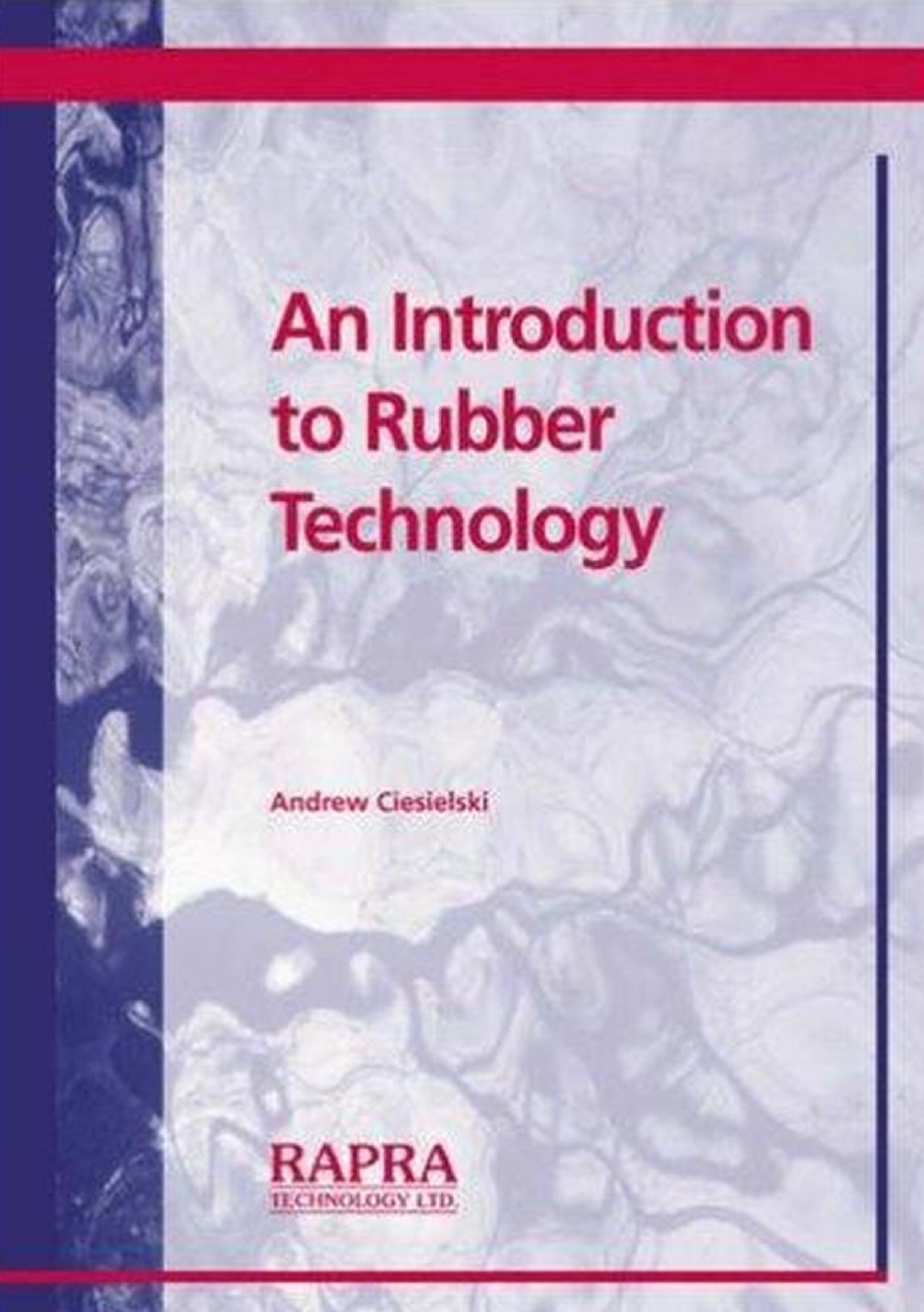

An Introduction to Rubber Technology

Andrew Ciesielski

RAPRA
TECHNOLOGY LTD.

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TECHNOLOGY LTD.

Rapra Technology Limited

Shawbury, Shrewsbury, Shropshire SY4 4NR, United Kingdom
Telephone: +44 (0)1939 250383 Fax: +44 (0)1939 251118
http://www.rapra.net

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Preface

This book is written as an introduction to the subject of rubber technology, leaving the in depth specialization to other texts. "Introduction to Rubber Technology" is aimed at those people who simply wish to gain a basic overall understanding of this field. Thus the purchasing agent, engineer, polymer chemist, student of rubber technology, shop floor manager, and indeed the president and upper management, involved in the industry will want to read this book. Customers who use rubber in their products can obtain an understanding of those technical aspects with which they are unfamiliar from this book. A knowledge of the content of the eight chapters will also provide the reader with a communication tool for discussing the subject with a rubber specialist.

Rubber technology has a fascinating history from the jungles of Brazil to its designation as a strategic material during World War II. The primary material comes in many variations, most of which are of synthetic origin. All of these variations have their own special property combination to help them find a niche in the product marketplace. The rubber technologist then formulates a blend of this primary raw gum elastomer with other chemicals to produce rubber formulations, drawing from a potentially infinite variation of material combinations. Machines mix, extrude, calender and mold the blend of materials in this formulation known as the rubber compound. At this point the rubber laboratory has an armoury of tests related to the compound to ensure that the customer is satisfied with the final product. Rubber chemistry and physics are used to explain why rubber behaves as it does and helps push the boundaries surrounding its use. With a greater understanding of the special deformation and elastic properties of this unusual engineering material the engineer can find unique solutions to some of his applications. One of the many rubbery materials, urethane, is ideally suited to be cast as a liquid into molds to produce products which exploit its high strength. This book opens the door to all of these areas.

I would like to thank the Holz Rubber Company for its support in my endeavor to produce this book, especially Mr. Ted Cooper for drawing many of the graphics. I would also like to express my appreciation to Mr. Robert Klingender of Zeon Chemicals Inc., for his helpful comments on the manuscript and to Mr. Nick Williams of The JR Clarkson Company for his contribution to the section on finite element analysis, and to Mr. Koh Murai (of the same company) for his observations relating to the engineering chapter. I would especially like to thank Dr. Alan Gent, Professor of Polymer Physics

and Polymer Engineering at The University of Akron, USA, for reviewing the chapter on Engineering. Thanks go to Uniroyal Chemical for a review of the urethane chapter and Mr. Wayne Cousins of Bayer for his useful comments on some of the elastomers mentioned in Chapter 2. A final thanks to Frances Powers, my technical editor for her insightful questions and enthusiasm during the editing of the manuscript.

Andrew Ciesielski
Holz Rubber Company

1 History

"So rubber comes from trees, or maybe it was invented by Charles Goodyear?"
...wondered Andrew.

"Well, some types we get from a tree, and good old Charles made it more useful"
...answered Lucy.

1.1 Natural rubber

There is much discussion about natural products which may yet be discovered in the fast disappearing rain forests, indeed a significant portion of pharmaceutical organic chemicals attribute their origin to the vast diversity of plant life found there. Even though alchemy has been left far behind there is a long way to go before all the elegant pathways which nature uses to synthesize her molecules are discovered. In the meantime we often rely on her to do it for us.

This book will focus on materials which owe their historical origin to a single chemical called polyisoprene, found in the sap of a tree named *Hevea braziliensis* (see Figure 1.1) found growing originally in the jungles of Brazil, and is also found in the milky latex of the humble milkweed (*Asclepias spp.*) and dandelion (*Taraxacum spp.*).

Polyisoprene, especially when chemically modified by vulcanization, has the remarkable ability to substantially return to its original shape after being stretched considerably. Any material which fulfills this requirement, is entitled to be called rubber. ASTM D 1566 gives a more detailed definition of rubber [1]. Polyisoprene extracted from *Hevea braziliensis* is called natural rubber (NR). This elastic property, as Suzuki points out, eventually led to a multi-billion dollar industry, and has affected the lives of the vast majority of the people on this planet [2].

Early 'rubber technologists' were found among the Aztecs and Mayas of South America, who used rubber for shoe soles, coated fabrics, and playballs, well over 2,000 years ago. An MRPRA (Malaysian Rubber Producers' Research Association) article [3] mentions that the Aztec king, Montezuma was paid tribute by the lowland tribes in the form of 16,000 rubber balls, and that ball courts have been excavated in Snaketown in the south-western United States dating back to AD 600-900.

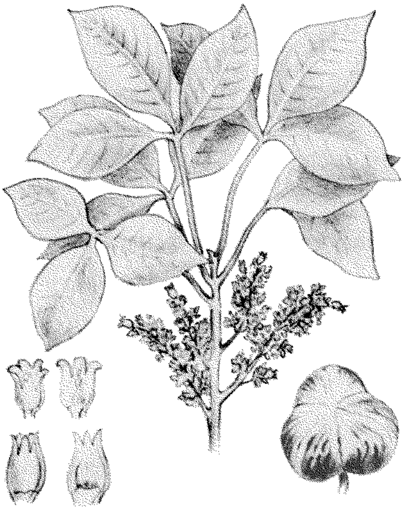

Figure 1.1 Leaf and seed from the *Hevea braziliensis* tree

Subramaniam, in the late Maurice Morton's book Rubber Technology [4], attributes Christopher Columbus as the first European to discover NR, in the early 1490s, when he found natives in Haiti playing ball with an extract from a tree. The book goes on to describe how, by the 18th century, uses for NR were well established in Europe, where the English chemist J. B. Priestley gave it its name since it 'rubbed' out pencil marks. Stern [5] mentions the Scotsman Macintosh who in 1823 used the solvent naphtha to dissolve rubber and applied the resulting solution to textiles to produce rainproof clothing.

Rubber at that time was supplied in hard blocks. Stern [5] notes that Thomas Hancock in London in 1830 used what can be described as the first internal mixing machine (see section 4.3), which mechanically worked the rubber, making it softer and therefore more easily processable. Stern mentions that Hancock moved on to two roll mills (see section 4.2), and that it took a hundred years before the internal mixer re-appeared, becoming a key element in the industry. Buist [6] says that Hancock's internal mixer was invented in 1820, and mentions that Hancock called it a 'pickle', as Buist puts it 'to confuse his competitors'. He also mentions that 'Hancock's company, James Lyne Hancock Ltd., in London was the first British Rubber company, founded in 1820'.

Rubber products, up to the 19th century, had a major flaw, they were sticky on hot days, and very stiff when cold. This doesn't seem like much of a problem until you sit down in your sticky rubber raincoat on a hot day and lift up the chair with you when you stand. This problem was solved by a major discovery attributed to Charles Goodyear of Woburn, Massachusetts, USA in 1839. Duerden [7] writes that Goodyear accidentally visited the rubber goods store of the Roxbury Company in New York, around 1832, and as a result became obsessed with the problems of rubber manufacture, to the extent of financial crisis, resulting in frequent visits to the pawnbrokers shop. Duerden comments that, in his search to modify rubber to make it more useful, 'Goodyear purchased the claim of combining sulfur with India Rubber' from Nathaniel Hayward. Goodyear was then awarded a contract from the US Government to manufacture mail bags. These bags were made from rubber containing sulfur and white lead. Before long the mail bags started to decompose. Instead of leading him to riches, Duerden mentions that it brought Goodyear and his large family to poverty. He must have been close to giving up when a momentous discovery took place. By chance he heated the raw rubber-sulfur-lead combination, and found that the material charred like leather, and vulcanized rubber, as we know it, was born. The resulting composition was a much stronger material and was no longer sticky at higher temperatures. Duerden writes that Goodyear took out a US patent for this momentous discovery in 1841 but that he profited little from it.

Later, in 1843, Hancock was also combining sulfur with rubber and using heat. Stern [8] states that an artist friend of Hancock, coined the term vulcanization for this process, after Vulcan, the god of fire. In this book, the words vulcanize, cure, and cross-linking will be used synonymously. This discovery expanded significantly the number of uses for rubber, since it achieved far more than just making a non-sticky material. In fact the vast majority of rubber products today, owe their existence to vulcanization. A relative newcomer on the scene, thermoplastic elastomers, do not need curing.

As time went on, the quantity of rubber consumed continuously increased. This created an intense demand from the jungles of Brazil, and the dark side of our human nature appeared in all its ugliness. Suzuki [1] mentions that the native people of the Amazon were ruthlessly exploited, and that a rubber tapper could be killed, simply for not bringing in the required quantity of rubber from the surrounding trees. Supply and transportation problems began to occur in the Amazon basin, which was the only known source of raw rubber at that time. White [9] describes how, in 1876, seeds were taken out of Brazil and grown into seedlings at Kew Gardens in England. They were then shipped to the Far East. Suzuki comments that virtually all of the supply of natural rubber today comes from millions of trees which owe their heritage to those few seedlings. This is food for thought, when the topic of preserving genetic diversity, in this case, the rainforest, arises.

In 1889 John Dunlop in England invented the first commercially successful pneumatic tire, which was at that time used for bicycles [10]. Dunlop produced his first vehicle pneumatic tire in 1906 [11]. An interesting observation by Stern, is that in 1904, in England, it was found that a powder called carbon black (see section 3.3.7), blended into rubber, significantly increased a number of its mechanical properties [12]. It seems surprising that this major discovery was then 'left on the shelf' for about eight years. By

1910 the motor car truly arrived and both the use and price of natural rubber exploded. Stern mentions that, after this time, with improved fabrics, the rubber treads on tires were wearing out before the fabric reinforcement. The hunt was on to improve the wear life of the rubber. The carbon black discovery was finally taken off the shelf [12].

1.2 Synthetic rubber

Around this time, chemists were actively searching for rubbery materials which could be manufactured artificially. Kuzma [13] notes that the Russians, in 1910, prepared such a rubber, known chemically as polybutadiene. In the 1930s, the Germans began commercial production of a synthetic rubber called Buna-S (styrene butadiene copolymer) [14, 15]. With the outbreak of the Second World War, both the USA and Europe were extremely vulnerable to a shortage of supply of natural rubber, which could have had a catastrophic effect on the war effort. A huge R & D project was initiated, between government and industry in the United States. Styrene butadiene rubber was improved, then manufactured on a large scale and called Government Rubber-Styrene (GR-S), later to be known generically as SBR, which today is a major material in the rubber industry.

Although SBR is the most significant synthetic rubber in terms of tonnage, other rubber materials were produced around the same time, and play an important role in today's market. A priest synthesized a chemical building block which led to the discovery of a rubber by DuPont who marketed it as Duprene [16], in 1931, then changed the name to Neoprene. Although the generic term for this material is polychloroprene (CR, chloroprene rubber) it is still most often referred to by its DuPont name. Bryant [17] points out that in 1934 production was started in Germany, of an oil resistant rubber called Buna-N, the name later changed in 1937 to Perbunan. Its generic name is nitrile rubber (NBR, nitrile butadiene rubber).

Butyl rubber (IIR, isobutylene isoprene copolymer) was developed in the 1940s. Other significant materials are Hypalon (CSM, chlorosulphonated polyethylene) and Viton (FKM, fluoroelastomer) by DuPont (now DuPont Dow Elastomers) in the 1950s and ethylene propylene terpolymer rubber (EPDM) in the 1960s. It is interesting to note that a commercially successful synthetic analogue of NR did not appear until around 1960, when it was commercialized by Shell as 'Shell Isoprene Rubber' and shortly after by Goodyear as Natsyn. It is chemically known as polyisoprene (IR), and while it has not in any way displaced its natural cousin, it has found a niche in the market place. An important material discovered by Bayer in the 1950s is polyurethane, which can be a coating or a rubber (and a rubbery stretch fabric), depending on its exact chemical composition (polyurethanes may have other forms such as thermoplastics and foams but these do not normally exhibit rubbery properties). A significant recent addition to the armory of the rubber industry is a class of materials called thermoplastic elastomers which are gaining increasing prominence in the marketplace. They behave like rubber at room temperature but soften like plastic when heated. When cooled down, they return to their rubbery state.

The rubber that started it all, NR, has survived the onslaught of the synthetic rubbers exceptionally well and today still represents nearly one-third of all rubber in the marketplace. The new awareness of our environment gives NR the added advantage of being seen as a renewable resource, because most synthetic elastomers are derived from petroleum oil based starting materials.

1.3 What exactly does the word 'rubber' mean?

Rubber seems to be a fairly straightforward word. The French call it caoutchouc recognizing its historically South American 'native' origin. The word derives from a South American Indian word, meaning 'weeping wood' [18, 19]. The dictionary definition of rubber is, 'a material that when stretched returns quickly to its approximate original shape'. This definition fits the vulcanized material quite well. ASTM Standard D 1566-98 [1] has a detailed definition of rubber implying the vulcanized material. Unfortunately the rubber industry tends to be somewhat casual in the use of the term rubber. When a rubber product is made, the primary raw material is a polymer. This polymer often has some elasticity, but not always. It is then mixed with chemicals to make a rubber 'compound' which is subsequently vulcanized. This compound is simply a physical mixture of chemicals and indeed a number of ingredients in the vulcanizate might be present only as a physical blend. The industry often calls both the polymer and the uncured compound, 'rubber'. Unvulcanized silicone, for example, (both polymer and uncured compound) does not fit the dictionary definition too well, since it can have the consistency of butter. The word used in this book for the primary raw polymer will be raw gum elastomer.

Some people use the term rubber, to mean NR only, but there have been instances when a customer asked for rubber (expecting the vendor to choose the right type, neoprene, natural, etc.), the vendor however assumed the customer was specifically asking for natural rubber, which in that case turned out to be the worst choice. Naturally, the vulcanized material is also called rubber, as indeed it should be. The word 'elastomer' and 'rubber' are often used by the industry to mean exactly the same thing, which is a waste of such an interesting word (elastomer), which maybe, could have been reserved exclusively to describe the raw polymer. Blow [20] makes comments similar to these, about the word 'rubber' having several meanings. He suggests that the vulcanized material be called 'elastomer'. ASTM Standard D 1566-98 defines 'elastomer' as 'a term often used for rubber and polymers that have properties similar to those of rubber'.

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2 Types of Rubber and Their Essential Properties

"But you told me this rubber product would be all right at 200 °C, and now it's all brittle and cracked!" said Andrew. "Well, you didn't tell me it was immersed in an alkaline liquid" ...replied Paul

2.1 Introduction

In the previous chapter we saw that there are many different types of rubbery materials. This chapter explains the features of some of these elastomers, which allows them to find their place and survive in the market. Only a cross section of significant types will be discussed with a brief summary of properties. A detailed analysis can be found in many texts, referenced in the appendix at the end of the book (and at the end of this chapter), as well as a wealth of detail from raw material suppliers. When properties of rubber are discussed, it is the attributes of the final vulcanized compound which are almost always referred to. The primary component of the compound is the raw gum elastomer (for NR this would be the dried latex from the tree) whose nature is the driving force for many of these properties. Little information is available as yet, for strictly mechanical engineering data, compared to the enormous wealth of similar detail for metals. Recent indications are that improvements are being made in this area.

2.2 Interpreting the properties

Choosing the correct rubber based on property data should be done by the rubber expert, since there are many potential pitfalls. The properties of specific types of rubber, especially chemical resistance are described in section 2.3. The following is an indication of some of the properties that a rubber chemist might consider.

2.2.1 Upper temperature aging limits - heat aging resistance

If someone mentions that a rubber is good for a certain temperature, the statement still has fuzzy edges. It might depend on whether short term or continuous exposure is being referred to. The chemist knows that many chemical reactions speed up as temperature rises, so that rubber can degrade more rapidly with increase in temperature. That means it will survive for progressively shorter time periods as the temperature increases. Thus the term 'good for' might need to be clarified in terms of, 'how long is the rubber good for' at a certain temperature. A good example is given in section 2.3.9, where Viton is discussed. Occasionally, the term 'good for continuous use' needs to be made clear. Does continuous use mean 1,000 hours, 10,000 hours, or maybe two years of continuous use? The answer to this question will be avoided for the moment (however see section 2.3.3). In the laboratory, upper temperature values are commonly established in a heat aging oven, which inevitably involves the presence of oxygen from the surrounding air. The upper temperature value is the maximum temperature that the product is exposed to such that any aging that occurs over time, does not interfere with the products' performance. In specific applications where oxygen is absent, these elastomers could have a somewhat higher heat aging resistance rating, see section 2.3.4.

2.2.2 Chemical resistance and concentration

Many chemicals are encountered in the form of an aqueous solution. For example hydrochloric acid (hydrogen chloride dissolved in water), ammonia, caustic soda solution, and chlorine water. Thus, to say that a rubber is resistant to sulfuric acid, for example, might not be the full story. The resistance might very much depend on the concentration of the chemical. For example NR is 'OK' (a deliberately vague term) in dilute sulfuric acid, but will deteriorate rapidly in the concentrated acid.

2.2.3 Chemical resistance and temperature

Some rubbers can be resistant to some chemicals at room temperature and deteriorate rapidly at a higher heat levels. These levels can be significantly below the 'upper temperature limits' discussed earlier. Thus a basic fluorocarbon elastomer, will perform reasonably well while immersed in dilute sodium hydroxide solution (alkaline) at 20 °C but, on immersion in an alkaline solution, at 121 °C will deteriorate. Without the offending solution, the fluoroelastomer can be given a continuous heat aging limit of 200 °C.

Degradation, as a rule, speeds up with temperature. For example ozone resistance for many elastomers will decrease as temperature rises. Yeoh [1] points out that butyl rubber at 50 °C has the same resistance to ozone as NR (NR has poor resistance to ozone) has at room temperature. Butyl rubber has good resistance to ozone at room temperature.

2.2.4 Mechanical properties and temperature

Some mechanical properties can change appreciably with temperature. When a vulcanizate is exposed to a higher temperature for a period of time, then cooled to room temperature and tested, it is heat aging properties that are being measured. The properties of vulcanizate can also be measured at the higher temperature. Properties of a vulcanizate can be significantly different when measured at a higher temperature (compared to room temperature) even if no aging has occurred. The following are examples of this.

Butyl rubber, a fairly non-resilient material at room temperature can have a significantly higher resilience at 80 °C. Resilience is the ratio of energy input to energy output in a rapid (or instantaneous) full recovery of a deformed specimen. The resistance of some nitrile elastomers to tearing can decrease at higher temperatures. The tensile strength of many rubbers might drop significantly as soon as a higher temperature is reached. For example MRPRA literature [2] indicates, that a cured NR compound which has a tensile strength of 30 MPa at 23 °C, can drop to 23 MPa at 80 °C, and 5MPa at 140 °C. At the other extreme, as temperatures are lowered, elastomeric materials reach a point when they stiffen appreciably (see section 6.3.3). When a low temperature limit is mentioned, the rubber might show some increase in stiffness well before that limit is reached.

2.2.5 Grades within a type of rubber

Virtually all synthetic (and natural) raw gum elastomers have subdivisions within their own family. In many cases this alters the level of a particular property possessed by the raw gum elastomer. An example might be nitrile, which is well known for its oil resistance. The latter can vary from moderate to excellent dependent on which grade is chosen, within the nitrile family.

2.2.6 The rubber compound

Since a rubber compound is a mixture of a number of different ingredients (see chapter 3), some of the ingredients might modify the basic properties of the raw gum elastomer within the compound. For example, carbon black, added to the mixture can give excellent resistance to UV light in an otherwise non-resistant elastomer. This is an incidental bonus for using carbon black, since it is normally added for other reasons. Certain chemicals added to a compound can distinctly improve resistance to ozone in a rubber that has no intrinsic protection.

2.2.7 Conclusion

The summary from all of this might be, 'well, let's leave it to the rubber chemist'. It is clear that properties should not be interpreted in isolation. Chemicals, concentration of a chemical, temperature, mechanical stress and stain, time duration, and compound variables might all interact. Thus individual properties can only be used as a guideline and must be treated in the context of the product and its specific application. Therefore, whenever a property is mentioned in this book the ideal conditions for that attribute are assumed. For example resistance to any material or mechanical deformation is taken to mean at room temperature, unless otherwise stated. Since most raw gum elastomers are sold in various grades, it should usually be assumed that a quoted property refers to the grade in which that property excels. It is worth repeating that properties including those in this book can only be treated as a guideline, to narrow down possible options. A final decision in choosing a compound for an application often depends on additional variables.

These are just a few points that the chemist or engineer needs to be aware of when interpreting rubber properties. Caution is advised and, professional assistance is always recommended. Some useful generic chemical resistance guides, are mentioned in the suggested further reading.

2.3 Specific elastomers

The following names refer to the raw gum elastomer and consequently are given to the name of the vulcanized compound. Only a few examples have been chosen, and given a brief description, to illustrate the 'flavor' of what is available. There are many texts describing rubber types in detail (see appendix) and raw gum rubber manufacturers provide a great amount of detailed information.

2.3.1 Natural rubber NR

Ironically, production of rubber trees in its original source in South America is negligible, with present suppliers being Malaysia, Indonesia, Sri Lanka, Nigeria and others. Attempts have been made to extract NR from the dandelion and poinsettia plants and more seriously from a Mexican shrub called Guayule (*Perthenium argentatum*) [3], but without economic success. Gutta-percha and balata are minor specialized sources [4]. Production of the natural product begins at the plantation where a slit is made into the bark of the rubber tree to allow the flow of a milky sap (see Figure 2.1). This latex consists of water, polyisoprene, and small quantities of other ingredients such as proteins and carbohydrates. It is collected and coagulated with formic acid [5] in large tanks.

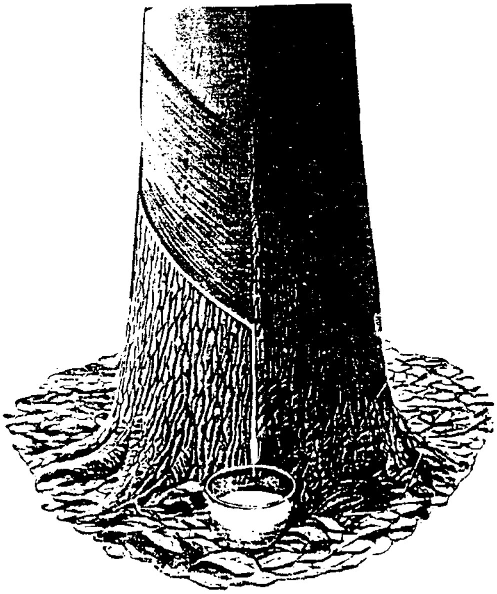


Figure 2.1 Tapping latex from a rubber tree

(Reproduced with permission from Lindley, NRPRA Technical Bulletin, No.8, Engineering Design, published by MRPRA)

The coagulum is then squeezed between rollers, to remove excess water and dried. Much of it is then baled and shipped off to the rubber processor. Some areas of the rubber industry use the latex directly for such items as medical gloves and condoms. In this case the latex is concentrated, mixed with ammonia for mechanical stabilization at the plantation, and shipped out.

Although the chemical building block of the polymer is always the same, polyisoprene, NR is available in many grades related to its 'dirt' content (remember it comes from a tree) and precise method of production. Popular grades are ribbed smoked sheet (RSS) and technically specified rubber such as SMR (Standard Malaysian Rubber) and SIR (Standard Indonesian Rubber). All of these are subgraded by dirt content. Grades are RSS1 to RSS5 and SMR 5,10 20, and 50; the lower the number, the cleaner the grade, and therefore the more expensive [6, 7]. ASTM D 2227 [8] also has standard specifications for technical grades. To achieve more consistent viscosity control of NR a specialized grade known as SMR CV (constant viscosity) is available. This grade has 0.15% of a hydroxylamine salt added to prevent a 'cross-linking' phenomenon known as storage hardening, which causes an increasing viscosity during storage. The quantity of the raw gum elastomer used in 1995 was 6.3 million metric tons with an estimate of around 8 million metric tons by the year 2005 [9].

Vulcanized products made from NR have high mechanical strength and can be compounded to have excellent elasticity (ability to snap back to their original shape). NR has very good abrasion resistance which, with its low relative cost, makes it a significant choice for slurry pump liners and impellers as well as for tank linings. It has very good dynamic mechanical properties and is therefore used in tires, rubber springs and vibration mounts. It is one of the few elastomers (polychloroprene (CR) is another good example) that have high strength in gum vulcanizates (cured, low hardness rubber, containing no fillers), which, combined with NR's good resilience, makes the gum excellent for fine particle impact applications. An NR rubber gum vulcanizate has a very high elasticity, thus most of the kinetic energy of an impacting particle is converted into deformation of the vulcanizate which then releases the energy by returning to its original undeformed state.

It also has very good low temperature resistance, down into the region of -57 °C at which its stiffness shows a considerable increase (see glass transition temperature in sections 6.3.3 and 7.7). Its high temperature heat aging resistance limit for 'continuous' use is in the region of 75 °C. Inherent weather resistance provided by the raw gum elastomer is poor. Significant components of weather, from the rubber technologists point of view, are UV light and ozone. Addition of carbon black to a compound gives resistance to UV, antiozonants (see section 6.3.6) and waxes, and helps with ozone resistance. Ozone attack is of most concern for thin products and those that are subjected to stretching in service. Electrical insulation is very good and, like all elastomers, is dependant on compounding. Dilute mineral acid (although not oxidizing acids such as nitric) and dilute base resistance is good. Solvents follow the polarity rule (see section 6.3.1), thus resistance to petroleum oils is poor while resistance to alcohols (such as ethanol and methanol) and ketones (such as methyl ethyl ketone (MEK) and acetone) is much better. Synthetic polyisoprene (IR) has basically similar properties to those of its natural cousin and has a more consistent rate of curing and processing characteristics, at a presently slightly higher relative price.

2.3.2 Styrene butadiene rubber SBR for an emulsion; SSBR for a solution

SBR and SSBR are derived from petroleum oil. This applies to most elastomers, with the obvious exception of NR. SBR represents half of all synthetic rubber production, and is much consumed in tires, where it competes with and complements NR. There are many subgroups of the raw gum elastomer, depending on the method of synthesis of the polymer, such as whether it is solution or emulsion polymerized, and the ratio of the two major chemical building blocks styrene and butadiene. In comparison with natural and CR, gum vulcanizates made from SBR have poor mechanical properties. The raw gum elastomer must have reinforcing fillers (see section 3.3.7), such as carbon black, in order to attain good mechanical strength and the filler increases hardness at the same time.

The properties of SBR are broadly similar to NR, for chemical, solvent, and weather resistance. The upper temperature heat aging resistance limit is a little higher. The cost of the raw gum elastomer is low on the relative scale for elastomers in general and is comparable with NR.

2.3.3 Polychloroprene CR

The CR in the heading stands for chloroprene rubber, more popularly known as Neoprene. Like all of the synthetic elastomers, CR is available to the rubber chemist in a number of grades to aid in compound mixing (blending the raw gum elastomer with a number of other ingredients to make the rubber compound) and to emphasize certain properties, such as reduction of crystallization rate in the vulcanizate (see section 6.3.4). CR might be considered somewhat more specialized than the two previous elastomers since it has a measure of both oil and weather resistance. The oil resistance would only be considered moderate. CR has similar dynamic mechanical characteristics to NR, including good mechanical strength when it is compounded as a gum vulcanizate. CR has some ability to retard flame, which means that when a source of flame is removed, the burning polymer will have a tendency to self extinguish, (this can be modified to improve or unintentionally diminish this property), while NR, EPDM, and SBR for example, will continue to burn. Upper continuous heat aging resistance temperature limits are of the order of 90 °C. Like a number of elastomers this can be raised somewhat by special compounding.

It is common to see the word continuous used in the literature without reference to time of exposure (is it a month, a year, ten years?) and also there is no definition of what constitutes ultimate failure of the material. This state of affairs is also common in this book. A very recent American standard SAE J2236 [10] defines continuous upper temperature resistance as, the temperature at which the material retains a minimum of 50% of both original elongation and tensile strength at break after 1008 hours (6 weeks). This will be a good precision reference for engineers and chemists as laboratories submit their materials to this standard. Leaving this kind of precision behind, one suggested upper range for CR in air is 99 °C for 1,000 cumulative hours and 85 °C for 10,000 cumulative hours. Other sources put it at 91 °C for 1,000 cumulative hours and 85 °C for 10,000 cumulative hours. Ultimately, application conditions decide, also not too many laboratories do precision aging tests for 10,000 hours on rubber vulcanizates. At the opposite end of the temperature range, CR shows some stiffening at around -18 °C, becoming brittle around -40 °C, although this can be lowered using certain compounding ingredients. Resistance of CR to dilute acids and bases is better than that of NR or SBR, while cost is somewhat higher. One last point, certain grades of CR are produced specifically for the adhesives marketplace.

2.3.4 Nitrile NBR

To the chemist this rubber is known as acrylonitrile butadiene rubber, to others it is called Buna-N but to many people in the industry, simply, nitrile. It is the workhorse of the marketplace for its oil resistant properties. The grades offered differ in the percentage of acrylonitrile (ACN) in the polymer chain as well as the overall viscosity of the polymer. The higher the amount of ACN in the elastomer the better the oil resistance; the lower end of the ACN distribution range being approximately equivalent to the oil resistance of CR and therefore only having a moderate level of oil resistance. NBR also has superior fuel resistance. The terms oil and fuel used here refers loosely to those products derived from petroleum. The weather resistance of NBR is poor, similar to NR and SBR, although it can be enhanced by blending with the plastic, polyvinyl chloride (PVC), at some 'cost' to its low temperature properties. This latter attribute of NBR also varies with ACN content; the lower the percentage of ACN in the polymer, the better the low temperature flexibility, and the poorer the oil resistance. A compound which has a nitrile raw gum elastomer in it, with a medium (33%) ACN content, would have good oil resistance and low temperature resistance down to the region of -40 °C. A low ACN (18%) nitrile would be useful down to -55 °C. NBR has better heat aging resistance than CR and is in the region of 107 °C for continuous (defined approximately as 1,000 hours) use. Special compounding ingredients can be added to increase heat aging resistance. Like SBR, NBR needs reinforcing fillers to give good mechanical properties.

NBR use is dominant in the oilfield, used in blow out preventors, packers and seals. However, sour gas wells containing hydrogen sulfide and amine corrosion inhibitors have been a problem for NBR based components because both chemicals can degrade nitrile elastomers causing embrittlement. The other major use for NBR is in the automotive sector. However, as 'under the hood' temperatures increase with reduced airflow and smaller engine compartments, NBR producers are searching for ways of increasing this elastomer's upper region of heat aging resistance. The term sour gas is also used in automotive applications, but here it means hydroperoxides (rather than hydrogen sulfide), which sometimes form in unleaded gasoline; this can be damaging to the 'average' NBR. Very high ACN NBR or NBR/PVC might be used in this situation.

The use of alcohol (methanol and ethanol) in gasoline, the so called oxygenated fuels, has made NBR processors look very closely at the effect of such a mixture on this elastomer, since alcohol concentrations at a certain level (around 10%) could be a problem. The alcohol causes NBR in contact with the gasoline alcohol blend to swell significantly. Blends above 5% should be treated with caution unless a resistant rubber type is used. It is worth noting that many applications of NBR exclude contact with oxygen (from the surrounding air), since the product is immersed in oil. This can increase the heat aging resistance temperature mentioned above. NBR is a distinctly polar rubber (see section

6.3.1), hence its excellent resistance to non polar petroleum oils. This also means that NBR has poor resistance to polar liquids such as ketones, esters, chlorinated solvents, and highly aromatic solvents such as benzene and toluene.

2.3.5 Ethylene propylene rubber EPM and EPDM

EPM is a copolymer consisting of ethylene and propylene units as part of the main polymer chain. It can be cross-linked with peroxides or radiation but not sulfur. EPM is used as an ethylene based plastic impact modifier and as a viscosity index improver for lubricating oils.

