CHAPTER 2
Materials and Compounds

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Contents

2.1 Introduction

Rubbers can be divided broadly into two types: thermosets and thermoplastics. Thermosets are three-dimensional molecular networks, with the long molecules held together by chemical bonds. They absorb solvent and swell, but do not dissolve; furthermore, they cannot be reprocessed simply by heating. The molecules of thermoplastic rubbers, on the other hand, are not connected by primary chemical bonds. Instead, they are joined by the physical aggregation of parts of the molecules into hard domains. Hence, thermoplastic rubbers dissolve in suitable solvents and soften on heating, so that they can be processed repeatedly. In many cases thermoplastic and thermoset rubbers may be used interchangeably. However, in demanding uses, such as in tires, engine mounts, and springs, thermoset elastomers are used exclusively because of their better elasticity, resistance to set, and durability.

The addition of various chemicals to raw rubber to impart desirable properties is termed rubber compounding or formulation. Typical ingredients include crosslinking agents (also called curatives), reinforcements, anti-degradants, process aids, extenders, and specialty additives, such as tackifiers, blowing agents, and colorants. Because thermoplastic rubbers contain hard domains that interconnect the molecules and impart strength and elasticity, they do not require crosslinking agents or reinforcing fillers. However, the selection of appropriate curatives and fillers is critical to the performance of thermoset elastomers.

This chapter deals only with thermoset rubbery materials and their formulation. We begin by describing the types of elastomers commercially available and then discuss fundamentals of their compounding.

2.2 Elastomer Types

2.2.1 General Purpose

General purpose elastomers are hydrocarbon polymers. They include styrene-butadiene rubber (SBR), butadiene rubber (BR), and polyisoprene rubber – both natural (NR) and synthetic (IR). These ''diene'' rubbers contain substantial chemical unsaturation in their backbones, causing them to be rather susceptible to attack by oxygen, and especially by ozone. Additionally, they are readily swollen by hydrocarbon fluids. The primary application of these elastomers is in automobile and truck tires.

2.2.1.1 Styrene-Butadiene Rubber (SBR)

SBR denotes a copolymer of styrene and butadiene, typically containing about 23% styrene, with a T_g of approximately –55 °C. It is the most widely used synthetic elastomer, with the largest volume production. It is synthesized via free-radical polymerization as an

emulsion in water, or anionically in solution. In emulsion polymerization, the emulsifier is usually a fatty acid or a rosin acid. The former gives a faster curing rubber with less tack and less staining. The molecular weight is controlled (to prevent gelation) by mercaptan chain transfer agents. When polymerization is complete, coagulation of the emulsion is carried out with salt, dilute sulfuric acid, or an alum solution. Alum coagulation results in a rubber with the highest electrical resistivity.

When emulsion polymerization is carried out at an elevated temperature ($\sim 50\,°C$), the rate of radical generation and chain transfer is high, and the polymer formed is highly branched. To overcome this, polymerization is carried out at low temperature ($\sim 5\,°C$), producing "cold" emulsion SBR, with less branching, and giving stronger vulcanizates.

A common initiator for anionic polymerization is butyl lithium. The vinyl butadiene content, and hence T_g, of SBRs polymerized in solution are increased by increasing solvent polarity. In comparison with emulsion polymers, the molecular weight distribution of anionically prepared SBR is narrow, and because the chain ends are "living," i.e., they remain reactive after polymerization, the molecules can be functionalized or coupled. For example, SBR macromolecules can be amine-terminated to provide increased interaction with carbon black, or coupled with $SnCl_4$ to give star-shaped macromolecules that break upon mastication in the presence of stearic acid to yield a material with lower viscosity. Solution SBR is also purer than emulsion SBR, because of the absence of emulsion residues. But, when compared at similar number-average molecular weights, emulsion SBRs are more extensible in the uncured (so-called "green") state than anionic SBRs.

2.2.1.2 Polyisoprene (NR, IR)

Natural rubber (NR) Natural rubber is produced from the latex of the Hevea brasiliensis tree. Before coagulation, the latex is stabilized with preservatives (e.g., ammonia, formaldehyde, sodium sulfite) and hydroxylamine may be added to produce technically-specified, constant-viscosity grades of NR. The T_g of NR is about $-70\,°C$ and its structure is thought to be completely *cis*-1,4-polyisoprene, except for the chain ends. NR contains small amounts of fatty acids and proteinaceous residues that promote sulfur vulcanization. Because NR macromolecules are configured identically (stereoregular), they spontaneously pack together as crystallites on standing at low temperature, with a maximum rate at temperatures around $-25\,°C$. NR also crystallizes upon straining. In fact, strain-induced crystallization imparts outstanding green strength and tack, and gives vulcanizates with high resistance to cut growth at severe deformations.

NR macromolecules are susceptible to fracture on shearing. High shearing stresses and oxygen promote the rate of molecular chain scission.

Several modified natural rubbers are available commercially. Some examples are:

a. Deproteinized, to reduce water adsorption, e.g., in electrical applications where maximum resistivity is required
b. Skim rubber, a high-protein, fast curing product used in cellular foams and pressure sensitive adhesives

c. Superior processing, in which ordinary and vulcanized latices are blended in about an 80:20 ratio before coagulation. Unfilled or lightly filled compounds made with superior processing NR give smoother and less swollen extrudates compared to those prepared from regular NR

d. Isomerized, prepared by milling NR with butadiene sulfone, resulting in cis/trans isomerization which inhibits crystallization

e. Epoxidized, an oil resistant rubber, which retains the ability to strain crystallize

Synthetic polyisoprene (IR) IR is produced both anionically and by Ziegler-Natta polymerization. The former material has up to 95% *cis*–1,4 microstructure, while the latter may be as much as 98% stereoregular. Even though the difference in stereoregularity is small, Ziegler-Natta IR is substantially more crystallizable. However, both types of IR have less green strength and tack than NR. IR compounds have lower modulus and higher breaking elongation than similarly formulated NR compositions. This is due, at least in part, to less strain-induced crystallization with IR, especially at high rates of deformation.

