

Vulcanization

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7.1 INTRODUCTION

The vulcanization process is necessary to produce most useful rubber articles, like tires and mechanical goods. Unvulcanized rubber is generally not strong, does not retract essentially to its original shape after a large deformation, and it can be very sticky. In short, unvulcanized rubber can have the same consistency as chewing gum.

The first commercial method for vulcanization has been attributed to Charles Goodyear. His process (heating natural rubber with sulfur) was first used in Springfield, Massachusetts, in 1841. Thomas Hancock used essentially the same process about a year later in England. However, Hancock filed his patent on November 21, 1843, 8 weeks before Goodyear filed his US Patent on January 30, 1844.

Since those early days, there has been continued progress toward the improvement of the process and in the resulting vulcanized rubber articles. In addition to natural rubber, over the years, many synthetic rubbers have been introduced. Also, in addition to sulfur, other substances have been introduced as components of curing (vulcanization) systems. This chapter is an overview of the science and technology of vulcanization. Emphasis is placed on general-purpose “high-diene” rubbers; for example, natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR), vulcanized by sulfur in the presence of organic accelerators.

The accelerated-sulfur vulcanization of these rubbers along with the vulcanization of other rubbers, which are vulcanized by closely related technology, comprises more than 90% of all vulcanization. These rubbers include ethylene-propylene-diene-monomer rubber (EPDM), butyl rubber (IIR), halobutyl rubbers, and nitrile rubber (NBR). Nevertheless, we give some consideration to vulcanization by the action of other vulcanization agents such as organic peroxides, phenolic curatives, and quinoid curatives.

Dynamic vulcanization (DV) is also considered. DV is the crosslinking of one polymer in a blend of polymers during its mixing, all polymers of the blend being in the molten state. The process is used in the preparation of thermoplastic elastomers from rubber-plastic blends.

7.2 DEFINITION OF VULCANIZATION

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process that increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network (Figure 7.1).

According to the theory of rubber elasticity (Flory, 1953), the retractile force to resist a deformation is proportional to the number of network-supporting polymer chains per unit volume of elastomer. A supporting polymer chain is a linear polymer molecular segment between network junctures. An increase in the number of junctures or crosslinks gives an increase in the number of supporting chains. In an unvulcanized linear high polymer (above its melting point) only molecular chain entanglements constitute junctures.

Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. A crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon-to-carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion.

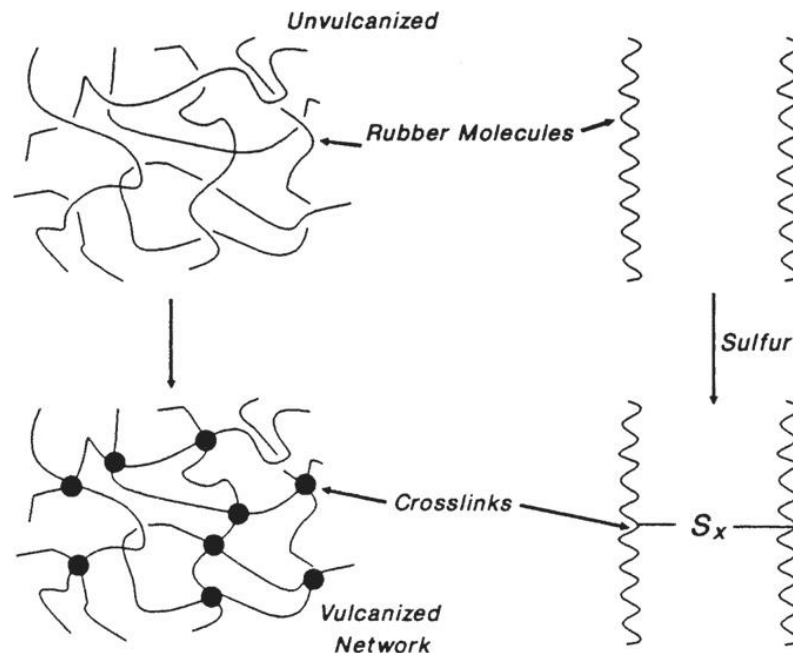


FIGURE 7.1 Network formation.

The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure. We note that, for extruded rubber goods, the compounded rubber extrudate can be heated in a salt bath or even in hot air.

7.3 EFFECTS OF VULCANIZATION ON VULCANIZATE PROPERTIES

Vulcanization causes highly significant changes at the molecular level. The long rubber molecules (molecular weight usually between 100,000 and 500,000 daltons) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4000 and 10,000 daltons. Because of network formation, the rubber becomes essentially insoluble in any solvent, and it cannot be processed by any means that requires it to flow, like processing in a mixer or extruder; on a mill or calendar; or during shaping, forming, or molding. Thus, it is essential that vulcanization occur only after the rubber article is in its final geometric form.

Effects of vulcanization (Bateman et al., 1963; Hofmann, 1967; Coran, 1978) on end-use properties are illustrated in Figure 7.2. It should be noted that static modulus increases with vulcanization to a greater extent than does the dynamic modulus. (Here, static modulus is more correctly the equilibrium modulus, approximated by a low-strain, slow-strain-rate modulus. Dynamic modulus is generally measured with the imposition of a sinusoidal, small strain at a frequency of 1–100 Hz.) The dynamic modulus is a composite of viscous

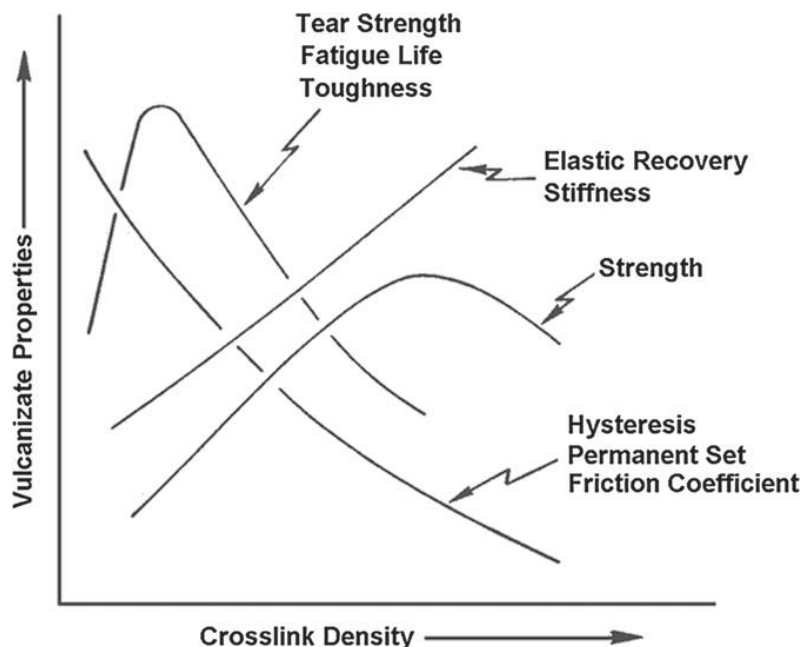


FIGURE 7.2 Vulcanizate properties as a function of the extent of vulcanization.

and elastic behavior, whereas static modulus is largely a measure of only the elastic component of rheological behavior.

Crosslink formation greatly reduces hysteresis. Hysteresis is the ratio of the rate dependent or viscous component to the elastic component of deformation resistance. It is also a measure of deformation energy, which is not stored (or borne by the elastic network), but is converted to heat. Vulcanization then causes a trade-off of elasticity for viscous or plastic behavior. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking but they are reduced by further crosslink formation. Properties related to the energy to break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density.

It should be noted that the properties given in Figure 7.2 are not functions only of crosslink density. The type of crosslink, the type of polymer, and type and amount of filler, and such also affects them.

Reversion is a term generally applied to the loss of network structures by nonoxidative thermal aging. It is usually associated with isoprene rubbers vulcanized by sulfur. It can be the result of too long of a vulcanization time (overcure) or of hot aging of thick sections. It is most severe at temperatures above about 155°C. It occurs in vulcanizates containing a large number of polysulfidic crosslinks. Though its mechanism is complex, a good deal about the chemical changes that occur during the reversion of natural rubber has been deduced (Morrison and Porter, 1984).

Sometimes the term reversion is applied to other types of nonoxidative degradation, especially with respect to rubbers not based on isoprene. For example, thermal aging of SBR (styrene-butadiene rubber), which can cause increased crosslink density and hardening, has been called reversion, since it can be the result of overcure and can also degrade a product's usefulness.

7.4 CHARACTERIZATION OF THE VULCANIZATION PROCESS

The time elapsed before crosslinking starts, the rate of crosslink formation once it starts, and the extent of crosslinking at the end of the process, are important characteristics related to the vulcanization process. There must be sufficient delay or scorch resistance (resistance to premature vulcanization) to permit mixing, shaping, forming, and flowing (e.g., in the mold) before vulcanization. After this necessary delay, or induction period, the formation of crosslinks should be rapid and the extent of crosslinking must be controlled (Figures 7.3 and 7.4).

Scorch resistance is usually measured by the time required, at a given temperature, for the onset of crosslink formation, as indicated by an abrupt increase in viscosity. The Mooney viscometer has been used for this

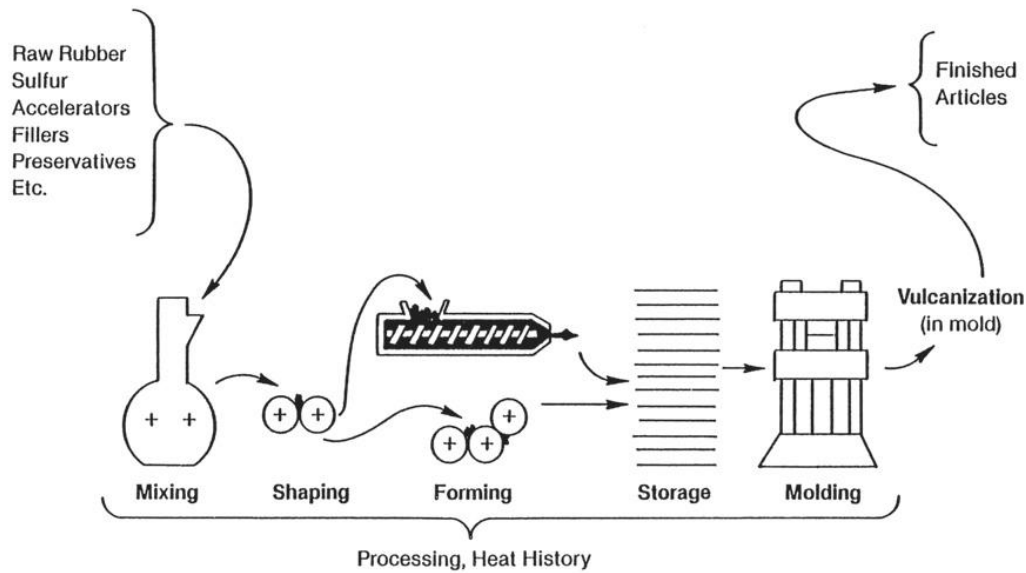


FIGURE 7.3 The effect of processing on heat history.

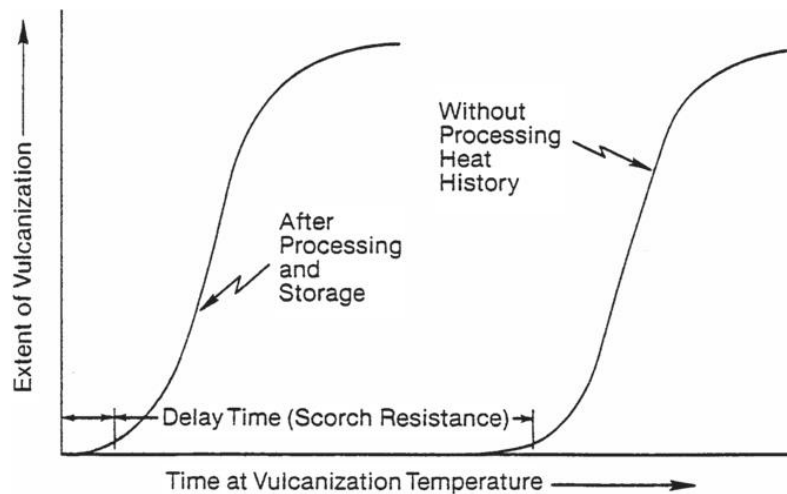


FIGURE 7.4 The effect of heat history (processing) on scorch safety.

(Coran, 1978). During this test, fully mixed but unvulcanized rubber is contained in a heated cavity. Imbedded in the rubber is a rotating disc. Viscosity is continuously measured (by the torque required to keep the rotor rotating at a constant rate) as a function of time. The temperature is selected to be characteristic of rather severe processing (extrusion, calendaring, etc.).

Both the rate of vulcanization after the scorch period and the final extent of vulcanization are now measured by using devices called cure meters. Many researchers have contributed to this development (Decker et al., 1963; Juve et al., 1964). Widely used cure meters are oscillating disc rheometers of the type introduced by the Monsanto Company around 1965. The development of the oscillating disc rheometer, largely through the efforts of Wise, was the beginning of modern vulcometry, which has become standard practice in the industry. Before the development of the cure meter, it was necessary to measure

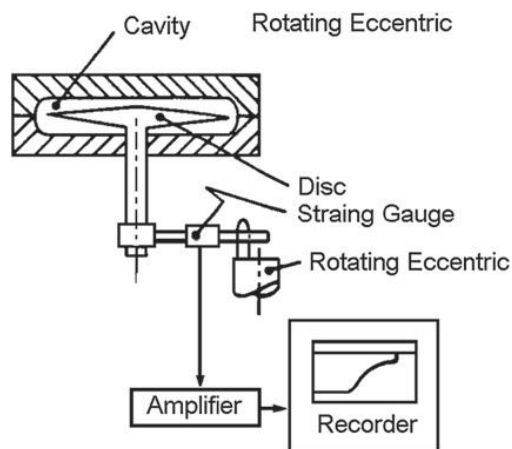


FIGURE 7.5 Oscillating disc rheometer.

mechanical properties of many specimens of a rubber sample, each vulcanized for a different length of time at a given temperature.

In order to measure the vulcanization characteristics the rubber is enclosed in a heated cavity (Figure 7.5). Imbedded in the rubber is a metal disc that oscillates sinusoidally in its plane about its axis. Vulcanization is measured by the increase in the torque required to maintain a given amplitude (e.g., degrees of arc) of oscillation at a given temperature. The torque is proportional to a low-strain modulus of elasticity. Since this torque is measured at the elevated temperature of vulcanization, the portion of it due to viscous effects is minimal. Thus, it has been assumed that the increase in torque during vulcanization is proportional to the number of crosslinks formed per unit volume of rubber. The torque is automatically plotted against time to give a so-called rheometer chart, rheograph, or cure curve.

Newer versions of the cure meter have been introduced (e.g., Figure 7.6). The cavity is much smaller and there is no rotor. In this type of cure meter, one-half of the die (e.g., the upper half) is stationary and the other half oscillates. These instruments are called moving-die rheometers. The sample is much smaller and heat transfer is faster. Also, because there is no rotor, the temperature of the cavity and sample can be changed more rapidly. In either case (oscillating disc or moving die), torque is automatically plotted against time. Such a chart is shown in Figure 7.7.