When a non-conjugated diene is grafted on to the main polymer chain it becomes a terpolymer, ethylene propylene diene (EPDM) and interchain sulfur cross-linking becomes possible. The names ethylene and propylene sound familiar because of their use in polyethylene and polypropylene (plastic) goods such as kitchenware. The chapter on chemistry and physics (see Chapter 6) will explain how they can be individually a plastic or, when combined at the molecular level, a rubber. Raw polymer suppliers offer the usual viscosity variations plus different ethylene/propylene ratio grades. A higher ethylene content gives more green strength (high elongation in the uncured state) which can help the rubber processor in the mill mixing. However, a high ethylene content gives poorer low temperature properties. Raw polymer manufacturers use a variety of diene monomers unit grafted on to the main polymer chain, which, amongst other things, allows variation in the ease of vulcanization, depending on the unit chosen and the amount in the polymer.

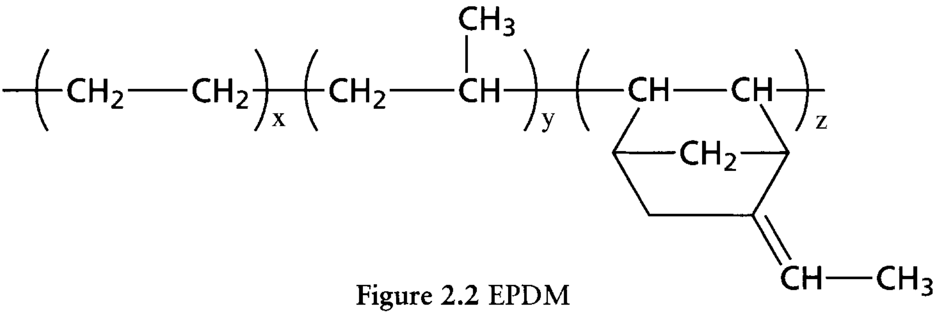
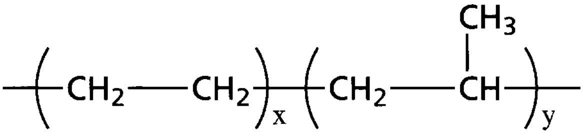


Figure 2.2 EPDM



$$-\left(CH_2-CH_2\right)_x\left(CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}\right)_y-$$

Figure 2.3 EPM

EPDM is largely unaffected by weather with very good resistance to ozone. Dupont literature [11] quotes EPDM products which were exposed to 10,000 parts per hundred million of ozone for 1,000 hours in air, at room temperature, without cracking. Raw gum elastomer manufacturers' literature [12, 13, 14, 15] indicate upper 'continuous' heat aging temperature limits in air, anywhere from 126 °C to around 150 °C. Introducing time into this equation, one scenario might be: one cumulative month at 165 °C, one cumulative year at 125 °C, and five cumulative years at 100 °C. This would depend on a number of variables such as avoiding a very high percentage of fillers, choice of antioxidants, and level of unsaturation in the raw gum elastomer.

Low temperature flexibility is very good and compares well with NR, and like NR and SBR, EPDM (with a lower polarity than NR) has very poor oil resistance. The price conscious rubber compounder is aware of the low specific gravity of the raw gum elastomer, which means he gets more elastomer (volume) per unit weight (see section 3.4.4). Like many commodities, rubber raw materials are sold by weight, while the vulcanized product is not. Also useful to the compounder is the ability of EPDM to accept large amounts of filler and oil-based compounding ingredients, which can be lower in cost than the raw gum elastomer. Resistance to a number of concentrated mineral acids and bases is significantly better than that of NR or SBR.

The use of EPDM is dominant in roof membrane linings and extruded channels for windows because of the above properties. EPDM has also been used as a blend with NR in tire sidewalls to improve resistance to cracking by ozone attack. The excellent electrical resistance of EPDM promotes its use in medium and high voltage cable covers. Its very good resistance to water absorption, combined with good mechanical properties and relatively low cost, make it a good choice for pond liners. Automotive applications of EPDM would include radiator and heater hoses and weather strips. Metallocene catalyst systems have recently been applied to the polymerization of EPDM [16, 17]. This new technology promises high precision in the control of the molecular architecture within the polymer. This, as with all elastomers, translates to highly consistent processing of the uncured compound and consistency of its final cured properties.

2.3.6 Butyl rubber IIR and halobutyl rubber CIIR and BIIR

Butyl rubber is a copolymer of isobutylene and isoprene, hence IIR. Its grades vary in isoprene content and viscosity, which is related to molecular weight. If a halogen, such as chlorine or bromine, is introduced into the polymer architecture, it becomes CIIR or BIIR, respectively.

IIR has some properties similar to those of EPDM, such as good mineral acid and base resistance (like EPDM some concentrated mineral acids are a problem), and weather resistance which is similar to that of EPDM. IIR has excellent resistance to permeability by gases. For example, Fusco [18] mentions its permeability to air being as low as 10% that of NR, at 65 °C. Like EPDM, the polarity (see section 6.3.1) of IIR is low which means poor resistance to petroleum oils and conversely low swell in many polar solvents, such as ketones. Resilience is poor, which translates to good damping ability. The upper continuous heat aging temperature limit is around 121 °C, which can be distinctly improved with IIR compounds containing resin (polymethylol-phenol) cure systems. For low temperature properties the vulcanizate becomes stiff and leathery at around -18 °C, although it is not brittle until around -70 °C.

Applications naturally following from these properties include mounts and bumpers for vibration and shock prevention, roof and tank linings, curing bladders and inner tubes for tires. A significant use is inner liners for tubeless tires, where halobutyl is preferred due to improved interply adhesion with the rest of the inner tire. Halobutyls can be blended with unsaturated elastomers such as NR, whereas for IIR it is not recommended (see section 3.4.2). Blending is not recommended for IIR since the rate of cure of the 'other elastomer' in the blend is often much faster than the rate of cure of the IIR, resulting in undercured IIR in the blend. IIR and halobutyl are used for pharmaceutical closures using high purity zinc oxide as the curative. Zinc oxide, is 'generally regarded as safe' by the United States Food and Drug Administration, i.e., has historically been in common use in contact with food or skin for many years without ill effect.

Recent elastomer modifications (from Exxon) are *p*-methylstyrene/isobutylene copolymers, which have the low permeability and high damping of IIR with the environmental and aging resistance of EPDM, and 'star branched' butyls, which have improved processing properties, prior to cure.

2.3.7 Silicone rubber MQ MPQ MVQ and MPVQ

As you can see, a number of symbols have been designated for significant variations within the silicone rubber family. The reader may refer to ASTM D 1418 [19] for abbreviations for elastomeric materials. Since all of the symbols for silicone rubber end in Q, this is the convention that will be used for silicone rubber in general, in this book.

Most elastomers have a carbon main chain, while Q has a silicone oxygen backbone. Silicone has an upper continuous heat aging temperature in the region of 205 °C. Caprino and Macander [20], give a table of estimated service life for Q as follows: 40 years at 90 °C, 2-5 years at 200 °C and two weeks at 315 °C. Moisture, such as might be found in a poorly ventilated environment, can be a problem at high temperature [21]. Silicone is among the best elastomers for both high and low temperature resistance. PVMQ heads the low temperature list at around -100 °C. Silicone rubber has excellent ozone, weather resistance and electrical insulation. Like CR, Q has a measure of flame retardant ability. Mechanical properties such as tensile strength, are low, but change very little when measured at higher temperatures; at 150 °C, it is catching up with other elastomers [22, 23]. Oil resistance is about the same as that of CR; acid and alkali resistance are not good. Applications include aerospace, medical, food contact, and automotive ignition cable. The cost of the raw gum elastomer is higher than any of the rubbers mentioned so far.

2.3.8 Hydrogenated nitrile HNBR (HSN)

This is a relatively new elastomer, making its first appearance in 1984. The symbol for the generic material is HNBR, although HSN is sometimes used in literature, standing for highly saturated nitrile. A chemical explanation for its special properties is found at the end of section 6.3.6. It has all the attributes of NBR plus a very much higher heat resistance, dependent on the grade chosen. It also has very good weather and abrasion resistance, plus good mechanical strength. It is used in oilfields where it has resistance to amine corrosion inhibitors and better hydrogen sulfide resistance than NBR. It has established itself in automotive applications for timing belts, gaskets and O-rings, where higher temperature resistant elastomers are needed. Peroxide cured HNBR has heat aging resistance up to 150 °C, based on around 1,000 hours, while sulfur donor cured (see sections 3.3.4 and 6.2.1) HNBR temperature resistance might drop to 135 °C. Cost is somewhat less than conventional fluorocarbon rubber (FKM) on a weight basis, also since the density (using g/cm^3, which approximates to specific gravity) of HNBR is about half that of FKM, more products can be made for the same weight purchased (see section 3.4.4).

2.3.9 Fluorocarbon rubber FKM (FPM)

In the United States fluorocarbon rubber is well known by its trade name of Viton (for other trade names see section 2.4). Based on vinylidene fluoride and hexafluoro-propylene the grades available differ in the chemical building blocks which were used to construct the polymer. Like silicone rubber, FKM has excellent high temperature resistance with an upper continuous heat aging temperature limit of 205 °C. DuPont literature [24] quotes continuous dry heat service to be >3,000 hours at 232 °C decreasing to >48 hours at 316 °C.

At the opposite end of the scale Nagdi [25] points out that conventional FKM is usually serviceable at temperatures down to -20 °C in dynamic applications, while for static use the temperature can be lower, although this will depend on the grade chosen. A primary variable in FKM grades is the level of fluorine in the elastomer molecule, FKMs being fluorohydrocarbons. Terpolymers tend to have a higher fluorine content than copolymers and therefore have better resistance to various media. In general, fluoroelastomers have excellent resistance to oxidation, ozone, fuels and petroleum oils and are resistant to most mineral acids at high concentrations. Although FKM has good resistance to many chemicals, excessive swelling occurs in some polar solvents such as low molecular weight ethers, esters and ketones. Chemicals such as alkalis and amines should be used with caution, with standard fluorocarbon grades, especially at higher temperatures because alkalis harden the general purpose FKM, which will eventually embrittle and then crack.

FKM has a tendency to self extinguish when a flame is removed. This is of benefit in situations where the results of a fire would be catastrophic, for example in a coal mine. Other elastomers might burn out of control, when the source of the originating flame (such as methane gas explosion) is removed. Applications for FKM include automotive fuel hose liners and seals and flue duct expansion joints, where high temperatures and acidic products from gas desulfurization are involved. The relative cost of FKM is high, more than any of the elastomers mentioned so far, also a high specific gravity (around 1.8) means less cured product (volume) per unit weight A recent addition to the FKM family is an 'alloy' of a polar ethylene copolymer with a fluoroelastomer [26] which optimizes cost, oil and heat resistance.

2.3.10 Aflas TFE/P

This is a copolymer of tetrafluoroethylene and propylene. It is a fluoroelastomer and has many of the attributes of FKM. Aflas has generally better resistance to both high temperature steam, and bases such as amines and concentrated alkalis, but poorer resistance to benzene and chlorinated solvents than conventional FKM [27]. Elastomers with a chemistry combining that of Aflas and FKM are available. Aflas has a specialized, small market consisting primarily of oil seals for the automotive industry, wires and cables and oilfield drilling (downhole).

2.3.11 Kalrez FFKM

To the chemist this material is a copolymer of perfluoromethyl vinyl ether and tetrafluoroethylene. The latter monomer is better known in the plastic material polytetrafluoroethylene (PTFE; Teflon is an example). FFKM (Perfluoroelastomer) has a chemical resistance close to the outstanding levels reached by PTFE. Its upper continuous dry heat aging temperature is about 260 °C [28]. Applications are those where all other elastomers are unsuitable. In terms of properties (chemical and heat resistance) FFKM is the closest thing to a universal elastomer. FFKM can be used for highly critical oilfield parts and in the chemical industry for parts which have to stand up to highly corrosive chemicals and extreme temperatures. The price, relative to other elastomers is extremely high [29] and molding of Kalrez compounds is usually performed by specialists.

2.3.12 Other elastomers

- *Polybutadiene rubber BR*

Although this is a significant elastomer it is most commonly used as a blend with other rubbers. Grades are very much dependent on the architecture of the repeating unit in the polymer chain [30]. BR is traditionally difficult to process on rubber machinery; this difficulty is not apparent when BR is blended with other non polar elastomers such as NR.

BR vulcanizates confer high resilience, therefore low heat build up, and good abrasion resistance to blends with other rubbers (its resilience is excellent and it has a low temperature flexibility second only to silicone rubber). In view of the above properties its major application area is in tires. Other applications are golf ball centers, modification of polystyrene to make high impact polystyrene and miscellaneous products needing improvements in abrasion, low temperature and resilience.

- *Polyacrylate ACM*

This family of polymers exhibit oil resistance. Their heat aging temperature limit is between 150 °C and 175 °C. The major application areas are automotive engine and transmission seals, gaskets and O-rings. The low temperature properties are not good, although some grades are flexible to -40 °C.

- *Epichlorohydrin ECO CO and GECO*

These halogenated polyethers are available in three forms: a homopolymer (CO), a copolymer (ECO) and a terpolymer (GECO). Attributes found within this group are: extremely low gas permeability, good oil and ozone resistance, and a good low and high temperature range. The high temperature performance is better than that of nitrile. They are used for automotive air ducts, fuel line hose tube and cover and some oilfield applications.

- *Chlorosulfonated polyethylene CSM*

Best known as Hypalon this material has excellent ozone, acid, and weathering resistance together with mild oil and heat aging resistance. It is used extensively for roofing, pond liners and applications needing resistance to strong mineral acids.

- *Polynorbornene*

This rubber has an extremely high molecular weight, allowing it to absorb from 150 to 300 phr of plasticizer and still retain good physical properties in very low hardness compounds. It is used for soft feed rolls for copiers and as the tread for dragster tires.

There are a number of other significant raw gum elastomers which have not been mentioned, such as polysulfides with their excellent solvent resistance, since the objective is simply to give a taste of the variety available. One recent material is a terpolymer of styrene, isoprene and butadiene (SIBR). This is exemplified in Goodyear's solution polymerized Sibrflex. There are many excellent books detailing specific elastomers, such as Hofmann's 'Rubber Technology Handbook' which contains a very exhaustive listing [27].

There are also a number of elastomeric materials, most of them of relatively recent origin, which melt like plastics whose role in rubber products continues to grow. They are called thermoplastic elastomers (TPE). It is not possible to deal with these in any great detail here. Information on TPE is available in references [31, 32, 33, 34, 35]. Terminology for thermoplastic elastomers is found in ASTM D 5538 [36].

2.4 Trade names

The following, Table 2.1, is a listing of just a few elastomer types, and some trade names, mainly American and European. For a detailed list, including grades, please see reference [37]. See also ISO 1629 [38] and ASTM D 1418 [19].

Table 2 1

Symbol	Generic name	Some trade names	Company
SBR	**Styrene butadiene rubber** Emulsion	Copo Cariflex Ameripol-Synpol	DSM Elastomers Shell Ameripol Synpol
SSBR	Solution	Duradene Soloflex Solprene	Firestone Soloflex Housmex
CR	**Chloroprene rubber**	Neoprene Baypren Denka	DuPont Dow Elastomers Bayer Denki Kabushiki Kaisha Kagaku Kogyo
NBR	**Nitrile**	Nipol Krynac Paracril Chemigum Perbunan N Nysyn	Zeon Bayer Uniroyal Goodyear Bayer DSM Copolymer

Table 2.1 *Continued*

Symbol	Generic name	Some trade names	Company
EPDM	**Ethylene propylene diene rubber**	Buna EP Nordel Vistalon Royalene Keltan	Bayer DuPont Dow Elastomers Exxon Uniroyal DSM Copolymer
IIR CIIR BIIR	**Butyl**	Exxon Butyl Polysar Butyl	Exxon Bayer
MQ	**Silicone elastomers**	Elastosil Silopren	Wacker Chemie Bayer FKM (FPM)
HNBR	**Highly saturated (*hydrogenated*) nitrile**	Zetpol Therban	Zeon Bayer
FKM	**Fluorocarbon**	Fluorel Viton Tecnoflon	Dyneon DuPont Dow Elastomers Montedison
BR	**Polybutadiene rubber**	Taktene Budene Diene Solprene Intene Buna	Bayer Goodyear Firestone Negromex EniChem Hüls GmbH
ACM	**Polyacrylate**	HyTemp Europrene AR	Zeon EniChem
ECO	**Epichlorhydrin ethylene oxide**	Hydrin C	Zeon
CSM	**Chorosulfonated polyethylene**	Hypalon	DuPont Dow Elastomers
EAM (EVM)	**Ethylene vinyl acetate**	Levapren	Bayer
AU	**Urethane (ester)** (see chapter 8)	Urepan Millathane Vibrathane	Bayer TSE Industries Uniroyal
EU	**Urethane (ether)** (see chapter 8)	Millathane Adiprene Vibrathane	TSE Industries Uniroyal Uniroyal

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3 The Basic Rubber Compound

"Tell me" ...said Andrew. *"Is the rubber compound more alchemy than science?"*

"Well" ...answered Debbie. *"It's more like a cake mix. You start with just the right blend of many ingredients which are designed to be processed smoothly during mixing and to take the correct shape in the mold when heat is applied, and then you produce a satisfied customer when he eats it."*

"So maybe it is a blend of art and science?' ...persisted Andrew.

3.1 Introduction

The rubber compound was first developed by Goodyear and Hancock and it continues to develop as new materials and new variations on old ones appear in the marketplace. The compound we see everyday as rubber, such as in a tire or pencil eraser, is a mixture of a number of different ingredients. It starts with the raw gum elastomer, supplied by the plantation owner as NR, or by the petrochemical complex converting petroleum products such as ethylene, propylene and butadiene into 'raw' bales or chips of rubbery polymers such as EPDM, BR, SBR, NBR or CR. It is shipped to the rubber processor who blends it with various ingredients. The raw gum elastomer itself has very limited use, although adhesives provide one example. Most are mechanically weak and subject to significant swelling in liquids, and will not retain their shape after molding. Many of its other properties could also benefit from enhancement. It is at this point that the rubber compounder takes over, and all of his art and science is dedicated to modifying the raw gum elastomer, changing it into a more useful material.

3.2 The basic compound formula

The specific formulation in Table 3.1 has 100 parts of raw gum elastomer and 160.15 parts of total material. After curing for 35 minutes at 140 °C its vulcanized properties are indicated as 57 IRHD, with a tensile strength of 30 MPa and elongation at break of 645%. The specific formulation and properties are taken from 'The Natural Rubber Formulary and Property Index' page 32, published by The Malaysian Rubber Producers Research Association (MRPRA)

Rubber chemists use the term phr (parts per hundred rubber), meaning parts of any non-rubbery material per hundred parts of raw gum elastomer (rubbery material). They prefer this rather than expressing an ingredient as a percentage of the total compound weight. Parts can mean any unit of weight (kg, lb, etc.) as long as the same weight unit is used throughout the formulation.

3.3 Raw materials

The compound formulation in Table 3.1 is a typical one in the rubber industry for most unsaturated (sulfur cross-linked) elastomers (see section 6.1). The following sections consider each ingredient individually.

3.3.1 Raw gum elastomer

This is the key ingredient (the one which is actually cross-linked) on which depend many of the properties of the final product. It is therefore always at the top of the formulation list and is expressed as 100 parts by weight of the total recipe. Thus, in the formulation in Table 3.1, for a 100 kg of raw gum elastomer there will always be 5 kg of zinc oxide.

Table 3.1

		Specific Formulation	
Material	**phr**	**For Example**	**phr**
Raw gum elastomer	100	SMR 20	100
Sulfur	from 0 to 4	Sulfur	0.35
Zinc oxide	5	Zinc oxide	5
Stearic acid	2	Stearic acid	2
Accelerators	from 0.5 to 3	MBS	1.4
		TMTD	0.4
Antioxidant	from 1 to 3	HPPD	2
Filler	from 0 to 150	N330 Black	45
Plasticizer	from 0 to 150	Aromatic petroleum oil	4
Miscellaneous		None	
		TOTAL	**160.15**

phr is defined as parts by weight of ingredient per 100 parts of raw gum elastomer.
The limits given are typical examples and are not intended to be absolute values.

3.3.2 Sulfur

It is interesting to note that sulfur is still by far the most used cross-linking agent in the rubber industry since its use by Goodyear and Hancock. Sulfur was known in archaic times as brimstone, and mentioned as an agent of divine retribution in the Bible [1]. It reacts chemically with the raw gum elastomer forming cross-links between the polymer chains, resulting in a more dimensionally stable and less heat-sensitive product. Its cost is relatively low but its function is essential. It is available in different particle sizes (fineness) as rubbermakers sulfur, and can also have a small quantity of oil added to reduce its dust in the air during handling. Rubbermakers sulfur is sulfur suitable for vulcanizing rubber; it has a low ash content, low acidity and sufficient fineness for adequate dispersion and reaction. The finer particle sizes, coated with magnesium carbonate, assist its dispersion in elastomers such as nitrile. Sometimes, as the sulfur level in a compound is increased, some of it can slowly bloom to the surface. For example Heinisch [2] mentions that sulfur levels as low as around 1 phr (at room temperature) might bloom. Blooming occurs if an additive dissolves totally in the polymer at the processing temperature but is only partially soluble at ambient temperature. In this situation some of the additive precipitates out of solution on cooling collecting on the surface of the polymer mass, causing a bloom. In this case, a highly 'polymeric' (amorphous) form of sulfur, known as insoluble sulfur, is available to reduce this problem, although dispersion in the compound can be more difficult. Although bloom does not generally affect a product's performance it is aesthetically displeasing. In the uncured compound bloom can reduce tack needed in building operations (such as plying up uncured sheets of rubber to obtain thicker sheets).

3.3.3 Zinc oxide and stearic acid

These two materials, together with sulfur and accelerator, constitute the 'cure system' for the formulation. Zinc oxide reacts with stearic acid to form zinc stearate (in some cases zinc stearate is used in place of zinc oxide and stearic acid) and together with the accelerator they speed up the rate at which sulfur vulcanization occurs. With sulfur alone, the curing process might take hours. With this curing system, it can be reduced to minutes.

3.3.4 Accelerators

The accelerator (not to be confused with a catalyst, which remains fully available at the end of a chemical reaction), is usually understood to mean an organic chemical, and as the name implies, it speeds up the rate of vulcanization. There are many accelerators available to the rubber chemist, grouped into several chemical classes. Some have a built in delay time, so that when heat is applied to the compound at the beginning of the curing process, no vulcanization (cross-linking) takes place for a specified initial period of time. They are appropriately called delayed action accelerators. An example would be the sulfenamides. This delay is highly beneficial if a compound takes a long time to completely fill a cavity in a heated mold. Sometimes, only a very short induction (delay) time is needed, and the dithiocarbamates provide this. Occasionally an accelerator with a slow rate of cure might be needed, such as the guanidines, or maybe a fast cure as given by the thiurams and dithiocarbamates.

Some accelerators are able to provide sulfur from their own chemical structure, so that the need for elemental sulfur might be reduced or eliminated in the formulation. They are called sulfur donors, and examples are tetramethylthiuram disulfide (TMTD), and dithiodimorpholine (DTDM). Sulfur donors provide monosulfidic cross-links which impart improved compression set and heat resistance (see section 6.2.1).

The rubber compounder also needs to consider the shelf life of chemicals during storage of the raw material prior to compounding; for example sulphenamide accelerators [3], are sensitive to high humidity levels, the presence of which will reduce shelf life. The accelerator story can get quite interesting, with variations in amount used and blends of different types, to get just the right amount of processing safety (protection from premature scorch), speed of cure (time is money) and final state of cure (which affects final properties). The cost of the accelerator also needs to be considered.

The type of elastomer chosen can dictate both the type and amount of accelerator used. For example EPDM, with few double bonds (double bonds are used for cross-linking) needs 'faster' curing accelerators to permit a reasonable state of cure. SBR needs a higher level of accelerators than NR.

The following is a summary of some typical chemical classes of accelerators available to the rubber chemist. When a level of scorch (see section 5.3.1) and cure are mentioned it refers to vulcanization temperatures of around 140 °C.

Dithiocarbamates	Example: Zinc dibutyl dithiocarbamate (ZDBC). Very scorchy and very fast curing. Useful in low temperature (down to 100 °C) vulcanization and in elastomers with low levels of unsaturation such as EPDM. Note that as temperature reduces scorch increases and cure rate decreases.
Thiurams	Example: Tetramethylthiuram disulfide (TMTD). Somewhat less scorchy than dithiocarbamates and fast curing. TMTD is less scorchy in the absence of sulfur. In this case its function would be that of a cross-linking agent rather than an accelerator. Tetramethylthiuram monosulfide (TMTM) gives good compression set.

Thiazoles	Example: Mercaptobenzothiazole (MBT). Moderate cure rate and scorch giving a low modulus (see Chapter 7) vulcanizate.
Guanidines	Example: Diphenyl guanidine (DPG). Scorchy and slow curing. Most often used in combination with other accelerators.
Sulfenamides	Example: *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS). Long scorch with medium to fast cure. It would be a good choice when mixing compounds containing reinforcing furnace blacks (see section 3.3.7) which generate more heat. The sulfenamide *N,N*-dicyclohexyl-2-benzothiazyl sulfenamide (DCBS) gives longer scorch and slower curing. DCBS gives excellent adhesion when bonding brass coated steel to rubber, for example in tire production.

A good overview on curing and accelerators is found in reference [4]. Standardized symbols for various accelerators are found in ASTM D 3853 [5].

3.3.5 Other cross-linking systems

- *Peroxides*

Peroxides are suitable for curing rubber but are not recommended for some elastomers such as IIR or CIIR. Peroxides can be used to cure many elastomers, since, unlike sulfur, they do not need unsaturated bonds (see section 6.1) in the polymer. Thus they may be used to cure ether-type polyurethanes, certain fluoroelastomers, silicones, and all of the previously mentioned saturated elastomers. Peroxides can also be used to cross-link CR.

Although not nearly as popular as sulfur, peroxides have a distinct place in rubber compounding, and are a major curative for silicone rubber. In the basic rubber compound formulation, the zinc oxide, stearic acid, sulfur and accelerator can all be replaced by a single material, the peroxide. Some care must be taken in compound formulation, to avoid unwanted interaction with peroxide. This applies, for example to antioxidant selection. Contact with oxygen (air) should be avoided during vulcanization (such as in hot air ovens or autoclave curing). Some ingredients, which are not part of the cure system, which are common in sulfur systems can interact with the peroxide in peroxide cure systems and thus interfere with cure. Use of peroxides as curing agents can confer some advantages. First an improvement in the heat aging resistance of the vulcanizate, thus upper temperature limits can be pushed up a little or the lifetime extended. Compression set (see section 5.4.5) is also improved. On the other hand, tensile strength, tear strength, and fatigue (dynamic deformation such as constant flexing) life are reduced. A post cure (continued cure outside of the mold) is sometimes undertaken with peroxide cured vulcanizates, to complete the cure and remove unwanted byproducts.

The cross-link density of a peroxide cured compound can be increased by addition of chemicals called coagents, of which methacrylates are a good example. This results in a higher state of cure with improvements in properties such as compression set.

• *Electron beam curing*

It is possible to achieve some vulcanization of rubber with a beam of electrons. Although not widely used throughout the industry such a process has found a place in partially cross-linking components of tires, as an aid to tire production, using a radiation dosage of about four megarads [6]. Much higher doses would be needed to fully vulcanize even thin rubber sections. Work has been carried out on the post curing of an SBR compound with electron beams, with claims of a significant improvement in resistance to ozone and crack initiation [7]. Other references to electron beam curing are [8, 9, 10, 11].

• *Miscellaneous*

Sulfur is the classical cross-linking agent for unsaturated elastomers (see section 6.2.1), such as NR, SBR, NBR, BR, and EPDM. In some cases, such as halogen-containing elastomers, the preferred agent is a metal oxide. For example, CR is typically cured with a blend of the oxides of magnesium and zinc, which cure by removing some chlorine from the polymer chain. CIIR can also be cured with zinc oxide. For both elastomers organic chemicals are typically added to increase the cure. Fluoroelastomers and polyacrylates may be cured with certain amines, and alternatively with bisphenols.

3.3.6 Antioxidants, age resistors and antidegradants

In the human body free radicals (which play a part in the aging process) are neutralized by antioxidants (in the form of some vitamins). In the same way antioxidants are also necessary to protect other organic materials, such as most elastomers' from aging. Many vulcanizates become brittle when they age. Aging can be caused by the ravages of oxygen, accelerated by heat. Antioxidants are designed to slow down this process and can act as free radical scavengers. Like accelerators, there are many antioxidants available, grouped into a number of chemical classes. The chemist needs to be careful when choosing age resistors, for example, in light colored compounds or where the product comes into contact with a surface that can not tolerate a stain. The chemist also needs to be aware of the volatility of some antioxidants (a material is not much use, if it evaporates during high temperature mixing of a compound). Some antioxidants excel in applications involving a high level of flexing of the product (anti-flex cracking antioxidants). Antiozonants, such as the *p*-phenylene diamines, which provide sacrificial protection against ozone, are also important, and are often added to a compound. This chemical group also has very good antioxidant activity. ASTM D 3853 - 96a [5] contains standardized symbols for antioxidant chemical names. Classification of antidegradants is found in ASTM D 4676 [12]. An antidegradant is a compounding material used to retard the deterioration caused by oxidation, ozone, light or combinations of these.

3.3.7 Fillers

This section explains why so many rubber products are black. It is much more than just putting black color into them. While the cured raw gum elastomers of NR and CR are mechanically strong, most gums are weak when vulcanized and they need reinforcing fillers. As the term implies, there is a reinforcement effect, the empirical results of which are to increase mechanical strength (for example tensile strength and resistance to tearing) in the vulcanizate, and to increase stiffness. Addition of filler increases hardness of the cured product. All fillers are not created equal, so that there is a range of reinforcement from very high to very low, corresponding to the primary size of the filler particle, from around 10 nm for very fine particle carbon blacks giving high reinforcement, to greater than 300 nm for some calcium carbonates which give low reinforcement. Use of the latter reduces compound cost. The shape and surface chemistry of the filler particle also play an important part in reinforcement. Some popular fillers are, in order of decreasing reinforcement, carbon blacks and silicas, clays and then whitings (calcium carbonate, otherwise known as chalk).

• Carbon black

This is a material of major significance to the rubber industry, so it is no surprise that most rubber products we see in the market place are black in color. We have moved a long way from collecting carbon from smokey oil flames, which produced a material called lampblack. The next historical step was to burn natural gas against iron channels, then scrape off the carbon to produce a highly reinforcing material called channel black. Both the use of this black in the rubber industry and its source of supply is currently limited and its cost is somewhat high. There are two common methods of producing carbon black today. Heating natural gas in a silica brick furnace to form hydrogen and carbon, produces a moderately reinforcing material called thermal black. Alternatively, if we incompletely burn heavy petroleum fractions, then furnace blacks are produced. These are the most important blacks in terms of quantity used and available types [13, 14].

Carbon black consists of extremely small particles (from around 10 to 300 nm) in a grape-like aggregate [15]. This gives two primary properties allowing a whole range of grades designated by both a particular particle size (surface area) and a specific level of structure. The rubber compounder thus has a whole range of properties available to him. The American Society for Testing and Materials (ASTM) specifies generic codes for these grades (ASTM D 1765 [16]). Numbers after the letter N in this ASTM code relate to particle size but they do not relate to structure. For example, one such code name is an oil furnace black type called N110, which is a grade with a very small particle size (therefore highly reinforcing) and fairly high structure. An example of a thermal black type is N990. It has a large particle size, and low structure resulting in a much lower level of reinforcement but higher resilience.

For two carbon blacks with the same particle size, an increase in structure, as in changing from an N326 to an N341, can mean smoother and more dimensionally stable extrusions and calendered compounds.

A decrease in carbon black particle size (increase in overall surface area to volume ratio) increases the tensile strength of the cured vulcanizate. For example, Cabot Corporation literature [17], illustrates an SBR elastomer with 20 phr of oil. Its compound is adjusted to equal vulcanized hardness of 65 Shore A by adjusting the loading level of each black. It gives a tensile strength at break of around 17.9 MPa for an N550 black and about 22.8 MPa for an N347 black. Both blacks have approximately the same structure but the N347 has the smaller particle size, and therefore gives the higher tensile strength at break. Carbon black is also a powerful UV absorber and therefore will give a measure of protection against sunlight to the rubber. This is especially important for unsaturated elastomers such as NR and SBR.

• *Precipitated silica*

Silica is a material found in abundance, to the delight of small children (and some adults) building sandcastles by the sea. The story is told that the Venetian traders of long ago supported wood on blocks of soda ash (sodium carbonate) to build their fires on the beach. In the intense heat, the soda ash reacted with the sand (otherwise known as silica, or to the chemist, hydrated silicone dioxide) to form sodium silicate known to most of us as glass. Venetian glass became famous throughout the known world. Possibly less famous is the reaction of sodium silicate with sulfuric acid to turn it back to silica. There is one important difference, the resulting silica is precipitated out of solution as a fine particle and its amorphous nature does not have the same potential for silicosis associated with the finely powdered version of its crystalline counterpart.

The humble shoe sole probably marked the beginning of the use of silica in the rubber industry. Like carbon black, it reinforces raw gum elastomers, and by virtue of its white color, it does not impose a restriction on the color of the vulcanized products. Since silica is white, any color can be mixed in and be seen in the compound.

For some properties it has the edge over carbon black. For example, it improves the tear strength of the vulcanized product and also better heat aging is claimed [18]. However, it does not offer carbon black's wide range of grades. Precipitated silica can be associated with certain unusual processing and curing characteristics within the rubber compound. Stiff and 'boardy' uncured compounds may result from higher filler levels. Also, its addition to a rubber compound requires greater accelerator levels for adequate cure, although this situation is somewhat mitigated by addition of triethanolamine (TEA) or diethylene glycol. Recent introduction of chemicals such as organosilanes, added to the compound, produce a lower mixed viscosity and an improvement in mechanical and some dynamic properties. Although silica is more expensive than carbon black, there is a huge supply of the raw material in nature.

• *More about silica, including tires (green tires)*

One of the reasons for using precipitated silica in rubber compounds, known about for some time, is low dynamic heat build up, i.e., low hysteresis (see section 7.5). This property is very useful to automotive tire compound designers, and tire tread compounds are now designed to benefit from this low hysteresis, assisted by addition of precipitated silica to the compound without a loss of traction (resistance between the tire and the road surface) [19] usually associated with addition of carbon black. Lower hysteresis translates into lower rolling resistance of tires which means lower fuel consumption.

Since carbon black is presently the dominant filler used in tires, which are a very large market in the rubber industry, there is also no doubt that carbon black manufacturers are closely watching the silica 'competition' [20]. An 'all silica' tire opens up the possibility of green, blue, or other colored tires, although it should be remembered that carbon black gives automatic UV resistance.

Precipitated silica is microscopically a very porous material and also contains a variable amount of free and adsorbed water. Wagner [21] mentions the dependence of viscosity and cure rate of a compound on the moisture present in precipitated silica, and suggests addition of diethylene glycol or polyethylene glycol to reduce accelerator requirement and buffer the effects of variable moisture. Hepburn [22] suggests that the silica interferes with zinc-accelerator-sulfur complexes, retarding cure. Silica tends to agglomerate, so that high shear is desirable when a compound is being mixed, to break down these agglomerates. This is necessary for good reinforcement. Silicas which claim easy dispersibility have recently appeared in the marketplace.

• *Other fillers*

A specialized form of silica called fumed silica is very highly reinforcing, and is not easy to disperse in a typical rubber mix (very low bulk density). One method of producing this material is to burn a mixture of hydrogen, air and silicone tetrachloride. It is used with silicone rubber. At the other end of the reinforcement scale is ground calcium carbonate (known as chalk, limestone or whiting to the rubber compounder). The ground material is used as a low cost filler with no reinforcing properties. In its precipitated form it has some reinforcement. Another group of fillers are the clays which are naturally occurring hydrated aluminum silicates. The grades available are lower in cost than silica and reflect a choice of reinforcement (soft or hard). The soft clays have some reinforcing properties and larger quantities (than hard clay), a few hundred phr, can be added to a rubber compound. The hard clays confer a distinctly improved level of reinforcement than the softer version. Hard clay can be calcined (heated to remove water) to produce a product with superior electrical (insulating) properties. Organic chemicals, added as a surface treatment to the filler [23], can improve some properties. Other fillers available are aluminum hydroxide, coal dust, lignin, silicates and talc [24].