2.2.1.3 Polybutadiene (BR)

Like isoprene, BR can be synthesized anionically or via Ziegler-Natta catalysis. Cold emulsion BR is also available. Anionic BR, prepared in hydrocarbon solvent, contains about 90% 1,4 structure and 10% 1,2 (i.e., vinyl). The vinyl content can be increased by adding an amine or ether as co-solvent during polymerization. The 1,4 structure is an approximately equal mix of cis and trans. Because it consists of mixed isomers, anionically-prepared BR does not crystallize. Emulsion BR has a mostly trans microstructure and also does not crystallize. On the other hand, the Ziegler-Natta product has a very high cis content and can crystallize. The T_g of low-vinyl BRs is about –100 °C, among the lowest of all rubbers, while that of high-vinyl BRs can reach 0 °C. Low-vinyl BRs are highly resilient and are often blended with SBR, NR, and IR to make tire treads with good abrasion resistance. Unlike NR, BR is resistant to chain scission during mastication.

2.2.2 Specialty Elastomers

In many applications, general purpose elastomers are unsuitable due to their insufficient resistance to swelling, aging, and/or elevated temperatures. Specialty elastomers have been developed to meet these needs.

2.2.2.1 Polychloroprene (CR)

Polychloroprene is an emulsion polymer of 2-chlorobutadiene and has a T_g of about –50 °C. The electron-withdrawing chlorine atom deactivates the double bond towards attack by oxygen and ozone and imparts polarity to the rubber, making it resistant to swelling by hydrocarbons. Compared to general-purpose elastomers, CR has superior

weatherability, heat resistance, flame resistance, and adhesion to polar substrates, such as metals. In addition, CR has lower permeability to air and water vapor.

The microstructure of CR is mostly trans-1,4 and homopolymer grades crystallize upon standing or straining, even though they are not as stereoregular as NR. Apparently, C-Cl dipoles enhance interchain interaction and promote crystallization. Copolymer grades of CR crystallize less or not at all. Applications include wire, cable, hose, and some mechanical goods.

2.2.2.2   Acrylonitrile-Butadiene Rubber (NBR)

NBR, also termed nitrile rubber, is an emulsion copolymer of acrylonitrile and butadiene. Acrylonitrile content varies from 18 to 50%. Unlike CR, polarity in NBR is introduced by copolymerization with the polar monomer, acrylonitrile, which imparts excellent fuel and oil resistance. With increased acrylonitrile content, there is an increase in T_g, reduction in resilience, lower die swell, decreased gas permeability, increased heat resistance, and increased strength. Because of unsaturation in the butadiene portion, NBR is still rather susceptible to attack by oxygen and ozone. Aging behavior can be improved by blending with small amounts of polyvinyl chloride. Nitrile rubber is widely used for seals and fuel and oil hoses.

2.2.2.3   Hydrogenated Nitrile Rubber (HNBR)

Nitrile rubber can be hydrogenated to eliminate most of the unsaturation and hence greatly improve aging and heat resistance. Fuel resistance is maintained. HNBR is used especially in oil field applications, where resistance to hydrocarbons at elevated temperatures is required.

2.2.2.4   Butyl Rubber (IIR)

Butyl rubber is a copolymer of isobutylene with a small percentage of isoprene to provide sites for curing. IIR has unusually low resilience for an elastomer with such a low T_g (about $-70\,^{\circ}C$). Because IIR is largely saturated, it has excellent aging stability. Another outstanding feature of butyl rubber is its low permeability to gases. Thus, it is widely used in inner tubes and tire innerliners. Brominated (BIIR) and chlorinated (CIIR) modifications of IIR are also available. They have enhanced cure compatibility with general purpose diene elastomers.

2.2.2.5   Ethylene-Propylene Rubber (EPR, EPDM)

The commercial rubbers with the lowest density are ethylene-propylene copolymers made by Ziegler-Natta and metallocene polymerization. To introduce unsaturated cure sites, a

non-conjugated diene termonomer, such as 1,4 hexadiene, ethylidene norbornene, or dicyclopentadiene, is employed. EPDM (ethylene-propylene diene monomer) has a small number of double bonds, external to the backbone, introduced in this way. The ratio of ethylene to propylene in commercial grades varies from 50/50 to 75/25, and a typical T_g is –60 °C. EPRs and EPDMs have excellent resistance to weathering and good heat stability. They can be made partially crystalline to give high green strength, but they possess poor building tack. Applications including roofing, seals, gaskets, and hose.

2.2.2.6 Silicone Rubber (MQ)

Unlike the previously discussed elastomers, which have carbon-carbon backbones, silicone rubbers contain very flexible siloxane backbones, and have very low glass transition temperatures. The most common silicone elastomer is polydimethyl siloxane with a T_g of –127 °C. Silicone rubbers have both excellent high temperature resistance and low temperature flexibility. In addition, they possess good biocompatibility and thus are used in implants and prostheses. Other uses include gaskets, seals, and O-rings.

2.2.2.7 Polysulfide Rubber (T)

Polysulfide rubbers contain a substantial proportion of sulfur in their structure. For example, the polysulfide rubber made by reacting dichloroethane with sodium tetrasulfide contains about 80% sulfur by weight. This results in high density (1.34 g/cm^3) and outstanding resistance to ketones, esters, and most solvents. Major uses of polysulfide rubbers include permanent putties for fuel tank sealants, fuel hose liners, and gaskets.

2.2.2.8 Chlorosulfonated Polyethylene (CSM)

When polyethylene is chlorosulfonated, its crystallinity is disrupted and a chemically stable elastomer results. Commercial grades contain 25 to 45% chlorine and 1 to 1.4 % sulfur. These elastomers have excellent weatherability and good flame resistance. Oil resistance increases with increasing chlorine content, while low temperature flexibility and heat aging resistance are improved when the chlorine content is low.

2.2.2.9 Chlorinated Polyethylene (CM)

Another modification of polyethylene to produce an elastomer is simple chlorination (25 to 42%, typically about 36%). CMs are less expensive than CSMs and provide vulcanizates with lower compression set. Increased chlorine content improves oil, fuel, and flame resistance, but results in poorer heat resistance. CM has excellent weatherability and heat resistance to 150 °C to 175 °C, even when immersed in many types of oil. Hose and wire and cable coverings are typical applications.

