RUBBER COMPOUNDING

1. Introduction

Rubber compounding is the complex, multidisiplinary science of selecting and blending the appropriate combination of elastomers and other ingredients to meet the performance, manufacturing, environmental, and cost requirements for rubber goods made and used in commerce. There is a wide variety of elastomers and ingredients that are available in making rubber goods, which include all of the following types of products: tires, innertubes, retreaded tires, footwear, rubber rolls, hoses, belts, weatherstripping, O-rings, seals, diaphragms, tubing, rubber and latex gloves, ball bladders, medical devices, bumpers, and numerous other products. This is a review of the basic materials used in designing many common types of rubber products. The development of the combination of materials contained in a usable rubber compound involve many disciplines that include chemistry, physics, mathematics, and polymer science. In many cases, classical scientific methods can predict the interaction effects and estimate the properties expected from rubber compounds. However, discovery and development of new materials that modify the rubber compound to produce new, useful, and beneficial properties are appearing regularly. Also, environmental concerns are creating an interest in utilizing recycled rubber products into new rubber compounds.

2. Compounding Hierarchy

Compounding is a term that has evolved within the plastics and rubber industry and in many respects is a misnomer for the material science of modifying a polymer or polymer blend through addition of other materials to achieve a set of mechanical properties for a specific service application. Compounding is therefore a highly complex science involving many traditional disiplines such as organic chemistry, polymer chemistry, materials physics, mathematics, and engineering mechanics.

There are some excellent reviews and discussion papers on the science of rubber compounding (1–8). The purpose of this discussion is to provide an introductory overview of the range of materials used by the materials scientist in compounding elastomers. In designing or making the selection of ingredients for use in a rubber article, the technologist relies upon published literature, experimental work, competitive benchmark information, and various information sources such as raw material supplier data, technical documents, and reports. Raw materials for a compound are generally selected in the following order:

1. polymer (natural or synthetic rubber)
2. fillers or reinforcing agent
3. antioxidants and antiozonants
4. plasticizers or oils
5. bonding agent or adhesive (if needed)
6. tackifer (if needed)
7. vulcanization system [curing agent, accelerator(s), or coagent]

Performance requirements of the final product often dictate which specific type of elastomer can be used. The expected usable life for the product is controlled by many factors such as end-customer needs, competitive situation in the marketplace, safety, and reliability. Rubber products are almost always used as a functional part of another system. For example, tires, hoses, belts, O-rings, and numerous rubber components are used in manufacturing automobiles and trucks. The overall life of the vehicle as well as its performance level often relates to the service life or quality level of the rubber parts.

3. Elastomers Used in Rubber Compounding

Elastomers can be divided into two general categories, natural rubber and synthetic rubbers. Synthetic elastomers in turn are either termed *general purpose rubbers* (GPR) or *special purpose rubbers*. Natural rubber is generally obtained from southeast Asia or Africa. Synthetic rubbers are produced from monomers obtained from the cracking and refining of petroleum. The most common monomers are styrene, butadiene, isoprene, isobutylene, ethylene, propylene, and acrylonitrile. There are monomers for specialty elastomers which include acrylics, chlorosulfonated polyethylene, chlorinated polyethylene, epichlorohydrin, ethylene–acrylic, ethylene–octene rubber, ethylene–propylene rubber, fluoroelastomers, polynorbornene, polysulfides, silicone rubber, thermoplastic elastomers, urethanes, and ethylene–vinyl acetate.

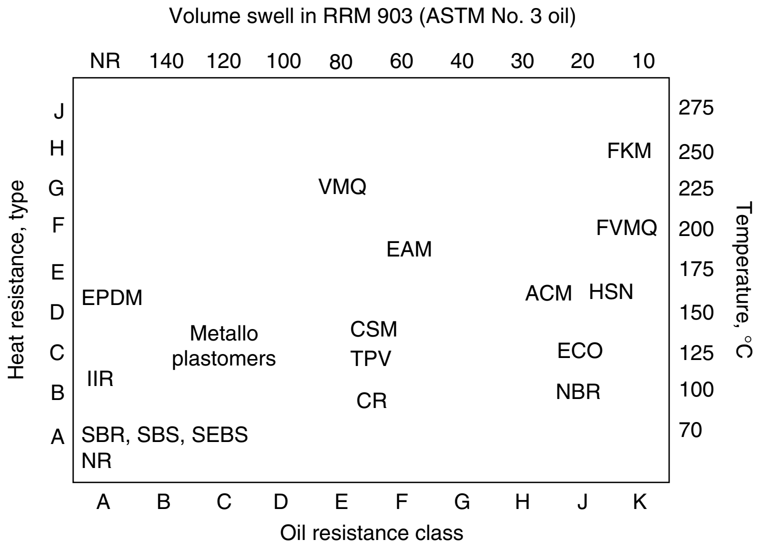


Fig. 1. SAE J200 classification systems for IRM 903 (ASTM No. 3) oil, where, for volume swell, NR = no requirement. Polymer abbreviations are defined in Table 1 (9,10).

Elastomers can be classified by their heat resistance and resistance to swelling (Fig. 1). The Society of Automotive Engineers (SAE) has developed a specification, SAE J200 (9), for classifying special-purpose elastomers by swelling in a special oil denoted IRM 903, which replaced ASTM (American Society for Testing and Materials) Number 3 (10). Properties for evaluating elastomers include hardness, tensile strength, change in tensile strength, elongation, and change in volume, tensile strength, and hardness after exposure to IRM 903 oil. However, probably the most effective classification system has been published by the International Standards Organization in specification ISO 1629 (11). Polymers containing residual unsaturation such as polybutadiene have abbreviations ending in −R (eg, BR), methylene containing polymers ending in −M (eg, ethylene propylene diene monomer, EPDM), silicone rubbers ending in −Q, oxygenates ending in −O, and urethanes ending in −U. A list of International Institute of Synthetic Rubber Producers (IISRP) abbreviations are shown in Table 1 (12). Table 2 displays typical general physical properties for a selection of the different types of elastomers including specifc gravity, hardness, tensile strength, and ratings for resilience, compression set, and permeability.

3.1. Natural Rubber. Natural Rubber is a biological homopolymer of isoprene and has the general structure illustrated in equation 1. The principal producing countries are Malaysia, Indonesia, Thailand, India, China, and Sri Lanka (see Rubber, natural). New sources are also being developed. To obtain natural rubber (NR), the Hevea brasiliensis tree is tapped for its sap. An off-white sap is collected and is coagulated by the addition of a strong acid such as sulfuric acid. The tapped latex consists of between 30% and 35% rubber, 60% aqueous serum, and 5 to 10% of other constituents such as fatty acids, amino acids and proteins, starches, sterols, esters, and salts. Some of the nonrubber substances, such as

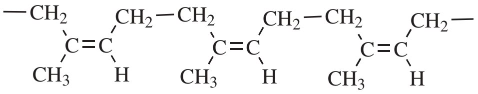
Table 1. **IUPAC Nomenclature for Selected Elastomers**[a]

AU	polyester urethane
BR	polybutadiene
BIIR	brominated isobutylene–isoprene (bromobutyl)
CIIR	chlorinated isobutylene–isoprene (chlorobutyl)
CPE	chlorinated polyethylene
CR	chloroprene rubber
CSM	chlorosulfonyl polyethylene
EAM	ethylene–vinyl acetate coploymer
EPDM	terpolymer of ethylene, propylene, and a diene with a residual unsaturated portion in the chain
EPM	ethylene–propylene copolymer
EU	polyether urethane
HNBR	hydrogenated acrylonitrile–butadiene rubber (highly saturated nitrile rubber)
IIR	isobutylene–isoprene rubber
IR	synthetic polyisoprene
NBR	acrylonitrile–butadiene rubber
SBR	styrene–butadiene rubber
E-SBR	emulsion styrene–butadiene rubber
S-SBR	solution styrene–butadiene rubber
X-NBR	carboxylated nitrile–butadiene rubber
X-SBR	carboxylated styrene–butadiene rubber
YSBR	block copolymers of styrene and butadiene

[a] From Ref. 12.

lipids, carotenoid pigments, sterols, triglycerides, glygolipids, and phospholipids, can influence the final properties of rubber such as compounded vulcanization characteristics and classical mechanical properties. Natural rubber is predominantly of the cis structure though the trans isomer, or *Gutta Percha*, can be found in latex tapped from the trees of the genus *Dichopsis*.

There are several systems that define the quality and uniformity of natural rubber. One system of grading natural rubber is based on form and visual observation of color and cleanliness. This is known as the International Natural Rubber Specification. The principal types and grades presented in Table 3 (13).



(1)

cis-Polyisoprene

Malaysian and Indonesian natural rubber growers have established a system based on technical characteristics. A summary of the standard technical specification scheme shown in Table 4 for natural rubber can be found in ISO 2000 (14,15). In addition to the solid form of natural rubber, it is available as a suspension in water and is known as latex. Synthetic rubbers are also available in latex form. Latex has become an important commodity used in the manufacture of

Table 2. **Physical Properties of Elastomers**[a]

Elastomer[b]	Specific gravity	Hardness Shore A	Tensile strength,[c] MPa[d]	Elongation,[c] %	Resilience[e]	Compression set[e]	Impermeability to gases[e]
NR	0.93	30–100	27.6	750	E	G	F
polyisoprene	0.92	30–100	24.1	750	E	F	F
SBR	0.94	35–100	20.7	600	G	G	F
butyl	0.92	30–90	17.2	700	P–F	P–F	E
polybutadiene	0.91	45–80	17.2	500	E	F	F
EPDM	0.86	30–90	20.7	600	G	G	F
chloroprene	1.23	35–95	20.7	600	G–E	F–G	F–G
nitrile	1.00	30–100	20.7	600	F–G	G	G
thiokol	1.25–1.35	20–80	10.3	450	P–F	P–F	E
urethane	1.02–1.25	55–100	55.2	750	F–E	G–E	P–F
silicone	0.98–1.60	25–90	10.3	800	F–G	G–E	P–F
CSM	1.12–1.28	40–95	20.7	600	F–G	F	G
acrylic	1.09	40–90	13.8	400	F–G	G	F–G
fluorocarbon	1.85	55–95	20.7	450	F	G–E	G–E
epichlorohydrin	1.27–1.36	40–90	17.2	400	F–G	F	E
chlorinated PE	1.16–1.25	45–95	24.1	600	F–G	F–G	G
cross-linked PE	0.92	90+	20.7	500	P	F	G

[a] Ref. 7.

[b] NR = natural rubber; SBR = styrene–butadiene rubber; EPDM = ethylene–propylene–diene monomer; CSM = chlorosulfonated polyethylene; and PE = polyethylene.

[c] Maximum value at room temperature.

[d] To convert MPa to psi, multiply by 145.

[e] E = excellent; G = good; F = fair, and P = poor.

Table 3. **Selected Categories of Visually Inspected Natural Rubber**[a]

Type	Grade	Description
1	ribbed smoked sheet	coagulated sheets, dried and smoked latex. Five grades are available
2	white and pale crepe	coagulated natural rubber latex milled to produce a crepe
3	estate brown crepe	fresh lump and other high quality scrap generated on the plantation
4	compo crepe	lump, tree scrapes, and smoked sheet cuttings milled to a crepe
5	thin brown crepe	unsmoked sheet, wet slab, lump, and other scrap from estates and small holdings
6	thick blanket crepe	wet slab, lump, and unsmoked sheets milled to give a crepe
7	flat bark crepe	all types of scrap natural rubber including earth scrap
8	pure smoked blanket crepe	milled smoked rubber derived exclusively from ribbed smoked sheet

[a] Ref. 13.

dipped goods for pharmaceutical applications. The principal uses of natural rubber are as follows: tires and tire retreading, 70%; latex (eg, gloves), 12%; mechanical goods, 9%; load-bearing components, 4%; and other, 5%.

3.2. Styrene–Butadiene Rubber. Styrene–butadiene rubber (SBR) is made by either an emulsion or solution process (eq. 2). The classification systems for emulsion SBR is shown in Table 5. In the emulsion process, it is more difficult to control polymer microstructure and the final product is not as pure as the solution form. However it tends to show a higher tensile strength and tear strength, and is easier to process. It is used in applications such as tire treads, sidewalls,

Table 4. **Technically Specified Rubbers Defined by ISO 2000**[a]

	Grade					
	TSR CV	TSR L	TSR S	TSR 10	TSR 20	TSR 50
dirt content, %wt max	0.05	0.05	0.05	0.1	0.2	0.5
ash content, %wt max	0.6	0.6	0.5	0.75	1	1.5
nitrogen content, %wt max	0.6	0.6	0.5	0.6	0.6	0.6
volatile matter, %wt max	0.8	0.8	0.8	0.8	0.8	0.8
initial Wallace plasticity $P_{0,\min}$		30	30	30	30	30
plasticity retention index, min	60	60	60	50	40	30
color, max (lovibond units)		6				
mooney viscosity	60 ± 5					

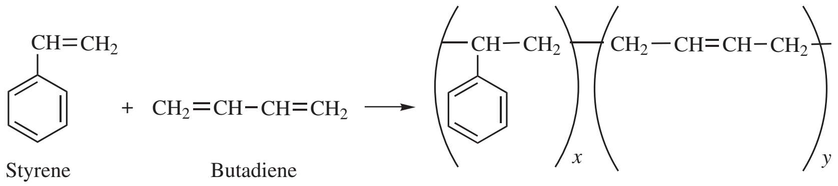
[a] Ref. 15.

Table 5. **Classification of Emulsion Polymerized Synthetic Elastomers by IISRP**[a]

Series	Description
1000	hot, nonpigmented emulsion SBR; polymerized above 38°C
1500	cold, nonpigmented emulsion SBR; polymerized below 10°C
1600	cold, nonpigmented emulsion SBR; carbon black/oil master batch/14 phr oil max
1700	oil extended cold emulsion SBR
1800	cold, nonpigmented emulsion SBR; carbon black/oil master batch. More than 14 phr oil
1900	emulsion resin rubber master batches

[a] Ref. 12.

bead wire insulation, ply and breaker compounds of bias tires, conveyor belt covers, and other industrial products not requiring oil resistance.



(2)

Solution SBR is classified as shown in Table 6. The principal use of solution polymerized SBR is in the tire industry as a major component of passenger and light truck tire treads (see STYRENE-BUTADIENE RUBBER). It is also finding application in radial medium truck tire drive axle tire tread, aircraft, farm tire treads, and large, off-the-road tires. It can replace emulsion SBR in ply compounds and even in sidewalls where a lower modulus is required. SBR uses in North America are tires, 75%; automotive mechanical goods, 8%; and other, 17% (14). Important properties of SBR are relatively low cost, good physical properties with the proper reinforcing agent, good abrasion, and skid resistance. A deficiency of SBR is its tendency to have fairly high heat generation (hysteresis).

3.3. Polybutadiene. The many forms that can result from the polymerization of butadiene, depending on the catalysts used, include high cis, medium cis, low cis, trans, and high vinyl polybutadiene (BR) as illustrated in equation 3

Table 6. **IISRP Classification of Solution Polymerized Stereo Polymers**[a]

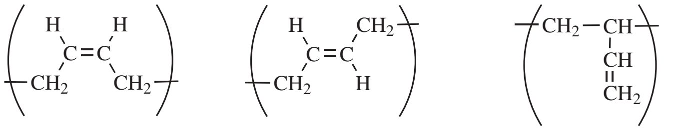
Category	Butadiene and copolymers	Isoprene and copolymers	Butadiene, isoprene, and styrene copolymers
dry polymer	1200–1249	2200–2249	2250–2599
oil extended	1250–1299	2250–2299	
black master batch	1300–1349	2300–2349	
oil-black master batch	1350–1399	2350–2399	
latex	1400–1449	2400–2449	
miscellaneous	1450–1499	2450–2499	

[a] Ref. 12.

Table 7. **Microstructure of Commercially Available Polybutadiene**

Catalyst	Typical expected microstructure		
	Cis, %	Trans, %	Vinyl, %
		(levels to ± 1%)	
Li	35	55	10
Ti	92–94	2–4	4
Co	96	2	2
Nd	98	1	1
Ni	96–98	0–1	2–4

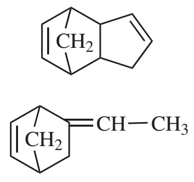
(see BUTADIENE). The property of polybutadiene of most interest to the rubber compounder is abrasion resistance coupled with good resilience (14). The polymer has very high rebound and low heat-generation values. With a few exceptions, such as the core of solid golf balls, the polymer is blended with other polymers to take advantage of its excellent abrasion resistance and hysteretic properties. Table 7 illustrates the effect the cataysts system has on polymer microstructure.


(3)

cis-1, 4-Polybutadiene *trans*-1, 4-Polybutadiene Vinyl-1, 2-Polybutadiene

3.4. Ethylene–Propylene Rubber.

Ethylene and propylene can be copolymerized to produce a wide range of elastomeric and thermoplastic polymers. Often a third monomer such as dicyclopentadiene, hexadiene, or ethylidene norbornene, illustrated in equation 4, is incorporated at between 2 and 12% into the polymer backbone, and therefore leads to the designation ethylene–propylene–diene monomer (EPDM) rubber (see ETHYLENE-ACRYLIC ELASTOMERS). The diene monomer introduces sites of unsaturation in the polymer that allow vulcanization by conventional sulfur curatives (16). At high levels of a third monomer, it is possible to achieve cure rates that are equivalent to conventional rubbers such as SBR and BR. Ethylene–propylene rubber (EPR) is typically vulcanized using a peroxide-based cure system.