3.3.8 Plasticizers

Oils and other 'slippery' materials are called plasticizers (a somewhat vague term). ASTM D 1566 defines them as 'a compounding material used to enhance the deformability of a polymeric material'. Their function at low levels is to aid in the dispersion of fillers. At higher amounts they reduce uncured compound viscosity, often lower compound cost, reduce vulcanizate stiffness (hardness) and in some cases improve low temperature flexibility. They also improve flow in extrusion and molding by making the uncured compound less elastic and reducing viscosity and friction.

Petroleum oils are one of the major sources of plasticizers. These oils are divided into three chemical categories, aromatic, naphthenic and paraffinic. Morris [25] points out that the latter category gives better rebound resilience and lower hysteresis (see section 7.5), while aromatics are better for tensile strength and resistance to crack growth. It comes as no surprise that those elastomers which have little or no oil (petroleum) resistance are the ones most suited for compounding with petroleum oils.

For oil resistant elastomers such as NBR, liquid plasticizers such as esters (polar liquids) are used. Esters can also improve low temperature flexibility. A few elastomers can hold large amounts of plasticizer (and filler) without appreciable degradation of properties, for example EPDM and polynorbornene. Since a compound with large amounts of plasticizer can be difficult to mix, the compounder may purchase some raw gum elastomers with the plasticizer already mixed in (for example oil extended rubber). Chlorinated oils are used in some compounds to enhance flame retardation properties.

3.3.9 Miscellaneous materials

There are many miscellaneous materials which have been used in rubber compounds. For example, molybdenum disulfide and graphite to reduce the coefficient of friction in the vulcanizate, and blowing agents (to make a cellular product), such as benzenesulfohydrazide. Vulcanized vegetable oil (well known as Factice), a friable solid which is a reaction product of vegetable oil and sulfur, has a similar role to plasticizers. Process aids are materials added in relatively small quantities (a couple of phr would be sufficient in some cases), in order to assist in some aspect of compound processing. For example, phenolic resins or pine tar are added to some compounds to improve tack, while fatty acids or metal salts of fatty acids, are added to improve dispersion of fillers. A small quantity of low molecular weight polyethylene in CR compounds aids in reducing sticking to mill and calender rolls. There are also microcrystalline waxes designed to deliberately bloom to the surface of a vulcanizate to provide a measure of ozone protection in static applications. These waxes are no good in situations where the product is constantly being flexed (dynamic deformation), because the coating is broken, thus exposing the surface to potential ozone attack. That still leaves bituminous materials, titanium dioxide (inorganic pigment for white color), organic colors, ground walnuts and many more materials. One last thought: for those of you whose vulcanizates are plagued by termites, try phosphoric acid esters in the compound.

• Using recycled tires as a compounding ingredient

Used tires can be incinerated [26], they are an efficient fuel source for steam in the generation of electricity. High temperature burning means no black smoke, but keep in mind that some sulfur goes into a tire rubber compound. It is converted to sulfur dioxide during incineration. Scrubbers are available for removal of this gas.

Recycled tires can also be used in some rubber compounds. The process for making rubber reclaim from cured rubber has been known and used for over a hundred years [27], moving through successive refinements. In one method the rubber is ground up and digested with chemicals and high pressure steam in an autoclave to produce rubber reclaim, which is then sheeted off a mill. Cost is an inhibiting factor in this process. Reclaimed rubber has breaks in the primary elastomer chain and so is considered a useful compounding ingredient for less demanding product applications. Recent methods discuss breaking the sulfur cross-links [28], such that the primary polymer chain remains relatively undamaged, producing a potentially more useful material.

Another alternative, known as far back as the time of Charles Goodyear, is to grind the tires very finely and use the grindings (rubber crumb) as a compounding ingredient. Crumb is used for cost reduction and to help expel air during the rubber molding process for some rubber compounds. Ground rubber is used, as part of paving materials, for athletic courts and roads. Recent standards are being developed for ground rubber and related commodity trading [29]. The interest in finding a use for discarded tires has increased significantly in recent years, and the rubber industry is playing a part in reducing the 'tire problem' (which logically should also include longer lasting tires). Rubber & Plastics News [30] mentions that 266 million tires were scrapped in 1996 in the USA, of which 75% 'found their way into some market'. About 12.5 million tires were ground into crumb.

3.4 Compound design

It is quite a challenge to the rubber chemist, to produce the 'perfect ' compound out of the raw materials available to him. The number of possible permutations is immense. In order to design a compound, he must have the best understanding possible, of both the application of the product and the machinery used to process the compound.

3.4.1 Compound design for product application

If a product undergoes flexing the chemist might add a specific antioxidant that maximizes flex crack resistance, or he may choose a level of 2.5 phr of sulfur, to enhance the fatigue life of the vulcanizate. If low cost is a primary consideration, then large quantities of whiting and petroleum oil, combined with a general purpose raw gum elastomer might work. For extreme toughness and strength in an application, a compound might require a fine particle N110 carbon black.

3.4.2 Elastomer blends

A single raw gum elastomer in a compound might not give just the combination of properties required for a specific application. The following are a few examples of blends which may meet these needs.

1. To achieve a combination of strength and very high resilience, a blend of BR with NR could be used. An application for this would be the high bounce balls, used for example in shaker screen applications for sieving building aggregates. The rubber balls bounce to shake the material through a screen and thus prevent the screens from clogging up.

2. A truck tire might have a mix of NR, SBR and BR, to achieve a balance of abrasion resistance, cost, etc. Also different parts of the tire perform different functions and will need their own specific blend. For example, the tire sidewall can have EPDM blended into its compound.

3. For CR, if the full level of properties of CR are not required, it might be blended with SBR to reduce cost.

4. Interply adhesion in a hand fabricated NBR might require some CR blended into it to improve tack (the ability of one piece of uncured compound to stick to another).

5. A BR/NR blend might be needed for very low temperature flexibility.

6. EPDM mixed in with NR lends it some weather resistance.

7. For severe grinding operations after vulcanization, some NR compounds can become sticky, due to the high frictional heat of the operation. A blend of NR with SBR reduces this nuisance.

8. NBR blended with the plastic PVC (available premixed from suppliers), is used for weather resistance, but at some cost to low temperature flexibility.

The list is endless and is only limited by the knowledge and imagination of the compound designer.

3.4.3 Blending for cured hardness

ASTM D 2240 [31], ASTM D 1415 - 88 [32], ISO 48 [33], ISO 7267-1 [34], ISO 7267-2 [35]. For other standards relating to hardness, see section 5.4.2.

If a compound with a new vulcanized hardness is required, it is sometimes more convenient to blend two pre-existing compounds of different vulcanized hardness, rather than formulating and mixing a new compound. One reason for doing this might be to reduce total inventory.

The following example provides a rule of thumb for doing this:

Required hardness of vulcanized compound: 50 Shore A

Hardness of available compounds: 40 Shore A and 80 Shore A

Quantity of 40 Shore A material required = (80 - 50) = 30 parts

Quantity of 80 Shore A material required = (50 - 40) = 10 parts

Therefore, 30 kg of 40 Shore A material + 10 kg of 80 Shore A material can be blended to provide 40 kg of material of hardness 50 Shore A

Shore A and IRHD are approximately the same.

3.4.4 Processing

Even after the 'perfect compound' has been designed, providing just the combination of properties the customer needs, it may still have to be mixed, extruded, calendered or molded. If this is not designed into the original formulation, there could be major problems.

For example, a large quantity of oil in a compound formulation would reduce friction (some friction is essential to mixing) between other compounding ingredients' to such an extent as to make mixing very difficult even when the oil is added incrementally. Using an oil extended rubber (where the raw gum elastomer manufacturer blends in the oil), as a partial replacement for the oil might help.

A compound which is too elastic might produce an extrusion which is rough and difficult to control dimensionally, as it exits the extruder (many elastomers do have a measure of elasticity in the uncured state). Adding Factice may help, or a low Mooney (see section 5.3.1) raw gum elastomer could be tried.

Some formulations begin to cure so quickly that they do not have the chance to fully take the shape of the cavity in a mold before they begins to vulcanize. A delayed action accelerator should be used in this situation.

The 'novice' compounder may formulate a compound with a large amount of very highly reinforcing carbon black (say N110), in order to achieve high vulcanized strength and hardness requirements. One might then find, that due to the very high level of N110 in the formulation, it is incapable of being mixed. The shear forces during mixing would create a great amount of frictional heat and risk making the process uncontrollable. The resultant dispersion of carbon black in the compound could also be poor. Process aids, such as fatty acids might help here. Alternatively, a three-stage mix might be considered. Here some of the black is added in a first mixing and the balance after dumping the batch, cooling it and returning it to the mixing machine. The sulfur and accelerators are added in a third mixing operation. In this alternative, one needs to be aware that some raw gum elastomers are sensitive to the extra mixing (in effect extra mastication) resulting in lower uncured viscosity and lower cured modulus. As a last (or first) resort one might consider abandoning that particular formulation.

Focusing on the other end of the spectrum, if one is mixing a compound containing oil as a compounding ingredient to produce a very soft, low vulcanized hardness formulation, it might mix well but give lots of problems in later processing, for example during a compression molding stage. Its low viscosity, and consequent inability to expel air from the mold during compression may cause voids and 'air blisters' in the product. Replacing all (or part) of the oil with Factice and using a high Mooney raw gum elastomer might be beneficial. A possible further option is to consider adding some partially cross-linked elastomer, if available, making sure it is fully blended with the primary raw gum elastomer.

Compound formulation is often the art of compromise between properties, processing requirements, and cost. A more expensive ($ per kg), low specific gravity compound might make more cured parts (more volume) than a less expensive ($ per kg) high specific gravity material, and therefore might be cheaper in terms of $ per unit volume. Therefore the compounder must translate cost per kg of the raw materials in the compound into cost per unit volume, before he makes any assessment of 'cheaper' or 'more expensive'.

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4 Rubber Equipment and Its Use

"Look" ...said Charlie. *"I've just mixed this compound according to your instructions and it's too nervy so it won't extrude right, and the viscosity is too high, it's barely flowing in the mold, and if I were you, I would keep away from the shop floor manager for a while!"*

"Don't worry" ...replied Andrew. *"Just put it back in the Banbury and mix it for a couple of minutes: that will break up the raw gum elastomer a bit more, thus reducing the elasticity and soften it up at the same time."*

"Sure" ...exclaimed Charlie, *"very impressive; it gets quite hot in the Banbury, what happens when you lose all your scorch time?"*

"Oh," ...reflected Andrew.

4.1 Introduction

The rubber technologist's mixing department has bags of powders, drums of liquids and bales or granules or chips of raw gum elastomer. These are weighed out precisely, to match both the batch weight needed and the ratio of ingredients in the formulation. Machines are necessary to mix these chemicals, resulting in a finely blended, solid homogeneous mixture. In many cases, the compounder and process operator expend their energy reducing the elastic component of the uncured rubber compound, to help it process, and then increase that component again during vulcanization.

Mixing is accomplished using mills and/or internal mixing machines. The resulting compound is then preshaped by mills, extruders or calenders, to prepare it for vulcanization. The latter is achieved using molds (which further shape the product), autoclaves, and sometimes ovens. That just leaves finishing operations, such as removing flash (see section 4.6.1 for an explanation of flash), or maybe the grinding of rubber rollers (cured in an autoclave) to a finished dimension, and then packaging the product.

4.2 Mills

These were used at the beginning of the rubber industry and are still an essential piece of rubber processing equipment.

A mill consists of two horizontally placed hollow metal cylinders rotating towards each other (see Figure 4.1). The distance between the cylinders (mill rolls) can be varied, typically between 0.25 to 2.0 cm. This gap between the rolls is called a nip.

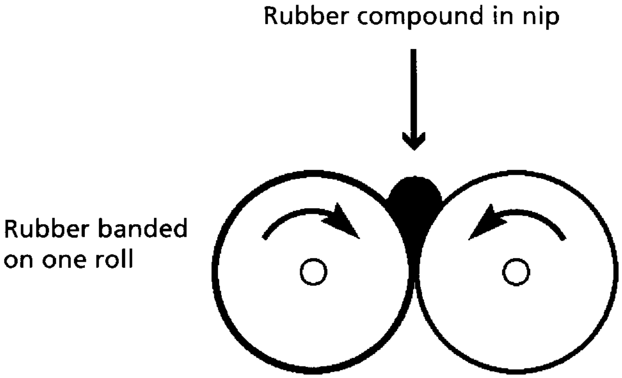

Figure 4.1 Conceptual view of rubber mill rolls
(courtesy of the Holz Rubber Company)

4.2.1 Operation

Raw gum elastomer is placed into the gap between the two mill rolls, the mill nip. It then bands, as a continuous sheet, onto one of the rolls. The speeds of the two rolls are often different, the back roll rotating faster than the front. The difference in speed between the two rolls is called the friction ratio and allows a shearing action (friction) at the nip to disperse the ingredients and to force the compound to stay on one roll, preferably the front one. A friction ratio of 1.25:1 is common. Powders, liquids, etc., are then added to the nip in a specific way (see section 4.2.3). The process produces friction which creates heat. This excess heat needs to be removed, either by spraying or flooding the inside of the roll with cooling water or by passing water through drilled channels in the wall of the roll.

A device is necessary to prevent the rubber from moving past the end of the rollers. This is accomplished by a piece of metal called a guide, positioned at each end of the roll, so as to almost touch the surface. At the beginning of the mixing process, pieces of material tend to fall off the mill rolls, so a tray (mill pan) is provided to catch them, to be swept up and returned to the rolls. When all the ingredients are completely blended (dispersed), rotating knives, in the shape of a disc, can be automatically applied to the rubber covered roll (this method can eventually cause scoring of the rolls), to take off one continuous sheet. Alternatively the operator can use a hand-held mill knife, and take off individual sheets.

A knowledge of safety procedures is critical to a mill operator, as with all rubber equipment, however only a very brief mention will be made here. Older production mills have a wire string or bar above the operator, while other mills have the bar in front of the millperson. When the bar is pushed, or the string pulled, roll rotation quickly stops. Safety standards stipulate the maximum permissible rotation of the roll after the bar or wire is activated. Some mills will throw the rolls into reverse.

The mill needs its own protection. This is commonly provided by driving motor overload devices. Also, if the compound exerts too much force in the nip, metal breaker plates deliberately break, allowing the rolls to quickly move apart and release the force, thus preventing more serious damage. These emergency devices are very useful if an unfortunate mill operator should quickly put an excessive amount of a ‘cold’ (room temperature), very stiff compound onto the mill.

4.2.2 Mill processing

The following description relates primarily to compounds which use sulfur as the cross-linking agent.

The key to mixing (in a Banbury mixer or a mill) (see Figure 4.2) is to maintain sufficient viscosity to ensure an adequate shearing action, to distribute the non-rubber ingredients into the raw gum elastomer, or to force the raw gum elastomer into the microscopic spaces of each filler particle. Both mechanisms have been hypothesized and one typical mixing sequence might be as follows:

The raw gum elastomer is placed into the nip and allowed to band onto the front roll. In the case of NR, it needs to move though the nip quite a few times to reduce its nerve (elasticity) and to lower its high viscosity (low viscosity grades are available). It then forms a smooth, more plastic, band on the roll. Normally most powders (other than accelerators and sometimes sulfur) are then added. If significant heat is produced, then cross-linking agents and accelerator addition will be delayed to the last part of the mixing process.

In some cases, when excessive heat is produced, it may be necessary to remove the compound from the mill before the accelerator is added, to avoid scorching (pre-vulcanization) (see section 5.3.1). The compound at this point is known as a masterbatch,

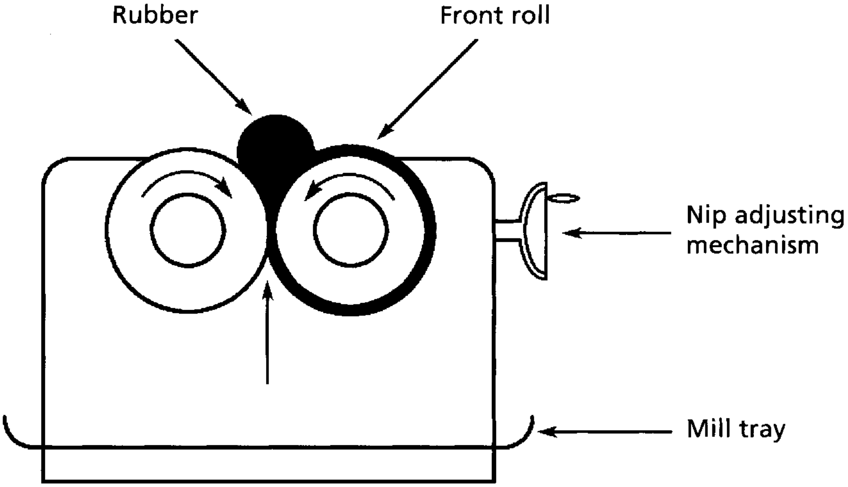

Figure 4.2 Mixing in a mill

defined in ASTM D 1566 as a homogeneous mixture of rubber and one or more materials in known proportions for use as a raw material in the preparation of the final compounds. The masterbatch is allowed to cool and subsequently returned to the mill for addition of the accelerator.

If the compound formulation calls for large amounts of fillers, it may be necessary to add small amounts of process aids with the filler to aid dispersion. Oils are then normally poured on incrementally (as are the fillers), after most of the fillers have been mixed in.

The art and skill of the mill operator plays a significant part in mixing. For example, he needs to know that some compounds based on CR tend to stick to the mill rolls, which require 'extra' cooling time to reduce this problem. The compounder also plays his part, in such a case, by adding waxy materials to the mix formulation to reduce this sticking. If the mill cooling is adequate and the temperature of the mix (frictional heat) is well below the level that would initiate vulcanization, then the cross-linking agent and accelerators can be added. During the mixing process, the mill operator uses a hand knife, at one end of the roll, to cut through the rubber, remove it, and place it in the nip at the other end, thus ensuring a homogeneous end-to-end blend. If no separate ingredients are visible, and the mixed compound is well blended, it can now be taken off in sheets or strips, cooled if necessary, ready for its journey towards a cured product.

These days mill mixing tends to be reserved for rubber compound development in the laboratory, or for small quantity production. Some companies prefer mill mixing, feeling that it gives superior control of dispersion and distribution of ingredients. However, the most common use of mills is in 'warming up' (by passing the room temperature compound through the mill nip a number of times) previously mixed rubber compound for immediate use in the next stage of the process, for example, calendering. In times gone by, the mill was associated with black powder (carbon black) or indeed any filler, 'flying around' the mill, settling on everything in sight, including the mill operator. Extraction systems above the mill have significantly reduced this problem, as has the move to the use of internal mixing machines.

4.3 Internal mixing machines

If the rolls of a mill are twisted to produce a corkscrew effect (they would now be called rotors), and then a block of steel is placed over the mill nip with the block connected to a steel rod above it, this would be called a ram. The ram would move up, to allow addition of ingredients to the nip, and it would move down to force the compound ingredients into the nip. If the whole thing is surrounded in a heavy metal jacket with a chute at the top to put ingredients in and a door at the bottom (underneath the rotors), to let the mixed material out, the result will be an internal mixing machine.

4.3.1 Operation

In 1916 Mr. Fernley H. Banbury, improved on an 'internal mixing machine' built by Werner & Pfleiderer [1] by designing the Banbury mixer. The Banbury mixer had modified rotors and the addition of a floating weight (see Figure 4.3). The internal mixer rapidly became an essential part of the rubber industry. At the present time, mixers are available in sizes ranging from those capable of mixing a kg or so, to those that can mix more than 500 kg per load, equivalent to many large mills. The internal mixer is faster, cleaner, (produces less dust from powdery materials such as carbon black, silica and clay), uses less floor space, and is probably less operator sensitive. It has thus displaced the mill for most compounding operations. However, the variable nip opening on a mill, plus immediate visual feedback of the state of the mix, allows a good mill operator a high degree of control and consequently dispersion.

The internal mixer has a fast mixing capability, from around two to ten minutes, and thus requires an efficient cooling system. This is provided by drilled channels in the walls of the mixing chamber, through which water passes to control the mix temperature. The rotors and discharge door can also be water cooled. The temperature of the compound being mixed is measured by a thermocouple in the side of the mixing chamber. Other parameters which can be measured and controlled during the mixing process are electrical power (amperage or watts) and time.

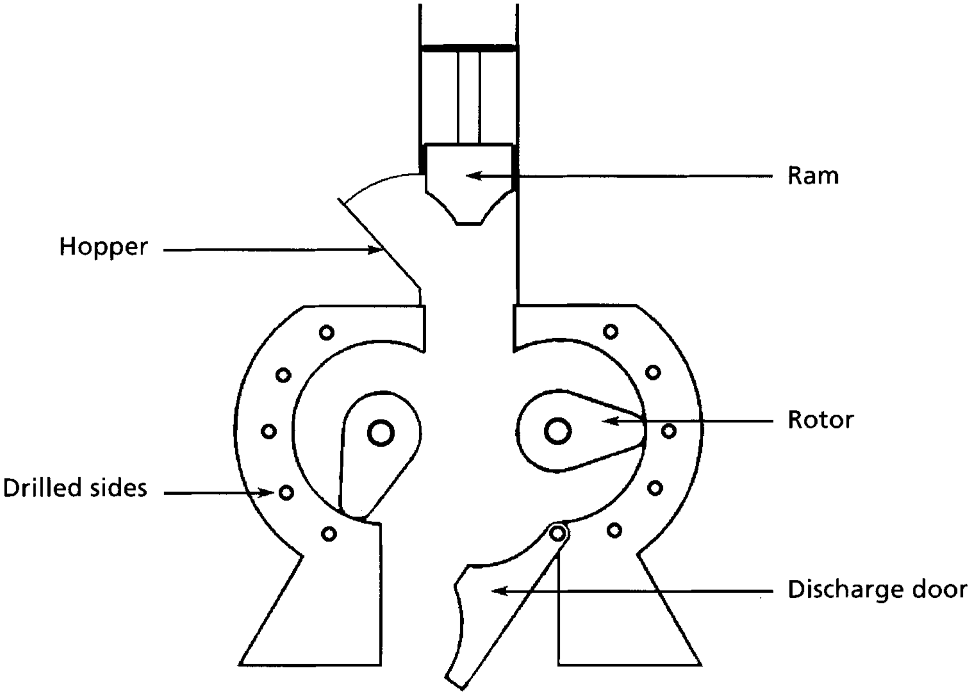

Figure 4.3 Conceptual cross-section through an internal mixing machine, with tangential rotors (*courtesy of the Holz Rubber Company*)

Raw gum elastomer is dropped through the hopper into the mixing chamber where it is mixed by the rotors. The ram, pressing on to the rubber mixture, is forced down by a pneumatically or hydraulically controlled cylinder, whose pressure is adjusted to give the best control of the mixing process. Oil may be poured in from the hopper, or injected through a valve in the hopper wall just above the mixing chamber. Mixing can occur between the rotors (intermeshing rotors) or between the mixing chamber walls and the rotors (tangential rotors), depending on the machine. The rotor to rotor, or rotor to wall, clearance is very important to correct mixing. Recent modifications are the Banbury ST rotors (synchronous technology) and Pomini's VIC (variable intermeshing clearance) design, where the distance between the rotors can be varied. Rotor design has recently been the subject of much research, using finite element analysis techniques (see section 7.11). The mixed rubber can be discharged from the machine, either by rotation of the whole mixing chamber or through a discharge door at the bottom of the mixer, depending on the machine design.

4.3.2 Processing

In this section, the mixing process will be discussed primarily with reference to unsaturated elastomers which are sulfur cured, unless otherwise stated.

The mixing principles are similar to those for the mill. One possible scenario is as follows: the raw gum elastomer is dropped into the hopper and the ram allowed to move down under pressure; the ram is raised for each addition of material and then lowered, to compact the mixture in the mixing chamber. When the rotors in the mixing chamber have masticated the raw gum elastomer so that it achieves a coherent mass, small quantity materials, such as antioxidants, zinc oxide and stearic acid, may be added.

For NR, the time taken to achieve coherence can be somewhat long, due to its high initial viscosity which needs to be reduced by mastication. Sometimes this involves a separate step, where the mixer is exclusively and completely filled with NR raw gum elastomer, which is worked to reduce its elasticity and increase its plasticity. It is then dumped from the mixer, and after resting, a portion of it is returned to be mixed with other compounding ingredients. Controlled, lower viscosity NR (such as SMR CV) is available which can eliminate this extra step.

Fillers are then added; large total amounts can be added incrementally and after most of the filler has been mixed in, any oil in the formulation may be then be introduced. If oil addition is delayed too long, the filler becomes totally ‘encapsulated’ by the elastomer and, the oil addition (especially larger quantities) can cause a loss of shearing action, resulting in a slippery mess in the mixing chamber (and an unhappy mixing operator).

During the mixing operation, feedback is received from the electrical power usage indicator, the temperature gauge, the time clock, and, for experienced operators, the sucking sound of the batch and the sound of the electrical motor driving the mixer. The noise of increased power from the motor is a happy sound for compounds with high levels of oil addition because it indicates that mixing is finally occurring. Often a particular temperature is chosen at which to complete the mixing process and dump the batch. Total time to mix the batch should correlate with this temperature. Since dump temperatures vary with heat transfer efficiency of the machine, the temperatures mentioned later in this section are only indicative. Upper temperature limits will be dictated by factors such as safety, for example exceeding the flashpoint of a plasticizer, and the risk of damage to the compound, for example scorch. Some rubber companies might use a value for total power consumed as an indicator to dump the batch.

Compounds with larger quantities of reinforcing filler can often reach temperatures over 150 °C by the time they are mixed. They would therefore be dumped from the mixer, often without sulfur and definitely without any accelerators (called a first stage mix or masterbatch), as otherwise the vulcanization process could commence in the mixer. The masterbatch would then be cooled, prior to being returned to the mixer for the addition of these materials, allowing the batch to be dumped at a final temperature closer to 100 °C.

Since the heat generated during mixing is often associated with reinforcing fillers, a compound without this raw material (or with some non-reinforcing filler) can reach full mixing (complete dispersion and distribution) at a much lower temperature than a compound with reinforcing fillers. This temperature will generally be comfortably below that needed to initiate vulcanization. Thus it may be feasible to experiment with adding the whole cure system in the first stage, i.e., as a single stage mix. This would be done with due regard to the required compound scorch time (see section 5.3.1) and plasticity of the mix for further processing.

For compounds with very high filler content such as a very high clay loading, the ram may plough through the clay like quicksand. Early addition of some oil is one solution, the idea being to bind the filler particles, thus increasing its coherence and encouraging shear.

Sometimes, a temperature of 150 °C may be too high for some heat-sensitive masterbatches. An example would be CR, where a dump temperature around 107 °C might be recommended, since the raw gum elastomer has the potential to show some curing activity without the addition of any other ingredients. For this elastomer, trace contamination of the mixing chamber with zinc oxide should also be avoided, (remember this is a curative for CR; see section 3.3.3). Also when the CR compound is dumped from the mixing machine on to a mill (see below), cool rolls are sometimes preferred to prevent possible sticking of the compound to the rolls.

For both mill and internal mixing, the proportions of ingredients must be exactly as the written formulation. Also, the internal mixer, unlike a mill, has a fixed volume mixing chamber and therefore only one particular total amount of ingredients is the correct one. The prediction of this amount is essential to successful mixing, and is not as straightforward as it first appears. The compounder calculates the total theoretical amount of ingredients for a batch, based on the specific gravity (or more precisely, density) of the ingredients and volume of the mixing chamber. This amount is then multiplied by a so-called fill factor, which is an empirical constant for that particular batch and mixing machine, and is dependent on a number of factors. Variables dictating the fill factor can be void spaces in the mixing chamber, the viscosity of the mix, the level of reinforcement of the fillers, the amount of filler and oil, and most importantly, the experience of the compounder and mixing operator. The fill factor is always numerically less than one, and can decrease significantly with higher levels of reinforcing fillers, and high viscosity raw gum elastomers. The result of this multiplication is chosen as the actual batch size to be used.

This represents only a glimpse of the art and technology of compound mixing, where the internal mixing machine strives to break down the size of solid ingredients (dispersive mixing) and distribute the particles evenly throughout the mix (distributive mixing). Its success is all the more important since, being at the beginning of the process, it affects all subsequent steps. The mixed compound drops under gravity from the mixer, usually onto a mill, where it is passed through the nip to cool the batch as quickly as possible, then banded onto the front roll. It is then either transferred immediately to the next operation, or taken off the mill as sheet, strip or a continuous length, and immediately cooled further to room temperature (for example by a water, anti-stick spray or dip) and stacked for future use.

4.4 Extruders

Extruders (see Figure 4.4) are conceptually a pump, consisting of a screw to move the material forwards, a barrel around the screw to contain the material, help it move, and provide part of the temperature control. The back end has a hopper, sometimes with feed rollers, to put rubber into the screw, and the front end has a 'head' to hold a die, through which the rubber extrudes.

An alternative to the screw extruder is the ram extruder, a well known trade name being Barwell. The ram extruder pre-dates the screw extruder, but it is still used in certain specialized applications. Here, the screw is replaced by a ram, which forces the material through the die. Since the process is discontinuous (a slug of rubber is placed in the

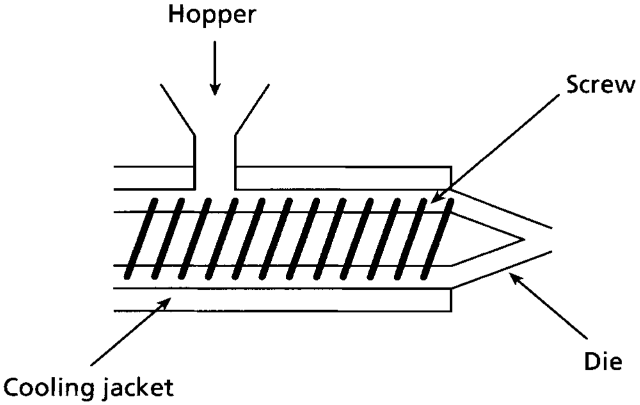

Figure 4.4 Conceptual view of a basic extruder
(courtesy of the Holz Rubber Company)

barrel, extruded, then another slug introduced), it is suited to making preforms for further use, such as placing into the cavities of molds. Thus a rotating blade is fitted in front of the die to chop the extrusion into volumetrically accurate preforms.

4.4.1 Introduction

Lambright [2] states that in 1845, extruders were used to cover wires with rubber (gutta-percha), which met the challenge of a waterproof electrical insulation for the newly expanding telegraphy. Extruders are used to make hose and general profiles such as window channels, coated wires, and preforms for further processing. They can also be used to produce sheet rubber, where a large extruder makes a tube, which is immediately slit, producing a continuous sheet.

4.4.2 Operation and processing

The system is designed to build up compression at the discharge end, to ensure consolidation of the material in the head. This can be realized in a number of ways, such as reducing the screw pitch towards the front. An important design variable is the ratio of the length to the diameter of the screw, the L/D ratio.

Extruders that use pre-warmed rubber compound, hot feed extruders, (pre-warming on a mill for example) use a small ratio, for example 6:1, while those using rubber compound at room temperature, cold feed extruders, need a larger ratio, for example 12:1. This longer length is needed since the initial part of the screw is used to heat up the compound. Some extruders have a vent from the screw cavity through the barrel to the outside, to allow the escape of any air trapped in the compound.

4.4.3 Die swell

The die is designed to avoid sudden discontinuities, as the compound moves through it and thus often has a contoured lead (entrance) section. As the extrusion exits the die, the extrusion can shorten in length and increase in cross section. This is known as die swell, which is dependent on die design, screw speed (i.e., shear rate), temperature and the compound's viscosity and its elastic component (see section 5.3.3). In practice, die swell can be quite complex and it might be necessary to modify the die a number of times, before the required extrusion shape is achieved. This recognizes that even uncured rubber has complex elastic and plastic behavior. Like an elastic band it can undergo elastic recovery on exiting the die. The chemist tries to formulate his compound to decrease uncured elastic behavior and increase plasticity. For example, he might do this by adding a material called Factice or other process aids to the formulation. Increased plasticity can also be achieved if the temperature of the compound moving through the extruder is progressively increased as it moves towards the die and it then becomes softer (lower viscosity) and more plastic. A very low hardness vulcanizate is often made from a low viscosity uncured compound. This can sometimes cause sagging of the extrusion before it is cured. If some of the raw gum elastomer in the compound is replaced by a partially cross-linked grade, then the firmness of the extrudate is improved. This helps control the extrudate dimensions. Such elastomer grades are available for CR, NBR, NR and SBR.

4.4.4 Recent extruder design

A problem with traditional extruders is the potential for reduced interblending of material as it moves along the screw. This causes uneven temperature distribution in the extrudate, which translates to a variable viscosity and therefore a continuously changing die swell. Layers of compound move along without intermingling, i.e., in laminar flow.

A relatively recent idea, introduced in the 1970s, is to introduce pins protruding from the inside of the barrel towards the screw. This breaks up the layers, mixes them, reducing thermal variation and increasing homogenization. Such a machine is known as a pin barrel extruder. An extension of this concept is described by Capelle [3], and is called a Pinconvert extruder. After a conventional pin section, there is a portion which has hydraulically adjustable pins protruding into a helically grooved liner on the inside of the barrel. This gives it a high degree of flexibility for controlling temperature and output. The device Capelle describes has an L/D ratio of 8:1, making it quite compact for a cold feed extruder. Capelle also mentions its use as a calender feed extruder.

An alternative concept is to introduce small bowl shaped cavities into the end section of the screw and the inside of the barrel. This creates turbulent flow in the cavities and therefore increased physical and thermal blending. Such an arrangement would be added onto the end of a standard extruder, and is called a cavity transfer mixer. This idea has been developed and patented by Rapra Technology Limited [4]. These concepts are most important in cold feed extruders running at higher speeds.

4.5 Calenders

A calender can be crudely thought of as a very high precision mill, with the rolls stacked on top of one another, with anything from two to four rolls in various configurations. The distance between the rolls can be varied to control calendered thickness.

4.5.1 Introduction

As with the extruder, the calender (see Figure 4.5) further processes the compound after it has been mixed in the internal mixer or on the mill. Calendering is a useful technique, if the final product is to be a roof or tank lining, fabricated hose, expansion joint or indeed any further product which needs accurately dimensioned continuous sheet. Calendering is also used for applying rubber compound to textiles. Sheet from a mill will have a thickness which is much too imprecise, can have a rough surface and may contain some trapped 'bubbles' of air. This makes it less desirable for processing into the above products. A more precise machine is preferred, and the calender fits this need.

A three roll calender is very popular, where the middle roll is fixed, while the ones above and below it can be moved vertically to adjust the gap between the rolls. A four roll 'S' configuration might be considered more 'state of the art'. Calenders are extremely robust and solidly built machines, and may provide service for many decades. Some of the rolls can be a substantial size, i.e., 90 cm in diameter and 250 cm in length. The early calenders must have appeared as quite imposing pieces of machinery. Willshaw [5] mentions 'Chaffee's Monster' and 'The Iron Duke', which were machines built in the first half of the 19th century. Willshaw also mentions that there are many calenders, which are around a hundred years old, still providing good service.