2.2.2.10 Ethylene-Methyl Acrylate Rubber (AEM)

This elastomer is a terpolymer of ethylene, methyl acrylate, and a small amount of carboxylic monomer as a cure site. Amines and peroxides are used as curatives. AEM has a heat resistance between that of CSM and MQ elastomers. It is resistant to aliphatics, but has poor resistance to strong acids and other hydrolyzing agents. Weathering and heat aging resistance are good up to 150 °C. Example applications are power steering hose, spark plug boots, and transmission seals.

2.2.2.11 Acrylic Rubber (ACM)

ACMs are copolymers of a dominant acrylate monomer (ethyl or butyl) and a cure site monomer, such as 2-chloroethyl vinyl ether. Butyl acrylate results in a lower T_g, but poorer oil resistance compared to ethyl acrylate. Copolymerization with acrylonitrile improves oil resistance. Although acrylate rubbers have good heat resistance, they have poor resistance to alkali and acids. Applications include gaskets, O-rings, oil hose, and transmission seals.

2.2.2.12 Fluorocarbon Rubbers

Fluorocarbon rubbers are made in emulsion and are among the most inert and expensive elastomers. A typical one is made by copolymerizing the fluorinated analogs of ethylene and propylene. This rubber has a density of 1.85 g/cm^3 and has a service temperature exceeding 250 °C. It is little affected by immersion in acids, bases, or aromatic solvents; however, ketones and acetates attack the material. There are many aircraft applications for fluororubbers including O-rings, seals, and gaskets.

2.2.2.13 Epichlorohydrin Rubber (CO, ECO)

Two common types are polyepichlorohydrin (CO) and copolymers with ethylene oxide (ECO), which have lower T_g. Epichlorohydrin rubbers are quite resistant to aliphatic and aromatic fluids, and have good building tack. Other notable properties include good ozone resistance, low gas permeability (about one third that of butyl rubber), and heat resistance up to 150 °C. Applications include wire and cable jackets, hose and belting, and packings.

2.2.2.14 Urethane Rubber

Polyester and polyether type millable urethane rubbers are available. The latter have better hydrolytic stability, but somewhat worse mechanical properties. Urethane rubbers can be cured with sulfur or peroxide, and vulcanizates have excellent resistance to

weathering, abrasion, and swelling by oil. Some applications are industrial rolls, caster wheels, gaskets, shoe soles, and conveyor belts.

2.3   Compounding

None of the elastomers discussed in the previous section have useful properties until they have been properly formulated. Although some of the science of compounding is understood, much art still remains in preparing technical rubber compositions. In this section, the science and technology of the various ingredients used in rubber are discussed.

2.3.1   Vulcanization and Curing

An elastomer, as synthesized, is basically a high molecular weight liquid with low elasticity and strength. Although the molecules are entangled, they can readily disentangle upon stressing, leading to viscous flow. Vulcanization or curing is the process in which the chains are chemically linked together to form a network, thereby transforming the material from a viscous liquid to a tough elastic solid. Strength and modulus increase, while set and hysteresis decrease. Various curing systems are used to vulcanize different types of elastomers, but complete coverage is beyond the scope of this chapter. Rather, discussion here is primarily on the curing of general purpose diene elastomers with sulfur, with only brief mention of other cure systems.

2.3.1.1 Sulfur Curing

The most widely used vulcanizing agent is sulfur. For sulfur to effectively crosslink a rubber, an elastomer must contain double bonds with *allylic* hydrogens. General purpose diene elastomers such as BR, SBR, NR, and IR meet this basic requirement.

   Two forms of sulfur are used in vulcanization: soluble (rhombic crystals of S_8 rings) and insoluble (amorphous, polymeric sulfur). Sometimes, in compounds containing high levels of sulfur, insoluble sulfur is used to prevent sulfur blooming, a process by which the sulfur migrates to the surface of a compound and crystallizes there. Blooming can occur when large amounts of soluble sulfur are used, because at high mixing temperatures, the solubility of S_8 is high, enabling large amounts to dissolve, but upon cooling the solubility decreases. When the solubility limit is reached, excess sulfur blooms to the surface. Sulfur bloom reduces the "tack" of a rubber compound, a necessary property if layers of rubber are to be plied up to make a composite structure, such as a tire. Insoluble sulfur does not bloom because it disperses in rubber as discrete particles, which cannot readily diffuse through the rubber. However, above 120 °C, insoluble sulfur transforms into soluble sulfur. Thus, mixing temperatures must be kept below 120 °C to take advantage of the bloom resistance of insoluble sulfur.

Crosslinking with sulfur alone is quite inefficient and requires curing times of several hours. For every crosslink, 40 to 55 sulfur atoms are combined with the rubber. The structure contains polysulfide linkages, dangling sulfur fragments, and cyclic sulfides. Much of the sulfur is not involved in crosslinks between chains. Moreover, such networks are unstable and have poor aging resistance.

To increase the rate and efficiency of sulfur crosslinking, accelerators are normally added. These are organic bases and can be divided into five major categories: guanidines, thiazoles, dithiocarbamates, xanthates, and thiurams. Of these, the guanidine-type accelerators, such as diphenyl guanidine (DPG), give the lowest rate of vulcanization as well as a relatively slow onset of vulcanization. Delayed onset of vulcanization is a desirable feature of rubber compounds. It allows shaping processes to be carried out before vulcanization starts and the material becomes set in its final shape. Premature vulcanization is known as "scorch."

Guanidines are seldom used alone, but rather are combined with another type of accelerator. The accelerators that increase the rate of curing the most are the xanthate types. These ultra-accelerators cause crosslinking so readily that they are seldom used in solid rubber because curing would be initiated just from the heat generated while mixing. Rather, xanthates are used mainly for crosslinking rubber as a latex.

The accelerators with the widest application are the thiazoles, a subcategory of which is the delayed-action sulfenamides. Compounds containing sulfenamides may be sheared for long times without premature vulcanization (scorch). This is particularly important in the tire industry, where a compound may be mixed, repeatedly milled, and then calendered or extruded before being fabricated into a tire.

Thiurams and dithiocarbamates are considered ultra-accelerators, although they are not as active as the xanthates. Because these accelerators have a short scorch time, care must be taken to keep processing temperatures low. Some compounds with ultra-accelerators may begin curing within one day at room temperature, so they must be processed soon after mixing. Crosslinking is efficient when ultra-accelerators are used, and especially when the ratio of accelerator to sulfur is high, so that only low levels of sulfur are required for proper vulcanization.

