

# Chemistry of the Vulcanization and Protection of Elastomers: A Review of the Achievements

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**ABSTRACT:** The chemistry of vulcanization and its effects on vulcanizate properties are reviewed. Also, the chemistry of the protection of rubber vulcanizates from the effects

of oxidation and ozonation is reviewed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 24–30, 2003

**Key words:** vulcanization; antioxidants

## INTRODUCTION

Rubber must be vulcanized to obtain useful elastomeric properties. Then, a technology must be developed for the preservation of those properties for as long as the end use requires. This review considers the chemistry of vulcanization, and its effects on vulcanizate properties are reviewed. Also, the chemistry of the protection of rubber vulcanizates from the effects of oxidation and ozonation is reviewed.

## VULCANIZATION

Vulcanization increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force. It is generally accomplished by the formation of a crosslinked molecular network.<sup>1</sup> The accelerated sulfur vulcanization of unsaturated rubbers (e.g., NR, SBR, and BR) by sulfur in the presence of organic accelerators and other rubbers, which are vulcanized by a closely related technology (e.g., EPDM, IIR, and NBR), comprises more than 90% of all vulcanizations.

During vulcanization, the long rubber molecules (usually having molecular weights of 100,000–500,000) become linked in junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4000–10,000. As a result, the rubber becomes insoluble, and it cannot flow. Therefore, vulcanization can only occur after the rubber article is in its final form. Figure 1 illustrates the main effects of vulcanization on use-related properties.<sup>2</sup> Reversion is network

loss due to nonoxidative thermal aging. It is usually associated with isoprene rubbers containing polysulfidic crosslinks. It can be the result of an overly long vulcanization time or hot aging of thick sections. It is most severe above 155°C.

Characteristics related to the vulcanization process are the time elapsing before crosslinking starts, the rate of crosslink formation, and the final extent of crosslinking. There must be sufficient delay or scorch resistance to permit shaping, forming, and flowing in the mold. Then, crosslink formation should be rapid. Both the rate of vulcanization and the final extent of vulcanization are measured with oscillating-disk or moving-die rheometers. The rheometer chart in Figure 2 gives the overall kinetics of crosslink formation and reversion or overcure.

A patent for the vulcanization of natural rubber by sulfur was issued to Charles Goodyear in 1839. Metal oxides (e.g., ZnO) enhanced the effect of sulfur and reduced the time required for vulcanization. Organic chemical accelerators were not used until 1906, when Oenslager<sup>3</sup> discovered the effect of aniline on sulfur vulcanization. The first delayed-action vulcanization systems were introduced in 1925 with the use of 2-mercaptobenzothiazole (MBT) and 2,2-dithiobisbenzothiazole (MBTS).<sup>4</sup> This nearly coincided with the introduction of cord-ply construction (1920–1930). Even more delayed action and yet faster curing vulcanization systems were made possible in 1937 with thiazole sulfenamide accelerators.<sup>5</sup>

However, thiazole sulfenamides were the last new accelerator class of great commercial significance to be introduced. A faster cure rate could not be maintained along with greater processing safety. There were acidic retarders, which would retard the onset of vulcanization, but they reduced the rate. The next major innovation in chemicals for vulcanization occurred in 1968, with the introduction of *N*-(cyclohexylthio)phthalimide.<sup>6</sup> This agent provided, for the first time,

