

A. H. Delgado and R. M. Paroli

14.1 Introduction

Natural and synthetic elastomeric materials have a variety of applications in the construction industry. No matter where one looks, one will see rubber-based materials in their dwellings and offices. Their use ranges from buildings through automotive accessories, roads, household articles, shoes, to computer accessories [1]. Many articles contain references to rubber in construction [1-27]. Bucksbee [25] gives an example of the broad applications of elastomeric materials in the construction industry. Essentially, no matter where you are whether it is in a building, or a residential street or on a highway an elastomer of some sort is at work. In building applications, rubber can help in the control or isolation of vibration and noise from motors generated from the building itself. In a rapid transit system, it supports the rails and vehicles thus reducing noise and vibration to adjacent buildings.

The use of rubber materials in buildings, both for construction and decoration, continues to increase due to their advantages, e.g., reduced weight, better performance and lower cost, in construction terms and in the provision of so-called 'maintenance free' structures. For example, without the use of rubber O-rings and compression gaskets a push-fit system would be impractical.

Building designers and users appreciate the inherent properties of synthetic rubbers. These properties are [11]:

- Soundproofing effects - Buildings are required to eliminate noises. Glass panes occupy a large area in the curtain wall construction and sounds and noises from motor vehicles and airplanes are easily transmitted into the rooms. The synthetic rubber gaskets eliminate the noises more effectively.
- Anti-quake performance - In the event of earthquakes, especially in Japan where earthquakes are frequent, falling objects, and broken glass are feared. Synthetic rubbers provide excellent anti-vibration property.

- Easy fabrication and installation.
- Sealing properties - Modern buildings are exposed to severe climatic conditions and the building structures are required to be well sealed against weather. Synthetic rubber provides excellent sealing properties.

The field is also further extended by the use of thermoplastic elastomers or thermoplastic polyolefins (TPE/TPO). This group includes polyurethanes, styrene-butadiene-styrene copolymers and a whole variety of plastics-rubber alloys. They are used in roofing, waterproofing, electrical coverings, sealants, etc.

Detailed discussion of the applications of rubber and rubber-based material in each area of construction is beyond the scope of this chapter. Only the applications of natural rubber and natural rubber-based composites in the construction of buildings will be considered.

14.2 Vibration control

There is a need in many buildings to prevent external vibrations from affecting sensitive equipment within the building. Hence, it is necessary to incorporate anti-vibration mounts during the construction of the buildings. Rubber vibration isolating systems have been known for many years but, it is only in the last 10 years that they have become available for designing high efficiency compounds. Laminated elastomeric bearings are usually used in the UK whereas steel coil springs are more often used in France and Germany.

Rubber springs are less massive than the equivalent steel springs. Also, the dynamic properties of rubber can provide a wider range of frequencies, especially for high frequencies.

Rubber mounts (see Figures 14.1 and 14.2) are also used for isolating individual items such as air conditioning and refrigeration equipment from the main structure of the building. Sounds within buildings resulting from general noise transmitted through walls and floors or from vibrating machinery, can be improved or eliminated by using rubber mounts. Airborne noise can also be a problem and must be taken into account when designing sound insulation systems.

Traditionally, thick and heavy walls were used to deal with general noise but as buildings become lighter, other methods of sound insulation can be obtained by light and complex construction. It is in this area where the rubber material finds its applications.

Prior to 1940, some of the ways of supporting large building were on vibration-absorbing springs. For example, in 1915 the New York Grand Central station was supported on lead/asbestos bearing that failed after a very short life. Another approach was the use of

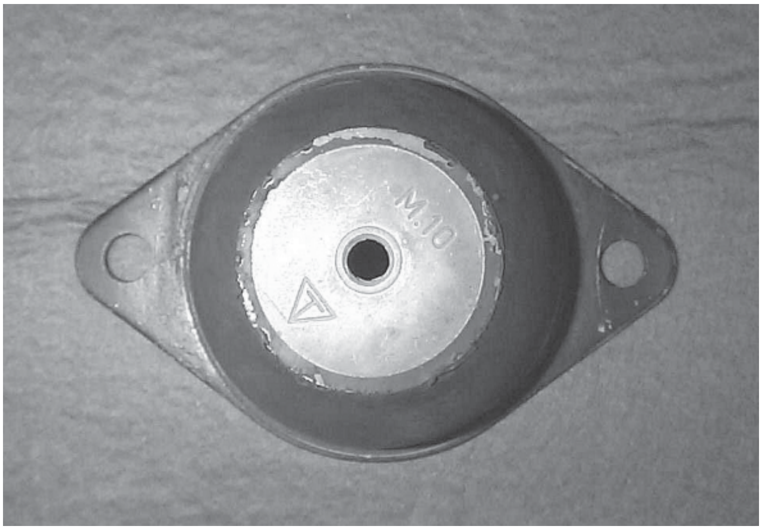

Figure 14.1 Rubber mount

Reproduced with permission from Gerry Pernica and Roch Glazer

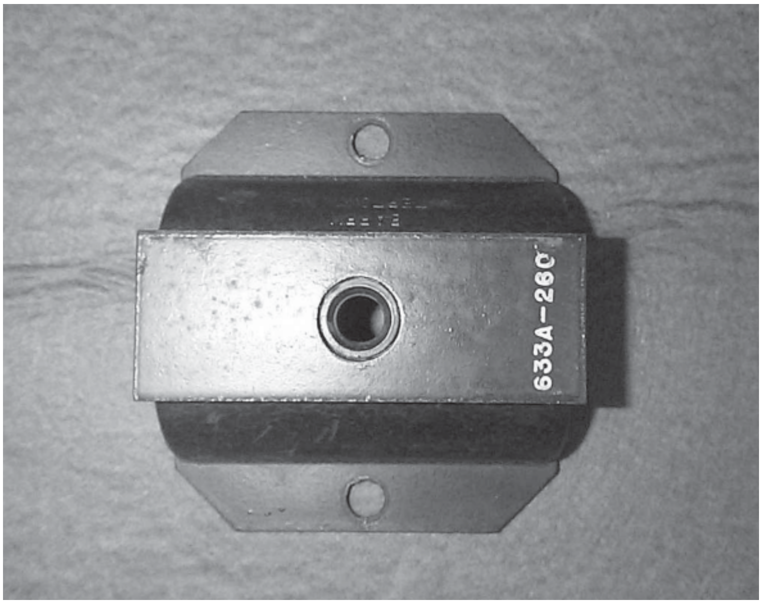

Figure 14.2 Rubber mount

Reproduced with permission from Gerry Pernica and Roch Glazer cork as a support medium, first used in the UK in 1938. This system worked well for light structures but it proved to be unsatisfactory for large buildings. The interest for rubber as a vibration absorbent started to grow towards the end of 1940 thanks to the work carried out by the Admiralty and the André Rubber Company [12], on shock absorbent mountings for ships where equipment required protection against shock.

In crowded countries such as the UK there are a large number of lots, which in the past were considered unsuitable for domestic accommodation. Now this land is seriously considered as sites for houses and apartment buildings. The unsuitability of the land had been due to ground-transmitted vibration from nearby roads or railways, especially the latter, which transmits heavy vibrations through the ground resulting in detriment to structures and occupants. Even in the worst case of vibrations, the applications of rubber springs to the foundation of buildings so that the building is supported on vibration-absorbing rubber pads has proven to be successful [12].

One of the most interesting developments using rubber springs is the Camden 16 housing project in London, UK [12]. This is a low-rise apartment building and housing complex on a site considered unsuitable for anything other than industrial building because it is surrounded by railway marshalling yards on each side and by two eight-track railway lines carrying all classes of traffic 24 hours a day. Moreover, the soil is soft clay, originating from the rail workings and transmits vibrations to a high degree. In addition to the soil problem, the vibration frequency to be damped is low and the springs must be designed with a service-life of approximately 100 years. Considering the cold climate, rubber was selected as the first and best choice of material for this type of application. Working together, André Rubber and J.H.A. Crockeet manufactured 482 springs, broken down into four load groups ranging from 160 to 645 tonnes. Each spring, in each group, had to meet a tolerance limit of not more than 6%. To this end, a 100 per cent test of the whole production had to be carried out and each one had to be certified to be a match on site. To shield against a wide range of frequencies generated by railway traffic, each spring had to damp-out frequencies of 400 Hz as well as the most disturbing 20 Hz. The long life expected for the springs has meant that deterioration of the rubber had to be considered. Considerable problems were encountered during the construction but they were overcome.

One of the most interesting features of the above complex is the ability to carry out a comparative test of the new, sprung building against a conventionally built terrace of victorian housing on the same site. Tests have shown that the rubber springing has produced a marked difference between the two types of buildings and proved that the system works [12].

In high seismic areas, base isolation in buildings and bridges is an accepted structural design technique [13]. Most of the completed buildings and those under construction use this approach. By using elastomeric bearings, predominantly natural rubber, the building or structure is decoupled from the horizontal components of the earthquake ground motion by interposing a layer with horizontal stiffness between the structure and the foundation. As a result, the fundamental frequency of the structure is lower than the fixed base frequency and lower than the predominant ground motion frequency.

Rubber isolation bearings for earthquake protection were first used in 1969 in the construction of an elementary school in Skapje, Yugoslavia. The building rests on large unreinforced blocks of natural rubber. Since the technology of reinforcing rubber blocks with steel plates was not well developed at that time, the weight of the three-story building resulted in the building bouncing and rocking backwards and forward during an earthquake.

In 1976, the Earthquake Engineering Research Centre (EERC) of the University of California at Berkeley began its research on the development of natural rubber bearings to protect buildings from earthquakes. The Malaysian Rubber Produce Research Association (MRPRA) in the UK sponsored the ten-year research project and the concept has led not only to a high degree of acceptance by structural engineers but to the construction of several buildings. The project started with hand-made bearings of extremely low-modulus rubber with a single three-story, single-bay, twenty-ton model. It was shown that using a rubber isolation bearing system reduced acceleration by as much as ten times when compared to conventional designs but the approach was not ideal. Further research led to modern approaches to quake isolation where the bearings were made by vulcanisation bonding of sheets of rubber to the reinforcing thin steel plates. To isolate the building from the horizontal components of the earthquake ground movement, the bearings are very stiff in the vertical direction and very flexible in the horizontal direction. Moreover, the bearing provides the building isolation from high-frequency vertical vibration produced by underground railways and local traffic.

A building constructed on rubber bearings will be simultaneously protected from both unwanted vibrations and earthquakes. The first earthquake data from the rubber base-isolated structure in the USA was provided by the February 1990 Upland and the June 1991 Sierra Madre earthquakes where the ground acceleration was recorded.

The first base-isolated building in the USA is the four-story building for the Foothill Communities Law and Justice Centre in the municipality of Rancho Cucamonga in San Bernardino County, California. The rubber isolators are made of highly filled natural rubber with ideal mechanical properties for a base isolation system. The new building for the Fire Department Command and Control Facility for Los Angeles County adopted the high-damping rubber system. A five-building complex for the Italian Telephone Company and SIP. recently completed in Italy has also used the system, which is the first of its type in Europe.

14.3 Floors

Rubber-based flooring has been used for a very long time. They are durable and are known to last 20–30 years [1]. Today, plastic-based flooring, e.g., PVC, is more predominant than rubber-based flooring. Rubber-based flooring however should not be overlooked because some new synthetic materials can lead to attractive, hardwearing flooring. However, there is little or no true natural rubber flooring. Most of them, if not all, are blends with general-purpose synthetic rubbers. One example is the Britcork ® a combination of cork and synthetic rubber. According to the manufacturer, Britcork is available in seven colours and gives the warmth of cork and the resilience of rubber. Another example is chlorosulphonated polyethylene (Hypalon), a synthetic rubber, which is resistant to flame, weather and to a variety of chemicals. Some of the properties of Hypalon floors are:

- super abrasion resistance,
- easy to clean,
- available in a wide range of stable colours,
- good resistance to ageing and weathering,
- dimensionally stable, resilient and flexible. According to the manufacturer (DuPont) Hypalon tiles have residual indentations 8 times lower than asphalt, 14 times lower than rubber and 16 times lower than linoleum,
- deadens sound,
- heat resistant and is not damaged by cigarette ends,
- resistant to chemicals: animal, vegetable, and mineral oils and greases.

Floating floors or suspended ceilings are required to meet lightweight construction regulations. In a floating floor, an air gap created by placing a resilient material such as rubber or foamed plastic between the timber raft and the concrete floor can achieve the desired result. The continuous demand of lightweight construction will provide an increasing outlet for rubber and foamed materials.

The source of rubber material used in construction is not only from natural rubber or synthetic rubber [18]. Recently, tyre companies in the USA disposed of thousands of tyres. Due to environmental laws, the tyres had to be recycled [18, 19]. One potential method of recycling is utilisation of powdered rubber obtained from grinding tyres and it is classified as crumb rubber. The crumb rubber is added to a non-polar matrix compound based on natural rubber and to an elastomer (NBR) of different polarity. Rubber powder can be applied to sports surfaces as a rubber mat when bonded with a polymer binder [20, 21]. It is commercially used in golf ranges, industrial floorings and pathways. Crumb rubber can also be used for roofing material because conventional bitumen roofing material tends to crack. Carpet underlay, produced by mixing crumb rubber with latex [22] is another attractive field. This opened a new market for the rubber industry. One example is the Guajarat Reclaim and Rubber Products Ltd. Company, which developed vulcanite (a product made from reclaimed rubber) for use in construction and other related industries. Vulcanite products are claimed to be water, acid and termite proof. The material can be glued with adhesives and has good screwing, good riveting properties, as well as good sound insulation properties and good electrical resistance. Applications of Vulcanite include flooring, mats, traffic signs, board and building partitioning material [22].

14.4 Walls and windows

Windows frames have to be water tight sealed to the concrete structure and brickwork. This can be achieved by bedding the frame in silicone rubber and by injecting a silicone rubber bead along all joints.