Often, a combination of accelerators is used to obtain the desired scorch resistance and cure rate. Generally, if two accelerators of the same type are combined, then cure characteristics are approximately the average of those for each accelerator alone. However, there is no general rule when combining accelerators of different types. Moreover, the type of accelerator is much more important than the level of accelerator in controlling scorch time. Although increased levels of accelerator increase the degree of crosslinking attained, generally accelerator concentration has only a small effect on scorch time.

Accelerated sulfur curing is more efficient when the activators zinc oxide and stearic acid are added. It is thought that these additives combine to create soluble zinc ions that activate intermediate reactions involved in crosslink formation.

One instrument used to determine the kinetics of crosslinking is the oscillating disc rheometer (ODR). An oscillating rotor is surrounded by a test compound, which is enclosed in a heated chamber. The torque required to oscillate the rotor is monitored as a function of time. Another instrument to follow curing is the rotor-less moving-die
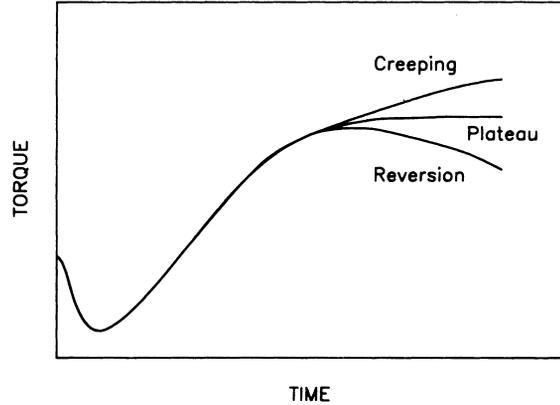
Figure 2.1 Three types of response from an oscillating disk rheometer.

rheometer (MDR), which uses thinner samples, and hence, has faster thermal response than the ODR. Examples of curemeter responses are shown in Fig. 2.1.

Initially, there is a sudden increase in torque as the chamber is closed. Then, as the rubber is heated, its viscosity decreases, causing a decrease in torque. Eventually, the rubber compound begins to vulcanize and transform into an elastic solid, and the torque rises. Molecular chain scission also may be occurring; however, an increasing torque indicates that crosslinking is dominant. If the torque reaches a plateau, this indicates completion of curing and the formation of a stable network. If chain scission and/or crosslink breakage become dominant during prolonged heating, the torque passes through a maximum and then decreases, a phenomenon termed reversion. Some NR compounds, particularly at high curing temperatures, exhibit reversion. On the other hand, some compounds show a slowly increasing torque at long cure times, or "creeping cure." This behavior often occurs in compounds that initially form many polysulfidic linkages. With extended cure times, these linkages may break down and reform into new crosslinks of lower sulfur rank, thereby increasing the total number of crosslinks.

2.3.1.2 Determination of Crosslink Density

The crosslink density of an elastomer can be determined from swelling or mechanical measurements. An elastomer crosslinked above its gel point absorbs solvent and swells, sometimes highly, but does not dissolve. Swelling continues until the retractive forces in the extended molecular strands in the network balance the forces tending to swell the network. For unfilled elastomers, the Flory-Rehner equation is widely used to relate the amount of swelling to the crosslink density:

$$N' = -\frac{1}{2V_s} \frac{ln(1 - v_r) + v_r + \chi v_r^2}{v_r^{1/3} - v_r/2} \tag{2.1}$$

where N' is the number of moles of crosslinks per unit volume, V_s is the molar volume of the swelling solvent, v_r is the volume fraction of rubber in the swollen gel, and χ is the polymer-solvent interaction parameter.

For vulcanizates containing reinforcing fillers such as carbon black, v_r for use in the Flory-Rehner equation may be obtained from the following expression derived by Kraus:

$$\frac{v_r}{v_{rf}} = 1 - \left\{ 3c\left[1 - v_r^{1/3}\right] + v_r - 1 \right\}\frac{\phi}{1 - \phi} \tag{2.2}$$

where v_{rf} is the volume fraction of filled rubber in the swollen gel, ϕ is the volume fraction of filler in the unswollen filled rubber, and c is the filler-rubber interaction parameter.

Crosslink densities of unfilled rubbers have also been determined from equilibrium stress-strain measurements using the Mooney-Rivlin equation:

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \tag{2.3}$$

where σ is the engineering stress, λ is the extension ratio, and C_1, C_2 are elastic constants. On plotting $\sigma/2(\lambda - \lambda^{-2})$, vs. $1/\lambda$ and extrapolating to $1/\lambda = O_1$ a value of C_1 can be obtained from the intercept. From the theory of rubber elasticity, $C_1 = N'RT$, where N' is the crosslink density, R is the gas constant, and T is the absolute temperature (see Chapter 3). To assure near equilibrium response, stress-strain measurements should be carried out at a low strain rate.

2.3.1.3 Influence of Crosslink Density

Mechanical properties of an elastomer depend strongly on crosslink density. Modulus and hardness increase monotonically with increasing crosslink density, and the material becomes more elastic, or stated alternatively, less hysteretic. Fracture properties, such as tear and tensile strength, pass through a maximum as crosslinking is increased. To understand this behavior, it is helpful first to consider fracture in an uncrosslinked elastomer, and then to discuss changes in the mechanism of fracture as crosslinks are introduced.

When an uncrosslinked elastomer is stressed, chains may readily slide past one another and disentangle. At slow rates, fracture occurs at low stresses by viscous flow without breaking chemical bonds. The effect of a few crosslinks is to increase the molecular weight, creating branched molecules and a broader molecular weight distribution. It is more difficult for these branched molecules to disentangle and hence, strength increases. As crosslinking is increased further, the gel point is eventually reached when a three-dimensional network forms. Some chains may not be attached to the network (soluble sol phase), but the whole composition no longer dissolves in a solvent. A gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, because chemical bonds must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking.

When an elastomer is deformed by an external force, part of the input energy is stored elastically in the chains and is available (released upon crack growth) as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat,

and in this manner, is made unavailable to break chains. At high crosslink levels, chain motions become restricted, and the "tight" network is incapable of dissipating much energy. This results in relatively easy, brittle fracture at low elongation. Elastomers have an optimum crosslink density range for practical use. Crosslink levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure.