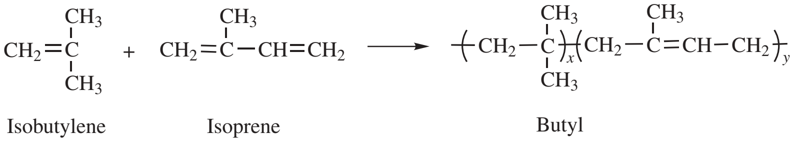
Dicyclopentadiene (DCPD)

Ethylidene norbornene (ENB) (4)

$H_2C{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$ 1,4-hexadiene (1,4-HD)

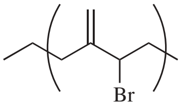
Variation of the ethylene–propylene ratio changes the viscoelastic properties of the rubber. The hardness can be varied widely by the filler and plasticizer level. In addition, EPDM can be highly extended with black and nonblack fillers, and oils. At high levels of fillers, EPDM can display very good resistance to swelling by the IRM 903 oil. The principal properties of EPR and EPDM are excellent weathering, good heat and water resistance, electrical insulation, and low temperature brittleness. As a result, EPDM is used in a wide variety of rubber goods. EPR elastomers are used in applications such as roofing, 20%; plastic modification, thermoplastic olefins (TPOs) and thermoplastic vulcanizates (TPVs), 17%; weather stripping, 15%; hoses and belts, 14%; oil viscosity modification, 10%; wire and cable, 6%; molded goods, 5%; tires, 3%; carpet backing, 2%; and other, 9% (14). EPR and EPDM have been made by either solution or emulsion polymerization processes and by gas-phase polymerization using metallocene catalysts.

3.5. Butyl and Halobutyl Rubber. Butyl rubber is made by the copolymerization of isobutylene with 1–3% isoprene (eq. 5), which is added to provide sites for curing. It is designated IIR because of these monomers. Halogenation of butyl rubber with bromine or chlorine increases the reaction rate for vulcanization (eq. 6). It is estimated that of the 200,000 kt of butyl (IIR) and halobutyl (HIIR) rubber manufactured in North America, over 90% is used in tire applications. The halogenated polymer is used in the innerliner of tubeless tires.



$$CH_2{=}C(CH_3)_2 + CH_2{=}C(CH_3){-}CH{=}CH_2 \longrightarrow {-}\!\left(CH_2{-}C(CH_3)_2\right)_x\!\left(CH_2{-}C(CH_3){=}CH{-}CH_2\right)_y\!{-} \qquad (5)$$

Butyl rubber is used to make innertubes and curing bladders (see BUTYL RUBBER). Butyl polymers are about eight times more resistant to air permeability compared to natural rubber and have excellent resistance to heat, steam, and water. This accounts for its use in gaskets and diaphragms for hot water and steam services. In addition, butyl rubber can be compounded to have low resilience properties and has found use in high damping mounts for engines, motors, and similar devices (6,17,18).



(6)

Most common isomer of bromobutyl (or chlorobutyl) rubber

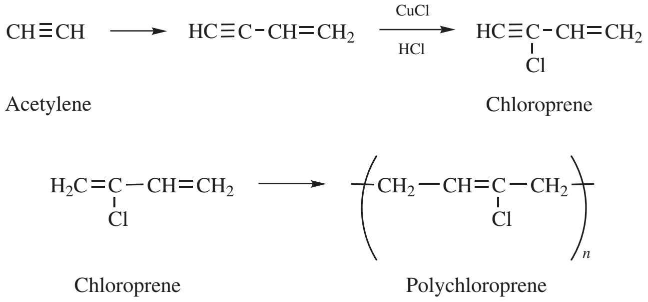
3.6. Special-Purpose Elastomers. Polychloroprene and polysulfide rubber were the first synthetic specialty elastomers discovered. Since their invention in the 1930s the total number of classes of synthetic rubbers has grown to almost 30. Table 1 has listed standard acronyms by the International Institute of Synthetic Rubber Producers (12).

Chloroprene Elastomers. Polychloroprene is made by polymerizing 2-chloro-1,3-butadiene (eq. 7). The elastomer is largely composed of the trans isomer. There are three major polymer types: the G-type, the W-type, and the T-type.

1. G-types are made by using a sulfur-modified process. G-type polymers possess excellent processing and dynamic properties, and are thus used in applications such as V-belts. However, they have poorer aging properties than W-types. They contain sulfur and tetramethylthiaram disulfide (TMTD) and they can be cured with only a metal oxide.
2. W-types use no sulfur modification. The W-type polymers tend to be used in applications requiring better aging, such as rolls and mechanical goods (see Chloroprene). W-type polychloroprenes require an organic accelerator.
3. T-types are similar to W-type polychloroprenes but contain a high level of gel, which in this instance offers improvements in processing. They find use where fast, uniform extrusions and calendering is required.

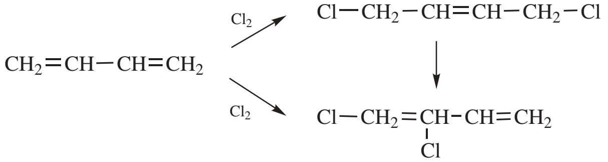
Polychloroprene is made from one of two starting materials, acetylene or butadiene. Acetylene can be dimerized and then chloronated to form chloroprene. Alternatively, when adequate butadiene is available, this can be directly halogenated (eqs. 7 and 8). In either case, the chloroprene product can then be polymerized to polychloroprene. Essentially a butadiene elastomer with chlorine present in the backbone,the polymer exhibits excellent tensile strength and low hysteresis, much like natural rubber. Tensile strength properties up to 28 MPa are possible with the proper reinforcing system (see Fillers). The polarity imparted by the chlorine atom improves the oil and solvent resistance approaching those of nitrile polymers. The polymer can be protected with *para*-phenylenediamine antiozonants to give ozone resistance, and heat aging is also good. As a result, chloroprene elastomers are used in a wide variety of applications needing a balance of such properties.

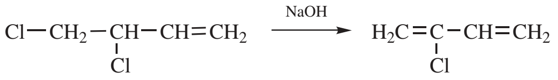
Principal uses include automotive V-belts, industrial and hydraulic hoses, specialty roofing, heels and soles in footwear, wire covering, and a wide variety of coated fabric uses, eg, rafts. Polychloroprene elastomers are also used extensively in adhesives. It is estimated that about 77,000 ton of polychloroprene are used each year in the United States (4,7,19).



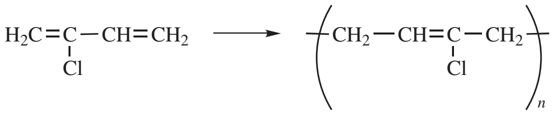
$$\mathrm{CH{\equiv}CH} \longrightarrow \mathrm{HC{\equiv}C{-}CH{=}CH_2} \xrightarrow[\mathrm{HCl}]{\mathrm{CuCl}} \mathrm{HC{\equiv}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2}$$

$$\mathrm{H_2C{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2} \longrightarrow \left(\mathrm{CH_2{-}CH{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH_2}\right)_n \tag{7}$$





$$\mathrm{Cl{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH{=}CH_2 \xrightarrow{NaOH} H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2} \tag{8}$$



$$\mathrm{H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left(CH_2{-}CH{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_2 \right)_n}$$

Chloroprene Polychloroprene

Chlorinated Polyethylene. Under pressure, polyethylene can be chlorinated to produce a polymer having a halogenated monomer content varying from 25 to 42%. The polymer requires the incorporation of carbon black and minerals for achieving good physical properties. The polymers handle like conventional polymers and can be mixed and processed on conventional rubber equipment. Chlorinated polyethylene (CPE) has excellent ozone, oil, and heat resistance, and as a result chlorinated polyethylene has replaced chloroprene elastomers. CPE has a lower specific gravity than chloroprene compounds and produces compounds that are similar to CR in properties but with lower costs. Also, because of high levels of chlorine, the flame resistance of compounds of CPE are high.

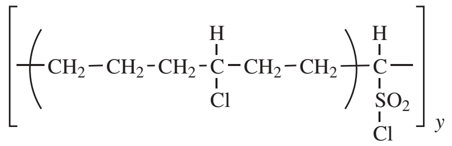
$$\mathrm{\left[CH_2{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n} \tag{9}$$

Chlorinated polythylene

An estimated 18 kt of these elastomers is used per year. The main uses of CPE are in construction, automotive, and electrical applications. These include power steering hose, electrical cords used in low voltage applications (extension cords, ignition wire), pond liners, and as a plastic modifier to improve impact modification.

Chlorosulfonated Polyethylene. This elastomer is made by the simultaneous chlorination and chlorosulfonation of polyethylene in an inert solvent. The resulting polymer is an odorless, colorless chip that is mixed and processed on conventional rubber equipment (2). The polymer (eq. 10) typically contains between 20 and 40% chlorine and 1% sulfur (see ETHYLENE POLYMERS, CHLOROSULFONATED). The polymer requires compounding with normal fillers to produce useful properties. Chlorosulfonated polyethylene (CSM) excels in resistance to attack by oxygen, ozone, corrosive chemicals, and oil, and in addition has very good electrical properties. The physical properties and abrasion resistance are also good. Light-colored articles made from CSM have excellent color-fastness.

Because of the presence of chlorine atoms, this elastomer also shows good flame resistance.



$$\left[\left(-CH_2-CH_2-CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-CH_2- \right) -\underset{\underset{Cl}{SO_2}}{\overset{H}{C}}- \right]_y \qquad (10)$$

Chlorosulfonated polyethylene

CSM is extensively used in construction and electrical applications. This includes roofing membranes, automotive ignition boots and wires, roll compounds, and some automotive hoses requiring good heat and oil resistance, eg, air conditioning and power steering hoses. It is also used in nuclear power plants because of its excellent resistance to radiation degradation. Chlorosulfonated polyethylene is sold under the trade name Hypalon.

Fluoroelastomers. Fluoroelastomers were introduced to the rubber industry in the late 1950s. They were made by modification of Teflon polymers and designed to have excellent heat and chemical resistance, but remain elastomeric in nature. With the increasing demand in the automotive and industrial market for improved reliability and longer in-service life, fluoroelastomers have made significant inroads into these applications (see FLUOROCARBON ELASTOMERS). Compared to all other elastomers, fluoroelastomers excel in heat, chemical, flame, weathering, fuel, and ozone resistance. In addition, oil, oxygen, and water resistance are very good. Fluoroelastomers, however, are attacked by amines and some highly polar solvents. Abrasion resistance and low temperature properties are adequate for most applications.

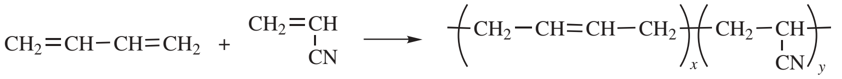
Seals and gaskets in the marine, oilfield, and chemical processing industries employ fluoroelastomers. In addition, many hoses in the automotive and chemical industry are made entirely of fluoroelastomer compounds or have a veneer of the fluoroelastomer as a barrier exposed to the harsh environment.

Epichlorohydrin. Commercial polyester elastomers include both the homopolymer and the copolymer of epichlorohydrin with ethylene oxide. The very polar chloromethyl group creates basic resistance to oil for these polymers, and they have been extensively used in fuel lines; however, the desire for lower fuel permeation is causing a search to be made for other polymers (20). Epichlorohydrin (ECO) has excellent resistance to fuel and oil swell. The ECOs show a volume swell of 35% at room temperature compared to 70% for a medium ACN–nitrile rubber in ASTM Reference Fuel C. The copolymer has a low temperature brittle point of −40°C; and the homopolymer, −15°C. An interesting property of these elastomers is a stable dynamic performance over a wide temperature range; however, the electrical properties are only average.

The principal uses of ECO are in automotive applications; eg, for fuel line and fuel vapor recirculation. There are also some downhole seal applications where ECO is used.

3.7. Nitrile and Acrylic Rubber. Nitrile rubbers are made by the emulsion copolymerization of acrylonitrile (9–50%) and butadiene (21) and are abbreviated NBR (eq. 11). The ratio of acrylonitrile (ACN) to butadiene has a direct effect on the properties and the nature of the polymers. As the ACN content increases, the oil resistance of the polymer increases (14). As the butadiene content increases, the low temperature properties of the polymer are improved. Nitrile rubber is much like SBR in its physical properties. It can be compounded for physical strength and abrasion resistance using traditional fillers such as carbon black, silica, and reinforcing clays. The primary benefit of the polymer is its oil and solvent resistance. At a medium ACN content of 34% the volume swell in IRM 903 oil at 70°C is typically 25–30%. Nitrile rubber can be processed on conventional rubber equipment and can be compression, transfer, or injection molded. It can also be extruded easily. Nitrile rubber compounds have good abrasion and water resistance. They can have compression set properties as low as 25% with the selection of a proper cure system. The temperature range for the elastomers is from −30 to 125°C. The compounds are also plasticized using polar ester plasticizers.

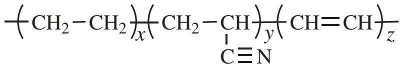
Applications requiring good oil resistance and moderate heat aging are the principal uses of nitrile rubber compounds. The automotive industry has been the primary consumer of nitrile rubber based products with hoses, fuel lines, and numerous O-rings and seals representing typical applications. In addition many rolls in the printing industry are made from nitrile rubber. However, fluoroelastomers, silicone, epichlorohydrin, and acrylic elastomers have been replacing nitrile rubber for better durability and longer service life.



$$CH_2{=}CH{-}CH{=}CH_2 + \underset{CN}{\underset{|}{CH_2{=}CH}} \longrightarrow \left(CH_2{-}CH{=}CH{-}CH_2\right)_x\left(CH_2{-}\underset{CN}{\underset{|}{CH}}\right)_y \tag{11}$$

Nitrile elastomers

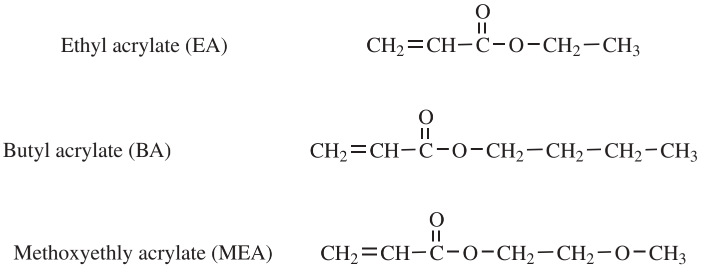
For compounding of nitrile elastomers, reference should be made to model formulations for a range of applications where such polymers are used (22). Hydrogenation of nitrile rubber improves the aging properties of the oil-resistant backbone. The polymers are available with acrylonitrile contents from 17 to 50% and residual double-bond unsaturation from 2 to 20% (eq. 12). In addition to outstanding oil resistance and improved aging properties, the abrasion resistance of the polymers is very good. The basic polymer is quite polar, giving inherent resistance to swelling in oils or gasoline, but can be affected by ketones, halogenated solvents and oils, and oxygenated solvents. They have a service range from −45 to 149°C. Hydrogenated nitrile rubber (HSN or HNBR) compounds compete with FKM, FVMQ, ECO, ACM, and high ACN content nitrile rubbers. Major applications include automotive timing belts, blow-out preventors, drill pipe protectors, and numerous oil and fuel pump components.



$$\left(CH_2{-}CH_2\right)_x\left(CH_2{-}\underset{C\equiv N}{\underset{|}{CH}}\right)_y\left(CH{=}CH\right)_z \tag{12}$$

Hydrogenated NBR
y = 17–50%
z = 1–15%

Acrylic elastomers possess good oil and heat resistance. They are made by polymerizing monomeric acid esters of ethyl or butyl acrylate and methoxyethyl acrylate or ethoxyethyl acrylate. They can be polymerized in emulsion, suspension, or solution systems (8). The polyacrylates are inherently tacky and soft. They require compounding with carbon black or mineral fillers for achieving useful properties. Their main properties are a temperature performance range of −40 to 175°C. They have good resistance to oils, oxidation, ozone, aliphatic solvents, sunlight, and weathering, and exhibit low permeability to gases. The tensile strength is usually 7 to 14 MPa (1000–2000 psi). Compounds can be fabricated with Shore A hardness values ranging from 40 to 90.



Ethyl acrylate (EA) $CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3$

Butyl acrylate (BA) $CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ (13)

Methoxyethly acrylate (MEA) $CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}O{-}CH_3$

The major monomers used in in polyacrylates are shown in equation 13. It is estimated that 9000 ton of these elastomers are used annually in the United States, principally in automotive applications requiring both oil and heat resistance. These include transmission, valve stem, crankshaft, pinion, and oilpan gaskets and seals. In addition, hoses, tubing, rolls, and belts are made from acrylic polymers (2,7).

3.8. Other Special Polymers. There are a variety of other polymers which, though when compared to the general-purpose polymers such as SBR, are used in low quantities but still merit discussion. These include elastomers such as polysulfides, silicone rubbers, and polyurethanes. Each are considered in turn.

Polysulfides. Polysulfides are also called Thiokol's (T) after the company that originally made them. They were discovered in 1927 (see POLYMERS CONTAINING SULFUR, POLYSULFIDES). Thiokol elastomers have low tensile strength and tear strength properties. However, they have good resistance to both aliphatic and aromatic solvents at room temperature and at slightly elevated temperatures. It is estimated that 1.4 to1.6 kt are used annually in the United States. The primary use of polysulfide elastomers are in seals, gaskets, rolls, and diaphragms where solvent resistance and low permeability are required.

Silicones. Silicone elastomers have a siloxane (–Si–O–Si–) backbone with methyl, vinyl, or phenyl groups attached. The elastomers are designated by their chemical composition as follows: methyl silicone (MQ), methyl vinyl silicone (VMQ), methyl phenyl silicone (PMQ), methyl phenyl vinyl silicone (PVMQ), and fluorovinyl methyl silicone (FVMQ). Silicone elastomers possess good resistance to heat aging. The siloxane backbone imparts resistance to oxygen, ozone, UV light, and to some polar fluids. However, the tensile strength of these elastomers is usually low. They also have low abrasion resistance and tear strength (see SILICONES). By fluorinating the silicone polymer it is possible to improve the solvent, fuel, and oil resistance of this already heat-resistant class of elastomers. The resulting polymers are especially useful in select automotive seals and gaskets, military, and oilfield equipment parts. Fluorosilicones (FVMQ) have excellent low temperature flexibility properties coupled with good oil, fuel, and solvent resistance and excellent aging properties. The materials are compounded and reinforced with fine particle fillers such as silica. The materials are mixed and processed on especially clean equipment and are peroxide-cured. The primary uses of these elastomers are in O-rings, shaft seals, wire and cable, and electrical connectors.