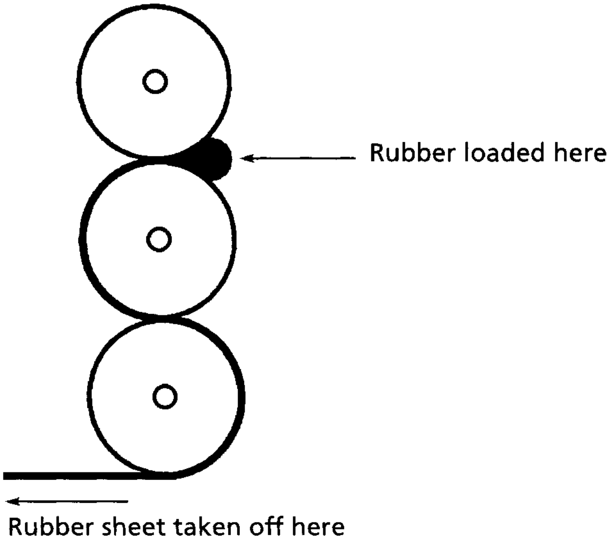

Figure 4.5 Conceptual end view of a basic, three roll vertical calender
(courtesy of the Holz Rubber Company)

4.5.2 Material thickness control

The compound in the nip can generate very large reaction forces pushing against the rolls. Bauman [6] states that a force of 43,000 kg per m of nip is possible for a product gauge of 0.25 mm, which is enough to deflect the surface of the rolls. Since the middle of the roll length is furthest away from a solid support (the bearing that houses the roll journal), it will deflect the most, resulting in a curve shaped deflection with a maximum at the middle which can be 0.13 mm or more. Even this apparently small variation can result in significant material wastage and complications in further processing. To counteract this, an opposing curve called a crown is put into the roll by grinding it. This only goes some way to solving the problem, since deflection forces vary with the compound used, and the thickness of the rubber to be calendered. Therefore some calenders are designed so that the rolls can swivel through a small angle, relative to each other, in the horizontal plane. This has the effect of creating a crown which can be varied, according to the amount of swivel chosen. The rolls can also be deliberately bent with a roll bending device, to introduce a crown. Here hydraulic cylinders act on the ends of the rolls through additional bearings.

Temperature control of the rolls is critical to the thickness of the product and is achieved in much the same way as in the internal mixer: flood cooling for older machines and drilled cores near the surface for modern ones. Since there is such a mass of metal in a calender roll, it takes a substantial time for temperatures to stabilize.

In order to avoid air blisters in the calendered sheet, a maximum for single plies of material might sometimes have to be as low as 0.13 mm. In order to achieve a greater thickness, the calendered sheet has to be reintroduced to the rolls and be 'plied up' with more compound from the nip. This process is then repeated until the desired final gauge is achieved.

4.5.3 Feeding the calender

If cold (room temperature) compound were to be fed to the nip, it would heat up erratically and produce a variable viscosity. This would cause uncontrolled deflection forces on the rolls and hence an unacceptable thickness variation and surface quality of the rubber. The simplest way to feed the calender, is to 'roll' small pieces of compound off a mill (called pigs or billets), and immediately put them in the nip. The pieces then spread along the length of the nip and form a 'rolling bank'. The bank actually circulates, by turning round and round in the nip. This is an improvement but the billets and rolling bank still show some continuous change in temperature. Also the the manual and batch nature of this process lends itself to some variability. A refinement is a continuous strip feed from a mill (via a conveyor belt), with the strip being mechanically moved along the length of the calender roll as it enters the nip. This gives a more even bank, which is kept as small as possible, since large banks trap air and are thermally variable. This refinement also gives better temperature control of the feed. However to achieve this improvement more automatic equipment is needed and therefore more initial capital outlay.

A 'state-of-the-art' system requires a whole sheet (rather than the above strip), virtually free of entrapped air (which a mill would have difficulty providing), with a very even temperature, directly entering the calender nip. Such a system is achieved with a roller head die arrangement. Here compound is fed to a pin barrel extruder, preferably of the Pinconvert type. Then a whole sheet is directly extruded into the nip of the calender, at a thickness very close to that which is finally required. In this case there is no rolling bank to cause air traps or thermal problems. Capelle [7] discusses such a system and states that single plies of material can be produced up to 18 mm thick.

4.6 Curing equipment

At last Goodyear's discovery of vulcanization can be utilized. The rolls of sheeting have been calendered, the extrusions have been made, the Barwell has produced its preformed pieces, and shapes have been cut from milled sheet. The final step is to provide sufficient heat to change the uncured compound from a somewhat plastic state, to a dimensionally stable elastic substance, and additionally, in the case of molding, to achieve a final shape. An engineer would interpret curing as an increase in elastic modulus (G'; see section 7.6.4). The chemist sees it as the formation of links between the chains, locking them together. The company owner sees it as a significant step in the transfer of money from a satisfied customer to the profit side of his financial ledger. Typical equipment used to achieve this change could be molds, autoclaves or even air curing ovens.

4.6.1 Molding

A mold might be described simplistically as at least two pieces of material (typically steel), which when fitted together form a cavity, resembling the shape of the product. This would be a very basic mold. Molding is by far the most important curing process, where uncross-linked rubber is placed into a heated mold, which gives it the final product shape, and then vulcanizes the material.

• *The mold*

It can vary in size from a clenched fist to that of an automobile, and can have a single cavity to make one product at a time, or enough cavities to make a hundred or more.

Most rubber molding is based on introducing a solid compound into a mold, although urethanes and silicones can be introduced as solids or liquids. Only solids will be discussed in this chapter. It takes a fairly high mechanical pressure, to close the mold, and thus form the product shape; this pressure is provided by a press. Thus the mold must be strong enough to avoid being crushed. Tool steel hardened to a Rockwell C hardness of about 60 might be needed.

• *Mold design*

A basic compression mold design is illustrated in Figure 4.6 which shows a cross section through the center. It is very important that the two halves of the mold register (fit accurately together). In this case, pins built into the top section fit snugly into holes drilled into the bottom half. Any looseness between the pin and the hole may cause the top half of the product to be out of alignment with the bottom half. If the fit is too tight, attempts to manually open the mold may prove difficult.

Since a number of compound materials expand with heat (the raw gum elastomer is of primary concern) by at least an order of magnitude more than steel, they will also shrink correspondingly as they cool when taken from the steel mold. Thus the mold dimensions are typically designed to be around 1.5% (based on linear dimensions) greater than

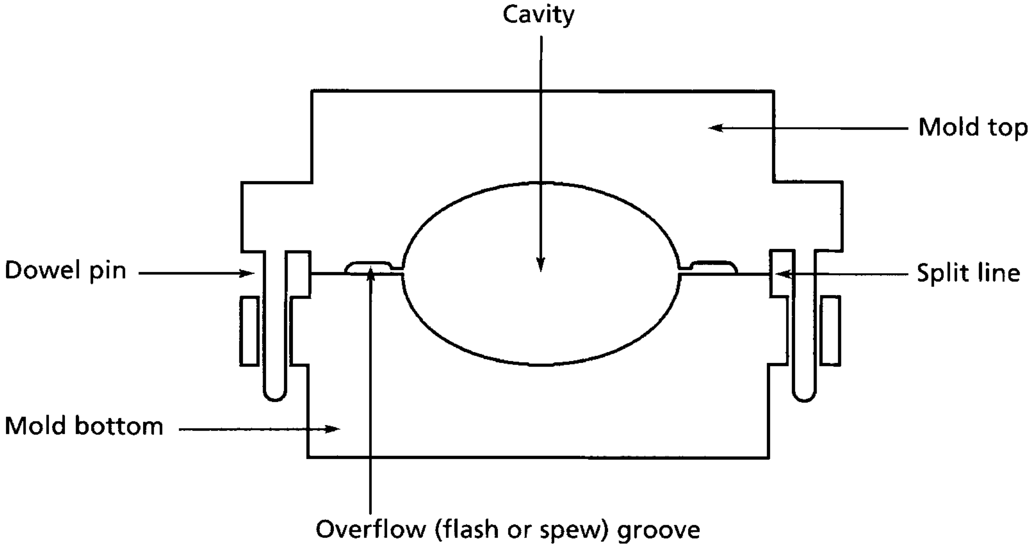

Figure 4.6 Closed empty compression mold
(courtesy of the Holz Rubber Company)

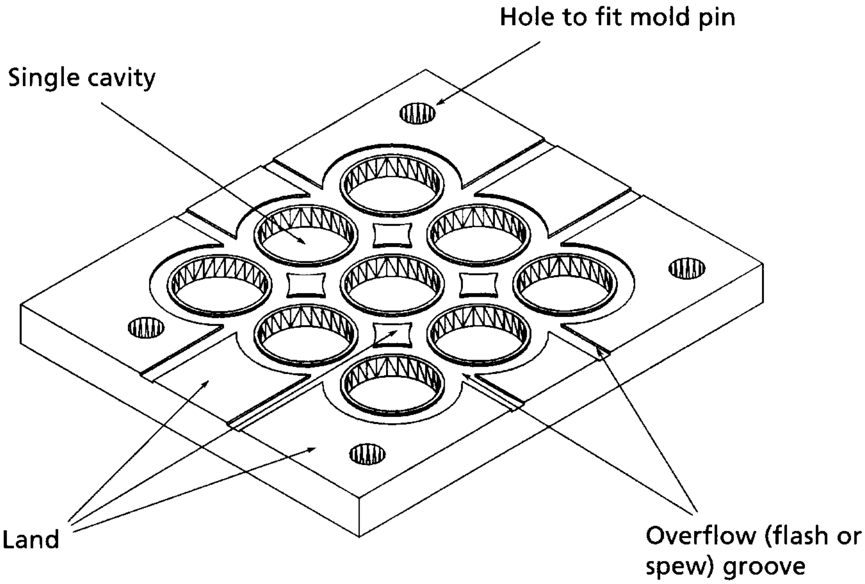

Figure 4.7: The bottom half of a nine cavity mold
(courtesy of the Holz Rubber Company)

those required in the rubber product, to compensate for the difference in expansion between the rubber and steel. This percentage vulcanizate shrinkage might be greater for FKM and silicone compounds and less for compounds with high amounts of filler.

Overflow (flash or spew) grooves are machined around the mold cavity. In theory, this is to contain rubber in excess of the cavity volume. In practice for compression molds, it is not unusual to see during mold closure, material filling the cavity, then spilling out of the overflow grooves, and even across an area outside the grooves known as the land, and then out of the mold. This excess material is known as flash.

• *Introducing compound to the mold*

There are different ways of introducing compound into the mold, some of which involve modifications to the basic design in Figure 4.6. They each confer certain advantages not found in the others.

a) In the most basic design, (see Figure 4.6, compression molding), pieces of rubber compound are placed in the bottom cavity and compressed using the top half of the mold.

b) The first modification is transfer molding, which can be visualized as drilling holes through the outside of the top mold half of a compression mold through to the cavity. Thus the mold can stay closed while rubber compound is introduced through these holes into the cavity by using the force exerted by the press platen.

c) If a separate device is used, not related to the press platen, which injects the compound through the holes, this would be injection molding.

4.6.2 Compression molding

This is the simplest, cheapest, and probably the most widespread of the three basic molding techniques. It is ideally suited to small quantity production, say, from around fifty to a few thousand of each product annually. Figures 4.8a and 4.8b show the various stages in the molding process. One of the keys to successful molding is adequate removal of air while the mold cavity is filling up with rubber.

The uncured pieces of compound placed in the mold are known variously as preforms, billets or load weights. For a ball, one might use an elliptically shaped extrusion, cut to an appropriate length from a Barwell (see section 4.4.4). This shape is important and deliberately chosen so that air in the mold cavity will have a free path of escape when the mold begins to close, see Figure 4.8a.

Normally the weight of this preform will be chosen to be a few percent (from two to ten percent) above the weight of the final product, to ensure a fully formed product and to give an extra ‘push’ for expulsion of any residual trapped air. The preform is placed in the bottom cavity and the top mold section placed on it by hand. If a significant number of moldings are to be made, it is often advantageous to fix the two halves of the mold to their respective press platens, as in Figure 4.9 thus reducing manual handling and therefore labor costs.

The mold is continuously heated to a temperature, typically between 120 °C and 180 °C. A cure time for a smaller part might be 20 minutes, at 150 °C, for thin cross sections (6 mm). In this case, temperatures above 150 °C could reduce the cure time to 10 minutes or less.

The chemist plays his part in achieving a smooth flow of material in the mold, by striving to control the uncured compound viscosity. This needs to be high enough to create the backpressure required to expel air efficiently as the mold closes, and low enough to permit completion of flow into all parts of the cavity before vulcanization begins. If we look at a low cured-hardness rubber, it usually contains little or no filler (NR & CR), or alternatively fillers plus a large quantity of oil. This can often make its viscosity too low for successful compression molding and the compounder may strive to increase its viscosity, by choosing a raw gum elastomer grade with a high Mooney viscosity (see section 5.3.1). At the other

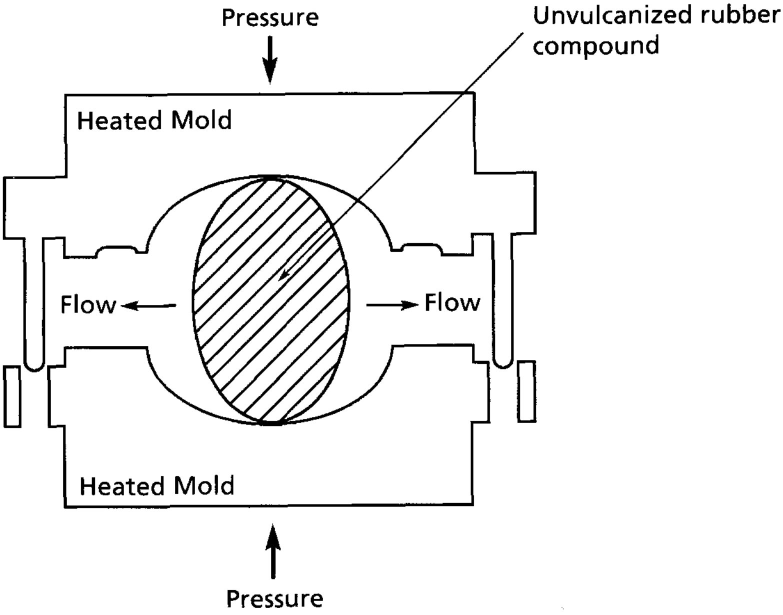

Figure 4.8a A loaded mold closing
(courtesy of the Holz Rubber Company)

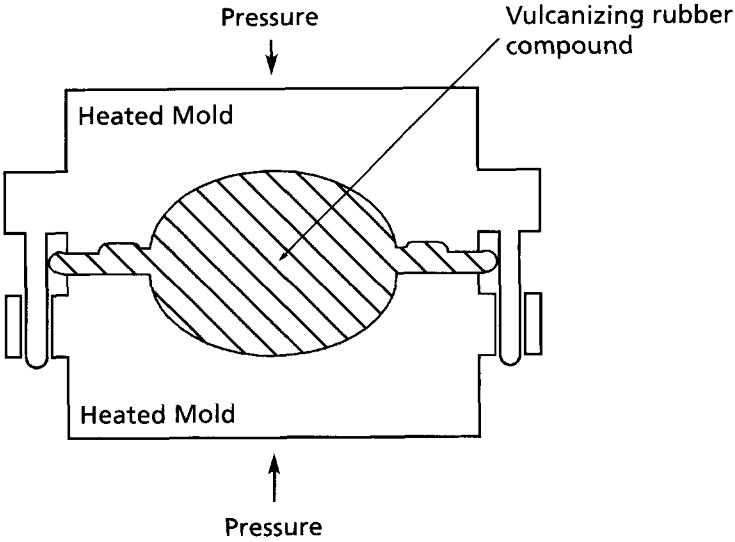

Figure 4.8b A loaded mold, closed under heat and pressure
(courtesy of the Holz Rubber Company)

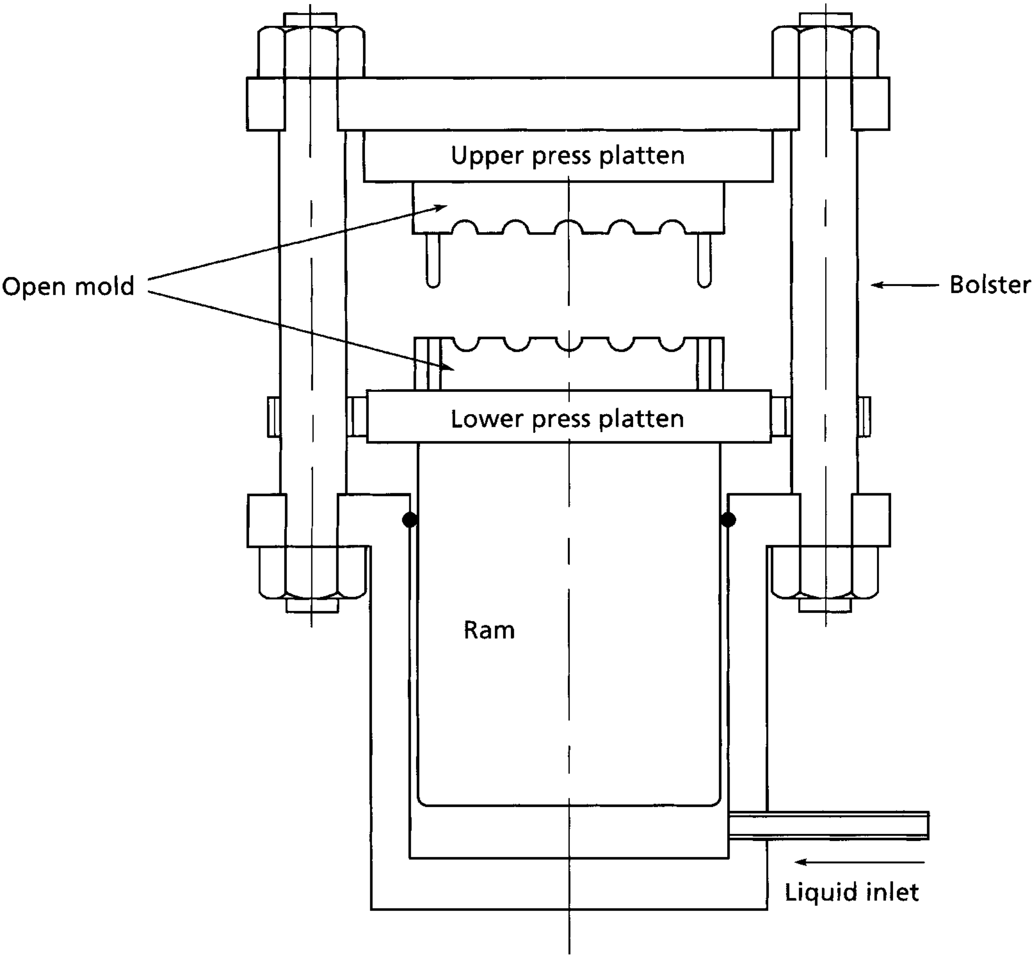

Figure 4.9 A basic press for compression and transfer molding
(courtesy of the Holz Rubber Company)

end of the scale, high vulcanized-hardness compounds with lots of highly reinforcing fillers will need specialized process aids and low Mooney viscosity raw gum elastomers, to reduce viscosity, in order to promote the flow of the compound in the mold.

As the press platens close the mold, excess compound begins to squeeze out into the flash grooves, taking air with it. Often, residual air remains and various methods have been devised to remove it. One method is to bring the mold pressure back down to zero and then return to full pressure by quickly lowering and raising the press platens a number of times. This 'shock' treatment is called 'bumping'. An additional line of attack is to find where air is being trapped in the final cured product and drill a small diameter hole through the mold cavity in the equivalent area; these are called bleeder holes. They permit an alternative escape route for the trapped air (together with some rubber). The shape of the preform and also its placement in the mold is important. The uncured rubber, placed in the cavity, might be a single piece or a number of pieces. This method is very much an art.

Since flash often spills over the land during compression, it is possible that a large land area between the flash groove and the outside of the mold might 'fine tune' backpressure control. A large land distance restricts flow at the time when the mold is almost closed and thus might increase backpressure, which would be of assistance with low viscosity compounds. For high viscosity materials the opposite might apply, i.e., a small land area and deep flash grooves would be desirable. This would also promote greater pressure at the moment before full mold closure for the same force exerted by the press ram. Radial grooves connecting the flash grooves with the outside of the mold should also assist in high viscosity compounds exiting the mold.

The press needs to exert a certain amount of pressure to allow the compound to flow into the cavities and for the mold to properly close. The objective is to obtain a thin flash, 'ideally', around 0.05 mm.

The area of the press rams, divided by the projected area of rubber and flash between the mold halves, multiplied by the line pressure at the press, will give the pressure exerted on the product in the mold at closure. The required pressure is typically 7-10.5 MPa and will vary acording to such things as the viscosity of the compound and the complexity of the mold cavity. The mold is designed to take the high stress involved.

It is interesting to note that the area of projected rubber can be smaller at the beginning of mold closure, since the rubber has not yet fully spread over all of the mold cavity. More of the force from the ram might briefly act on delicate inserts or parts of the mold, depending on the exact set up involved. This sometimes has the potential to cause damage if not taken into account.

The flow of material in a mold is a complex process, especially in compression molding. The rubber in the cavity is undergoing large temperature changes, which translate to viscosity variations thus continuously altering the flow characteristics of the compound. In recent years finite element analysis packages (see section 7.11), which describe the material flow patterns in the mold, have become available to mold designers. The use of such design aids is at an early stage in most of the rubber industry.

• *Backrind*

Once the compression mold has closed, the compound continues to heat up and attempts to thermally expand. Its coefficient of expansion can be a least fifteen times greater than

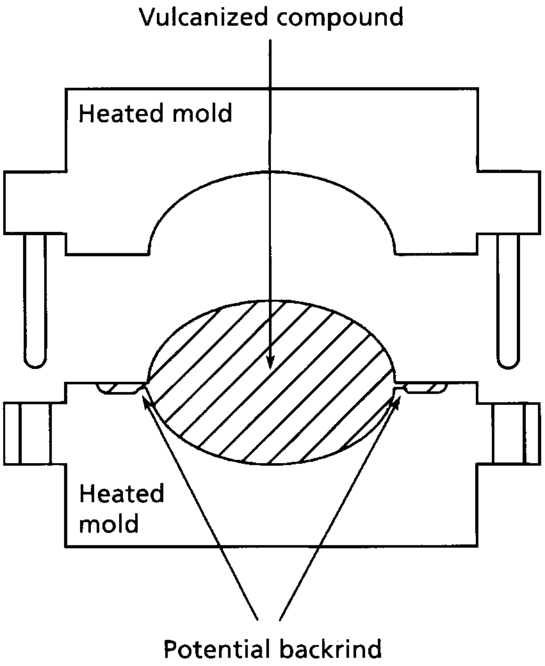

Figure 4.10 An open mold after rubber curing
(courtesy of the Holz Rubber Company)

that of the steel mold. For moldings with large cross sections or high volume to surface area ratios, such as a ball, phenomena such as backrind [8] can occur. When the product is taken out of the mold, it looks chewed up and torn in the area of the flashline; this is described as backrind. If this occurs there is likely to be a flurry of activity between the shift foreman, chemist and engineer.

Backrind is thought to be caused because as the rubber heats up (heat transfers first from the mold to the outside layers of compound) the outer layers of the molding cure first, while the colder uncured inner layers are still heating up and attempting to thermally expand. Since the inner layers are restricted by the closed mold and cured outer layer of compound, they develop a continuously increasing internal pressure. If this internal pressure exceeds that applied by the press, the mold will open for an instant, relieving the internal pressure and causing a rupture at the 'cured' parting line; the mold will then instantly reclose. If this occurs a number of times during the cure it is called chattering.

Another theory is that at the end of the cure time, at the instant the press is opened, the removal of the external clamping force instantaneously releases the internal pressure in the product, opening the mold slightly and causing a rupture at the parting line of the vulcanizate. Sometimes, only some areas of the parting line are affected, suggesting that in these cases the mold is opening unevenly.

Possible solutions that might alleviate the backrind and chatter problem are:

a) Pre-heating the preform.

b) Designing a 'sacrificial' section into the product at which backrind will occur between this section and the flash line. This section is then removed after cure, leaving only a small blemish where it is connected to the product.

c) A more intriguing idea is to drill 6 mm holes through the mold into the cavity, into a less important section of the product. As the compound heats up and expands in the heated closed mold, it freely extrudes through these holes; in a large product, uncured compound can extrude for quite some time, (this may be analogous to moving water not freezing in an otherwise frozen stream). The mold is designed so that there is still sufficient backpressure to allow air and product to flow into the flash grooves. This last method might be used for large products, 11 kg or more in weight, since backrind is a more serious problem in larger products.

d) For certain simple product geometries, it is possible to place in the mold an amount of rubber, which is actually slightly less than the amount required to fill the cavity at room temperature. As it heats up in the closed mold it expands and completely fills the cavity without the consequent build up of to much internal pressure. This would need precise control of preform dimensions and assumes the closed mold is not totally airtight.

e) A compound formulated for long scorch time might delay curing of the outer layers during thermal expansion, thus preventing any rupture of these layers during the presumed instantaneous mold opening during cure.

f) Reduction of the temperature of cure would decrease thermal expansion or possibly, in effect, increase scorch time of the compound. This would be at the price of increased cure time.

g) Cooling the mold after cure, before reducing the pressure applied by the press, and then opening the mold, might reduce internal pressure and therefore possibly reduce backrind.

• *Heat transfer*

How long should it take to cure a compound in a mold? The rubber laboratory uses a rheometer to help determine this (see section 5.3.2) using small samples of compound. The rheometer might indicate a cure time to be 25 minutes at 150 °C. If this is then applied to a shop floor molding, it must be remembered that the 25 minutes is based on all of the compound in the rheometer being at 150 °C at approximately the beginning of the 25 minute period. Rubber can be very poor at transferring heat, so that for a large bulky part in a shop floor compression mold, it may take hours for heat to be transferred from the mold to the center of the part. The rheometer estimate of 25 minutes must now be revized, to take into account a constantly changing temperature (with time) throughout the part as the cure progresses. Carbon black is significantly better at transferring heat than a raw gum elastomer, thus for the same bulky part, a carbon black filled compound will vulcanize, through to its center, much sooner than a non-filled gum compound.

An experiment performed by Bose [9] at Accurate Continental Rubber illustrates the point quite well. He compression molded a cylindrical ‘block’ 10 cm high by 9 cm diameter of NR compound, with a thermocouple inserted into the center of the block. The press platen temperature was at 150 °C and the mold was allowed to reach thermal equilibrium. At this point the compound was introduced and the clock started. For a gumstock NR compound (30 Shore A), it took 2 hours for the probe to register 130 °C. For a carbon black filled compound (76 phr carbon black, 70 Shore A), the time taken to register 130 °C was only 1.1 hours. This clearly indicates that a shorter overall time in the press is sufficient for the carbon black filled compound but not for the gum. If it takes time for heat to transfer in, it also takes time for heat to transfer out, on removal of the product from the mold. This might theoretically suggest completing the cure outside the mold. There are however dangers in such a practice, such as distortion of product shape and porosity in the center of the part.

4.6.3 Transfer molding

If we take the top half of a compression mold, then drill transfer holes through it and place a metal collar (transfer pot) on the closed mold so as to surround all of the holes, we have in effect converted it into a transfer mold.

All that is needed now is to put rubber compound into the pot and force it through the holes by placing a piston (plunger) into the pot and using the press platens to force the piston to push the compound down through the pot into the closed mold cavity, see Figures 4.11a and 4.11b. This conversion is used in the rubber industry. Alternatively, the transfer pot can be designed to be an integral part of the mold and the piston can be fixed to the upper press platen.

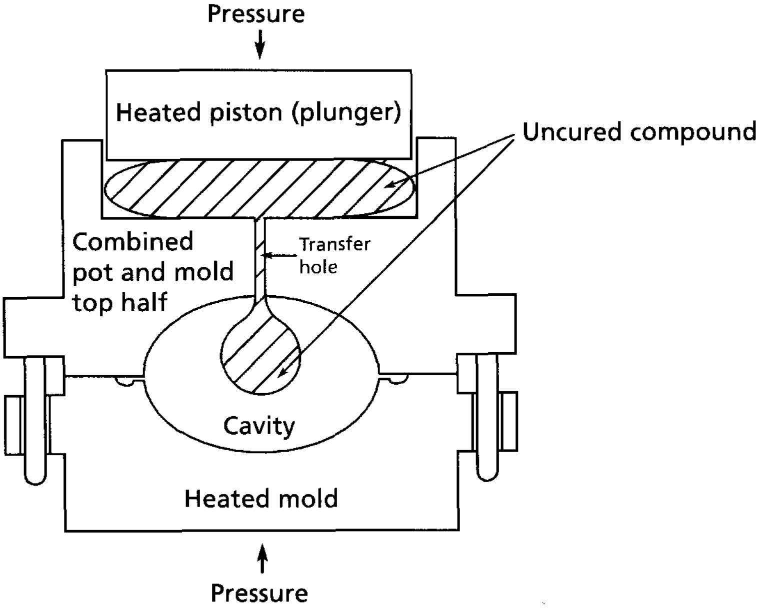

Figure 4.11a Conceptual cross section through a transfer mold - compound moving from pot to cavity *(courtesy of the Holz Rubber Company)*

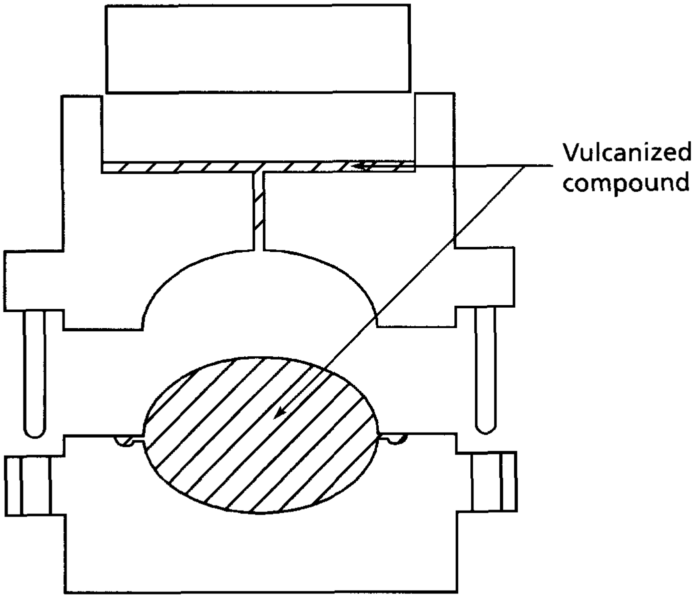

Figure 4.11b Conceptual cross section through a transfer mold - transfer mold opened after cure *(courtesy of the Holz Rubber Company)*

Since rubber can be considered a thixotropic non-Newtonian fluid, the shear between it and the walls of the transfer holes reduces its viscosity, thus allowing the compound to enter the mold cavity more easily. Shear also heats the compound which reduces viscosity and speeds up cure.

• *Design considerations*

The piston can be slightly tapered to allow easier removal of the product after cure. One point to note is that now, the mold consists of three sections, the piston or plunger, the top half of the mold, and the bottom half. The middle section can potentially float upwards as the piston moves down before transfer is complete. If the surface area of the pot is smaller than the total projected area of rubber between the top and bottom mold halves, the 'reaction' force pushing the top mold section up, will be greater than the force of the piston, through the rubber in the pot, keeping it down. The top half of the mold will tend to float up, allowing compound to leak out between the now open parting line, until the piston bottoms out, closing the mold. This results in excessive flash between the mold halves. If the area of the pot is sufficiently large, as it should be, the mold stays closed with minimal flash. Transfer molding may use pressures around 14 MPa, somewhat higher than compression molding.

• *Advantages*

a) The mold stays closed throughout cure, leading to a far better chance of reduced flash thickness and therefore a better closure dimension tolerance (the product dimension which includes the variable flash thickness, assumed theoretically to be zero).

b) Due to frictional heating during transfer, the compound enters the cavities at a higher temperature, thus reducing overall cure time, especially for large parts.

c) As some compounds 'sit on the shelf' before use, there is the possibility of ingredients blooming to the surface (see section 3.3.2), which might interfere when the compound is bonded to metal. It is suggested that in transfer molding, as the compound moves through the transfer holes, this bloom tends to 're-dissolve', thus improving the prospect of a consistent bond.

d) There is no need for complex preform preparation, nor careful positioning in the mold cavity.

e) The technique is generally better for rubber to metal bonding.

• *Disadvantages*

a) The plunger and transfer pot are an extra cost.

b) The pad of cured rubber left behind in the transfer pot should be sufficiently thick to be removed as one piece. The pad represents waste material and the amount can be more than the flash waste in a compression mold.

c) There is the risk of compound sweeping across cemented inserts and removing some of the cement. The adhesive manufacturer needs to be consulted if this might be the case.

d) When the cured rubber attached to the product in the transfer holes is cut off, it will leave a blemish. This might be a concern, for example, if all surfaces of the product act as a seal.

4.6.4 Injection molding

An injection mold consists of a cylinder (injection barrel) with a ram or screw inside it, so that the rubber compound can be moved towards a nozzle at its end. The nozzle is then pressed against a hole made in the top half of a closed mold. This hole is then connected to smaller holes (gates and runners) which enter the cavities of the mold.

The compound can be presented to the barrel as a continuous strip, or in granulated form through a hopper, as in plastics injection molding. A ram has a tighter fit in the barrel than a screw and therefore there is less leakage backwards through the barrel; it is also cheaper than a screw. The screw 'mixes' the compound as it moves towards the nozzle, creating more frictional heat and therefore higher temperatures which translate to easier flow and shorter cure times. A combination of ram and screw is popular.

• *Advantages*

a) The cure temperatures used can be much higher than those used for compression or transfer molding. For example, MRPRA literature [10], mentions NR injection temperatures of 160 °C and mold temperatures of 180-190 °C. High temperatures mean shorter cure times; one or two minutes are possible for thin cross sections.

b) Since the temperature of the compound entering the cavity is closer to the molding temperature, there is much less thermal volume expansion of the rubber during cure, therefore much less internal pressure build-up, resulting in a much reduced tendency to backrind.

c) No complex preform is needed.

d) Flash is significantly reduced or eliminated.

e) Air entrapment is significantly reduced.

f) The system is capable of a high level of automation, reminiscent of plastics injection molding.

g) It is suited to fast, high quantity production.

- ***Disadvantages***

a) The molds need to withstand very high injection pressures. This entails use of high hardness steel molds and higher precision tooling.

b) If gates and runners are added to the mold its cost becomes significantly higher than compression ortransfer molding.

4.6.5 Autoclave curing

An autoclave is a cylindrical steel pressure vessel, used to cure extrusions, sheeting and all manner of hand fabricated parts. They can be very small or huge, for example, 30 m long and 3 m or more in diameter. The heat needed to cure is commonly provided by wet steam, often at 0.3 MPa, although some curing processes might need pressures of 0.7 MPa or more. In special cases carbon dioxide or nitrogen might be used, either separately or in combination with wet steam, to provide higher pressures than the wet steam alone could produce at a given temperature. The pressure of wet steam is restrained by its temperature/pressure equivalence. Choosing 150 °C as the desired cure temperature would only generate 0.3 MPa from the wet steam. In cases where porosity in the product is a problem it might be advantageous to independently increase the pressure in the autoclave. If enough nitrogen is introduced to give an extra 0.6 MPa pressure, there is now a total of 0.9 MPa, which might significantly reduce any porosity problems encountered at the lower pressures. It is clearly understood that the autoclave must be kept within its design capability.

Another point to note is that any oxygen in the autoclave can react with compounds containing peroxide cross-linking agents, causing an uncured layer on the surface of the final product. An exclusively nitrogen or carbon dioxide atmosphere in the autoclave might be a way to resolve this problem. However, this would require a source of heat other than steam.