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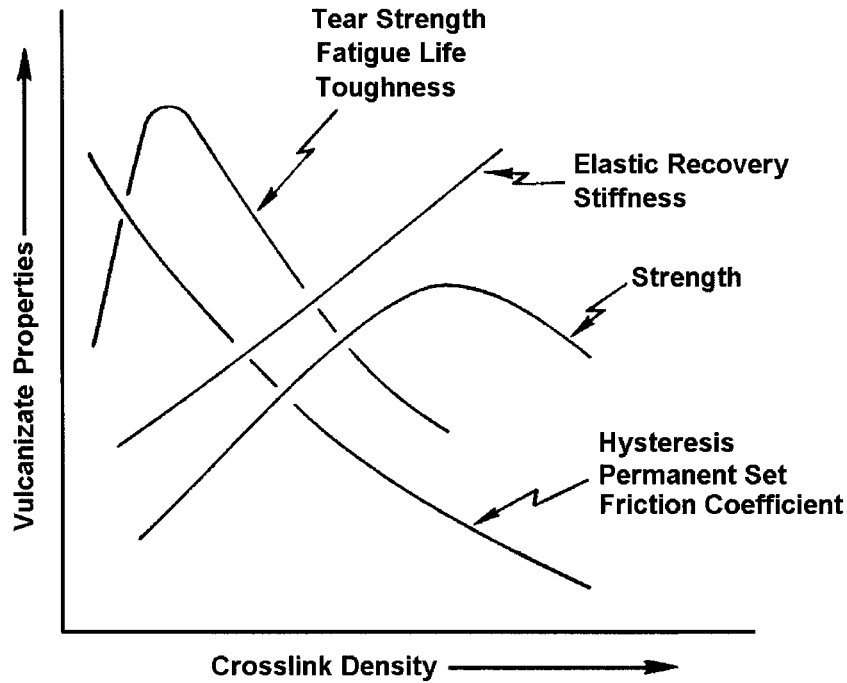
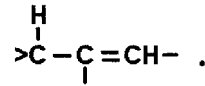


Figure 1 Properties versus the crosslinks.

control of the delay time nearly independent of the cure rate. The vulcanization characteristics given by various accelerators and combinations are given in Figure 3.

The reactive moiety for accelerated sulfur vulcanization<sup>7</sup> can be represented by



Typically, a recipe for the vulcanization system for one of the aforementioned elastomers contains 2-10 phr

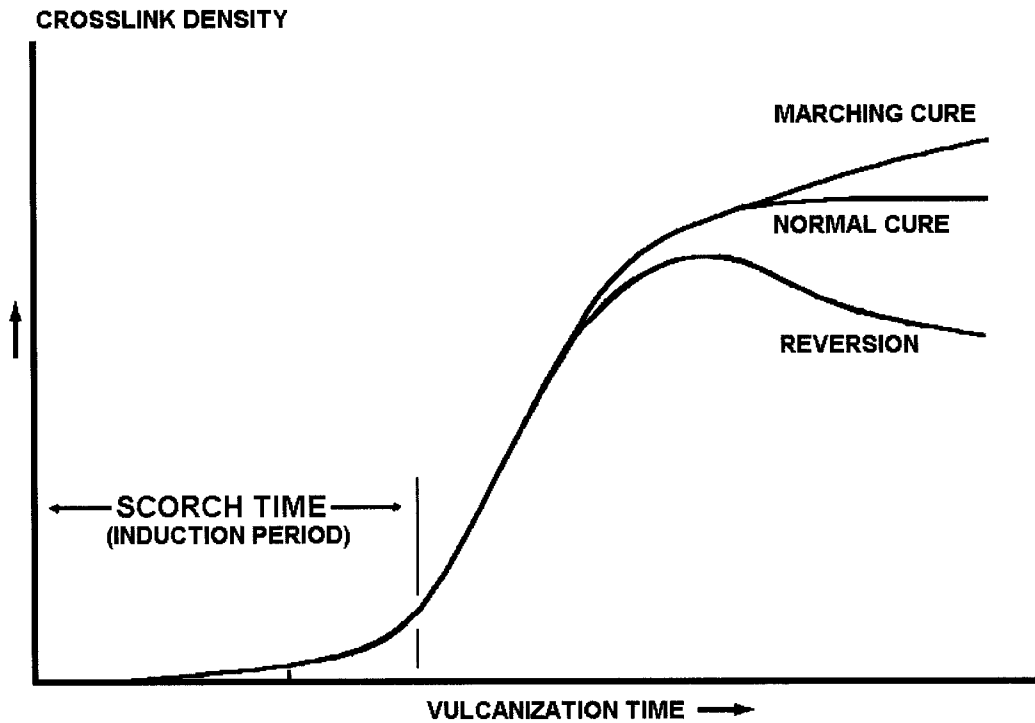


Figure 2 Rheometer chart showing the curing characteristics.