Urethanes. Urethane elastomers are prepared by the reaction of an isocyanate molecule with a high molecular weight ester or ether molecule. The result is either an elastomeric rubber form or a liquid prepolymer that can be vulcanized with an amine or a hydroxyl molecule (see POLYURETHANES). Urethanes are processed as rubber-like elastomers, cast systems, or thermoplastic elastomers. The elastomer form is mixed and processed on conventional rubber mills and internal mixers, and can be compression, transfer, or injection molded. The liquid prepolymers are cast using automatic metered casting machines, and the thermoplastic pellets are processed like all thermoplastic materials on traditional plastic equipment. The unique property of polyurethane is high abrasion resistance and moderately high Shore A (75–95) hardness. In addition, tear strength, tensile strength, and resistance to swelling by many oils is very high. The main deficiencies of the urethanes are their resistance to heat over 100°C and that shear and sliding abrasion tend to make the polymers soft and gummy. It is estimated that close to 68,000 ton of these rubbers are used per year in the United States if all forms are included. Uses include sport wheels (roller blades, ski wheels); printing, paper, and steel processing rolls; gears; pump liners; appliance components; and solid industrial tires.

Vinyl Acetate–Ethylene Copolymers. Vinyl Acetate–Ethylene copolymers would also fall into this category. In these random copolymers, the ratio of ethylene to vinyl acetate (EVA) is varied from 30 to 60%. As the vinyl acetate content increases, the oil and heat resistance increases. With higher ethylene content the physical strength, tensile, and tear increases. The polymers are cured with peroxides. The main properties of these elastomers include heat resistance, moderate oil and solvent resistance, low compression set, good weather resistance, high damping, and excellent ozone resistance, and they can be easily colored (see VINYL ACETATE POLYMRS). Applications include automotive electrical system components, eg, ignition cable, footwear, weather stripping, and miscellaneous O-rings and seals for industrial applications.

4. Fillers for Rubber

Fillers are particulate materials added to improve the physical properties and optimize the cost of the rubber compound (see FILLERS). All particulate fillers increase the hardness and stiffness of rubber compounds. The chemical composition and its effect on rubber compound physical properties typically classify fillers into three broad categories: nonreinforcing, semireinforcing or extending, and reinforcing fillers. Reinforcing fillers improve the physical properties of the rubber vulcanizate, while some fillers simply act as diluents or extenders.

Improvements in rubber compound physical properties are directly related to the filler particle size, whereby the smaller particulate fillers impart greater reinforcement. Particle-size distribution and particle shape also have significant effects on composite reinforcement. Filler structure ranges from precise geometrical forms, such as spheres or hexagonal plates, to irregular masses. A particle with a high aspect ratio has higher reinforcement than a more spherical one. Fillers having a broad particle-size distribution have better packing in the rubber matrix and provide lower viscosity than that provided by an equal volume of the filler with a narrow particle-size distribution. The properties of particulate-filled elastomers are determined by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the polymer-filler interfacial interactions.

A wide variety of particulate fillers are used in the rubber industry. Carbon black is the filler of choice. All grades, with the exceptions of N880 and N990 thermal blacks, reinforce rubber with the finest particle-size carbon blacks imparting the highest degree of reinforcement based upon improved abrasion resistance, tear strength, tensile strength, and stiffness. A number of mineral fillers are used in the rubber industry to extend and/or reinforce elastomers. They include carbonates, clays, silicas, silicates, and talc. However, when compared to carbon black, the use of nonblack fillers by the tire and rubber industry is limited.

4.1. Carbon Black. This is the primary reinforcing filler used in the rubber industry. Carbon black can be made by three processes: the furnace process, the thermal process, and the channel process. Over 97% of black is made by the furnace process (see CARBON BLACK).

The furnace process involves spray injection of a low end fraction of crude oil into a heated chamber. The temperature, shape of the injectors of the oil, rate of injection, shape of the reactor, and other factors are controlled to produce carbon black fillers of different particle sizes and structures. The particle size and structure control and the reinforcing character of carbon black are the bases of their classification system (Table 8). There are approximately 30 common grades of carbon black used in the rubber industry. There are also numerous specialty grades produced for use in plastics, conductive applications, and proprietary grades produced for use in tires and other special-purpose products (14).

Carbon black primarily owes its reinforcing character to the size and shape of the aggregate structure; for example see Figure 2. An aggregate

Table 8. **Tire and Industrial Products Carbon Black Categories**[a]

Type	ASTM designation	Particle size, nm	Application
SAF	N110	11–19	tires
ISAF	N220	20–25	tires
HAF	N330	26–30	tires
FF	N475	31–39	industrial products
FEF	N550	40–48	tires, industrial products
GPF	N660	49–60	tires, industrial products
SRF	N762	61–100	industrial products

[a] Ref. 14.

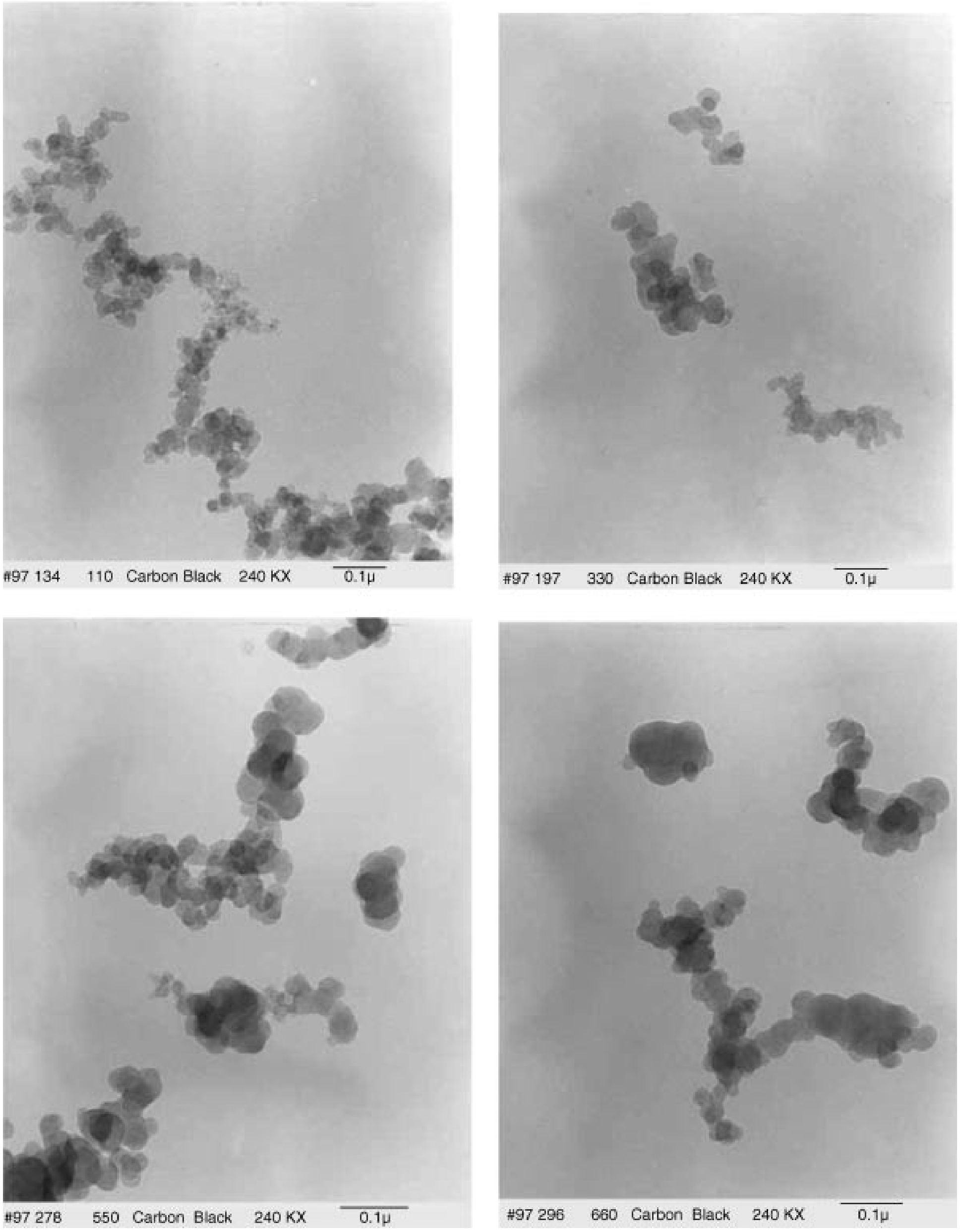


Fig. 2. Electron micrographs illustrating particle structure of carbon blacks N110, N330, N550, and N660.

consists of primary particles essentially spherical in shape that are chemically bonded (fused) to one another. The two most important properties of carbon black are surface area and structure. Surface area depends inversely upon the size of the primary particles, and is one measure of the area available for physical interaction with an elastomer. The structure of carbon black depends upon the size and grouping of these primary particles in the aggregate. The more the primary particles in the aggregate, the higher is the structure of the carbon black due to the more complex shape and void volume (porosity). Surface activity refers to the strength of the carbon black/rubber interaction either from nonbonded physical interactions or chemisorption. The small (2–3%) but significant amount of noncarbon atoms, such as hydrogen, oxygen, and sulfur, that are present on the carbon black surface results in surface activity differences. During mechanical mixing with polymers, it is desirable to minimize the presence of agglomerates, which are physically associated aggregates. Aggregate structures are not thought to be broken down into primary particles by simple mechanical processes such as mixing, milling, etc.

The structure of the carbon black is determined by dibutyl phthalate (DBP) absorption and the surface area is estimated by nitrogen or CTAB absorption (Table 9).

Carbon blacks are also classified into reinforcing, semireinforcing, and extender blacks. The furnace blacks from N100 through N300 are considered reinforcing blacks based on the increase in tensile strength observed when they are incorporated into rubber. They are sometimes referred to as *hard blacks*, and are used in treads, black sidewalls, casings, and breaker compounds of radial passenger and truck tires. In addition, they are commonly used in the covers of belts, a few select hose compounds, and other rubber goods requiring high tensile strength, tear strength, modulus, and good abrasion resistance.

Table 9. **Common Commercial Grades of Carbon Black**[a]

ASTM Designation	Iodine number	DBP	Compressed DBP	CTAB	Nitrogen absorption	Tint strength
N110	145	113	98	126	143	124
N115	160	113	96	128	145	123
N121	121	132	112	121	132	121
N220	121	114	100	111	119	115
N231	121	92	86	108	117	117
N234	120	125	100	119	126	124
N299	108	125	105	104	108	113
N326	82	72	69	83	84	112
N330	82	102	88	82	83	103
N339	90	120	101	93	96	110
N347	90	124	100	87	90	103
N351	68	120	97	73	73	100
N375	90	114	97	96	100	115
N472	250	178	114	145	270	
N550	43	121	88	42	42	
N630	36	78	62	35	38	
N660	36	90	75	36	35	
N762	27	65	57	29	36	
N772	30	65	58	33	29	
N990		43	40	9	6	
N991		35	38	8	7	

[a] Refs. 14,23.

The N500 through N700 series carbon blacks are considered semi-reinforcing blacks. These are used widely in bias and radial tire casings, innerliners, beads, squeeges, and other tire components not requiring the ultimate in strength and abrasion. They are also used in matting, roofing, curing bladders, and innertubes.The N900 series thermal blacks are viewed as extender blacks because of the limited reinforcement they provide for the rubber compound. All semi-reinforcing carbon blacks are often referred to as *soft blacks*.

4.2. Mineral Fillers.

Mineral fillers are naturally occurring materials that are mined and are ground to a specified particle size (24,25). Grinding may be done dry using mechanical mills. For a finer product the ore is ground wet. Wet grinding may be autogenous where the ore grinds by attrition with itself or a grinding media may be employed. Additional processing may include a combination of steps. They include (*1*) separation of fine and coarse particles by use of screens, by air or water flotation, or by centrifugal filtration (*2*) removal of impurities by washing, heat treatment, magnetic separation, or chemical treatment and/or (*3*) surface treatment with a variety of chemicals to improve the compatibility with the rubber matrix.

Calcium carbonate is usually derived from a naturally occurring source, such as calcite or whiting, by wet grinding. Precipitated and synthetic calcium carbonates are available in high purity; typically have a higher surface area, finer particle size, and narrower particle-size distribution; and thus a higher degree of reinforcement. Kaolin clay, a hydrated aluminum silicate, is one of the most abundant silicate minerals. Depending upon the type of processing, kaolin can be categorized as air-floated, water-washed, calcined, or surface-treated. Kaolin has the finest particle-size range of any naturally occurring mineral. Silicas are categorized as naturally occurring such as crystalline and diatomaceous earth, or as synthetic silicas which include precipitated silica, pyrogenic (fumed) silica, and silica gel. Crystalline silica is an inert, abrasive, large particle obtained from grinding sand or quartz. Diatomaceous earth or dolomite is obtained from sedimentary rocks and often contains up to 30% organic matter and inorganic impurities such as sand, clay, and soluble salts. Precipitated and pyrogenic silicas are high surface areas, fine-particle reinforcing fillers (see Fig. 3). Talc is a hydrated magnesium silicate with a morphology and purity varying according to the mining location.

Among the nonblack fillers, the highest hardness is provided by rod-shaped or plate-like particles, which can orient parallel during processing, compared to spherical particles of similar diameter. Uses of clay in rubber produces compounds with high hardness values. Clay is further classified as a hard clay if it reinforces rubber also imparting high modulus, tensile strength, and resistance to abrasion, or as a soft clay if it produces a compound with lower physical properties. Of the spherical particulate fillers, precipitated silicas, surface-treated clays, and calcium silicates also produce high hardness and high modulus compounds (see Fig. 4). The highest tensile strengths are produced in rubber compounds by using precipitated silicas. Calcium silicate and surface-modified clay also afford high tensile strength compounds, followed by use of zinc oxide, carbonates, and hard clay. No other nonblack filler approaches the precipitated silicas for imparting abrasion resistance.

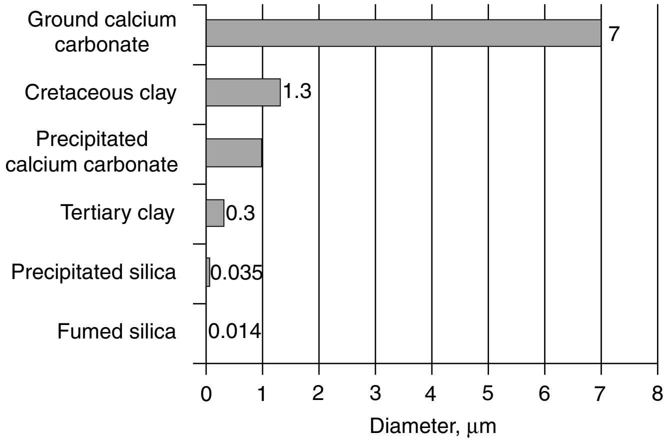


Fig. 3. Median particle diameters of nonblack fillers.

Calcium Carbonate. Calcium carbonate ($CaCO_3$) is also known as whiting, limestone, marble, chalk, or calcite. It has been ground and added to rubber compounds to reduce cost and to impart hardness and opacity to rubber articles. Particle sizes range from 2 to 80 µm for dry-ground product and from 0.5 to 11 µm for wet-ground product. The chemical composition and crystalline nature depend on the limestone deposit that is mined, for example chalk or marble, and the color of the deposit.

Important applications of calcium carbonate in the rubber industry include use in electrical wire and cable insulation where the low moisture content and natural insulating properties make it a preferred filler, in the production of articles where low cost and smooth surface appearance are desired, such as footwear, and in extruded hoses and automotive sealing parts.

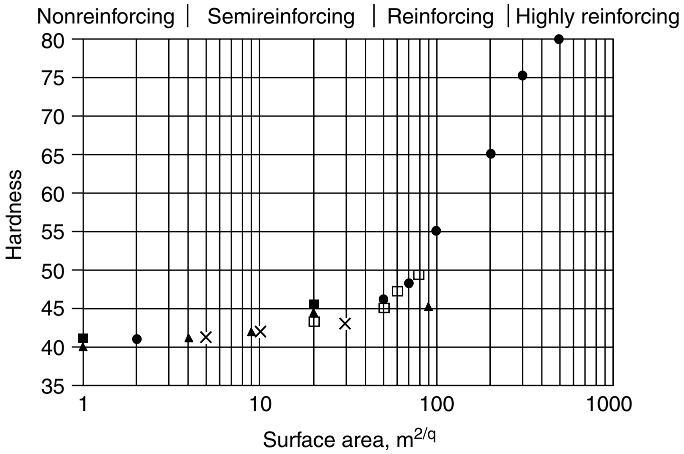


Fig. 4. Reinforcing effect on hardness of nonblack fillers with different surface areas. ● Silica, ■ talc, ▲ calcium carbonate, × soft clay, □ hard clay.

Clay. Kaolin clay, also called kaolinite or China clay, is hydrous aluminum silicate [$Al_2Si_2O_5(OH)_4$] consisting of platelets with alternating layers of silica and alumina in the structure. The weathering of granite forms fine particles of clay. Clay deposits are classified as primary, secondary, and tertiary. Primary deposits are mixtures of clay and granite found where they were originally weathered, and contain only 40 to 50% particles less than 2 μm in diameter. Secondary deposits form when fine particles from primary deposits flow and are deposited in a new location. Tertiary deposits are the most important commercial deposits because of their fine particle size, with >80% of the particles being less than 2 μm in diameter. Their high purity results when water carries the fine particles of a secondary deposit to a new location.