Both the level and type of crosslinking are important. When curing with sulfur, the type of crosslinks depends on (1) sulfur level (2) accelerator type (3) accelerator/sulfur ratio and (4) cure time. Generally, high accelerator/sulfur ratio and longer cure time increase the number of monosulfidic linkages at the expense of polysulfidic ones. Vulcanizates containing predominately monosulfidic crosslinks have better heat stability, set resistance, and reversion resistance than those with polysulfidic links. This is attributed to greater stability of C-S bonds compared to S-S bonds. On the other hand, compounds containing a high proportion of polysulfidic crosslinks possess greater tensile strength and fatigue cracking resistance compared to compositions with monosulfidic links. This is thought to be due to the ability of S-S bonds in polysulfidic linkages to break reversibly, thereby relieving locally high stresses that could initiate failure.

2.3.1.4 Other Cure Systems

Peroxides are another type of curing agent for elastomers. Unlike sulfur vulcanization, carbon-carbon double bonds are not required for peroxide curing and thus, peroxides may be used to crosslink saturated elastomers, e.g., ethylene-propylene copolymers, chlorinated polyethylene, chlorosulfonated polyethylene, and silicone rubber. In addition, peroxides readily crosslink diene elastomers. Peroxide curing takes place via a free-radical mechanism and leads to carbon-carbon crosslinks, which are quite stable. The crosslinked materials show good aging resistance and low compression set.

Some elastomers, particularly polychloroprene, can be crosslinked with the metal oxides ZnO and MgO. It has been proposed that the crosslinking occurs via allylic chlorines on the polymer molecules. Generally, mixtures of ZnO and MgO are used because ZnO by itself is too scorchy and MgO alone is inefficient.

Butyl rubber cannot be cured with peroxides and sulfur vulcanization is often inefficient. Instead, polymethylol phenolic resins with metallic chlorides are often used. They give crosslinked materials with excellent resistance to high temperatures.

2.3.2 Reinforcement

Particulate fillers can increase the strength of an amorphous rubber more than 10-fold. For a filler to cause significant reinforcement, it must possess high specific surface area, i.e., the particles must be small, less than 1 μm in size. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. They can be produced with a primary particle size as small as 100 Å, corresponding to a surface area of a few hundred m^2 per gram of filler.

Two other important characteristics of fillers are structure and surface chemistry. Structure relates to irregularity in shape of filler aggregates (Fig. 2.2), determined by the extent and manner of clustering of primary particles. A filler aggregate with high structure has a large void volume within the space it pervades, in which rubber molecules may become "occluded." The combination of occluded rubber and filler then becomes the reinforcing entity, so that the effective volume fraction of filler is increased (Aggregates are not broken down into primary particles upon mixing with rubber.). Generally, reinforcement is enhanced by high structure and strong bonding between filler and rubber. Silica fillers are often treated with silane coupling agents to bond them chemically to rubber, or the coupling agents may be added directly to the rubber compound.
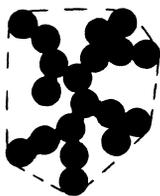

Figure 2.2   Schematic of a carbon black aggregate consisting of fused primary particles. The dotted line (a surface in 3D) depicts the volume pervaded by the aggregate. The larger the ratio of pervaded to actual volume is, the higher the "structure".

During shear mixing, rubber and carbon black become chemically linked. This has been demonstrated by attempting to dissolve filled, uncrosslinked compounds in good solvents. Only a portion of the rubber dissolves, leaving a "carbon gel" containing all of the carbon black and the remainder of the rubber which is strongly bound to the filler, termed "bound rubber." The interactions between rubber and carbon black include a spectrum of strengths, with some chains chemically attached to the black and others with physical bonds of varying magnitude. The importance of bonding between rubber and carbon black is illustrated by exposing carbon black to extreme heating (graphitization) in an inert atmosphere before mixing it into rubber. Graphitization removes active functional sites on the black, decreases the amount of bound rubber, and reduces the reinforcing effect, as shown in Fig. 2.3. Compared to the vulcanizate reinforced with normal furnace black, the vulcanizate containing graphitized black has lower modulus, higher ultimate elongation, and reduced strength. However, the rubber filled with graphitized black is much stronger than a simple unfilled (gum) vulcanizate or one filled with an equal volume fraction of larger-sized particles (e.g., clay).

Before addition to rubber, carbon black aggregates are "clumped" together as so-called agglomerates. To provide the greatest reinforcement, these black agglomerates must be broken down into aggregates and thoroughly dispersed in the rubber. This requires mixing at high shear stress. The viscosity of the rubber must not be too low, or the shear stresses will be insufficient to break apart the filler agglomerates. Thus, when oil is to be added to a stock, it should be added toward the end of the mixing cycle, after the carbon black has been well dispersed.

Besides enhancing strength, carbon black also improves processability by greatly reducing melt elasticity. This allows shaping operations, such as extrusion and calendering, to occur with less shrinkage and melt distortion.

Carbon black is most effective for strengthening non-crystallizing elastomers such as SBR. Strain-crystallizing elastomers such as NR already have a self-reinforcing
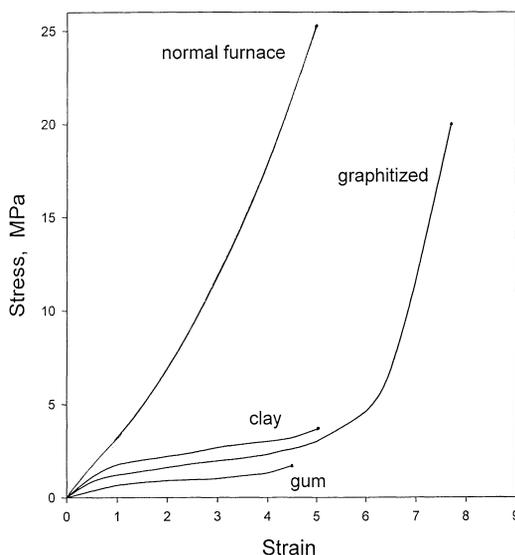
Figure 2.3 Typical stress-strain curves for an unfilled (gum) vulcanizate and ones filled with normal furnace black, graphitized black, and a filler consisting of micron-sized particles (e.g., clay).

mechanism. Indeed, unfilled and black-filled NR vulcanizates have comparable tensile strengths, although the latter have improved resistance to tearing and abrasion.