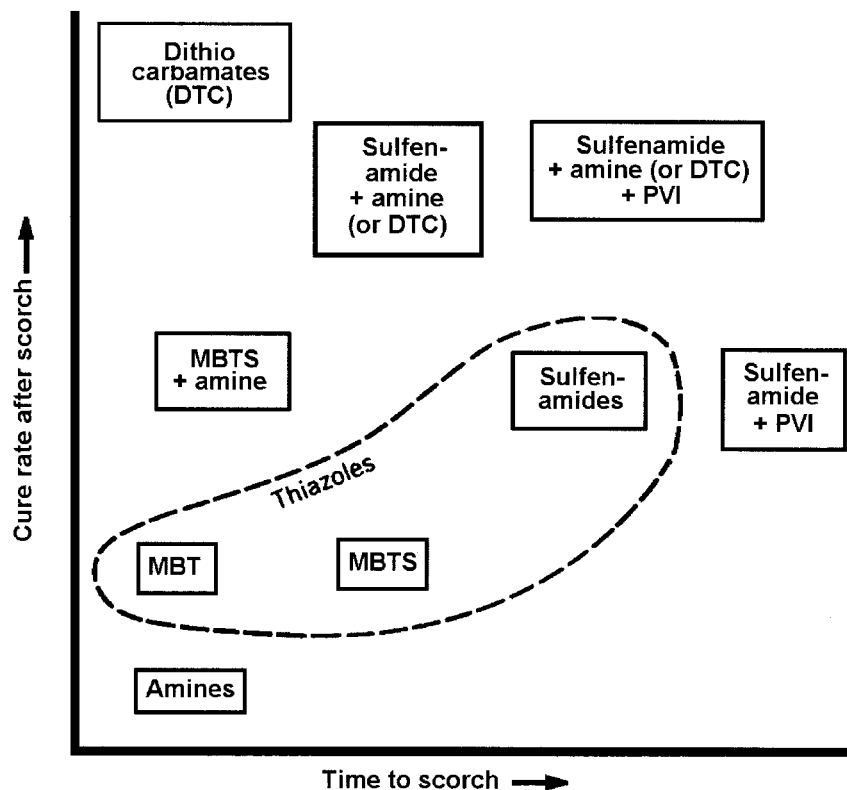


Figure 3 Map of the vulcanization characteristics for the accelerators and combinations.

zinc oxide, 1–4 phr fatty acid (stearic), 0.5–4 phr sulfur, and 0.5–2 phr accelerator. The fatty acid with zinc oxide forms a salt that can complex with accelerators, and its reaction products can complex with sulfur. Frequently, mixtures of accelerators are used.

### Chemistry

The general reaction path of accelerated sulfur vulcanization is thought to be as follows.<sup>2,8</sup> The 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., 2-benzothiazyl). The monomeric polysulfides interact with the rubber to form polymeric polysulfides, such as rubber- $\text{S}_x\text{-Ac}$  (sulfurated rubber). During this reaction, MBT is formed when a benzothiazole-derived accelerator is used and the elastomer is natural rubber. In SBR, the MBT becomes bound to the elastomer molecular chain, probably as the thioether rubber- $\text{S-Ac}$ . Finally, the rubber polysulfides react, either directly or through an intermediate, to give crosslinks (rubber- $\text{S}_x\text{-rubber}$ ). Accelerated vulcanization gives both improved crosslinking efficiencies and rates. The mechanisms and reactions of delayed action vulcanization are illustrated in Figure 4, in which the accelerator is a benzothiazolesulfenamide.