4.7 Product dimensional specifications

Once a product is manufactured, both the customer and manufacturer want to be sure that the dimensional tolerances are adequate for the application. Overly strict tolerances might mean more expense in producing the product. On the other hand loose tolerances might prevent the product from doing its job, for example a seal might not seat correctly in its housing. In order to achieve harmony, both customer and vendor need a communication language to which they both agree. The US Rubber Manufacturers Association (RMA) [see appendix 20] is an example of an organization that provides such a language. This extends to molded goods, extrusions, hose, linings, etc. If we take a rubber extrusion cross section as an example, it could be classed from high precision (E1) through to commercial tolerances (E3), each with its own table of numerical values. Thus if both parties agree to E1 tolerances, there is a clearer understanding of what is expected.

4.8 Storage of rubber parts

Now that the rubber products are vulcanized and ready for use, it is appropriate to mention some of the generalizations, related to preferred storage, assuming immediate use is not required.

a) The storage temperature should be kept below 25 °C because heat can accelerate the aging process.

b) Avoid direct sunlight. Sunlight (a source of UV radiation) has the potential to degrade light colored (non-black) compounds of unsaturated polymer chains.

c) Avoid ozone, such as storage in proximity to equipment that produces ozone. Ozone can cause cracking if there is even a small tensile stress present. This applies to unsaturated elastomers.

d) Mechanical stress, such as excessive stacking of one product on top of the other, should be avoided because it can promote/cause increased ozone attack and in addition might cause a permanent deformation.

The shelf life of a rubber product could be some months or it might be many years.

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5 The Rubber Laboratory

"Look", ...said Andrew, *"All you need to do is to make sure all the compound ingredients are correct and weigh them accurately and then all the batches will come out the same."*

5.1 Introduction

The introductory sentence is certainly an ideal state that all rubber technologists strive for, and the philosophy of modern quality assurance is to control the process of manufacture to such an extent that product testing is virtually eliminated. For the raw materials this would also mean the vendor's process being in total control and so on down the line. Although the rubber industry has moved a long way towards this state, it presupposes a total understanding of the process involved. When raw materials are chosen and mixed to form a compound, there is still a need to confirm that the compound possesses the expected properties, that allow it to process well on rubber machinery, and that the product will perform according to the customer's expectations. The test properties chosen, must also reflect the 'real world' requirements of the compound and its subsequent product.

5.2 Raw material

A rubber product manufacturer might decide to rely on the vendor for total quality assurance of the raw materials that are purchased. Certificates of compliance can be requested from the vendor. Such certificates will specify the property requirements and test results, for the purchased consignment of raw material. The vendor might state melting point for purity of accelerators and antioxidants, particle size and structure for carbon black, specific gravity and aniline point for oils. Raw gum elastomers are generally checked for Mooney viscosity (see section 5.3.1). Tests specific to particular raw gum elastomers might apply. For example EPDM is tested for its ethylene content, NBR for the level of acrylonitrile, SBR for styrene content, and so on. A change in vendor for an 'equivalent' raw material, sometimes does not mean 'exactly the same'. For example, a raw gum elastomer with the same Mooney viscosity and copolymer composition might differ in molecular weight distribution (see section 6.1.2), and therefore could process differently on the shop floor.

5.3 Properties of the uncured compound

The molding operator needs to be confident that the compound he is getting from the mixing department, will have a reasonably consistent flow behavior, each time a batch is mixed. The extruder and calender personnel also need consistent smooth processing. The time lag between application of heat to a compound and the beginning of cure (scorch time), is often essential to its success in molding on the shop floor. Attention must also be focused on characteristics of the cross-linking process itself. There are lots of instruments available to measure all of these essential properties, all of which come under the heading of rheology.

5.3.1 Mooney viscometer

In the early days of the rubber industry, Mooney devised an instrument to measure the 'stiffness' of uncured compounds, otherwise known as the compound's viscosity. The appropriate standards associated with this test are:

ISO 289 [1], ASTM D 1646 [2], BS 903: Part A58 [3], DIN 53523-3 [4]

The units of measure used by all of the standards are simply Mooney units.

Figure 5.1 shows an instrument for measuring viscosity, the Mooney viscometer, in which a knurled knob (rotor) rotates (at two revolutions per minute) in a closed heated cavity (like a mold), filled with uncured rubber. A shearing action develops between the compound and the rotor, and the resulting torque (resistance of the rubber to the turning rotor) is measured in arbitrary units called Mooney units, which directly relate to torque. The higher the number, the higher the viscosity.

A shorthand language is used to express the results:

e.g. 40 ML 1+4 (100 °C)

Where: 40 refers to viscosity in Mooney units
M indicates Mooney
L indicates that a large rotor was used (S would indicate the use of a small rotor)
1 refers to a one minute pre-heating time, after the cavity is closed but before the rotor is switched on, during which the rubber warms up to the cavity temperature.
4 refers to the time in minutes, after starting the rotor, at which the reading is taken
100 °C is the temperature of the test

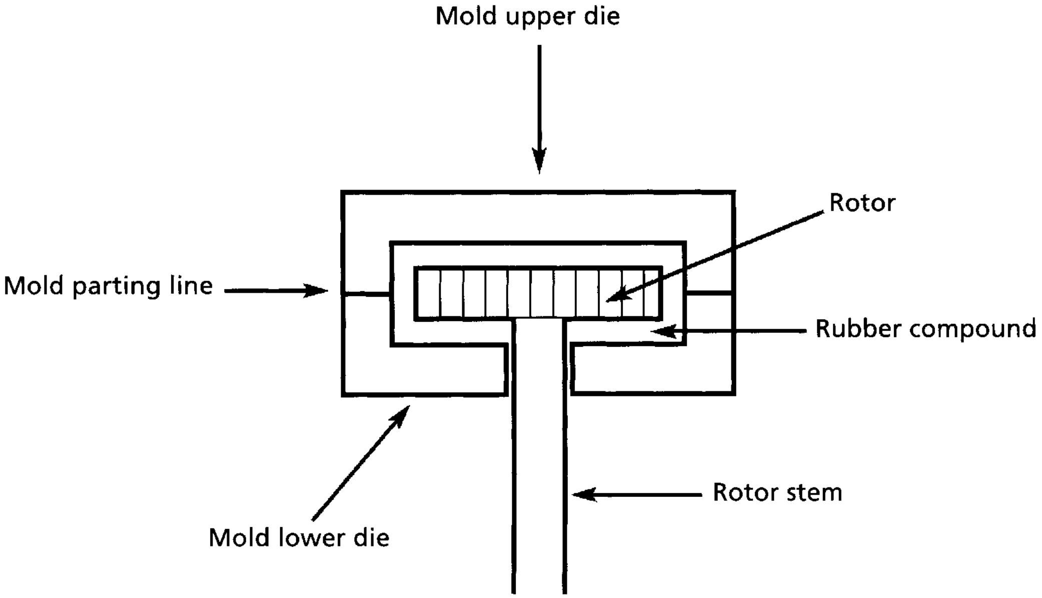

Figure 5.1 Principles of the Mooney viscometer
(courtesy of the Holz Rubber Company)

• *Mooney scorch*

The Mooney viscometer is also used to measure the time it takes, from initial exposure of the compound to a particular temperature, to the time of onset of cure (rapid increase in torque experienced by the rotor) at that temperature. This is known as the scorch time. A knowledge of scorch time is important to the rubber processor as a short time may lead to problems of premature vulcanization. This period is taken as the number of minutes to reach a 3 Mooney unit rise in torque for a small rotor, and 5 Mooney units for a large rotor, from the moment the cavity is closed. A standard temperature for this test can be chosen, for example from ASTM D 1349-87 (1992) [5]. A typical temperature is 125 °C. It is a compliment to Mooney that his instrument will survive into the year 2000. However, there is a basic limitation. As the test is taken past the onset of cure, the rotor tears the cured rubber, and therefore this device cannot be used to investigate rheological properties after the scorch time.

5.3.2 Oscillating disc curemeter

ISO 3417 [6], ASTM D 2084 [7], BS 903: Part A60: Section 60.2 [8]

The oscillating disc curemeter or rheometer (ODR) solves the problem of not being able to make any rheological measurements after the scorch time (as with the Mooney viscometer), by changing the rotor from a rotating mode to an oscillating one. Since cured rubber can stretch to some extent without breaking, the oscillations are kept within this limit. The magnitude of the oscillation is measured in degrees of arc, 1° and 3° are most common, and the rate of oscillation is suggested as 1.7 Hz. The curemeter is an essential piece of equipment and used extensively in the rubber laboratory. The machine plots a graph of torque verses time for any given curing temperature. The full extent of cure and beyond can now be recorded. For example reversion, the point at which the vulcanized compound breaks down due to prolonged heating can now be measured.

• *Testing procedure*

A piece of uncured compound rubber is placed on the heated rotor, and the heated top die cavity is immediately brought down on to the lower die thus filling the cavity. In Figure 5.2, the curve shows an immediate initial rise in torque upon closure of the heated cavity. At the top of this first 'hump', the compound has not had much chance to absorb heat from its surroundings, and since viscosity is temperature dependent it will be somewhat higher in these first few seconds. As the compound absorbs heat from the instrument, it softens. Its temperature then stabilizes, and its viscosity has a constant value prior to the onset of cure. This assumes that it is not masked by a very short scorch time. This is the first important feature on the curve. It is the minimum viscosity of the rubber at the chosen temperature and degree of oscillation; and it has the symbol M_L. Note, ASTM nomenclature is used throughout this chapter.

After a certain time, the viscosity (torque) begins to increase, indicating that the curing process (vulcanization or cross-linking) has begun. The time from the closure of the cavity to this moment is the next important property, the scorch time. It has the symbol t_s1, which means, the number of minutes to a 1 dN.m rise above M_L (used with a 1° arc). If a 3° arc is chosen, then a scorch time with the symbol t_s2 is used, which is a 2 dN.m rise above M_L.

The torque continues to increase, until there is no more significant rise. At this point the compound is vulcanized, and this maximum torque value is designated by the symbol M_H.

The last major piece of information to be extracted is the time it takes to complete the cure, known as the cure time. The symbol for this property is t'x. This is defined with some

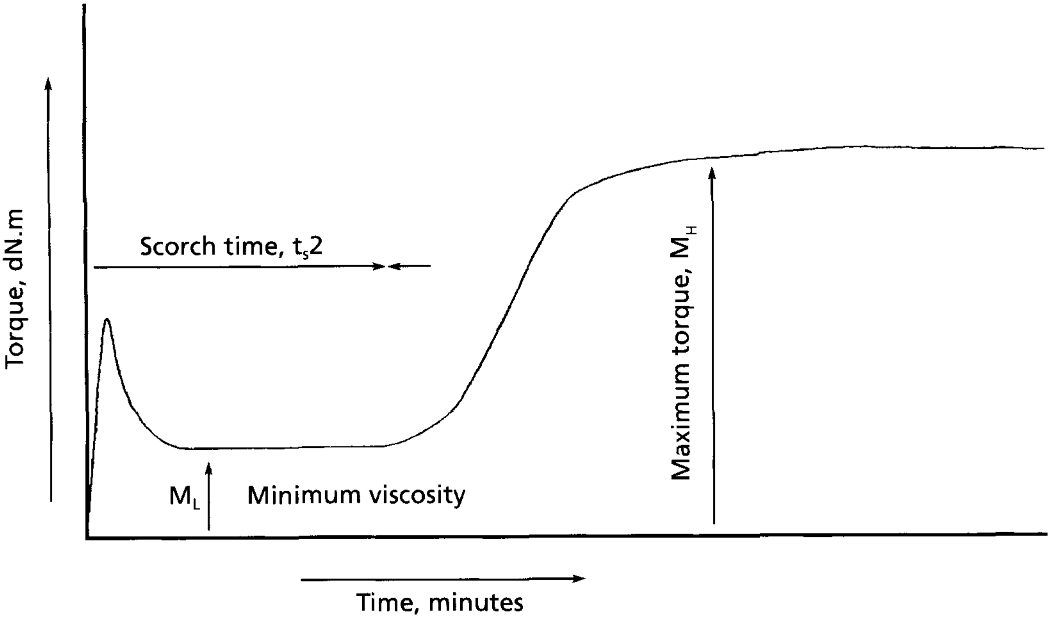

Figure 5.2 Typical oscillating disc curemeter curve

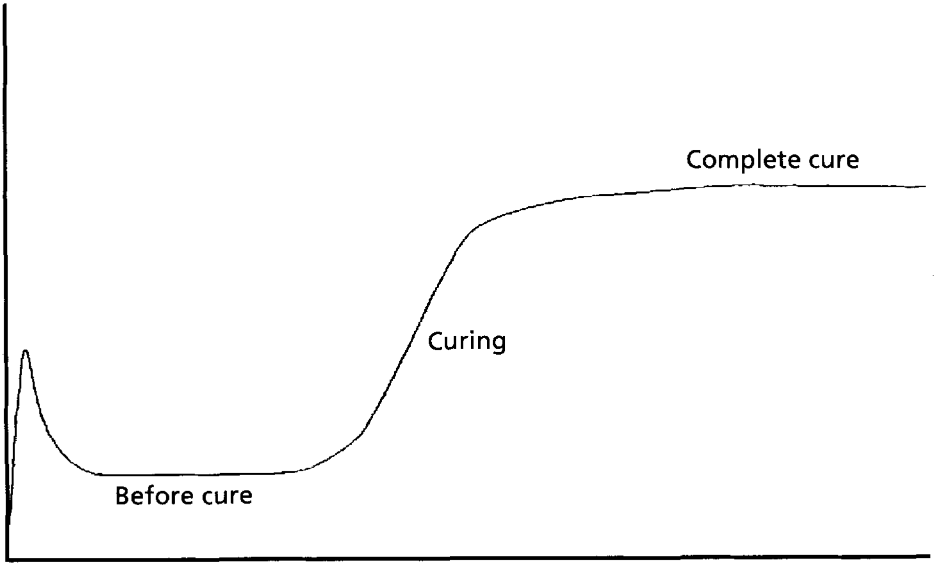

Figure 5.3a Normal ODR curve

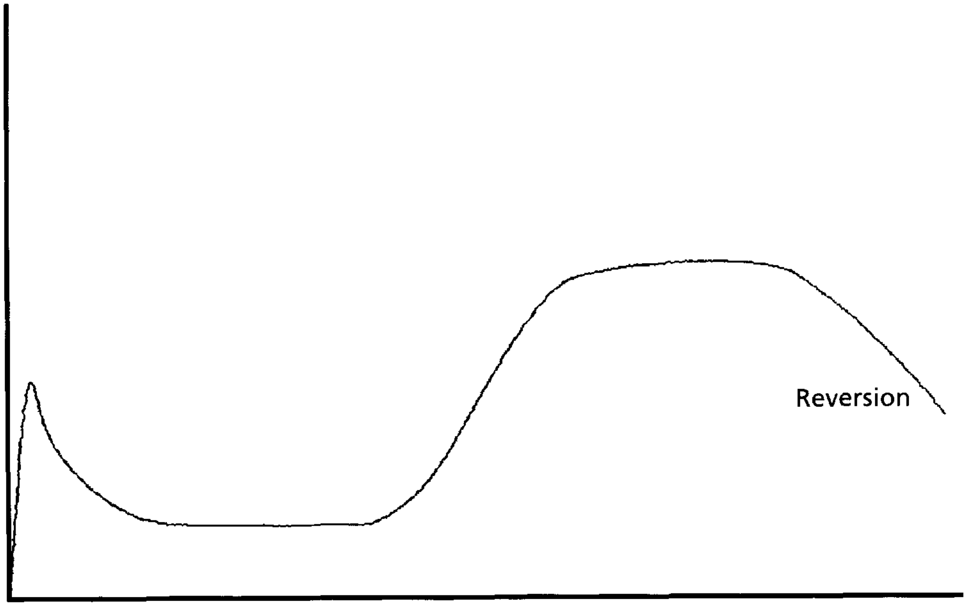

Figure 5.3b ODR reversion curve

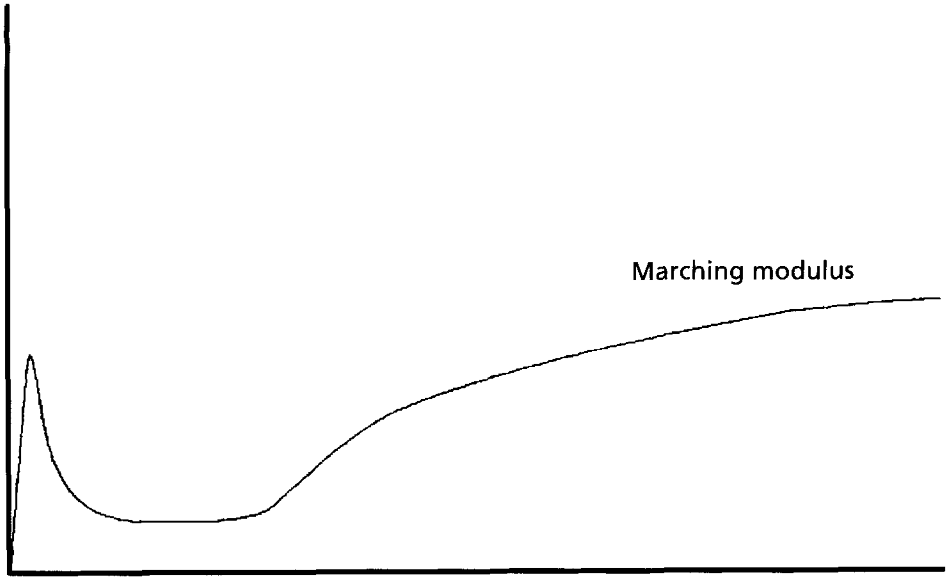

Figure 5.4 Marching modulus curve

precision as 'the time taken for the curve to reach a height expressed as the value of M_L plus a 'percentage' of the difference between M_H and M_L'. If we think of this 'percentage' as a decimal, then 90% is 0.9 (this number is commonly chosen), and mathematically this height would be expressed as $0.9(M_H-M_L)+M_L$. This 'cut off' at 90% is often known as the technical cure time of the compound, and has the symbol t'90.

Some compounds exhibit what is sometimes known as marching modulus, see Figure 5.4, where the rate or speed of vulcanization 'marches' on more and more slowly as the cure proceeds. This is often seen in compounds containing CR.

• *What the symbols really mean*

For a given compound, the chemist will establish a numerical value and permitted variation for the rheological properties that have been discussed.

If the M_L value is outside the permitted variance it might indicate the following:

If too much carbon black or too little oil is in the batch of compound, it will show up as having an anomolously high M_L. Too little carbon black or too much oil would give the opposite result.

Certain raw gum elastomers tend to reduce their viscosity with mixing, notably NR. If the compound is excessively processed, such as in too much mixing relative to normal, the viscosity can drop sufficiently to give an abnormally low M_L.

t_S1 or t_S2: Establishment of a minimum scorch time is essential to the safe processing of a rubber compound, on any rubber machinery that further shapes the compound while heating it up. A mold is a good example. A large complex mold requiring a long time to fill with uncured rubber at its chosen mold temperature, might need a long scorch time. Here, a low scorch life could result in premature vulcanization, before the cavity has properly filled, resulting in a high level of rejected product.

It should also be noted that a compound which contains curatives will cure whilst sitting unused on 'the shelf'. Scorch and cure, for a given compound, are purely a function of temperature and time. At 150 °C scorch and cure occur a lot faster than at 20 °C. The shelf life of a compound waiting to be used can be measured in days or even a year, depending on a number of factors. A shorter t_S2, caused for example by dumping a batch (with curatives) from the internal mixer at too high a temperature, might result in a shorter shelf life.

M_H: If a constant value for M_L is assumed then M_H gives information about the curative system, and therefore the degree of cross-linking of the elastomer. If insufficient curatives are mixed into the batch, then M_H will be low. The reverse applies for an excessively high level of curatives. For the basic formula described in this book, the chemist must then discover whether the anomalous M_H is due to the presence of sulfur or accelerators. Zinc oxide or stearic acid levels do not have as dramatic an effect on M_H as sulfur or accelerators. This example is related to the basic cure system for unsaturated elastomers.

t'90: This symbol refers to the cure time but it also gives information on the cure system as a whole. When Goodyear finally used heat on his sulfur containing rubber, the t'90 times would have been extremely long, since he did not have the benefit of the zinc oxide/stearic acid, accelerator 'booster package'. The arguments used for variations to M_H also apply to t'90.

5.3.3 Rotorless curemeter

ISO 6502 [9], ASTM D 5289 [10]

Although the ODR has been the 'workhorse' of the industry, an instrument called the rotorless curemeter has recently become established in this role. A popular example of such an instrument is the moving die rheometer (MDR). The MDR has a number of advantages over the ODR. The oscillating disc in the ODR is replaced with an oscillating die. A top and bottom die form the cavity which contains the rubber sample. ASTM D 5289 prefers a frequency of oscillation of 1.7 Hz and for the torsion type of a rotorless curemeter an amplitude of oscillation +1°/+0.5°. The two dies allow the instrument to separate the elastic and viscous components (see section 7.6.1) of the compound, and plot them as two separate curves [11].

Although the two curves can be shown as S' (elastic stress) and S'' (viscous stress), very often it is preferred to display S' and tan delta (tan δ) which is S''/S'. For an explanation of tan δ see section 7.6.3. Tan δ follows a somewhat similar path to that of S''. Figure 5.5 illustrates tan δ decreasing as the cross-linking process continues, reaching a minimum limit at completion of cure. The final value of tan δ indicated in Figure 5.5 is 0.22, indicating a higher damping (less elastic) material.

Further MDR instrument evolution has added sweeps of frequency, strain, and temperature of the sample being tested [12, 13].

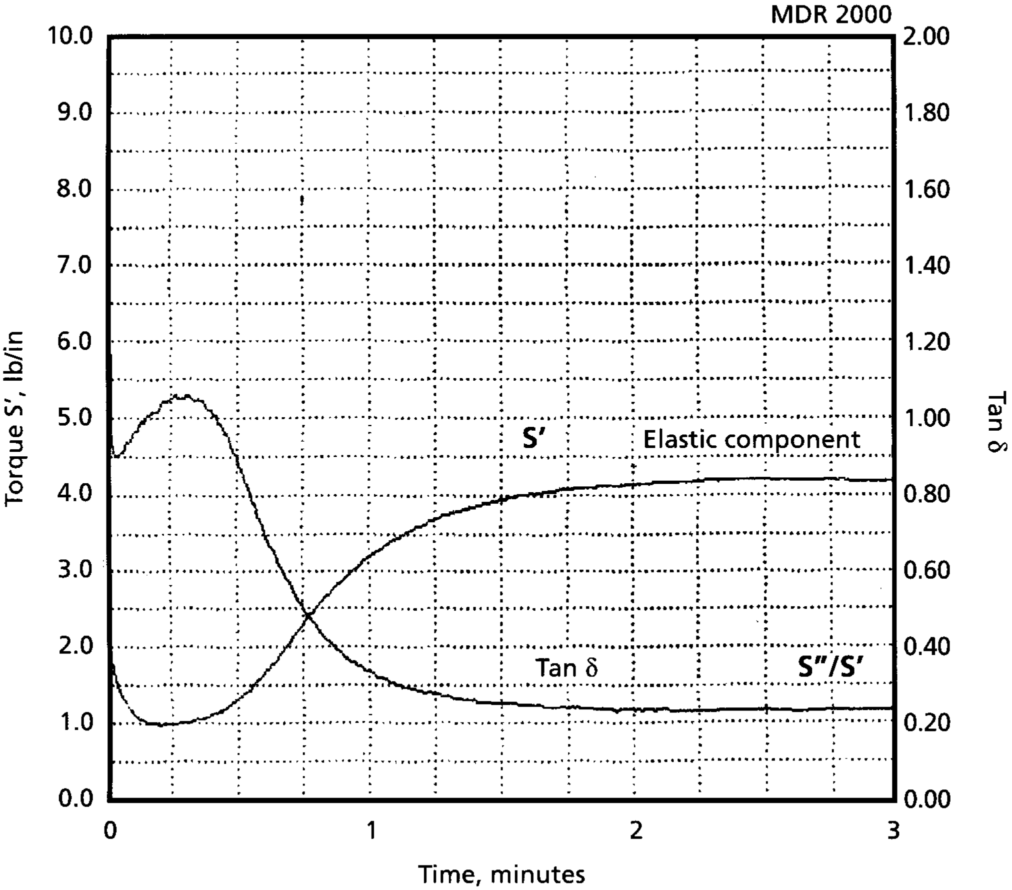

Figure 5.5 Moving die rheometer curve
(courtesy of the Holz Rubber Company)

5.3.4 Other instruments

There are a number of other instruments used to measure uncured properties of compounds. Just a few will be mentioned here. Small laboratory extruders are available with specially contoured dies (Garvey die), to provide information on extrudate smoothness and die swell. Refer to ASTM D 2230 [14]. A capillary rheometer is also available, in which the uncured compound is extruded through a small orifice and the change in dimensions of the extrudate are measured with a laser. This instrument generates high shear rates, more typical of shop floor conditions than say, a Mooney rheometer. The capillary rheometer can thus represent flow of compounds on rubber processing machinery, such as injection molds.

5.4 Properties of the cured compound

5.4.1 Introduction

Since there are numerous applications for rubber products, this has resulted in many different kinds of tests, all based on the premise that the results they produce correlate with the desired end use property. For example, a test for ozone attack gives clear information as to how the material will behave in an ozone atmosphere. However there is some doubt as to whether a compression set test or a stress relaxation test is the more appropriate in determining how well a seal will perform. Compression set is, historically, a much older test, and therefore well established, and it might have been originally introduced as a test for state of cure, before rheometers were used. As curing proceeds, compression set decreases. At the point when the curemeter trace levels out, cure is complete and compression set is practically at a minimal value.

5.4.2 Hardness

ISO 48 [15], ISO 1400 [16], ISO 7619 [17], ISO 1818 [18], ASTM D 2240 [19], ASTM D 1415 [20], BS 903: Part A26 [21], BS 903: Part A57 [22], DIN 53519-1 [23]

They say if you wish 'hard' enough, your wish will come true, at least to within one or two points on the hardness scale of measurement (see Figure 5.6). The scientist might rephrase the statement and say, the hardness test is somewhat subjective. An extremely

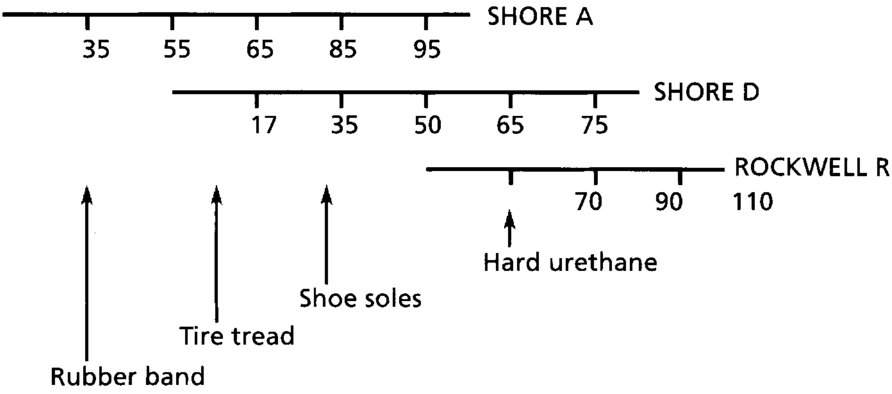

Figure 5.6 Approximate equivalence of hardness scales
(adapted from 'Engineering Properties of Adiprene', published by Uniroyal, Inc.)

convenient and very widely used measuring device, that can be carried anywhere, is the 'pocket Durometer' hardness tester. The principle of operation of this instrument can be likened to pressing a ball point pen into the material to be tested, and relating the depth of penetration of the point to an agreed scale of numbers. The greater the penetration of the point the lower the hardness. Hardness is probably the most widely used, cured property of rubber.

Note: A Shore A value of 100 is the same as a Shore D value of 100, thus the scale value for Shore A from 95 to 100 (stiffness increases exponentially in this region) corresponds approximately to the scale value for Shore D from 50 to 100.

• *Use of a pocket durometer*

There has occasionally been debate between the product manufacturer and the customer about the validity of hardness results obtained using a pocket durometer. The following suggestions on using a pocket durometer are taken from personal experience and perusal of standards.

The speed of application of the durometer will affect the reading (i.e., whether it is slammed on the rubber sample or gently pressed against the vulcanizate). Quickly applying the instrument to the rubber will give higher readings. This might be analogous to jumping into a swimming pool from a high diving board (high speed of application); in this case, the water would feel 'harder' and so does the rubber. Also, if the reading is taken instantly after application of the instrument, it might give a higher value than if it were taken even a second later. Some vulcanizates can produce a lower value within one second of time. This is significant for rubber with a high viscous component (see section 7.6.1). For example, a butyl compound might be less elastic than a NR gum and when the instrument is pressed into the vulcanized rubber, the indicator will instantly give a reading, which then decays to a lower value. This decay might be negligible for the NR gum, which is highly elastic, but might be in the order of 3 or 4 units for some butyl vulcanizates. The amount of decay gives an indication of the viscous component in a vulcanizate, thus an undercured product would have a larger decay than a correctly cured one. The more elastic a vulcanizate is, the less the decay. All of this would be regarded as a semi-quantitative measure to be used cautiously by the experienced chemist.

It is preferable to bring the durometer down vertically on to the rubber, (rather than pressing it down at an angle then bringing it to vertical). The standard ASTM D 2240 allows the tester to read the instrument at any time within one second, after applying the instrument to the rubber. The reading could change a few points in this time. The shape of the rubber surface being measured also makes a difference. A concave rubber surface might produce a slightly lower reading, while a convex surface would produce a slightly higher value. ASTM D 2240 specifies a minimum rubber sample thickness of 6 mm and testing at a minimum distance of at least 12 mm from its edge. The variability of the pocket durometer has to be set against its convenience. A variance of ± 5 hardness units is a typical industry standard. In North America the Shore scale is widely used, a rubber band would be around 30 points on the Shore A scale, a car tire, maybe 60 points. At values above 90 Shore A, the stiffness that hardness approximately correlates with, begins to increase exponentially, and it is recommended that a Shore D scale be used. Thus the Shore D scale in effect expands the higher end of the Shore A scale. Incidentally both Shore A and Shore D scales give a value of 100 points for glass.

In order to reduce variance, but at the expense of portability, the pocket durometer can have a weight fixed on to it and this combination moves down a stand, onto the rubber test piece. This reduces operator variability. There are also specific bench instruments, dead load hardness testers, operating similarly to the durometer described previously. ISO 48 states that the reading is to be taken at a specific time of 30 seconds after contact with the test piece, using these instruments.

One additional hardness measuring instrument, which should be mentioned in passing, is the Pusey and Jones (ASTM D 531) [24]. It is still used in the rubber roller industry, and is a large bench instrument. Its numerical values are not the same as Shore A or IRHD although there is a correlation between them.

For both IRHD and Shore scales, numerical values at the high or low end of a particular scale suggest moving to the next higher or lower scale available. For example if values above 90 on the Shore A scale are obtained, a move to a Shore D scale is recommended. The standards for methods of determining hardness are ISO 1818, ISO 48 and ISO 1400, which cover the ranges 10-35 IRHD, 10-100 IRHD and 85-100 IRHD, respectively.

As an approximation, the Shore A scale is equivalent to IRHD. However ASTM D 1415 (similar to ISO 48) is a test method specifically for IRHD (International Rubber Hardness Degrees).

5.4.3 Tensile properties

ISO 37 [25], ASTM D 412 [26], BS 903: Part A2 [27], DIN 53504 [28]

If rubber is stretched, squashed or otherwise mechanically deformed, the scientist says that a deformation (change in shape) called strain has been applied to the material, as a result of an applied pressure called stress. There are certain clearly defined modes of strain, such as tensile (stretch), compression (squash), shear (a combination of tensile and compression), and torsion (twist).

The most used strain mode in the quality control rubber laboratory is tensile. In this test, a piece of rubber is stretched until it snaps (tensile at break). The test piece often goes through a considerable amount of elongation before break occurs (up to around 900%, depending on the compound). It is interesting that this test is so popular, since there are very few product applications where the rubber is stretched so much.

• *Tensile testing*

Tensile testing is accomplished by first molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces are die cut (see Figure 5.7).

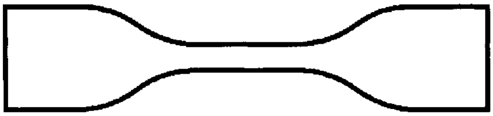

Figure 5.7 Dumbbell shaped test piece for tensile testing

The test pieces are then stretched in a tensile testing machine and the force required to stretch the samples is measured. Values of stress (force divided by the unstretched cross sectional area of the straight portion of the dumbbell) are recorded at various levels of extension, up to the break point. The extension is measured as percent elongation and is defined as:

$$\frac{L - Lo}{Lo} \times 100$$

Where: L is the stretched length.
Lo is the original length.

Tensile values before the sample breaks, give the modulus of the sample. For the rubber chemist, modulus means the tensile value (stress) at a given elongation. Modulus numbers at 100%, 200% and 300% elongation are commonly measured. Note that the modulus, as defined here, is not equivalent to the modulus as understood by an engineer, which is equal to stress over strain. See section 7.3 for further explanation.

• *Significance of tensile testing*

An important function of tensile testing is to determine how well ingredients are dispersed in the rubber compound, during the mixing stage. For example, if carbon black is is poorly dispersed, the tensile strength (at break) of the cured compound will be lower than it should be. A low state of cure, due to insufficient curative, as well as inadequate cure time or temperature, will also give a lowered tensile strength.

If a compound has too much carbon black, not enough oil, or too high a state of cure, perhaps due to excessive sulfur or accelerator, it will be reflected in a higher modulus value. A severely overprocessed NR compound might have a lowered modulus value. Compounds used in the rubber industry have tensile strengths from less than 7 MPa to around 28 MPa. Urethanes can have even higher tensile strengths. There are cases where tensile strength is specifically relevant to an application, for example an elastic band. A higher tensile strength is also preferred for highly dynamic applications.

5.4.4 Tear

ISO 34 [29], ISO1816 [30], ASTM D 624 [31], BS 903: Part A3 [32], DIN 53515 [33]

This test measures a rubber's ability to resist tearing. A shape is cut from a flat sheet and stretched in a tensile machine. The most common shape in North America is that cut by die C, where the sample is designed to tear at the apex of a V, as in figure 5.8.

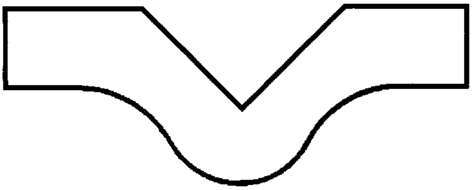

Figure 5.8 Rubber tear test piece (ASTM die C)

If this apex in the die is not kept sharp and well defined, it can result in higher apparent values of tear. ISO 34 describes a trouser shaped test piece which might avoid this problem. In general interpretation of tear tests should be treated with caution. Brown [34] makes the comments that a distinction should be made between the force required to initiate a tear and that needed to continue or propagate the tear, and also that results are sensitive to test piece geometry.

5.4.5 Compression set

ISO 815 [35], ASTM D 395 method B [36], ASTM D 1414 [37], BS 903: Part A6 [38], DIN 53517-1 [39]

This test measures a rubber's ability to recover from a compressive deformation. A popular variation, such as ASTM D 395 method B, compresses a sample by 25% of its original thickness. It is then held in this state, between two steel plates, for a specified time and temperature. The steel plates are then removed, and the test piece allowed to cool at room temperature for 30 minutes, and then the thickness is re-measured. If the sample recovers to its original thickness (that prior to compression) completely, it would have a zero percent compression set. If there is no recovery at all, it would have 100% compression set. Thus a poor compression set has a high number and a good compression set has a low numerical value. For example, applying ASTM D 395 method B, a good quality NR vulcanizate, might have a compression set of 15%, when compressed for 22 hours at 70 °C and then released. This would indicate a healthy ability to recover from compression.