Clay can be generally divided into soft and hard clays on the basis of their producing softer and harder rubber compounds at a given loading level. There are several processes for producing clay for rubber reinforcement from the mined form: (*1*) Air-floated clay, in which the ore is milled to break up lumps and air classified, is the least expensive form of clay and imparts moderate reinforcement. (*2*) Water-washed clay involves gravity separation of impurities, bleaching, magnetic separation to improve color properties, and centrifuging to produce the desired particle size range to impart higher reinforcement by the control of pH, color, and particle size. (*3*) Delaminated kaolin uses chemical and/or mechanical means to break apart the platelet structure of the clay, which further increases the available surface area and reinforcement properties. (*4*) Metakaolin is partially calcined by heat treating to 600°C. (*5*) Calcined clay is formed by heating to 1000°C, which produces a very white, high surface area mineral with an inert surface.

Clays are used as a filler for many rubber goods. The natural air-floated and water-washed clays are considered semi-reinforcing fillers for most rubber compounds. They are used in large volumes by the footwear, mat, industrial tire, and mechanical goods manufacturers. In addition, a small amount of clay is used by the tire industry in innerliners and white sidewalls, using the clay as an extender filler in low to medium dynamic stress applications. Clays are also used as partitioning agents in slab dips and antitacks. Clays were formerly used as fillers for bias tire carcasses; however, radial tires require better flex fatigue resistance than clay can impart.

Talc. Talc [$Mg_3Si_4O_{10}(OH)_2$] is a platelet form of magnesium silicate with a high aspect ratio. Platelets can orient in the extrusion process, thus providing rubber extrudates with smooth surfaces that can be extruded at high rates. It is commonly used in compounds, which have critical surface appearance such as exterior automotive components or consumer goods.

Talc is used in tires in white sidewall compounds to provide a smooth appearance to the buffed sidewall. The large platelets of talc provide a barrier to gas and moisture permeability in compounds, which allows talc to be used in applications such as hydraulic and automotive hoses, barrier films, and tire innerliners.

4.3. Synthetic Fillers. Synthetic fillers are generally manufactured by precipitation of soluble materials under carefully controlled conditions to provide tailored properties. They may be found as colloidal particles which may be spherical, ellipsoid, rod, or tube shaped; as aggregates which are covalently bonded groupings of individual particles, or as agglomerates that are loosely held associations of aggregates physically interacting. Reinforcement properties are a function of the colloidal particle size and shape, the aggregate dimensions and morphology, and the ability of agglomerates to break down during mixing. Additionally, the composition and surface chemistry of the filler plays a significant role.

Precipitated Calcium Carbonate. Precipitated calcium carbonate is formed by dissolving limestone and precipitating $CaCO_3$ as very fine particles using carbon dioxide (Aroganite Process) or sodium carbonate (Solvay Process). Typical particle sizes range from 0.02 to 2 μm. Most commercially available precipitated calcium carbonate is spherical colloidal particles or aggregates consisting of a few spherical particles. Additional shapes and aggregates of varying morphology are possible and provide increased reinforcement. Precipitated calcium carbonate is used as a semi-reinforcing filler in shoe products and industrial rubber goods, particularly when resistance to alkali solutions is needed. The low moisture content and good reinforcement allow precipitated calcium carbonate to be used in wire and cable insulation applications.

Metal Oxides. Zinc oxide, which is formed from the burning of zinc metal, was the first nonblack filler used for reinforcement of rubber compounds. Although zinc oxide and magnesium oxide are still used as a reinforcing filler in some specialty compounds, particularly those that require heat resistance, their role in rubber compounding in the last several decades is that of an activator for the sulfur cure system or as curatives for chloroprene rubber compounds.

The rutile form of titanium dioxide (TiO_2) is an important filler for white and colored rubber articles. The ability of the titanium dioxide particle to scatter light provides high whiteness and opacity to rubber, which gives the filler particle the ability to cover background colors. The anatase crystalline form of titanium dioxide is also used.

Silicates. Amorphous silicates are precipitated from aqueous blends of soluble silicate, typically sodium silicate, and soluble salts of other metals. The most important types for reinforcement of elastomers are aluminosilicates with mixed Al_2O_3 and SiO_2 structures, magnesium aluminosilicates, and calcium silicates. The silicates have surface areas and resultant reinforcement which span the range from the highest surface area clays (ca 30 m^2/g) to the lower end of the precipitated silicas (ca 100 m^2/g).

Silica. Because of its small particle size and complex aggregate structure (see Fig. 5), precipitated silica imparts the highest degree of reinforcement to rubber among all of the nonblack particulate fillers. The main uses of silica are in the treads of passenger and truck tires for traction and low rolling resistance, in the treads of off-the-road tires for improved chunking and tear resistance, and as a component of the bonding system for adhering brass and zinc-plated steel cord to rubber. Silica is used in shoe soles for its resistance to wear and tearing, its nonscuffing characteristics, and to obtain compounds with light color. It is used to improve the tear strength and resistance to flex fatigue (cracking, cut-growth) and heat aging in a wide variety of manufactured rubber goods including conveyor and power transmission belts, hoses, motor and dock mounts, bumper pads, and rubber rolls. For comparative purposes, some properties of silica and their applications are illustrated in Tables 10 and 11.

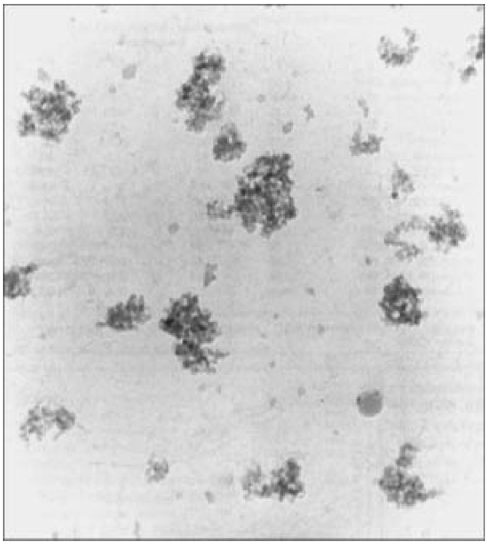


Fig. 5. Transmission electron micrograph of precipitated silica showing aggregate structure (27).

Table 10. **Properties of Commercial Amorphous Silica**[a]

	Colloidal silica	Precipitated silica	Pyrogenic silica	Silica gels
SiO_2	15–50	85–95	98–99	96.5–99.5
weight loss at 105°C	50–80	4–7	0.5–2.5	
particle size, nm	4–60	5–50	5–50	1–100

Table 11. **Application of Amorphous Silica by Partical Size and Form**

	Surface area, m^2/gm		
	90–130	130–180	180 –220
conventional	tire casing; Non-tire internal and external components	tire treads; tire casings and non-tire products external components	tire treads and non-tire external components for abrasion resistance
semi highly dispersible	tire casing; non-tire products external components	tire treads; tire casings	tire treads
highly dispersible	tire casings; tire treads	tire treads	high performance tire treads

The reaction of a bifunctional organosilane with precipitated silica involves the hydrophobation of the alkoxy group of the silane with a surface silanol group of the silica, followed by reaction of the sulfur-containing function of the silane with an olefin group of the elastomer to afford a covalently bonded structure. This silane-coupled silica is useful in improving the abrasion resistance of silicas to levels of carbon blacks, and promoted their use in the treads of radial passenger tires.

For comparative purposes, the effects of nonblack fillers, both natural rubber and SBR compounds, are shown in Tables (12) and (13). For example it illustrates how tensile can vary from 11 MPa for ground whiting or calcium carbonate filled NR to 25 MPa for HiSil 233 or silica-filled compounds.

4.4. Surface Treatment. Carbon black remains the particulate filler of choice for rubber articles since the inherent reinforcing effect of the nonblack fillers in hydrocarbon elastomers is not comparable. This is primarily due to the nonbonded interactions established between the particulate filler and polymer functionality (28). Surface chemistry plays an important role in the interaction of the nonblack fillers and the polymer with contributions ranging from electrostatic interactions to covalent bonding to the polymer backbone. However, surface chemistry also strongly affects the interaction of the nonblack filler with other chemicals in the rubber compound, particularly active metal oxides, curatives, and antidegradants.

Both surface morphology and surface chemistry play an important role in the interaction of a filler with coupling agents. For example, the dipole-induced dipole interactions between the polar groups such as siloxane and silanol on the surface of silicas to the nonpolar groups (methyl, alkenyl, aryl) of hydrocarbon elastomers are weak compared to the dipole–dipole interactions resulting from hydrogen bonding between surface silanol groups in silica aggregates. In addition, the dispersive forces between a nonpolar molecule and silica are low, while those between a nonpolar molecule and carbon black are high. Thus, materials to improve the compatibility between hydrocarbon elastomers and mineral fillers are of considerable interest. Organosilane coupling agents have been successfully utilized to further increase the physical properties of a number of nonblack fillers including calcium silicate, clays, mica, silica, and talc. Clays pretreated with an amino-functional or mercapto-functional silanes, and silicas pretreated with the mercapto-functional or tetrasulfide-containing silanes are commercially available. A manual of commercial coupling agents to promote adhesion between polymers and various substrates is available (29). The reaction of a bifunctional organosilane with a silica or silicate particulate filler involves the hydrophobation of the alkoxy group of the silane with a surface silanol group of the silica or silicate, followed by reaction of the sulfur-containing function of the silane with an olefin group of the elastomer to afford a covalently bonded structure (see Fig. 6).

Silane-modified clays have found broad acceptance in a wide variety of rubber goods. The silane serves as a bridge between the organic rubber molecule and the inorganic filler particle. The result is a filler with higher reinforcing properties than regular clay. However, the dynamic properties and the degree of reinforcing improvement usually does not permit their use as a carbon black substitute or replacement.

Table 12. **Effects of Nonblack Fillers on Natural Rubber Properties**[a,b]

Filler loading	Volume, parts	Mooney viscosity	Optimum cure (at 141°C), min	Modulus (at 300%), MPa[c]	Tensile strength, MPa[c]	Elongation, %	Hardness, shore A	NBS abrasion, ASTM D1630	Rebound, %
pure gum		21	15	2.1	24.2	680	43		81.2
barytes	30	27	20	2.1	15.0	640	49	22.1	80.5
	50	24	20	2.1	11.5	610	56	19.4	
ground whiting	30	32	20	2.1	15.0	640	50	24.1	81.5
	50	43	15	1.9	10.7	590	57	21.6	
soft clay	30	35	25	7.2	17.9	500	49	44.4	81.5
	50	41	25	12.4	16.4	390	58	36.4	
hard clay	30	29	25	9.2	19.9	500	55	54.4	68.2
	50	31	25	14.9	18.4	370	64	43.8	
Purecal U	30	37	15	5.0	19.0	580	53	42.2	75.9
	50	46	15	6.1	14.9	540	57	31.8	
Calcene TM	30	32	15	3.7	19.2	640	48	50.0	70.5
	50	42	15	5.1	16.6	610	58	39.6	
zinc oxide	30	22	20	5.2	21.8	600	55	54.1	73.1
	50	23	20	5.5	15.4	550	64	48.1	
Zeolex	20	23	10	3.5	22.6	660	49	51.4	
	30	65	10	5.3	19.3	600	53	46.0	67.3
	40	62	10	7.9	18.0	540	64	39.4	
Silene EF[d]	20	47	10	4.0	24.8	670	52	59.7	
	30	51	10	5.2	20.1	610	61	48.9	67.3
	40	56	10	7.9	17.4	540	67	45.6	
Hisil 233[e]	20	64	10	5.6	27.2	640	58	57.2	77.5
	30	81	10	9.2	25.3	590	73	60.9	65.9
	40	89	10	13.0	23.9	500	78	79.6	53.9

[a] Ref. 7.

[b] Recipe, in parts by wt: smoked sheets, 100.00; zinc oxide, 5.00; filler, as indicated; nondiscoloring antioxidant, 1.00; MBTS, 1.00; TMTD, 0.10; sulfure, 2.75; stearic acid, 3.00.

[c] To convert MPa to psi, multiply by 145.

[d] Silene EF stocks contain 2.4, 3.8, and 5.0 parts of diethylene glycol, respectively.

[e] In addition to the 1 part of MBTS shown in recipe, the 20 vol HiSil 233 stock contains 0.25 parts TMTD and 0.5 parts triethanolamine; the 30 vol stock contains 0.5 parts TMTD and 2 parts triethanolamine; and the 40 vol stock contains 0.5 parts TMTD and 3 parts triethanolamine.

Table 13. **Effect of Nonblack Fillers on the Properties of SBR**[a,b]

Filler loading	Volume, parts	Mooney viscosity	Optimum cure (at 141°C), min	Modulus (at 300%), MPa[c]	Tensile strength, MPa[c]	Elongation, %	Hardness, shore A	NBS abrasion, ASTM D1630
pure gum		26	45	0.6	1.4	680	30	13.3
barytes	30	37	45	1.6	3.8	620	46	15.2
	50	48	45	2.3	3.8	530	54	15.3
ground whiting	30	40	45	1.2	4.0	620	48	16.5
	50	47	45	1.4	5.0	680	50	15.7
soft clay	30	42	90	2.1	9.0	1080	42	28.8
	50	51	90	2.8	7.0	1130	46	33.5
hard clay	30	41	90	2.8	11.4	890	50	34.2
	50	42	90	3.5	10.1	960	51	37.2
Calcene TM	30	45	45	1.6	12.6	860	45	26.6
	50	61	45	1.9	11.9	830	49	16.0
Purecal U	30	46	45	1.7	14.0	710	45	27.7
	50	65	45	2.5	15.2	680	52	27.3
zinc oxide	30	28	45	1.4	14.5	840	45	30.7
	50	39	45	2.1	14.9	760	54	25.6
Zeolex	20	50	30	2.1	14.0	680	47	34.1
	30	62	30	3.3	16.2	670	53	33.7
	40	79	30	4.2	14.0	620	56	32.1
Silene EF[d]	20	58	15	5.4	14.1	520	56	34.2
	30	72	15	5.3	15.9	570	60	42.0
	40	77	15	6.6	15.0	510	63	46.7
Hisil 233[e]	20	53	60	4.0	18.7	610	51	48.7
	30	81	30	5.8	23.5	610	56	45.9
	40	112	30	7.7	21.9	560	67	40.3

[a] Ref. 7.

[b] Recipe, in parts by wt: SBR 1502, 100.0; zinc oxide, 5.00; filler, as indicated; nondiscoloring antioxidant, 1.00; MBTS, 1.50; TMTD, 0.10; sulfur, 3.00; Cumar MH 2.5, 15.00; stearic acid, 1.00.

[c] To convert MPa to psi, multiply by 145.

[d] Silene EF stocks contain 2.4, 3.8, and 5.0 parts of diethylene glycol, respectively.

[e] The HiSil 233 stocks contain 2.3, 3.5, and 4.8 parts of diethylene glycol, respectively. The 30 vol stock contains 1.2 parts MBTS and 0.15 parts TMTD instead of the combination in the recipe; the 20 and 40 vol stocks contain 1.5 parts MBTS and 0.1 parts TMTD.

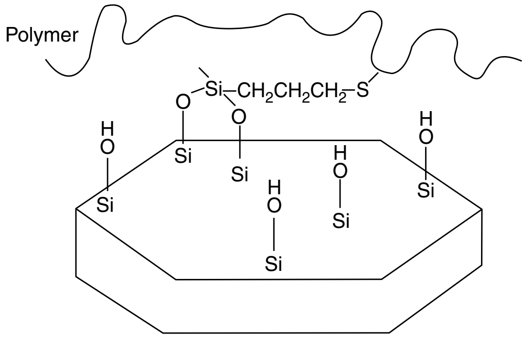


Fig. 6. Illustration of silane coupling of polymer to a silicate surface.

Silane-modified silicas are used in tire tread compounds to reduce rolling resistance, increase wear resistance, and improve wet and snow traction properties.

4.5. Reclaim Rubber. Reclaimed and recycled rubber is considered as a filler in this discussion. The process of reclaiming rubber by chemical digestion has been in use since the late 1800s. Early processes involved the treatment of the rubber cord mix with acid. Acids attack cotton, rayon, and nylon. The acid treatment was used to remove the reinforcing components. The rubber was ground and treated. It was then washed, steam devulcanized, and shaped so it could then be reincorporated into new rubber compounds. An improvement on this technique was the use of alkali digestion. The principal benefit of using reclaim is its lower cost compared to new polymers. Reclaim typically sells for 20–30% of the cost of its nonreclaimed counterparts. Reclaimed rubber also imparts some desirable improvements in processing such as lower nerve, seen when milled or extruded components tend to snap back or develop distortions, than new polymers. As a result, compounds containing reclaim have a much lower die swell and faster extrusion rates. It also increases calendering rates and improves flow and mold filling. One of the shortcomings of reclaim is that it lowers the green strength and tensile strength of the compounds in which it is used. Reclaim is in fact a mixture of rubber, carbon black, oil, zinc oxide, stearic acid, and other compounding ingredients used in the original compounds. The levels of reclaim used are generally 15 to 25 phr, about half of which is rubber and the other half compounding ingredients. In some low performance requirement rubber products, such as mats, much higher levels can be used.

Reclaim can be used in many tire applications such as internal casings components and innerliner compounds, sidewalls, chafers, and rubber used in bead components. The introduction of radial tires changed the property needs for compounds used in tire manufacturing and reduced the volume of reclaim. Butyl reclaim made from tubes is used in the innerliner of both bias and radial tire compounds and some reclaim is used in low speed bias tires. There is a fairly large volume of some high quality rubbers such as natural rubber and butyl being reclaimed and used in some solid tires and other mechanical goods to extend the compound without having too adverse of an effect on the product. Ground rubber has replaced reclaim in many tire applications including treads, innerliners, subtreads, and bead components. It is also used in mechanical goods, footwear, solid tires, mats, and retreads. Cryogenic and wet-ground rubbers which are of smaller particle size can be used at moderately high levels and still allow compounds to be processible. A comprehensive discussion on reclaim and recycled elestomers is available (31).