An increase in the concentration of fatty acid, with the accompanying increase in the concentration of

available  $\text{Zn}^{2+}$ , raises the overall rate in the early reactions, during the delay period, which lead to the formation of rubber- $\text{S}_x\text{-Ac}$ . However, the rate of crosslink formation is reduced, but the extent of crosslinking is increased. Here zinc chelation changes the position of the  $\text{S-S}$  bond most likely to break. Because a stronger bond must break, the rate is lower; however, the extent of crosslink formation is increased because less sulfur is used in each crosslink.<sup>9</sup> This is illustrated in Figure 5.

In natural rubber, increases in sulfur or accelerator concentrations result in higher crosslink densities; however, as the ratio of the concentration of accelerator to that of sulfur increases, the proportion of monosulfidic crosslinks increases. Greater amounts of accelerator (with respect to sulfur) also increase the number of pendent groups of the type  $\text{S}_x\text{-Ac}$ , which dangle from the rubber molecular chains. Higher ratios of the sulfur concentration to the accelerator concentration give both more polysulfide crosslinks and more sulfur combined with the rubber chains as sulfur-containing six-membered heterocyclic rings along the rubber molecular chains. In addition, conjugated olefinic double bonds appear along the polymer backbone chain. Such changes in the vulcanizate network structure are responsible for changes that occur in vulcanizate properties as a result of changes in the curing-system recipe. The best mechanical properties are obtained with long-chain polysulfidic crosslinks