2.3.3 Anti-Degradants

Oxygen and ozone can react with elastomers and alter network structure by causing chain scission and/or crosslinking. Antioxidants and antiozonants, which can function chemically or physically, have been developed to inhibit the action of these reactive components of air.

Chemical protectants are capable of reacting with the degradant or interfering with the chain of reactions that otherwise would culminate in degradation of the rubber. The most common types are aromatic amines, phenolics, and phosphites. The first type is staining, while the other two are not. Physical protectants function by migrating, i.e., blooming, to the rubber surface and providing a barrier to attack by degradants. Microcrystalline waxes, which are mixtures of alkanes, isoalkanes, and cyclo-aliphatic hydrocarbons, are commonly used. The rate and extent of blooming are important and depend on the level of compatibility with the elastomer.

2.3.3.1 Ozone Attack

Ozone, even when present in the atmosphere at only a few parts per hundred million, readily cleaves carbon-carbon double bonds in elastomers. As a result, an unsaturated rubber, exposed to ozone in the strained state, quickly develops surface cracks. The severity of cracking increases rapidly if the applied strain is above a small threshold level, of the order of 10%. Para-phenylenediamines (PPDs) are effective in reducing ozone

cracking in diene rubbers and there is good evidence that they react directly with ozone, competing with the ozone-rubber reaction. However, there are no additives that enable unsaturated elastomers to resist ozone as well as saturated ones.

2.3.3.2 Oxidation

In general, the reaction of oxygen with elastomers causes both chain scission and crosslinking. If chain scission dominates during aging, the elastomer softens and eventually may become sticky. This is the usual behavior of unfilled NR and IIR vulcanizates. However, most technical elastomer compounds eventually harden and embrittle during oxidation, a consequence of the dominant crosslinking reactions. For some compounds, in the early stages of oxidation, there is a fortuitous equality in the extent of chain scission and crosslinking, such that modulus does not change. Nonetheless, the altered network now contains increased chain-end defects, and strength and elongation are reduced.

A concentration of only 1 to 2% of reacted oxygen is normally sufficient to cause severe deterioration in an elastomer. The principal mechanism of oxygen attack involves an autocatalytic, free radical reaction. The first step is the creation of macroradicals as a result of hydrogen abstraction from rubber chains by a proton acceptor. Oxidation continues by reaction of macroradicals with oxygen and the subsequent formation of peroxy radicals and hydroperoxides, which are readily detected by infrared spectroscopy. Oxidation is accelerated by heat, exposure to ultraviolet light, and the presence of some metals, notably copper, cobalt, and manganese. Also, stress hastens oxidation. For sulfur-cured vulcanizates, the oxidation rate increases as sulfur content increases. It is believed that the allylic crosslink site is particularly susceptible to oxidation.

Antioxidants are employed to slow oxidation. They fall into two classes, with different functions. The first type, called preventive antioxidants, react with hydroperoxides to form harmless, non-radical products. In the process, the antioxidant is oxidized. The second type, chain-breaking antioxidants, destroy peroxy-radicals that would otherwise propagate. Chain-breaking antioxidants are aromatic and contain labile protons, which are ''donated'' to the peroxy-radicals. This occurs readily because the resulting antioxidant radical is highly resonance-stabilized. A listing of some common amine antioxidants, which are quite effective in diene elastomers, is given in Table 2.1.

Usually, accelerated aging tests are used to determine the resistance of a vulcanizate to oxidation. However, caution should be used in attempting to infer long-term aging performance from short-term tests carried out at temperatures much higher than the service temperature. The reason is well illustrated in Fig. 2.4. A black-filled NR vulcanizate was oxidized at various temperatures, while the degree of oxidation was determined directly by the quantity of oxygen absorbed. Stress-strain measurements were carried out on the aged samples. Stiffness at room temperature is plotted schematically against oxygen uptake at various temperatures. It is noteworthy that, when aged at 50 °C, the vulcanizate stiffened, while when it was aged at 110 °C, it softened. Clearly, in this case, relative rates of chain scission and crosslinking depend on aging temperature.

Table 2.1 Some Amine Antioxidants and Their Common Abbreviations

Phenyl-α-naphthylamine (PAN)
N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)
N-(1,3 dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD)
N,N'-diphenyl-p-phenylenediamine (DPPD)
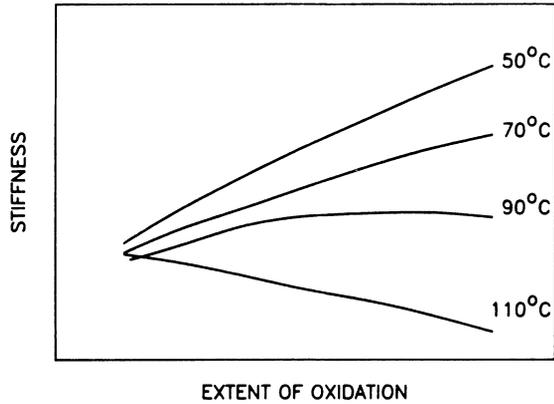Poly-1,2-dihydro-2,2,4-trimethylquinoline (TMQ)

Figure 2.4 Stiffness of an NR vulcanizate determined at room temperature after oxidative aging at the temperatures indicated.

A convenient way to determine separately the extent of chain scission and crosslinking during aging is to carry out two types of stress relaxation test: continuous stress relaxation (CSR), and intermittent stress measurement (ISM). The procedures are as follows:

In CSR, a sample of the rubber to be aged is stretched to a given low extension ratio, λ. The stress is allowed to decay to an equilibrium value, $\sigma(0)$. Then, while the extension is maintained, the sample is placed in an aging chamber and stress, $\sigma_c(t)$, is monitored continuously as a function of aging time, t. Newly formed network chains resulting from additional crosslinking are non-load bearing because they are introduced in the strained state. Only scission of the original network chains causes $\sigma_c(t)$ to be reduced. In ISM testing, on the other hand, a sample is aged in the unstretched state; then periodically, the equilibrium stress, $\sigma_i(t)$, required to impose the extension ratio, λ, is determined. In this case, the measured stress depends on the net difference between crosslinking and chain scission.