The cure curve gives a rather complete picture of the overall kinetics of crosslink formation and even crosslink disappearance (reversion) for a given rubber mix. In some cases, instead of reversion, a long plateau or marching cure can occur. The cure meter is, therefore, extensively used to control the quality and uniformity of rubber stocks (also called rubber compounds).

Vulcometry started as a research tool to study vulcanization. It was then used to control uniformity of rubber mixed in the factory. Also, programmed temperature-profile vulcometry has been used to develop recipes for industrial use. The cure temperature-time profile of an industrial mold can be imposed on the curing cavity of the cure meter. The test sample can then be vulcanized in

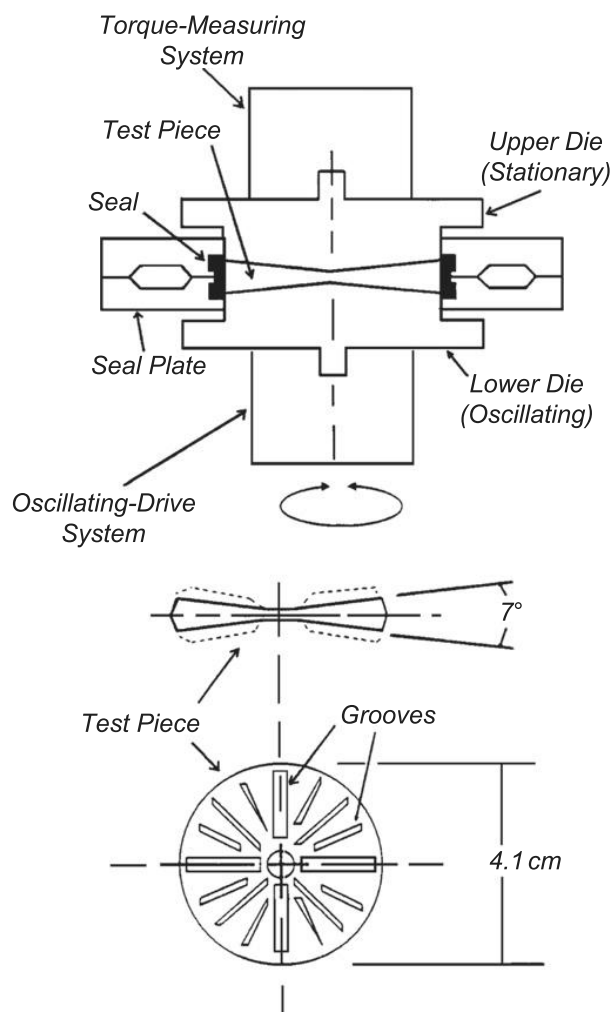


FIGURE 7.6 Moving-die rheometer.

the cure meter under the same conditions as those encountered in the factory. Both the extent of cure and temperature can be simultaneously displayed as functions of time.

7.5 VULCANIZATION BY SULFUR WITHOUT ACCELERATOR

Initially, vulcanization was accomplished by using elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr). It required 5 h at 140°C. The addition of zinc oxide reduced the time to 3 h. The use of accelerators, in concentrations as low as 0.5 phr, has since reduced the time to as short as 1–3 min. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial interest. (An exception to this is the use of about 30 or more phr of sulfur, with little or no accelerator to produce molded products of hard rubber or “ebonite.”) Even though unaccelerated-sulfur vulcanization is not of commercial significance, its chemistry has been the object of much of the early research and study.

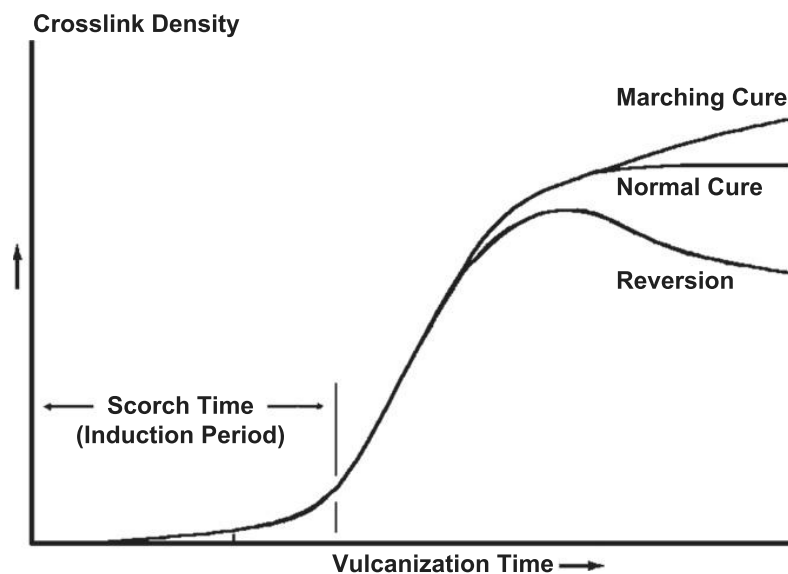
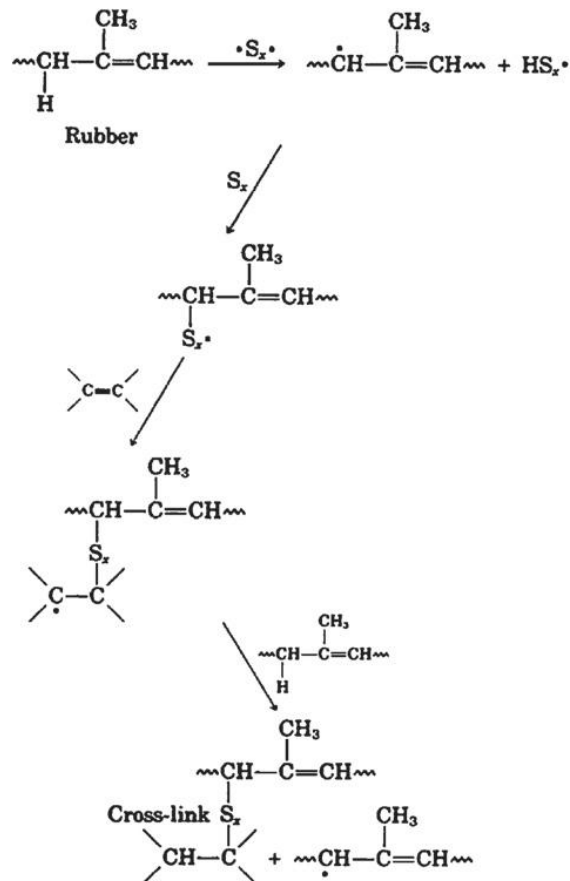
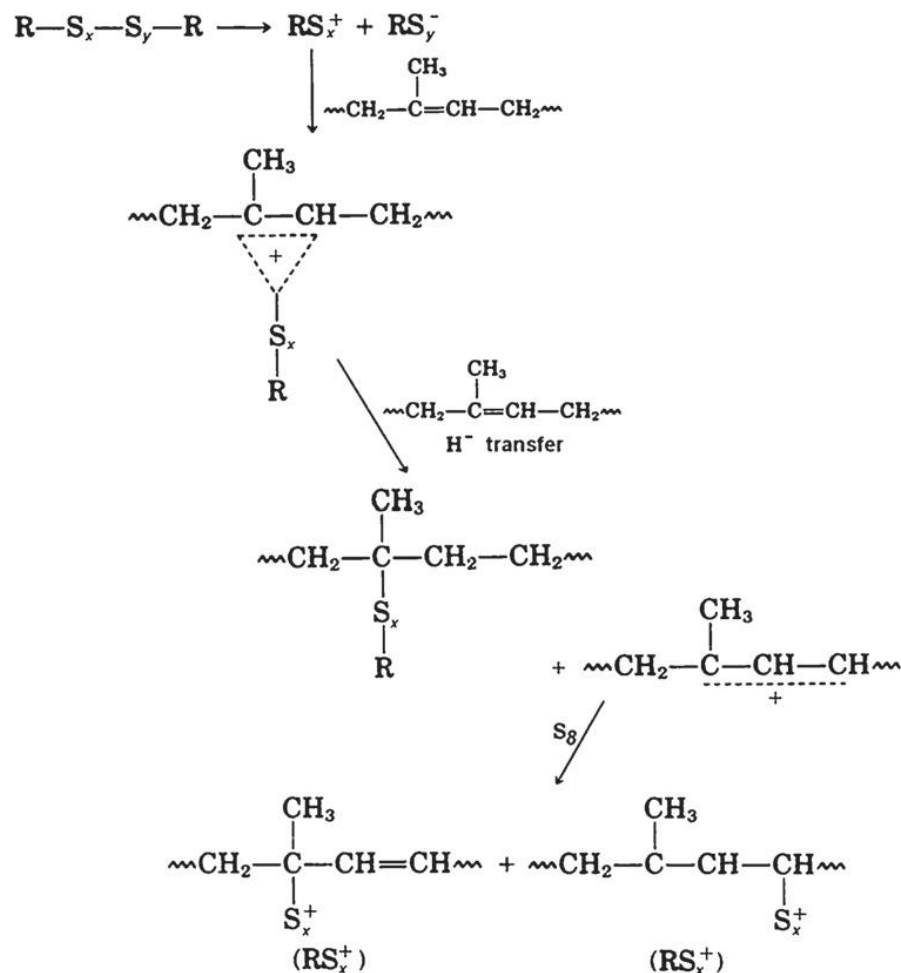


FIGURE 7.7 Rheometer cure curve.

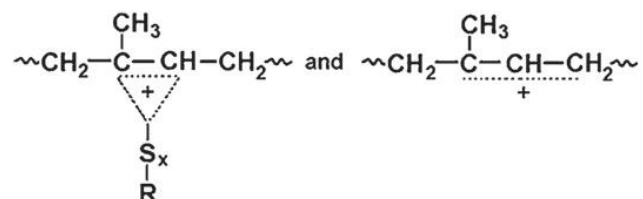
The chemistry of unaccelerated vulcanization is controversial. Many slow reactions occur over the long period of vulcanization. Some investigators have felt that the mechanisms involved free radicals (Farmer and Shipley, 1946; Farmer, 1947a,b):



Other investigators have promoted ionic mechanisms (Bateman et al., 1958):



The intermediates



were proposed in Scheme 2 to explain the fact that model compound reactions gave both unsaturated and saturated products, sulfur atoms being connected to both secondary and tertiary carbon atoms.

7.6 ACCELERATED-SULFUR VULCANIZATION

Organic-chemical accelerators were not used until 1906 (65 years after the Goodyear-Hancock development of unaccelerated vulcanization; Figure 7.8),

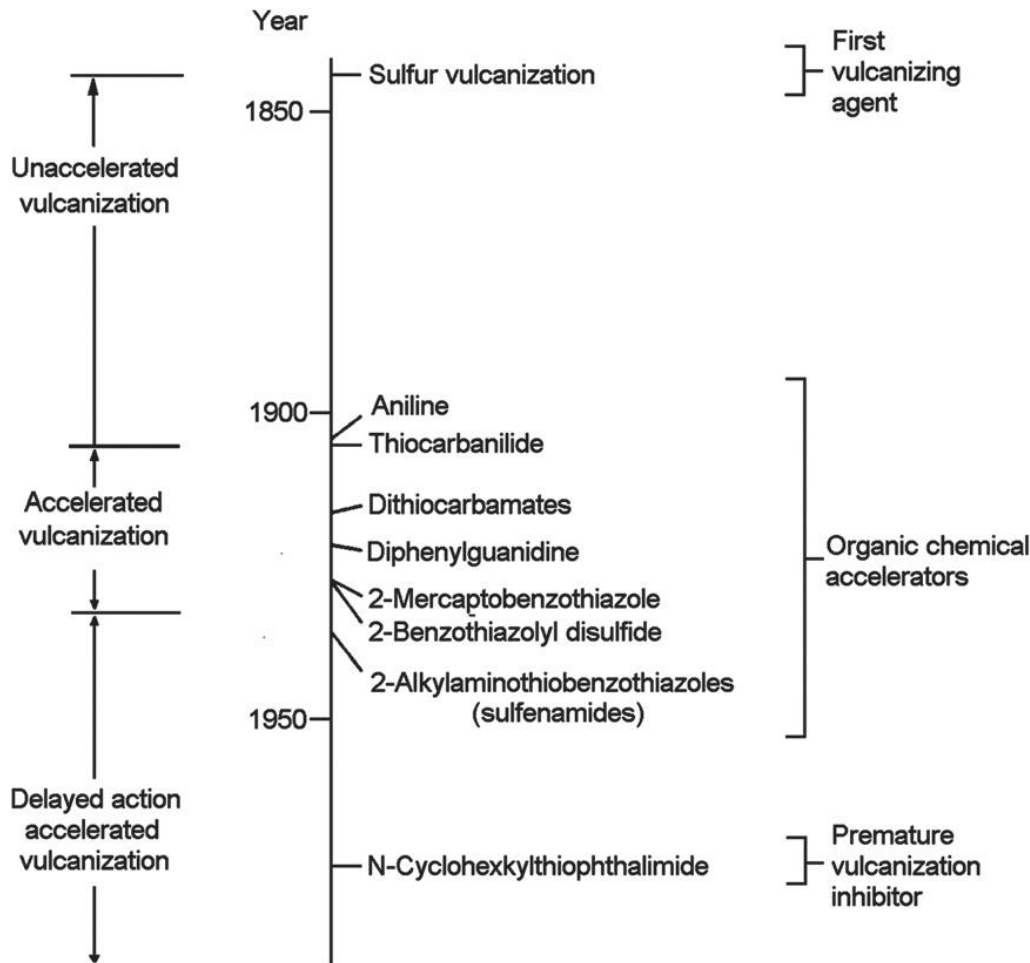


FIGURE 7.8 The history of vulcanization by sulfur.

when Oenslager discovered the effect of aniline on sulfur vulcanization (Oenslager, 1933). This could have been, at least partially, in response to the development of pneumatic tires and automobiles near the turn of the century. Aniline, however, is too toxic for use in rubber products. Its less toxic reaction product with carbon disulfide (i.e., thiocarbanilide) was introduced as an accelerator in 1907. Further developments led to guanidine accelerators (Weiss, 1922). Reaction products formed between carbon disulfide and aliphatic amines (dithiocarbamates) were first used as accelerators in 1919 (Malony, 1920). These were and are still the most active accelerators with respect to both crosslinking rate and extent of crosslink formation. However, most of the dithiocarbamate accelerators give little or no scorch resistance and their use is impossible in many factory-processing situations. The first delayed-action accelerators were introduced in 1925 with the development of 2-mercaptobenzothiazole (MBT) and 2-benzothiazole disulfide (or 2,2'-dithiobisbenzothiazole) (MBTS) (Bedford, 1921; Sebrell and Bedford, 1925; Bruni and Romani, 1921). This nearly coincided with the deployment of cord-ply construction (1920–1930),

which enabled mass production of automobile tires. Even more delayed-action and yet faster curing vulcanization were possible in 1937 with the introduction of the first commercial benzothiazolesulfenamide accelerator (Zaucker et al., 1934; Harmon, 1937). Still more delay became possible in 1968, with the availability of an extremely effective premature vulcanization inhibitor (PVI). This compound was N-(cyclohexylthio)phthalimide (CTP), small concentrations of which were used along with benzothiazolesulfenamide accelerators. Figures 7.8–7.10 illustrate the history of the progress toward faster vulcanization, but with better control of premature vulcanization or scorch resistance.