The use of thermoplastic elastomeric (TPE) materials is becoming more popular in the building industry when the rubber performance is required for curtain wall, storefront and skylight glazing seal applications [10]. For example, they are used in pre-set exterior glazing bar seals; interior foam lined vertical seals; multiple material combinations of tape-silicone and TPE forming vertical cavity fillers; store front seals and packing seals; seals in leaf, circular, bulb and finned section for opening doors and windows (see Figure 14.3). Manufacturers of TPEs claim that the weathering resistance, retention properties at high temperature and resistance to permanent loads are better than the thermoset rubber compounds such as EPDM and polychloroprene (Neoprene). Two phase elastomeric alloys, Santoprene thermoplastic rubber and Vyram thermoplastic rubber, marketed by Advanced Elastomer Systems (AES) for sealing applications, are claimed to have properties, which are superior to conventional thermoset rubbers such as EPDM and polychloroprene. An outdoor test performed on the TPE in harsh ageing sites (Arizona and South Florida) showed good retention of tensile strength over a 48-month exposure [10]. The EPDM and polychloroprene maintained their tensile strength but with a detrimental effect to the elasticity. Most elastomeric alloys are compatible with polycarbonate and acrylic materials used in skylights. The use of thermoset rubbers such as EPDM and polychloroprene are limited in glazing systems because they can cause loss of silicone seal and adhesion. The silicone rubber can be used in this application but at a

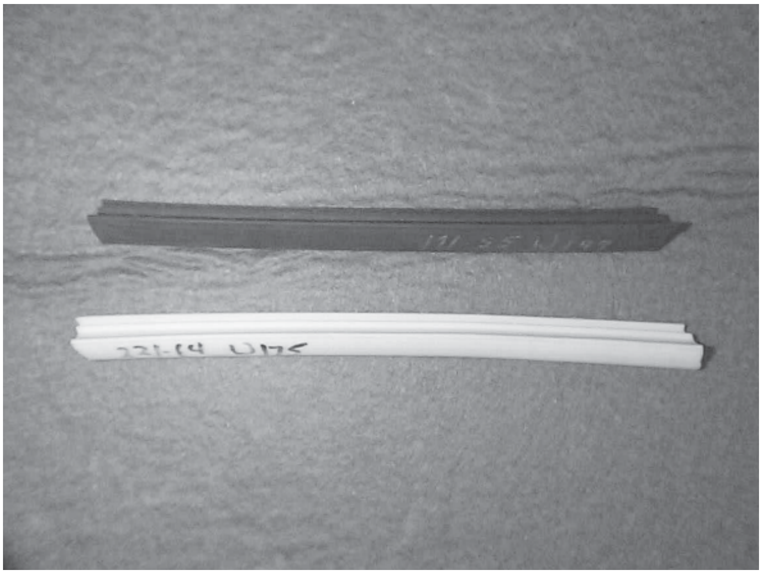

Figure 14.3 Seal gasket

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much higher cost. According to Cooke [10], independent tests have indicated that the adhesion loss and staining are minimal when elastomeric alloys are used for this application. Therefore, in curtain wall installation, these materials can be used for head and sill gasket in non-structural applications with minimal staining and loss of adhesion to silicone sealant.

Neoprene and Hypalon synthetic rubbers are extensively used in the Osaka Hilton International Hotel in Japan in rain gutters, window stool (a flat piece of moulding that covers the interior portion of a windowsill, to block out drafts), and curtain wall gaskets [11]. For example, Hypalon is used in rain gutters and leader heads, which are believed to be the first applications in the world. Also, it is used in glass window stool of the building, whereas the curtain wall gaskets, top-light gaskets and ring-like joint gaskets are made in Neoprene. The reason for switching from the traditional aluminum or stainless steel rain gutter to Hypalon is its weather resistance, durability, colour stability to keep matching the surrounding walls, cost advantages over the metal products and greater ease of fabrication as well as subsequent handling because of rubber-like elasticity.

14.5 Adhesives and sealants

New rubber-based adhesive products have created new uses for synthetic rubbers in the construction industry [24]. These products are known as construction adhesives and bring a variety of benefits to builders and occupants of dwellings and commercial buildings. Synthetic rubber-based construction adhesives help builders to reduce material costs, utilise highly paid skilled labour more efficiently and reduce construction time. The ones benefiting the most are owners and tenants because these adhesives help slow-down the rising cost of housing. Moreover, these construction adhesives provide a stronger and longer-lasting method of construction thus reducing maintenance costs. In addition, they eliminate squeaks and other sounds typical of structures nailed without adhesives.

Elastomeric materials have been used to manufacture elastomer-based construction adhesives such as 3M5230 Scotch Grip Wood adhesives [14]. This type of adhesive forms relatively thick bond lines with low shear moduli contrary to conventional synthetic resin structural adhesives.

The recent growing interest in energy saving is forcing many countries to manufacture fully insulated timber frame buildings [16]. Even well insulated floors and walls may still have weak points. This has strengthened the position of some rubber manufacturers such as Värnamo Rubber in Sweden. As one of Europe's leading manufacturers of cellular rubber, it can offer a wide range of sealing strips for DIY with the emphasis on draught excluder strips for windows and doors, and products for other environmental applications such as noise control, dust, damping, etc. The seals are of EPDM rubber, a popular material in the building industry. According to the manufacturer, the material is unaffected by water and water vapour, resistant to ozone, UV and ageing. It also remains resilient down to –40 °C. They also manufacture chloroprene (neoprene) strips, which are known to have excellent ageing characteristics, and are resistant to oils and solvents. Värnamo seals are made in solid and cellular rubber. Those made of solid rubber are ideal for gaps that vary greatly in size because they are soft and pliable with closed cells and an external 'skin' around.

The applications of the seals (manufactured from black EPDM cellular rubber with closed cells and skin covered) are:

- floor plate sealing,
- wall plate sealing,
- wall unit sealing,
- take up movement in joints and components,

- to keep wind out, keep heat in.

The sound absorbing EPDM cellular rubber strips have been developed as a sound insulation joint against a ceiling, wall or floor.

The threshold and draught seals are used mainly under interior doors in hospitals where it excludes corridor dust and noise and makes the moving of patients easy. Another application of the threshold and draught seals would be in schools and public buildings especially for wheelchair accessibility.

Another example of the rubber-based materials for applications in the building industry is the Devcon Silit 100 silicone rubber, an adhesive/sealant for industrial maintenance, production and building construction [17]. Its applications in building construction are:

- joints in curtain wall construction and flashing seams,
- glass block and skylights,
- glazing windows sash,
- caulking bathroom and shower fixtures and ceramic tile,
- expansion and contraction seals in precast concrete façade panels, joints in bridges and tunnels.

Another application of rubber-based adhesives in construction is in the mounting of prefinished, decorative panels to wall studding [24]. Once the adhesive is applied, the panels require less nailing. Since the panels will be permanently bonded, there is little chance of vibration, which is usually responsible for nails popping, panel sagging and unidentified sounds. Another application is to mount ceramic tiles in the kitchen and bath, as well as plastic bricks. They are also used to mount weather-stripping and install many types of floor covering, which may use hot-melt adhesives for self-adhesive tiles.

Rubber-based construction adhesives are also used beneath floor coverings. The adhesive is used to bond the plywood sub-floor panels to the supporting beams by applying the adhesive onto the wooden beams [24]. Fewer nails are required to secure the panel until the adhesive sets. This results in a floor system where the stress from the nails is shifted to the adhesive, thus, eliminating most, if not all, nail popping and squeak problems resulting from wood shrinkage. Builders have found that by using this type of floor system, the cost of material is reduced by 50% because only one layer of plywood is required.

14.6 Roofing and waterproofing

Polymer-based synthetic roofing emerged in Europe in the 1950s as an alternative to built-up roofing. European roof manufacturers went from fabricating tear-resistant polymer plastic to producing single-ply sheets. They also modified bitumen with polymers to achieve greater elasticity and weather resistance by manufacturing the bitumen in single sheets reinforced with glass fibre or polyesters. In the early 1960s, the North American rubber roofing industry began to market single-ply synthetic rubber roofing sheets as waterproofing. The development of this industry resulted in the market of liquid-applied polymer roofs, which were limited to the USA throughout the 1960s and early 1970s because of technical problems such as poor UV and tear-resistance.

The 1930s saw the first uses of an elastomer-like material in construction waterproofing. The sheeting was a compound from high molecular weight polyisobutylene, a butyl rubber-like polymer having a fully saturated structure with no mechanism for conventional vulcanisation [27]. The system was selected because of its resistance to effects of immersion, good tear resistance and compression/puncture resistance. By 1952, black-pigmented butyl canal membrane had been installed on a roofing deck in Logan, Utah, USA. Tests showed that after 15 years of exposure, the material had full retention of flexibility and more than 70% retention of original stress/strain properties. The tightly packed methyl side group in the backbone of the butyl and polyisobutylene polymer, gives the material low permeation characteristics but the diene location in the backbone of the butyl rubber molecule makes the butyls vulnerable to ozone attack. While much superior in that property to highly unsaturated rubbers, NR, BR, SBR, etc., this feature of butyl's molecular structure eventually caused the demise of butyl sheeting as a major contender for exposed canal/pond liners and elastomeric roofing.

Another commercially available synthetic rubber is polychloroprene, developed in the 1930s and first used as roofing in the early 1960s [23]. Due to the cured nature of the membrane, polychloroprene roof membranes have excellent resistance to weather, heat, oils, solvents, abrasion, acid, alkalis as well as a high degree of resistance to ozone, maintaining low temperature flexibility. Unfortunately it is susceptible to UV degradation, certain acids, solvents (they show poor resistance to aromatic, halogenated and aliphatic solvents, causing swelling and distortion of the membrane), and peroxides thus requiring a liquid CSM coating. When uncured, polychloroprene is used in flashing applications because it conforms to the sharp angles of the flashing.

Hypalon, a thermoplastics material, became one of the first synthetic roofing materials used in the USA in the early 1960s. It is resistant to UV, most chemicals, oils, grease, bitumen, salts, acids, fire (self-extinguishing), ponded water, abrasion, ozone and extreme temperatures. However, it is sensitive to leaded gasoline and jet fuel and it is difficult to solvent weld. Its main applications are in sheet form on lightweight, exposed roofs.

The first uses of EPDM and chlorosulphonated polyethylene (CSM), during the early 1960s, as roof sheeting in a stand-alone application was a milestone. Both elastomers brought a new level of weathering and ozone resistance to the application for a good and novel structural reason. The reason for the EPDM centres on the fact that its diene unsaturation, through which normal vulcanisation occurs, is outside of the polymer backbone. For CSM, the situation is parallel, with the pendant sulphonate groups providing crosslinked sites out of the polymer backbone, which is protected from attack from oxidants.

The international oil shortage in 1973, resulted in a shortage of asphalt, essential for built-up roofing (BUR), and a substantial increase in price. Hence, prices for BUR roofs increased and building owners became more concerned with fuel costs. This gave rise to an opportunity for non-asphalt-based roofing and waterproofing membranes to gain a share of the market. As the price of BUR increased, the EPDM costs decreased because of the competition. By the early 1980s, the cost for installing BUR and ballasted EPDM systems was almost the same.

The reasons for EPDM's acceptance were its good flexibility at low temperatures, large elongation, high vapour permeance, resistance to ozone, coal tar and most atmospheric pollutants. EPDM has become the largest selling synthetic roofing material in the USA since 1963. EPDM comes in black or white. Because of its reflective characteristics, white EPDM is used in places with high air conditioning costs (reflectivity prevents the solar radiant energy from entering the building and helps reduce the overall use of air conditioning). Membranes can be installed as ballasted, adhered, mechanically attached or used in Protected Membrane Roofing (PMR) systems. As any other material, it has limitations. It burns, swells when in contact with grease, animal fats, leaded gasoline solvent and oils. For this reason manufacturers call for insertion of polychloroprene under rooftop equipment or at air exhausts from restaurants [23]. Difficulties are also encountered with bonding two EPDM sheets during installation. If surface preparation is not properly done, good bonding between sheets is not achieved and seam problems may result. It is believed that the new tape-adhesives currently used will alleviate this problem.

Elastomeric roofing today has achieved its significant commercial success mostly because of efficiencies arising from the loose laying of large panels - adhered to substrates only at roofing terminations and at needed penetrations. A low-sloped roof residence in Northern Ireland in mid-1965 was a very early, if not the first, such installation using rounded river gravel over 0.76 mm thick homogenous butyl, cushioned underneath with 1 mm thickness of loose-laid bitumen saturated felt.

Elastomer manufacturers have made minor changes in the physical form of the elastomers to provide ease of mixing without adversely affecting physical and chemical resistance properties of the membranes. Current emphasis is directed towards ease of installation of the membrane, e.g., use of tape adhesives instead of liquid adhesives, and the performance on the roof. This work encompasses the roofing industry, raw material suppliers, membrane and adhesive manufacturers, architects and roofer.

Butadiene acrylonitrile (NBR) is another type of material used for roofing applications. Copolymers of butadiene and acrylonitrile are known by the names of Buna N, nitrile rubber, and NBR. Nitrile rubber, offers the following advantages: resilience and flexibility at low temperatures; excellent weatherability, (resistant to ozone and UV radiation); outstanding abrasion and tear resistance and impact strength; resistance to attack by most common chemicals. By blending NBR with the right thermoplastic resin and polymer additives, additional properties such as flame resistance, mildew resistance, heat-welded-ability and adhesion to fabrics and metal can be achieved.

Spray-applied polyurethane foams (PUF) roofing systems are widely used [23]. However, PUF are susceptible to UV radiation and weather degradation. Therefore, after curing, spray-applied PUF roofing systems must be protected from environmental factors by using a suitable UV resistant elastomeric coating. Among the rubber-based materials used successfully in this application are: silicone rubbers, butyls, chlorosulphonated polyethylenes (Hypalon), and Neoprenes. Since butyls and chloroprenes do not have weather-resistance, they must be treated with a weather-resistant coating such as Hypalon. The top coatings on the polyurethane foam may be selected to provide a breathable membrane or a moisture vapour retarder. In cold storage or freezer storage areas the top coating will act as a vapour retarder, preventing moisture from penetrating the PUF, and condensing or freezing on the cold surface.

Solvent system coatings of polychloroprene have the ability to bridge cracks (up to 1.5 mm wide), which occur after the coatings have cured. As mentioned earlier, neoprene coatings are susceptible to sunlight, hence, they are usually coated with CSM coatings.

