ELASTOMERS, SYNTHETIC

1. Introduction

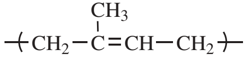
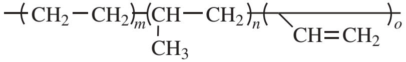
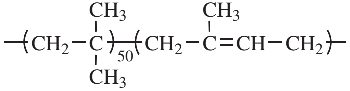
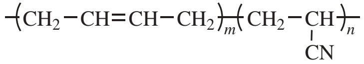
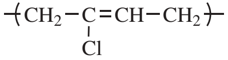
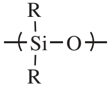
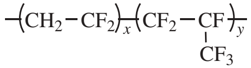
The purpose of this article is to provide a brief overview of the materials designated synthetic elastomers and the elastomeric or rubbery state. Subsequent entries describe the individual classes of elastomers in detail. Table 1 provides a fundamental description of the principal classes of synthetic elastomers. Table 2 gives the widely accepted ASTM abbreviations for synthetic rubbers.

2. Definition of Elastomers

The term elastomer is the modern word to describe a material that exhibits rubbery properties, ie, that can recover most of its original dimensions after extension or compression. Ever since the pioneering work of Staudinger in the early 1900s (1), it has been accepted that such rubbery behavior results from the fact that the material is composed of a tangled mass of long-chain, flexible polymer molecules. When such a material is extended or stretched, the individual long-chain molecules are partially uncoiled, but will retract or coil up again when the force is removed because of the kinetic energy of the segments of the polymer chain. The flexibility of such polymer-chain molecules is actually the result of the ability of the atoms comprising the chain to rotate around the single bonds between them. Theories of rubberlike elasticity are well-developed (2).

The properties of elastomeric materials are also greatly influenced by the presence of strong interchain, ie, intermolecular, forces which can result in the formation of crystalline domains. Thus the elastomeric properties are those of an

Table 1. **Elastomers[a] and Their Characteristics**

Name	CAS Registry number	Chemical name	Repeat unit structure	Vulcanizing agent	Stretching crystallization	Gum tensile strength
natural rubber	[9006-04-6]	*cis*-1,4-polyisoprene (>99%)	[b]	sulfur	good	good
styrene–butadiene rubber	[9003-55-8]	poly(butadiene-*co*-styrene)	 $(CH_2-CH=CH-CH_2)_m(CH_2-\underset{C_6H_5}{CH})_n$	sulfur	poor	poor
butadiene rubber	[9003-17-0]	polybutadiene (>97% cis,-1,4)	$(CH_2-CH=CH-CH_2)$	sulfur	poor to fair	poor to fair
isoprene rubber	[9003-31-0]	*cis*-1,4-polyisoprene (>97%)	 $(CH_2-\overset{CH_3}{C}=CH-CH_2)$	sulfur	good	good
EP(D)M	[c,d]	poly(ethylene-*co*-propylene-*co*-diene)[c]	 $(CH_2-CH_2)_m(\underset{CH_3}{CH}-CH_2)_n(\underset{CH=CH_2}{\quad})_o$	sulfur	poor	poor
butyl rubber	[9010-85-9]	poly(isobutyene-*co*-isoprene)	 $(CH_2-\overset{CH_3}{\underset{CH_3}{C}})_{50}(CH_2-\overset{CH_3}{C}=CH-CH_2)$	sulfur	good	good
nitrile rubber	[9003-18-3]	poly(butadiene-*co*-acrylonitrile)	 $(CH_2-CH=CH-CH_2)_m(CH_2-\underset{CN}{CH})_n$	sulfur	poor	poor
chloroprene rubber	[9010-98-4]	polychloroprene (mainly trans)	 $(CH_2-\underset{Cl}{C}=CH-CH_2)$	MgO or ZnO	good	good
silicones		polydialkylsiloxane (mainly polydimethyl siloxane)	 $(\overset{R}{\underset{R}{Si}}-O)$	peroxides	poor	poor
fluorocarbon elastomers		poly(vinylidene fluoride-*co*-hexafluoropropene)	 $(CH_2-CF_2)_x(CF_2-\underset{CF_3}{CF})_y$	diamines	poor	poor
polysulfide rubber		poly(alkylene sulfide)	$(CH_2-CH_2-S_{2-4})$	metal oxides	fair	poor
polyurethanes		polyurethanes	$HO(R-OCONHR'NHCOO)_xR-OH$	diisocyanate	fair	good

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[a] Not inclusive; see also ACRYLIC ELASTOMERS, PHOSPHAZENES, CHLOROSULFONATED POLYETHYLENE, EETHYLENE–ACRYLIC ELASTOMERS, POLYETHERS under the title ELASTOMERS, SYNTHETIC.

[b] See ISOPRENE RUBBER.

[c] o = zero for ethylene–propylene rubber; poly(ethylene-*co*-propylene) [9010-79-1].