Accelerated-sulfur vulcanization is the most widely used method. For many applications, it is the only rapid crosslinking technique that can, in a

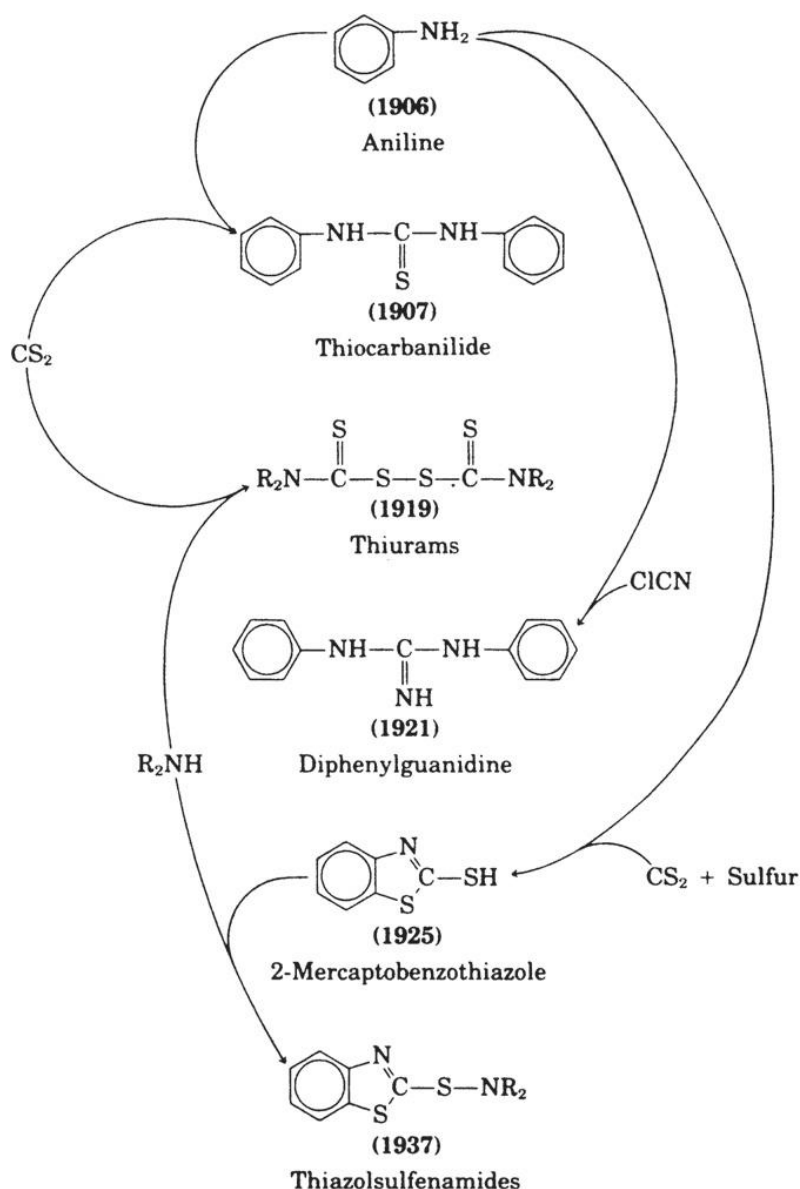


FIGURE 7.9 The chemistry of accelerator synthesis.

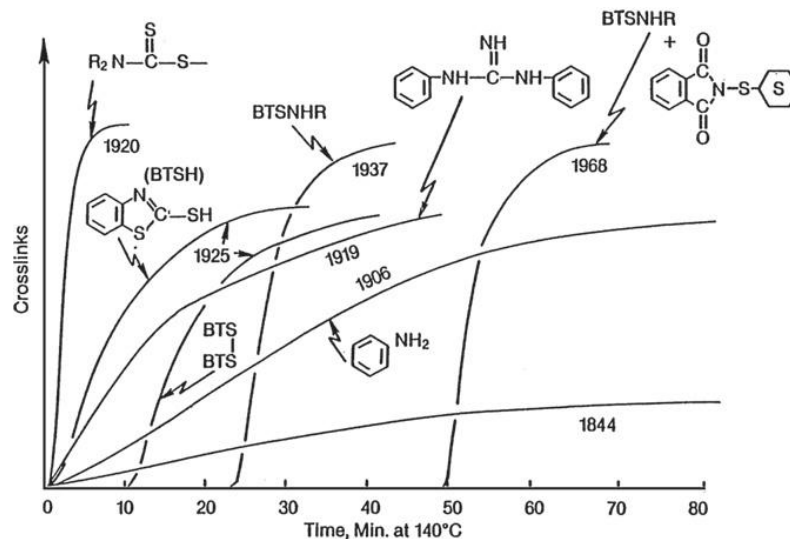
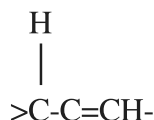


FIGURE 7.10 Improvements in the accelerated-sulfur vulcanization of natural rubber.

practical manner, give the delayed action required for processing, shaping, and forming before the formation of the intractable vulcanized network. It is used to vulcanize natural rubber (NR), synthetic isoprene rubber (IR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber (IIR), chlorobutyl rubber (CIIR), bromobutyl rubber (BIIR), and ethylene-propylene-diene-monomer rubber (EPDM). The reactive moiety for all of these elastomers can be represented by



Typically a recipe for the vulcanization system for one of these elastomers contains 2–10 phr of zinc oxide, 1–4 phr of fatty acid (e.g., stearic), 0.5–4 phr of sulfur, and 0.5–2 phr of accelerator. Zinc oxide and the fatty acid are vulcanization-system activators. The fatty acid with zinc oxide forms a salt, which can form complexes with accelerators and reaction products, formed between accelerators and sulfur. Accelerators are classified and illustrated in Table 7.1.

Frequently, mixtures of accelerators are used. Typically, a benzothiazole type is used with smaller amounts of a dithiocarbamate (thiuram) or an amine type. An effect of using a mixture of two different types of accelerators can be that each activates the other and better-than-expected crosslinking rates can be obtained. Mixing accelerators of the same type gives intermediate or average results.

We should note here that there is a need to reduce the use of accelerators based on secondary amines, which can react with nitrogen oxides to form suspected carcinogenic nitrosamines. This is especially a problem

TABLE 7.1 Accelerators for Sulfur Vulcanization

Compound	Abbreviation	Structure
<i>Benzothiazoles</i>		
2-Mercaptobenzothiazole	MBT	
2,2'-Dithiobisbenzothiazole	MBTS	
<i>Benzothiazolesulfenamides</i>		
N-Cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-butylbenzothiazole-2-sulfenamide	TBBS	
2-Morpholinothiobenzo-thiazole	MBS	
N-Dicyclohexylbenzo-thiazole-2-sulfenamide	DCBS	
<i>Dithiocarbamates</i>		
Tetramethylthiuram monosulfide	TMTM	
Tetramethylthiuram disulfide	TMTD	
Zinc diethyldithiocarbamate	ZDEC	
<i>Amines</i>		
Diphenylguanidine	DPG	
Di-o-tolylguanidine	DOTG	

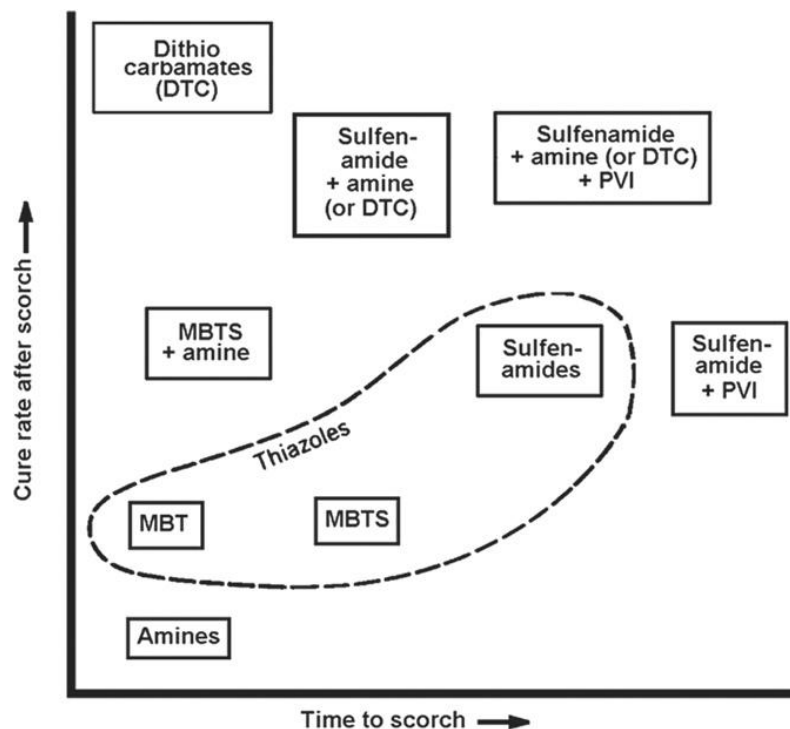


FIGURE 7.11 Vulcanization characteristics given by various accelerators and combinations.

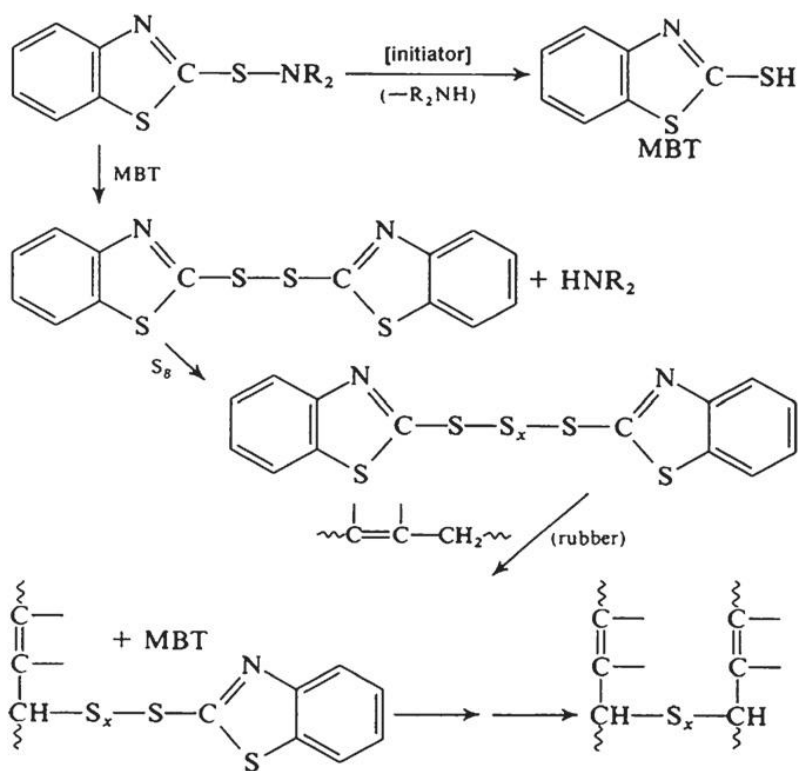
with dithiocarbamate-type accelerators. Proposed accelerators, which do not give carcinogenic nitrosamine derivatives, include dibenzylamine-derived dithiocarbamates and those based on sterically hindered amines.

Different types of accelerators impart vulcanization characteristics that differ with respect to both scorch resistance and crosslinking rate. Figure 7.11 is a map of accelerator system characteristics. Within groups or types, differences can be obtained by choosing the individual accelerators. In the group of benzothiazolesulfenamides, the scorch resistance and vulcanization time increase in the order: TBBS or CBS, MBS, DCBS.

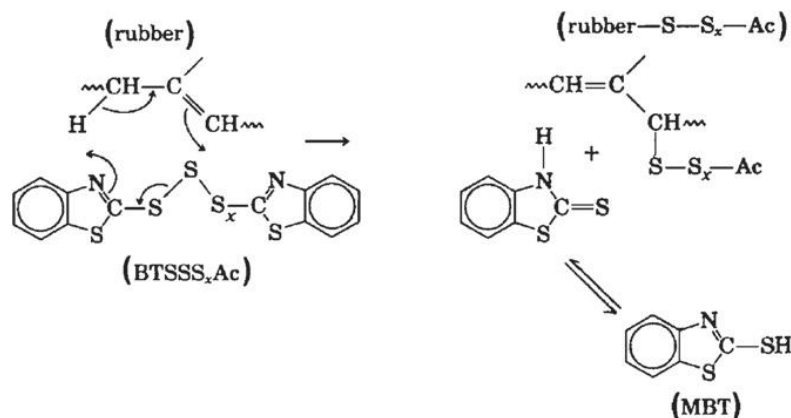
The effect of the addition of small concentrations of the premature vulcanization inhibitor (PVI), N-(cyclohexylthio)phthalimide, is also given by Figure 7.11. This retarder (Coran and Kerwood, 1970) is frequently used to independently control scorch resistance with little effect on the rate of crosslinking (Coran, 1978). Before the development of N-(cyclohexylthio)phthalimide as a PVI, acidic retarders like salicylic acid, acetylsalicylic acid, phthalic anhydride, and benzoic acid were used. These additives improved scorch resistance but also gave greatly reduced rates of crosslink formation after the delay. Another retarder of the past was N-nitrosodiphenylamine, which is less active and not now used because of toxicological concerns.