The following materials are suitable for waterproofing barrier systems to the movement of water under pressure.

- *Rubberised asphalt* - are liquid membranes that cure by solvent evaporation. Their formulation is based on a high quality polymeric rubber, asphalt and solvent. They are used in mechanical room floors, laboratory and testing areas, hospital floors, shower room floors, wall areas and enclosed parking garages. Rubberised asphalt (modified bitumen) sheets are likely to be mainly asphalt with a small percentage of styrene-butadiene-styrene. The rubberised asphalt is usually encased between layers of polyethylene. Although rubberised asphalt is used as waterproofing, water may find its way into it and cause blistering and emulsification of the asphalt. Rubberised asphalt sheets are claimed to have a life expectancy of 10–15 years if used underground [23].

- *Chlorinated rubber* - Resin coatings made from chlorinated rubber may be used to coat the interior of swimming pools. They may also be used as waterproof barriers where the temperature reaches 60 °C. A pigmented coating must be used if exposed to sunlight.

- *Butyl rubber sheet* - a copolymer of isobutylene with a small amount of isoprene, is supplied as a non-breathing sheet membrane. The membrane is loosely laid with overlaps, which are sealed with solvent. Application to vertical surfaces is extremely difficult because the sheet stretches under its own weight, especially in warm weather.

- *Chlorosulphonated polyethylene (CSM) sheets* - most common tradename is Hypalon. They are sometimes used underground and have similar properties to neoprene liquid applied coatings.

- *Ethylene-propylene-diene monomer (EPDM) sheet* - is a material (see Figure 14.4) of extremely low permeability to water and is more resistant to UV than butyl rubber. Contrary to butyl, EPDM sheets have the advantage of allowing entrapped water vapour to escape. Like butyl sheets, it is sealed at the laps with solvent or tape-adhesives and stretches under its own weight. Therefore, it may not be suitable for vertical surfaces.

- *Polychloroprene (tradename – Neoprene) sheet* - can be bonded to concrete with neoprene adhesives. Liquid neoprene can be used to complete the barrier over areas where the sheet does not readily conform to the surface geometry.

Changes in the design of roofing towards lighter, better-insulated structures have produced a requirement for waterproofing layers able to resist greater strains over a longer period of time but still based on bitumen materials [26]. Therefore, blending of waterproofing and durability properties of bitumen with an appropriate synthetic polymer was developed to obtain blending with good tensile elastic characteristics. Polybutadiene and polyisoprene-based thermoplastic rubber have been found to be particularly suitable for modifying the properties of bituminous roofing products to produce materials capable of successful applications for a wide range of modern roofing systems. Polybutadiene segments provide rubber elasticity and the polystyrene blocks together to give a form of physical vulcanisation.

Lastly, roofing is beginning to see the development of thermoplastic polyolefin (TPO) based systems. TPO roofing membranes have been in service in Europe for approximately 10 years and their use in North America is increasing. As expected with any new material,

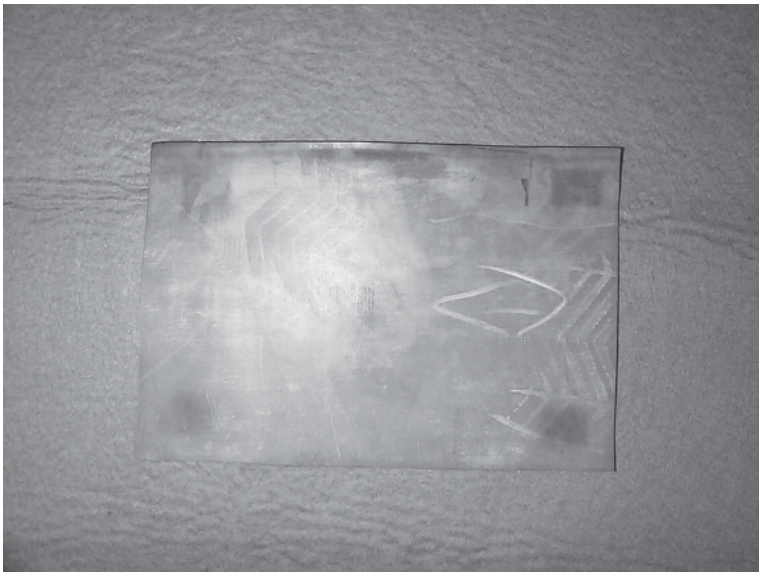

Figure 14.4 EPDM

Reproduced with permission from Gerry Pernica and Roch Glazer

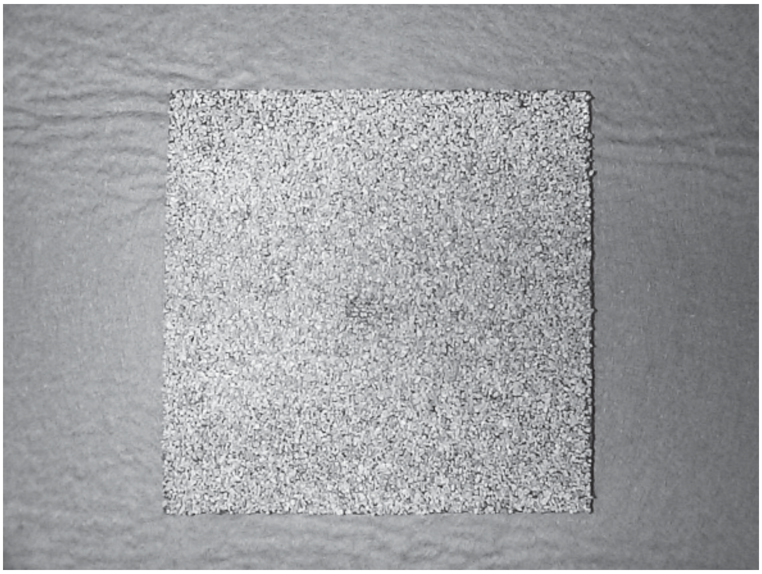

Figure 14.5 Modified bitumen

Reproduced with permission from Gerry Pernica and Roch Glazer there has been a learning period associated with the installation and maintenance of TPO and as yet, little information is available regarding their durability. The first appearance of a 'TPO-type' roofing product in the United States was around 1987, the second in 1991, the third in 1993, the fourth in 1996 and two more appeared in 1999. The confusion associated with TPO comes from both the chemical terminology and the marketing of the product. The marketing has focused mainly on the EPDM-like characteristics of TPO, i.e., being rubber with the benefits of welded seams (which EPDMs do not have). Another focus has been on the chemical resistance attributed to the olefin component of the polymers. Unfortunately, some confusion has occurred, especially regarding the use of the term thermoplastic. It is important to remember that TPOs are thermoplastic but only some thermoplastics are TPO.

In general, TPO membranes are being marketed as a product that combines the properties of EPDM and PVC without the associated drawbacks that these two materials have. In other words, they are supposed to be as UV- and heat-resistant as EPDM and as heat-weldable as PVC. The following benefits/characteristics have been reported for TPO: they are environmentally friendly and recyclable; welded seams as opposed to having to use adhesives; available in a wide variety of colours; resistant to heat, UV degradation; resistant to many chemicals, animal fats, vegetable oils; good cold-temperature flexibility; and, no external plasticisers added. TPO membranes do not have the same feel, e.g., flexibility, texture, etc., handling and application as the other thermoplastic membranes on the market. They are lighter in weight and thus easier to handle, but while flexible, they have a rather rigid feel. They have a tendency to hold their shape, and do not relax quickly.

14.7 Summary

As can be seen from this chapter the application of rubber in construction is very extensive. Although most of the applications described apply to the envelope or shell of the building, there are many more which are in the process of being developed or should be developed to serve our needs.

For example, with an ageing population, the risk and consequences of falling is greater. The properties of rubber make it an ideal material to minimise the injuries people will encounter when they fall. As a result, rubber-based products can be used in gymnasiums, houses, hospitals, etc. It is not uncommon for people to fall in bathrooms so there is good reason to have more rubber-based materials used in this area. This could help create a 'soft' environment, i.e., no matter where you fall, your chances of serious injury would be greatly reduced. This is not limited to washrooms and can be extended to kitchens or even around swimming pools. It would not need to be used only in new construction but could also be added during renovations or retrofitting.

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15 Rubber Recycling

A.I. Isayev

15.1 Introduction

The process of fabricating rubber products involves vulcanisation, an irreversible reaction between the elastomer, sulphur and other chemicals producing cross-links between the elastomer molecular chains and leading to the formation of a three-dimensional chemical network. The cross-linked elastomers are solid, insoluble and infusible thermoset materials. The presence of this network creates a tremendous problem in rubber recycling. In contrast to thermoplastics, which can be melted and reprocessed, it is not possible to restore thermoset rubber to its virgin state by any means including the use of heat, chemicals or mechanical action. Goodyear, who invented the sulphur vulcanisation process more than 150 years ago [1], was also the first who initiated efforts to recycle cured rubber wastes through a grinding process [2]. Nowadays, even after so many years of efforts in recycling, the development of a suitable technology to utilise waste rubbers is an important issue facing the rubber industry.

Among the various rubber wastes, accumulation of used tyres is an enormous environmental problem due to the large number of tyres scrapped each year. Particular concerns in the recycling of waste rubbers and used tyres are not only their valuable content of hydrocarbon resources, but also their potential environmental hazard [3]. According to a recent survey of the Scrap Tyre Management Council of the Rubber Manufacturers Association, approximately 270 million scrap tyres are generated annually in the United States alone [4]. The market for scrap tyres is currently consuming about 66% of that total amount while the rest is added to an existing stockpile of an estimated 800 million scrap tyres located around the USA. These stockpiled tyres create serious fire dangers and provide breeding grounds for rodents, snakes, mosquitoes, and other pests causing health hazards and environmental problems [5]. Moreover, the major use of scrap tyres in the US is to generate the so-called tyre-derived energy by burning used tyres. However, burning tyres may create a danger of air pollution [6]. About 64% of the consumed scrap tyres have been burnt in 1998, and only 13% of the total consumed amount have been turned into ground rubber tyre (GRT) which is the initial material for the tyre rubber recycling processes [4]. Also, the management of other waste rubbers has become a growing problem in rubber industry. It is estimated that over 150,000 tonnes or more of rubber are scrapped from the production of non-tyre goods in the form of runners, trim and pads [7].

Waste tyres and rubbers, being made of high quality rubbers, represent a large potential source of raw material for the rubber industry. The main reasons for the low scale current application of tyre and rubber recycling are: more stringent requirements for quality of rubber articles, and hence for that of reclaimed rubber, the substitution of raw rubber by other materials, for example by plastics in some cases; rising cost of reclaim production from tyres and rubber waste due to the more stringent regulations for environmental protection; a comparatively high labour input into reclaim production; and as a result of all this, the high cost of reclaimed rubber [8]. However, the increasing legislation restricting landfills is demanding the search for economical and environmentally sound methods of recycling discarded tyres and waste rubbers. Recent aggressive policies of the automotive industry are aimed to increase the usage of recycled plastic and rubber materials [9, 10, 11, 12]. This may serve as an example of the growing industrial demand for such technologies. Although recycling of metals, papers and glass is well utilised in practice, rubber recycling is still in its infancy. The latter further enhances the importance of the development of a suitable technology to recycle waste rubbers.

The main objective of this chapter is to provide an up-to-date account of rubber recycling including existing methods and emerging technologies of devulcanisation and also the possibility for recycled rubber utilisation into products. Rubber devulcanisation is a process in which the scrap rubber or vulcanised waste rubber is converted, using mechanical, thermal or chemical energy, into a state in which it can be mixed, processed and vulcanised again [13]. Strictly speaking, devulcanisation in sulphur-cured rubber can be defined as the process of cleaving, totally or partially, poly-, di- and mono-sulphidic cross-links formed during the initial vulcanisation [14]. However, in the present context, devulcanisation is assumed to lead to breakage of the chemical network taking place along with further shortening of the macromolecular chains [15].

A number of methods [14, 16-19] have been applied in an attempt to solve the problem and to find more effective ways of rubber recycling and waste utilisation. These methods include pyrolysis and incineration, reclaiming, grinding, pulverisation, microwave and ultrasonic processes. Processes for utilisation of recycled rubber are also being developed including the usage of reclaimed rubber to manufacture rubber products and thermoplastic/rubber blends and the usage of GRT to modify asphalt and cement.

15.2 Recycling of rubber vulcanisates

15.2.1. Pyrolysis and incineration

One particular method suitable for recycling used tyres is pyrolysis [20, 21]. Pyrolysis is the thermal decomposition of rubbers in the absence of air and oxygen to produce oils and gases for reuse by petrochemical industries. Carbon black and other solid content remaining after pyrolysis can be utilised as fillers. Pyrolysis is typically carried out in boilers, autoclaves, rotary kilns, screw conveyors and fluidised beds. Also, hydrogenation has been performed using a tubing bomb reactor [22]. Research activities in tyre rubber pyrolysis to recover hydrocarbon liquid and carbon black were quite extensive in the 1960-1970s and led to plant construction for pyrolysis of scrap tyres in the 1970s. Since then significant studies were carried out on tyre pyrolysis concerning evolution of volatiles [23], utilisation of oil and carbon black [24, 25]. However, these attempts proved to be economically unsuccessful due to the low price of crude oil. Also, pyrolysis plants produce toxic waste as a byproduct of operation [26].

Another established method of utilising worn rubber tyres is to burn them for their energy value. This is the incineration method. It is advocated by a number of the major tyre and rubber companies and also by the major utility companies. However, in doing so, valuable rubber materials are lost. In fact, 128 J of energy is consumed to make one kilogram (60,000 BTU per pound) of synthetic tyre rubber [27]. In contrast, the calorific value recovered by burning is 27–33 J/kg (13,000 to16,000 BTU per pound) of rubber which is not much higher than that of burning much cheaper coal. Moreover, burning of tyres for energy may lead to atmospheric pollution [28].