• *Compression set as a predictor of seal performance*

Compression set is a test which measures the ability of cured rubber to recover to its original shape after the deforming force is removed. The ability of a seal to prevent leakage would seem to rely on properties of a rubber during compression, not after release from compression, as exemplified by compression set where the deforming force is removed. This is certainly the case when a functioning seal stays compressed, i.e., the deforming force is not removed, during the whole of its lifetime. In such a situation a compression set test would only be an indirect measure of the seal's ability to function.

The compression set test is very simple, and is widely used in the industry. However, a test called stress relaxation might be more appropriate, as it would be a more direct measure of the seal's ability to function. Here a sample is compressed in a housing and the amount of force (backpressure) exerted by the sample on the housing is recorded as a function of time. Since rubber is not perfectly elastic, this force (stress) will decrease with time. If this force were to become lower than that exerted by a fluid contained by a seal, it would indicate the likelihood of leakage. The debate about the use of compression set and stress relaxation as a predictor of seal performance is not a new one, but theoretically, the latter test seems the obvious choice [40, 41]. The production of extensive data correlating stress relaxation, compression set and seal performance might settle this debate. ASTM D 1390 [42] is a very recently introduced test for stress relaxation; ISO 3384 [43] is also a test for stress relaxation.

5.4.6 Shear modulus

ISO 1827 [44], ASTM D 4014 Annex A [45], BS 903: Part A14 [46]

There is no test listed specifically for Young's modulus (see section 7.3) or shear modulus in the two standard volumes of ASTM standards designated for rubber (Vols. 09.01 [47] and 09.02 [48]). However Annex A in ASTM D 4014, Elastomeric Bearings for Bridges, does have a method for shear modulus. ASTM D 797, A Test for Young's Modulus by Bending Beam was withdrawn in 1995. There is an ASTM test for rubber properties in compression, ASTM D 575 [49]. Shear and Young's modulus for metals are addressed in ASTM E 143 [50] and ASTM E 111 [51], respectively. The latter also discusses tangent and chord modulus.

The following information is found in ASTM D 4014 Annex A. The test piece (quadrupole) shown in Figure 5.9 is designed to prevent twisting when shearing the sample. It is important that a full bond remains between the rubber and steel plates, at all times. The middle steel plates are placed into the grips of a tensile testing machine. When the grips are moved apart, this causes shear in the rubber blocks. Data are measured from the sixth force deflection cycle, using the chord modulus (see section 7.3.1) at the specified strain. A discussion of shear modulus and its use as a rubber laboratory test can be found in Peacock [52].

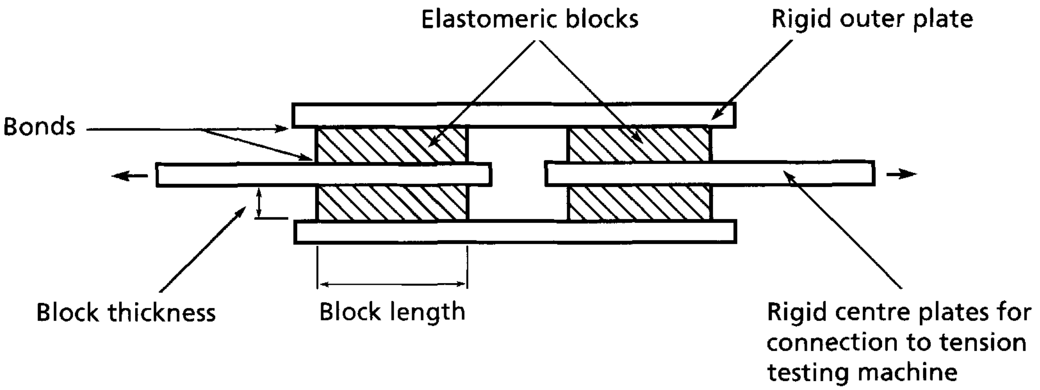

Figure 5.9 Shear modulus test piece, copyright ASTM
(reprinted with permission)

5.4.7 Other laboratory tests

There are numerous other tests available. Electrical properties such as volume resistivity, are found in ASTM D 991 [53], where an antistatic rubber is described as one having a resistance of 10^4-10^8 Ω, while a conductive rubber has a resistance less than 10^4 W at 120 volts. Both properties are achieved by the use of special carbon blacks in the rubber compound. Interestingly, poor dispersion of standard carbon black in a rubber compound will give a low value for electrical resistance; as dispersion improves, resistivity increases. Other tests include ozone resistance, heat aging, swell in liquids, low temperature brittleness and flame propagation. For material analysis of a compound, (details of methods can be found in ASTM volume 09.01), the traditional tools of chemistry such as infra-red analysis and chromatography are used to determine elastomer type, carbon black and non-black filler level, plasticizer content, sulfur, accelerator and antioxidant levels. This information can be augmented by instruments which measure how heat interacts with rubber. Such instruments are called thermal analysers, such as differential scanning calorimeters (DSC), thermogravimetric analysers (TGA), and thermomechanical analysers (TMA) [54, 55].

Dynamic mechanical thermal analysers and dynamic mechanical rheological testers [56] are being used significantly more now than in the past. They are able to generate rheological and engineering data on cured rubber by applying various deformation modes at different frequencies and temperatures.

References

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   Part 1: Determination of Mooney Viscosity

   ISO 289-2:1994
   Rubber, Unvulcanized - Determinations Using a Shearing-Disc Viscometer
   Part 2: Determination of Pre-Vulcanization Characteristics

2. ASTM D 1646-96a
   Test Methods for Rubber-Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)

3. BS 903:Part A58: 1990
   Physical Testing of Rubber
   Part A58. Methods Using the Mooney Viscometer

4. DIN 53523-3
Testing of Rubber and Elastomers; Testing with the Mooney Shearing Disk Viscometer; Determining the Mooney Viscosity

5. ASTM D 1349-87 (Reapproved 1992)
Standard Practice for Rubber - Standard Temperatures for Testing

6. ISO 3417:1991
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7. ASTM D 2084-95
Test Method for Rubber Property - Vulcanization Using Oscillating Disk Cure Meter

8. BS 903:Part A60: Section 60.2
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6

Chemistry

"What? Chemistry is like architecture?" ...said Andrew.

"Molecular architecture, you need to know how to design a polymer and understand what each part does and how the parts fit together", ...said Robert.

6.1 Building a rubber molecule

Just like a house built from bricks, the raw gum elastomer is also built from small discrete units, called monomers. Both monomers and polymers are molecules, the former are small, the latter are very large. Monomers are simple chemicals, such as ethylene, propylene, isoprene, and butadiene, most of which originate from petroleum oil.

To a chemist a butadiene monomer would look like this: $CH_2{=}CH{-}CH{=}CH_2$.

All of the carbon atoms are linked together like a small chain. Two methods of representing the structure are shown in Figure 6.1.

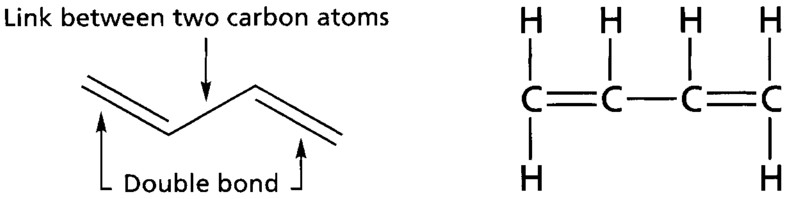

Figure 6.1 A butadiene molecule (monomer) used for creating BR and other rubbers

The end carbon atoms have two bonds, linking them to the adjacent carbon atom. These are called double bonds (also known as unsaturated bonds), and they are much more chemically reactive than a single bond. It is the double bonds that allow the carbon atom on the end of this small chain to link up with a carbon atom on the end of another butadiene molecule, and start a 'chain reaction' (polymerization) to build up a 'superchain' containing thousands of monomers, all linked together.

Due to the small size of the butadiene molecule it is highly mobile at room temperature and pressure, i.e., it is a gas. As the butadiene chain grows, a given amount of thermal energy cannot move the larger molecule around as easily, and it becomes a liquid. Eventually it reaches 'supermolecule' status, i.e., a polymer or in this case, more specifically an elastomer. The molecule is so large that it becomes a solid, or maybe more accurately, an ultra slow moving liquid, and is referred to as polybutadiene rubber. In fact, a bale of BR can literally flow off a shelf, after a long period of storage, depending upon the storage temperature and assuming the material has unrestricted movements. To the rubber compounder it is now a raw gum elastomer, and it can be used as a primary ingredient to mix a rubber compound.

In the language of chemistry, the elastomer's chemical formula is:

$(\text{-}CH_2\text{-}CH\text{=}CH\text{-}CH_2\text{-})_n$

where the chemical species inside the brackets is the basic repeating unit (monomer) and *n* is the number of monomers in the elastomer chain. There are still some double bonds in the polymeric chain and these are essential to the cross-linking process, using sulfur as the vulcanizing agent.

6.1.1 Other building blocks

The architecture of butadiene can be altered to produce an entirely new rubber. By reaction with chlorine a monomer called 2-chloro-1,3,-butadiene ($CH_2 = CCl\text{-}CH = CH_2$) results, which when polymerized, produces polychloroprene, also known as neoprene. Alternatively another monomer can be polymerized with the butadiene molecule, a process described as copolymerization. If the other building block is styrene, styrene butadiene (SBR) is produced. If instead of styrene the other monomer is acrylonitrile, the polymerization will produce butadiene acrylonitrile copolymer (NBR) or nitrile rubber. Naturally, butadiene's versatility does not extend to all elastomers.

When either ethylene or propylene are polymerized on their own, polyethylene or polypropylene is the outcome, popular as plastic kitchenware. If an element of 'randomness' is introduced into the architecture of the polypropylene, such as introducing ethylene into a growing polypropylene chain, the resulting polymer has the characteristics of an elastomer. The result of this copolymerization of both ethylene and propylene is EPM rubber. Its chemical structure is shown in Figure 6.2. Note that this simplified structure does not imply a 1:1 ratio of ethylene to propylene.

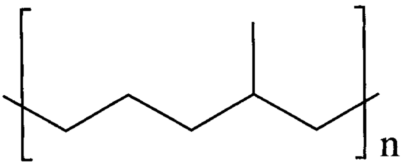

Figure 6.2 EPM

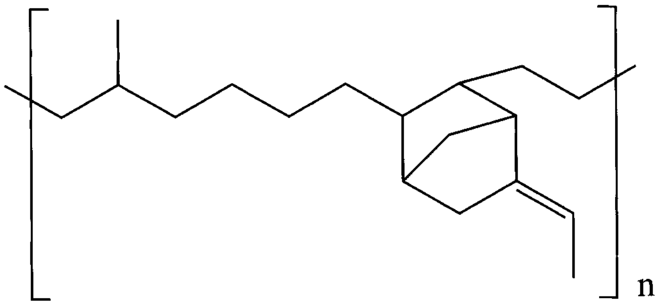

Figure 6.3 EPDM

The elastomer has no double bonds and therefore can not be cured with sulfur, so the cure of choice would be peroxide. An extra chemical species with unsaturated bonds, locked into the side of the main polymer chain, would mean that sulfur vulcanization could occur, and the raw gum elastomer produced is called EPDM. Since the main chain has no double bonds it cannot be so easily attacked by oxygen or ozone. Figure 6.3 shows the chemical structure of EPDM. Note the double bond which allows sulfur cross-linking to take place. The double bond is not part of the main chain. Various diene monomers are used to introduce the double bond into EPDM.

6.1.2 Shop floor significance of molecular weight

During the manufacture of the raw gum elastomer, the polymerization process can be stopped at any given point. However, in order for it to have useful properties, the polymer must grow to a certain minimum chain length with a certain molecular weight. In practice there will be an assortment of many differently sized chain lengths in the elastomer, i.e., it will have chains of many different molecular weights. This is known as the molecular weight distribution of the elastomer. The average molecular weight will correlate with laboratory determinations of Mooney viscosity.

Low hardness compounds can often contain larger amounts of incorporated oil in order to achieve a low Shore A value. However, the incorporated oil also reduces the compound's uncured viscosity to such an extent that molding becomes difficult because of too little backpressure. A high molecular weight grade of raw gum elastomer has a high viscosity. Thus if it replaces a medium molecular weight raw gum elastomer in the compound, the final compound viscosity might now be high enough for efficient molding without affecting the requirement of low vulcanized hardness. Raw gum elastomer manufacturers sometimes sell their product with oil already incorporated.

When the scientist looks at the solid raw gum elastomer, he sees long chain molecules which are relatively free to slide past one another, in the bulk polymer. Hence the ability of polybutadiene mentioned earlier to 'pour off the shelf'.

The ability to totally control the molecular architecture of the polymer is not absolute, and thus there will be some variation in properties during the continued production of an elastomer. However, recent work with metallocene catalysts holds the promise of improved control.

6.2 Vulcanization

A piece of unvulcanized rubber is a mass of long polymer chains, all entangled, like a bowl of spaghetti. When it is stretched, two things occur: the chains disentangle to some extent and there is a degree of slippage, the chains slipping and sliding past one another, and they also tend to straighten out. When the rubber is released from stretching the straight chains recoil and re-entangle.

Vulcanization significantly increases the overall elasticity, by locking the chains to each other (see section 6.2.1), which greatly decreases the amount of slipping the chains can undergo. This is the process of cross-linking. Cured rubber is a much more dimensionally stable and heat resistant material. This is somewhat analogous to a coil spring mattress. If the coils were not linked (uncured rubber), the mattress would distort and wobble drastically. Linking the coils (vulcanization) makes the mattress firm (dimensionally stable) and provides it with plenty of bounce (elasticity).

6.2.1 Sulfur vulcanization

The first and by far the most important cross-linking agent is sulfur, which is relatively inexpensive and plentiful, and yet vital to the rubber industry. For a number of elastomers, the double bonds (unsaturation) discussed earlier are in plentiful supply on the polymer chain. Sulfur links one chain to another through these double bonds. Elastomers such as NR and SBR need only a small percentage of these double bonds to be utilized to produce a useful product; however this leaves the larger percentage unused and therefore vulnerable to attack by oxygen, ozone and heat.

Reaction of the small percentage of double bonds actually used for vulcanization can be achieved with 2-3 phr of sulfur in a conventional cure system. If more sulfur (30 phr) is added to the compound, many more of the available sites are cross-linked and the movement of the chains is so restricted after vulcanization that the rubber can barely stretch. It becomes very stiff (without the aid of any fillers) having a hardness of around 70 plus on the Shore D scale, and an inevitably reduced elongation at break of around 5%. The resulting material is called ebonite, so called because, when polished, it resembled the wood, ebony and indeed, before the days of plastic, polished ebonite was used for the handles of cutlery. Ebonite is still used today in tank linings and hair combs with a soft feel. The dense packing of cross-links in ebonite reduces swelling of the rubber in liquids and the lower number of double bonds reduces attack by ozone and UV light. By far the best known ebonite is that produced from NR, although ebonites can easily be produced from both SBR and NBR.

• *The sulfur cross-link*

At one extreme, a single sulfur atom connects the carbon atom of one chain to that of another. In practice the single sulfur atom is the predominant link, see Figure 6.5a. The rubber chemist knows that this is a result of using an efficient vulcanization (EV) system. EV can be achieved by adding to the rubber formulation, a particular type of accelerator, which has available sulfur atoms in its molecule, and avoids using elemental sulfur altogether. In this case the accelerator, now more appropriately called a cross-linking agent becomes a sulfur donor (see section 3.3.4). EV can also be achieved by using small amounts of elemental sulfur, about 0.3 to 0.8 phr, together with larger amounts of accelerator (2-5 phr). At the other extreme is a conventional cure system comprising 2-3 phr elemental sulfur and smaller quantities of accelerator (approximately 0.5-1.0 phr). This produces predominantly multiple sulfur atoms in the cross-link, known as polysulfidic cross-links, see Figure 6.4b. In between these two extremes lies the semi-EV system using about 1.5 phr elemental sulfur and a correspondingly adjusted accelerator level. The symbol S_x in Figure 6.4b represents the multiple sulfur link.

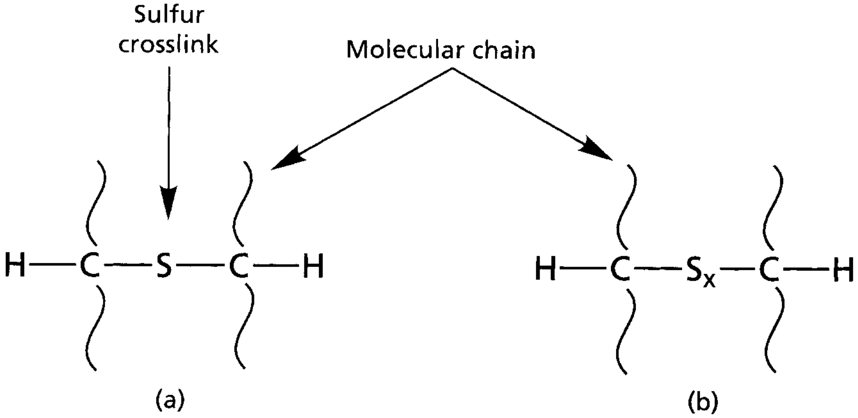

Figure 6.4 (a) Single sulfur atom linking two polymer chains. (b) Multiple sulfur link

• *Sulfur cross-links and properties*

Intuitively it might be expected that a cross-link consisting of many sulfur atoms would be more 'flexible' than a cross-link consisting of a single sulfur atom. In terms of properties, this means that vulcanizates with a conventional cure system are generally better at relieving stress when flexed, thus they have a better fatigue life in a repetitious (cyclic) deformation environment. A disadvantage is that sulfur to sulfur bonds are weaker (less thermally stable) than a sulfur to carbon link, the conventionally cured system is therefore, less heat resistant than a semi EV or EV system. The conventionally cured system also has poorer compression set.

6.2.2 Peroxides

Although sulfur is the best known and most used vulcanizing agent, there is another class of cross-linking agents known as peroxides. They do not need the reactivity of a double bond to cure, nor do they need accelerators, although chemicals known as co-agents are often used to improve overall vulcanization. Peroxides typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymer, thus creating highly active sites on the chain, called radicals, which attach to a similar site on another chain, creating a carbon to carbon cross-link, which is stronger than a sulfur carbon link and more thermally stable, see Figure 6.5.

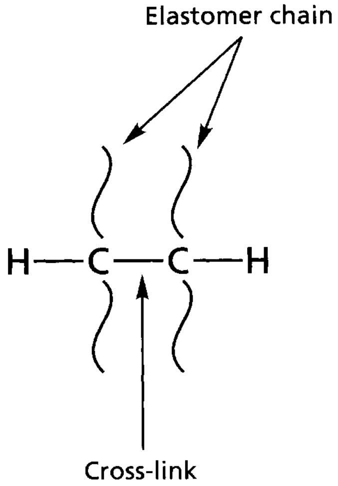

Figure 6.5 Two polymer chains directly linked through a carbon atom from each elastomer chain

Peroxide cross-linking confers a higher heat aging resistance. Heat aging implies the effects of increased temperature over time, not the effects as soon as a given temperature is reached. Peroxide cross-linking gives better compression set than sulfur cured cross-linking, at the expense of fatigue life and some tensile strength. Peroxide curing can vulcanize certain elastomers which cannot be cured with sulfur, because of a total lack of double bonds, for example the copolymer of ethylene and propylene rubber (EPM). Elastomers which can be cured with peroxides are EPDM, EP, SBR, NR, BR, CR, certain FKMs and silicones. Butyl rubber cannot be cured in this way, as the peroxide causes degradation of the rubber. However bromobutyl rubber can be peroxide cured for use in certain applications.

6.3 The cured product

6.3.1 Swelling in liquids

The way in which rubber products behave when in contact with liquids is of crucial importance to many applications such as hoses, pumps, and expansion joints, as well as in the seal industry.

In cases where swelling in liquids occurs it is often a physical phenomenon, without chemical interaction, so that even if the vulcanizate is allowed to freely swell, then when the liquid environment is removed, the rubber often returns to its original state relatively unharmed, since the cross-links are not ruptured. This assumes that no excessive stress (internal or external) is imposed on the rubber when it is swollen. If chemical interaction occurs as well, then the outcome changes. It should be noted that there is sometimes the possibility of some compounding ingredients, such as antioxidants or plasticizers, being extracted by the liquid.

A low swell in a test can sometimes be interpreted in more than one way. Consider the case of a cured compound, immersed in a liquid, which causes the raw gum elastomer portion to swell. If that liquid is also capable of extracting plasticizer from the compound, at the same time as the raw gum elastomer content is causing it to swell, the result might be, a 'zero apparent change in volume'.

• *Polarity*

The chemist uses the concept of polarity as a guide to determine how rubber will behave in a liquid. Certain atoms in a polymer chain can preferentially draw electrons towards themselves from their neighbors.

The chlorine atom, such as that in CR, draws electrical charge from the adjacent carbon atom, causing the chlorine to be slightly negative (electronegative) and the carbon to be slightly positive (electropositive), as follows:

$$^{\text{positive}}\,\mathrm{C\text{-}Cl}^{\text{negative}}$$

This makes CR a polar elastomer. A chemical group such as acrylonitrile (ACN) also has this ability in nitrile rubber.

Double bonds in a polymer chain also provide a measure of mobility for movement of electrical charge, introducing somewhat less polarity than the chlorine atom or ACN group. Double bonds are found in the main chain of NR, SBR and BR. EPDM has a low level of polarity, consisting of only carbon and hydrogen atoms with little unsaturation (the main chain has no double bonds) and no significantly electronegative side groups.

The same principle applies to liquids. Those with chlorine in the molecule such as methylene chloride are highly polar. Liquids with a combination of oxygen and carbon (the former draws electrons from the latter) with an unsaturated link between them such as is found in acetone and MEK (a chemical class known as ketones) are also quite polar. Benzene, although containing only carbon and hydrogen has many conjugated double bonds (highly unsaturated) giving it some polarity. Even the humble water molecule has some polarity between its oxygen and hydrogen atoms.

Liquid hydrocarbons, such as those derived from petroleum, have carbon and hydrogen atoms, with variable unsaturation. This means that some, such as benzene, are polar while others are not. Those with few or no double bonds, i.e., paraffinic oils are non polar.

• *How the chemist uses polarity*

Rubber will swell the most in a liquid of similar polarity to itself. Thus EPDM (low polarity) will swell little in methylene chloride or acetone (high polarity) and greatly in paraffinic oil (low polarity). Nitrile rubber, on the other hand, will do the opposite; hence its use as an oil resistant elastomer. However not all nitrile is created equal. It is sold with the polymer chain containing different percentages of ACN. As that percentage increases, so does the polarity of the rubber and thus the oil resistance improves. A low ACN content might only confer the oil resistance of CR.

If the common elastomers are arranged in order of increasing polarity it looks like this: EPDM, NR, SBR, CR, NBR. If the petroleum oils are arranged in the same way, it looks like this: paraffinic, naphthenic, aromatic. A word of warning however, polarity is not the only explanation for swelling, and there may be exceptions to the 'rule', nonetheless it does explain quite a lot.

6.3.2 Permeability to liquids

Some elastomers allow liquids or gases to move through them more or less easily; this is known as permeability. For example IIR is quite impermeable to pure water and therefore makes a good lining for vessels holding pure water. In the tank lining industry, water is a common liquid in contact with rubber. If the water is very pure with no dissolved salts, it might slowly permeate natural rubber linings. In this case, the rubber manufacturer might recommend that a lining consisting of an ebonite layer, sandwiched between two gum layers, be bonded on to the wall of the tank. The dense ebonite layer will significantly reduce permeation, and be physically cushioned from mechanical damage by the gum layers. The outer gum layer will provide good abrasion resistance to any fine particle undissolved slurry. If there are dissolved salts in the water, they will significantly slow down permeation of water molecules from the solution, and an ebonite layer might not be needed. In this case, a possible explanation is that the electrically charged species produced by the salt, 'hold back' movement of water through the lining.

6.3.3 Effects of low temperature - glass transition

An elastomer is envisioned as a coiled polymer chain. Applied deformation results in movement of the molecular chain, such as stretching. This is possible due to open spaces within the coil. As the temperature is lowered, this open space (free volume) becomes smaller, restricting chain mobility. In our "macro" world this reveals itself as a stiffening of the elastomer. Eventually a temperature is reached at which there is insufficient free volume to allow any mobility and a significant (thousandfold) increase in stiffness occurs. With continued cooling, a temperature is eventually reached where if some rubbers are hit with a hammer, it can shatter like glass. This state is the glass transition temperature or the glass transition point, although it is more a region than a point.

The stiffening is a purely physical phenomenon and is totally reversible. The glass transition temperature (*Tg*), will depend primarily on the raw gum elastomer, although there is the possibility of modifying it with plasticizers. *Tg* can be explained by considering chemical entities attached to the elastomer's main backbone. Thermal energy allows them to rotate around this main chain. If the rubber is cooled, then as the *Tg* is reached, rotation stops. If these chemical monomer groups are large (bulky), and if there are many of them, the *Tg* will be reached sooner, i.e., at a higher temperature.

For nitrile rubber, the ACN group is somewhat large. The number of ACN monomer groups polymerized in the main chain can also vary, depending on the grade of NBR rubber purchased. A low ACN nitrile (a low percentage of acrylonitrile groups) therefore has fewer bulky groups, which permits its *Tg* to be lower. Thus a nitrile with a 25% ACN content, will have a *Tg* around -48 °C, compared to a high ACN content of 45% with a *Tg* about -14 °C.

The use of dioctyl sebacate, and similar plasticizers, can lower the *Tg* of NR, CR and NBR. Speed of deformation (strain rate in dynamic deformation) of the rubber vulcanizate also has an effect on *Tg* (see section 7.7).

6.3.4 Effects of low temperature - crystallization

Certain elastomers undergo a less dramatic stiffening at low temperatures, for reasons other than glass transition. The effect occurs at warmer temperatures than *Tg*, and is also fully reversible; it might be equivalent to a 20 point increase on the IRHD scale. As the temperature is lowered, the polymer chain takes on a more ordered orientation, and a phenomenon called crystallization occurs. Crystallization requires a regular structure, and the best known elastomers which demonstrate this phenomenon are CR and NR. Crystallization may take days or months to reach maximum stiffness. The rate at which crystallization occurs in vulcanizates is maximal at -25 °C for NR and at around -10 °C for CR. Addition of plasticizers may increase the crystallization rate. The level of sulfur in an NR formulation significantly alters the crystallization rate of the vulcanizate. A sulfur level of 2.5 phr in the compound will substantially reduce the rate compared to a level of 0.5 phr. The grade of raw gum elastomer used in CR can also affect the crystallization rate. The stiffening effect may not be too much of a concern in some applications, since dynamic movement of the vulcanizate quickly 'dissolves' the crystalline regions removing the problem. Effects of low temperatures on NR are discussed in MRPRA literature [1].

6.3.5 Stretching - strain induced crystallization

The term crystallization is also used to describe the behavior of CR and NR when a vulcanizate is stretched at room temperature. Upon stretching, an ordered alignment occurs in the polymer chain and crystalline regions form. Here it occurs extremely rapidly and is called strain induced crystallization. The crystalline regions 'dissolve' just as rapidly when the strain (stretching) is removed. The cured gum elastomer becomes very strong when stretched, as shown by a high tensile strength. Most elastomers do not demonstrate strain induced crystallization and are mechanically weak as a vulcanized gum. This gives NR and CR an advantage where soft vulcanizates are needed in certain engineering applications.

6.3.6 Aging

Like the human body, rubber is subject to the ravages of aging and some of the reasons might be similar. Aging can be caused through attack by oxygen, ozone, and constant flexing. Surprisingly, or maybe not, the means of protection from aging for both people and rubber sometimes coincide. Antioxidants in vegetables and vitamin supplements provide resistance to free radicals, while antioxidants and antiozonants provided by the industrial chemist protect rubber.

The double bonds, so important for vulcanization, have an 'achilles heel'. They can be the site for attack by ozone, even in concentrations as low as 10 parts per hundred million. If the cured rubber is kept stretched, even slightly, the rate of ozone attack dramatically increases. Cracks appear perpendicular to the stretched direction, with the potential to cause destructive tearing, which could be catastrophic in a thinner product.

Oxygen can cause the chains to break, softening the rubber, or in many cases providing sites for further cross-linking, thus making the vulcanizate hard and brittle. NR, as well as the other unsaturated elastomers, are prone to damage by oxygen and ozone. EPDM however has no unsaturation in its main chain and is far more resistant. Ultraviolet light, as well as copper and manganese compounds soluble in rubber, can all accelerate oxygen attack (oxidation).

As a rule, heat tends to increase chemical reactions, which means, all of the above aging processes will tend to be much faster as the temperature rises. Carbon black is an excellent UV absorber and will give good protection from the effects of UV light.

If the double bonds are chemically removed from the rubber, it becomes less vulnerable to heat aging and 'weathering'. Thus if the double bonds in nitrile are mostly or totally used up, by adding hydrogen atoms (hydrogenation), during the manufacture of the raw gum elastomer, it still retains its oil resistance and in addition, like EPDM, gains heat aging, oxygen and ozone resistance. Such a rubber is highly saturated nitrile (HSN, HNBR), described in Chapter 2.

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7 Engineering

"So what's the elastic tensile modulus of the rubber?" said Andrew. "Depends on how much you are going to stretch it", ...answered Jerry.

"Look, just tell me what the modulus is, will you" ...replied Andrew.

7.1 Introduction

The engineer, used to the precision of metals, tends to consider rubber to be a somewhat undisciplined material. In the past, engineers have tended to leave it in the hands of the chemist. Meanwhile rubber, which was clearly an engineering material, waited patiently to be fully utilized by the engineer. One problem is that complete engineering data are in short supply. It is to be hoped that this situation will change and indeed recent indications over the past few years are that such changes are beginning to take place.

Products made from a range of materials can be 'elastic' due to their method of construction, for example a helical metal or plastic spring. The compressed air in a balloon will allow it to return to its original shape after deformation, and this concept has been incorporated into products combining bubbles of air or other gases with viscous materials to produce a viscoelastic effect for highly efficient shock absorption [1]. Elasticity can also be an intrinsic property of the material which nature achieves in a spider's web. The capture silk within the spider's web can stretch 300% [2]. It is suggested from studies of the golden orb-weaving spider that segments of protein in the silk contain long spring-like shapes. Another material with intrinsic elastic properties is of course, rubber.

7.2 Rubber and steel

The engineer is familiar with metals, so it might be of interest to briefly compare them with elastomers. It could be argued that steel is more elastic than rubber. The catch is that steel can only be stretched to about 2% of its original dimension, while still remaining elastic. Rubber, on the other hand, while possibly not being as resilient (see section 2.2.4), can keep most of its elasticity when stretched anywhere from around a hundred to several hundred percent. When an elastic material is stressed, then upon release of the stress, no permanent strain remains.

Consider next, tensile strength at break. Rubber at its best, has a value around 35 MPa, whilst that of carbon steel is about 500 MPa. It would appear that steel is vastly stronger than rubber. However, Lindley [3] argues that if we take the cross section of the rubber at the point when it breaks, since it is still elastic up to this point, rather than the original cross section, and then recalculate the tensile strength (force/area), it begins to approach that of steel. It could also be argued that we should be comparing a yield tensile strength of carbon steel, which is around 250 MPa, since vulcanized rubber's tensile strength at break is virtually its yield point (in practical terms rubber will break before a yield point is reached).

Rubber can be thought of as an energy storage device, converting kinetic energy and storing it as potential energy, and as such is capable of storing 150 times more energy than steel [4].

A tall block of rubber can be compressed more per unit thickness, than a short block, even though the cross sectional area, and load on that area is the same for both blocks. The tall block is apparently 'softer' than the short block! With steel, both blocks will deflect to the same extent per unit thickness. This makes rubber extremely versatile since a rubber product's stiffness can be altered by a simple change in its shape (see section 7.4.1).

The next property considered by the engineer is 'elastic' modulus. For steel this is the same as Young's modulus. It is a measure of stiffness intrinsic to the material and independent of geometry. For steel it is very much a constant, and can be relied on like the sun coming up each morning. For rubber, this is not quite the case. Stretch it and its modulus changes as it is stretching. Warm it up or cool it down, stretch it quickly or stretch it slowly, it keeps changing. It even changes from one stretch cycle to the next.

Steel, with a Young's modulus of around 200,000 MPa is a vastly stiffer material than rubber, whose tensile modulus is 1-2 MPa for a NR gum compound vulcanizate. This increases to around 10 MPa, for an 80 IRHD (80 Shore A) cured NR material.

A final point, is that rubber does not 'corrode' as steel does. This makes rubber in applications such as bridge bearing effectively 'maintenance free'.

7.3 Stress, strain and modulus

Many rubber products are used in situations where a load is applied to them, such as the weight of a motor vehicle and its motion on the road, against the tires. This causes a deformation in the rubber. Other simple examples of deformation are stretching of a rubber band or the compression of a rubber seal. The engineer prefers to use a more precise language to describe this mechanical behavior.

Stress is the force applied to the product, divided by its original cross sectional area. Thus a force of one Newton on an area of one square meter would produce a stress of one Pascal.

Strain is the change in size as a single dimension such as length, due to the applied force.

$$\text{Strain} = \frac{L - L_o}{L_o}$$

Where: L is the strained dimension
L_o is the original dimension

If a strip of rubber stretches from 1 cm to 1.1 cm, strain will be 0.1/1.0 = 0.1

The chemist prefers to use percentage elongation which in this case would be 10%.

To obtain a measure of stiffness for a material, the chemist uses hardness, as in IRHD or Shore A. The engineer is more familiar with modulus.

$$\text{Modulus} = \frac{\text{stress}}{\text{strain}}$$

If a strip of rubber were stretched with a stress of 2.0 MPa resulting in a strain of 0.5 (50%) the modulus would be 2.0/0.5 = 4.0 MPa, in this case referred to as tensile modulus.

A word of caution, chemists use the term modulus in a different context, and define it as the tensile stress for a given elongation. Thus compound property specifications commonly use modulus with the understanding that it is defined as stress for a given strain.

Modulus is important to the engineer and he uses it in various deformation modes of the material (see figure 7.1), such as tension, shear, compression (strictly speaking, effective compression, where the rubber is allowed to bulge) and bulk compression (where the rubber is compressed but is physically restricted from bulging).

The engineer also makes a distinction between static modulus, such as in a gasket where there is no dynamic movement, and dynamic modulus such as in a tire rotating against the road, where there is lots of dynamic movement. Dynamic modulus is higher than static modulus because the rate of change of the load alters the value of the viscous

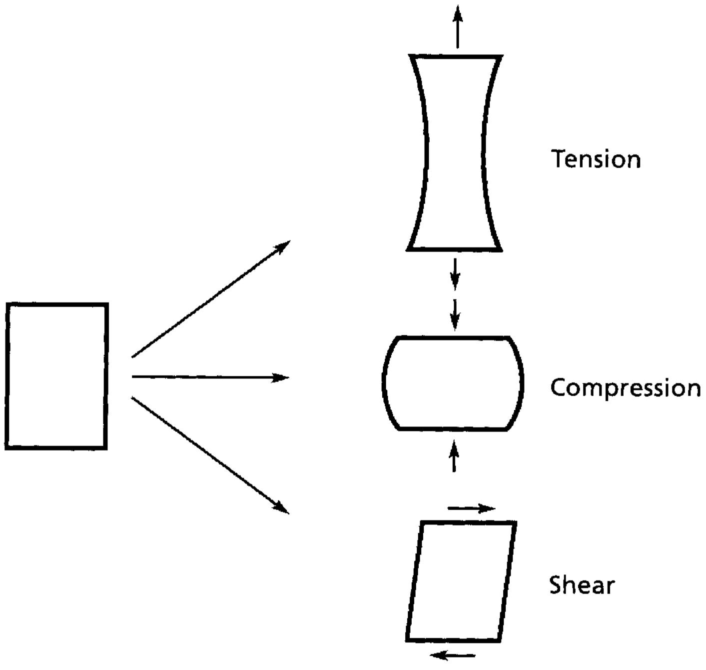

Figure 7.1 Some deformation modes for rubber
(courtesy of the Holz Rubber Company)

component of the modulus (Newton's Law of viscosity, see section 7.6.4). An example of the use of modulus properties would be the design of seismic bearings for earthquake protection, where both shear and compression properties are critical.