[d] [25038-36-2] when the diene is norbornene.

Table 2. **ASTM Elastomer (Rubber) Designations**

Abbreviation	Elastomer
ABR	acrylate–butadiene
BR	butadiene
CR	chloroprene
EPM	ethylene–propylene
EPDM	ethylene–propylene–diene[a]
IR	isoprene
IM	isobutylene
IIR	isobutylene–isoprene or butyl rubber
SBR	styrene–butadiene
SIR	styrene–isoprene
NBR	acrylonitrile–butadiene
NCR	acrylonitrile–chloroprene
PBR	vinylpyridine–butadiene
PSBR	vinylpyridine–styrene–butadiene
XNBR	carboxylic-acrylonitrile–butadiene
XSBR	carboxylic-styrene–butadiene
CIIR	chloroisobutylene–isoprene or chlorobutyl rubber
BIIR	bromoisobutylene–isoprene or bromobutyl rubber
MQ	dialkysiloxane
GPO	poly(propylene oxide)
AU	polyesterurethanes
EU	polyetherurethanes

[a] Nonconjugated diene; residual unsaturation from the diene is in the pendent group.

amorphous material having weak interchain interactions and hence no crystallization. At the other extreme of polymer properties are fiber-forming polymers, such as nylon, which when properly oriented lead to the formation of permanent, crystalline fibers. In between these two extremes is a whole range of polymers, from purely amorphous elastomers to partially crystalline plastics, such as polyethylene, polypropylene, polycarbonates, etc.

A most interesting class of materials is comprised of those amorphous elastomers that show the ability to undergo a temporary crystallization when stretched to a high extension, thus virtually becoming fibers, but that retract to their original dimension when the force is removed. Such crystallizing rubbers can thus demonstrate unusually high tensile strength in the stretched condition, but revert to the amorphous state when the force is relaxed because of relatively weak interchain forces.

3. Effect of Temperature on Polymer Properties

There are two principal forces that govern the ability of a polymer to crystallize: the interchain attractive forces, which are a function of the chain structure, and the countervailing kinetic energy of the chain segments, which is a function of the temperature. The fact that polymers consist of long-chain molecules also introduces a third parameter, ie, the imposition of a mechanical force,

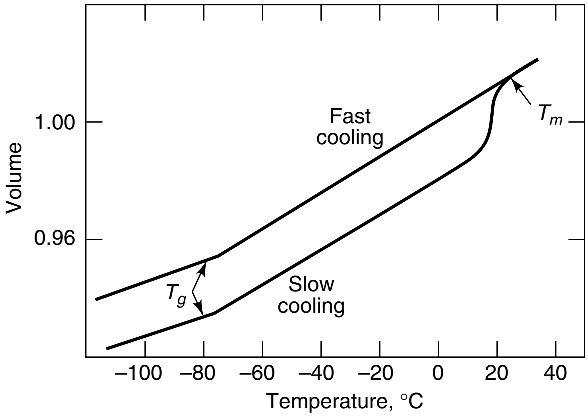


Fig. 1. Phase transition in Hevea rubber. T_g is glass-transition temperature; T_m is melting point.

eg, stretching, which can also enhance interchain orientation and favor crystallization.

In addition to the phenomena of crystallization and melting, which both represent a change of state in the material, there is a third transition which plays a strong role in the behavior of polymers, although it is by no means absent in the behavior of simple liquids. This is the glass-transition temperature, T_g. The role of these transitions in the behavior of elastomers is shown in Figure 1, which depicts the volume–temperature relations during the cooling or heating of a sample of natural rubber. The volume is expressed in arbitrary units. This type of measurement is usually performed by noting the shrinkage or expansion of a fluid in a pycnometer containing a sample of rubber in a neutral liquid, which can be heated or cooled.

If a sample of natural rubber is first heated above room temperature, eg, to 30–40°C, and then slowly cooled, the volume shows a linear decrease until the temperature approaches about 20°C, at which point there is a sharp drop in volume. This represents a true change of state, ie, the onset of crystallization or the freezing/melting point of the rubber. On further cooling, the volume continues to show a linear decrease, but on a different line than that of the original. This continues until a temperature of −72°C is reached, at which point there is no discontinuity, as in the case of the freezing/melting point, but a change in the slope of the volume–temperature line. This point does not represent a true change of state but a second-order transition known as the glass-transition temperature or "glass point" (3). Thus the freezing/melting point, T_m, of the rubber is the temperature at which crystallization or melting occurs, a true first-order transition, whereas the T_g of the rubber is the point at which the liquid state becomes a glassy state, ie, the molecular chain segments lose their ability to move around.

A further examination of Figure 1 shows that it is possible to avoid the freezing/melting point entirely by quenching the rubber, ie, cooling too fast for crystallization to take place, and shrinkage continues along the original volume–temperature line.