7.6.1 The Chemistry of Accelerated-Sulfur Vulcanization

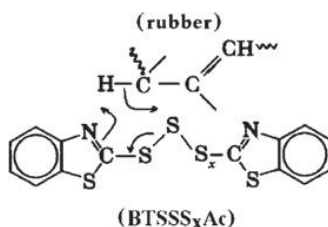
The general reaction path of accelerated-sulfur vulcanization is thought to be as follows (Coran, 1978; Campbell and Wise, 1964a,b; Hu and Scheele, 1962; Morrison and Porter, 1984; Ghosh et al., 2003): Accelerator reacts with sulfur to give monomeric polysulfides of the structure $\text{Ac-S}_x\text{-Ac}$ where Ac is an organic radical derived from the accelerator (e.g., benzothiazyl-). The monomeric polysulfides interact with rubber to form polymeric polysulfides (e.g., rubber- $\text{S}_x\text{-Ac}$). During this reaction, 2-mercaptobenzothiazole (MBT) is formed if the accelerator is a benzothiazole derivative and if the elastomer is natural rubber. (In SBR the MBT becomes bound to the elastomer molecular chain probably as the thioether rubber- $\text{S}_x\text{-Ac}$.) When MBT itself is the accelerator in natural rubber, it first disappears then reforms with the formation of rubber- $\text{S}_x\text{-Ac}$. Finally, the rubber polysulfides react, either directly or through an intermediate, to give crosslinks, rubber- $\text{S}_x\text{-rubber}$. A reaction scheme can be written as follows:



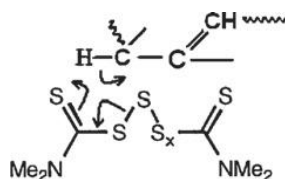
There are obvious differences between accelerated vulcanization and unaccelerated vulcanization. (Greater crosslinking efficiencies and greater crosslinking rates are obtained with accelerated vulcanization.) But there are more subtle differences. Results from model reactions with curing ingredients indicate that sulfur becomes attached to the rubber hydrocarbon almost exclusively at allylic positions (Skinner, 1972). This is not the case with unaccelerated-sulfur vulcanization, thus:



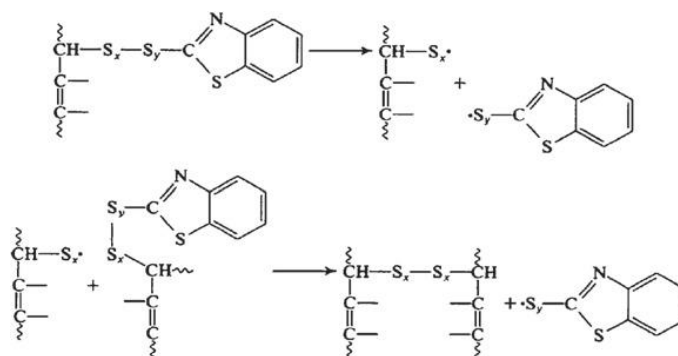
Rather than the eight-membered-ring intermediate shown above, one could propose a six-membered-ring sulfurization intermediate:



This is similar to what was suggested by Nieuwenhuizen et al. with respect to their work on dithiocarbamate acceleration (Nieuwenhuizen et al., 1997):

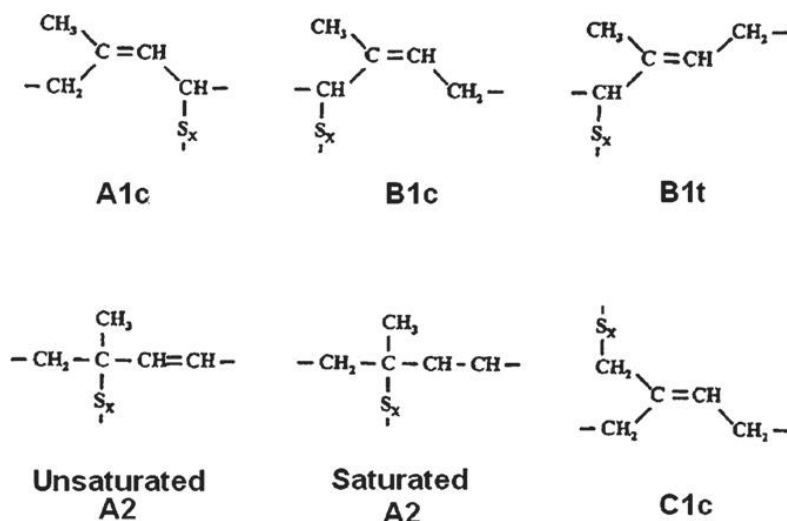


Others have proposed that zinc must be present for sulfuration (Ignatz-Hoover et al., 1999). At any rate, crosslinks could then form, in a number of ways; for example:



By using solid-state C-13 NMR spectroscopy, Koenig and his group (Koenig, 2000; Pelliccioli et al., 2002) have added much detail to the chemical structure of the sulfurated network backbone. Following are the types of

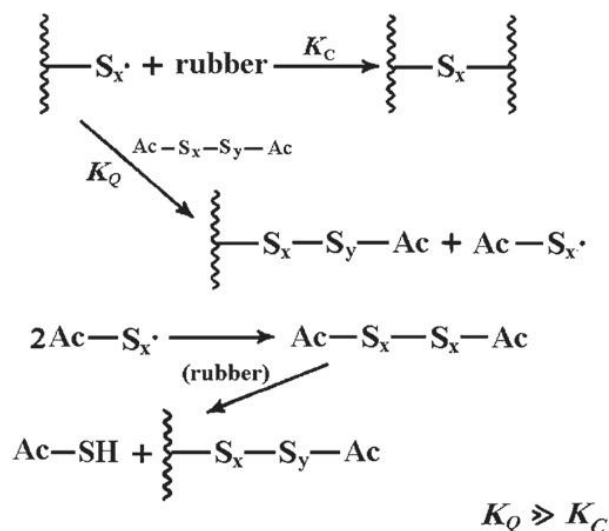
structures that have been assigned to the attachment points of the sulfur atoms to the rubber molecular backbone:



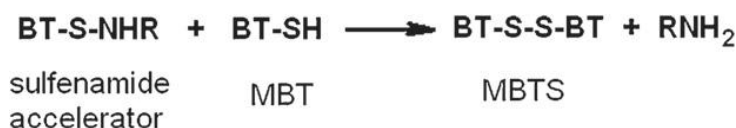
Koenig's group has done much work on conditions that change the relative amounts of the various types of attachments. For example, concentrations of both the B1c- and B1t-type polysulfides increase with the level of carbon black loading (for types N110, N220, N326, N330, N550, and N765) (Mori and Koenig, 1995).

7.6.2 Delayed-Action Accelerated Vulcanization

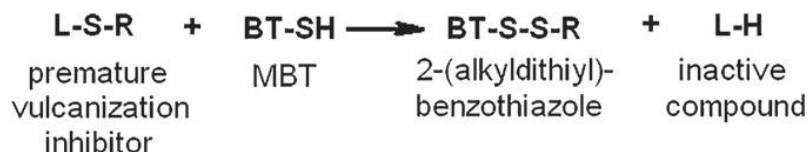
If crosslink formation is by a free radical mechanism, delayed action could be the result of a quenching action by the monomeric polysulfides formed by reactions between accelerator and sulfur. If the polymeric polythiyl radicals (crosslink precursors) are rapidly quenched by an exchange reaction before they are able to form crosslinks, crosslink formation would be impeded until substantial depletion of the monomeric polysulfides (Coran, 1978). This is illustrated as follows:



Thus, one theory for delayed action is the quenching of free radical crosslink precursors by monomeric polysulfides. It has been found that, if bisalkylpolysulfides are mixed with uncured rubber stocks, more delay results. It is also been shown that the early reaction products formed by the interaction between accelerator and sulfur ($\text{Ac-S}_x\text{-Ac}$) are inhibitors of crosslink formation. The very substances that give rise to the formation of the crosslink precursor (rubber- $\text{S}_x\text{-Ac}$) inhibit the formation of the crosslinks. We note that other mechanisms for delayed action have been proposed. In the case of acceleration by benzothiazolesulfenamides, the accelerator is depleted in an autocatalytic fashion with the formation of 2-mercaptobenzothiazole (MBT). The rate of this depletion is about proportional to the amount of MBT present. There is strong evidence, which indicates that the following reactions occur in sulfenamide-accelerated systems:



If MBT could be taken out of the system as fast as it forms, substantial increases in processing safety would result. Such is the case when the premature vulcanization inhibitor, N-(cyclohexylthio)phthalimide (CTP), is present. This compound (Coran and Kerwood, 1970) and others like it react rapidly with MBT to form 2-(alkyldithio)benzothiazoles, R-S-S-BT , which are active accelerators but which do not interact rapidly with the sulfenamide accelerator:



where L is a “leaving group” of the premature vulcanization inhibitor (e.g., N-phthalimido- for CTP).

Gradwell and Stephenson have also studied prevulcanization inhibition by using CTP (Gradwell and Stephenson, 2004).

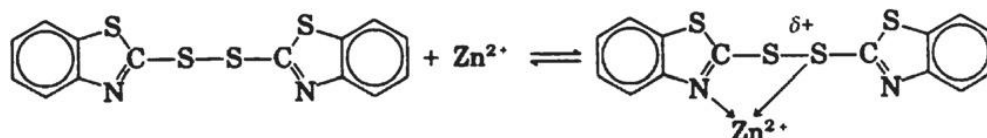
The importance of scorch control cannot be overemphasized. Present-day tire plants could not compete without good control of scorch resistance or processing safety as it is commonly called. Such safety is necessary in order to rapidly process rubber mixes at high temperatures (through extrusion, calendaring, etc.) into preforms for molding (e.g., tire components).

Delayed-action mechanisms and reaction kinetics have also been discussed and reviewed elsewhere (Ignatz-Hoover et al., 1999; Koenig, 2000;

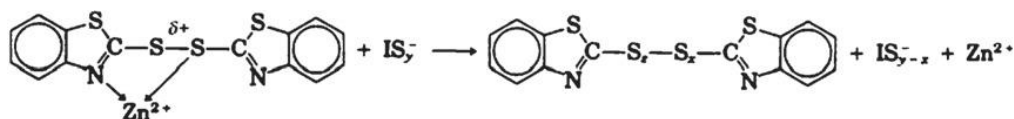
Pellicioli et al., 2002; Mori and Koenig, 1995; Fan et al., 2002; Coran, 1983; Leib et al., 1188; Son, 1973; Sullivan et al., 1061; Ding et al., 1996; Choi, 2006; Gradwell and Stephenson, 2004; Arem et al., 1999; Heideman et al., 2004).

7.6.3 The Role of Zinc in Benzothiazole-Accelerated Vulcanization

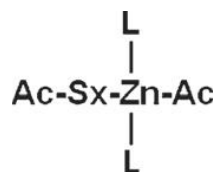
An increase in the concentration of fatty acid and hence increases in the concentration of available Zn^{++} causes an increased overall rate in the early reactions (during the delay period), which lead to the formation of rubber- S_x -Ac. However, it gives rise to a decrease in the rate of crosslink formation but an increase in the extent of crosslinking (Coran, 1965). The increase in the rates of the early reactions has been explained by the interaction:



where the chelated form of the accelerator is more reactive than the free accelerator during the early reactions:

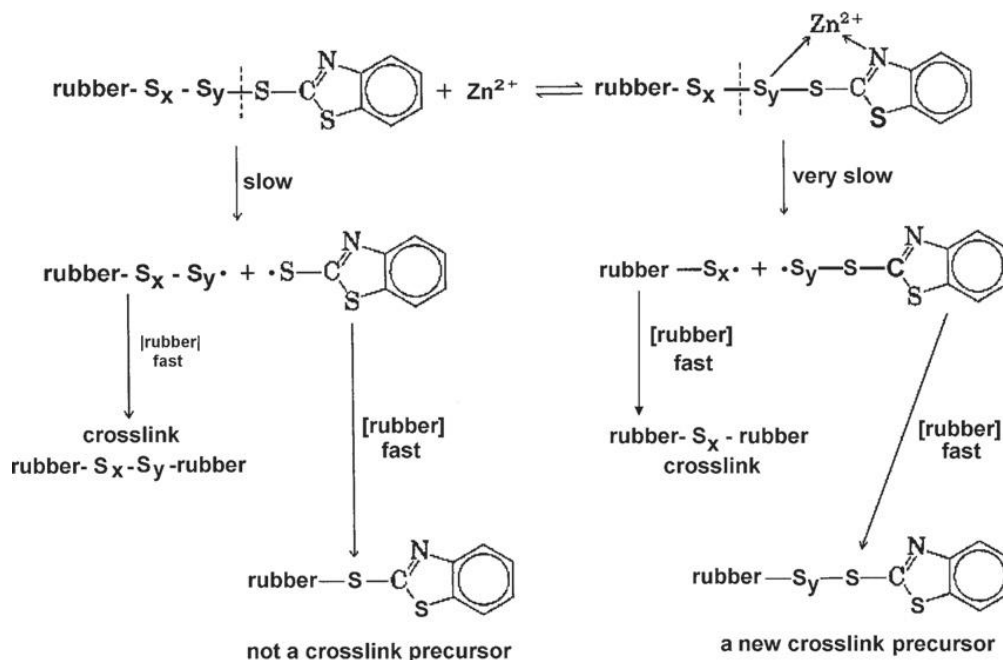


Here, I-S_y is an ionized form of linear sulfur. It could be rapidly formed in a reaction between sulfur and any number of initiating species. Others have proposed that the presence of Zn^{++} can increase the rate of sulfurization through the formation of complexes of the type:



where L is a ligand such as an amine molecule (Ignatz-Hoover et al., 1999; Choi, 2006).

The decreased specific rate of crosslink formation, and the increased extent of crosslinking due to the presence of Zn^{++} in benzothiazole-accelerated vulcanization, have been explained by the following scheme (Coran, 1965):



Zinc chelation changes the position of the S-S bond most likely to break. Since a stronger bond must break, the rate is slower. Though the rate of crosslinking is slower, the extent of crosslink formation is increased since less sulfur is used in each crosslink. That is, the crosslinks are of lower sulfidic rank.

The presence of zinc compounds can also promote the reduction of the sulfur rank of crosslinks during high-temperature aging of the vulcanizate, for example, during reversion (Layer, 1992). In some cases zinc compounds actually promote the decomposition of crosslinks (Morrison and Porter, 1984).

More recently, Heideman et al. have particularly discussed the role of the zinc activator system (ZnO + fatty acid) (Heideman et al., 2004).

7.6.4 Achieving Specified Vulcanization Characteristics

It has been difficult, for many years, to independently control the two main vulcanization characteristics, scorch resistance (processing safety) and rate of crosslink formation. In the case of natural rubber (NR), if one had chosen a fast accelerator system in order to obtain short curing times in the press, then process safety would have suffered greatly. If one had chosen a delayed-action acceleration system, then the rate of vulcanization in the press would have been limited. The development of the highly efficient premature vulcanization inhibitor N-(cyclohexyl-thio)-phthalimide (CTP) changed all of that, since great improvements in scorch resistance with little or no change in crosslinking rate became possible (Trivette et al., 1977). Thus, the rate of crosslink formation can be adjusted by the selection of accelerators. For example, the moderately fast delayed-action accelerator t-butylbenzothiazolesulfenamide (TBBS) can be partially replaced by a small amount of a coaccelerator (e.g., 0.1–0.2 phr

of tetramethylthiuram disulfide [TMTD] or tetramethylthiuram monosulfide [TMTM]) to obtain a greatly increased cure rate; however, the scorch resistance will be significantly reduced. In such a case, the scorch resistance can be regained by the addition of 0.05–0.25 phr of CTP, without a noticeable decrease in the rate of crosslinking (Coran, 1978; Rodger and Roebuck, 1976).

It is true that merely increasing the concentration of TBBS will give an increase in cure rate with only a small change in scorch resistance. However, the increase in accelerator concentration will generally be rather large and the concentration of sulfur will be adjusted downward to keep the hardness and stiffness constant (maintaining constant crosslink density). The relatively large change in the concentrations of sulfur and accelerator will cause changes in vulcanizate-performance properties. (See the later section on vulcanizate properties.)