15.2.2 Grinding methods

There have been many proposals to recycle vulcanised rubber and utilise it in the vulcanised state. Use of waste rubber in the vulcanised state most often requires reduction of particle size and/or surface area. Another method for the utilisation of scrap rubber and wastes is a grinding method. This method was invented by Goodyear about 150 years ago [2]. Presently, there are three methods of grinding waste rubber: ambient grinding, cryogenic grinding and wet-ambient grinding [29-31]. Vulcanised scrap rubber is first reduced to a 50 mm x 50 mm or 25 mm x 25 mm chip. Then a magnetic separator and a fibre separator remove all the steel and polyester fragments. This can then be further reduced using ambient ground mill or ground into fine particles while frozen using cryogenic grinding [7].

A method for obtaining fine-mesh rubber is cooling scrap tyres in liquid nitrogen below their glass transition temperature and then pulverising the brittle material in a hammer mill. Cryogenically ground rubber has a much finer particle size varying from 30 to 100 mesh. But for inexpensive rubbers such as tyre rubbers, the process is not economical because of the amount of liquid nitrogen or other cryogenic liquids needed to freeze the rubber [32]. However, the process may be economical for expensive rubbers such as fluorocarbon rubbers. Also, the smaller is the desired particle size, the more expensive is the process. The cryogenic process produces fairly smooth fracture surfaces. Little or no heat is generated in the process. This results in less degradation of the rubber. In addition the most significant feature of the process is that almost all fibre or steel is liberated from the rubber resulting in a high yield of usable product and little loss of rubber [7].

Because of the high cost of cryogenic size reduction at liquid nitrogen temperature, mechanical size reduction by chopping and grinding is used often. The ambient process often uses a conventional high-powered rubber mill set at a close nip. The vulcanised rubber is sheared and ground into small particles. Using this relatively inexpensive method it is common to produce 10 to 30 mesh material and relatively large crumb. In addition, multiple grinds can be used to further reduce the particle size. The lower particle limit for the process is the production of 40 mesh material. The process, however, generates a significant amount of heat. Excess heat can degrade the rubber and if not cooled properly combustion can occur upon storage. In addition, ambient grinding produces an irregular shaped particle with many small hair-like appendages that attach to the virgin rubber matrix producing an intimate bonded mixture [33].

Other suggested recycling processes include mechanical and thermo-mechanical methods, which only comminute the vulcanisates in rubber and do not devulcanise them. A process using a wet grinding method to achieve a crumb fineness of approximately 200 mesh has been reported [34]. When this product, which had a much higher surface to mass ratio, was devulcanised, no chemicals and only minimal heating and mechanical processing were required. Wet or solution process grinding may yield the smallest particle size ranging from 400 to 500 mesh. The advantage of fine particle wet ground rubber is that it allows good processing, producing relatively smooth extrudates and calendered sheets [34].

15.2.3 Pulverisation methods

The pulverisation techniques for rubbers are also being developed based on the concept of polymer pulverisation originally proposed for plastics. The process manufactures polymer powder using a twin-screw extruder imposing compressive shear on the polymer at specific temperatures that depend on the polymer [35]. Based on this method solid-state shear extrusion pulverisation of rubber waste is also proposed [36-38]. The rubber particles obtained were fluffy and exhibited a unique elongated shape.

Recently, this process was further developed to carry out pulverisation of rubbers in a single screw extruder to obtain particles varying in size from 40 to 1700 μm [38]. A schematic diagram of the pulverisation technique based on a single screw extruder is shown in Figures 15.1a and 15.1b [38]. As indicated in Figure 15.1a, the extruder consists of three zones: feeding (Zone 1), compression (Zone 2) and pulverisation (Zone 3). The screw is square pitched with the compression zone having a uniform taper to create a

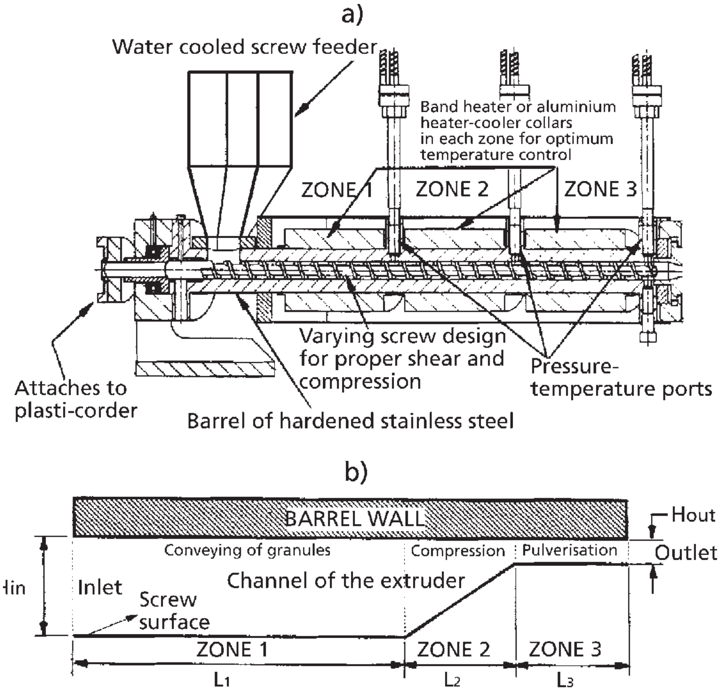

Figure 15.1. Schematic diagram of the single screw extruder for pulverisation of rubbers a) and geometry of the extruder channel with variable depth b) [38]

Reproduced with permission from E. Bilgili, H. Arastoopour and B. Bernstein, Rubber Chemistry and Technology, 2000, 73, 2, 340, Figure 1. Copyright 2000, Rubber Division, American Chemical Society

compression ratio of 5. The water-cooling channel is located in the barrel in order to remove the heat generated by pulverisation of rubber. Experimental studies showed that during the pulverisation of vulcanised scrap rubber in the extruder, a significant amount of heat was generated, due to friction, leading to partial degradation of the rubber [38]. The rubber granulates are fed into the hopper of the extruder and conveyed into the compression zone where they are subjected to a high compressive shear. Under the simultaneous action of this compressive shear and torsion due to the screw rotation, granulates are pulverised and emerge from the pulverisation zone as rubber powder of a smaller particle size. Surface oxidation of the rubber particles and initiation of agglomeration of a fraction of the produced particles may also take place. The particles produced exhibit irregular shapes with rough surfaces and have a porous structure. The cross-link density and gel fraction of the particles are reduced in comparison with those of the initial rubber granulates. This indicates the occurrence of partial devulcanisation.

Due to this effect, the particles obtained in this process can be moulded into products after an exposure to high heat and high pressure for a period of at least one hour [39].

15.2.4 Reclaiming processes

Reclaiming is a procedure in which the scrap rubber or vulcanised waste is converted, using mechanical and thermal energy and chemicals, into a state in which it can be mixed, processed and vulcanised again. The principle of the process is devulcanisation [13]. In devulcanisation, it is assumed that the cleavage of intermolecular bonds of the chemical network, such as carbon-sulphur and/or sulphur-sulphur bonds takes place, with further shortening of the chains [15]. Devulcanisation in sulphur-cured rubber can be defined as the process of cleaving, totally or partially, poly-, di- and mono-sulphidic cross-links which are formed during the initial vulcanisation [14].

Many different reclaiming processes [8, 14, 16-19, 40-42] have been applied through the years in an attempt to solve the problem of rubber recycling. Generally ground rubber scrap is, in most cases, the feedstock for the devulcanisation step. Recently, Warner [14] presented an excellent review of the existing literature that is relevant to various methods of devulcanisation.

Reclaiming is the most important process in rubber recycling. Many different reclaiming processes [7, 8, 14, 32, 43-49] have been used throughout the years depending on scrap characteristics and economics. Generally, ground rubber scrap is, in most cases, the feedstock for the reclaiming. The pan process, digester process (either wet or dry), and mechanical or reclaimator process are currently the most common processes used for reclaiming. The pan process [8, 14, 43, 44, 46-49] was widely used in the early stages of the reclaim industry before the advent of the wet digester. Its use is now limited to speciality type rubbers such as light coloured natural rubber (NR) reclaim [47]. In this process, the ground rubber is mixed with various reclaiming oils before being added to bins or boats. These bins are inserted into an autoclave which is then subjected to steam pressure (1.0–2.0 MPa) and temperature (175–205 °C) for cycle times of 5 to 12 hours.

The digester process [8, 14, 43, 44, 46–49] uses a steam vessel equipped with a paddle agitator for continuous stirring of the crumb rubber while steam is being applied. The wet process may use caustic and water mixed with the rubber crumb while the dry process uses steam only. If necessary, various reclaiming oils may be added to the mixer in the vessel. The dry digester has the advantage of less pollution being generated and was adopted after the Clean Air and Water Act was enacted.

A mechanical or reclaimator process [32, 33, 49, 50] has been used for the continuous reclaiming of whole tyre scrap. Fine rubber crumb (typically 30 mesh) mixed with various reclaiming oils is subjected to high temperature with intense mechanical working in a modified extruder for reclaiming the rubber scrap.

Depending on the specification of the finished products, fillers may be added to the devulcanised product before further processing. The devulcanised rubber from each process is then strained and refined as dictated by the specification of the finished product before being powdered, baled, sheeted or extruded into the finished form.

Chemical processing is a possible method for devulcanising the vulcanised network through the use of chemical agents that attack the C—S or S—S bonds. However, this process of devulcanisation is very slow and creates further problems with the removal of the solvents and additional waste is generated in the form of sludges. Also, some processes require elaborate chemical process techniques, therefore handling and safety become a concern.

Saville and Watson [51] wrote a masterful and extensive review of the structural characterisation of sulphur-vulcanised rubber network and chemical probes. Their approach opened the way to distinguish among polysulphide, disulphide and monosulphide bonds in carbon-black filled NR vulcanisates. This can be achieved by measuring the chemical cross-link density before and after treatment with chemical reagents which specifically break particular types of cross-links. They also discussed the ability of methyl iodide to cleave cross-links. Selker and Kemp [52] and Selker [53] reported a study indicating the specificity of methyl iodide to break monosulphide bonds in rubber vulcanisates. Moore [54] treated tetramethylthiuram disulphide/zinc oxide vulcanisates with methyl iodide and found that most of the cross-links were broken. Manik and Banerjee [55] used the method of Moore to confirm the results of a study of the mechanism of acceleration with CBS. Selker and Kemp [56] even applied methyl iodide to reduce the amount of combined sulphur in ebonite. But, methyl iodide was reported to be a carcinogen.

Nicholas [17] has reported phase transfer catalysis as a means of transporting hydroxide ions from water into swollen rubber particles to cleave polysulphidic cross-links with little or no main chain scission. The devulcanisation of rubber by this process was incomplete. Although many chemical cross-links have been broken, reaction residues remaining in the devulcanised particles caused scorch problems and were difficult to remove.

Kawabata and co-workers [57, 58] investigated the degradation of a vulcanised synthetic isoprene rubber. This was done by soaking the rubber in a mixture of phenylhydrazine, iron chloride, benzene and methanol at 30 °C with stirring to reclaim the rubber by chemical degradation. They showed that the network chain underwent a severance reaction by the phenylhydrazine-iron chloride system in the following order of ease: polysulphide linkage > monosulphide linkage > carbon—carbon cross-link. They only studied the mechanism of degradation of vulcanised rubber by the phenylhydrazine-iron chloride system.

Adam and co-workers [59] reported the work done to modify rubber granulate chemically for the purpose of increasing the quantity of useful rubber waste in the rubber industry. They grafted ethyl acrylate onto ground polybutadiene vulcanisate waste rubber using a redox method and also via gamma rays. The properties of the waste rubber were found to have worsened as a result of the treatment. The quantity of grafted monomer was larger when gamma irradiation was used.

Siuru [19] reported that researchers at the Pacific Northwest National Laboratory developed bioreactor technology. They tried to make used synthetic rubber reusable by increasing the surface reactivity of ground tyre rubber using sulphur-loving microorganisms. Microorganisms metabolising rubber hydrocarbon have been reported and referenced, but these microorganisms are known to be eliminated by the toxic substances usually present in a compounded rubber [60]. An overview of the existing biotechnological possibilities, namely, microbial desulphurisation, of waste rubber recycling is given by Holst and co-workers [61].

De and coworkers [41, 62] reported that sulphur cured styrene-butadiene copolymer (SBR) and natural rubbers can be reclaimed by a vegetable product (renewable resource material) and diallyl disulphide under various reclaiming conditions. The results have revealed a definite influence of the reclaiming agent and the milling conditions on the molecular weight of the sol, sol content, and viscosity of the reclaim rubber.

It is known that sulphur vulcanised NR can be completely recycled at 200–225 °C by using diphenyldisulphide [63]. Recently, the efficacy of various disulphides as recycling agents for NR and ethylene-propylene-diene monomer (EPDM) vulcanisates were reported [64]. While complete devulcanisation was observed on sulphur cured NR at 200 °C, a decrease in cross-link density of 90% was found when EPDM sulphur vulcanisates with diphenyldisulphide was heated to 275 °C in a closed mould for 2 hours. At the same time, EPDM cured by peroxide showed a decrease in cross-link density of about 40% under the same conditions.

Another chemical method was recently proposed by Hunt and Kovalak [65]. It is based on the use of 2-butanol as a devulcanising agent for sulphur cured rubber under high temperature and pressure. The use of devulcanisation retains the molecular weight of the rubber and does not significantly alter its microstructure. However, the process is extremely slow and requires separation of the devulcanised rubber from the 2-butanol.

15.2.5 Wave methods

15.2.5.1 Microwave method

Microwave technology has also been proposed as a technique to devulcanise waste rubber [16, 66]. This process applies the heat very quickly and uniformly on the waste rubber. The method uses the application of a controlled amount of microwave energy to devulcanise a sulphur vulcanised elastomer, containing polar groups or components, to a state in which it could be compounded and revulcanised to useful products requiring significant physical properties, such as hoses. On the basis of the relative bond energies of carbon—carbon, carbon—sulphur, and sulphur—sulphur bonds, it was presumed that the scission of the sulphur—sulphur and sulphur—carbon cross-links actually occurred. However, the material to be used in the microwave process must be polar enough to accept energy at a rate sufficient to generate the heat necessary for devulcanisation. This method is a batch process and requires expensive equipment.