Steam digestion of silicone rubber produces a silicone reclaim, used to reduce the cost of silicone compounds. It has been widely used by silicone automobile ignition systems. The resulting compounds have excellent aging characteristics and still possess outstanding electrical properties.

5. Antidegradants

Good aging properties of rubber compounds are essential for providing required service life of rubber products. The type of elastomer used is the principal factor in considering aging properties. In general, the more saturated the backbone of the elastomer, the better is the aging properties. For example, EPDM and butyl rubbers are quite stable when compared to more unsaturated polymers such as polyisoprene, sytrene-butadiene rubber, and polybutadiene. Unsaturated polymers are susceptible to oxidation thermally or by reaction with ozone; thus antioxidants and antiozonants are needed to extend the useful service lives of products made with these elastomers. The factors affecting the aging of general-purpose rubber having conventional sulfur and accelerator systems are as follows (6,32,33).

5.1. Oxygen. Addition of only 1 to 2% of oxygen is sufficient to cause deterioration of properties for most general-purpose elastomers. Oxidation proceeds by free-radical mechanisms and leads to chain scissioning and cross-linking (34). In the chain scission reaction, free radicals attack the unsaturated polymer backbone causing chain breaking, which results in softening and weakening. This is the primary effect observed for oxidation of natural rubber and butyl rubber. Brittle stocks result from attack at cross-links, resulting in formation of new cross-links. This is a predominant reaction with SBR, neoprene, nitrile, and EPDM rubbers. A drop in ultimate elongation is the most sensitive physical criterion for the aging measurement regardless of mechanism, and is a favored method compared to measurement of tensile loss for cured compounds. In synthetic rubber production (SBR, in particular), viscosity increases with aging and can affect processing if not prevented.

5.2. Heat. As expected, heat accelerates oxidation. Therefore, the effects described previously are observed earlier in product use and are more severe as the service temperature of the product is increased. Because oxidation is a chemical reaction, a temperature increase of 10°C almost doubles the rate of oxidation.

5.3. Flexing. Flex cracking is a common mode of fatigue failure in rubber compounds. Flex cracking involves not only a mechanical fatigue but also oxidation that is accelerated by heat generated during the flexing cycle. The higher the rate of flexing, the greater is the heat generation, and the worse is the fatigue life of the compound or product.

5.4. Ozone. Although ozone concentration in the atmosphere is only a few parts per hundred million (pphm), it rapidly reacts with an elastomer's carbon–carbon double bonds, particularly the backbone unsaturations, causing cracking of the rubber products. This reaction is especially accelerated by stress (stretching and bending) of the elastomer. For every rubber compound, there is a critical elongation below which cracks do not form. Usually, this is in the range of 5–10% elongation. Ozone reacts with double bonds so rapidly that it cannot diffuse into the rubber and therefore all action is at the surface. Thus, surface-protective agents are most useful against ozone attack. For example, waxes that bloom to the surface of rubber to form an inert film are used effectively for static protection (34). Effective antiozonants protect rubber surfaces initially by a sacrificial reaction with ozone, and then by the formation of a protective surface layer on the ruber surface by the reaction products called ozonides (7,14) which are formed in reaction with ozone, but which can also further react to protect the rubber. Certain polymers also provide good ozone protection. The use of 40–50 parts of a low diene rubber, such as brominated isobutylene-*co*-*p*-methylstyrene, chlorobutyl, or EPDM, in natural rubber, polybutadiene or SBR compounds significantly increases ozone resistance.

5.5. Light. Ultraviolet (UV) light promotes free-radical oxidation at the rubber surface causing discoloration and formation of a brittle film of oxidized rubber. This skin cracks in random directions to form a pattern called crazing but can be minimized by the addition of carbon black fillers or UV stabilizers. Carbon black filled rubber compounds are more resistant to UV light than are gum (unfilled) or light-colored stocks containing mineral fillers. Nonblack compounds require use of larger quantities of nonstaining antioxidants which should continually bloom to the product surface as the UV stabilizers on the surface are depleted.

5.6. Sulfur. Low sulfur compounds and *efficient vulcanized* (EV) sulfur-accelerated systems have better aging resistance. Normally, the oxidation rate increases with the amount of sulfur used in the cure. The increased rate may be due to activation of adjacent C–H groups by high levels of combined sulfur. Saturated sulfides are more inert to oxidation than allylic sulfides. Polysulfidic cross-links impart excessive hardening of SBR as compared to more stable monosulfidic cross-links.

5.7. Metals. Transition-metal ions, such as iron, copper, manganese, and cobalt, when present even in small amounts, catalyze rubber oxidative reactions by affecting the breakdown of peroxides in such a way as to accelerate further attack by oxygen. Natural rubber vulcanizates are especially affected. Therefore, these metals and their soluble salts, such as oleates and stearates, should be avoided.

5.8. Selection of Proper Antidegradant. Because the various antioxidants function by different mechanisms, an antioxidant under one condition may become an oxidation promoter in a different condition. Therefore, an antioxidant should be carefully selected depending on service requirements. Most antioxidants are either amines, phenols, or phosphates. The following are some important properties in the selection of proper antidegradant that should be considered.

Persistence in Service (Volatility, Leachability, etc). Volatility is related to molecular weight, and type of antioxidant molecule. In general, the higher the molecular weight, the less the volatility (37). The type of molecule also has an effect. For example, hindered phenols have higher volatility than amine types of the same molecular weight. Volatility is also important from the standpoint of loss of antioxidant during service and depends on surface exposed, temperature of service, flexing, etc. Comparative loss studies for amine and phenolic-type antioxidants have been done (17). Rubber testing is affected by the volatility of antidegradants and widely varying results are obtained depending on whether open or closed aging chambers are used.

Solubility. Another desirable property of an antidegradant is its high solubility in rubber, but poor solubility in water and solvents that come in contact with rubber. Poor solubility in the rubber means that only small quantities of antioxidants can be dissolved without producing a bloom, a migration to the surface. As an example, *N*-isopropy-*N*′-phenyl-*p*-phenylenediamine (IPPD) has limited use because of its poor solubility in, for example, natural rubber (less than 2.0 phr). On the other hand, phenolic and phosphite antioxidants have high solubility and bloom is not a concern. Solubility of antiozonants in rubber is especially important because their effectiveness depends on the use of small amounts, ie 2 to 5 phr, which must be soluble in the rubber but which also must migrate to the rubber surface in sufficient concentrations to establish a protective layer.

Protection Against Flex Cracking. Most antioxidants including waxes provide oxidation protection under static conditions. However, most of them are not effective in rubber products subjected to dynamic flexing, such as sidewall compounds in tires. The best dynamic protection is provided by *N*-alkyl-*N*′-phenyl-*p*-phenylenediamines.

Stability. In order to have maximum effectiveness over long periods of time, an antioxidant should be stable upon exposure to heat, light, oxygen, water, etc. Many antioxidants, especially in the presence of an impurity when exposed to light and oxygen, are subject to oxidation reactions with the development of colored species. Alkylated diphenylamines are least susceptible and the *p*-phenylenediamine derivatives the most susceptible to direct oxidation.

Physical Form. Physical form is an important characteristic. Compounders prefer solid, free-flowing, nondusty materials, whereas polymer manufacturers prefer materials that are liquid. Less desirable forms are semicrystalline materials which may stratify during storage. Also, substances to be avoided are highly viscous liquids and low melting resins which may solidify upon storage.

Staining Properties. For rubbers containing carbon black, discoloration is not generally a problem and the more potent staining amine antioxidants are used. For white or light-colored rubber products, nonstaining antidegradants are required. Functional classes of nonstaining antioxidants include substituted monophenols, hindered bisphenols and thiobisphenols, substituted hydroquinones, organic phosphites, and thioesters. Triphenyl phosphine, substituted thioureas and isothioureas, thiosemicarbazides, esters of dithiocarbamates, lactams, and olefinic and enamine compounds are reported to be nonstaining antiozonants. Approaches to completely replace the para-phenylenediamine antiozonants with a non-discoloring antiozonant have had only limited success leading to the development of new classes of nonstaining antiozonants (30).

Metal Deactivation. Compounds capable of forming coordination complexes with metal ions are needed for this purpose. A chelating agent such as ethylene–diaminetetraacetic acid (EDTA) is a good example.

Condition of Use. The selection of suitable antioxidants is highly dependent on the conditions under which the rubber product is to be used. It is difficult to find a single material that meets all requirements of a product. Consequently, quite often, blends of antioxidants are used. Table 14 provides a summary of characteristics of commercially important antidegradants (7).

Table 14. **Antidegradants**[a]

			Resistance[b] to				
Type	Example (trade name)	Staining	Oxygen	Heat	Flexing	Metal catalysis	Ozone
hindered phenols	2,6-di-*t*-butyl-*p*-cresol (CAO-1)	None to slight	F	F	F–P	P	P
hindered bisphenols	2,2′-methylenebis-(4-methyl-6-*t*-butylphenol) (Antioxidant 2246)	None to slight	G–F	G–F	F–P	G	P
hindered thiobisphenols	4,4′-thiobis(6-*tert*-butyl-*m*-cresol) (Santowhite Crystals)	Slight	G–F	G–F	F–P	F	P
hydroquinones	2,5-di(*tert*-amyl)hydroquinone (Santovar A)	None to slight	G–F	F	F–P	P	P
phosphites	tri(mixed mono- and dinonylphenyl)-phosphite (Polygard)	None to slight	G–F	F	F–P	P	P
diphenylamines	octylated diphenylamine (Cyanox 8)	Slight to moderate	G–F	G–F	F	P	P
naphthylamines	phenyl-α-naphthylamine (Akrochem PANA)	Moderate	G	G	G–F	F	P
quinolines	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (AgeRite Resin D)	Slight to moderate	G	E	F	P	F–P
carbonylamines condensation products	reaction product of diphenylamine/acetone (BLE-25)	Considerable	G	E	E–G	P	F–P
para-phenylene-diamines	mixed diaryl-*p*-phenylene-diamines (Wingstay 100)	Considerable to severe	E–G	E–G	E–G	E	E–G

[a] Ref. 7.

[b] E = excellent, G = good, F = fair, and P = poor.

5.9. Antioxidant Types. Commercially available antioxidants may be divided into three general classes: secondary amines, phenolics, and phosphites. In general, the amines are more active than the phenolics which in turn are more active than the phosphites. Amine antioxidants, however, often cause staining problems and are therefore used mainly in black-colored compounds. The phenolics and phosphites are relatively nonstaining and are normally used in light-colored elastomer formulas. Many antioxidants in these classes are volatile to some extent at elevated temperatures and almost all antioxidants are readily extracted from their vulcanizates by the proper solvent. These disadvantages have become more pronounced as performance requirements for rubber products have been increased. Higher operating temperatures and the need for improved oxidation resistance under conditions of repeated extraction have accelerated the search for new techniques for polymer stabilization. Seals, gaskets, and hoses are some examples where high temperatures and solvent extraction can combine to deplete a rubber product of its antioxidant and thus lead to its oxidative deterioration faster (38,39).

Techniques for providing increased protection against oxidation under severe temperature and solvent extraction conditions include the use of polymer-bound antioxidants. Chemical attachment of the antioxidant molecule to the polymer backbone eliminates volatility and extraction by making the antioxidant essentially infinite in molecular weight after curing. Two general methods of accomplishing this attachment have been used:

1. functionalized macromolecules react with antioxidant molecules to provide the bound antioxidant, and
2. antioxidant molecules containing polymerizable functional groups may be copolymerized with conventional monomers during polymer production.

5.10. Test Methods. The most common methods used for determining the efficiency of antioxidants in vulcanized elastomers involve accelerated aging tests rather than oxygen absorption experiments. The standard tests involve aging dumbbell specimens cut from tensile strength test sheets under varying conditions of time, temperature, and oxygen content. They are as follows:

1. air oven (ASTM D573) at 70°C for 1, 3, 5, 7, and 14 days, or in a test tube (ASTM D865) to eliminate cross-contamination (40,41);
2. oxygen pressure (oxygen bomb, ASTM D572) of 2 MPa (300 psi) at 70°C for 2, 48, 72, and 96 h (42); and
3. air pressure heat test (air bomb, ASTM D454) at 126°C, and at 80 psi of air for 3, 5, 8, 12, 20, and 30 h (43).

Because of the simplicity of the first test method, most of the comparisons are made using this technique. The effects of the aging process are usually measured on tensile properties such as breaking strength, elongation, and stress (modulus) at 300% elongation. In general, one day of oven aging at 70°C corresponds to one year of shelf aging (a minimum requirement for rubber products), whereas the oxygen and air bomb methods are more drastic. By varying the amounts, types, or combinations of antioxidants, the relative effectiveness of these materials against oxygen deterioration can be determined.

6. Processing Agents

To improve processing and to plasticize the rubber compound, numerous processing agents have been used over the years, such as petroleum and ester plasticizers, resins and tars, liquid rubber peptizers, peptizers, fatty acids and derivatives from vegetable oils, and polyethylene and hydrocarbon waxes. Benefits from the use of plasticizers are illustrated in Table 15 (6).

Petroleum plasticizers are the most universally used plasticizers for all rubber compounds. They improve flow and processing properties and also reduce the cost of the final compound. Aromatic process oils are the most common plasticizer for general-purpose rubbers. Naphthenic process oils are used where a minimum of discoloring or staining is required. Paraffinic process oils are used in the low polarity rubbers where high loadings and good solubility are required to avoid bleeding and maximize the plasticizing action.

Ester plasticizers are used in highly polar elastomers, such as neoprene and nitrile rubber, to improve low or high temperature performance or impart particular oil or solvent resistance to a compound. From 5 to 40 phr are commonly used (see PLASTICIZERS). Resins and tars are added to impart tack, soften the compound, improve flow, and in some cases improve filler dispersion, as is the case with organic resins in mineral-filled SBR. Resinous substances are also used as processing agents for homogenizing elastomer blends.

Table 15. **Benefits Through Use of Processing Aids**[a]

Operation	Benefit of processing aids	Controlling materials parameters
mixing	faster filler incorporation	reduced viscosity
	better dispersion	hydrophobation reaction in silica compounds
	reduced viscosity	
	improved release	homogenization
	lower dump temperature	
	reduce mix times	
processing	faster and easier calendering and extrusion	rheological properties
	improved release	viscosity
	less energy consumption	green strength
		tack, bloom
curing and molding	faster cavity fill at lower operating pressure	scorch resistance
	reduced stress in molded parts through easy cavity fill	rheological properties
	shorter cycle times	clean
	improved release	mold

[a] Refs. 6,7 and 44.

Stearic acid is used in many compounds as a cure activator and in addition may serve as a processing agent to improve mill and processing equipment release properties. Thus stearic acid may be the most widely used processing agent in the rubber industry. Stearic acid is typically used at 1 to 3 phr, and may also be added as a zinc salt (ie, zinc stearate). Because of its low molecular weight it has limited solubility in many elastomers. The term *stearate* often refers to a fatty acid mixture containing palmitates and small quantities of other fatty acids such as oleic acid and linoleaic acid.

Processing agents can be prepared by blending fatty acids, zinc, and calcium soaps into waxes, such as myricyl palmitate, to overcome solubility limitations of individual products. The result is a blend of organic fatty acids, usually in paste form, which serves to improve processing. In some cases, processing agents contain blends of fatty-acid chemicals and an ester-type plasticizer. This makes the processing agent more effective in highly polar elastomers such as nitrile rubber.

Table 16 illustrates how specific classes of processing aids may be used depending on the need. For example, should the rubber technologist encounter difficulties in the product-building operation, tackifiers can be used to assist in ensuring that the respective components in the product will come together in an efficient manner. Further upstream in mixing, peptizers, dispersion aids, or homogenizing agents can be varied to give the desired throughput and compound quality at the mixers. A comphensive review of processing aids has been prepared (44).

7. Vulcanization

Vulcanization is a chemical process where sulfur or other materials form crosslinks in the elastomer and thereby improve the polymer's mechanical properties. In many instances, not all of the desired properties reach an optimum level simultaneously. The task is to achieve a balance of the most important property requirements through design of the cure system and time–temperature cure cycle so as to attain the necessary compound mechanical properties. Frequently, the curing equipment available, such as presses or autoclaves, do not allow the curing conditions to be varied as desired, and so a cure system compatible with the existing equipment must be designed and also meet the compound performance requirements.

7.1. Measuring Vulcanization. The formation of a three-dimensional cross-linked structure during vulcanization increases the stiffness (modulus) of the compound. Therefore, following the modulus increase versus cure time provides a continuous picture of the vulcanization process. Oscillating disk rheometers (ODR) and moving die rheometers (MDR) provide useful methods (45,46). In these tests, a preweighed sample of uncured rubber is placed into a preheated cavity containing a conical rotor. The cavity is closed and the rotor is set to oscillate within the rubber sample. As vulcanization proceeds, the compound's resistance to rotor movement increases and this resistance is followed as a function of time, thereby generating a continuous profile of cure behavior. A cure

Table 16. **Operations Using Processing Aid, Types, Examples, and Function**[a]

Processing operation	Processing aid	Examples	Function
mixing	chemical peptizer	2,2′-dibenzamididiphenyldisulfide	reduces polymer viscosity by chain scission; reduces molecular weight
		pentachlorothiophenol	
	physical peptizer	zinc soaps	reduces polymer viscosity by internal chain lubrication
	dispersing agent	mineral oils	improves filler dispersion; reduces mixing time; reduces mixing energy
		fatty acid esters	
		metal soaps	
		fatty alcohols	
	homogenizing agent	resin blends	improves polymer blend compatibility; improves compound uniformity
mixing extruding	lubrication agent	mineral oils	improves compound flow and release
		metal soaps	
		fatty acid esters	
		fatty acid amides	
	fatty acids		
	softening agent	mineral oils	lower hardness
	plasticizer	aromatic di and tri esters	improves product performance at low and high temperatures
		aliphatic di esters	
		alkyl and alkylether monoesters	
building product assembly	tackifier	hydrocarbon resins	improves green tack; use hydrocarbon resins in summer, phenolics in winter, or as temperature varies
		phenolic resins	
curing	stiffening agent	high styrene resin—rubber masterbatches	increased hardness
		phenolic resins	
		trans-polyoctenamer	
	mold release agent	organosilicones	easier product release from mold; decreased mold contamination
		fatty acid esters	
		metal soaps	
		fatty acid amides	

[a] Refs. 6,7 and 44.