In rubber mixes containing only a synthetic rubber, such as styrene-butadiene rubber (SBR) or butadiene rubber (BR), the effects of cure-system changes may not be as pronounced as they are in the case of NR. However, if even a relatively small amount of NR is present, the effects of cure-system changes on the vulcanization process parameters resemble those obtained with NR alone.

One of the curing characteristics that we would like to control is reversion, which can occur in compounds containing natural rubber. There is more than one approach to reducing the amount of reversion. We can use sulfur donors or increase the ratio of accelerator concentration to sulfur concentration, or we could carry out the vulcanization at a reduced temperature for a longer period. However, these approaches give rise to effects that will have to be compensated. Another approach is use of additives such as certain bisimides, e.g., N,N'-*m*-phenylene-biscitraconimide and N,N'-*m*-phenylene-bismaleimides (Datta et al., 1997, 1998; Datta and Ivan, 1995) or trialkoxysilylalkylpoly-sulfides such as bis-(3-triethoxysilylpropyl)-tetrasulfide (Tan and Wolff, 1985).

7.6.5 Effects on Adhesion to Brass-Plated Steel

The adhesion between rubber and brass-plated steel (e.g., steel tire cords for belted radial tires) has been the subject of much study and speculation. Brass plating is the major method of obtaining adhesion between natural rubber and the steel of tire cords. Over the years there has been much speculation about its mechanism, but there is agreement on one aspect of the adhesion of natural rubber to brass-plated steel: the actual adhesion between the natural rubber and the brass-plated cord, formed *in situ* during the vulcanization process, is an interfacial layer of sulfides and oxides of copper (Buchan, 1959; van Ooij, 1979, 1984).

The adhesive layer between the rubber and cord is generally considered to be formed by the interaction between the copper and the vulcanization system. As a result of this, optimization of the vulcanization system with respect to

adhesion is critical. Also, a change in the composition of the brass coating on the steel wires, or a change in the thickness, can require a change in the vulcanization system in order to maintain the optimum level of adhesion.

van Ooij, who has done much of the work in the field, has written reviews on the subject of brass-plated steel cord/natural rubber adhesion. van Ooij (1979, 1984) has given a model for rubber-brass adhesion in which a copper sulfide layer forms on the brass before the onset of crosslink formation. The thin film of copper sulfide has good adhesion and cohesion. In addition, the film is so porous that rubber molecules can become entangled with it. It is not required that the film forms simultaneously with the formation of crosslinks during vulcanization; but, rather, it is required that the copper sulfide film be completely formed before crosslinking starts. Indeed, adhesion between brass-plated steel and natural rubber can frequently be improved by the use of the retarder, CTP (Coran, 1978), or by using a more delayed-action accelerator such as N-dicyclohexylbenzothiazole-2-sulfenamide (DCBS) (Albrecht, 1973).

Failure rarely occurs between the rubber and the copper sulfide film. It generally occurs cohesively within the sulfide film or adhesively in a layer below the sulfide film.

Sulfidation of the brass surface is not due to its interaction with elemental sulfur, but it is the result of the interaction between the brass surface and accelerator-sulfur reaction products, which can be represented by the general structure, $\text{Ac-S}_y\text{-Ac}$ and $\text{Ac-S}_y\text{-H}$, where Ac is an accelerator-derived moiety (e.g., benzothiazolyl group). The value of the subscript, y , increases with the ratio of the concentration of sulfur to the concentration of accelerator used in the curing system. Generally, high sulfur levels and high ratios of sulfur concentration to accelerator concentration favor good rubber-to-brass adhesion.

Recently, van Ooij et al. have reviewed adhesion of steel tire cord to rubber (van Ooij et al., 2009). The authors reviewed the literature extensively and provided an updated model for adhesion to brass-plated tire cord, which incorporated observations made by many techniques. They discussed the effects of different compounding ingredients and the possible alternatives to the current brass coatings. They note that the use of cobalt compounds improves the adhesion between rubber and brass-coated cords, but new adhesion promoters have been developed as replacements for Co, or for combined use with Co. They also discussed the use of phenolic-resin adhesion promoters. They describe the various techniques that have been developed to study the rubber-brass interface and its aging mechanism.

7.6.6 The Effect on Vulcanizate Properties

Increases in sulfur and accelerator concentrations give higher crosslink densities and, therefore higher moduli, stiffness, hardness, and so on. However, as the ratio of the concentration of accelerator to the concentration of sulfur increases, the proportion of monosulfidic crosslinks increases in natural rubber

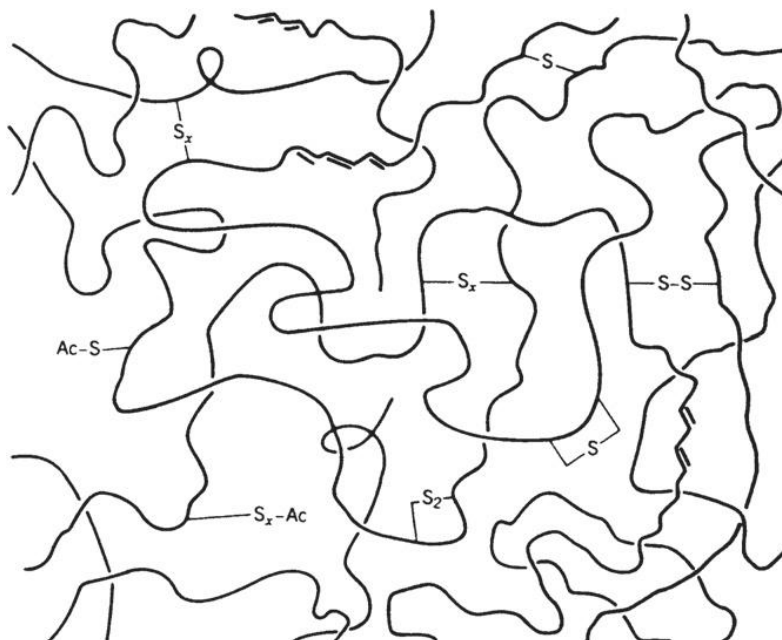


FIGURE 7.12 Crosslink types and chain modifications.

stocks (also called rubber compounds). Greater amounts of accelerator (with respect to sulfur) also give an abundance of pendant groups of the type, $-S_x\text{-Ac}$, which are attached to and “dangle” from the rubber molecular chains. Higher ratios of sulfur concentration to accelerator concentration give both more polysulfide crosslinks and more sulfur combined with the rubber chains to form sulfur-containing six-membered heterocyclic rings along the rubber molecular chains. In addition, conjugated olefinic double bonds appear along the polymer backbone chain. Figure 7.12 indicates these features. Such changes in the vulcanizate network structure, no doubt, are responsible for changes, which occur in vulcanizate properties as a result of changes made in the curing-system recipe (Studebaker, 1966; Moore et al., 1961; Moore and Trego, 1961; Skinner and Watson, 1969; Russell et al., 1969; Lewis, 1986).

Effects of changes in the concentrations of accelerator and sulfur on vulcanizate properties have been studied by using the following recipe (parts by weight): natural rubber, 100; N330 carbon black, 50; N-isopropyl-N'-phenyl-*p*-phenylenediamine (IPPD antidegradant) 2; zinc oxide, 5; stearic acid, 3; plasticizer, 3; sulfur, variable; N-cylohexylbenzothiazolesulfenamide (CBS), variable (Coran, 1978).

The effects of changes in the accelerator concentration on 300% modulus (jargon for stress at 300% tensile strain), thermal-oxidative aging and fatigue life (DeMattia flex crack) are given in Figure 7.13. The effects on 300% modulus are indicated by the diagonal contours of negative slope. They are parallel and show that the stress at 300% strain increases with an increase in either sulfur or accelerator concentration. The contours for % retention of ultimate

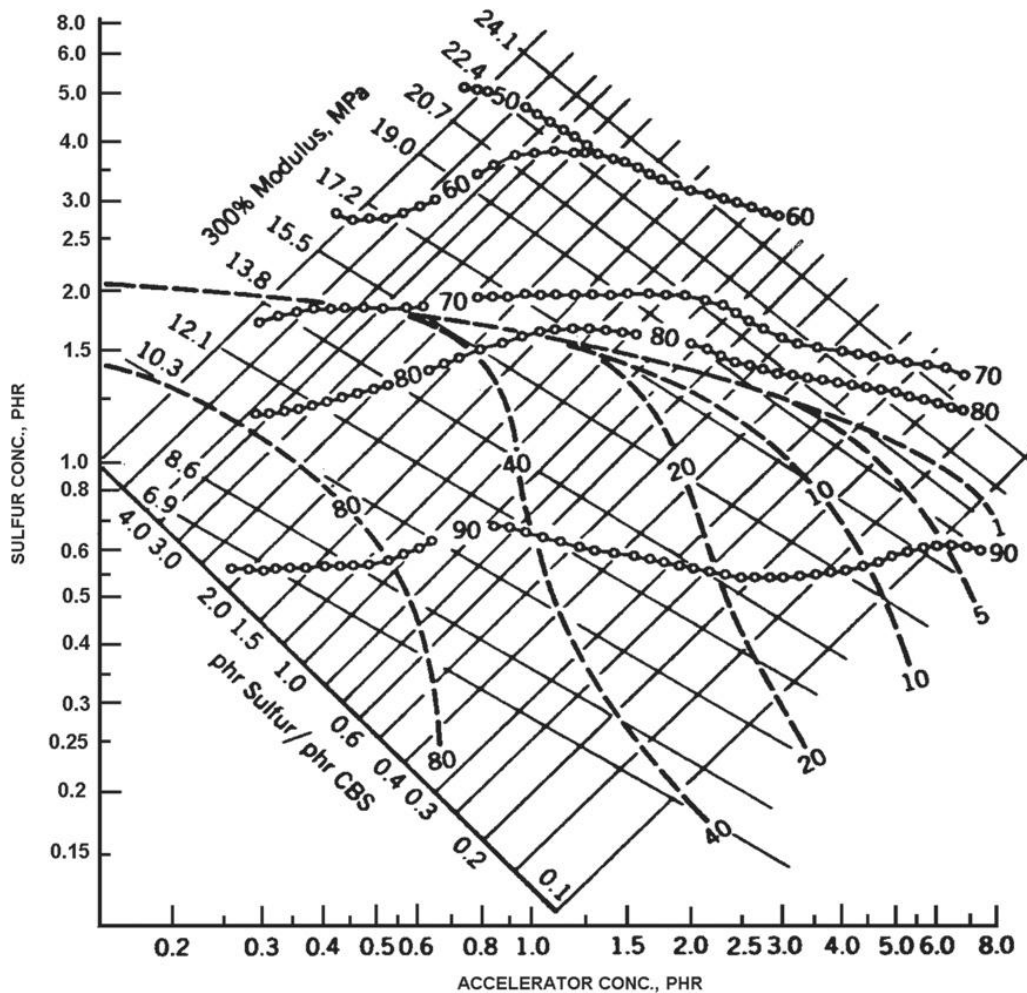


FIGURE 7.13 Vulcanizate properties: —, 300% modulus (Mpa); ---, DeMattia flex fatigue life ($\text{kHz} \times 10^{-1}$); -o-o-o-, % retention of ultimate elongation after 2 days at 100°C.

elongation after hot air aging (at 100°C for 2 days) indicate that oxidative aging, in the presence of IPPD, depends only on the concentration of sulfur. Higher concentrations of sulfur give poor aging characteristics in correlation with the higher number of points of chain sulfuration. This suggests that sulfur substitution along the chain can activate chain scission by reactions with oxygen (Lorenz, 1963). Another view is that sulfur interferes with the antidegradant activity (in this case with IPPD) (Bell and Cuneen, 1967).

The contours for flex fatigue life are complex. The test is run such that the specimens are about equally strained; however, there is some question as to whether the tests should be run at equal strain or at equal strain energy (Gent et al., 1964; McCall, 1969). For some cases, where strain is restricted by fabric reinforcement, fatigue test data should be compared at equal strain amplitude. For other applications, where the strain is not limited, the tests should be run at equal strain energy. The contours as presented here can be interpreted in terms of either constant strain or constant strain energy: All points on the chart can be compared at an approximately equal strain per cycle; however, if we interpolate

TABLE 7.2 Fatigue Life at Constant 300% Modulus

p/hr Sulfur/p/hr Sulfenamide	Flex Life, kc
6	400
5	500
4	530
3	550
2	550
1	400
0.6	350
0.4	270
0.3	250
0.2	190

between the flex-life contours but only along a constant modulus contour, we can extract values corresponding to approximately equal strain energy per cycle. By choosing higher modulus contours, we are considering higher strain energies.

Considering the group of flex-life contours as a whole, or at approximately constant strain energy per cycle, we may conclude the following: a high level of either sulfur or accelerator gives poor flex life. However, by the selection of the proper ratio of sulfur concentration to accelerator concentration, higher modulus vulcanizates can be obtained with at least some optimization of fatigue life. The flex life at approximately equal strain energy per cycle can be illustrated by extracting values along the 13.8 Mpa modulus contour line. Table 7.2 can then be constructed.

For the strain energy corresponding to a 300% modulus of 13.8 Mpa, the maximum flex life (as measured by the DeMattia flex test) is obtained when 2.5 times as much sulfur as accelerator is used. Other optimum ratios for various 300% moduli can be obtained from the contours. Some of these are given in Table 7.3.

These optimum ratios and fatigue life data should not be considered to be universal values. Different recipes, different types of antidegradants, different types of fillers, different concentrations of antidegradants and fillers, different base polymers, different types of fatigue tests, and such give rise to different optimum sulfur concentration/accelerator concentration ratios and different optimum fatigue life values. Nevertheless, the trends given here have been generally noted.

The effects of concentrations of sulfur and accelerator on network structure and vulcanizate properties have been studied (McCall, 1969; Datta et al., 2007; Fan et al., 2001; Dijkhuis et al., 2009; Campbell, 1409; Cooper, 1958). The low values for fatigue life at low levels of sulfur, but high levels of accelerator,

TABLE 7.3 Optimized Fatigue Life

Stress at 300% Strain, 300% Modulus, MPa	Optimum Sulfur Conc./ Accelerator Conc. Ratio	Optimized Flex Life, kc
6.9	3.50	800
10.4	3.00	800
13.8	2.50	550
15.5	1.00	300
17.2	0.45	120
19.0	0.27	70

have been attributed to high concentrations of accelerator-terminated appended groups (Campbell, 1409) and high concentrations of monosulfidic crosslinks. Monosulfidic crosslinks are not able to exchange, rearrange, or break to relieve stresses without the breakage of main chains.

On the other hand, polysulfidic crosslinks are able to rearrange under stress (Bateman et al., 1963; Coran, 1978; Cooper, 1958). The rearrangement of a crosslink occurs in two steps: (1) breaking and (2) reforming. Work by Brown et al. (1987) indicates that only the breaking of the weak polysulfide crosslinks is required for the strengthening of the vulcanizate network. It is only required that enough of the crosslinks be weak (in comparison to backbone bonds) for the rubber to be strong. At any rate, when moderately high concentrations of sulfur (with respect to accelerator) are used, flex life improves, presumably due to the presence of enough weak or rearrangeable polysulfidic crosslinks.