15.2.5.2 Ultrasonic method

Numerous recent publications are devoted to the study of the effect of ultrasound on polymer solutions at low concentrations [67-69] and on polymer melts during extrusion [70-75]. Significant efforts have also been made to understand the mechanism of the effect of ultrasound on fluids [76, 77].

The application of ultrasonic waves to the process of devulcanising rubber is a very recent field of study. Most references indicate that rubber is vulcanised by ultrasound rather than devulcanised. Rubber devulcanisation by using ultrasonic energy was been first discussed by Okuda and Hatano [78]. It was a batch process in which a vulcanised rubber was devulcanised at 50 kHz ultrasonic waves after treatment for twenty minutes. The process claimed to break down carbon—sulphur bonds and sulphur—sulphur bonds, but not carbon—carbon bonds. The properties of the revulcanised rubber were found to be very similar to those of the original vulcanisates.

Recently, a novel, patented, continuous process has been developed for devulcanisation of waste rubbers and is considered as a suitable way to recycle waste rubbers [79-97]. This technology is based on the use of the high power ultrasound. The ultrasonic waves at certain levels, in the presence of pressure and heat, can break up the three-dimensional network in cross-linked rubber. The process of ultrasonic devulcanisation is very fast, simple, efficient and solvent and chemical free. Devulcanisation occurs in seconds and may lead to the preferential breakage of sulphidic cross-links in vulcanised rubbers. The process is also suitable for the decross-linking of the peroxide cured rubbers and plastics. A schematic diagram of the devulcanisation reactor suitable to carry out this process is shown in Figure 15.2. This devulcanisation reactor was developed in cooperation with National Feedscrews and Machining, Inc. The reactor consists of a 38.1 mm single-screw rubber extruder and an ultrasonic die attachment. A cone-shaped die and the ultrasonic horn have sealed inner cavities for running water for cooling. The shredded rubber is fed into the extruder by a feeder with adjustable output. Thus, the rubber flow rate in the process is controlled by the feed rate. An ultrasonic power supply, an acoustic converter, booster and a cone-tipped horn are used. The horn vibrates longitudinally with a frequency of 20 kHz and various amplitudes. The ultrasonic unit is mounted onto the extruder flange. The convex tip of the horn matches the concave surface of the die, so that the clearance between the horn and the die is uniform. The clearance is controlled, and the die plate and the horn are cooled with tap water.

Isayev and co-workers [79-98] have carried out extensive studies on the application of ultrasound to polymer processing. It was shown that this continuous process allows one to recycle various types of rubbers and thermosets. As a most desirable consequence, ultrasonically devulcanised rubber became soft, therefore, enabling this material to be reprocessed, shaped and revulcanised in very much the same way as the virgin rubber.

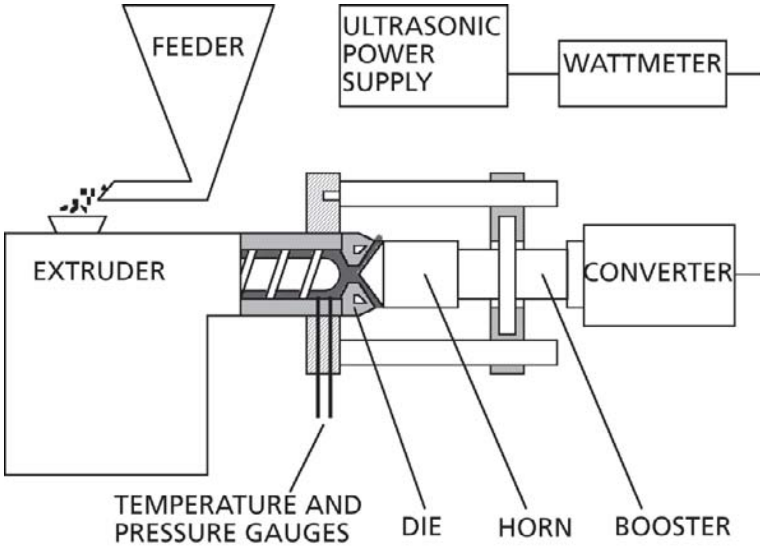

Figure 15.2 Schematic diagram of the continuous devulcanisation reactor with ultrasonic die attachment

This new technology has been used successfully in the laboratory to devulcanise a ground tyre rubber [82, 83, 93], unfilled NR [94], guayule rubber [99], unfilled and filled SBR [82, 85-92, 96], unfilled silicone rubber [79, 98], fluoroelastomer, ethylene vinyl acetate foam and cross-linked polyethylene [80, 81]. After revulcanisation, rubber samples exhibit good mechanical properties, which in some cases, are comparable to or exceed those of virgin vulcanisates [87, 94, 98].

It is believed that the process of ultrasonic devulcanisation is based on a phenomenon called cavitation. In this case, acoustic cavitation occurs in a solid body. This is in contrast to cavitation typically known to occur in liquids in the regions subjected to rapidly alternating pressures of high amplitude generated by high power ultrasonics [100]. During the negative half of the pressure cycle the liquid is subjected to a tensile stress and during the positive half cycle it experiences a compression. Any bubble present in the liquid will thus expand and contract alternately. The bubble can also collapse suddenly during the compression. This sudden collapse is known as cavitation and can result in almost instantaneous release of a comparatively large amount of energy. The magnitude of the energy released in this way depends on the value of the acoustic pressure amplitude and, hence, the acoustic intensity.

Although the presence of bubbles facilitates the onset of cavitation, it can also occur in gas-free liquids when the acoustic pressure amplitude exceeds the hydrostatic pressure in the liquid. For a part of the negative half of the pressure cycle the liquid is in a state of tension. Where this occurs, the forces of cohesion between neighbouring molecules are opposed and voids are formed at weak points in the structure of the liquid. These voids grow in size and then collapse in the same way as gas-filled bubbles. Cavitation may be induced in a gas free liquid by introducing defects, such as impurities, in its lattice structure.

In the case of polymer solutions, it is well known that the irradiation of a solution by ultrasound waves produces cavitation of bubbles [67, 101]. The formation and collapse of the bubble plays an important role in the degradation of polymers in solution. Most of the physical and chemical effects caused by ultrasound are usually attributed to cavitation, the growth and very rapid, explosive collapse of microbubbles as the ultrasound wave propagates through the solution. The intense shock wave radiated from a cavitating bubble at the final stage of the collapse, is undoubtedly the cause of the most severe reactions. This shock wave is capable of causing the scission of macromolecules that lie in its path. The degradation arises as a result of the effect of the ultrasound on the solvent.

In any medium, cavities, voids and density fluctuations exist. It is believed that these induce cavitation, leading to molecular rupture. In solid polymers, the microvoids present intrinsically, are responsible for cavitation when they are subjected to a hydrostatic pressure in the manner of an impulse. One of the main causes of microvoid generation in polymer materials is the interatomic bond rupture when they are subjected to mechanical and thermal stresses.

Zhurkov and co-workers [102] have carried out extensive studies related to microvoid formation in stressed polymers.

When applied to rubbers, the cavitation usually corresponds to the effect of formation and unrestricted growth of voids in gas-saturated rubber samples after a sudden depressurisation [103, 104]. In general, this has a broader sense and may be understood as the phenomenon related to the formation and dynamics of cavities in continuous media [97]. In materials science, for example, it means a fracture mode characterised by formation of internal cavities [105]. In the acoustic field, cavitation denotes the phenomenon relating to the dynamics of bubbles in sonically irradiated liquids [106].

Structural studies of ultrasonically treated rubber show that the breakup of chemical cross-links is accompanied by the partial degradation of the rubber chains [82, 89, 92, 93, 96]. The mechanism of rubber devulcanisation under ultrasonic treatment is presently unclear, unlike the mechanism of the degradation of long-chain polymer in solutions irradiated with ultrasound [101]. Specially, the mechanisms governing the conversion of mechanical ultrasonic energy to chemical energy are not understood. However, it has been shown that devulcanisation of rubber under ultrasonic treatment requires local energy concentration, since uniformly distributed ultrasonic energy among all chemical bonds is not capable of rubber devulcanisation [84, 85, 107].

It is well known that some amounts of cavities or small bubbles are present in rubber during any type of rubber processing [108]. The formation of bubbles can be nucleated by precursor cavities of appropriate size [103]. The proposed model [83-85] is based upon a mechanism of rubber network breakdown caused by cavitation, which is created by high intensity ultrasonic waves in the presence of pressure and heat. Driven by ultrasound, the cavities pulsate with amplitude depending mostly upon the ratio between ambient and ultrasonic pressures (acoustic cavitation).

It is known that, in contrast to plastics, rubber chains break down only when they are fully stretched [109, 110]. An ultrasonic field creates high frequency extension-contraction stresses in cross-linked media. Therefore, the effects of rubber viscoelasticity have been incorporated into the description of dynamics of cavitation [97, 111]. The devulcanisation of the rubber network can occur primarily around pulsating cavities due to the highest level of strain produced by the powerful ultrasound [111].

Generally, cleavage in polymer chains results in the production of macroradicals [112, 117], the existence of which have been confirmed spectroscopically by the use of radical scavengers such as diphenyl picrylhydrazyl (DPPH). Obviously, in the absence of scavengers, the macroradicals are free to combine by either disproportionation or combination termination, the former leading to smaller-sized macromolecules whilst the latter will give a distribution dependent upon the size of the combining fragments [114].

By utilising differential scanning calorimetry (DSC) it was reported [90] that the ultrasonically devulcanised sulphur cured SBR indicated an increase in the glass transition temperature of the devulcanised rubber even at cross-link density much lower than that of the original vulcanisates. Solid-state nuclear magnetic resonance (NMR) studies confirmed that these changes in glass transition temperature were due to a decrease of molecular mobility as measured by a decrease in spin-spin relaxation time [90]. Ultrasonic devulcanisation was also accompanied by a significant increase in *cis-trans* isomerisation. It was suggested that the changes observed under ultrasound treatment were due to the transformation of interchain sulphur bonds to cyclic sulphur structure [88], thus modifying the backbone chain. It was also reported [87] that under some processing conditions the tensile strength of unfilled revulcanised SBR was found to be much higher than that of the original vulcanisate with elongation at break being practically unchanged. In particular, Figure 15.3 shows the stress-strain curves of unfilled virgin vulcanisates and revulcanised SBR obtained from devulcanised rubbers at various values of amplitudes A. The devulcanised rubbers were obtained by using the ultrasonic reactor depicted in Figure 15.2

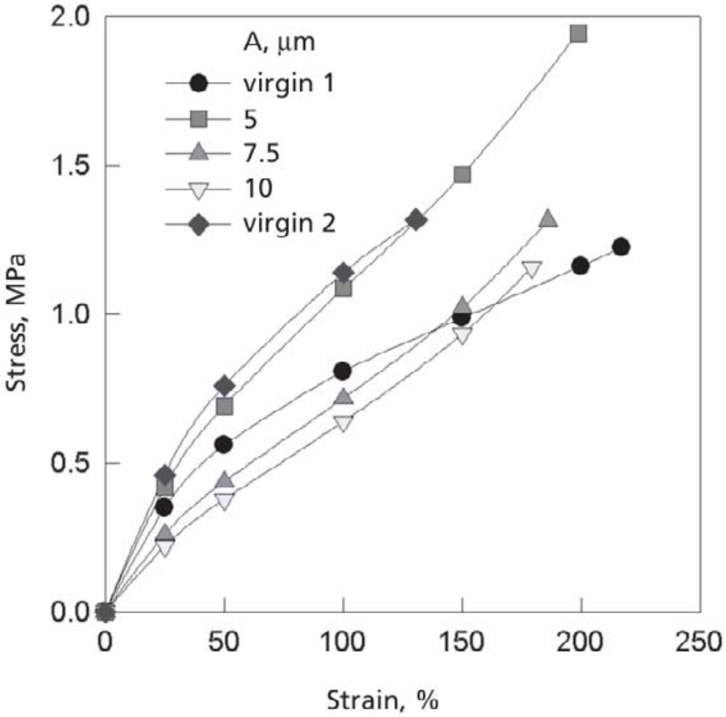

Figure 15.3 Stress-strain curves of unfilled SBR virgin rubbers and revulcanised rubbers obtained at various amplitudes and a gap of 1.52 mm. Virgin 1: 2 phr of sulphur and and 1.3 phr of Santocure, virgin 2: 4 phr of sulphur and 2.6 phr of Santocure

at the barrel temperature of 120 °C, the screw speed of 20 rpm, flow rate of 0.63 g/s. The ultrasonic horn diameter was 76.2 mm. In contrast to the usual findings that the mechanical properties of reclaimed rubber obtained by using different techniques are inferior to those of virgin vulcanisates, the present data are rather unexpected. It was proposed that the improvement in the mechanical properties of revulcanised SBR was primarily due to the extent of non-affine deformation of the bimodal network which appears in the process of revulcanisation of ultrasonically devulcanised rubber. It was found [91] that the revulcanisation process of devulcanised SBR was essentially different from that of the virgin SBR. The induction period is shorter or absent for revulcanisation of the devulcanised SBR. It was suggested that a decrease or disappearance of the induction period is due to an interaction between rubber molecules chemically modified in the course of devulcanisation and unmodified rubber molecules resulting in cross-linking. It was shown that approximately 85% of the accelerator remained in the ultrasonically devulcanised rubber.

It is also interesting to note that unfilled revulcanised NR obtained by means of the ultrasonic reactor, depicted in Figure 15.2, retains the ability to undergo the strain-induced crystallisation during stretching as evidenced by the stress-strain behaviour shown in Figure 15.4. This figure shows behaviour of NR vulcanisates which were ultrasonically devulcanised at different barrel temperatures and amplitudes along with the virgin vulcanisates. Strain-induced crystallisation was observed in all the revulcanised samples. The stress-strain characteristics of the vulcanisates prepared from devulcanised GRT indicate that tensile strength and elongation at break can be as high as 10 MPa and 250%, respectively, from 10–16 mesh scrap tyre rubber. Ultrasonically devulcanised rubbers consist of sol and gel. The gel typically exhibits a low cross-link density. It is interesting to note that the tensile strength of the vulcanisate obtained from GRT correlates with the cross-link density of the gel of the devulcanised GRT, as shown by Figure 15.5. This figure shows the tensile strength data obtained in all the samples devulcanised in a wide range of processing conditions.