7.3.1 Tensile modulus and Young's modulus

The chemist tests the tensile strength of a cured compound and uses the information to confirm that a compound was mixed correctly, including the dispersion of fillers. He might only use one or two points on a graphical plot of tensile stress against strain. The engineer can extract a wealth of additional information from parts or even all of the graph.

Consider the typical curve in Figure 7.2. The gradient of the curve changes as it is stretched. Since the gradient represents stress/strain it provides the value for the modulus of the material. The curve represents the sixth stress cycle, i.e., the test piece was cyclically deformed six times.

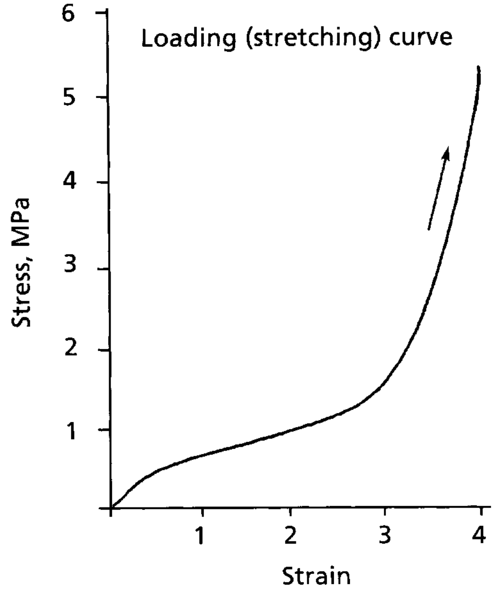

Figure 7.2 Tensile stress/strain curve representing the sixth stress cycle

An engineer will usually define Young's modulus as the gradient of the curve, where it meets the origin (where the stress and strain axis meet at zero). This is fine for steel, which follows Hooke's law (stress is directly proportional to strain) up to its elastic limit, and cannot stretch elastically more than about 2% anyway. However, elastomers are elastically useful far beyond this value and Young's modulus at 2% might not have much meaning for rubber if the intended application is above this value. At 2% elongation the stress/strain curve for rubber is substantially linear (assuming that temperature and strain rate are held constant). If temperature or strain rate is changed, Young's modulus will alter its value. It will decrease as temperature increases, and increase as strain rate increases. Such behavior will apply to all modes of deformation. However, elastomers can be substantially elastic up to several hundred percent strain. Figure 7.2 indicates that in the very small strain region, tensile modulus is fairly linear and therefore might qualify as Young's modulus (which follows Hooke's law). As strain is increased the stress/strain gradient has clearly begun to change, indicating a material with an apparently lower tensile modulus. The rubber is now 'softer' and has lost its linear nature but it is still a rubbery elastic material. Lindley [5] states that 'for non-linear stress/strain behavior, it is necessary to specify the strain at which the modulus is evaluated'. He also suggests that a distinction be made between the tangent modulus, i.e., the slope of the tangent to the stress/strain curve, and the chord modulus, i.e., the slope of the line from the specified strain to the origin.

The tensile curves in Figures 7.2, 7.5 and 7.6 are all from the same rubber sheet (2 mm thick), cured for 25 minutes at 150 °C. The compound is NR with a highly reinforcing carbon black filler and oil for processing purposes. It has a tensile stress at break of 28 MPa and an elongation at break of 620% (a strain of 6.2) with a Shore A hardness of 50. All samples were tested at a strain rate of 50 cm/minute at 20 °C.

7.3.2 Young's modulus equals three times the shear modulus?

For an isotropic, incompressible material there is a relationship between Young's modulus and Shear modulus, such that $E = 3G$.

Lindley [6], provides a table with values of Young's modulus (E) and shear modulus (G) for natural rubber vulcanizates. If we look at the 30 IRHD values (where the rubber contains no carbon black filler) and divide its Young's modulus by its shear modulus an E/G value of 3 is obtained.

This rearranges to $E = 3G$

Classical mechanics also indicates that $E = 2G\,(1 + \nu)$

Where ν = Poisson's ratio

$$\text{Poisson's ratio} = \frac{\text{normal strain}}{\text{lateral strain}}$$

Rubber, with some properties of a liquid, is virtually incompressible. (Elastomers just seem to be compressible, because they bulge). This incompressibility gives them a Poisson's ratio value very close to 0.5 for smaller strain levels. If this value is substituted into the above equation:

$$E = 2G\,(1 + 0.5)$$

Giving us the same relationship again: $E = 3G$

Unfortunately this relationship only appears to apply to unfilled rubbers, and becomes more complicated when carbon black is added. Using Lindley's [6] numbers for E and G for a 65 IRHD vulcanizate.

$$E = 4.2G$$

Thus it seems that the gum rubber follows classical mechanics, while carbon black complicates the issue. In other words, it would seem that a highly elastic material, such as the NR gum compound, gives a much better fit to the equation $E = 3G$, while a less elastic rubber, such as the 65 IRHD does not. Even the gum's fit with the classical equation might falter, when other factors, for example a higher strain level, are introduced.

A later edition of Lindley's work [7], gives a value for a particular gum natural vulcanizate, of:

$E = 1.5$ MPa

and $G = 0.49$ MPa, and for a particular 65 IRHD rubber,

where: $G = 1.3$ MPa, this latter value for 0-2% strain. Lindley also states that linearity for unfilled vulcanizates is limited to strains of up to a few percent.

7.4 Compression modulus, Young's modulus and shape factor

Measurement of tensile strength at break is useful to the chemist. However, far more actual rubber product applications experience compression. The engineer recognizes this and uses this property far more than the chemist.

True compression modulus is an intrinsic material property. It is a measure of an actual change in volume due to compression, not a change in shape, such as bulging, where the overall volume remains the same. If we physically restrain rubber from bulging and apply a compressive force, its compression modulus would be extremely high, since rubber is virtually incompressible. Gent [8] uses the term modulus of bulk compression, E_b, for this property intrinsic to the material.

If compression is applied and the rubber is allowed to bulge, the correct term would be, as Gent points out, effective compression modulus, E_c. In this book the term compression modulus will be used to mean effective compression modulus.

Now let's link together Young's modulus (taken at small strain values) and effective compression modulus.

Gent states that for a flat sandwich block:

$$E_c = E(1+2\phi S^2)$$

Where: E_c is the effective compression modulus

E is Young's modulus

S is the shape factor of the block (see section 7.4.1)

ϕ is the elastomer compression coefficient

The relationship will change for different shaped rubber samples.

7.4.1 Shape factor

An interesting property of vulcanized rubber in compression is that it can be stiff or soft, depending on its shape. This has the potential of making a complex engineering problem simpler to solve. The key is in rubber's ability to bulge, when a load is applied, see Figure 7.3.

As we reduce the area that is 'free to bulge', the rubber product becomes stiffer.

For example, assume that there are two disks, both with the same diameter, but one is 1 cm thick and the other is 5 cm thick. If the disks are compressed so that the thickness of both is reduced by the same percentage amount, more force will have to be applied to the 1 cm disk than to the 5 cm disk to achieve the same percentage reduction in thickness. The 1 cm disk has a smaller 'wall area' (therefore less area free to bulge) that the 5 cm disk which translates into a higher compression modulus (E_c) for the 1 cm disk.

The distilled essence of this knowledge is something called the shape factor which is defined as, 'the loaded area of a piece of rubber divided by the total area free to bulge'. A cube with a load sitting on it will have a shape factor of the area of the loaded face, divided by the total area of the four sides which are free to bulge (the remaining side is assumed to be resting on a surface and therefore not free to bulge). This very simple calculation gives a shape factor of 0.25. The smaller the numerical value of the shape factor, the 'softer' the rubber component will be.

Data provided in a book from the Goodyear Tire and Rubber Company [9] demonstrates the relationship between compression and shape factor for a particular compound. For a 20% compressive deflection and a particular 30 Shore A vulcanizate, it shows the following variation of compression with shape factor. For a shape factor of 1.0, its approximate compression stiffness value is 0.9 MPa. At a shape factor of 2.0, it becomes 2.2 MPa, and at a shape factor 3.0 it is 3.8 MPa, a significant increase in compression stiffness.

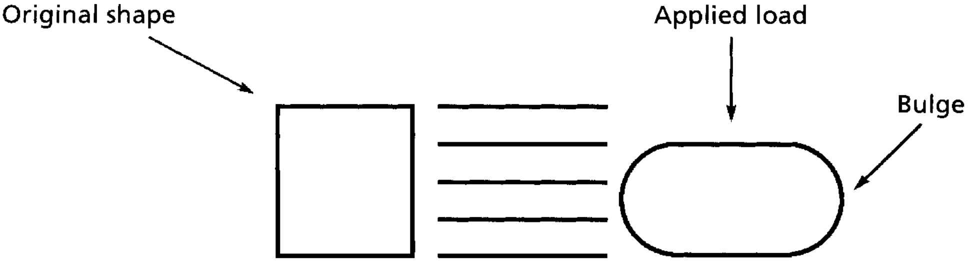

Figure 7.3 Uncompressed and compressed rubber. The top and bottom of the test piece are restricted from bulging when a load is applied
(courtesy of the Holz Rubber Company)

As the area free to bulge moves towards total restriction, the shape factor increases dramatically, and with it the compression modulus. At total restriction it is given the name bulk modulus, and values of a few GPa [10] have been quoted.

7.4.2 Construction bearings

The shape factor becomes more complicated when a stiff material such as steel plate or fabric is inserted into the rubber, like a sandwich. This composite would be molded as a single unit. Here, the geometry stays the same but the compression stiffness increases, since the stiff laminates decrease the rubber product's ability to bulge.

If the laminations are horizontal, the increased stiffness will be in the vertical direction. We now have a rubber 'spring' which is stiffer vertically, to take heavy loads, and softer horizontally. Figure 7.4 shows a cross section through a rubber pad with steel laminations.

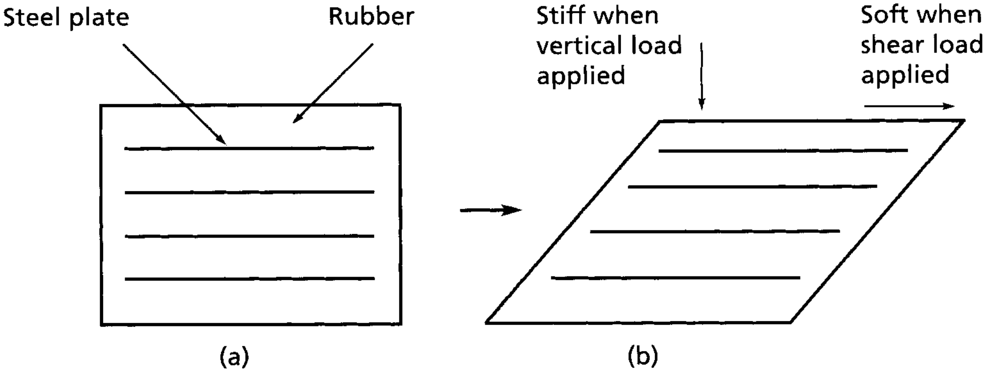

Figure 7.4 (a) Original shape of bearing; (b) Shape after applying both a vertical and shear load

Thus the weight of structures such as bridges can be supported, and at the same time moved horizontally. The rubber bearing, being stiff vertically can take the heavy load of the bridge, while its 'softness horizontally' will allow a larger displacement for horizontal movement of the bridge due to thermal expansion and contraction. As an added bonus, it is virtually maintainance free.

A natural extension of the use of bearings for bridges, would be to use such a concept for reducing the damage that earthquakes can cause to buildings and their contents, and most importantly, to the people inside. An important requirement would be the bearing's ability to undergo significant horizontal displacements. The first building in the USA to be protected by natural rubber seismic bearings was built in California in 1983 [11]. Indeed a small earth tremor soon after installation showed excellent isolation of the building from the seismic disturbance. Since that time, these bearings have been installed in a number of buildings throughout the USA. Other countries, such as Japan have also adopted this relatively new concept of seismic base isolation.

Bearings are used to absorb other vibrations, such as those from underground railways and one well documented case is that of Albany Court, London, UK [12]. An extensive study has been made over 15 years of the building mounts in Albany Court. Detailed measurements of creep have been made and it is predicted that creep will be less than 6 mm after 100 years' service.

A natural concern of the engineer is that a bridge or a building is intended to last a long time. This leads to the question: how long will the rubber bearings last? Bridge bearing pads have already been in use for a considerable period of time, and some made from NR removed for inspection after decades of use, have been shown to be in very good condition [13]. Stevenson and Campion [14] mention a NR pad, which still remained in good condition after supporting a bridge structure for a hundred years. This suggests that the inherent lack of weather resistance in NR (it normally has protective chemicals added to it), is not a factor, when dealing with large bulky products such as rubber bridge bearings, which undergo small but frequent deformations. This evidence, relating to longevity, also supports the argument that NR is the material of choice for seismic bearings in base isolation of buildings. Seismic bearings are designed to undergo higher deformations than bridge pads but one assumes that this will occur infrequently.

Two elastomers are commonly used for bearing pads for bridges, CR (Neoprene) and NR. The Tg (see section 6.4.3) for CR is around -45 °C whilst that of NR is approximately -70 °C. Thus NR should be the rubber of choice for use in very cold climates.

7.5 Tensile stress/strain and hysteresis

Figure 7.5 shows a tensile stress applied to rubber up to a strain value of 4.0 (400%). At this point the stress is gradually removed and then some interesting things occur. The first surprise is that the return journey to zero stress does not follow the original path. High school physics tells us that work is force multiplied by distance ('stress x strain') which is represented by the area under both the loading and unloading curve. Since the area under the former is larger, more work is expended in stretching the rubber than in returning it to its original shape. Since it takes energy to perform work, less energy is expended during the rubber's return to its original state. Since energy cannot be created nor destroyed, then where did the difference in energy go? It is converted into heat, by an amount equivalent to

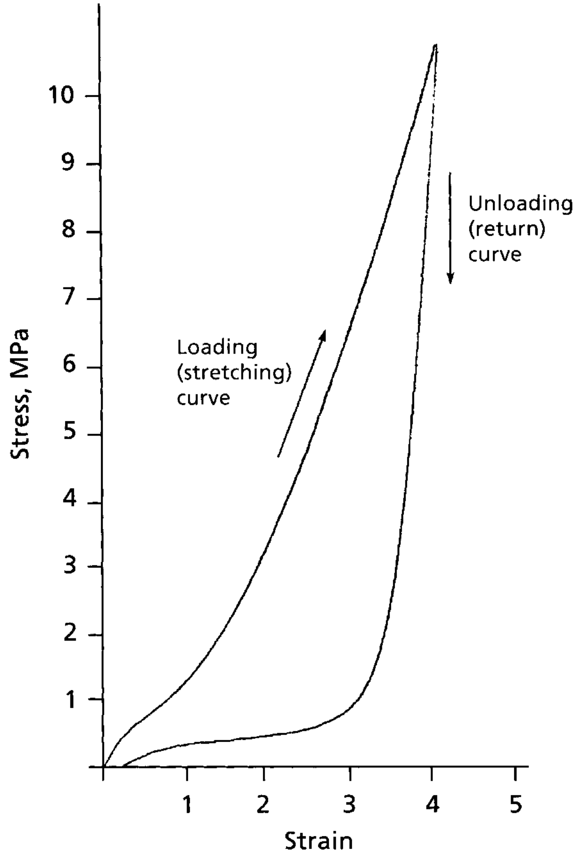

Figure 7.5 A tensile stress/strain curve, representing the first cycle, taken to a strain of 4.0

Note: strain is a ratio and therefore does not have units of measurement.

the area in the loop formed by the two curves. This conversion is known as hysteresis and it is due to the viscous damping component of the rubber (see section 7.6.1). The area is called the hysteresis loop (and is related to tan δ, see section 7.6.4). The larger the area of the loop, the greater the heat produced and the less elastic the rubber.

The second point of interest is that the return curve does not quite reach zero strain at the end of the return journey. This is because rubber is not a completely elastic material and therefore does not return fully to its original undeformed state. If allowed to relax for some time, this gap will narrow. The area of the loop is smaller for a NR gum compound vulcanizate (more elastic) than for one with filler (less elastic).

Hysteresis can occur in any deformation mode. For example, imagine a heavily loaded solid fork-lift tire moving rapidly. The engineer calls this cyclic deformation at high strain and high frequency. Each time a section of the tire impacts (compression deformation) and then releases from the floor it can be described in the form of a hysteresis loop. The viscous component is rapidly converting kinetic energy into heat. If these conditions are taken to excess, they have the potential to cause a considerable temperature rise within the tire with consequent heat degradation.

Delving a little deeper, what would happen if the curves are continuously cycled, if the rubber is stretched and relaxed a number of times, as in Figure 7.6, which represents the sixth cycle?

With each cycle the material becomes softer (lower modulus), and the loops become thinner (less hysteresis). This change stabilizes after a number of cycles. The effect is smaller for a NR gum elastomer (more elastic) where the initial and final loop area would be smaller. The effect is more pronounced for a compound filled with a reinforcing filler such as carbon black. The 'softening' effect, indicated by the lower modulus (smaller gradient of the initial part of the return curve on the first cycle in Figure 7.5 and subsequent curves in Figure 7.6) of the stressed rubber is known as the Mullins effect [15]. If the vulcanizate is

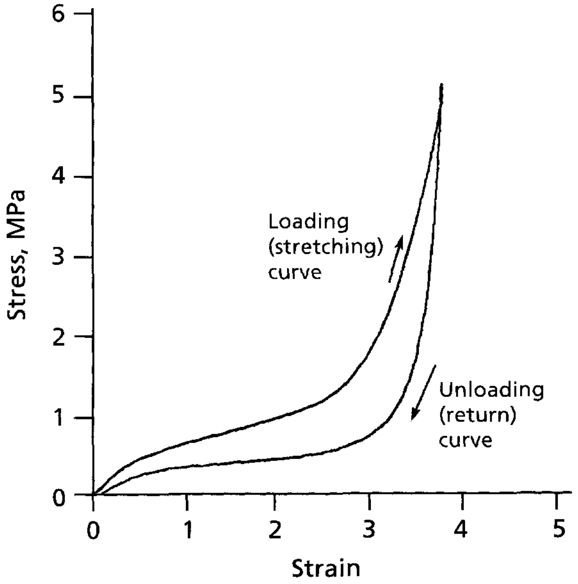

Figure 7.6: A tensile stress/strain hysteresis loop at the sixth cycle, taken to a strain of 4.0

Note the significantly reduced value for stress at a strain of 4.0, relative to Figure 7.5.

allowed to rest for some time, after multiple cycles (see Figure 7.6), it will regain some of the characteristics of the curve in Figure 7.5.

We can use this information to our advantage. Creep and stress relaxation (see section 7.6.2) are caused by the viscous component, which is smaller after a number of cycles. In other words the loop area is now smaller, therefore the viscous component is smaller. Thus if we cyclically pre-stress a rubber product, a process known as scragging, just prior to use, the viscous component and therefore both creep and stress relaxation are reduced. An important point for the engineer might be to ignore the first few cycles of a deformation test if the application involves many cycles in reasonably quick succession, since the first few (giving a higher modulus value) are not representative of the many that follow. A good example is a rubber spring which would have a higher spring rate (compression deflection characteristics) in the first few cycles, than all subsequent ones. The rubber product does show some recovery to its original state after deformation, followed by a resting phase. One point to mention is that the two curves in Figures 7.5 and 7.6, which are taken from the same material, clearly show that rubber properties, such as modulus, are influenced by previous deformation history.

7.6 Viscoelasticity

Although rubber is highly elastic it is not completely so. The best the chemist can achieve is probably represented by the high bounce rubber ball from the toy store, which is a rubber compound with an extremely high proportion of BR and a vulcanization system designed for a high state of cure. The chemist can also design a compound, so that a ball made from it hardly bounces at all; toy stores probably have them too. This low bounce ball is said to have a significant viscous component and a low elastic component. This combination of viscous and elastic properties results in the definition of viscoelasticity.

7.6.1 The spring and the dashpot

An engineer would visualize viscoelasticity as a combination of two separate mechanisms occurring at the same time in rubber. A spring represents the elastic portion, and a dashpot represents the viscous component, as shown in Figure 7.7. When a force is applied to this combination, causing a deformation, the spring and dashpot behave quite differently. The spring will store deformational energy, and then release it (by returning to its original shape) when the deformation is removed. When the piston in the dashpot moves, it cannot return to its original position when the force is removed. The energy that the piston has when it is moving, kinetic energy, is irreversibly converted into heat. No energy remains to move it back to its original position.

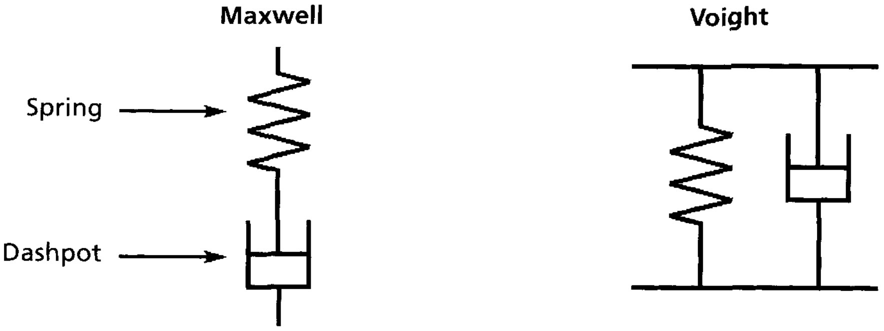

Figure 7.7 Representation of rubber elastic and viscous components using Maxwell & Voight models

Both drawings in Figure 7.7 are conceptualized ideas of viscoelasticity (viscoelastic models) and reflect different aspects of rubber-like properties [16, 17]. According to Gent [18], in practice it is more convenient to describe stress relaxation experiments by a generalized Maxwell model and creep experiments by a generalized Voight model. Dynamic mechanical experiments can be described equally well by either model, although the Voight model is commonly used. The rubber balls discussed previously would be represented by the engineer as in Figure 7.8.

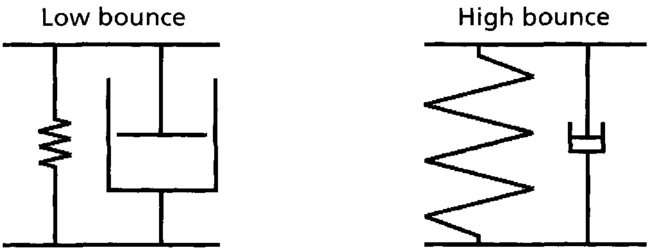

Figure 7.8 Spring and dashpot concept of the low and high bounce ball. It would also be representative of a rubber compound (a) before cure and (b) after cure.

7.6.2 Consequences of the viscous component

The way in which the viscosity component explains some of the properties of rubber has been discussed. Next the effect of viscosity on two specific engineering properties, creep and stress relaxation are considered.

• *Creep*

When a weight is placed on a block of rubber, the block thickness will decrease as it takes up the load and the sides will instantaneously bulge. After this time, the thickness continues to reduce, at an ever decreasing rate. Usually, after a few weeks, this rate becomes extremely small. This phenomenon is known as creep and in engineering terms it would be defined as a change in strain with time at constant stress. Fortunately, creep can often be predicted over a long period of time [19], which is useful to the civil engineer who may have to figure out how much a building will settle, due to the compression of the rubber bearing blocks on which it is resting. At room temperature, creep is proportional to the logarithm of time. As temperature increases, its proportionality moves towards straight time. Creep is due to the viscous component of the rubber, and therefore a more viscous rubber will have a higher level of creep.

• *Stress relaxation*

In some instances, a rubber component will clearly be compressed to a fixed dimension. An example might be a seal or gasket compressed by its housing. The elastomer will exert an opposing force, consisting of an elastic and viscous component. This force is exerted against the housing as the gasket resists the deformation and the force seals it against leakage. However the viscous component of the force will slowly decay with time, with the possibility that the gasket might eventually not be able to resist the pressure of fluid in the system. In this case the gasket or seal might leak. This phenomenon is called stress relaxation, (see section 5.4.5), defined by the engineer as change in stress with time, at constant strain. Like creep, it is higher in rubber with a higher viscous component.

The numerical values of both creep and stress relaxation will change over time if air (oxygen) attacks the rubber (aging). This is most significant for thin sections. Fortunately, as the rubber's thickness increases, the overall aging effect diminishes.

7.6.3 Viscoelasticity and modulus

In the viscoelastic model, both the spring and the dashpot change their position, in response to an applied force. The applied force provides the stress, and the change in position of the spring and the dashpots relate to the strain. Stress divided by strain equals modulus.

That part of the modulus provided by the dashpot is called loss modulus (G'') which is related to energy lost as heat, while the spring's contribution is called storage modulus (G') which is related to the storage of converted kinetic energy as potential energy. Both play an important part in how rubber behaves in dynamic situations. An engineer may need to know the value of one component of the modulus relative to the other. The ratio, G''/G' is referred to as tan delta (tan δ). The choice of name for this ratio will become more evident later in this chapter.

Knowledge of the ratio tan δ of a rubber vulcanizate, is useful for understanding the distribution of elastic and viscous components. Tan δ will allow determination of the amount of damping (see section 7.8.1) that the rubber will provide when used as a spring. A knowledge of tan δ will also be useful in determining how much heat will be produced in dynamic applications; too much heat could destroy a product. An example of the use of tan δ would be its value in a tire compound. A high tan δ gives a tire tread with better traction against a road surface and therefore improved braking in the wet. This will usually be at the expense of fuel consumption, since there is more rolling resistance to movement of the automobile.

7.6.4 Viscoelasticity in cyclic deformation

A number of rubber engineering applications involve deformation of the product in a repetitious manner, called cyclic deformation. A vibration mounting on an engine, moves repeatedly through a deformation mode; a section of a tire on a vehicle is cyclically subjected to deformation against the road surface. To simplify the situation consider the case of an elastic band stretched through only a few percent, to represent the origin point for movement. The behavior of the band may be followed, moving a few percent above this point, then back through the origin to a few percent less, and finally back to its origin point. This should keep the band approximately within its mathematically linear region and will be one full cycle of movement. This is then repeated through many repetitions or cycles, as illustrated in figure 7.9. Rather than showing the stretching (elongation) in linear dimensions (centimeters or inches), an engineer might prefer to display it as angular strain, thus a full cycle of movement is 360°. A similar cyclic viscoelastic curve is shown in ASTM D 2231 [20].

The curves provide some intriguing insight into the differing behavior of the elastic and viscous components.

The elastic stress curve in Figure 7.9, shows what might be expected intuitively. When the rubber band is fully stretched (90° in angular strain language), the elastic stress related to it is at a maximum. The elastic stress perfectly follows the elastic strain. This is very familiar to engineers, and is expressed as Hooke's law where stress is directly proportional to strain, or put another way, stress/strain is a constant. This constant is the elastic modulus of the material. In this idealized example (tensile deformation), this would be equal to Young's modulus.

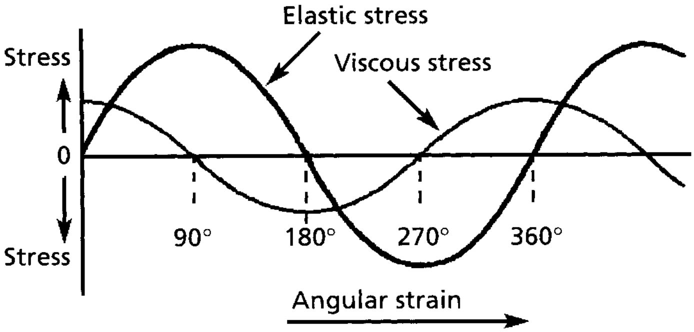

Figure 7.9 Idealized cyclic stress-strain, showing the viscoelastic curve split up into its two primary components, elastic and viscous

The viscous stress curve in Figure 7.9 might seem a little surprising to some of us. Here, at the point of maximum stretch (at 90° strain), the viscous stress is not a maximum, it is zero. Isaac Newton figured this one out, and expressed it as Newton's law of viscosity, which states that, viscous stress is proportional to strain rate, or, put another way, stress/ strain rate is a constant. This constant is the viscosity of the material.

Rubber has some properties of a liquid. At the point when our elastic band is fully stretched and is about to return (90° and 270°), its 'velocity' or strain rate, is zero, and therefore its viscous stress is also zero. In other words, the dashpot is not moving at that instant. Considering Figure 7.9 again, any point chosen on the elastic curve (for example its maximum or zero stress level), the viscous curve is always lagging behind the elastic curve, by an angular distance of 90°. The engineer would say that the viscous stress is out of phase with the elastic stress by 90°. It takes 90° of movement for the viscous stress to reach the equivalent stress value as the elastic stress.

Figure 7.10 shows the total stress curve (a combination of the the viscous and elastic), so not surprisingly, it is called the viscoelastic curve. It is following (out of phase), the elastic one, by a distance, equivalent to a certain number of degrees, known as delta (δ) or it might be thought of as an angle δ (loss angle, since it can represent energy lost as heat). There is a simple mathematical relationship between this angle and modulus, as shown in Figure 7.11. Translating this into the language of vector analysis, the vector diagram shows that:

$\tan \delta = \frac{G''}{G'}$ where G'' is loss (viscous) modulus and G' is storage (elastic) modulus

which is equivalent to $\frac{S''}{S'}$ where S'' is viscous stress and S' is elastic stress

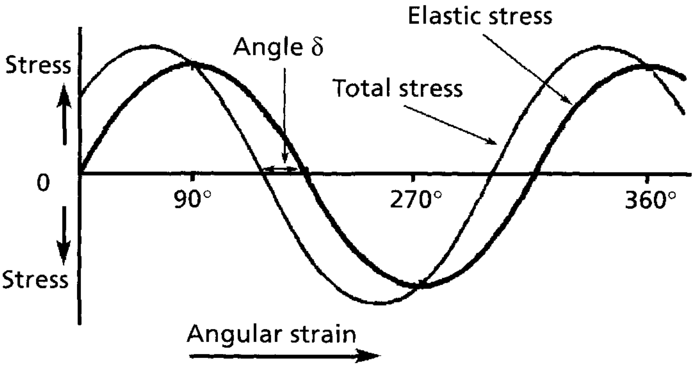

Figure 7.10 Idealized cyclic stress/strain curve, showing the full viscoelastic curve (total stress) together with its elastic component.

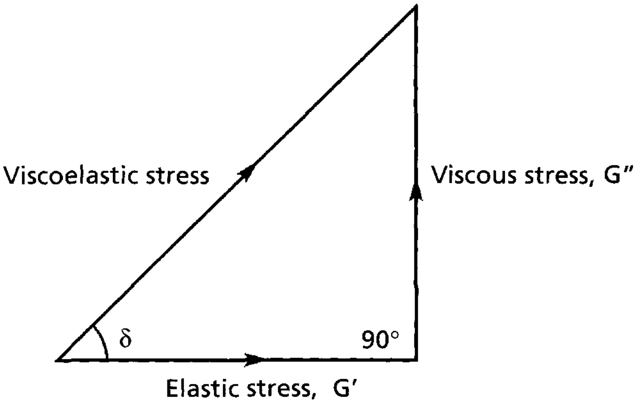

Figure 7.11 Vector diagram, showing the viscous component 90° out of phase with the elastic component using trigonometry

$$\tan \delta = \frac{\text{opposite}}{\text{adjacent}} = \frac{G''}{G'}$$

7.6.5 Dynamic viscoelasticity - some warnings

An important aspect of rubber behavior is described by the cyclic curves in Figures 7.9 and 7.10, but that is only part of the story. Both Hooke's and Newton's laws describe an ideal situation called linear viscoelasticity, where everything changes in a simple, mathematically linear manner. The good news is that it does provide a reasonable description of rubber deformation, if the latter is kept small and therefore linear. Even in this situation, both frequency (speed or number of cycles per second) and temperature need to be kept constant, to achieve linearity. 'Real life' is often non-linear, and represents an area in which all the answers are not known, although mathematical models of rubber non-linearity are improving, allowing a technique known as finite element analysis (see section 7.11) to make inroads into the non-linear world. References for viscoelasticity in cyclic deformation are [21, 22, 23, 24].

7.7 Rubber turns to glass

This topic has been discussed in the chapter on chemistry (see section 6.3.3). From the engineer's viewpoint all rubbery materials undergo an increase in modulus as temperature is decreased. Lindley [25], referring to unfilled, vulcanized NR, mentions that an increase in stiffness occurs as the temperature is lowered, proportional to absolute temperature, from above 70 °C down to around -20 °C. He then states that a more significant increase occurs, until at -60 °C, the rubber is glass-like and brittle. This is known as its glass transition temperature *Tg*, more accurately described as a temperature region. The rubber will return to its original state as the temperature is increased.

Now let us speculate on how an engineer might be able to combine the knowledge of *Tg* with Newton's law relating to viscous stress (see section 7.6.4). Imagine a rubber product undergoing cyclic deformation. Increased frequency, (rate of deformation or strain rate), increases the viscous stress, (Newton's Law - viscous stress is proportional to strain rate), and the rubber gets 'stiffer'. This has the effect of moving *Tg* to a higher temperature for the product. For example an MRPRA data sheet [26] states that the *Tg* of NR of -70 °C (taken at a low deformation rate) is increased by 6 to 8 °C (*Tg* becomes -64 °C to -62 °C) by a ten-fold increase in deformation rate. This might be of significance, for example, in dynamic applications for cold climates, where *Tg* could be higher (warmer) than for the same product in a static mode. If the engineer is not aware of this, he may assume that the product is still operating safely above *Tg* based on static values. As a rule, the engineer will wish to avoid the *Tg* region, since at this temperature, many useful rubbery properties are lost. Fortunately, Williams, Landel and Ferry came to the rescue on this one. Using their equation (WLF equation), engineers can calculate this shift in *Tg* for any given change in deformation frequency [27].

7.8 Rubber and vibration

The ability of an elastomer to convert energy of motion, allows it to absorb vibration. Its viscous component, converting kinetic energy into heat, is most useful for absorbing shock (very low frequency stress) such as a single large impact, and thus a rubber compound (for example based on butyl raw gum elastomer) would have this component maximized in its formulation if it is to be used as a low frequency shock absorber. On the other hand, the elastic component can return the product quickly to its original state, ready for the next cycle of deformation, and thus it can cope with higher frequency stress. This component would be maximized in a formulation where rapid smaller impacts (stresses) occur. The engine of the motor car creates vibration, which must be isolated from the rest of the vehicle. Rubber satisfies this need for an isolating material.

7.8.1 Transmissibility

Using the motor vehicle as an example, the engineer needs to know how much vibration (force) is getting past the engine, through the vibration mount, to the rest of the vehicle, affecting, amongst other things, passenger comfort. He defines this as transmissibility, T, which is the transmitted force divided by the imposed force. Since the engine is transmitting vibration, the latter will have an associated frequency, which can be used to calculate transmissibility. Warley [28] and Lindley [29] express this in terms of the following equation which assumes linear viscoelasticity and that the system moves along one linear dimension only, i.e., one degree of freedom. Lindley states that the equation applies to a linear spring with stiffness and damping independent of frequency. This equation is:

$$T = \left[\frac{1 + \tan^2 \delta}{\left(1 - r^2\right)^2 + \tan^2 \delta} \right]^{1/2}$$

where: T is transmissibility

tan δ is equal to loss modulus/storage modulus as defined in section 7.6

r is the ratio of input frequency divided by the natural frequency, f/f_n
(f being the input frequency from the engine and f_n the natural frequency at which the vibration mount would vibrate freely)

The engineer will also wish to know the minimum amount of damping needed, to just prevent the vibrations getting from the engine to the vehicle body. This is the critical damping coefficient, Cc. Davey and Payne [30] define critical damping as: the smallest amount of damping that will prevent free oscillations, i.e., resonance, in a system including a rubber spring, when disturbed from its equilibrium position, the rubber being assumed to have a linear stress/strain relationship.