Figure 1 thus helps to define the general features of the physical state of polymers. Polymers fall into two classes, those that are capable of crystallization and those that are not. A noncrystalline (amorphous) polymer is considered a liquid (although a highly viscous one), which becomes a glass at reduced temperatures. Thus, atactic polystyrene is always amorphous, but it is in a "glassy" state at room temperature, since its T_g is about 105°C. Above its T_g it becomes rubbery although its chemical stability in air at that temperature is so poor as to render it useless. On the other hand, polyethylene and isotactic polypropylene are crystalline, to a greater or lesser extent, at room temperature, and hence do not exhibit rubbery behavior.

The class of rubbers that show the ability to crystallize when stretched represent a special class of rubbers. In the listing of the various principal elastomers in Table 1, this unique property is shown to increase the strength of rupture of these elastomers.

4. Compounding and Vulcanization of Elastomers

In order to "cure" or "vulcanize" an elastomer, ie, cross-link the macromolecular chains (Fig. 2), certain chemical ingredients are mixed or compounded with the rubber, depending on its nature (4,5). The mixing process depends on the type of elastomer: a high viscosity type, eg, natural rubber, requires powerful mixers (such as the Banbury type or rubber mills), while the more liquid polymers can be handled by ordinary rotary mixers, etc (see RUBBER COMPOUNDING).

The principal rubbers, eg, natural, SBR, or polybutadiene, being unsaturated hydrocarbons, are subjected to sulfur vulcanization, and this process requires certain ingredients in the rubber compound, besides the sulfur, eg, accelerator, zinc oxide, and stearic acid. Accelerators are catalysts that accelerate the cross-linking reaction so that reaction time drops from many hours to perhaps 20–30 min at about 130°C. There are a large number of such accelerators, mainly organic compounds, but the most popular are of the thiol or disulfide type.

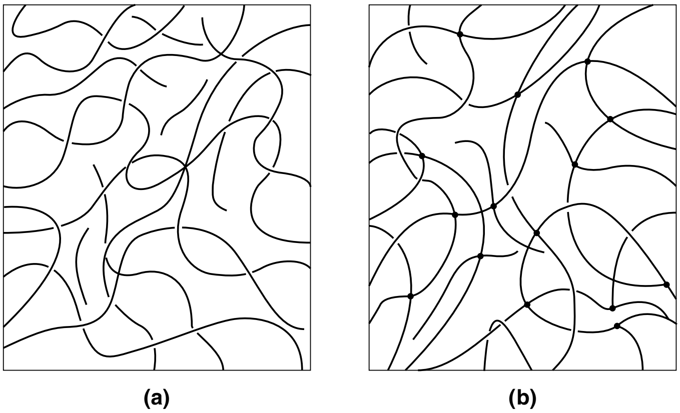


Fig. 2. Vulcanization of rubber macromolecles: (**a**), before cross-linking; (**b**), after cross-linking.

Zinc oxide is required to activate the accelerator by forming zinc salts. Stearic acid, or another fatty acid, helps to solubilize the zinc compounds.

In addition to the ingredients that play a role in the actual vulcanization process, there are other components that make up a typical rubber compound (see RUBBER CHEMICALS). Softeners and extenders, generally inexpensive petroleum oils, help in the mastication and mixing of the compound. Antioxidants (qv) are necessary because the unsaturated rubbers can degrade rapidly unless protected from atmospheric oxygen. They are generally organic compounds of the amine or phenol type (see also ANTIOZONANTS). Reinforcing fillers, eg, carbon black or silica, can help enormously in strengthening the rubber against rupture or abrasion. Nonreinforcing fillers, eg, clay or chalk, are used only as extenders and stiffeners to reduce cost.

5. General-Purpose Elastomers

The main thrust of the early attempts to create synthetic rubber was aimed at a general-purpose elastomer to displace natural rubber. Such attempts only became possible after Greville Williams, in 1860, showed that natural rubber could be pyrolyzed to yield isoprene (and its homologues) (6). Hence, there were many attempts during the last part of the nineteenth century to "convert" isoprene into a rubber. However, because this involved a polymerization reaction, and because the concept of polymers had not yet been developed, it is not surprising that such efforts were all unsuccessful. Among the more noteworthy work was that of Bouchardat who was able, in 1879, to produce a rubbery substance by heating isoprene, obtained from natural rubber, with hydrochloric acid (7). Tilden, in 1884, showed that the same results could be achieved with isoprene obtained from other sources than rubber, so that there was nothing unusual about the isoprene used by Bouchardat (8).

In the early part of the twentieth century, success began to crown some efforts at the synthesis of rubber. Thus Matthews and Strange, in 1910, showed that metallic sodium can react with isoprene to convert it to a rubbery substance, and Harries, in 1913, showed the same effect with butadiene and sodium (9). It was the latter work that ultimately resulted in the first commercial production of a general-purpose synthetic rubber, sodium polybutadiene. There had been a limited commercial production in Germany during World War I of "methyl rubber" prepared by the thermal polymerization of 2,3-dimethylbutadiene, but this rubber was of such poor quality and required such a difficult and unreliable process that it was hastily dropped at the conclusion of the war. Hence it was the polymerization of butadiene by means of sodium metal that became the first synthetic rubber process, giving rise to the Buna rubbers in Germany, and the SKF rubbers in the USSR during the 1920s.