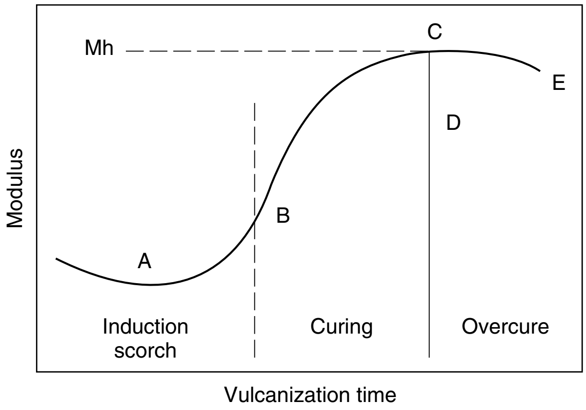


Fig. 7. Cure curve from oscillating disk rheometer where **A** represents scorch safety, **B** cure rate, **C** state of cure, **D** optimum cure, and **E** reversion.

curve, shown in Figure 7, provides information on scorch safety or cure induction time, cure rate, state of cure or stiffness developed, optimum cure time or time when modulus no longer increases significantly, and reversion or the tendency of the compound to degrade upon overcure.

Sulfur vulcanization is a complex reaction during which both the number (density) and type (structure) of cross-links are continuously evolving as the reaction proceeds. The chemical structures formed at any given time during cure may favor one set of properties such as tear strength while not being optimum for others such as hysteresis and compression set. A cure system designed to minimize these trade-offs is always an objective of the rubber technologist (47).

For example, modulus or stiffness increase as the number of cross-links increase because the three-dimensional structure which forms becomes more resistant to deformation under load, thereby requiring greater force to reach a given elongation. With overcure, cross-link structure either degrades and modulus drops as in the case of natural rubber, or it continues to build, resulting in a *marching modulus* as in the case of SBR.

Tensile strength, tear strength, and fatigue resistance frequently pass through a maximum as cure state or cross-link network evolution progresses. These ultimate properties are highly dependent on the presence of flaws in the material. As cross-linking proceeds and modulus builds, any applied load acting on a flaw (from poor dispersion, small nicks or tears, localized overcure due to inhomogeneity, etc) concentrates the stresses at the flaw and provides a mechanism for tensile failure and tear propagation or poor fatigue life (Fig. 8). Permanent set and low hysteresis properties depend on minimizing the viscous or plastic component of modulus. Because cross-linking increases elasticity, a high state of cure typically provides the best compression set and heat buildup properties.

Heat resistance is influenced by both the type and extent of cure. The greater the strength of the chemical bonds in the cross-link, the better is the compound's heat resistance. Peroxide cure systems, which result in carbon–carbon

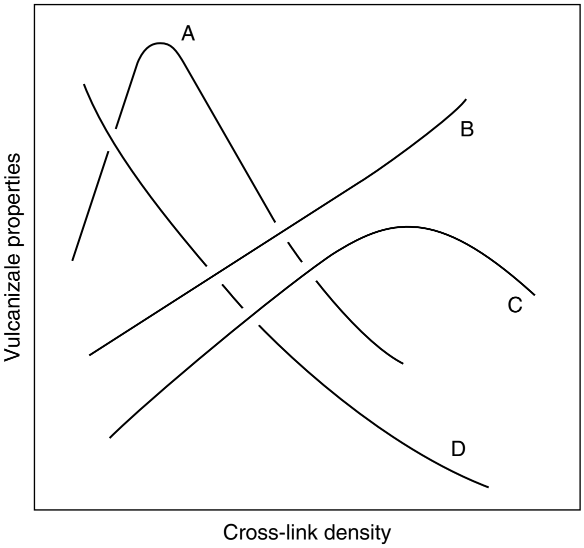


Fig. 8. Effect of cross-link density where **A** represents tear strength, fatigue life, and toughness; **B**, elastic recovery and stiffness; **C**, tensile strength; and **D**, hysteresis, permanent set, and friction coefficient.

bonds, show good heat resistance because of more thermally stable, short, cross-links. This is an important factor in designing the desired cure system.

Cross-Link density has only a minor effect on some compound properties such as thermal conductivity, electrical properties, and low temperature brittleness. Another cure system consideration is the compound scorch behavior. Prior to vulcanization, rubber is plastic-like and can be processed into desired shapes such as tires, hoses, belts, or other articles. The time available to accomplish this processing depends largely on the cure system and is referred to as the scorch time. If a compound cures prematurely during the processing step, it is usually scraped. Therefore, a key requirement of the vulcanization step is to minimize premature vulcanization or scorch (Fig. 7).

7.2. Vulcanizing Agents. Sulfur is the most common vulcanizing agent for the widely used diene-containing elastomers, such as natural rubber, SBR, and polybutadiene. Rubbermakers' sulfur is a rhombic form existing as a cyclic or eight-member ring structure. Insoluble sulfur is an amorphous polymeric form with molecular weights of 100,000–300,000. Because this material is insoluble in rubber, it resists migration to the surface prior to cure and this bloom-free attribute contributes to maintaining better building tack and better component-to-component adhesion (48,49). Sulfur-containing chemicals such as dimorpholinyl disulfide (DTDM) and tetramethylthiuram disulfide (TMTD) are not only effective accelerators, but they can also be used as sulfur donors. As such, they are effective in controlling sulfur cross-link length to form primarily mono- and disulfide cross-links. These short cross-links are more thermally stable than conventional sulfur curing and thereby provide better heat and set resistance. However, these accelerators are potentially nitrosamine-generating species, and research continues to replace them.

Peroxides are probably the most common materials used after sulfur because of their ability to cross-link a variety of diene- and nondiene-containing elastomers, and their ability to produce thermally stable carbon–carbon cross-links. Carbon–carbon bonds are inherently stronger than the carbon–sulfur bonds developed with sulfur vulcanization (49). Peroxides decompose when heated to produce active free radicals, which in turn react with the rubber to produce cross-links. The rate of peroxide cure is controlled by temperature and selection of the specific peroxide, based on half-life considerations (see INITIATORS, FREE-RADICAL). Although some chemicals, such as bismaleimides, triallyl isocyanurate, and diallyl phthalate, act as coagents in peroxide cures, they are not vulcanization accelerators. Instead, they act to improve cross-link efficiency (cross-linking vs scission), but not rate of cross-link formation.

Halogen-containing elastomers such as polychloroprene, chlorosulfonated polyethylene, and brominated isobutylene-*co*-*p*-methylstyrene are cross-linked by their reaction with metal oxides, typically zinc oxide. The metal oxide reacts with halogen groups in the polymer to produce an active intermediate which then reacts further to produce carbon–carbon bonds. Zinc chloride is liberated as a by-product and it serves as an autocatalyst for this reaction. Magnesium oxide is typically used with zinc oxide to control the cure rate and minimize premature cross-linking (scorch).

Two commercially important, high performance elastomers which are not normally sulfur-cured are the fluoroelastomers (FKM) and the polyacrylates (ACM). Polyacrylates typically contain a small percent of a reactive monomer designed to react with amine curatives such as hexamethylene–diamine carbamate (Diak #1). Because the type and level of reactive monomer varies with ACM type, it is important to match the curative type to the particular ACM in question. Sulfur and sulfur-bearing materials can be used as cure retarders; they also serve as age resistors (50). Fluoroelastomer cure systems typically utilize amines as the primary cross-linking agent and metal oxides as acid acceptors.

Other examples of difunctional compounds used for curing are epoxy resins for nitrile rubber, quinone dioximes for butyl rubber, and phenolic resins for butyl rubber, EPDM, and some EPDM-based thermoplastic elastomers (TPEs). The cross-linking mechanism involves a condensation reaction between each of the two curative difunctional groups with the polymer chain to form a three-dimensional network. Because only carbon–carbon linkages result, thermal stability and permanent set resistance are excellent, often approaching those of peroxide curing. A summary of the advantages and disadvantages of each of the various cross-linking agents appears in Table 17.

7.3. Rubber Vulcanization Chemicals. The vulcanization systems consist of the following components; the vulcanizing agent such as sulfur, the accelerator to activate the sulfur, a retarder to help control the rate of vulcanization, and an activator such as zinc oxide and stearic acid.

Accelerators. During sulfur vulcanization of rubber, accelerators serve to control time to onset of vulcanization, rate of vulcanization, and number and type of sulfur cross-links that form. These factors in turn play a significant role in determining the performance properties of the vulcanizate.There are seven principal classes of accelerators which include thiazoles, sulfenamides, guanidines, carbamates, thiurams, xanthates, and phosphates (Fig. 9). There are also miscellaneous

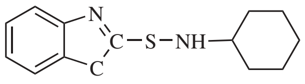
Table 17. **Vulcanization Agents**

Accelerator Class	Elastomer	Advantages	Disadvantages
sulfur	dienes	versatile	heat and compression set resistance
sulfur donors			
peroxides	saturateds polymers	heat and compression set resistance	cure rate control
	dienes		
resins	primarily butyl-based polymers	heat resistance	slow cure rate
metal oxides	halogenated polymers	preferred for CR, CSM	water resistance

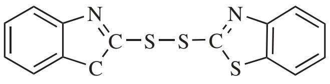
accelerators that do not fit into these categories. In addition, blends of several accelerators are prepared which are designed as cure packages for a specific applications. Choosing the best cure system requires extensive knowledge of each accelerator type and its applicability in each elastomer. Table 18 shows a simplified comparison of the scorch and cure rate attributes for the five most widely used classes of accelerators used in the high volume diene-based elastomers.

Although differences in accelerator response do occur from one rubber type to another because of inherent differences in their molecular structures, the guidelines in Figure 10 serve as an overview of the principal accelerators and their performance (see Rubber chemicals).

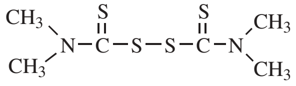
It is common practice in the rubber industry for a compounder to use combinations of several accelerators in developing a cure system. Typically, these cure



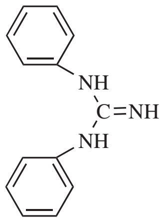
Cyclohexyl benzothiazole disulfide



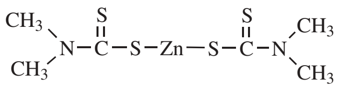
Mercaptobenzothiazole disulfide



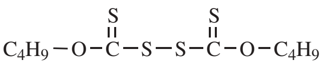
Tetramethylthiuram disulfide



Diphenyl guanidine

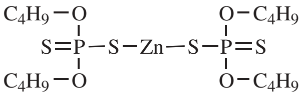


Zinc dimethyldithiocarbamate



$$C_4H_9-O-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-O-C_4H_9$$

Dibutyl xanthogen disulfide



$$S=\overset{\overset{C_4H_9-O}{|}}{\underset{\underset{C_4H_9-O}{|}}{P}}-S-Zn-S-\overset{\overset{O-C_4H_9}{|}}{\underset{\underset{O-C_4H_9}{|}}{P}}=S$$

Zinc dibutylphosphorodithiate

Fig. 9. Structure of a selection of accelerators.

Table 18. **Accelerated Sulfur Vulcanization**

Accelerator class	Example	Abbreviation	Scorch safety	Cure rate	Expected sulfur cross-link length
none present	sulfur only			slow	S4–S8
guanidines	diphenyl guanidine	DPG	moderate	moderate	S2–S4
mercapto-benzothioazoles	mercaoptobenzothiazole	MBT	moderate	moderate	S2–S4
	mercaptobenzothiazole disulfide	MBTS	moderate	moderate	S2–S4
sulfenamides	cyclohexyl-2-benzothiazole-sulfenamide	CBS	long	fast	S2–S4
	tert-Butyl-2-benzothiazole-sulfenamide	TBBS	long	fast	S2–S4
thiurams	tetramethylthiuram disulfide	TMTD	short	very fast	S2
dithiocarbamates	zinc dimethyldithiocarbamate	ZDMC	very short	very fast	S2

systems comprise a primary accelerator and one or more secondary types. Primary accelerators are generally the thiazole and sulfenamide classes; the secondary accelerators are the thiurams, dithiocarbamates, guanidines, and to a much lesser extent, certain amines and the dialkylphosphorodithioates (32). Typically, secondary accelerators are more basic than the primary or major accelerator.

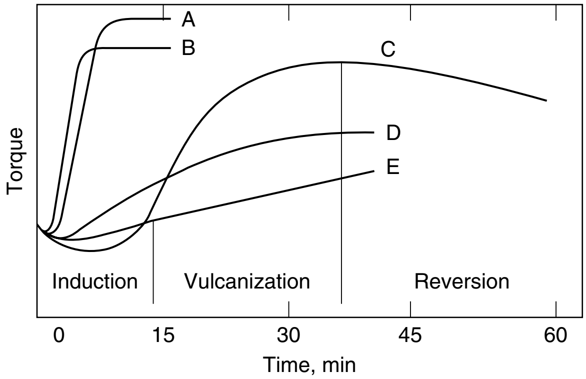
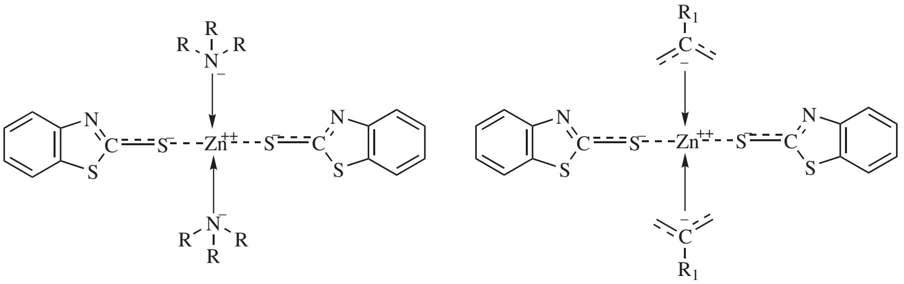
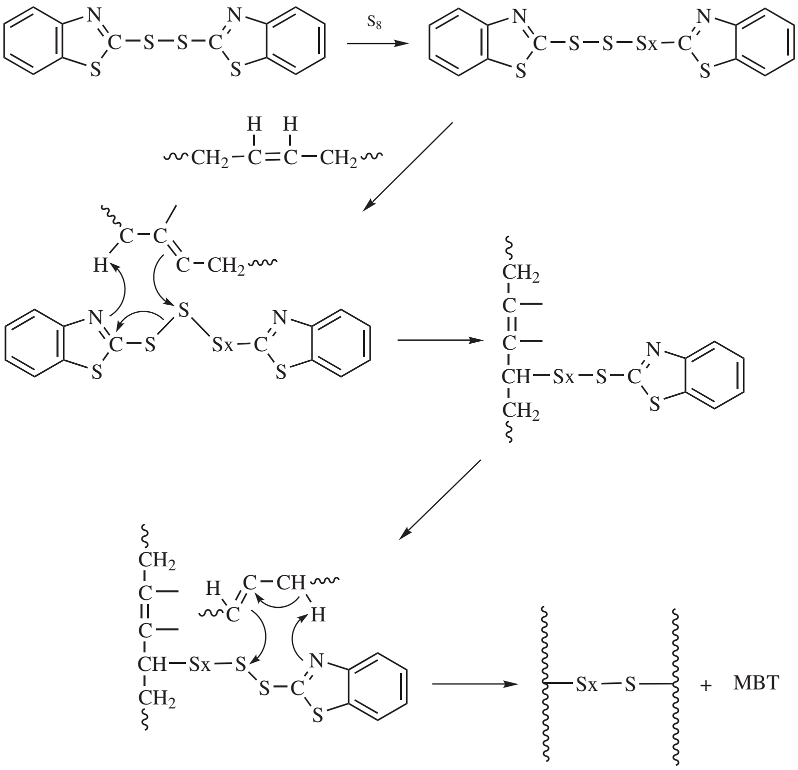


Fig. 10. Cure characteristics of accelerators: A, thiurams; B, dithiocarbamates; C, sulfenamides; D, thiazoles; E, guanidines. The induction period represents scorch time.

The role of activators in the mechanism of vulcanization is as follows. The soluble zinc salt forms a complex with the accelerator and sulfur termed the sulfurating agent (eq. 14). The sulfurating agent


(14)

is stabilized by amine from the accelerator or COO−ligands. This complex then reacts with a diene elastomer to form a rubber−sulfur−accelerator cross-link cursor while also liberating the zinc ion. For simplicity the vulcanization mechanism leading to completion of the sulfur cross-link to another rubber diene segment can be illustrated in the schematic in equation (15) (50). As a general rule the sulfenamides exhibit faster cure rate than the thiazoles. If secondary accelerators are used, dithiocarbamates give the fastest cure followed by the thiurams, then the guanidines.



(15)

Comprehensive reviews on the mechanism of vulcanization, roll of the sulfurating complex, metal oxide vulcanization, etc, are available (50,51).

Activators. *Activators* are chemicals that increase the rate of vulcanization by reacting first with the accelerators to form rubber-soluble complexes. These complexes then react with the sulfur to form sulfurating agents (eqs. 14,15). The most common activators are combinations of zinc oxide and stearic acid. Other fatty acids used include lauric, and oleic, acids. Soluble zinc salts of fatty acid such as zinc 2-ethylhexanoate are also used, and these rubber-soluble activators are effective in natural rubber to produce low set, low creep compounds used in load-bearing applications. Weak amines and amino alcohols have also been used as activators in combination with the metal oxides. Natural rubber usually contains sufficient levels of naturally occurring fatty acids to solubilize the zinc salt. However, if these fatty acids are first extracted by acetone, the resultant "clean" natural rubber exhibits a much lower state of cure. Therefore, to ensure consistent cure rate, fatty acids are usually added. Synthetic rubbers, especially the solution polymerized elastomers, do not contain fatty acids and require their addition to the cure system.