When even higher concentrations of sulfur are used (with the maintenance of constant modulus), flex life decreases. It is possible that this is due to the large amount of cyclic chain modification associated with high levels of sulfur.

Natural rubber compositions, vulcanized by high levels of accelerator and low levels of sulfur, have been called EV and semi-EV vulcanizates. Here, "EV" means efficient vulcanization, since sulfur is used efficiently in the production of crosslinks. On the average, the crosslinks are shorter than in the case of conventional vulcanization; they contain more monosulfidic crosslinks and less polysulfidic ones, or their average sulfur rank is lower. Though EV vulcanizates suffer with respect to fatigue resistance, they are frequently used because of their excellent reversion resistance (resistance to nonoxidative thermal aging or overcure) and good resistance to thermal-oxidative aging. The resistance to reversion or thermally induced loss of crosslinks is thought to be the result of the greater intrinsic stability of the lower rank (disulfidic and especially monosulfidic) crosslinks. Semi-EV vulcanizates (wherein the sulfur concentration to accelerator-moiety concentration ratio is at an intermediate value) are an advantageous compromise in which fairly good unaged fatigue life is obtained, but maintained after aging.

Rather than using high levels of accelerator to obtain EV and semi-EV vulcanizates, it is sometimes advantageous to replace some of the sulfur with a so-called sulfur donor. Examples of these are tetramethylthiuram disulfide (TMTD) and 4,4'-dithiodimorpholine (DTDM).

This type of vulcanization-system design was reported by McCall (1969). He found that by judiciously balancing the levels of accelerator, sulfur, and DTDM, he could obtain good vulcanization characteristics, good thermal stability, good flex life, and superior retention of flex life. Others have reported on more recent work on the effects of crosslink type on reversion (Datta et al., 2007; Fan et al., 2001).

7.6.7 Accelerated-Sulfur Vulcanization of Various Unsaturated Rubbers

Over the years, much of the research on accelerated-sulfur vulcanization was done by using natural rubber as a model substrate. Natural rubber was the first elastomer and therefore the search for the understanding of vulcanization originated with work on natural rubber. Most of the work cited in the previous sections is related to natural rubber. However, some rather early studies have been directed to the vulcanization of butadiene 1,4-polymers (Skinner and Watson, 1969; Wolfe et al., 1929; Gregg and Katrenick, 1970). More recent is the work of Pellicioli and coworkers. Early basic work on the vulcanization of ethylene-propylene-diene-monomer rubber (EPDM) has been carried out (van den Berg et al., 1984a,b). Recently, Kuno and coworkers did basic work on EPDM networks. They found that, essentially, the vulcanizate properties depend only on the crosslink density, not on the type of curing system (Dijkhuis et al., 2009).

The chemistry of the accelerated vulcanization of BR, SBR, and EPDM appears to have much in common with the vulcanization of natural rubber: Before the formation of crosslinks the rubber is first sulfurated by accelerator-derived polysulfides ($\text{Ac-S}_x\text{-Ac}$) to give macromolecular, polysulfidic intermediates ($\text{rubber-S}_x\text{-Ac}$). However, whereas in the case of MBTS- or benzothiazolesulfenamide-accelerated sulfur vulcanization of natural rubber, MBT is given off during the formation of $\text{rubber-S}_x\text{-BT}$ from the attack of rubber by $\text{BT-S}_x\text{-BT}$, in the case of BR and SBR, MBT is not eliminated and remains unextractable presumably because it becomes bound as the macromolecular thioether $\text{rubber-S}_x\text{-BT}$. (BT is a 2-benzothiazolyl group.) As in the case of natural rubber, the average length of a crosslink (its sulfidic rank, the value of x in the crosslink, $\text{rubber-S}_x\text{-rubber}$) increases with the ratio of sulfur concentration to accelerator concentration (S/Ac) used in the compounded rubber mix. However, in the case of BR or SBR, the crosslink sulfidic rank is not nearly as sensitive to S/Ac as it is in the case of natural rubber. Model compound studies of the vulcanization of EPDM (e.g., wherein ethylenenorbornane was used as a model for EPDM) (van den Berg et al., 1984a,b) indicate that the polysulfidic rank of the EPDM crosslinks probably responds to changes in

S/Ac in a natural rubber-like fashion. A difference here is that evidence for model monosulfidic crosslinks was lacking while model disulfidic crosslinks were more apparent than in the case of natural rubber vulcanization.

Reversion (when defined as the loss of crosslinks during nonoxidative thermal vulcanizate aging) is a problem associated mainly with natural rubber or synthetic isoprene polymers. It can occur only under severe conditions in butadiene rubber; in SBR, instead of the softening associated with the nonoxidative aging of natural rubber, we can observe hardening (the so-called marching modulus) during extensive overcure. In natural rubber and synthetic isoprene-polymer rubbers, the crosslinks tend to be more polysulfidic than in the case of BR or SBR. The highly polysulfidic crosslinks are more heat-labile than their lower rank cousins in BR and SBR; they are more likely to break and then form cyclic chain modifications. But the reason for the formation of the crosslinks of higher polysulfidic rank in isoprene rubbers than in butadiene polymers is grandly elusive, though it almost has to be related to the methyl groups, which are substituents along the isoprene-polymer chains but which are absent from butadiene-polymer chains.

The effect of zinc is much greater in the vulcanization of isoprene rubbers than it is in the vulcanization of BR and SBR. Again, the reason for the difference is not known, but a strong speculation is that this difference is also related to the presence of methyl groups only in the case of the isoprene rubbers.

7.6.8 Selected Accelerated-Sulfur System Recipes

Examples of recipes are given in Table 7.4. These recipes are not intended as ultimate solutions to compounding problems. Variations will undoubtedly be necessary to meet particular requirements.

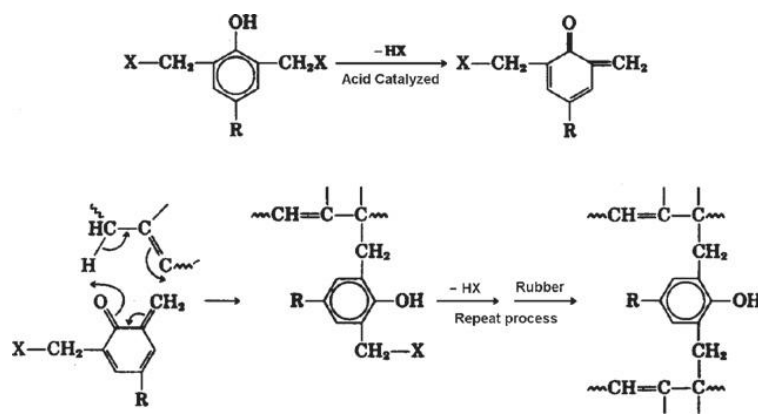
7.7 VULCANIZATION BY PHENOLIC CURATIVES, BENZOQUINONE DERIVATIVES, OR BISMALEIMIDES

Diene rubbers such as natural rubber, SBR, and BR can be vulcanized by the action of phenolic compounds (van der Meer, 1943; Thelamon, 1963; Giller, 1966; Van Duin and Souphanthong, 1995), which are (usually di-)substituted by $-\text{CH}_2\text{-X}$ groups where X is an $-\text{OH}$ group or a halogen atom substituent. A high-diene rubber can also be vulcanized by the action of a dinitrosobenzene, which forms *in situ* by the oxidation of a quinonedioxime (Rehner and Flory, 1946; Martell and Smith, 1962; Sullivan, 1966; Baker et al., 1962; Gan and Chew, 1983), which had been incorporated into the rubber along with the oxidizing agent, lead peroxide.

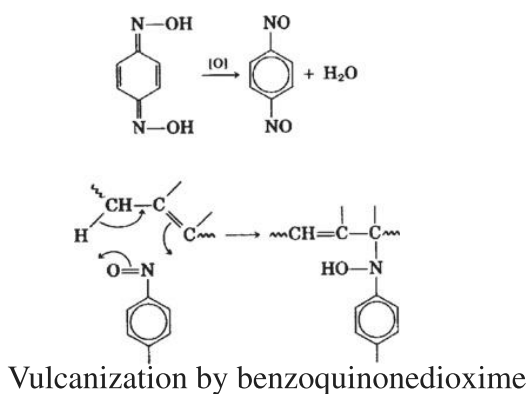
The attack upon rubber molecules by the vulcanization system can be visualized in a way similar to that which was postulated for the sulfurization of the rubber molecules by the action of accelerated-sulfur vulcanization systems. Reaction schemes for these two types of vulcanization can be written as follows:

TABLE 7.4 Recipes for Accelerated-Sulfur Vulcanization Systems^a

	NR	SBR	Nitrile (NBR)		Butyl (IIR)	EPDM
			1	2		
Zinc oxide	5.00	5.00	3.00	2.00	3.00	5.00
Stearic acid	2.00	2.00	0.50	0.50	2.00	1.00
Sulfur	2.50	1.80	0.50	0.25	2.00	1.50
DTDM ^b	—	—	—	1.00	—	—
TBBS ^b	0.60	1.20	—	—	—	—
MBTS ^b	—	—	2.00	—	0.50	—
MBT ^b	—	—	—	—	—	0.50
TMTD ^b	—	—	1.00	1.00	1.00	1.50
Vulcanization conditions ^c						
Temperature (°C)	148	153	140	140	153	160
Time (min)	25	30	60	60	20	20

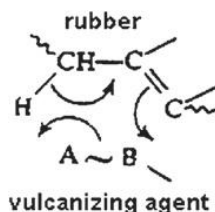
^aConcentrations in phr.

Vulcanization by phenolic curatives

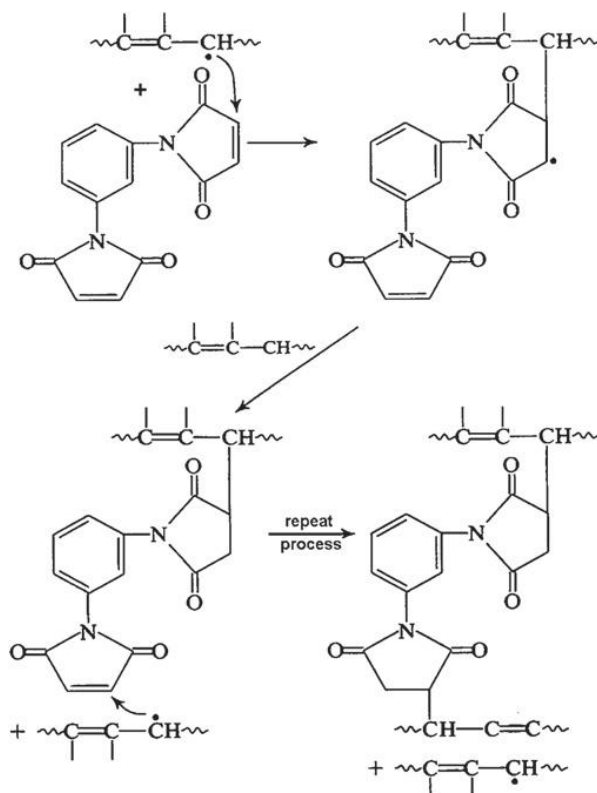


Vulcanization by benzoquinonedioxime

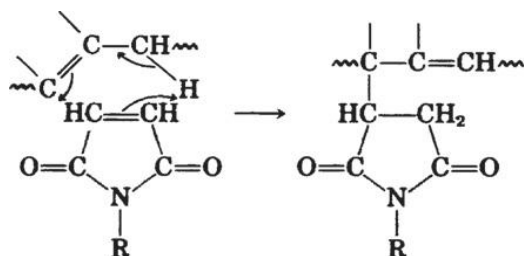
As shown above, the chemical structural requirements for these types of vulcanization are that the elastomer molecules contain allylic hydrogen atoms. The attacking species from the vulcanization system must contain sites for proton acceptance and electron acceptance in proper steric relationship. This will then permit the following rearrangement, where A is the proton acceptor site and B is the electron acceptor site:



This is an explanation for the fact that this type of vulcanization is not enabled by double bonds per se, without allylic hydrogens in the elastomer molecules (Coran, 1978; Baldwin et al., 1970). (It should be pointed out that the phenolic curative could also act by a slightly different mechanism to give crosslinks, which contain chromane structural moieties (Greth, 1951) the allylic hydrogens still being required.) Another vulcanizing agent for high-diene rubbers is *m*-phenylenedibismaleimide. A catalytic free radical source such as dicumyl peroxide or benzothiazyl disulfide (MBTS) is usually used to initiate the reaction. A reaction scheme for this type of vulcanization, adapted from Kovacic and Hein (1962), is as follows:



Although a free radical source is frequently used with a maleimide vulcanizing agent, at high enough vulcanization temperatures, the maleimides react with the rubber without the need for a free radical source. This could occur as shown here:



This is another example of what has variously been called a pseudo-Diels-Alder, ene, or “no-mechanism” reaction (Hoffmann, 1969). It is similar to the reaction written for the attack of rubber molecules by phenolic curatives or the *in situ* formed nitroso derivative of the quinoid (e.g., benzoquinonedioxime) vulcanization system. It is also closely related to the sulfurization scheme written for accelerated-sulfur vulcanization. Comparisons between accelerated sulfur, phenolic, quinoid, and maleimide vulcanization can then be visualized as follows:

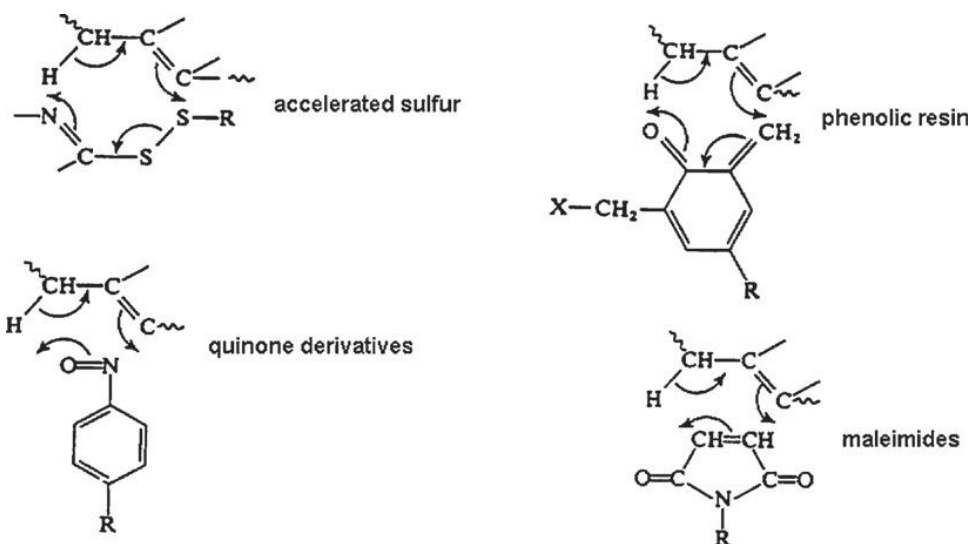


Table 7.5 gives selected recipes for vulcanization by phenolic curatives, benzoquinone-dioxime, or *m*-phenylenebismaleimide. Vulcanizates based on these types of curatives are particularly useful in cases where thermal stability is required.