Now, based on rubber elasticity theory, it is assumed that the stress $\sigma(t)$ is directly proportional to network chain density, $N(t)$, thus

$$\frac{\sigma(t)}{\sigma(0)} = \frac{N(t)}{N(0)} \tag{2.4}$$

where N(0) is the network chain density at the start of aging. Furthermore,

$$N_c(t) = N(0) - N_s(t) \tag{2.5}$$

and

$$N_i(t) = N(0) + N_x(t) - N_s(t) \tag{2.6}$$

where $N_c(t)$, $N_s(t)$ and $N_x(t)$ are, respectively, the number of molecular chains remaining after aging time t, the number of chain scissions that occurred and the number of new crosslinks introduced per unit volume. $N_c(t)$ is determined from Eq. (2.4) and the results of CSR, and $N_i(t)$ likewise from ISM. Thus, the number of chain scissions $N_s(t)$ is obtained directly from CSM, and the number of new crosslinks, $N_x(t)$, is obtained from $N_s(t)$ when combined with the results of ISM.

2.3.4 Process Aids

Process aids are additives that lower viscosity and thus enable a rubber compound to be fabricated with less energy. They also increase melt stability so that the rate of processing can be increased. There are two general kinds of process aids: chemical peptizers and physical plasticizers. Chemical peptizers, typically added at 1 to 3 parts by weight per hundred parts of elastomer (phr), reduce molecular weight by increasing oxidative chain scission. Examples include sulfonic acids and pentachlorothiophenol, which are commonly used in NR. Excess peptizer must be avoided, because it results in reduced vulcanizate strength.

Physical plasticizers soften a compound by reducing entanglements and decreasing internal friction. The entanglement plateau modulus (indicative of entanglement density) depends on the concentration of rubber in a rubber/plasticizer mixture to a power of 2.0 to 2.3. An additional benefit of physical plasticization may be improvement in low temperature flexibility. Plasticizers should have good compatibility, which can become a problem at low temperatures, because a poorly compatible plasticizer may ''bleed'' from the compound. Common plasticizers include oils, fatty acids, esters, pine tar, liquid polymers, and rosin.

2.3.5 Extenders

Extenders are added to rubber compositions to reduce cost. Usually, this results in a decrease in physical properties, which limits the amount of extender that can be used. Oil extension of rubber, especially in tire treads, is widely practiced. Oil levels of 30 to 40 phr are typical. Oil addition permits the use of elastomers with higher molecular weights and the addition of greater amounts of filler than would be possible otherwise. These two factors compensate for the dilution of network chains, so that good physical properties are obtainable even at rather high oil levels.

Other types of extenders are particulate solids with primary particle sizes greater than about 1 μm. These stiffen rubber compositions, but either have little effect on strength or diminish it. Examples include clay, calcium carbonate, and ground coal.

Resins are hard brittle solids which can dissolve in rubber at processing temperatures, but may separate out as another phase in the vulcanized material and stiffen it. Some are

two-component systems, which react chemically at vulcanization temperatures. A phenolic resin that reacts with a formaldehyde donor is an example.

2.3.6 Tackifiers

Tack is the ability of two materials to resist separation after being in contact for a short time under light pressure. Tackifiers are a class of resins added to elastomers to improve tack. Several types are available:

1. Rosin derivatives that are chemical mixtures of abietic and related acids are usually esterified by polyhydric alcohols, then hydrogenated, dimerized, or disproportionated to improve aging and heat stability
2. Coumarone-indene resins consisting of indene, coumarone, styrene, methyl styrene, methyl indene, etc., are obtained from coal coke oven light oils
3. Aliphatic petroleum resins made from unsaturates obtained while cracking crude oil
4. Terpene oligomers of alpha- or beta-pinene obtained from pine tree stumps
5. Alkyl modified phenol-formaldehyde resins

Tackifiers generally have molecular weights in the 500 to 2000 range. Ring and ball softening points vary from 50 to 150 °C and tackifiers often have limited compatibility with the elastomer to which they are added; they are less compatible than a plasticizer, but more compatible than a filler. The function of tackifiers, typically added in the range 1 to 10 phr, is two-fold: to increase initial tack and to prevent tack degradation that can occur after a stock has been processed. In NR stocks, the latter function is the more important one, while for SBR and NR/SBR blends, the tackifier serves both functions.

A tackifier must be compatible with the rubber. This is dependent on chemical composition and molecular weight. For modified phenolics, the para-alkyl group must be large, t-butyl or greater, to improve compatibility with a non-polar hydrocarbon elastomer. When the alkyl group is t-octyl, the most effective tackifying action occurs at a molecular weight of about 2000.

2.4 Typical Rubber Compositions

This chapter concludes with a few typical rubber formulations and some physical properties of the vulcanizates obtained from them, taken in part from the Vanderbilt Rubber Handbook, edited by R. F. Ohm (R.T. Vanderbilt Co., Inc., 1990).

Table 2.2 An Unfilled Natural Rubber Formulation

Ingredient	Amount (phr*)
Natural rubber	100
Process oil	2
Stearic acid	2
Zinc oxide	5
Antioxidant: 6PPD	1
Sulfur	2.75
Cure accelerator: benzothiazyl disulfide	1
Cure accelerator: tetramethyl thiuram disulfide	0.1

*Parts by weight per 100 parts by weight of rubber

Cure: 10 minutes at 150°C

Shore A Hardness	39
Tensile Strength (MPa)	24
Breaking Elongation (%)	750

Table 2.3 Carbon Black-Filled Natural Rubber Formulations for General-Purpose Engineering Use

Ingredient	Amount (phr*)
Natural rubber	100
Process oil	5
Stearic acid	2
Zinc oxide	5
N-550 carbon black	25, 50, 75
Phenylamine antioxidant	1.5
Sulfur	2.5
Cure accelerator: benzothiazyl disulfide	1.0
Cure accelerator: tetramethyl thiuram disulfide	0.1

*Parts by weight per 100 parts by weight of rubber

Cure: 20 minutes at 150° C

	N550 carbon black (phr)		
	25	50	75
Shore A Hardness	51	62	72
300% Modulus (MPa)	7	9	11
Tensile Strength (MPa)	22	24	25
Breaking Elongation (%)	700	600	550