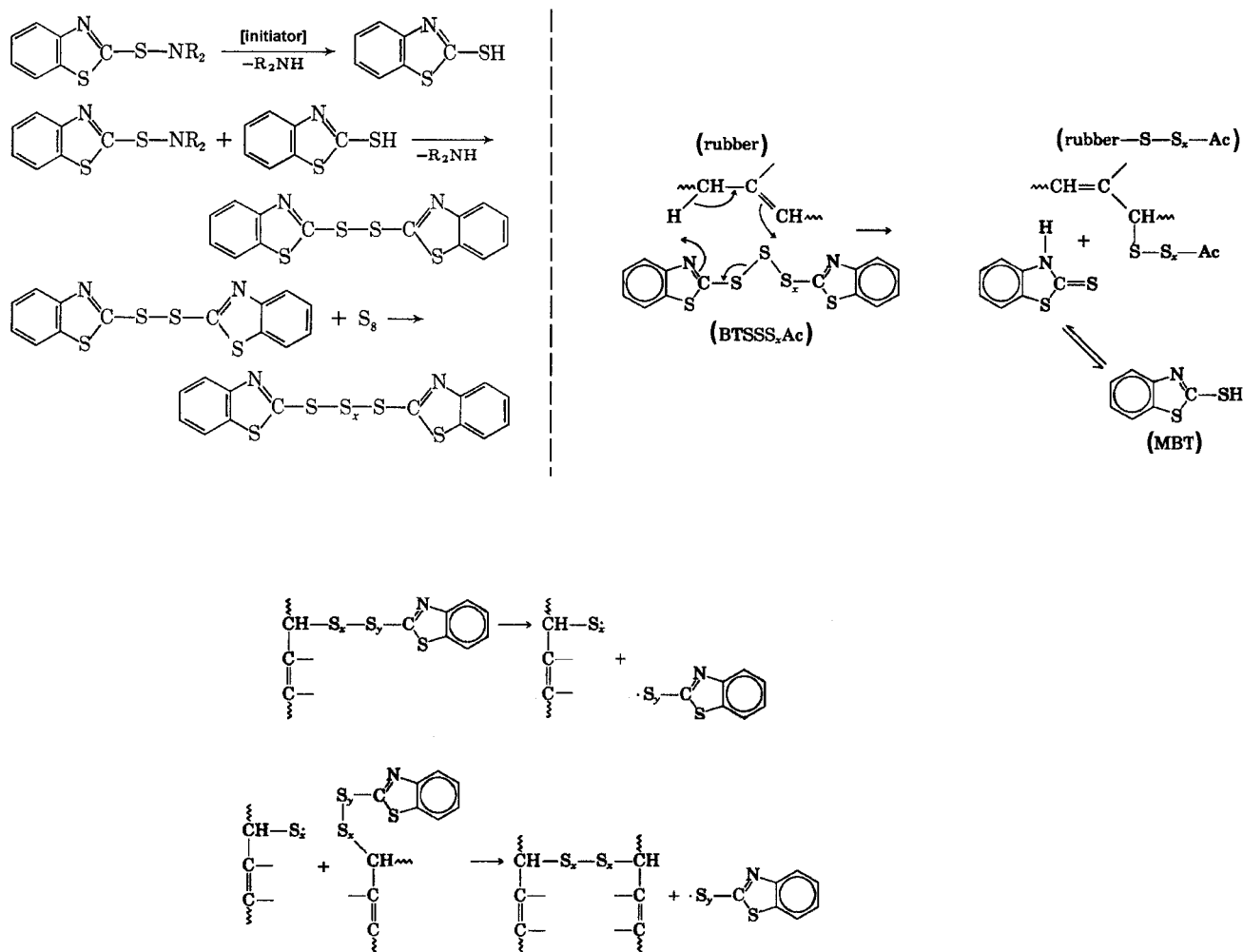


Figure 4 Reaction scheme for a benzothiazolesulfenamide-accelerated sulfur vulcanization.

but with little rubber main-chain modification (dangling groups and cyclic structures). Figure 6 schematically gives types of network structures found in natural rubber vulcanizates.

The chemistry of the accelerated vulcanization of BR, SBR, and EPDM has much in common with that of natural rubber. Before the formation of crosslinks, the rubber is first sulfurated by accelerator-derived polysulfides (Ac-S<sub>x</sub>-Ac) to give macromolecular, polysulfidic intermediates (rubber-S<sub>x</sub>-Ac). However, although with the MBTS- or benzothiazole-sulfenamide-accelerated sulfur vulcanization of natural rubber, MBT is given off during the formation of rubber-S<sub>x</sub>-BT (from the attack of rubber by BT-S<sub>x</sub>-BT), for BR and SBR, MBT is not eliminated and remains unextractable because it becomes bound as the thioether rubber-S-BT (BT is a 2-benzothiazolyl group.)

Non-sulfur vulcanizing agents include phenolic curatives, benzoquinone derivatives, bismaleimides, metal oxides, and organic peroxides.

### Delayed-action accelerated vulcanization

If the polymeric polythiyl free radicals (crosslink precursors) are rapidly quenched by an exchange reaction, with the monomeric polysulfides formed by reactions between the accelerator and sulfur, before they are able to form crosslinks, crosslink formation is impeded until there is substantial depletion of the monomeric polysulfides formed early in the process.<sup>10</sup> Also, the delay can be increased by the premature addition of a vulcanization inhibitor, *N*-cyclohexylthiophthalimide, which removes small amounts of MBT that form early in the process and are responsible for a reduction in the length of the induction period.

### Current and future research trends

<sup>13</sup>C-NMR methods have recently been used to study the chemistry of accelerated sulfur vulcanization with elastomer substrates.<sup>11</sup> <sup>1</sup>H-NMR (band broadening) and network visualization microscopy are being used