Sulfenamide accelerators generally require lower levels of fatty acid because they release an amine during the vulcanization process which acts to solubilize the zinc. Guanidines and similar amine accelerators also serve to both activate and accelerate vulcanization. A study of the effect of stearic acid and zinc oxide on a sulfenamide-accelerated, sulfur-cured natural rubber compound showed the need for both zinc and fatty acid activators is presented in Figure 11 (52).

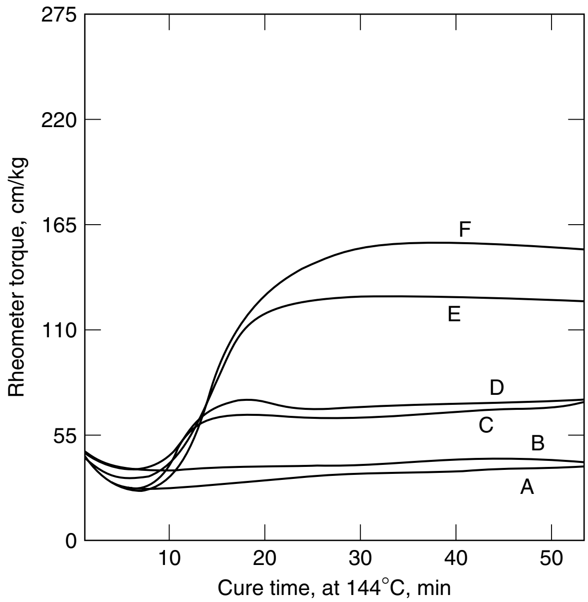
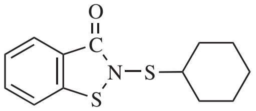


Fig. 11. Effect of activators on cure rate, where A is 2.5 phr sulfur, B sulfur plus stearic acid (2 phr) plus zinc oxide (5 phr), C sulfur plus TBBS (0.6 phr), D sulfur plus stearic acid, E sulfur plus TBBS plus ZnO, F sulfur plus TBBS plus stearic acid plus ZnO.

Retarders. The purpose of vulcanization retarders is to delay the initial onset of cure in order to allow sufficient time to process the unvulcanized rubber. Several main classes of materials are used commercially such as organic acids and anhydrides, cyclohexylthiophthalimide (Santogard PVI), and a sulfenamide (Vulkalent E). Examples of organic acid retarders include phthalic anhydride, benzoic acid, and salicylic acids. These materials are thought to function by reaction with basic components present as accelerator fragments, from other basic compounding ingredients, and from impurities. These basic moieties, which would normally serve to accelerate vulcanization and produce a higher state of cure, are neutralized by the acid retarders. Therefore, they are effective in delaying the initial onset of cure. However, some retarders also lower the rate of vulcanization and in many cases detract from the final mechanical properties (22).



(16)

N-(cyclohexylthio) phthalimide

The thiophthalimide (CTP) and sulfenamide classes of retarders differ from the organic acid types by their ability to retard scorch (onset of vulcanization) without significantly affecting cure rate or performance properties. Much has been published on the mechanism of CTP retardation. It functions particularly well with sulfenamide-accelerated diene polymers, typically those used in the tire industry. During the initial stages of vulcanization, sulfenamides decompose to form mercaptobenzothiazole (MBT) and an amine. The MBT that is formed reacts with additional sulfenamide to complete the vulcanization process. If the MBT initially formed is removed as soon as it forms, vulcanization does not occur. It is the role of CTP to *temporarily* remove MBT as it is formed. The retardation effect is linear with CTP concentration and allows for excellent control of scorch behavior.

7.4. Cure System Design. There are three generally recognized classifications for sulfur vulcanization: conventional, efficient (EV) cures, and semiefficient (semi-EV) cures. These differ primarily in the type of sulfur cross-links that form as shown in Figure 12, which in turn significantly influences the vulcanizate properties (33). The term *efficient* refers to the number of sulfur atoms per cross-link (32).

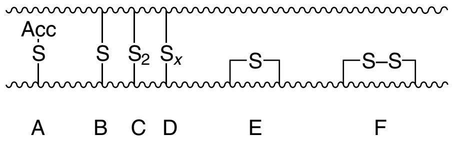


Fig. 12. Sulfur-based cure system designs where conventional systems are polysulfidic, EV systems are mono- to disulfidic, and semi-EV are di- to polysulfidic. A is pendent sulfide group terminated with accelerator residue, B monosulfidic cross-link, C disulfidic cross-link, D polysulfidic cross-link ($x > 20$), E cyclic monosulfidic cross-link, F cyclic polysulfidic cross-link, and Acc accelerator residue.

Conventional cure systems use relatively high levels (2.5 phr and higher) of sulfur combined with lower levels of accelerator(s). These typically provide high initial physical properties, tensile strength, tear strength, and good initial fatigue resistance, but with a greater tendency to lose these properties after heat aging. In contrast, EV cure systems employ much lower levels of free sulfur (0.1 to 1.0 phr) or they use sulfur donors such as TMTD or DTDM combined with higher accelerator levels. The short mono- and disulfide cross-links that form often do not exhibit the physical properties afforded by the conventional systems, but they better retain properties after aging. Semi-EV cures represent a compromise between conventional and EV cures. Although semi-EV cures do yield polysulfide cross-links, they tend to minimize formation of inefficient moieties such as sulfur bridging with itself, accelerator-terminated sulfur linkages, etc. This cleaner usage of sulfur is the reason for their affording a properties between conventional and EV cures.

The reason for the greater loss in properties with conventional cure systems can be understood by examining cross-link bond strengths. Polysulfide bond strengths are significantly lower than are the bond strengths from the shorter cross-links obtained with EV cure systems. The relatively unstable S_x bonds break and rearrange to form mono- and disulfide linkages plus non-cross-linking cyclic and accelerator-terminated fragments. These reactions are observed as changes in properties with increased aging severity. However, conventional systems in natural rubber do provide better flex life than EV cures, and this is one of the limitations of EV curing. The short monosulfide bonds are less able to rearrange to relieve localized stresses which can build during flexing, whereas the longer S_x bonds can rearrange. This ability for stress relief is thought to be one mechanism for the superior flex life of conventional cures. If natural rubber compounds are subjected to thermal aging plus fatigue, the conventional systems perform no better than EV systems. The compromise obtained by using semi-EV systems involves the balance between heat aging and flex life.

Table 19 illustrates formulas for conventional, semi-EV, and EV cure systems in a simple, carbon black-filled natural rubber compound cured to optimum cure (t90).

Table 19. **Cure System Classification**

Material	Conventional cure system, phr	Semi-EV (semiefficient vulcanization system), phr	EV (efficient vulcanization system), phr
natural rubber	100	100	100
N330 carbon black	50	50	50
ZnO	4	4	4
stearic acid	1	1	1
6PPD[a]	1	1	1
sulfur	2.5	1.5	0.15
CBS[b]	0.5	1	2
TMTD[c]			2.5

[a] 6PPD = *N*-1,3-Dimethylbutyl-*N*′-phenyl-*p*-phenylene diamine.

[b] CBS = Cyclohexyl-2-benzothiazole-sulfenamide.

[c] TMTD = Tetramethylthiuram disulfide.

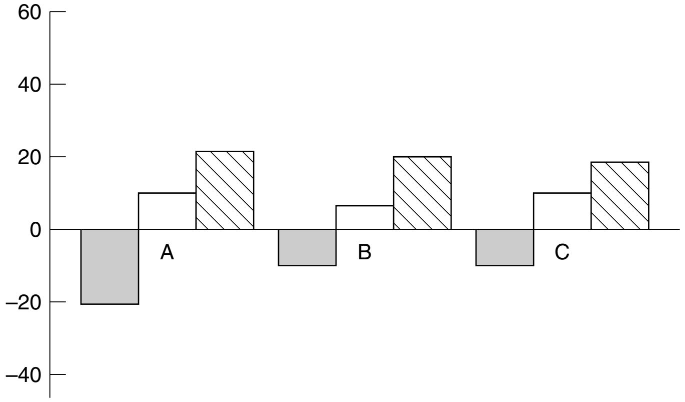


Fig. 13. Aging properties of cured natural rubber. **A** conventional cure system, **B** semi-EV, **C** EV system, ■ tensile strength loss (%), □ fatigue life, and ▨ hardness change.

All three systems give similar tensile strength, elongation, and hardness properties. Conventional and semi-EV systems tend to display better hysteresis (heat buildup) as measured by tangent delta and unaged fatigue resistance.

Figure 13 summarizes properties obtained after heat aging these compounds at 70°C. Both EV and semi-EV systems are superior in tensile strength and hardness retention. Loss of fatigue resistance is greatest for the conventional cure. These observations illustrate the importance of achieving the necessary cross-link structures for an optimum balance of properties. These illustrations are for compounds subjected to ideal or t90 cure conditions at a relatively mild temperature of 140°C. Extremely high cure temperatures, such as those used in injection molding, can be expected to alter these results, but not the overall trends.

In a study of how cross-link structure of a conventionally cured compound changes as a function of cure time, it was observed that total cross-links decrease rapidly past optimum cure (reversion) and that most of the cross-links lost are the S_x types as cure progresses (7). Cure temperature affects cross-link density; there is a dramatic decrease in cross-link density as cure temperature increases. This is a serious concern for the compounder charged with increasing productivity by going to higher temperature, shorter cure cycles. Although plant efficiencies might improve, compound performance is likely to deteriorate.

7.5. Cure Systems of Butyl Rubber and EPDM. Regular (nonhalogenated) butyl rubber is a copolymer of isobutylene with a small percentage of isoprene which provides cross-linking sites. Because the level of unsaturation is low relative to that of natural rubber BR, or SBR, cure system design generally requires higher levels of fast accelerators such as the dithiocarbamates and thiurams. Examples of typical butyl rubber cure systems, their attributes, and principal applications have been reviewed (18). Use of conventional and semi-EV techniques can be used in butyl rubber as shown in Table 20 (4).

EPDM is a terpolymer of ethylene, propylene, and a small amount of an unsaturated diene as a third monomer to provide a cure site. Unlike the elastomers previously discussed, the unsaturation in EPDM is not in the main chain, but it is pendent to the chain. Peroxide-based cure systems afford better aging

Table 20. **Conventional and Semi-EV Cure Systems for Butyl Rubber (in PHR)**[a,b]

Ingredient	Semi-EV	Conventional
sulfur	0.5	2.0
TMTD	1.0	1.0
MBT		0.5
DTDM	1.2	
TBBS	0.5	
mooney scorch at 121°C t15, min	36.2	18.5
rheometer at 165°C t90, min	21.0	21.8
cured to t90 at 165°C		
hardness, Shore A	68	68
300% modulus, MPa	5.5	7.1
ultimate tensile, MPa	11.0	11.3
ultimate elongation, %	600	510
heat age resistance, 70 h at 121°C		
retained tensile, %	76	57
compression set, %	56	81

[a] Ref. 7.

[b] Master batch: butyl polymer, 100 phr; GPF carbon black grade N660, 70 phr; paraffinic oil, 25 phr; zinc oxide, 5 phr.

resistance and low compression set. A comparison of a sulfur-based cure to two different peroxides in EPDM is shown in Table 21 (4). Initial properties for these three compounds are reasonably close. However, after air aging, the advantages of peroxide curing are apparent. Most dramatic is the improved compression set obtained by the highly stable C−C cross-links developed with peroxides. Other advantages include ability to achieve high transparency or nondiscoloring and very low creep or stress relaxation. Disadvantages limiting the use of peroxides include poor hot tensile and tear strengths, slow cure rate, a tendency for scorch problems, and somewhat more difficult storage and handling problems in the factory.

7.6. Effect of Other Compounding Ingredients on Vulcanization. Other ingredients besides the elastomer and the cure system itself influence cure and scorch behavior. Usually the effect of a material on compound vulcanization is dependent upon the pH of the material. Ingredients which are basic in nature tend to accelerate the rate of both scorch and cure, whereas acidic materials exhibit the opposite effect. Reviews of the effect of antidegradants, fillers, process oils, and plasticizers are available (6,14,32,33).

Amine-type antioxidants or antiozonants such as the *p*-phenylenediamines (PPD) can decrease scorch time. As the PPD degrades and liberates free amine, scorch time decreases and cure rate is increased.

Nonblack fillers such as the precipitated silicas can reduce both rate and state of cure because of their strong physical interactions with the polar activator and accelerator chemicals. Neutral fillers such as calcium carbonate (whiting) and clays have little or no effect on the cure properties. Carbon black effects are small.

7.7. General Strategy (Statistical Techniques). Often statistically designed experiments are used to optimize curative levels (53). By using properly

Table 21. **Peroxide Versus Sulfur Cured EPDM**[a]

Product	Sulfur	Di-cup	Vul-cup
nordel[b] 1040	100	100	100
HAF black, phr	50	50	50
ZnO, phr	5.0	5.0	5.0
stearic acid, phr	1.0		
sulfur, phr	1.5		
TMTM,[c] phr	1.5		
MBT,[d] phr	0.5		
40KE, phr		6.5	
			4.1
TMQ,[e] phr	0.5	0.5	0.5
cure temperature, °C	160	171	177
cure time, min	20	20	20
original properties modulus, MPa[f]			
100%	2.2	1.8	1.9
200%	6.2	5	5.4
tensile strength, MPa[f]	17.9	17.2	18.1
elongation, %	400	375	375
hardness, points	68	62	60
air-aged, 70 h at 150°C			
modulus, MPa[f]			
100%	5.38	1.7	2.1
200%	12.8	4.7	5.2
tensile strength, MPa[f]	15	17.4	16.8
elongation, %	220	400	350
hardness, points	78	58	60
compression set, %	77	21	19

[a] Ref. 7.

[b] E. I. du Pont de Nemours & Co., Inc.

[c] TMTM = tetramethylthiuram monosulfide.

[d] MBT = 2-mercaptobenzothiazole.

[e] TMQ = polymerized trimethyldihydroquinoline.

[f] To convert MPa to psi, multiply by 145.

designed experiments, ie, balanced and/or orthogonal arrays of curative levels, regression analyses can be performed which quantify the effect of each ingredient, and combination of ingredients (interactions), on the properties of interest. From this, an optimum balance of properties is obtained much more efficiently than via the traditional approach of linearly varying one ingredient at a time. It is encouraged that this technique be used for solving problems in cure system design or any problem involving optimizing combinations of materials and identifying interactions between materials.

8. Tire Compounding

The pneumatic tire consists of two basic areas: the tread area which is responsible for ground contact, and the casing which is responsible for supporting load and transmitting power to the tread area. Each of these areas has several components with different properties which serve specific and unique functions, and all of which must interact for maximum performance (8,54). The role of the rubber compounds which are used in these basic components is threefold: (*1*) to provide the contact area between the vehicle and the surface; (*2*) to provide the cohesive material that holds the tire together such that it acts as an integral unit; and, (*3*) to provide protection for the ultimate strength bearing components, ie, the textile, steel beads, and steel or fabric breakers or belts in radial tires.

8.1. Tire Component Parts.

Desired properties in the components of a radial steel belted passenger car (PC) tire are as follows. The tread is designed and compounded for abrasion resistance, traction, low rolling resistance, vehicle handling characteristics, and protection of the casing from road hazards and obstacles. Often it is divided into two subcomponents to maximize performance: the outer tread for surface contact and the undertread for tying into the casing while reducing tire rolling resistance through decreased hysteresis.

The steel belt, which provides strength and protection for the ply or plies, is encased in a compound that must possess adhesion to the steel which provides stress transfer from the very rigid steel to the considerably more flexible tread, sidewall, and textile carcass components. The wedge compound is formulated to reduce belt-edge sheer stresses while tying the belt to the carcass and reducing hysteresis.

The casing ply coat compound functions are similar to the steel breaker compound. Normally in the steel belted passenger car tire, the ply is a textile cord of polyester or nylon fabrics which are soft and flexible. The truck radial steel tire normally uses a steel cord ply. Earthmover tires are of two basic constructions, ie, radial using steel and bias using textiles. The sidewall compound is formulated to protect the ply and must possess resistance to weathering, ozone, abrasion, and tearing while providing excellent flex fatigue resistance. The innerliner compound must provide good air-permeation resistance and resist moist, hot-air aging.

The apex (often referred to as bead filler) compound must be formulated for dynamic stiffness to facilitate stress distribution and provide good car-handling properties. The bead insulation compound must possess good adhesion to this most important component for enclosing the plies of the tire and holding the tire to the rim. The chafer or rim strip compound protects the plies from rim abrasion and seals the tire to the rim.

There are many ways to measure these properties, some of which are proprietary. However, most laboratory tests are standardized by the American Society for Testing Materials (ASTM). Many of them are interactive to various degrees. The rate and state of vulcanization is especially important to consider for components of heavier and thicker tires. The heat used to vulcanize the tire in a mold under pressure requires time to penetrate from both sides, of the larger tire to the innermost portions. Securing a balanced state of cure, ie, the maximizing of physical properties in all the components, results in the innermost components having a faster rate of cure. The peripheral compounds should have a cure system which holds its physical properties well when overcured. Most tire companies utilize their own physical and chemical laboratories in addition to extensive tire-testing facilities which include laboratory and field vehicle tests. These facilities are augmented by the availability of private commercial companies which operate worldwide.

Table 22. **General Composition of Tire Tread Compounds by Application**[a]

Compound	Material	Standard, phr	High performance, phr	Low rolling resistance, phr	Radial medium truck, phr
polymer	NR			0–40	60–100
	SBR	50–100	0–100	60–100	0–30
	BR	0–50			0–40
carbon black grades	N100 Series	N100 Series			N100 Series
	N200 Series	N200 Series	N200 Series	N200 Series	N200 Series
	N300 Series	N300 Series	N300 Series	N300 Series	
carbon black loading		70–80	70–85	40–65	45–60
oil		30–60	25–45	0–30	0–20
antioxidants, antiozonants		1–2	1–2	1–2	1–3
sulfur		1	1	1	1
accelerator		1–2	1–2	1–2	1–2
stearic acid		1–2	1–2	1–2	1–2
ZnO		3	3	3	3

[a] Ref. 7.