Since most real world systems do not approach critical damping (the car body still vibrates to some extent), the engineer expresses this in terms of a fraction of critical damping:

$\frac{C}{Cc}$ Where C is the damping coefficient.

Davey and Payne [30] define the damping coefficient, C, as the force required to produce a unit rate of shear in the rubber spring.

For f=fn, $\frac{C}{Cc} = \frac{\tan\delta}{2}$ for hysteric damping.

Warley suggests using a value of tan δ specific to the strain level and frequency of the mount. Using this equation, a tan δ of 0.24 would provide 12% critical damping.

It needs to be stressed that a 'real world' engine mount will vibrate with more than one degree of freedom and the system will be non-linear. However the simplified model does provide insight into the subject of transmissibility.

7.8.2 Translating the transmissibility curve

The curves in Figure 7.12 provides a wealth of information about the behavior of a vibrating system. As the imposed frequency increases, f/fn increases, and the value begins to move towards that of the natural frequency and the transmissibility actually exceeds 100% (T = 1.0) so that the vibration on the output side of the motor mount is worse than that in the engine (see previous equation for transmissibility).

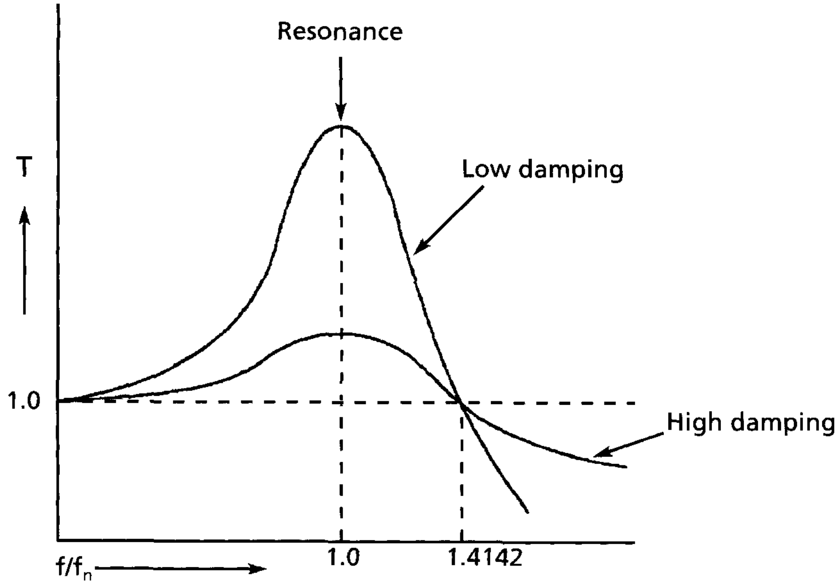

Figure 7.12 Transmissibility curves of high and low damping rubbers

When f is equal to f_n (and therefore $f/f_n = 1$) this is called resonance. This is like the opera singer, sending vibrations through the air at the same frequency as the natural frequency of a wine glass, leading to maximum vibration and breakage of the glass. Transmissibility (T) will be highest at this point.

Things improve as the ratio moves through 1.0, until at $f/fn = \sqrt{2}$ (i.e., 1.4142), there is a balance, where the imposed force equals the transmitted force (the curve crosses 100% transmission at $\sqrt{2}$). It is only after this point that absorption of vibration occurs. From then on, the higher the ratio, the better the vibration absorption will be, as transmissibility falls from 100%.

The viscous component reduces transmissibility at resonance. IIR, being a high damping rubber, has a higher tan δ than NR, which reflects in IIR's lower value of T, at resonance. Thus some damping component is needed to reduce potentially harmful vibration, if the engine vibrates below $f/fn = \sqrt{2}$, or moves through this region. Above this value, all the advantage of the viscous component is lost, as can be seen from the curve for NR (low damping, therefore lower tan δ), which is now more effective at reducing the transmissibility of the vibration force.

Therefore it is logical to select a material having the smallest value of tan δ needed to get safely through resonance and the smallest practical numerical value for its natural frequency. Low frequency equates to long wavelength, which equates to a rubber which stretches to a large length for a given force as it dynamically cycles, and that means a softer rubber. Additional references to rubber in vibration are [31, 32, 33].

7.9 Rubber gets stiffer as the temperature rises!

A DuPont (now DuPont Dow Elastomers) booklet [34] shows an illustration of a highly elastic strip of gum vulcanizate, with a load on the end of it, stretched to greater than 10%. When the rubber is warmed up, it retracts, thus reducing its length. From the engineer's point of view, the elastomer's modulus (stiffness) has increased, and yet a decrease would have been expected. This unusual phenomenon is called the Gough-Joule effect [35]. It is assumed that the elastomer is significantly above its *Tg*. This effect might need to be allowed for in some highly elastic rubber products, such as springs. DuPont state that this effect occurs when the rubber is first stressed, then heated.

7.10 Life time prediction

Rubber degradation over time when exposed to air (oxidation due to oxygen) has already been discussed (see section 6.3.6). As the temperature rises, the aging process speeds up. This principle should also apply to other degrading chemicals as well as oxygen. Traditional methods of evaluating the effects of long term exposure to chemicals have involved prolonged immersion. However an equation derived by Arrhenius relates reactivity with temperature, so that the results of tests at higher temperatures can be used to predict the effects of exposure for longer time periods at lower temperatures.

The Arrhenius equation is $k = Ae^{-Ea/RT}$

where: k is the rate constant of a chemical reaction

A is a proportionality constant related to collision frequency and orientation of molecules

e is the base for natural logarithms

Ea is the activation energy

R is the gas constant

T is the absolute temperature

This alternative approach is discussed in detail for chemicals used in oilfield drilling, to predict the lifetimes of elastomeric seals in the order of one or two decades [36]. For products with a large cross section, the rate of diffusion of any degrading chemical needs to be taken into account. An example would be the bridge bearing pads discussed earlier in section 7.4.2, where the diffusing chemicals are ozone and oxygen.

7.11 Finite element analysis

A discussion of engineering would not be complete without some mention of Finite Element Analysis (FEA). This is a technique that takes a complex geometric problem and divides it into many, discrete, easier to solve, parts. For rubber, we might take the complex geometry of a corrugated elastomeric boot, and on a computer, divide it into many sections each of which has a simple geometric shape. These are known as finite elements, which can take the shape of a two-dimensional triangle as in Figure 7.13, or a quadrilateral or a more complex three-dimensional brick form or hexahedra. Load, strain or pressure can effectively be applied to the individual elements in order to understand the behavior of the whole.

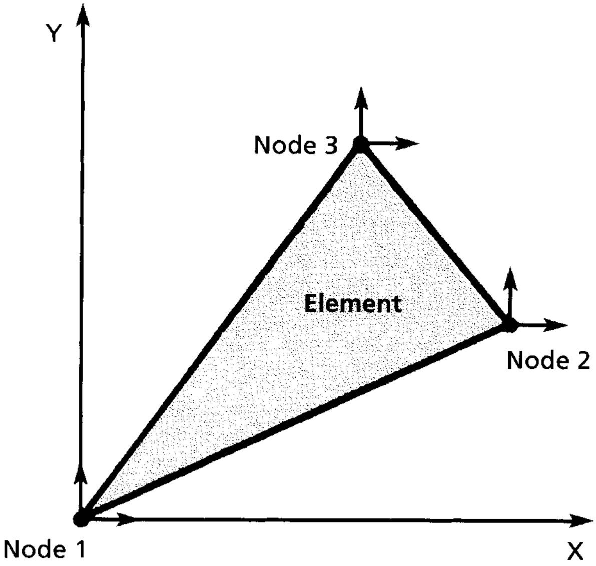

Figure 7.13 Triangular finite element

(reproduced with permission from MARC Analysis Research Corporation, Nonlinear Finite Element Analysis of Elastomers (white paper), published by MARC, 1992)

Menough [37] uses the interesting analogy of a brick wall. Imagine the bricks (elements) to be made of rubber and a force applied to one brick. FEA would be used to calculate the resulting stress/strain value for that brick, and then it would apply that information to the next brick, and so on, until all the bricks in the wall have specified stress/strain values. Stress would be calculated via the cross sectional area of the brick and then computed through the modulus of the material. The result would be the stress deformation pattern for the whole wall. This can be displayed on the computer in various colored contours so that high stress or strain areas, or other potential points of interest can be easily highlighted.

Figure 7.14 and Figure 7.15 illustrate finite elements in an uncompressed and then a compressed O-ring. Only a two-dimensional cross section is shown.

For a more formal definition of FEA, MARC [38] states that 'FEA is a computer aided engineering technique, for obtaining approximate numerical solutions to boundary value problems, which predict the response of physical systems, subjected to external loads'. They also mention that this is accomplished by a computer solving thousands of simultaneous equations, with high end PCs now solving, medium sized, real world, non-linear problems. Finney [39] mentions that the FEA of elastomers became a reality for design engineers in the early 1970s.

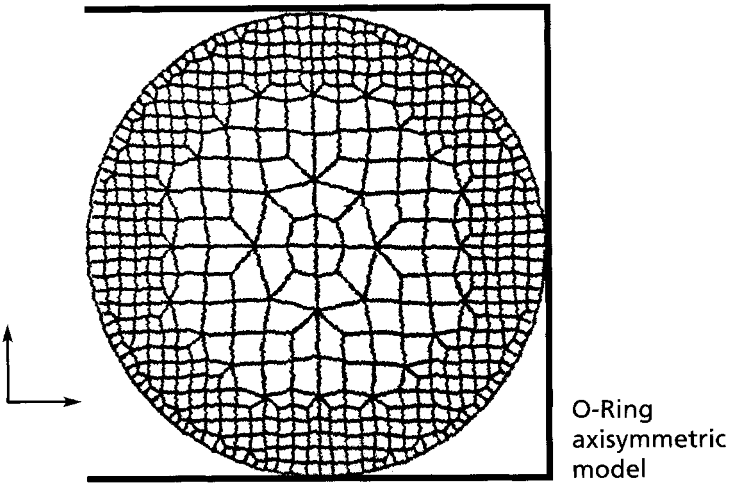

Figure 7.14 Cross section of an uncompressed O-ring in a housing, using a larger number of elements, where most change is likely to be observed, away from the center

(reproduced with permission from MARC Analysis Research Corporation, Nonlinear Finite Element Analysis of Elastomers (white paper), published by MARC, 1992)

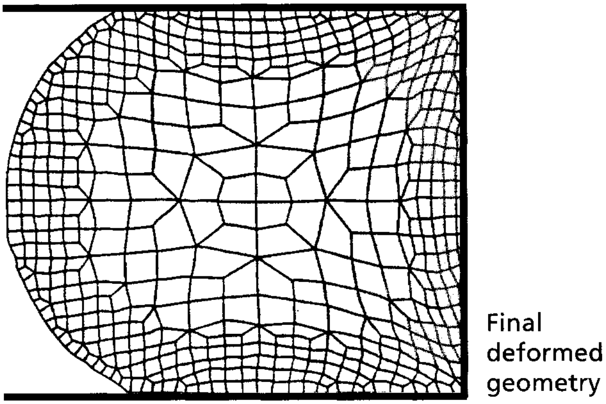

Figure 7.15 Finite element distribution in a compressed O-ring cross-section

(reproduced with permission from MARC Analysis Research Corporation, Nonlinear Finite Element Analysis of Elastomers (white paper), published by MARC, 1992)

The O-ring example has a high level of geometric symmetry. Thus two-dimensional geometry can be used along the axis of symmetry providing the information needed for the three-dimensional O-ring. This greatly reduces the number of equations that need to be solved.

If a product is constrained in some way in the real world, the FEA must represent this. Considering the housing surrounding the O-ring example, boundary conditions are constraints that are applied to specific elements in an FEA model. Constraints are required to allow or restrict movement (degrees of freedom) of a whole or partial element. Such constraints are typically translations or rotations. By carefully applying constraints, an accurate representation of the real world problem is achieved. Selection of correct boundary conditions is critical to achieve an accurate FEA solution. Some FEA systems allow the analyst to apply boundary conditions to complete faces or surfaces of the FEA model.

Mesh density is the number of elements that comprise the FEA model. Increasing the number of elements in a particular model will generally produce a more accurate result. The downside to increasing the mesh density is that the time required to solve the equations increases. A technique to determine what the correct number of elements should be, is a convergence study. For a given model the reported maximum stress is noted and the number of elements in this area is increased. The analysis is re-run and the reported maximum stress is again determined. This exercise is then repeated several times more. At some point the difference between the maximum stress of two consecutive runs will be very small.

Once the province of such organizations as large tire companies, use of FEA has grown significantly and is now being adopted by smaller rubber companies. Designers of FEA systems create programs (codes) to solve analysis problems. Some examples are, Texgap, MARC, ABAQUS, Ansys, and Algor.

For FEA to work, it needs, amongst other things, a mathematical model of rubber behavior. Models such as those of Mooney-Rivlin and Ogden are popular examples. Other models have been introduced to cope with some of the divergent behavioral properties of rubber [40, 41], discussed earlier in this chapter. The models require stress/strain data, which is supplied by laboratory tests, specific to the particular rubber compound which is to be used for the product. This could involve testing for uniaxial and biaxial tensile strength, compression and various types of shear. FEA models use strain energy functions, and they assume that the material is isotropic and elastic. This is known as hyperelasticity.

7.11.1 Rubber presents challenges to FEA

The high bulk modulus of rubber (see section 7.4) leading to a Poisson's ratio very close to 0.5, can lead to complications in the analysis, especially if freedom to bulge (see section 7.4.1) is severely restricted in the product to be analyzed. As rubber begins to deform it quickly leaves the ordered realm of linear equations such as Hooke's Law. At the present time FEA codes cannot accurately predict a stress value for large, single jumps in deformation, such as elongation. The FEA analyst tries to solve the equation using small deformation jumps. Small elongations are solved in a step-wise manner until the final elongation is reached. Changes in temperature can alter the rubber's physical characteristics (see section 2.2.4), and if relevant, would be taken into account in the FEA. Properties at a rubber to metal (or any rigid substrate) interface could also be a point of concern [42]. At such interfaces a great deal of care needs to be exercised by the analyst because of the very large differences in modulus between the interface materials. These are some of the factors that present a challenge to the designers of FEA codes and the users of FEA.

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8 Castable Polyurethanes

"You mean, all you do is mix a few liquids together and you get rubber", ...said Andrew.

"Sure, and no powders flying around like that black stuff you like so much", ...answered Paul.

8.1 Introduction

In 1937 Professor Otto Bayer determined the principles of polyurethane chemistry. As a result of his work, polyurethane now has a myriad of wonderful uses. Fitness and sports enthusiasts will find urethane (polyurethane) woven into textiles and sold under trade names such as Spandex and Lycra. Since it is elastic, it hugs the body and adjusts comfortably to movement. The skier has boots and parts of his skis made from polyurethane. The family truck might have a urethane liner. The wooden desk or deck in the garden could be protected with a urethane varnish. The warehouse floor might have a tough urethane coating. The fork-lift truck moving around the warehouse could well have solid urethane tires. The favorite couch in the living room may have flexible urethane foam filling.

In this chapter, a material will be discussed which applies to only some of these diverse areas - castable urethanes. These are viscoelastic materials and many of them clearly qualify to be called rubber. However, at the high end of the urethane hardness spectrum, the qualification of 'rubber' might not be so clear.

So far in this book, solid raw gum elastomers have been described which are converted into useful products, using large and relatively expensive machinery, such as the internal mixer. Large amounts of energy are needed to mix and shape these solid starting materials. When liquids are the starting materials such machinery is not required.

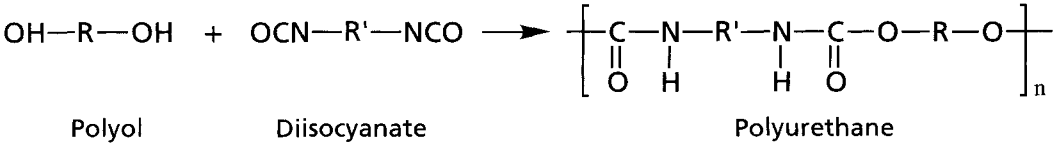
If a diisocyanate is stirred into a polyether or polyester polymer of low molecular weight, followed by a 'curative', and then thoroughly mixed, and poured into a mold, the result can be a solid elastomer. The product produced could be a bowling ball, ski-boot shell, roller covering for printing or heavy industrial use, skateboard wheel, the list goes on. Polyurethane can be obtained in bright colors, which are used to advantage in bicycle tires, where it also makes use of its most important assets, abrasion resistance and general physical toughness. These two properties are also used in mining applications, such as pump parts for slurry applications. Tensile strengths are easily above the best that other elastomers can achieve; 50 MPa is possible.

Most elastomers of 80 IRHD and above have poor physical properties. At 90 IRHD properties are extremely low. However castable urethanes have very high strength at 80 IRHD and above. Urethane compounds can also be formulated to reach 80 Shore D. At this point, they are more plastic than rubber. Urethanes can also be translucent, which can be advantageous. They also have very good electrical insulating properties, making them ideal potting materials for electrical encapsulations. Urethanes have good weather and petroleum oil resistance (not aromatic), and generally have a dry upper aging temperature around 100 °C. A number of attempts have been made over the years to use urethane for automobile tires but so far efforts to enter this lucrative market have been without success.

8.2 Chemistry

Chemistry and chemical terminology play a more important role in urethane production than in the more traditional rubber industry.

In simple terms, if a low molecular weight (from a few hundred to several thousand) polyester or polyether, which has OH groups at either end of the polymeric molecule (a polyol) reacts with a chemical containing two isocyanate groups, also one at each end (diisocyanate) a hydroxyl group from the end of the polyol combines with one of the isocyanate groups from the diisocyanate, to form a structural link called a urethane, see Figure 8.1.



$$\mathrm{OH{-}R{-}OH} + \mathrm{OCN{-}R'{-}NCO} \longrightarrow \left[\underset{\underset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle H}{|}}{N} - R' - \underset{\underset{\displaystyle H}{|}}{N} - \underset{\underset{\displaystyle O}{\|}}{C} - O - R - O \right]_n$$

Figure 8.1 Synthesis of urethane link in polyurethane

Ends can continue to link up to form a low molecular weight polymer (liquid) called a prepolymer. In practice, prepolymers commonly contain a small amount of excess unreacted diisocyanate, called 'free isocyanate', to ensure that the final chain ends contain only isocyanate groups. All that is then required is what is loosely called the curative, although strictly speaking it is a chain extender, to produce the final solid polyurethane elastomer.

8.2.1 The 'curing chemicals' - chain extenders

Like the diisocyanate, the prepolymer also has isocyanate groups on the ends of its molecular chains. Isocyanates react with what is called 'active hydrogen'; an example would be the hydrogen on the hydroxyl group of the polyol. Water also provides such hydrogen and so can act as a curative. This can be a blessing or a curse, depending on whether you are deliberately adding it to create a foam (the reaction liberates carbon dioxide) or trying to keep moisture (H_2O) out of the reaction, to avoid bubbles in the product.

The most commonly used 'active hydrogen' chemicals are those containing two $-NH_2$ groups, called diamines, and other chemicals containing two hydroxyl groups (like the polyols), called diols. Diols are small chemical units compared to polyols. If a diamine curative is used, then its $-NH_2$ groups will link up end to end with isocyanate groups on the prepolymer. As the polymer (elastomer) grows, in our 'primordial soup', it changes from liquid to solid, at the temperature of the curing process. The link between the diamine and the isocyanate is called a urea. In the case of a diol curative, a urethane link is formed.

In some instances it is appropriate to mix the polyol, isocyanate, and curative all at once. This is the one shot system. However, a popular method is for a vendor to sell the prepolymer to the processor, who then simply adds curative to make his solid urethane.

In discussing elastomers earlier in the book, hardness was achieved by adding fillers such as carbon black, so why are they not needed in castable urethanes? Smith [1] suggests that in the cured urethane polymer, the isocyanate and some types of curatives act as hard segments or blocks in the chain, which give it stiffness and strength. The polymer chain is also interspersed with soft segments (the polyol portion), which provide chemical resistance, flexibility and low temperature properties. Prepolymers with a high level of isocyanate would contribute more to the hard segments. This concept of hard and soft segments is similar to that arising in thermoplastic elastomers (see section 2.3.12).

A few common examples of chemicals used in urethane elastomers are:

Polyols might be ethers such as polytetramethylene ether glycol (PTMEG) and polypropylene ether glycol (PPEG) or esters such as polyethylene adipate glycol (PEAG) and polycaprolactone glycol (PCLG).

Diisocyanates, toluene diisocyanate (TDI), and diphenylmethane diisocyanate (MDI).

Diamines, 4,4'-methylene-*bis*(2-chloroaniline) (MOCA, sometimes MCBA) and methylene dianiline salt complex (Caytur 21).

Diols, 1,4-butanediol (BDO) and hydroquinone *bis*(β-hydroxyethyl) ether (HQEE).

Triols, trimethylol propane (TMP) and triisopropanolamine (TIPA).

8.2.2 Linking chemistry to properties

- *Polyols*

The polyol may be thought of as the main polymer backbone. They may in fact be branched structures, with more than two hydroxyl end groups. Polyester polyols confer better oil resistance, abrasion and tear properties. Polyethers, on the other hand, have improved low temperature resilience, and lower hysteresis than polyesters, and better stability in water. Urethanes have the potential to suffer from a chemical degradation process in water known as hydrolysis [2] which increases with temperature rise and acidity or alkalinity of the water.

- *Diisocyanates*

MDIs are more resistant to hydrolysis compared to TDIs and are usually used with diol curatives, rather than diamines, with which they react much too quickly. TDIs, on the other hand, cure perfectly with diamines but slowly with diols, and have better higher temperature resistance than MDIs. The right combination of polyol and isocyanate can maximize a property. For example, an MDI/polyether system would be a good combination for better resistance to hydrolysis. Naphthalene diisocyanate (NDI) is also used for two-stage processing but not in one-stage processing.

- *Curatives*

Diamines and diols have a functional group at either end allowing the growing polymer chain to extend. Use of diamines, rather than diols, tends to be associated with harder urethanes. Triols have an extra functional group (a third OH group) which can be available for cross-linking which improves compression set in the cured product. This is a distinct advantage in products such as soft printing rollers.

- *Miscellaneous*

Plasticizers can be used, such as dioctyl phthalate (DOP), and anhydrous dipropylene glycol dibenzoate, which when blended into the reaction mixture, reduce the hardness of the final cured product without reacting with it. It is also possible to use catalysts, such as stannous octoate and oleic acid to accelerate the curing process. Fillers are sometimes incorporated to increase hardness, e.g., for printers rollers.

8.2.3 Stoichiometry during cure

When making a urethane product, the chemically correct proportions of reactive chemicals are critical to the properties of the cured part (this is called stoichiometry). If the actual relative quantities of ingredients involved in producing urethane are calculated using the chemical equation for the curing reaction, this would represent the 'chemically correct' theoretical ratio of ingredients. In urethane processing this is termed the 100% theoretical amount of material, e.g., curative (100% theory). Uniroyal literature [3] indicates the following effect of % theory of curative on properties of a particular urethane. Tensile strength maximizes at 90-95% theory, flex life increases dramatically with % theory (100-105% theory is preferred), while abrasion resistance falls rapidly above 105% (flat in the 85-105% theory region). This demonstrates that the processor must pay great attention to the ratio of reactants in the process, relative to the product property requirements.

8.2.4 Cure temperature

Since there can be various reactions going on at different reaction rates during the curing process, changes in temperature might make a relatively slow reaction become a faster one. As a result, this may change the final chemistry and thus the properties of the product. Uniroyal [4] states that the effect of increasing the curing temperature from 80 °C to 120 °C on the MCBA cured polyether L83, is to cause hardness, modulus, tear strength, and elongation to decrease, while tensile strength increases. It should be noted that there can be an increase in viscosity of a prepolymer when it is subjected to repeated heating/cooling cycles. This is because the terminal isocyanate groups react with each other which extends the polymer, which automatically increases viscosity. An example of this would be heating a drum of solid prepolymer to liquefy it in order to remove a portion of the contents and then repeating this process later. Therefore, it is good shop floor practice to keep such cumulative heating to a minimum, in order to minimise available isocyanate losses. Available isocyanate is needed for subsequent curing of the prepolymer.

8.2.5 The cured product, properties versus temperature

Like most elastomers, many of the characteristics of cured urethanes are sensitive to heat. A mechanical property at room temperature will be different to that at a higher temperature. The property will change immediately as the cured product increases in temperature from room temperature and recover as the temperature decreases, assuming that no heat aging has occurred in the meantime. This is illustrated by literature from TSE industries, discussing millithane millable urethane [5]. At room temperature, the tensile strength and elongation at break of a particular urethane are 27.6 MPa and 440%, respectively, and the Shore A hardness is 89. At 121 °C this rapidly changes to 10.3 MPa, 350% and 88 Shore A, respectively.

8.3 Making the product - processing

Once the chemistry of the process is understood it is possible to make solid urethane elastomers with simple, inexpensive equipment. For this reason there are many small businesses making urethane products. Care is needed because of health protection; some of the chemicals used in urethane processing, such as isocyanates and MOCA, are covered by health regulations.

In essence, if a curative is added to a container of prepolymer, and the two are thoroughly mixed and then poured into a mold, a solid urethane product can be taken out, providing a suitable cure time and temperature are used.

8.3.1 Handbatching

In the above basic description no machines are involved. The prepolymer and curative are heated to the exact temperature required in separate containers. Accurately weighed portions are poured out and then mixed very carefully with a spatula to avoid air bubbles appearing in the mix, blending in any component adhering to the inside wall of the container. This process is known as handbatching. At this moment, cure begins, so pot life is of concern (the time taken for the viscosity of the mix to increase so much that it can not be adequately poured, this is equivalent to scorch time, see section 5.3.1). Additionally, urethanes (particularly higher hardness materials) can generate their own heat (exothermic reaction) which needs to be anticipated when trying to maintain the correct temperature. The mixture is then poured into a pre-heated mold, and held at a specified temperature.

Techniques have been developed to prevent air getting into the mix during pour, such as those illustrated by Blaich [6]. The mold often has release agent applied to it, and once it is filled, it is usually kept heated in an oven during cure, which might last thirty minutes. After this time, the product is removed and often given a post cure. This means continuing the cure outside the mold, at a temperature of approximately 100 °C, for a much longer period of time, to ensure that all the chemicals have fully reacted, thus maximizing properties. Since moisture can act as a curative, the by-product of which is carbon dioxide bubbles, any humidity in the air is a potential problem. It is not unusual to apply a vacuum to the liquid reactants, just prior to mixing, to extract both dissolved gas and moisture.

8.3.2 Machine mixing

If large quantities of urethane are being mixed on a regular basis, there comes a point, where using a machine for the actual mixing is more economical. The principle of such a machine is shown in Figure 8.2.

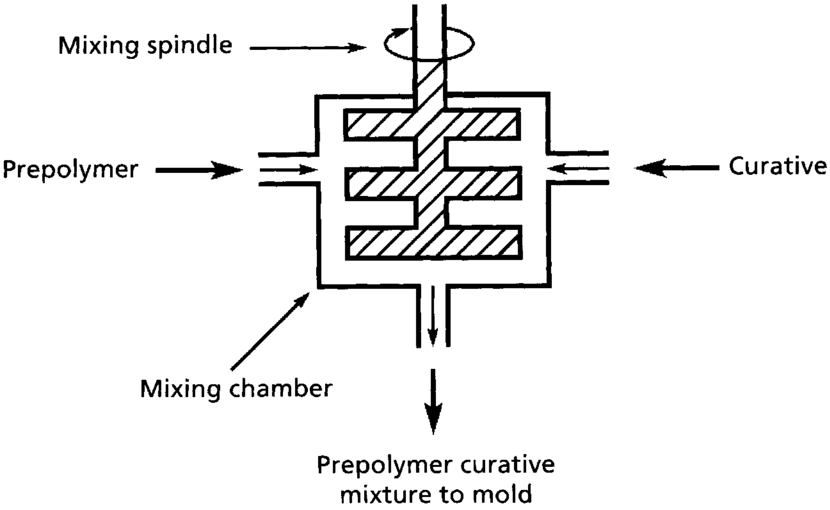


Figure 8.2 Representation of the mixing chamber in a urethane mixing machine, *(courtesy of the Holz Rubber Company)*

It is essential that any machine should reliably deliver the exact quantity of each ingredient to the mixing chamber, blend the mix perfectly every time, and the mixing chamber should be able to be thoroughly cleaned after each pour. More detailed information about machine mixing is indicated in the suggested further reading, at the end of this chapter.

8.3.3 Variations of the basic molding process

Quite a number of variations of basic molding are used in the industry. For centrifugal casting the mold is placed into a centrifuge, the high 'G' forces push the liquid into the 'hard to reach' areas of the mold and displace air bubbles which have a much lower mass. An application for this process would be production of thin cross section products such as sheeting.

For rotational casting the mold is turned on two axes, in order to coat the inside of the mold to make objects such as a hollow ball.

Compression molding similar to that discussed earlier in section 4.6.1 can also be used. Here the mixture is poured into the heated bottom mold half or both halves, and allowed to partially 'cure', so that there is a distinct increase in the viscosity of the liquid mixture.

The two halves of the mold are quickly brought together under pressure (before gravity takes over) and heated until cure is complete. Practice enables the molder to know just when to pour the mixture, as well as the exact moment to close and quickly compress the mold. If the viscosity is too low, air will be trapped and if it is too high the product will fracture. This method can be useful where compression molds are already in existence, also, as there are no open surfaces, problems related to the presence of a meniscus affecting appearance or performance do not arise. Compression molding can be used in cases where bubble removal would be a significant problem in a cast mold.

A method popular in the production of items such as automobile fascias is reaction injection molding (RIM). Conceptually it is a speeded up version of machine mixing. Pressure at the mixing head is dramatically increased and the spindle in the mixing head is replaced by a fast turbulent flow of the ingredients. Chemicals with fast cure times are chosen and the mold is fixed onto the mixing head. Cycle times with this method are fast, well suited to high volume production and the manufacture of large products. Rigid foam parts can be made with a solid 'skin', which forms against the walls of the mold.

8.4 Millable urethanes

Since there is a whole industry devoted to processing of solid raw gum elastomers, to which most of this book is devoted, it is reasonable that solid raw gum urethane elastomers exist to take advantage of it. Like castables, the millable gum is made from a polyol and diisocyanate, only here there are insufficient of the latter, so that all the OH groups on the polyol are not used. The result is a solid gum which can be peroxide cured. Double bonds can be incorporated in the polyol, if sulfur vulcanization is required. Carbon black fillers can be added to increase hardness, and plasticizers to make the product softer. Millable urethanes have similar properties to the castables including their reputation for toughness.

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Some Web Sites Related to Rubber

Rubber Division, American Chemical Society	www.rubber.org
Rubber Manufacturers Association (RMA) USA	www.rma.org
Rapra Technology Limited (RAPRA)	www.rapra.net
TARRC (MRPRA) Tun Abdul Razak Research Centre (Malaysian Rubber Producers Research Association)	www.tcom.co.uk/tarrc/
British Plastics & Rubber	www.polymer-age.co.uk
Energy Rubber Group (USA)	www.star.telegram.com/homes/erg/
Rubber & Plastics News (USA)	www.rubbernews.com
Rubber World Magazine	www.rubberworld.com
European Rubber Journal	www.crain.co.uk/erj/
Institute of Materials (Rubber Division) (UK)	www.instmat.co.uk/regorg/rubber.htm
American Society for Testing and Materials (ASTM)	www.astm.org

Abbreviations and Acronyms

ACM	polyacrylate
ACN	acrylonitrile
ASTM	American Society for Testing and Materials
AU	urethane (ester)
BDO	1,4-butanediol
BIIR	bromobutyl rubber
BR	polybutadiene rubber
BS	British Standards
CBS	*N*-cyclohexyl-2-benzothiazolesulphenamide
CIIR	chlorobutyl rubber
CO	epichlorohydrin homopolymer
CR	polychloroprene rubber chloroprene rubber
CSM	chlorosulfonated polyethylene, i.e., Hypalon
DCBS	*N,N*-dicyclohexyl-2-benzothiazyl sulfenamide
DIN	Deutsches Institut für Normung
DOP	dioctyl phthalate
DPG	diphenyl guanidine
DSC	differential scanning calorimeter
DTDM	dithiodimorpholine
EAM	ethylene vinyl acetate
ECO	epichlorohydrin copolymer
EPM	ethylene propylene copolymer rubber
EPDM	ethylene propylene terpolymer rubber
EU	urethane (ether)
EV	efficient vulcanization
EVM	ethylene vinyl acetate
FDA	Food and Drug Administration (USA)
FEA	finite element analysis
FFKM	perfluoromethyl vinyl ether and tetrafluoroethylene copolymer
FKM	fluoroelastomer, i.e., Viton

GECO	epichlorhydrin terpolymer
GR-S	Government rubber-styrene
HPPD	N-(1,3-dimethyl)-N¢-phenyl-*p*-phenylenediamine
HQEE	hydroquinone bis (-b-hydroxyethyl)ether
HNBR	hydrogenated nitrile
HSN	hydrogenated nitrile
IIR	butyl rubber isobutylene isoprene rubber
IR	polyisoprene
IRHD	International rubber hardness degrees
ISO	International Standards Organisation
MBS	2-(morpholinothio)benzothiazolesulphenamide
MBT	mercaptobenzothiazole
MCBA	4,4’-methylene bis (2-chloroaniline)
MDI	methylene diisocyanate
MDR	moving die rheometer
MEK	methyl ethyl ketone
MRPRA	Malaysian Rubber Producers’ Research Association
NBR	nitrile butadiene rubber
nm	nanometers
NR	natural rubber
NRPRA	Natural Rubber Producers’ Association
ODR	oscillating disc rheometer
PCLG	polycaprolactone glycol
PEAG	polyethylene adipate glycol
PMA	Polyurethane Manufacturers Association
PEG	polypropylene ether glycol
PTMEG	polytetramethylene ether glycol
PVC	polyvinyl chloride
PVMQ	see astm D1418
Q	silicone elastomers
RIM	reaction injection molding
RMA	Rubber Manufacturers Association
RSS	Ribbed smoked sheet

SAE	Society of Automotive Engineers
SBR	styrene butadiene rubber
SIBR	styrene-isoprene-butadiene rubber
SIR	Standard Indonesian Rubber
SMR	Standard Malaysian Rubber
SMR CV	Standard Malaysian Rubber Constant Viscosity
SSBR	styrene butadiene rubber (solution)
ST	synchronous technology
TDI	toluene diisocyanate
TEA	triethanolamine
TFE/P	tetrafluoroethylene propylene copolymer
TGA	thermogravimetric analyser
TIPA	tiisopropanolamine
TMA	thermomechanical analysers
TMP	trimethylol propane
TMTD	tetramethyl thiuram disulfide
TMTM	tetramethyl thiuram monosulfide
TPE	thermoplastic elastomer
VIC	variable intermeshing clearance
ZDBC	zinc dibutyl dithiocarbamate

Chart for Converting SI Units to Imperial Units

SI Unit	Conversion Factor	Imperial Unit
MPa	x 145	lb/in
cm	x 0.3937	inches
kg	x 2.2046	lb
kPa	x 0.00987	atm
N	x 0.2248	lbf
°C	x 1.8 + (32)	°F

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