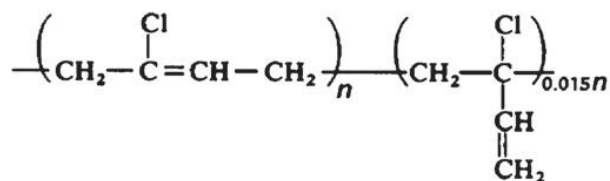
TABLE 7.5 Recipes for Vulcanization by Phenolic Curatives, Quinone Derivatives, or Maleimides^a

	IIR		SBR		NBR
	1	2	1	2	
Zinc oxide	5.00	5.00	—	—	—
Lead peroxide (Pb ₃ O ₄)	—	10.00	—	—	—
Stearic acid	1.00	—	—	—	—
Phenolic curative (SP-1056) ^b	12.00	—	—	—	—
Benzoquinonedioxime (GMF)	—	2.00	—	—	—
<i>m</i> -Phenylenebismaleamide (HVA-2) ^c	—	—	0.85	0.85	3.00
2-Benzothiazyl disulfide (MBTS)	—	—	2.00	—	—
Dicumyl peroxide	—	—	—	0.30	0.30
Vulcanization condition ^d					
Temperature (°C)	180	153	153	153	153
Time (min)	30	20	25	25	30

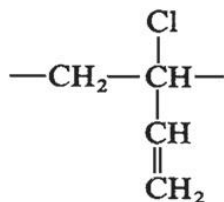
^aConcentrations in phr.^bSchenectady Chemicals.^cDuPont.^dConditions change depending on other aspects of the compositions.

7.8 VULCANIZATION BY THE ACTION OF METAL OXIDES

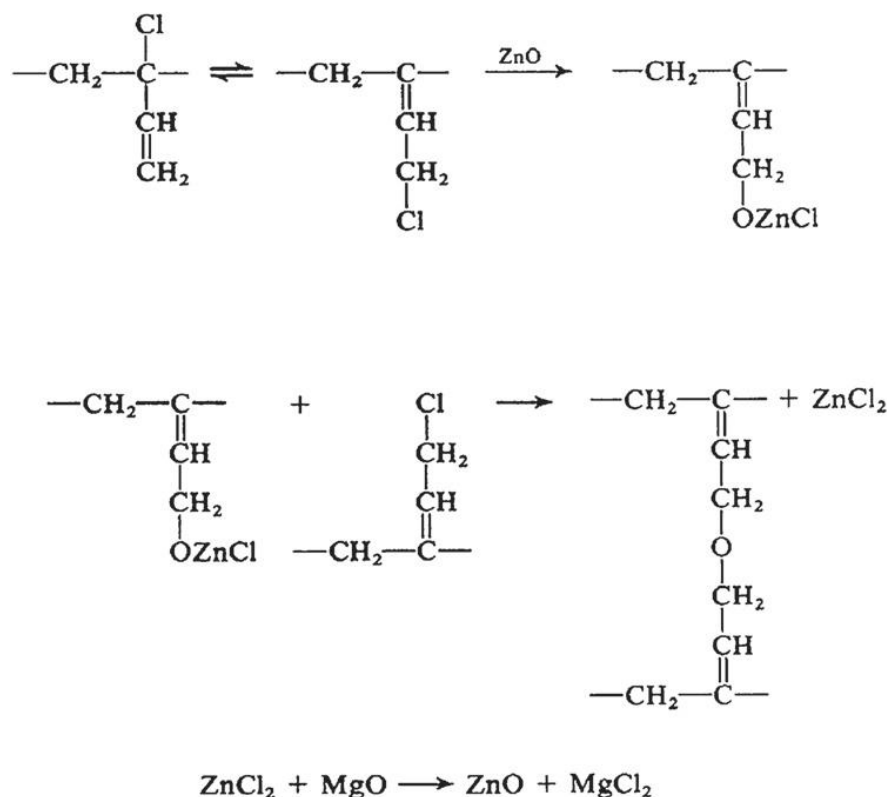
Chlorobutadiene or chloroprene rubbers (CR), also called neoprene rubbers, are generally vulcanized by the action of metal oxides. CR can be represented by the structure:



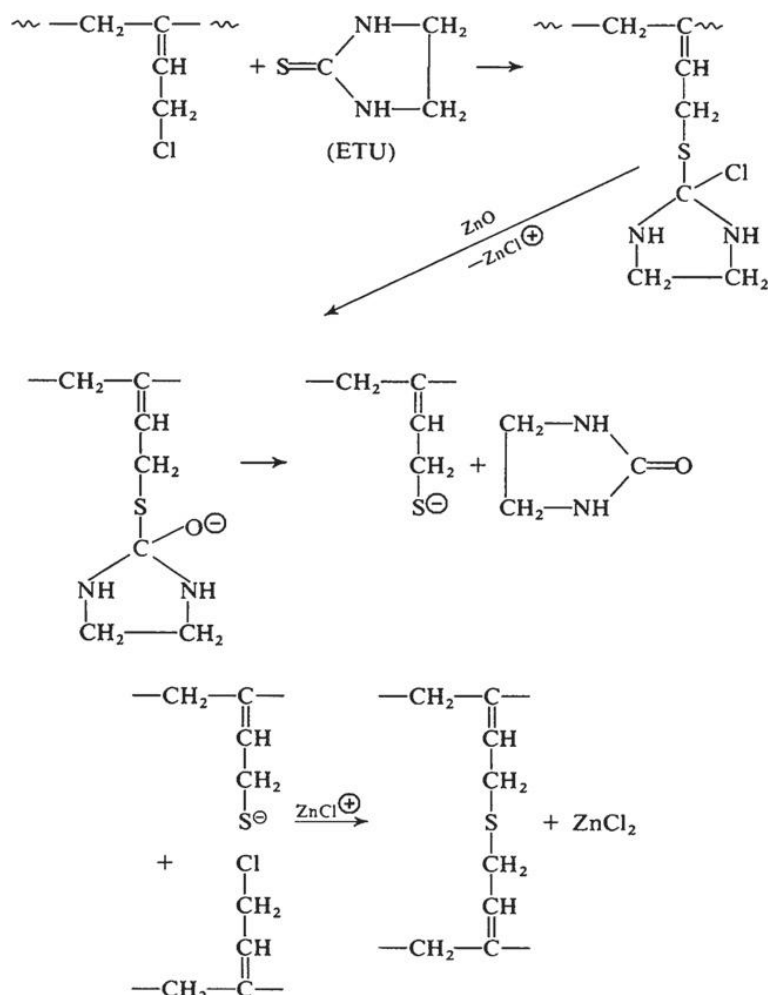
The crosslinking agent is usually zinc oxide, which is used along with magnesium oxide. CR can be vulcanized in the presence of zinc oxide alone; however, magnesium oxide is necessary to give scorch resistance. The reaction is thought to involve the allylic chlorine atom, which is the result of the small amount of 1,2-polymerization:



A mechanism, which has been written for the vulcanization of CR by the action of zinc oxide and magnesium oxide, is as follows (Hofmann, 1967):



Most accelerators used in the accelerated-sulfur vulcanization of other high-diene rubbers are not applicable to the metal oxide vulcanization of neoprene rubbers. An exception to this is in the use of the so-called mixed curing system for CR, in which metal oxide vulcanization is combined with accelerated-sulfur vulcanization. Along with the metal oxides, tetramethylthiuram disulfide (TMTD), N,N'-di-o-tolylguanidine (DOTG), and sulfur are used. This may be desirable for high resilience or for good dimensional stability. The accelerator, which has been most widely used with metal oxide cures, is ethylenethiourea (ETU) or 2-mercaptoimidazoline. Further extensive use of ETU in the vulcanization of CR is somewhat in doubt since it is a suspected carcinogen. The related compound, thiocarbanalide, an old accelerator for sulfur vulcanization, has been revived for CR vulcanization. Other substitutes for ETU have been proposed (Mori and Nakamura, 1984; Kato and Jujita, 1982). A mechanism for ETU acceleration has been given by Pariser (1960):



Examples of recipes for metal oxide vulcanization are given in Table 7.6. It should be noted that in one case, calcium stearate was used instead of magnesium oxide to obtain better aging characteristics (Becker, 1964).

7.9 VULCANIZATION BY THE ACTION OF ORGANIC PEROXIDES

Most elastomers can be vulcanized by the action of organic peroxides (Loan, 1967; Dluzeski, 2001). Diacyl peroxides, dialkyl peroxides, and peresters have been used. Dialkyl peroxides and *t*-butyl perbenzoate give efficient crosslinking. Di-*t*-butyl peroxide and dicumyl peroxide give good vulcanizates, but the former is too volatile for general use. Dicumyl peroxide is widely used, however its vulcanizates have the odor of acetophenone, which is a byproduct of the vulcanization process. Other nonvolatile peroxides of the same class, which give vulcanizates free of the odor of acetophenone, are 1,1-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane and 2,5-dimethyl-2,5-bis(*t*-butylperoxy)hexane. This latter compound is particularly good for vulcanization at higher temperatures (as high as 180°C) since it is more thermally stable than the others.

TABLE 7.6 Vulcanization Systems for Chloroprene Rubber^a

ZnO	5.00	5.00	5.00
MgO	4.00		4.00
Calcium stearate	—	5.50	—
Stearic acid	—	—	1.00
TMTM	—	—	1.00
DOTG	—	—	1.00
ETU	0.5	0.5	—
Sulfur	—	—	1.0
Vulcanization condition ^b			
Temperature (°C)	153	153	153
Time (min)	15	15	15

^aConcentrations in parts by weight per 100 parts of neoprene W.

^bConditions change depending on other aspects of the compositions.

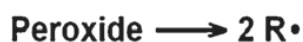
It should be noted that acidic compounding ingredients (fatty acids, certain carbon blacks, and acidic silicas) can catalyze nonradical-generating, wasteful decomposition of peroxides. Other compounding ingredients such as antidegradants can reduce crosslinking efficiency by quenching or altering the free radicals before they can react with the polymeric substrate.

Peroxides are vulcanizing agents for elastomers, which contain no sites for attack by other types of vulcanizing agents. They are useful for ethylene-propylene rubber (EPR), ethylene-vinyl acetate copolymers (EAM), certain millable urethane rubbers, and silicone rubbers. They generally are not useful for vulcanizing butyl rubber (poly[isobutylene-co-isoprene]) because of a tendency toward chain scission, rather than crosslinking, when the polymer is subjected to the action of peroxide.

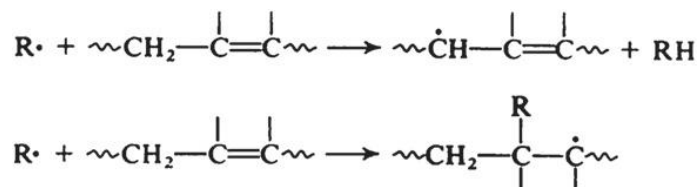
Elastomers derived from isoprene and butadiene are readily crosslinked by peroxides; but many of the vulcanizate properties are inferior to those of accelerated-sulfur vulcanizates. However, peroxide vulcanizates of these diene rubbers may be desirable in applications where improved thermal aging and compression set resistance are required.

7.9.1 Peroxide Vulcanization of Unsaturated Hydrocarbon Elastomers

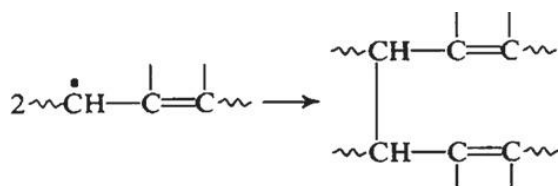
The initiation step in peroxide-induced vulcanization is the decomposition of the peroxide to give free radicals. Thus



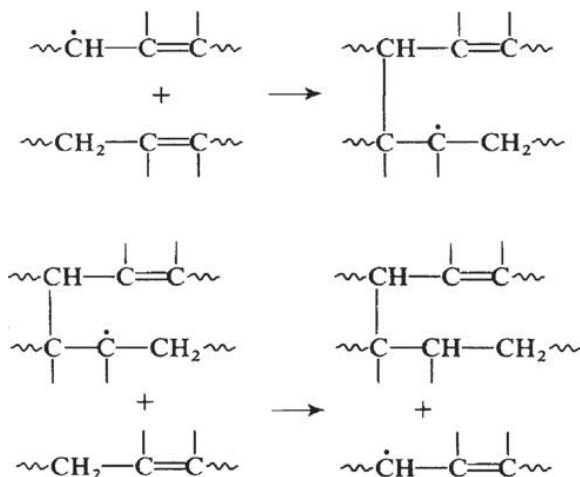
where R is an alkoxy, alkyl, or acyloxy radical, depending on the type of peroxide used. (Dibenzoyl peroxide gives benzoyloxy radicals but dicumyl peroxide gives cumyloxy and methyl radicals (Scanlan and Thomas, 1963).) If the elastomer is derived from butadiene or isoprene, the next step is either the abstraction of a hydrogen atom from an allylic position on the polymer molecule or the addition of the peroxide-derived radical to a double bond of the polymer molecule (Farmer and Michael, 1942; Farmer and Moore, 1951a,b).



For isoprene rubber, the abstraction route predominates over radical addition. Two polymeric free radicals then unite to give a crosslink.



Crosslinks could also form by a chain reaction, which involves the addition of polymeric free radicals to double bonds (Loan, 1967, 1963).



In this case crosslinking occurs without the loss of a free radical, so that the process can be repeated until termination by radical coupling. Coupling can be between two polymeric radicals to form a crosslink or by an unproductive process: a polymeric radical can unite with a radical derived from the peroxide. If a polymeric radical decomposes to give a vinyl group and a new polymeric radical, a scission of the polymer chain is the result.

Few monomeric radicals are lost by coupling with polymeric radicals when dialkyl peroxides are used as the curative. Also, if the elastomer is properly

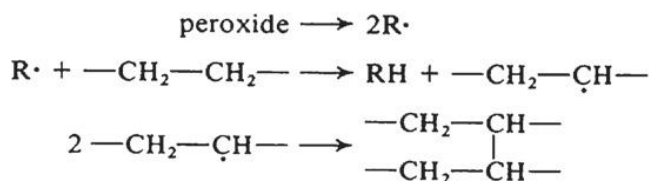
chosen, the scission reaction is not excessive (Loan, 1967; Dluzneski, 2001; Scanlan and Thomas, 1963; Farmer and Michael, 1942; Farmer and Moore, 1951a,b; Loan, 1963). For dicumyl peroxide in natural rubber, the crosslinking efficiency has been estimated at about 1.0. One “mole” of crosslinks is formed for each mole of peroxide; crosslinking is mainly by the coupling of two polymeric radicals (Thomas, 1962; Scott, 1962). One peroxide moiety gives two monomeric free radicals, which react with rubber to give two polymeric radicals that couple to form one crosslink.