8.2. Materials. Tire compounds contain the following generalized ingredients in the approximate proportions noted. Industry practice is to formulate starting with 100 parts per hundred weight of the rubber (phr). Table 22 offers examples for various treads.

There may be as many as 15 different compounds in a single tire. Each compound typically uses between 8 and 12 ingredients. There are approximately 1000 different chemicals or materials used in the tire compounding field. Thus, the potential combinations are extremely high. In addition, interactions between materials are encountered and must be controlled. For example, premixing of certain vulcanization ingredients must be avoided because of their reactions with each other and formation of end products that do not give the desired rate and state (number of elastomer cross-links) of cure in the finished tire. Interactions are not limited to the 8 to 12 ingredients within a single formula, but may also occur between the compounds of adjacent components, in preassembly of components for tire building, in storage of green (uncured) tires, in vulcanization of the tire, in warehousing, and during operation of the tire through its service life.

Migration of chemicals from adjoining compounds, in addition to preferential absorption of various materials into each other, makes knowledge of the chemistry and physics of materials most important in realizing specific, highly varying properties in the different compounds and components necessary to maximize tire performance and optimize cost. Some interactions of materials are desired. For example, without migration of resins at compound component interfaces, adhesion of one component to another is significantly weakened and intercomponent separation is enhanced. Solubility parameters of materials are important in processing of compounds and components. A material used in excess of this parameter can bloom (diffuse to the surface of the component) and render it difficult in final tire assembly or inhibit the desired migration of other ingredients and weaken component interfacial adhesion.

Tire Elastomers. For the mechanical strength requirements of tires, NR is better than SBR or BR and offers excellent tread chipping/chunking resistance with low tire running temperatures and improved rolling resistance. Although more difficult to mix and process, it is very good in downstream processes such as extruding, calendering, and tire building. Although good in chip/chunk-type wear and in severe stress wear, it is usually faster wearing in nominal passenger and truck over-the-road tires. It offers better ice traction and excellent flexibility in extreme low temperature service (ie, less than 40°C). It is by far the preferred rubber for wire belt and textile ply/breaker coat compounds.

SBR is by far the preferred polymer for passenger car tire treads, mainly owing to its good wear and traction. It is also the least expensive polymer when produced by the emulsion (water-based) process which is the most commonly used. In the 1980s, specialty solution polymerized SBRs (SSBR) were introduced. These rubbers, using hydrocarbon solvent such as hexane as media and special catalytic systems, were found to offer increased capabilities for compounders to improve rolling resistance for decreased fuel consumption while maintaining high levels of wear and traction. The specialty SSBRs accomplish this through control of the styrene–butadiene polymer backbone structure, coupling of polymers, and addition of reactive chemical units at the polymer ends. Not all of these changes are used in the same specialty polymer, but coupled polymers are common and can significantly affect polymer molecular weights; ie, larger (higher molecular weights) branched polymers which are more difficult to produce, are more expensive, and have some deficiencies in processing. Many of these polymers are available in the oil/black master batch (premixed blends) as is the emulsion SBR. SBR, whether emulsion or solution, is still not as resilient as NR or BR which limits applications in tires.

BR can be produced in both emulsion and hydrocarbon solution processes. It is the butadiene part of SBR that is controlled in specialty SSBRs. Originally polybutadiene found its niche in tires by offering excellent over-the-road wear characteristics because of its high cis, high linearity structure. This offers resilience (low hysteresis) and excellent flex fatigue resistance along with excellent wear and could only be achieved in the more expensive solvent process. BR is more difficult to process in the factory, particularly in milling operations. It does not possess the excellent tack of NR and makes tire building more difficult. BR is also very low in resistance to tearing.

Halobutyl rubber (HIIR) is used in innerliner and white sidewalls, and sometimes in treads to improve winter traction properties. This class of polymer offers marked improvements in tire-air retention owing to lower air permeability as well as excellent age resistance and flex fatigue life. Both the chlorine and bromine versions of isobutylene isoprene rubber (IIR) are used to improve covulcanization with the other commodity tire rubbers. It is an almost saturated polymer with few sites (1–2%) available for conventional sulfur curing. IIR offers high hysteresis at nominal tire operating temperatures and thus acts as a superior cushioning rubber. It is the preferred rubber for tire curing press bladders.

A new isobutylene polymer modified with p-methylstyrene and subsequently brominated is available which offers a fully saturated backbone to resist aging while improving compatibility with tire commodity rubbers. Use of such polymers may allow improvement in a broad range of tire performance parameters.

EPR has a fully saturated backbone and has only unsaturation points available for vulcanization cross-linking in very small percentages of the pendent diene modifier (EPDM). It is an excellent aging compound with high flex fatigue life even when heavily loaded with fillers and is utilized in PC tire white sidewalls.

It is common to use more than one type of rubber within a given compound. An example of this is the truck tire sidewall which must not only possess high strength but must also have excellent aging and flex fatigue life in order to survive multiple retreading, ie, vulcanizing a new tread to the worn original tire casing. The original casing of a radial truck tire, if properly maintained, can last for a million miles, while the original tread on this casing can deliver 100,000 to 300,000 miles. In passenger car tires, as many as four different polymers may be used for the tread compound totaling 100 phr; eg, 25 phr emulsion SBR, 25 phr SSBR, 30 phr BR, and 20 phr NR. If solution polymerized SBR categories can be considered as falling with a 10°C T_{g} range increments, there are at least nine groups of specialty SSBRs that are commercially available. In addition some large vertically interated, tire companies are producing for their own captive use. Natural rubber can be purchased in several grades. SBR also comes in different grades and is available in oil and oil/carbon black master batches (oil and/or carbon black added to the rubber at the rubber producers) which may use a different SBR (usually higher molecular weight) than if it were produced without master batching. The use of different materials within a single grouping is commonly encountered, ie, the use of two or more elastomers making up the 100 parts total as mentioned above.

Tire Compound Filler Reinforcement. The popular carbon blacks for tires and their application patterns are shown in Table 23. In tires, carbon black is important because of the high flex fatigue and tear strength requirements of this product. Poor dispersion may result in premature cracking in both treads and sidewalls. In off-the-road tires, poor dispersion could result in excessive chipping, chunk-outs, and cutting of tread material, causing a significant loss in treadwear in addition to tread "base-of-lug" cracking which can lead to loss of an entire lug. Because of demands for improved fuel consumption

Table 23. **Carbon Blacks and Their Applications in Tires**

		Tire components						
Series	Tire types	Tread	Sidewall	Ply breaker	Apex	Chafer	Bead	Liner
N100	truck	+				+		
N200	most	+				+		
N300	most	+	+	+	+	+	+	
N500	most			+			+	+
N600	most			+			+	+
N700	most			+				

through reduced rolling resistance, a new series of carbon blacks referred to as low hysteresis or LH, which are N220 or N300 series, have emerged. Basically these series of carbon blacks have a wider size range in both the primary particles and primary aggregates in addition to a more chemically active surface area.

Second in tonnage for tire use, silica's utilization has been increasing in spite of higher per kilogram cost because of increased compound tear strength and contribution to improvement in tire traction performance, and lower rolling resistance. Silica as a tire reinforcing filler was first introduced in earthmover tire treads owing to its ability to improve tear resistance and lower tire operating temperatures. These properties are of utmost importance in off-the-road tires, which function at high operating temperatures and encounter rocks that may cut and tear out large chunks of tread under high traction and torque conditions. With demand for improved rolling resistance, silica usage has expanded into other tire lines. This expansion has also been boosted by the introduction of a silane coupling agent, which forms a chemical bond between the silica and the rubber resulting in improved treadwear. With the use of the bifunctional silane coupling agent silica treads are equal in wear to some carbon blacks while still offering an improvement in rolling resistance. Silane use slightly reduces tear, but this is acceptable in most applications. Silica has also found applications in wire breaker coat compounds, where it stabilizes the copper sulfide bonding layer to the brass-coated steel cable, thus improving adhesion.

Reinforcement and stiffness of a compound can also be achieved with the use of reactive resins. Resins consisting of two-component systems of resorcinol or resorcinol condensation products and a methylene donor, such as hexamethoxymethylmelamine (HMMM) or hexamethyltetramine (HMT), are the most popular in tires. These materials can be prereacted and added to the formula, or for more effective results they can react *in situ*; ie, they can be added separately into the formula and react when the tire is vulcanized.

Softeners, Extenders, and Plasticizers. Other materials can affect the properties of rubber such as softeners, extenders, and plasticizers. In tires the most popular of these are petroleum oils. They are utilized for controlling green compound viscosity and vulcanized compound hardness. The term *extender* is used to denote their use to allow for increased use of reinforcing fillers as the oils are significantly less expensive than are the rubbers. These materials also act as processing aids. The term *plasticizer* is used to denote their ability to act as an internal lubricant for processing purposes as well as for improving low temperature flexibility in the vulcanized product. The synthetic phthalates are the most effective in meeting low temperature flexibility while also serving as softeners. Cost limits their application.

The petroleum oils are of three basic types: aromatic, naphthenic, and paraffinic. Naphthenic oil does not contain high levels of polynuclear aromatics and is therefore less hysteretic. Because of these considerations the naphthenic oil is gaining in usage at the expense of aromatics. Paraffinic oil is only used in very limited quantities in tire compounds. The petroleum oils are more specific to certain rubbers and therefore require compounding considerations for full optimized usage. All three softeners migrate from one compound to another, and this must be considered when compounding for a set range of stiffness (modulus) gradiations in the tire components designed to alleviate stress.

1. *Processing aids*. Petroleum oils are processing aids as well as functioning as softeners, extenders, and plasticizers.
2. *Peptizers* are materials used rather extensively in natural rubber (NR) compounds. When added to NR in premastication, they cleave or break the molecular backbone resulting in lower molecular weights which allows for easier processing. However, there has been a move to reduce usage in order to maximize strength. Some tire companies have gone to mixing variations which are more expensive to preserve molecular weight.
3. *Other processing aids* utilized in tires are vegetable oils (fatty acids, fatty acid esters, alcohols, and metal salts of these oils), naturally occurring resins such as pine tar, and hydrocarbon resins.

The main benefits of processing aids are as follows: (*1*) improving incorporation of fillers; (*2*) reducing mixing energies; (*3*) reducing internal friction for ease of milling, extruding, and calendering; (*4*) compatibilizing the different rubbers for improved processing as well as for better adhesion of one compound to a different compound in the vulcanized tire (compatibilizers have gained markedly in usage because of polarity differences of blended polymers); and (*5*) providing improved green tack (tackifiers) for better tire building.There is a definite trend in the industry to develop multifunctional materials with value-added properties.

Vulcanization System Components. Tire compounds are almost exclusively cured (cross-linked) with sulfur. Sulfenamides, thiazoles, thiurams, guanidine, and carbamates are the most popular choices to accelerate curing. Efficient vulcanization (EV), semiefficient (semi-EV), and the conventional curing systems are all used, sometimes in the same tire for different compounds and components. They are also varied depending on the elastomer or elastomer blend used within a given compound, such as a compound using a blend of NR and SBR which uses a more efficient cure system than NR alone may require.

Zinc oxide and stearic acid are used to activate the curing system as well as to preserve cured properties when overcuring, which is curing beyond the point of time and temperature at which maximum properties are obtained.

Overcuring is encountered to some degree in all compounds of any thickness because of the slow conduction of heat through rubber. Earthmover tires may have tire shoulder gauges in excess of 0.3 m (12 in.). The outside and inside of the tire are overcured to obtain a satisfactory state-of-cure in internal components. Even though heat is being conducted to the midpoint of the tire shoulder from both sides it can take many hours to reach the same temperature as the plies and that portion of rubber next to the mold. Although the earthmover tire epitomizes this phenomena, it is an excellent example of the problem of maximizing cured properties which change rather dramatically with state-of-cure. The properties of tear strength, resilience, modulus, tensile strength, elongation, and cut growth (fatigue) are significantly affected by state-of-cure. Of course many factors are involved in effecting the desired end goal of an optimized state-of-cure: the mold, the temperatures and media to effect the temperatures, the pressures, etc. Thus knowledge and understanding of engineering and physics, particularly thermodynamics, in addition to the chemistry of rubber and material reactions, are required.

An important consideration of any vulcanization system is scorch resistance. Scorch time is that period after heat has been applied until a significant change in compound stiffness occurs indicating that cross-linking of the polymer has initiated. As the rubber compound is hot when the accelerators and sulfur are added, it appears that the scorch period starts immediately. As the compound is processed through the factory to form tire components, it is heated and is subject to premature vulcanization (scarch) if heat is excessive (scorch). Scorched compounds are more difficult to process to their finished component.

To assist in control of the onset of vulcanization, a retarder or prevulcanization inhibiter (PVI) is used. Retardation of the onset of cure does not mean that the rate of cure is slowed; in fact, cure rate may actually be increased. Rather, there is an extension to the induction period prior to cure.

8.3. Compound Formulating. Generally two basic approaches are used to formulate for achieving desired tire performance: the use of known relationships of materials used in a given compound to a specific performance parameter, and computing relationships of materials to physical properties and in turn estimating the effect on a given performance parameter. Using physical properties relating to performance parameters facilitates development of regression equations to predict performance for laboratory screening of potential improvements. Many of these relationships are well established. The two main categories of measurement criteria are either classical mechanical or dynamic mechanical properties.

8.4. Mechanical Strength. Strength is measured in the laboratory with tests of stretch, compression, and torque in both uncured and cured compounds. Uncured or so-called green compounds are measured to assess processing characteristics. An example is plasticity of the green compound at a given temperature and torque to predict the ease or difficulty of milling, extruding, and calendering to secure a given profile and, or gauge of a component for subsequent tire building. Cured compounds are tested for mechanical or physical properties to relate them to a specific tire parameter. Both green and cured properties are run after mixing of a formula to assure its correctness before subsequent processing for given components. Testing is also conducted on the final component before tire building in some cases.

Some tests, while undergoing deformation, are usually referred to as static, in that they are performed at slow speeds or low cycles. Examples of these tests are stretch modulus, ultimate tensile strength, and elongation to break, ie, a measure of total energy capabilities or rupture phenomena. Dynamic properties are measured by continuous cycles of varying deformation (tension, compression, or shear), at varying frequencies which can be set close to that which a component would experience in a tire. These properties are more correlative to many tire performance parameters.

8.5. Aged and Fatigued Properties. Tire compounds are subjected to static and dynamic aging throughout their entire life cycle. Static aging begins even in the green (uncured) state with exposure to oxygen, ozone, light, heat, and humidity. In the tire factory, these effects can be minimized to the point where they barely exist. Factory tire compounders are assigned to tire plants to assure the integrity of their compounds throughout the production cycle. Even as tires are warehoused they are protected by regulations and procedures followed by the material's technologist or compounders. It is when tires are applied to the vehicle that this natural phenomenon of aging becomes most important.

Heat has a detrimental effect on rubber compounds. For example, the tensile strength of a tire compound at 150°C may only be 50% of its room temperature maximum. Furthermore, most of the strength properties, such as tear strength and modulus, are similarly affected. When a tire is heated up through use and allowed to cool again to ambient temperature, it loses some of its original strength and is subject to attack by ozone. This can sever molecular chains and leads to cracking at points of deflection. Finally, flex fatigue resistance diminishes markedly upon aging and repeated cycling because of chemical changes in the compound when heated by rolling and working. Low tire inflation means more work and more heat adding to degradation by a power factor.

Wire cords are particularly subject to degradation of their adhesion values by moisture. To combat this, halogenated butyl (HIIR) use is essential in tire innerliners because of its property of low air and water vapor diffusion rates. Moisture is present in most air pumps and many tires are mounted with water left in the tire on mounting. For these reasons, tires and tire compounds are tested extensively at simulated aging conditions in the laboratory and on test vehicles before they are sold to the customer.

9. Test Methods

Because of the long-range elasticity of soft rubber vulcanizates and the various special conditions under which they are degraded in use, special test methods have been developed which in many respects are unlike those used for wood, metals, and hard plastics. The American Society for Testing and Materials (ASTM), through its Committee D11 on Rubber and Rubber-like Materials, is constantly developing and promulgating new and improved methods for testing rubber and rubber products.

Test methods to characterize rubber compounds fall into four general catagories.

1. Rheological characterization, which would include measurement of compound viscosity using a Mooney Viscometer, indicating ease of processing, vulcanization and curing kinetics, and rheological information obtained from a capillary rheometer.
2. Classical mechanical properties such as tensile strength, tear strength, peel adhesion, hardness, and aged properties.
3. Dyanamic mechanical properties such as storage modulus and loss modulus obtained in tension, compression, and shear. A range of associated terms may be calculated from this data which in turn can be used to estimate final product performance parameters.
4. Secondary properties which might include properties such as permeability, fatigue resistance, rebound, and heat buildup.

The test protocol followed in a development program will depend on the nature of the final product under development. However, as a minimum, based curing properties, processing properties, and basic mechanical properties are required for decisions regarding selection of a compound formula to be used in a product such as a hose or belt.

10. Summary

The science of rubber compounding is among the most complex disiplines in industrial chemistry. The role of the modern materials scientist in the tire and rubber industry is to use materials to improve current products and develop new technology products. Four major factors govern this development process:

1. *Quality*. The product must meet the design expectations and be trouble-free.
2. *Performance*. The product must meet the customer's expectations.
3. *Environmental*. Products must be in compliance with regulatory requirements and present minimum concern with regard to disposal.
4. *Cost*. The product or system of which the rubber part is a component must provide value to the customer.

In meeting these objectives, the disipline of rubber compounding has evolved from an "art" 50 years ago to a highly complex science.

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