15.3 The usage of recycled rubber

15.3.1 General remarks

There are technical restraints in the devulcanisation of rubbers, and vulcanisation is, in fact, not truly reversible [12]. The partial devulcanisation of scrap rubber will result in a degradation of physical properties. In many cases, this may limit substitution levels in high-tech applications such as tyres. But it can provide the compounder of less stringent products with an excellent low cost polymer that can be used as the prime polymer or at very high substitution levels.

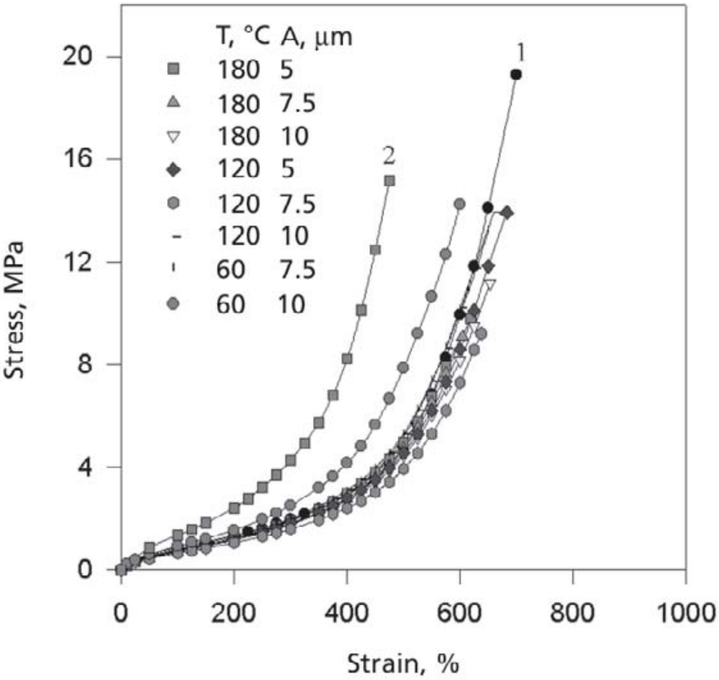

Figure 15.4 The stress-strain curves for unfilled NR recipe 1 ultrasonically devulcanised at different barrel temperatures and amplitures, die gap 2.54 mm, flow rate 0.63 g/s and revulcanised with recipe 2 and for NR recipe 1 (curve 1) and NR recipe 3 (curve 2). Recipe 1: 2 phr of sulphur, 1 phr of CBS, 5 phr of ZnO, 1 phr of stearic acid; recipe 2: 2 phr of sulphur, 2.5 phr of CBS, 0.5 phr of stearic acid; recipe 3: 4 phr of sulphur, 1 phr of CBS, 78.5 of Zn), 1.5 phr of stearic acid

Recycled rubber has widespread uses, but there are a considerable number of formulations to which it cannot be added. In tyres, reclaim cannot be used for tread compounds because every addition may decrease their resistance to wear [13]. Considerable amounts of reclaim are consumed for carcasses of bias ply tyres for cars if the compounds are of NR; for carcasses of radial tyres no reclaim is added. On the other hand, reclaim is added to compounds for bead wires and it may also added to sidewalls. Within the framework of direct recycling options a number of applications for ground rubber tyre outside the rubber industry have been proposed. Such applications include the use as fillers in asphalt for the surface treatment of roads and as a rubberised surface for sport facilities. The ground scrap rubber can be used as fillers in raw material [3, 115-119] and plastic compound [3, 120]. However, the problem of compatibility with its matrix and size of the filler, as well as the discontinuity at the interface between the two phases

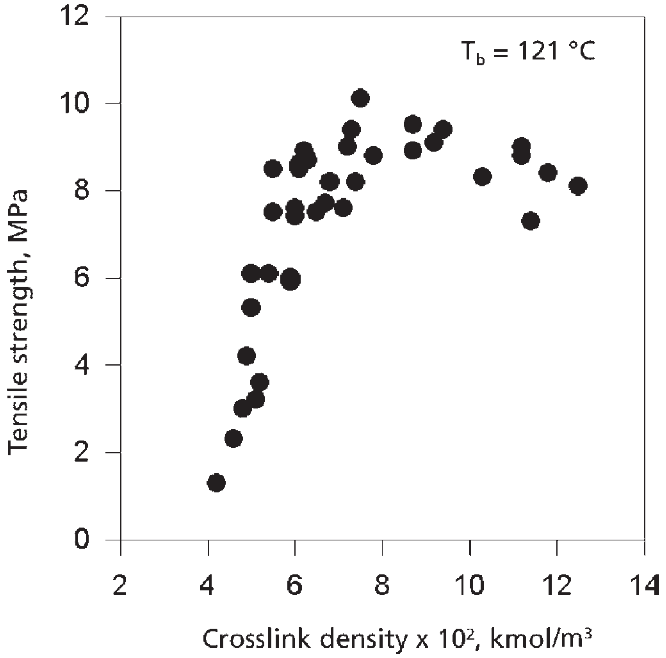

Figure 15.5 Correlation between tensile strength of revulcanised GRT and crosslink density of gel of devulcanised GRT obtained under different processing conditions

should be considered. Rubber products containing ground rubber have low tensile properties due to insufficient bonding between the ground rubber and the virgin matrix.

Compounds for the production of shoe heels and soles, tubes, conveyor belts, technical rubber mouldings, automobile floor mats, lower layers of floor coverings, various moulded and extruded profiles, sealing plates, battery boxes and other hard rubber goods, where certain vulcanisation problems can be solved in this manner, are the other major consumers of reclaim. Since almost all reclaim is black, it cannot therefore be used for light and coloured compounds unless produced from selected coloured waste. For every such use the reclaim must be tested from this point of view.

15.3.2 Rubber/recycled rubber blends

The recycled rubber can be blended with virgin material [115, 118, 119] and plastic compound [3, 120]. However, the compatibility with its matrix should be considered. Rubber products containing ground rubber typically have lower tensile properties due to insufficient bonding between the ground rubber and the virgin matrix. Gibala and co-workers [116, 117, 121] have carried out extensive studies on blending of carbon black filled ambiently and cryogenically ground SBR vulcanisates with the original, uncured compounds. They investigated Mooney viscosity and cure behaviour of the compounds and tensile and tear strength of the prepared vulcanisates. A composition containing ambiently ground rubber showed a higher viscosity than one with cryogenically ground rubber. This was attributed to occlusion of the matrix rubber phase within the sponge-like, ambiently ground rubber. This occlusion did not occur with the smooth, cryogenically ground particles. SBR compounds containing ground vulcanisates showed a lower scorch time and a lower maximum rheometer torque believed to be due to a migration of accelerator fragments from the ground vulcanisates to the matrix rubber and a migration of sulphur from the matrix rubber to the ground vulcanisate, respectively. Vulcanisates containing ambiently ground rubber exhibited reduced tensile strength and enhanced tear strength relative to the original vulcanisate. Nah and Kaang [122] measured mechanical properties of various SBR rubber vulcanisates containing rubber particles various concentration and sizes. A typical reclaimed rubber powder is also incorporated into virgin rubber. They indicated a power-law relationship between the tensile strength reduction and the particle size. Their findings concerning the scorch time, cure time and minimum torque are similar to those in reference [121]. The die swell of the compounds containing the rubber particles is reduced.

Hong and Isayev [123] studied blends of the ultrasonically devulcanised carbon black filled NR mixed with virgin carbon black filled NR compound. Curing behaviour and tensile properties were measured in comparison with those of blends of ambiently ground NR vulcanisates and virgin NR. Curing characteristics of the blends indicated that an increase in the devulcanised NR content decreased the scorch time and the cure time. The minimum torque of blends containing devulcanised NR was lower than those containing ground NR particles. As indicated in Figures 15.6 and 15.7, the tensile strength and elongation at break of the blends with ultrasonically devulcanised NR were much better than those with the ground rubber. It is also seen that as the proportion of the virgin NR in the blends with devulcanised NR increases, the mechanical properties progressively increased at or above the rule of mixtures.

15.3.3 Thermoplastic/recycled rubber blends

The technology of polymer blending has emerged as a useful tool in tailoring polymers to the needs of the end users. An exciting development in blending is the introduction of thermoplastic elastomers (TPE) based on plastic/rubber blends. These TPEs are becoming increasingly important because of their elastomeric properties and easy processability of the blends and their lower cost. TPEs are replacing many of the conventional rubbers as

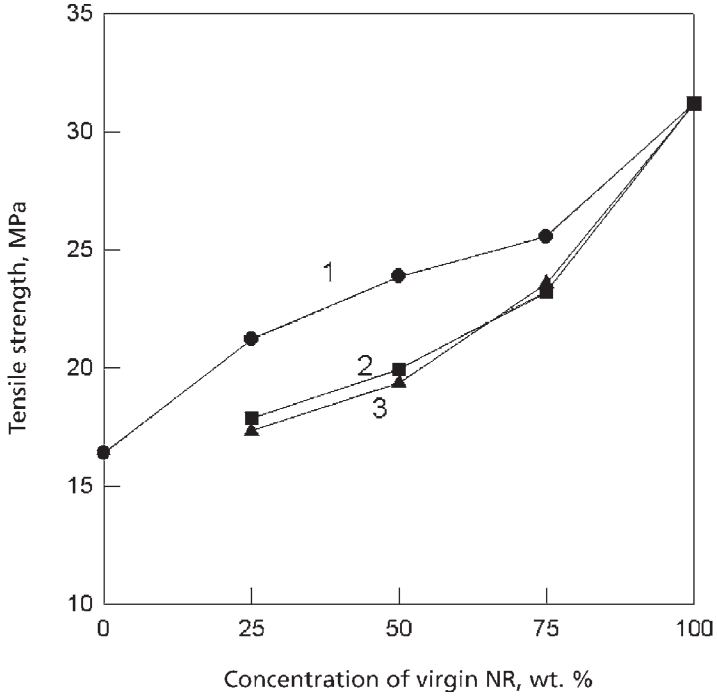

Figure 15.6 Tensile strength of carbon black filled (35 phr) devulcanised NR/virgin NR vulcanisates (curve 1) and ground NR/virgin NR vulcanisates (curves 2 and 3). Curve 1 is based on the curing recipe containing 2 phr of sulphur, 1 phr of CBS, 5 phr of ZnO, 1 phr of stearic acid. Curves 2 and 3 are based on the same curing recipe with the amount of curatives based on the virgin and total rubber content, respectively

well as leading thermoplastics. The disadvantages associated with TPEs are that they melt or soften at a specific temperature, and show creep behaviour on extended use. However, the many applications that have been successfully commercialised with TPEs are a testimony to the value of these materials in the rubber product market [124]. Also, TPEs have properties which bridge the gap between conventional rubber vulcanisates and thermoplastics.

For many end uses, the ideal plastic/elastomer blend comprises finely divided elastomer particles dispersed in a plastic phase. This favourable morphology should remain during the fabrication of the material into parts, and in use. Uncross-linked or partially cross-linked TPEs have either a dispersed-rubber phase morphology or, in some instances a co-

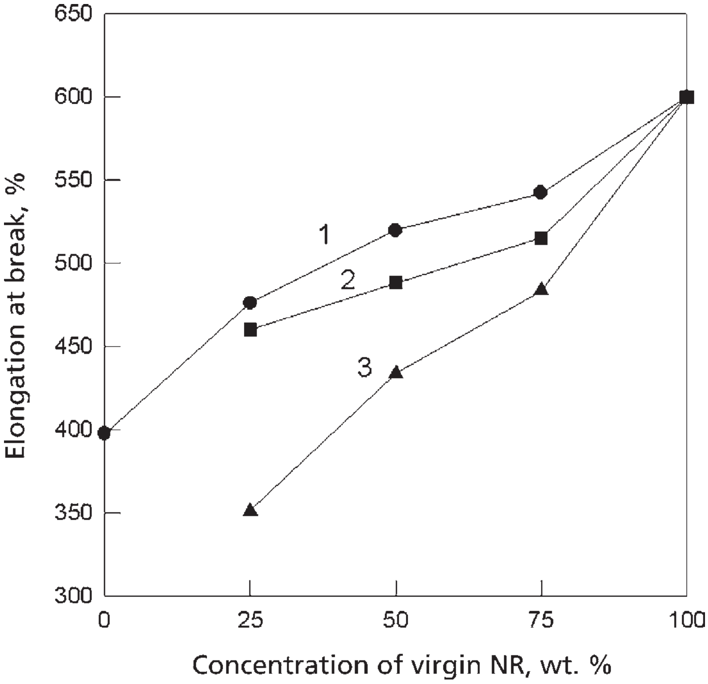

Figure 15.7 Elongation at break of carbon black filled devulcanised NR/virgin NR vulcanisates and ground NR/virgin NR vulcanisates. Notations are the same as in Figure 15.6

continuous morphology [125]. The uncross-linked rubber particles of a blend can coalesce after the removal of temperature and the shear of dynamic mixing. In the TPEs with cross-linked rubber particles, while dispersed in the less viscous molten thermoplastic, the rubber particles cannot reaggregate. Thus, they are trapped in this dispersed state. The surface area generated by their fine dispersion enables them to interact intimately and synergistically with the thermoplastic, to give a highly elastomeric composition.

Dynamic vulcanisation is a route to new thermoplastic elastomers having properties as good or even, in some cases, better than those of block copolymers [126]. Dynamic vulcanisation is the process of vulcanising the elastomer during its melt mixing with the molten plastic. With regrinding and reworking in the melt, the network of particles that touch and are loosely bound together, disintegrates and melt-processability of the material is restored. If the elastomer particles of such a blend are small enough and if they are fully vulcanised, then the properties of the blend are greatly improved.

The process of preparation of TPEs containing a plastic phase and a highly vulcanised rubber phase by dynamic vulcanisation, was described by Gessler [127] as well as by Coran and co-workers [128-130]. These pioneering works on dynamic vulcanisation led to the successful development of a new class of thermoplastic vulcanisates (TPV). It is important to note that the commercialisation of the technology was greatly aided by the discovery by Abdou-Sabet and Fath [131] of preferred compositions based on Lewis-acid catalysed methylol-phenolic vulcanisation systems for the new thermoplastic vulcanisates. Coran and co-workers [132] used a large number of elastomer-plastic combinations to prepare TPVs by dynamic vulcanisation.