At the same time, however, considerable research was being done, especially in Germany, on a novel process called emulsion polymerization, in which the monomer was polymerized as an emulsion in the presence of water and soap. This seemed advantageous since the product appeared as a latex, just like natural rubber, leading to low viscosity even at high solids content, while the presence of the water assured better temperature control. The final result, based mainly on work at the I.G. Farbenindustrie (IGF) (10), was the development of a butadiene–styrene copolymer prepared by emulsion polymerization, the forerunner of the present-day leading synthetic rubber, SBR.

The ESSO company had an agreement with IGF during the years prior to World War II for an interchange of information on petroleum products, including synthetic rubber, so that information on the production of SBR was available to the United States during the wartime emergency, which started with the seizure of Far East rubber plantations by Japan in 1941. Thus Germany continued to produce SBR emulsion and the USSR continued with sodium polybutadiene throughout the war, while the United States developed an "instant" synthetic rubber industry in 1942–1945 for the production of emulsion SBR.

5.1. Styrene–Butadiene Rubber (SBR). This is the most important synthetic rubber and represents more than half of all synthetic rubber production (Table 3) (see STYRENE–BUTADIENE RUBBER). It is a copolymer of 1,3-butadiene, $CH_2{=}CH{-}CH{=}CH_2$, and styrene, $C_6H_5CH{=}CH_2$, and is a descendant of the original Buna S first produced in Germany during the 1930s. The polymerization is carried out in an emulsion system where a mixture of the two monomers is mixed with a soap solution containing the necessary catalysts (initiators). The final product is an emulsion of the copolymer, ie, a fluid latex (see LATEX TECHNOLOGY).

The original recipe adopted by the U.S. Government Synthetic Rubber Program was known as the "Mutual Recipe" and is shown in Table 4. As can be seen, the reaction temperature was set at 50°C, which resulted in 75% conversion to polymer in about 12 h. The reaction was then stopped by addition of a "shortstop," such as 0.1 parts hydroquinone, which destroyed any residual catalyst (persulfate), and generated quinone, which helped inhibit any further polymerization.

An antioxidant such as phenyl-β-naphthylamine, was then added to the latex (1.25 parts) prior to coagulation by salt–acid mixtures and drying of the rubber crumb, which was compressed into 34-kg bales. The SBR produced by

Table 3. **World Synthetic Rubber Consumption[a,b], 10^3 t**

Rubber type	1987	1988	1989[c]	1993[c]
SBR solid	2324	2382	2405	2616
SBR latex	241	245	250	265
carboxylated latex	984	1049	1088	1189
polybutadiene	1044	1098	1117	1215
ethylene–propylene	498	540	557	642
polychloroprene	249	251	251	258
nitrile, solid and latex	221	237	240	262
other synthetics[d]	958	1022	1040	1163
Total	*6519*	*6824*	*6948*	*7610*

[a] Ref. 11.Courtesy of the International Institute of Synthetic Rubber Producers.

[b] Excludes Communist countries.

[c] Estimated.

[d] Includes butyl and polyisoprene.

Table 4. **The "Mutual Recipe" for Polymerization of SBR**

Component	Parts by weight
water	180
butadiene	75
styrene	25
soap	5
potassium persulfate	0.3
n-dodecyl mercaptan	0.5
polymerization temperature	50°C
polymerization time	12 h for 70% conversion

this recipe had a Mooney viscosity of about 50 and a number-average molecular weight M_n of 100,000–200,000.

The thiol (*n*-dodecyl mercaptan) used in this recipe played a prominent role in the quality control of the product. Such thiols are known as chain-transfer agents and help control the molecular weight of the SBR by means of the following reaction where M = monomer, eg, butadiene or styrene; $\mathrm{R(M)}_n =$ growing free-radical chain; $k_p =$ propagation − rate constant; $k_{\mathrm{tr}} =$ transfer− rate constant; and $k'_p =$ initiation − rate constant.

$$\mathrm{R(M)}_{n+1} + \mathrm{C_{12}H_{25}SH} \xrightarrow{k_{\mathrm{tr}}} \mathrm{R(M)}_{n+1}\mathrm{H} + \mathrm{R'S}$$

$$\mathrm{R'S} + \mathrm{M} \xrightarrow{k'_p k_p k'_p} \mathrm{R'S(M)}_n$$

Thus the thiol $\mathrm{C_{12}H_{25}SH}$ is capable of terminating a growing chain and also initiating a new chain. If the initiation-rate constant, k'_p is not much slower than the propagation-rate constant, k_p, the net result is the growth of a new chain without any effect on the overall polymerization rate (retardation). That represents a true chain transfer, ie, no effect on the rate but a substantial decrease in molecular weight (12).