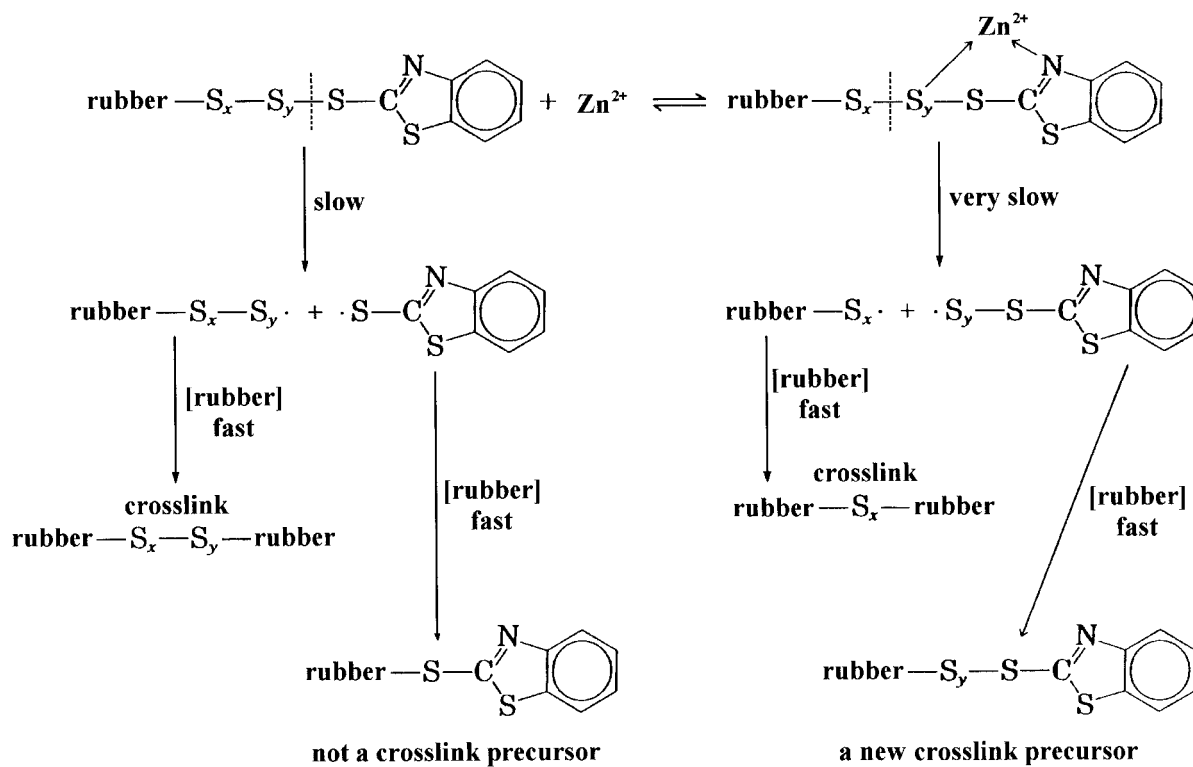


Figure 5 Reaction scheme for the effect of zinc ions on the rate and efficiency of crosslink formation.