Coran and Patel [130] investigated the relationship between the ultimate properties and the structures of thermoplastic vulcanisates. They indicated from experimental results that the ultimate properties of PP/EPDM system were an inverse function of the rubber particle diameter. The smaller the average rubber particle size, the better the stress/strain properties of the material. It was also found that only a small amount of curing agent was required for a large improvement in the tension set as the cross-link density of the rubber phase increased. Tensile strength improved rather continuously as the cross-link density of the elastomer phase increased, but the compositions remained processable as thermoplastics even at high elastomer cross-link density. However, only small changes in the stiffness of the compositions occurred with greater changes in the extent of cure.

Elastomeric alloys have been characterised as compositions containing rubber particulate domains approximately 1–2 μm in diameter in a matrix of thermoplastic resin [126]. The dynamic vulcanisation of a conventional thermosetting rubber within a thermoplastic matrix subjected to shear produces a fine dispersion of cross-linked micron-size rubber particles [133]. The process of dynamic vulcanisation, when done under prescribed conditions and with the optimum cross-linking system, produces a dispersed phase of particulate rubber in a continuous phase of plastic [128, 131]. This morphology has been disputed. However, Abdou-Sabet and Patel [125] have shown conclusively that this is the structure of dynamically vulcanised TPEs.

The blending of waste rubber with thermoplastics is important both from the point of view of disposal of waste and the reduction in the product cost. More attention has been focused on compounding GRT with thermoplastics which can be subsequently re-melted and formed into a wide range of moulded and extruded products [134, 135]. The mechanical properties of such compounds depend upon the concentration of GRT, polymer matrix type and adhesion between the GRT and polymer matrix, as well as the particle size and their dispersion and interaction between the GRT and matrix [130]. Generally, adhesion between the GRT and polymer matrix and size of the GRT particles are the two major factors controlling the mechanical properties of such composites. Also, dynamic vulcanisation techniques can be used to improve the properties of the blends of ultrasonically devulcanised GRT and thermoplastics [136]. Dynamic vulcanisation is the process of vulcanising the elastomer during its melt mixing with the molten plastic [127-130].

Blending with waste rubber is important both from the point of view of disposal of waste and the reduction in the product cost. More attention has been focused on compounding finely ground GRT with thermoplastics which can be subsequently re-melted and formed into a wide range of moulded and extruded products [3, 134].

The addition of GRT, however, results in significant deterioration in the mechanical properties of these composites. It is reported [137-149] that the GRT has a detrimental effect on most of the physical properties of cured rubber, the extent of deterioration increasing with the amount and size of the GRT. There have been several investigations into improving the adhesion between the GRT and polymer matrix.

Baker and coworkers [3, 140-142] studied the effects of various compatibilisers to promote the adhesion of PE/GRT blends. They reported that it was possible to achieve a partial recovery of the same properties through a melt blending process where each component was first conditioned with compatibilisers of similar structure before the actual blending was carried out [134]. Among the various compatibilisers, epoxydised NR [142], ethylene-co-acrylic acid copolymer [3, 141, 142] and ethylene-co-glycidyl methacrylate polymer [135, 141] were found to improve the impact properties of PE/GRT composites effectively. It was also reported that a smaller GRT particle size results in a small increase in the impact property of the composite and has a greater influence on the melt processability of the composites. The percentage improvement in the impact energy for linear low density polyethylene (LLDPE) and the composites prepared from them, was greater than for the corresponding high density polyethylene (HDPE) Composites. Deanin and Hashemiolya [143] also suggested that the low polarity and/or low crystallinity of the matrix polymer appeared to favor the compatibility with ground tyre rubber.

Phadke and De [139] investigated the influence of cryogenically ground rubber (CGR) on melt flow and mechanical properties of PP. They found that NR was essential as a dispersing agent. The dynamic mechanical properties revealed that PP is thermodynamically incompatible with NR and CGR. CGR in the powder form showed poor adhesion to a PP matrix and decreased the impact strength at higher loadings. However, addition of a masterbatch of CGR and NR improved the adhesion between CGR and PP and increased the impact strength of the blends.

Another approach to improving the compatibility of GRT and polymer is the modification of GRT particle surface. The polymeric surface modification can be carried out by chemical treatments like chromic acid etching [144], thermal oxidation [145] or by mechanical means. Stark and Leigton [146] found that surface treatment of ground rubber with a matrix of unsaturated curable polymer and a curing agent could also improve the performance of the blends. Rodriguez [147] determined the effect of CGR (approximately 250 microns) from old tyres on some mechanical properties of an unsaturated polyester resin. Composites made from silane-treated ground rubber showed better mechanical properties than composite made from untreated CGR. However, the particle size of the ground rubber was apparently too large to produce a toughening effect on the filled materials.

Zijp [148] patented thermoplastic elastomeric compositions which were prepared by mixing comminuted vulcanised rubber from waste products with thermoplastic olefins, particular PE. The addition of non-ionic surfactant greatly improved the bonding between the two main components, thus yielding compositions with a very low level of porosity and improved mechanical properties, particularly superior toughness. A non-ionic surfactant could control the porosity of vulcanised rubber particles and thermoplastic polymer by varying the relative quantity of rubber and dimensions of the rubber particles. However, a disadvantage of this method is that very low degrees of porosity could not be achieved at the more useful, somewhat higher rubber contents.

High-energy treatment including plasma [149, 150], corona discharge and electron-beam radiation were used to modify the surface of GRT [135]. Chidambaram and co-workers [149] studied the oxidation on the surface of GRT generated by chemical and physical treatment such as plasma and autoclave in oxygen atmosphere to improve adhesion between GRT and polyamide in the blend. Xu and co-workers [151] studied an epoxy resin compounded with tyre rubber particles modified by plasma surface treatment. They observed an improvement in mechanical properties of the resulting material over those containing the untreated rubber. Pramanik and Baker [141] investigated the effects of corona discharge treatment of GRT on the impact property of the thermoplastic composite containing the GRT. X-ray photoelectron spectroscopy analysis showed that the corona discharge treatment of GRT increased the oxygen containing groups on the ground rubber surface. In some composites it has been found that treated GRT marginally improved the impact property of the composites. However, prolonged times of treatment and higher power inputs for corona discharge of GRT reduced the impact strength of the composites.

Lal and Walters [152] described how the mechanical properties of uncured composites containing reclaimed rubber devulcanised using microwave energy, were significantly improved by adding crystalline or semi-crystalline *alpha*-olefin polymer, such as PE or PP. Improvements in solvent resistance and moulding properties of the uncured blends were also achieved.

Luo and Isayev [136] reported that the phenolic resin cure system and maleic anhydride grafted PP compatibiliser significantly improved mechanical properties of PP/ultrasonically devulcanised GRT blends prepared by dynamic vulcanisation. In addition, Hong and Isayev [153] blended GRT and ultrasonically devulcanised GRT with HDPE using a

Brabender internal mixer and a twin-screw extruder. The latter blend was dynamically vulcanised in these mixers. Also, HDPE and GRT blends mixed earlier by using a twin-screw extruder were passed through the ultrasonic devulcanisation extruder and subsequently dynamically vulcanised by means of the internal mixer and the twin-screw extruder. The blends mixed by using the twin-screw extruder prior to devulcanisation were found to have better tensile properties and impact strength than any other blends. Rheological properties of these blends were also studied.

Coran and Howard [154, 155] patented and studied blends of GRT and recycled HDPE from used milk containers. Effects of GRT particle size and concentration on mechanical and rheological properties were determined. The blend systems were optimised by a soft rubber-plastic binder produced from a mixture of HDPE and EPDM where EPDM is dynamically vulcanised during its mixing with the HDPE. It was concluded that the softening of the HDPE binder provides compositions of improved ultimate mechanical properties.

15.3.4 Asphalt modified by tyre rubber

The practice of modifying asphalts, i.e., blending with small amounts of polymers, has existed for many years already. The art of blending rubbers with asphalt has appealed to many workers in both the asphalt and the rubber fields. The main objective has been to improve the thermomechanical properties that cannot be achieved by asphalt through the manufacturing by conventional techniques, vacuum distillation or blowing of petroleum residues [156]. The use of blending GRT with asphalt has been in existence for quite some time. Depending on the type of tyre the composition of GRT may include different rubbers. These cross-linked rubbers are mostly immiscible in bitumen. The blends show an improvement in basic asphalt properties as well as rubber-like characteristics. The blend is thought of as a dispersion of undissolved swollen rubber particles acting as an elastic aggregate within asphalt modified by the portion of the rubber particles that have dissolved.

The use of blending GRT with asphalt began in the 1960s by McDonald who developed and patented a patching material consisted of 25% scrap and asphalt blended at 190 °C for 20 minutes [157]. McDonald continued his work by expanding it to actual road pavement test sections as a seal coat and in 1968, Sahmaro Petroleum and Asphalt used a blend of GRT and asphalt as a binder for a hot premix. The hot premix is a mixture of stone aggregate, sand and the tyre asphalt binder all premixed in a batch or drum type mixer. This material is then applied as a carpet on top of the road by means of a paving machine followed by a steel roller used to compact the material [158]. Thereafter, many variations of the basic process of hot premix described above with the blend of GRT and asphalt as the binder have been proposed, most of them involving replacing stone aggregate with GRT. However, this method does not truly modify the asphalt binder, thus the blending process of GRT and asphalt before preparing a mixture is the most efficient in improvement of properties. Typical use levels range from 15 to 30% [159].

GRT is obtained today predominantly from automotive tyres mostly composed of vulcanised SBR, NR and carbon black. However, the chemical composition can vary depending on the source of GRT. These sources can be defined as being obtained from automotive tyres, truck tyres, sidewall buttings, tread peel or whole carcass tyres. Truck tyres are composed mostly of natural rubber, while sidewall compositions for passenger tyres are usually blends of SBR with NR or butadiene rubber. The composition of the GRT does affect the properties of the resulting blend. In conjunction with composition, the method of processing the GRT also effects digestion, of the asphalt soluble fractions, as well as the optimal mixing times and resulting properties of the asphalt rubber blend. The surface morphologies between ambient and cryogenically ground particles are different. These differences affect surface area and thus mixing times. In addition to surface morphology, the size of the GRT particles is also important.

A limited amount of work has been done on the characterisation of the blends of GRT and asphalt. Blends are typically mixed at temperatures of 300 to 400 °C for a period of 0.5 to 2 hours. The mix increases in viscosity and has a consistency of slurry with discernable rubber particles spread throughout. At room temperature the resulting composition is a tough rubbery-elastic like material. This mixing period is often referred to as reaction or digestion time. Takallou and Takallou [159] suggest that the elastic quality of the blend is caused by the mechanical action of the undissolved rubber particles performing as a completely elastic aggregate within the asphalt, which is modified by a portion of the rubber particles that have dissolved. Roberts and Lytton [157] show that mixing times of two hours as opposed to times of half and one hour significantly improve elastic recovery while Schuller [42] reports that increasing mixing time reduces the amount of solid rubber in the mixture increases both high and low molecular weight fractions of dissolved rubber in the asphalt. This brings up a very interesting point for further investigation as to whether the increase in asphalt soluble rubber fractions that occurs with longer mixing times can be attributed to elastic properties. Al-Abdul-Wahhab and Al-Amri [160] have shown that the addition of GRT at levels of 10, 20 or 30% significantly increases the softening points and strain recovery over the base asphalt with a viscosity increase of similar magnitude for all three blends.

A renewed interest in the use of GRT came about in the late 1980s and continues on today. Incorporation of GRT in asphalt is an important issue since tyre stockpiles are building up as well as the landfills, the ones that will accept them [161]. There is a lot of activity in the USA, currently in the Government at the Federal Level addressing the issues of scrap tyres, as well as a bill to promote the use of scrap tyres in asphalt and roads [20].

The use of polymers in asphalt for paving applications is limited because of the high cost associated with road construction. SBR latex is the most predominant modifier followed by block copolymers and scrap tyres. Considering paving requirements and the usage costs for blending with GRT compared to latex or block copolymers with GRT being used at levels five times higher but one-tenth of the cost of latex and block copolymers, it is the most economical way to modify paving asphalt binders. In over thirty years of history it has been shown that the rubber modified asphalts last longer, twice that of conventional asphalt, reduce cracking, reduce or eliminate rutting and increase strength resulting in that it can replace conventional asphalt in pavement design by up to 50% [162].

The most recent study of asphalt-rubber binder is that reported by Billiter and co-workers [163]. They measured how rheological properties were affected by asphalt composition, rubber dissolution and temperature. Rubber content, rubber particle size and base asphalt composition were found to be the main factors affecting the rheology of asphalt-rubber binder. By controlling these variables, binders with improved cracking resistance and rutting resistance can be produced. Finally, scrap tyres used as a crumb rubber modifier in asphalt will improve paving performance and safety by being an excellent and cost effective modifier for highway pavement industry [164].

15.3.5 Cement modified by tyre rubber

Production of rubber-filled cement compositions is a possible area for a further expansion of usage of GRT [165-172]. The influence of the shape of rubber particles on mechanical properties, workability and chemical stability of rubber-filled cement was studied [165]. The composite containing rubber shreds was able to bridge the crack and prevent catastrophic failure of the specimen, while the composite containing granular rubber particles was unable to bridge the crack. The pull out test indicated poor interfacial bonding between the granular rubber particles and the matrix. In fact, many studies in this area indicated that the interface between the rubber and cement is weak. Attempts to improve the interface were made by washing the rubber particles [166, 170, 171]. Some improvement has been achieved by washing the particles by water [170], water and carbon tetrachloride mixture and water and latex mixture [173] leading to an enhanced adhesion in rubber-filled cement. Several surface modifications are also proposed including the treatment of rubber with sulphuric acid and nitric acid to chemically oxidise rubber and introduce polar groups. Contrary to expectation, the treatment with nitric acid led to a decrease of the strength of the composite [171]. On the other hand, the treatment with sulphuric acid improved the adhesion of rubber to concrete [174]. It was also found [175] that addition of rubber particles to the mortar led to a decrease in their compressive and flexural strengths due to pull out of particles. However, the treatment of rubber particles before mixing with bifunctional silane-coupling agent, such as *gamma* mercapto trimethoxy silane-coupling agent, improved the interface and led to increased ductility [175]. It is suggested to expand this research to find the effects of the type of coupling agent on the adhesion and the fracture behaviour of the rubber-filled cement paste, mortar and concrete. These materials can be utilised in highway pavement overlays, sidewalks, medians, sound barriers and other transportation non-structural uses.