The use of these transfer agents, known as modifiers, in SBR polymerization has a profound effect in producing an acceptable synthetic rubber because without them the SBR emulsion polymerization system produces a very high molecular-weight polymer, which can easily become sufficiently cross-linked to result in gel, ie, a rubber insoluble in any solvent. A high gel rubber is also difficult to process with the normal mixing equipment, ie, rubber mills or Banbury mixers. Hence the use of thiol modifiers made it possible to produce processible elastomers. Thus, in the Mutual Recipe of Table 4, the reaction was stopped at about 70% conversion in 12 h to obtain a gel-free SBR, having a Mooney viscosity of about 50. Increasing the conversion above this point would run the risk of gel formation because of depletion of the thiol modifier.

The most significant post-war development in SBR production was the introduction of low temperature polymerization recipes, capable of being used at a temperature near the freezing point of water, ie, 5°C. This "cold rubber" could be produced gel-free even at a Mooney viscosity of 100. Hence the average molecular weight was substantially higher than that of the 50°C SBR, with a smaller fraction of low molecular-weight "tails" that might introduce network defects in the final vulcanizate. The fact that this 100 Mooney cold rubber was more difficult to process during compounding could be easily circumvented by adding up to 25% of an emulsion of petroleum oil to the latex before coagulation. This “oil-extended cold rubber” became the standard SBR for use in tire treads, etc, because of its superior abrasion resistance, resilience, and strength.

Processing and Properties. Since SBR is an amorphous polymer (irregular chains), it does not exhibit crystallization either on stretching or cooling, and hence exhibits negligible strength unless it is reinforced with a fine-particle carbon black. It is compounded much like natural rubber, although it is not quite as easy to process and is also vulcanized with sulfur. It is not quite as tacky as natural rubber in the tire-building process and also shows a lower “green” strength of the unvulcanized compound.

However, the final properties of the tire show some points of superiority over natural rubber, ie, in higher abrasion resistance of cold SBR. Since the polymer has a T_g of −45°C compared with the −72°C of natural rubber, it shows poorer low temperature properties. Also, since the resilience of SBR is only about 50%, compared to at least 70% for the natural rubber, there is more heat build-up with SBR. In fact, although it is entirely possible to produce an all-synthetic automobile tire, this is not the case for truck tires because their greater mass leads to an unacceptable degree of heat build-up (13).

5.2. Polybutadiene. The homopolymer polybutadiene (PB) is next in importance to SBR, as shown by its world production (Table 3). It is prepared by polymerization of butadiene in solution, using organometallic initiators, either of the Ziegler-Natta type or lithium compounds. It is, therefore, a result of the discovery of stereospecific polymerization during the 1950s and 1960s (see ELASTOMERS, SYNTHETIC–POLYBUTADIENE).

Molecular Structure. The butadiene units in the chain are of three types: *cis*- and *trans*-1,4

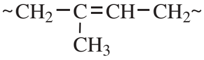
$$-\!\!\left(CH_2-CH{=}CH-CH_2\right)_m\!\!\left(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\right)_n\!\!-$$

1,2 units are atactic.

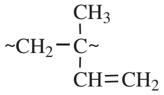
Ziegler-Natta type catalysts can generate a very high cis-1,4 structure (>90%), which is the choice polymer for tires. It is made to specifications similar to SBR, ie, molecular weight average of 100,000–200,000, Mooney viscosity 50, and oil-extended. Lithium catalysts on the other hand yield variable chain structures, depending on the solvent used, ie, mixed structures of cis-1,4 and trans-1,4 and 1,2. These polymers are generally in the lower molecular-weight range and are not used for tire rubber. They are also important in the production of block copolymers for thermoplastic elastomers.

Processing and Properties. Polybutadiene is compounded similarly to SBR and vulcanized with sulfur. The high cis-1,4 type crystallizes poorly on stretching so it is not suitable as a “gum” stock but requires carbon black reinforcement. It is generally used for automotive tires in mixtures with SBR and natural rubber. Its low T_g (−95°C) makes it an excellent choice for low temperature tire traction, and also leads to a high resilience (better than natural rubber) which in turn results in a lower heat build-up. Furthermore, the high *cis*-polybutadiene also has a high abrasion resistance, a plus for better tire tread wear.

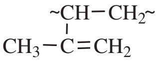
5.3. Polyisoprene (Synthetic). Polyisoprene has four possible chain unit geometric isomers: *cis*- and *trans*-1,4-polyisoprene, 1,2-vinyl, and 3,4-vinyl.