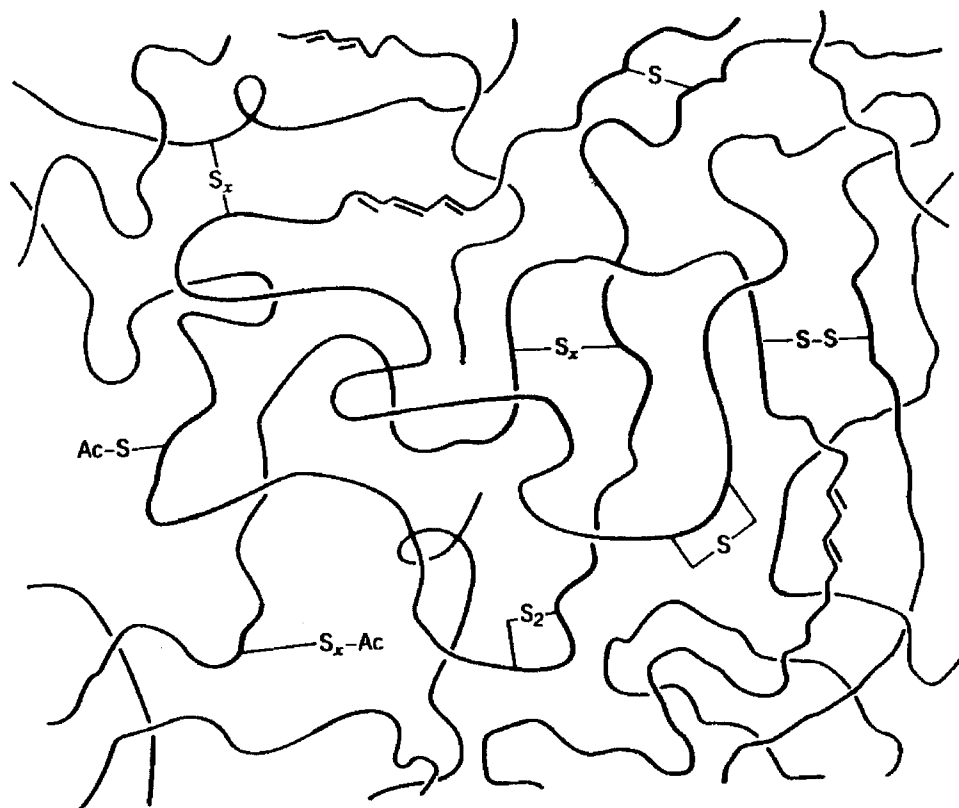


Figure 6 Crosslink types and chain modifications.

to determine crosslink densities in blend phases.<sup>12</sup> Model compound studies with dithiocarbamate-type accelerators have recently been carried out.<sup>13</sup> Here similarities and differences, with respect to benzothiazol-derived accelerators, have been found.

Accelerators based on secondary amines can release amines, which react with  $\text{NO}_x$  to form nitrosamines, suspected carcinogens. This is especially a problem with dithiocarbamate-type accelerators. Proposed accelerators that do not give carcinogenic nitrosamine derivatives include dibenzylamine-derived dithiocarbamates and accelerators based on sterically hindered amines.

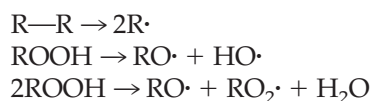
Thermoplastic elastomers are replacing some conventional rubbers, and those prepared by dynamic vulcanization, called thermoplastic vulcanizates, have finished properties very much like those of conventional rubbers, but they are processable like thermoplastics.

## PRESERVATION

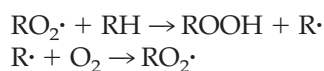
### Oxidation of polymers

The oxidative degradation of a polymer proceeds by a free-radical chain reaction mechanism. Initiation usually occurs by exposure to heat, light, or mechanical stress. The oxidation of hydrocarbons or related polymers by oxygen is an autocatalytic process, with the primary products being hydroperoxides.<sup>14</sup> Autoxidation occurs in three phases:

#### Initiation



#### Propagation



#### Termination



This uninhibited hydrocarbon oxidation model, however, ignores factors such as the relative differences between polymers, and it does not account for the fact that the nature and character of the propagating radicals are not the same for all polymers.

### Antioxidants

For rubber, the most effective antioxidants are the staining and discoloring derivatives of aryl amines; however, the need for nondiscoloring antioxidants has been met by the introduction of phenolic nonstaining antioxidants.<sup>15</sup> These types of antioxidants block the propagation of oxidation; in addition, there is an antioxidant regeneration process.<sup>16–19</sup>

Aromatic amines (e.g., *N,N'*-alkyl- and -aryl-substituted *p*-phenylene diamines) find applications as both raw polymer stabilizers and final vulcanizate stabilizers.<sup>19</sup> However, phenolics (i.e., 2,6-dialkyl-substituted) can be used in non-black-reinforced vulcanizates in which nonstaining and nondiscoloration are desired. With phenolic antioxidants, increased steric hindrance at the 2- and 6-positions results in improved antioxidant performance. Kuczkowski<sup>20</sup> proposed an optimum antioxidant hindrance of the phenolic group, which should be matched to the oxidizable matrix polymer.

In addition to the aforementioned phenolic and amine antioxidants, peroxide decomposers are used to harmlessly decompose peroxides, which otherwise could decompose to give free-radical propagating species, such as  $\text{R—O}\cdot$  and  $\text{H—O}\cdot$ . Examples of such peroxide decomposers, which act synergistically with phenolic and amine antioxidants, are dialauryl- $\beta,\beta$ -thiodipropionate and tris(*p*-nonylphenyl)phosphite.