15.4 Summary

Waste tyre and rubber is an important problem of international significance. The present work describes some routes available to solve this problem. Numerous technologies are being developed. Among them, in addition to the well-known grinding techniques, are continuous pulverisation methods based on a single or twin-screw extruder that may serve as a possible route to supply rubber powder as a feedstock for devulcanisation technologies. Ultrasonic technology is one of the most promising methods to make devulcanised rubber suitable for making rubber products from 100% recycled rubber and as well as for adding to virgin rubber, virgin and recycled plastics, asphalt, concrete and cement. Equipment has to be developed capable to achieve high output to make the process economically acceptable. The major challenge in industrial implementation of this process is the development of a high power ultrasonic generator capable to continuously operate under high pressure and temperature. There is also a lack of scientific understanding of various processes governing recycling of rubbers. Development of the science based technologies for rubber recycling would significantly reduce a world wide energy consumption, offer renewable rubbers from scrap tyres and rubber waste and would lead to less pollution of the environment.

Acknowledgment

This work is supported in part by grant DMI-9712043 from the National Science Foundation.

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Abbreviations and Acronyms

6PPD	*N*-(1,3-dimethylbutyl)-*N´*-phenyl-*p*-phenylene diamine
77PD	*N*,*N´*-bis-1,4-dimethyl pentyl-*p*-phenylene diamine
abs	Anti-lock brake system
ABS	Acrylonitrile-butadiene-styrene rubber
ACM	Acrylic rubber
ACN	Acyrlonitrile
ACTAS	Automated continuous tyre assembly
ADC	Azodicarbonamide
ADS	Air dried sheet
AES	Advanced Elastomer Systems
ASTM	American Society of Testing and Materials
ATBN	Amine terminated NBR
AU	Polyurethane rubber
BCI-MX	1,3 bis (citraconimidomethyl) benzene
BES	Benzoic acid
BET	Brunauer-Emmett-Teller Method
BHT	2,6-*t*-butyl-*p*-cresol
BIIR	Brominated IIR
BIMS	Brominated isobutylene-co-*para*-methylstyrene
BPSCE	Biphasic single component elastomer
BR	Butadiene rubber
BS	British standards
BSH	Benzenesulphohydrazide
BTPDE	Bis-(alkyl thiopropionate) diesters
BTU	British Thermal Unit
BUR	Built-up roofing
CAD	Computer aided design
CAE	Computer aided engineering

C3M	Continuous cold compounding
CAM	Computer aided manufacturing
CBS	*N*-cyclohexyl-2-benzothiazole sulphenamide
CDO	*p*-Benzoquinone dioxime
CFC	Chlorofluorocarbon
CFD	Computational fluid dynamics
CGR	Cryogenically ground rubber
CIIR	Chlorinated IIR
CIS	Commenwealth of Independent States
CLD	Caprolactam disulphide
CM	Chlorinated PE
CO	Epichlorohydrin homopolymer
COPQ	Cost of poor quality
CPE	Chlorinated polyethylene
CPU	Cast polyurethane elastomer
CR	Polychloroprene rubber
CSDPF	Carbon-silica dual phase filler
CSM	Chlorosulphonated polyethylene
CSR	ContiSafety Ring
CTAB	Cetyltrimethyl ammonium bromide
CTP	*N*-(cyclohexylthio) phthalimide
CTS	ContiTire system
CV	Constant viscosity
CWS	ContiWheel System
DBP	Dibutyl phthalate
DBPA	Dibutyl phthalate absorption test
DCBS	*N*, *N*-dicyclohexyl-2-benzothiazly sulphenamide
DCP	Dicumyl peroxide
DCPD	Dicyclopentadiene
DCPS	Disc centrifuge photo sedimentometry
DEG	Diethylene glycol
DETU	*N*, *N*´-diethylthiourea
DIN	Deutsch Institut fur Normung
DINP	Diisononyl phthalate

DIY	Do-it-yourself
DMTA	Dynamic mechanical thermal analysis
DNPT	Dinitrosopentamethylene tetramine
DOE	Design of experiments
DOP	Dioctyl phthalate
DOTG	Di-*o*-tolyl guanidine
DPG	*N*, *N*′-diphenyl guanidine
DPNR	Deproteinised NR
DPPH	Diphenyl picrylhydrazyl
DPTT	Dipentamethylene thiuram tetrasulphide
DRC	Dry rubber content
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTDM	Dithiomorpholine
EAM	Ethylene-acrylic elastomers
EB	Ethylene butylene copolymer
EBC	Estate brown crepe
ECH	Epichlorohydrin
ECO	Epichlorohyrin/ethylene oxide copolymer
EERC	Earthquake Engineering Research Centre
EFVF	Effective filler volume fraction
EMC	Epoxy moulding compound
ENB	Ethylidene norbornene
ENR	Epoxidised NR
EP	Ethylene propylene copolymer
EPDM	Ethylene-propylene-diene terpolymer
EPM	Ethylene-propylene rubber
EPR	Ethylene-propylene rubber
E-SBR	Emulsion polymerised styrene-butadiene
ESC	Environmental stress cracking
ESP	Electronic stability programmes
ETER	Epichlorohydrin/ethylene oxide terpolymer
ETU	Ethylene thiourea
EV	Efficient vulcanisation

EVA	Ethylene vinyl acetate
EVM	Ethylene vinyl acetate rubber
FCM	Farrel continuous mixer
FEA	Finite element analysis
FEF	Fast extrusion furnace
FKM	Fluorocarbon elastomer
FMEA	Failure mode and effects analysis
FMVE	Perfluoro (methylvinyl ether)
FPM	Fluorocarbon copolymer
FZ	Phosphazene
GCC	Ground calcium carbonate
GMF	*p*-Quinone dioxime
GPF	General purpose furnace
GPO-3	Propylene oxide/allyl glycidyl ether copolymer
GR-S	Government rubber styrene
GRT	Ground rubber tyre
HAF	High abrasion furnace
HDI	Hexamethylene diisocyanate
HDPE	High density polyethylene
HFC	Hydrofluorocarbon
HFP	Hexafluoropropylene
HFPE	1-Hydropentafluoropropylene
HIIR	Halogenated IIR
HNBR	Hydrogenated NBR
HPHT	High pressure - high temperature
HX	*Trans*-1,4 hexadiene
IEC	International Electrotechnical Commmission
IFP	French Institute of Petrol
IGC	Inverse gas chromatography
IIR	Isobutylene isoprene rubber (butyl rubber)
IISRP	International Institute of Synthetic Rubber Producers
IMPACT	Integrated Manufacturing Precision – Assembled Cellular Technology
IPP	Isopentenyl pyrophosphate
IPPD	*N*-isopropyl –*N*′-phenyl-*p*-phenylene diamine

IR	Polyisoprene rubber
IRHD	International rubber hardness degrees
ISAF	Intermediate super-abrasion furnace
ISNR	Indian Standard Natural Rubber
ISO	International Standards Organisation
IWS	Integrated wheel system
LATZ	Low ammonia-TMTD/zinc oxide
LLDPE	Linear low density polyethylene
LPO	Liquid petroleum olefin
MBI	2-Mercaptobenzimidazole
MBS	2-(4-Morpholinothio) benzothiazole
MBSS	2-Morpholino dithio benzothiazole
MBT	2-Mercaptobenzothiazole
MBTS	2,2´-Dithiobis (benzothiazole)
MDI	4,4´-Diphenylmethane diisocyante
MERL	Materials Engineering Research Laboratory
MIPS	Millions of instructions per second
MMA	Methyl methacrylate
MMP	Modular manufacturing process
M_n	Number average molecular weight
MOR	2,4-Morpholino mercapto benzothiazole
MPR	Melt processable rubber
MQ	Silicone rubber with methyl substituent
MRPRA	Malaysian Rubber Producers Research Association
MT	Medium thermal
MTBE	Methyl tertiary butyl ether
MVQ	Methyl vinyl polysiloxane (silicone rubber)
MVX	Mix-vent-extrude
MW	Molecular weight
M_w	Weight average molecular weight
MWD	Molecular weight distribution
N_2SA	Nitrogen surface area
NBR	Butadiene-acrylonitrile rubber
NDPA	*N*-nitrosodiphenylamine

NMR	Nuclear Magnetic Resonance
NR	Natural rubber
NST	Non-staining
OE	Original equipment
OENR	Oil extended NR
OESBR	Oil extended styrene-butadiene rubber
OTOS	*N*-oxydiethylene-*N*´-oxydiethylene thiocarbanyl sulphenamide
PA	Polyamide
PANA	Phenyl-a-naphthylamine
PBNA	Phenyl-*b*-naphthylamine
PCC	Precipitated calcium carbonate
PE	Polyethylene
PEA	Polyesteramide(s)
PEE	Polyether ester
PEEA	Poly(ether esteramide)(s)
PEG	Poly(ethylene glycol)
PEN	Poly(ethylene naphthalate)
PET	Poly(ethylene terephthalate)
phr	Parts per hundred rubber
PLC	Pale latex crepe
PMMA	Poly(methyl methacrylate)
PMQ	Silicone rubber with methyl and phenyl substituents
PMR	Protected membrane roofing
PNGCR	Papua New Guinea Classified Rubber
PNP	*Para*-nitrophenol
PO	Propylene oxide homopolymer rubber
POK	Polyolefin ketone
PP	Polypropylene
PPDC	Piperidinium *N*-pentamethylene dithiocarbamate
PRI	Plasticity retention index
PS	Polystyrene
PU	Polyurethane
PUF	Polyurethane foams
PUR	Polyurethane rubber

PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVI	Pre-vulcanisation inhibitor
Q	Silicone rubber
QC	Quality control
QDI	*N*-1,3-dimethyl butyl-*N*′-phenyl-*p*-quinone diimine
RCT	Radial - circumferential - thickness
R&D	Research & Development
RLT	Radial light truck
RMD	Radial medium duty
RSS	Ribbed smoked sheet
SAE	Society of Automotive Engineers
SAF	Super abrasion furnace
SBR	Styrene-butadiene rubber
SBS	Styrene-butadiene-styrene
SCS	Salicylic acid
SEBS	Styrene-ethylene-butylene-styrene
SEPS	Styrene-ethylene-propylene-styrene
SIR	Standard Indonesian rubber
SIS	Styrene-isoprene-styrene
SLR	Standard Sri Lankan rubber
SMR	Standard Malaysian rubber
SMR-CV	SMR-constant viscosity
SMR-L	SMR-light colour
SP	Superior processing
SPC	Statistical process control
SPF	Super processing furnace
SRF	Semi-reinforcing furnace
S-SBR	Solution polymerised styrene-butadiene rubber
SSR	Standard Singapore Rubber
ST	Staining
STR	Standard Thai Rubber
SWT	Sidewall torsion
TBBS	*N*-*tert*-butyl-2-benzothiazole sulphenamide

TBSI	*N-tert*-butyl-2-benzothiazole sulphenamide
TBzTD	Tetrabenzylthiuram disulphide
TDI	2,6-toluene diisocyanate
TDPE	Alkyl thiodipropionate esters
TEM	Transmission electron microscope
TESPT	Bis (3-triethoxy silyl propyl tetrasulphide
TETD	Tetraethyl thiuram disulphide
TFE	Tetrafluoroethylene
TFP	Tetrafluoropropylene
T_g	Glass transition temperature
TiBTD	Tetraisobutyl thiuram disulphide
TiBTM	Tetraisobutyl thiuram monosulphide
T_m	Melting point temperature
TM	Polysulphide rubber
TMA	Thermo mechanical analysis
TMQ	2,2,4-trimethyl-1,2-dihydroquinoline (polymerised)
TMTD	Tetramethyl thiuram disulphide
TMTM	Tetramethyl thiuram monosulphide
TNP	Tris (nonylphenyl) phosphite
TOR	*Trans*-cyclooctenamer
TP95	Di-(butoxy-ethoxy-ethyl) adipate
TPA	*Trans*-polypentenamer
TPD	Tapping Panel Dryness
TPE	Thermoplastic elastomer(s)
TPNR	Thermoplastic natural rubber
TPO	Thermoplastic polyolefins
TPU	Thermoplastic polyurethane
TPU-E	Thermoplastic polyurethane elastomer
TPV	Thermoplastic vulcanisate
TSR	Technically specified rubber
TTR	Thai tested rubber
TTZ	Tolyltriazole
UV	Ultraviolet
VDA	Vehicle dynamics analysis

VIC	Variable Intermeshing Clearance
VMQ	Silicone rubber with methyl and vinyl substituents
WLF	Williams Landel Ferry equation
XLD	Crosslink density
XLPE	Crosslinked polyethylene
XNBR	Carboxylated nitrile rubber
Z5MC	Zinc pentamethylene dithiocarbamate
ZBEC	Zinc dibenzylethyldithiocarbamate
ZBPD	Zinc dibutyl dithiophosphate
ZDBC	Zinc dibutyl dithiocarbamate
ZDEC	Zinc diethyl dithiocarbamate
ZDMC	Zinc dimethyl dithiocarbamate
ZEPC	Zinc ethyl phenyl dithiocarbamate
ZIX	Zinc isopropyl xanthate
ZMBT	Zinc 2-mercaptobenzothiazole
Zn-EMA	Zinc salt of poly(ethylene-co-methacrylic acid)
Zn-mEPDM	Zinc salt of maleated EPDM
Zn-mHDPE	Zinc salt of maleated HDPE
Zn-mPP	Zinc salt of maleated PP
Zn-PEA	Zinc salt of poly(ethylene-co-acrylic acid)
Zn-PPA	Zinc salt of poly(polypropylene-co-acrylic acid)
Zn-SEPDM	Zinc salt of sulphonated EPDM
Zn-XNBR	Zinc salt of carboxylated NBR

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