$\sim CH_2-\underset{CH_3}{C}=CH-CH_2\sim$



$\sim CH_2-\overset{CH_3}{\underset{CH=CH_2}{C}}\sim$



$\sim\underset{CH_3-C=CH_2}{CH}-CH_2\sim$

Natural rubber (Hevea) is 100% *cis*-1,4-polyisoprene, whereas another natural product, gutta-percha, a plastic, consists of the trans-1,4 isomer. Up until the mid-1900s, all attempts to polymerize isoprene led to polymers of mixed-chain structure.

The revolutionary development of stereospecific polymerization by the Ziegler-Natta catalysts also resulted in the accomplishment in the 1950s of a 100-year-old goal, the synthesis of *cis*-1,4-polyisoprene (natural rubber). This actually led to the immediate termination of the U.S. Government Synthetic Rubber Program in 1956 because the technical problem of duplicating the molecular structure of natural rubber was thereby solved, and also because the rubber plantations of the Far East were again available.

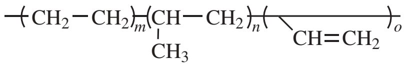
Polymerization and Molecular Structure. As in the case of polybutadiene, the Ziegler-Natta type of initiators are used to produce a polymer of high cis-1,4 structure (~98 – 99%) (natural rubber is 100% cis-1,4). Lithium organometallics can also be used in hydrocarbon solvents to produce relatively high cis-1,4 chain structures but not quite as high as either natural rubber or the Ziegler-Natta polymer. In practice it is the latter polymer that is produced commercially, generally to a high molecular weight (1–2 million), with some proportion of actual gel polymer (see Elastomers, synthetic–polyisoprene).

Processing and Properties. This polymer is compounded like natural rubber and has similar ease of processing. It is also vulcanized with sulfur. Like natural rubber, it can crystallize on stretching, leading to high gum strength. However, the slightly lower cis-1,4 content of the high cis polymer compared to natural rubber leads to lower strength. This slight deficiency also leads to lower "green strength" in tire building as well as lower "building tack."

Actually, production of synthetic polyisoprene is relatively small because of the sufficient and increasing supply of natural rubber. It is important, however, in ensuring that *cis*-1,4-polyisoprene (natural rubber), as a strategic material, is less subject to political uncertainties.

6. Age-Resistant Elastomers

6.1. Ethylene–Propylene (Diene) Rubber. The age-resistant elastomers are based on polymer chains having a very low unsaturation, sufficient for sulfur vulcanization but low enough to reduce oxidative degradation. EPDM can be depicted by the following chain structure:



where $m = \sim 1500$ (~60 mol%), $n = \sim 975$ (~39 mol%), and $o = 25$. The diene comonomer provides one double bond for the copolymerization and a residual double bond for sulfur vulcanization. Ethylene–propylene rubbers (EPR) are also commercial products (see ELASTOMERS, SYNTHETIC—ETHYLENE–PROPYLENE–DIENE RUBBER).

Processing and Properties. Because of its irregular chain structure, EPDM is amorphous at <60 wt% ethylene and shows no crystallization on stretching (or cooling). Hence it exhibits poor strength and requires the assistance of carbon black reinforcement. At higher ethylene contents, the materials are semicrystalline and exhibit controlled green strength and crystallization on stretching. The presence of unsaturation in the side chain makes it possible to use sulfur vulcanization, but a higher proportion of accelerators must be used because of the low unsaturation. This also makes it difficult to use blends of EPDM with the highly unsaturated elastomers (NR, SBR, and PB), since the unsaturated rubber uses up the sulfur too rapidly. It exhibits poor building tack in tire manufacturing. However, it has excellent aging properties and shows no ozone cracking because of no in-chain low saturation. It also has good low temperature behavior ($T_g \sim -$ °C) and resilience. Its excellent aging and low temperature properties make it ideal for use as a sheet rubber for roofing applications, where it has shown a rapid growth.

6.2. Butyl Rubber. Butyl rubber was the first low unsaturation elastomer, and was developed in the United States before World War II by the Standard Oil Co. (now Exxon Chemical). It is a copolymer of isobutylene and isoprene, with just enough of the latter to provide cross-linking sites for sulfur vulcanization. Its molecular structure is depicted in Table 1.

The polymerization system is of the cationic type, using coinitiators such as $AlCl_3$ and water at very low temperatures (−100°C) and leading to an almost instantaneous polymerization (see ELASTOMERS, SYNTHETIC–BUTYL RUBBER).

Molecular Structure. The chain structure is as shown in Table 1 and molecular weights of 300,000–500,000 are achieved. The Mooney viscosities are in the range of 40–70 leading to a soft elastomer, which requires carbon black reinforcement for higher modulus.