### Ozonation

Atmospheric ozone reacts readily with  $\text{C}=\text{C}$  double bonds, leading to the breakage of molecules lying on the surface. As a result, small, deep fissures (i.e., ozone cracks) are formed if the rubber is stretched by more than about 10%. Cracks 1 mm long appear in unprotected rubber after a few weeks of exposure to typical outdoor ozone (ca. 5 parts per 100 million). Figure 7 suggests a mechanism for ozone cracking.<sup>21</sup>

### Antiozonants

The problem of antiozonant protection for rubber products was first noted in the 1930s after the introduction of the antiozonants *N*-phenyl- $\beta$ -naphthylamine<sup>22</sup> and *N,N'*-diphenyl-*p*-phenylene diamine.

Therefore, diamines (e.g., alkyl-aryl *p*-phenylene diamines, the same ones used as antioxidants) prevent cracking, probably by competing with the  $\text{C}=\text{C}$  bonds in rubber for the reaction with ozone. These antiozonants bloom to the surface and react there, protecting the rubber. Therefore, 0.5 to about 2–3 phr of an antiozonant is commonly included in the mix formulation of rubber compounds based on unsaturated elastomers. Examples of commercial *p*-phenylene diamines are *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine, *N*-cyclohexyl-*N'*-phe-



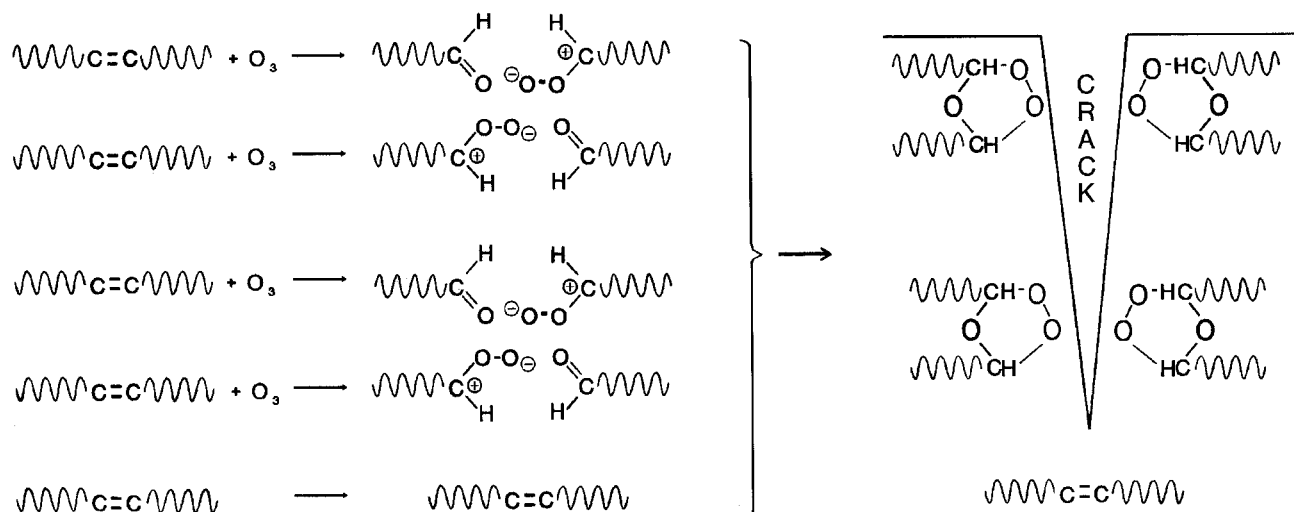


Figure 7 Suggested mechanism for ozone cracking.

nyl-*p*-phenylene diamine, and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine.

An additional method of protection (usually used with *p*-phenylene diamines) is the inclusion of a few parts per hundred parts of rubber of a microcrystalline paraffin wax in the formulation. The wax blooms to the surface and forms a protective skin. However, a protective skin from wax blooming to the rubber surface protects rubber goods only under the static conditions of application.

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