Table 2.4 Typical Styrene-Butadiene Rubber (SBR) Formulation

Ingredient	Amount (phr*)
SBR-1500	100
Process oil	4
Stearic acid	2
Zinc oxide	5
Antioxidant: DPPD	1.5
N-330 carbon black	50
Sulfur	2
Cure accelerator: benzothiazyl disulfide	2
Cure accelerator: tetramethyl thiuram disulfide	0.15

*Parts by weight per 100 parts by weight of rubber

Cure 25 minutes at 150°C

Shore A Hardness	65
300% Modulus (MPa)	13.5
Tensile Strength (MPa)	25
Breaking Elongation (%)	500

Table 2.5 A Butyl Rubber Formulation

Ingredient	Amount (phr*)
Butyl 268	100
Process oil	2
Stearic acid	1
Zinc oxide	5
N-330 carbon black	50
Sulfur	2
Cure accelerator: tetramethyl thiuram disulfide	1
Cure accelerator: mercaptobenzothiazole	0.5

*Parts by weight per 100 parts by weight of rubber

Cure: 20 minutes at 171°C

Shore A Hardness	62
300% Modulus (MPa)	8.5
Tensile Strength (MPa)	16.3
Breaking Elongation (%)	530

Table 2.6 Polychloroprene Formulations for General-Purpose Engineering Use

Ingredient	Amount (phr*)
Polychloroprene (Neoprene W)	100
Process aid	5
N550 carbon black	25, 50, 75
Stearic acid	2
Zinc oxide	5
Magnesium oxide	4
Antioxidant: octylated diphenylamine	2
Cure accelerator: activated thiadazine	1

*Parts by weight per 100 parts by weight of rubber

Cure: 20 minutes at 150°C

	N550 carbon black (phr)		
	25	50	75
Shore A Hardness	53	64	78
300% Modulus (MPa)	9	11	14
Tensile Strength (MPa)	20	21	24
Breaking Elongation (%)	400	350	300

Table 2.7 Acrylonitrile-Butadiene Rubber (NBR) Formulation

Ingredient	Amount (phr*)
NBR (Chemigum N689B)	100
Process aid	2
N330 carbon black	50
Zinc oxide	5
Stearic acid	1.5
Sulfur	1.75
Antioxidant: octylated diphenylamines	1.5
Plasticizer: dibutyl phthalate	12.5
Coumarone-indene resin	12.5
Cure accelerator: benzothiazyl disulfide	1.5

*Parts by weight per 100 parts by weight of rubber

Cure: 35 minutes at 150°C

Shore A Hardness	59
300% Modulus (MPa)	9.2
Tensile Strength (MPa)	18.5
Breaking Elongation (%)	510

Table 2.8 Ethylene-Propylene Diene Monomer (EPDM) Formulation

Ingredient	Amount (phr*)
EPDM (Nordel 2744)	100
Extender: paraffinic process oil	90
N-550 carbon black	100
Zinc oxide	5
Stearic acid	1
Sulfur	2
Cure accelerator: mercaptobenzothiazole	1.0
Cure accelerator: tetramethylthiuram monosulfide	1.5

*Parts by weight per 100 parts by weight of rubber

Cure: 20 minutes at 166° C

Shore A Hardness	64
300% Modulus (MPa)	6.8
Tensile Strength (MPa)	15.5
Breaking Elongation (%)	410

Acknowledgment

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Problems for Chapter 2

1. Polychloroprene, though containing more unsaturation, has higher resistance to ozone than nitrile rubber. Furthermore, nitrile rubber cures readily with sulfur, while polychloroprene does not. Explain.
2. Homopolymerization of ethylene or propylene results in a hard plastic, while a 50/50 copolymer is an elastomer. Why?
3. What are the two types of sulfur used as a curative for rubber? Which one is resistant to blooming? Why?
4. 1,2 polybutadiene and 1,4 polybutadiene have the same number of double bonds, but the former cures less effectively with sulfur. Explain.
5. Why does the stiffness of a black-filled vulcanizate increase with increasing black structure (at fixed specific surface area)?
6. Distinguish between preventive and chain-breaking antioxidants.
7. A vulcanizate is subjected to oxidative aging. The change in stress with time in both CSR and ISM experiments is the same. What does this signify?

Answers to Problems for Chapter 2

1. NBR is a copolymer of butadiene and acrylonitrile. As with BR, unprotected double bonds in the butadiene portion are readily cleaved by ozone and can undergo crosslinking via sulfur. The double bonds in CR are protected by a polar, electron-withdrawing chlorine group. This reduces reactivity of the double bonds towards ozone and towards the curing reaction with sulfur.
2. Homopolymers of ethylene and propylene have low glass transition temperatures, but they have regular structures and are crystalline solids at room temperature. Copolymerization creates molecular chains with an irregular microstructure that cannot fit together into a crystal lattice. Hence, the copolymer is an amorphous rubbery material with low T_g.
3. Crystalline soluble sulfur and amorphous insoluble sulfur are the two types. The latter does not bloom because it remains as discrete particles when mixed into rubber.
4. Accelerated sulfur vulcanization occurs through allylic hydrogens. Each monomer unit of 1,2-BR has one allylic hydrogen, while a 1,4 unit has four allylic hydrogens, with less steric hindrance.
5. Carbon black with increased structure can occlude more rubber. This effectively increases the volume fraction of filler by shielding a portion of the rubber from stress.
6. Two principal intermediates in the reactions leading to oxidative degradation of rubber are hydroperoxides and peroxy-radicals. Preventive antioxidants react with the first, and chain-breaking ones with the second.
7. Continuous stress relaxation (CSR) is sensitive only to chain scission, while ISM indicates the net difference between scission and crosslinking. Thus, if CSR and ISM give the same results, the vulcanizate must degrade by chain scission only.

Composite materials and material compounds are of increasing importance, because of the steadily rising relevance of resource saving lightweight constructions. Quality assurance with appropriate Nondestructive Testing (NDT) methods is a key aspect for reliable and efficient production. Quality changes have to be detected already in the manufacturing flow in order to take adequate corrective actions. For materials and compounds the classical NDT methods for defectoscopy, like X-ray and Ultrasound (US) are still predominant.