Processing and Properties. Sulfur vulcanization is generally used with higher accelerator levels, as in the case of EPDM. Unlike EPDM, this elastomer has sufficient chain regularity to permit crystallization on stretching so it can exhibit high gum strength. However, its low modulus requires carbon black for stiffening, not for strength. Butyl rubber has a T_g of −72°C, but has a broad loss peak; thus it shows low resilience at room temperature, with a high hysteresis loss. It is therefore a useful damping rubber. Butyl rubber is remarkable for its excellent impermeability to gases, which led to its widespread use for inner tubes for tires, and more recently for the barrier in tubeless tires. It cannot be blended with high unsaturation rubbers in sulfur vulcanization. However, its halogenated derivatives, chlorobutyl and bromobutyl, can be covulcanized with the unsaturated elastomers, eg, SBR in tubeless tires, because of the interaction with the zinc oxide in the compound.

7. Solvent-Resistant Elastomers

7.1. Nitrile Rubber (NBR). This is the most solvent-resistant of the synthetic elastomers, except for Thiokol, which, however, has rather severe limitations. NBR was developed both in Germany and the United States by private industry prior to World War II. It is a copolymer of butadiene, $CH_2{=}CH{-}CH{=}CH_2$, and acrylonitrile, $CH_2{=}CHCN$, corresponding to the molecular structure shown in Table 1.

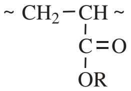
Molecular weights are in the same range as for SBR ($\sim$100,000), Mooney 20–90. Vulcanization is carried out with sulfur, as for SBR (see ELASTOMERS, SYNTHETIC–NITRILE RUBBER). It is the nitrile group, $-C{\equiv}N$, that confers oil resistance to this polymer, and the nitrile content can vary from 10 to 40%, leading to increasing solvent resistance.

Polymerization System. This elastomer is prepared by emulsion polymerization, similar to that used for SBR, but generally carried out to virtually 100% conversion. As for SBR, the chain irregularity leads to a noncrystallizing rubber, so that this polymer requires carbon black reinforcement for strength.

Processing and Properties. Nitrile rubber requires carbon black for strength. It exhibits excellent resistance to hydrocarbon solvents, but not as much to polar solvents. Because of its high T_g (strong interaction between nitrile groups) of -20 to -40°C, it has poor low temperature properties. Hence, for example, the desirability of a high nitrile content for solvent resistance, eg, gasoline hose, has to be balanced against low temperature stiffening.

Hydrogenated nitrile is a more recent development, in which the unsaturation of the polymer is markedly reduced leading to better aging.

7.2. Acrylic Elastomers. These materials are based principally on an acrylate chain structure, as follows:



$$\sim CH_2{-}\underset{\underset{OR}{|}}{\underset{C=O}{\underset{|}{CH}}}\sim$$

where R is generally an alkyl group. Because of the absence of unsaturation, vulcanization is carried out by amine compounds instead of sulfur, but this absence of unsaturation also confers good aging properties. This rubber also shows good resistance to hydrocarbon solvents because of the polar acrylic ester groups present (see ELASTOMERS, SYNTHETIC—ACRYLIC ELASTOMERS; ETHYLENE–ACRYLIC ELASTOMERS).

7.3. Chloroprene Rubber. Polychloroprene can be represented by the formula:

$$\sim CH_2{-}\underset{Cl}{\underset{|}{C}}{=}CH{-}CH_2\sim$$

The trans-1,4 configuration predominates but there are also small amounts of the three other isomeric structures, ie, cis-1,4, -1,2, and -3,4. It was one of the first synthetic rubbers produced in the United States as early as 1931, by the Du Pont Co., because of its good solvent resistance. Its Du Pont trade name is neoprene. Even though it is not as solvent resistant as nitrile rubber, it has many other advantageous properties (see ELASTOMERS, SYNTHETIC—POLYCHLOROPRENE).

Polymerization. The polymer is prepared by emulsion polymerization of chloroprene. Since *trans*-1,4-polychloroprene is capable of crystallizing on stretching (or cooling) it can exhibit a high gum tensile strength without carbon black just like natural rubber. In fact, it is the only elastomer, other than natural rubber, to be used for latex dipped goods. Hence, just like natural rubber latex, neoprene latex is used in many applications, eg, dipping (rubber gloves), coating, and impregnating. It is generally produced as a homopolymer, since copolymerization is difficult to achieve because of the high reactivity of chloroprene. Some grades of neoprene contain a few percent of a comonomer in order to reduce the tendency to crystallize (harden) on storage. This tendency results from the fact that the melting point (T_m) of neoprene crystals ($\sim$50°C) is substantially higher than that of natural rubber ($\sim$20°C).

Vulcanization. Some of the chlorine atoms along the chain (1,2 units) are very labile and reactive, and provide excellent sites for cross-linking. Hence neoprene is not vulcanized by sulfur but by metal oxides, eg, magnesium and zinc oxides, although sulfur is generally included in the compound to control the rate of vulcanization.