In the case of BR or SBR, the efficiency can be much greater than 1.0, especially if all antioxidant materials are removed. A chain reaction is indicated here. It might be explained by steric considerations. In butadiene-based rubbers, double bonds are quite accessible. Radical addition to double bonds could give highly reactive radicals, which would be likely to add to other polymer double bonds. A chain of additions might be more likely in butadiene rubber than in the presence of hindering methyl groups in isoprene rubbers.

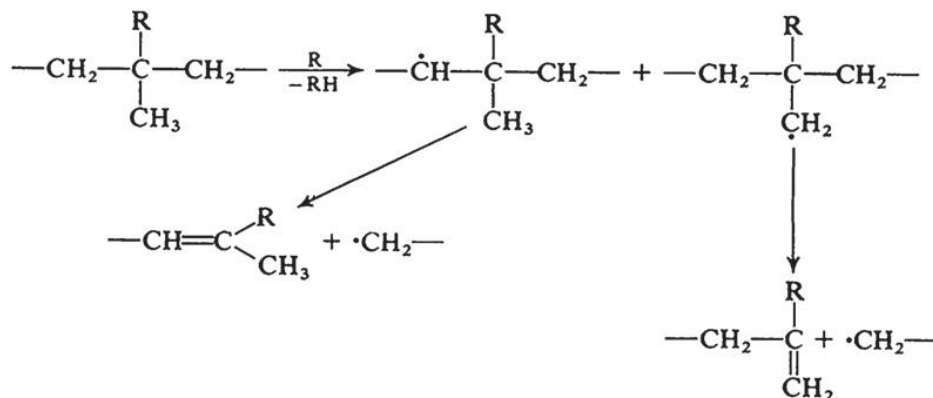
We might expect that nitrile rubber would also be vulcanized with efficiencies greater than 1.0; however, though the double bonds in nitrile rubber are highly accessible, the crosslinking efficiency is somewhat less than 1.0 (Loan, 1963).

7.9.2 Peroxide Vulcanization of Saturated Hydrocarbon Elastomers

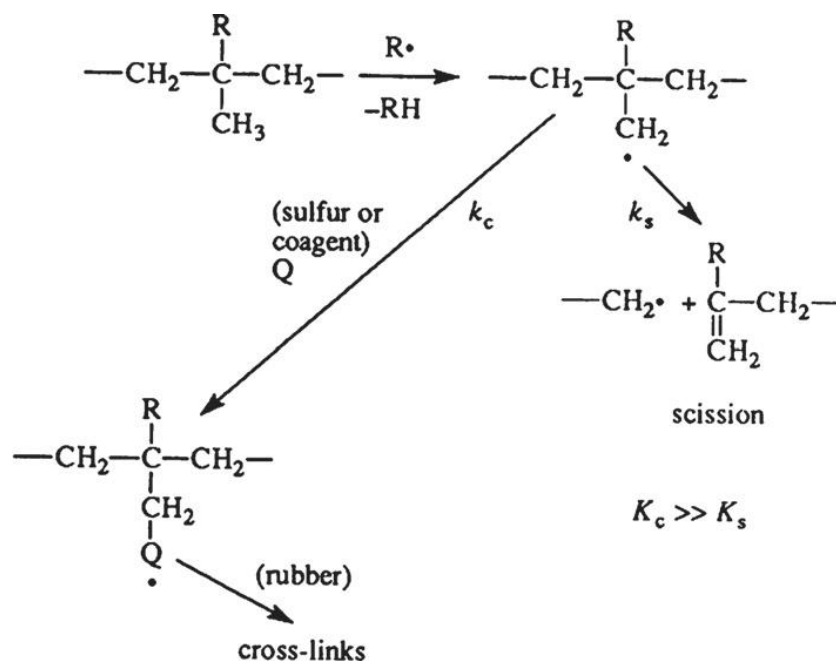
Saturated hydrocarbon polymers are also crosslinked by the action of organic peroxides, though branching reduces the efficiency. Polyethylene is crosslinked by dicumyl peroxide at an efficiency of about 1.0, saturated EPR gives an efficiency of about 0.4, while butyl rubber cannot be cured at all. For polyethylene, the reaction scheme is similar to that of the unsaturated elastomers.



However, branched polymers undergo other reactions.



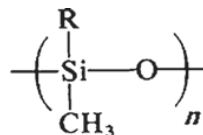
Sulfur, or the so-called coagents (Loan, 1963; Lenas, 1964), can be used to suppress scission. Examples of coagents are *m*-phenylenebismaleimide, high-1,2 (high-vinyl)polybutadiene, triallyl cyanurate, diallyl phthalate, and ethylene diacrylate. Their mechanism of action may be as follows:



Recent work with coagents has been reported by Alvarez-Grima and coworkers (Alvarez Grima et al., 2006). They point out that scorch is a common problem in peroxide cure, especially for injection molding and extrusion applications. Several additives can help to improve scorch safety; however, they always result in a lower peroxide efficiency, thus inferior vulcanizate properties. These authors presented work on the use of a combination of a bismaleimide-type coagent, like N,N'-*m*-phenylenedimaleimide (BMI-MP), and a sulfur-containing compound like dipentamethylenethiuram tetrasulfide (DPTT). This combination provides scorch safety and at the same time improves the mechanical properties of the vulcanizates. The concentrations of coagent and sulfur-containing compound have a big influence on the scorch time and on the mechanical properties. Optimum concentrations were 4 phr of coagent and 0.7–0.96 phr of the sulfur-containing compound. The chemistry of this type of vulcanization was also studied (Alvarez Grima et al., 2009).

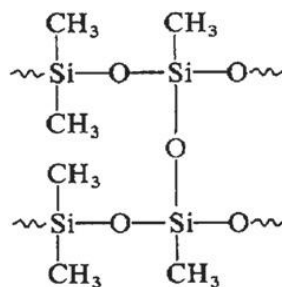
7.9.3 Peroxide Vulcanization of Silicone Rubbers

Silicone rubbers can be represented by



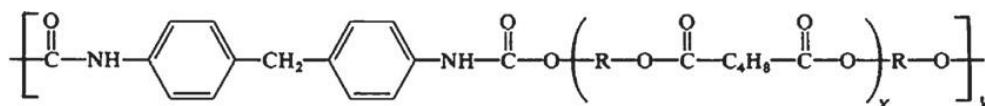
where R can be methyl, phenyl, vinyl, trifluoropropyl, or 2-cyanoethyl. Dialkyl peroxides such as dicumyl peroxide can cure silicone rubbers, which contain vinyl groups. Saturated silicone rubbers require diacyl peroxides such as bis-(2,4-dichlorobenzoyl)peroxide. In the case of saturated siloxane rubbers, the mechanism is hydrogen atom abstraction followed by polymeric radical coupling to give crosslinks. Nonproductive use of peroxide results from the coupling of the polymeric radicals with the lower-molecular-weight free radicals formed by the decomposition of the peroxide curative. The incorporation of vinyl groups improves the crosslinking efficiency (Lewis, 1962; Thomas, 1966).

Vulcanization is frequently done in two steps. After a preliminary vulcanization in a mold, a high-temperature (e.g., 180°C) postcure is carried out in air. The high-temperature postcure removes acidic materials that can catalyze hydrolytic decomposition of the vulcanizate (Roush et al., 1964). Also the high temperature enables the formation of additional crosslinks of the following type (Hofmann, 1967):



7.9.4 Peroxide Vulcanization of Urethane Elastomers

Urethane elastomers suitable for peroxide vulcanization typically are prepared from a hydroxyl-group-terminated oligomeric adipate polyester and 4,4'-methylenediphenylisocyanate (MDI). A typical structural representation is as follows:



Hydrogen atoms can be abstracted from arylated methylene groups, but hydrogen atoms may also be abstracted from α -methylene groups of the adipate moieties. Though they are usually sufficient, vulcanization efficiencies can be increased by the incorporation of urea structures into the polymer chain (Bork and Roush, 1964).

TABLE 7.7 Recipes for Peroxide Vulcanization^a

	NR	SBR	EPR	Silicone Rubber	Millable Urethane
Dicumyl peroxide	1.0	1.0	2.7		2
Bis(2,4-dichlorobenzoyl peroxide)	—			1.0	
Triallyl cyanurate			1.5		
Vulcanization conditions ^b					
Temperature (°C)	150	150	160	115, 250 ^c	153
Time (min)	45	45	30	14,1440 ^c	45

^aConcentrations in phr.^bConditions change depending on other aspects of the compositions.^cTemperature and time of postcure in air.

7.9.5 Recipes for Peroxide Vulcanization

Examples of starting-point recipes are given in Table 7.7. Outstanding characteristics of peroxide vulcanizates are low permanent set and thermal stability of the network.

7.10 DYNAMIC VULCANIZATION

Dynamic vulcanization (DV) is the vulcanizing or crosslinking of one polymer during its molten-state mixing with another polymer or with other polymers. The polymers are first thoroughly mixed and then, during further mixing, *one* of the polymers is obliged to become crosslinked, whereas the remaining other polymeric material remains uncrosslinked. The process produces a dispersion of crosslinked polymer in a matrix or continuous phase of uncrosslinked polymer. If the dispersed crosslinked material is elastomeric and the continuous or matrix material is of a melt-processable plastic, then the composition can be used as an impact resistant thermoplastic resin, or if there is a large enough proportion of rubber in the composition, it might be suitably used as a thermoplastic elastomer (TPE). Such materials are referred to as thermoplastic vulcanizates (TPVs).

TPVs combine the rapid molding of thermoplastics with the elastomeric properties of thermoset rubber. They are useful in a broad range of applications. TPVs comprise the second largest group of soft, rubbery thermoplastic elastomers, after styrenic-based block copolymers.

Fischer (1973) used the DV process to prepare compositions containing *partially* vulcanized rubber. It has since been found that improved, very strong elastomeric compositions of EPDM and polypropylene could be prepared by

dynamic vulcanization provided that the rubber was completely vulcanized (Coran and Patel, 1980).

The DV process for thermoplastic elastomers can be described as follows: After sufficient melt-mixing of plastic and rubber, vulcanizing agents are added. Vulcanization of the rubber phase occurs as mixing continues. After removal from the mixer, the cooled blend can be chopped, extruded, pelletized, injection molded, and so on. Such a composition is described as a dispersion of very small particles of vulcanized rubber in a thermoplastic resin matrix. Such compositions are prepared commercially by a continuous process by using a twin-screw extruder.

Dynamic vulcanization gives the following improvements, in comparison with blends which have not been dynamically vulcanized: reduced set, improved ultimate properties, improved fatigue resistance, improved resistance to attack by hot oils, greater stability of melt-phase morphology, greater melt strength, and so on.

Recent developments in dynamic vulcanization have been reviewed by Babu and Naskar (2011).

7.10.1 EPDM-Polyolefin Compositions

The dynamic vulcanization of blends of EPDM rubber with polyolefins (PP or PE) has been described (Coran and Patel, 1980). The rubber-plastic proportions and the extents of vulcanization were varied. In a few instances the rubber was first press-cured and then ground to various particle sizes. The ground rubber particles were then mixed with molten polypropylene. It was found that the ultimate properties (UE and UTS) varied inversely with rubber particle size. Since the smallest particle sizes of vulcanized rubber were obtained by dynamic vulcanization (not by grinding of cured rubber), the more durable compositions were obtained by dynamic vulcanization.

Only a small amount of crosslink formation is required for a large improvement in tension set. However, tensile strength improves rather continuously as the crosslink density of the rubber phase is increased. Compositions can be vulcanized by accelerated sulfur, methylolphenolic materials (e.g., catalyzed by SnCl_2), or other curatives (Coran and Patel, 1996).

As the concentration of the polyolefin resin increases, the compositions become less like rubber and more like plastic. Modulus, hardness, tension set, and strength increase.

7.10.2 NBR-Nylon Compositions

Excellent elastomeric NBR-nylon compositions have also been prepared by dynamic vulcanization during the melt-mixing of intimate blends of NBR with various nylons. In this case, the effect of curatives was complicated by the fact that some nitrile rubbers tend to self-cure at temperatures of mixing. Sulfur,

phenolic, maleimide, or peroxide curatives can be used. The thermoplastic elastomeric compositions prepared by the dynamic vulcanization of nylon-NBR blends are highly resistant to hot oil. As in the case of the EPDM-polyolefin blends, increases in the amount of rubber in the composition reduce stiffness but increase resistance to permanent set.

7.10.3 Other Elastomeric Compositions Prepared by Dynamic Vulcanization

In addition to EPDM-polyolefin and NBR-nylons combinations, a large number of other rubber-plastic combinations have been used to prepare thermoplastic vulcanizates by dynamic vulcanization (Coran et al., 1982).

The best compositions are prepared when the surface energies of the rubber and plastic material are matched, when the entanglement molecular length of the rubber molecule is small (i.e., molecular entanglement density of the rubber molecule is greatest), and when the plastic material is crystalline. It is also necessary that neither the plastic nor the rubber decomposes in the presence of the other at temperatures required for melt-mixing. Also, in each case, a curing system appropriate for the rubber under the conditions of melt-mixing is required.

7.10.4 Technological Applications

The lower cost of thermoplastic processing is the motivation for the development of thermoplastic elastomers. However, failure in the achievement of truly

TABLE 7.8 Commercially Available High-Performance TPVs^a

Grade Name	Elastomer Type	Matrix Phase	Supplier
TPSiV	Silicone	Polyamide (PA), thermoplastic polyurethane (TPU)	Dow Corning
Zeotherm	Polyacrylate (ACM)	Polypropylene (PP), PA, polyester	Zeon
E-TPV	Ethylene acrylate	Thermoplastic copolyester (COPE)	DuPont
Uniprene-XL	Hydrogenated-styrene block copolymer (H-SBC)	PP	Teknor-Apex
Serel	Styrene-butadiene (SSBR)	PP	Goodyear
Septon V	H-SBC, reactive hard block	SBC triblock	Kuraray

^aRobert Eller Associates Inc. (2004). <http://www.robertellerassoc.com/>.

rubber-like properties has impeded the acceptance of thermoplastic-elastomer technology. Nevertheless relatively recently commercialized compositions based on polypropylene and *completely* vulcanized EPDM have many of the excellent properties of the polyurethane and copolyester-type thermoplastic elastomers and even improved set and fatigue resistance. Applications of these materials can be listed as follows: caster wheels, convoluted bellows, diaphragms, gaskets, seals, tubing, mounts, bumpers, glazing seals, shields, suction cups, torque couplings, vibration isolators, plugs, connectors, rollers, oil-well injection lines, handles, grips, hose covers, vacuum tubing, bushings, grommets, protective sleeves, shock isolators, ducts, various hoses (e.g., hydraulic, agricultural spray, paint spray, plant air-water, mine hose, etc.), wire and cable insulation and strain relief, jacketing, and more.

7.10.5 Extra-High-Performance TPVs

TPVs have been developed that are more resistant to high temperatures, hot oils, oxidation fatigue, and so on. There is little open, published work on these materials. Some of these materials were discussed by Babu and Naskar (2011). This new TPV technology is expected to bridge the gap between PP/EPDM TPVs and the more costly engineering TPVs. Examples of commercialized extra-high-performance TPVs are given in Table 7.8.

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