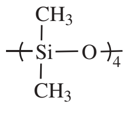
Processing and Properties. Neoprene has a variety of uses, both in latex and dry rubber form. The uses of the latex for dipping and coating have already been indicated. The dry rubber can be handled in the usual equipment, ie, rubber mills and Banbury mixers, to prepare various compounds. In addition to its excellent solvent resistance, polychloroprene is also much more resistant to oxidation or ozone attack than natural rubber. It is also more resistant to chemicals and has the additional property of flame resistance from the chlorine atoms. It exhibits good resilience at room temperature, but has poor low temperature properties (crystallization). An interesting feature is its high density (1.23) resulting from the presence of chlorine in the chain; this increases the price on a volume basis.

8. Temperature-Resistant Elastomers

8.1. Silicone Rubber.

These polymers are based on chains of silicon rather than carbon atoms, and owe their temperature properties to their unique structure. The most common types of silicone rubbers are specifically and almost exclusively the polysiloxanes. The Si–O–Si bonds can rotate much more freely than the C–C bond, or even the C–O bond, so the silicone chain is much more flexible and less affected by temperature (see Silicon compounds, silicones).

Polymerization. The polymer chain is formed by a ring-opening reaction caused by the action of alkalies on the monomer, a cyclic siloxane:



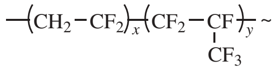
$$\left(\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - O \right)_4$$

Molecular weights are about 500,000 but the polymer is still a very viscous liquid and requires a silica filler to become an elastomer.

Vulcanization. Generally this is carried out by the action of peroxides, which can cross-link the chains by abstracting hydrogen atoms from the methyl groups and allowing the resulting free radicals to couple into a cross-link. Some varieties of polysiloxanes contain some vinylmethylsiloxane units, which permit sulfur vulcanization at the double bonds. Some liquid (short-chain) silicones can form networks at room temperature by interaction between their active end groups.

Processing and Properties. Silicones are soft, weak rubbers, even with silica fillers (carbon black does not work well), leading to tensile strength of about 5–8 MPa (700–1200 psi). However, they offer excellent resistance to stiffening at very low temperatures (dry ice), as well as softening at elevated temperatures, thus retaining their properties because of the great flexibility of the polymer chains. However, they cannot be considered high temperature stable elastomers because they can degrade (3 months at 250°C).

8.2. Fluorocarbon Elastomers. These elastomers were developed by both the Du Pont and 3M companies during the 1950s. They are the most resistant elastomers to heat, chemicals, and solvents known, but they are also the most expensive, ie, between \$22 and \$35 per kg. The most common types are copolymers of vinylidene fluoride and hexafluoropropene, thus:



$$-\!\!\left(CH_2-CF_2\right)_x\!\!\left(CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}}F\right)_y\!\sim$$

The fluorine atom confers chemical inertness, but some hydrogen atoms must be in the chain to maintain rubbery properties. Some fluorinated silicones are also available where superior low temperature properties are required (see ELASTOMERS, SYNTHETIC—FLUOROCARBON ELASTOMERS).

Polymerization. Emulsion polymerization is used, but the latex is too unstable for use and all the latex is coagulated to dry rubber. The molecular weight range is 100,000–200,000 with a Mooney viscosity of 50–70.

Vulcanization. Diamines are used to form cross-links by reacting with the fluorine atoms. Peroxides are also added to assist in the cross-linking and carbon black is used for reinforcement.

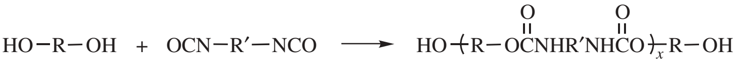
Processing and Properties. These elastomers are generally designed for high temperature use, with mechanical properties as a secondary consideration. Thus tensile strengths of only 12–15 MPa (1700–2200 psi) are common at ambient temperatures, but they change very little after exposure to high temperatures. Thus these elastomers have an indefinite life at 200°C and can be heated to 315°C up to 48 h. However, they have poor low temperature properties, reaching a brittle point at −30°C, compared to nitrile rubber at −40°C.

9. Liquid Rubber Technology

An entirely new concept was introduced into rubber technology with the idea of "castable" elastomers, ie, the use of liquid, low molecular-weight polymers that could be linked together (chain-extended) and cross-linked into rubbery networks. This was an appealing idea because it avoided the use of heavy machinery to masticate and mix a high viscosity rubber prior to molding and vulcanization.

In this development three types of polymers have played a dominant role, ie, polyurethanes, polysulfides, and thermoplastic elastomers.

9.1. Polyurethanes. The polyurethanes were developed in Germany and Great Britain just prior to World War II, largely because of the work of Otto Bayer in Germany (14). This was based on the reaction of liquid, low molecular-weight polyesters or polyethers, having hydroxyl end groups, with organic diisocyanates to yield solid elastomers, as follows, where HO–R–OH is a low molecular-weight polyester or polyether and OCN–R–NCO is an organic diisocyanate.



$$HO-R-OH + OCN-R'-NCO \longrightarrow HO\left(R-O\overset{O}{\overset{\|}{C}}NHR'NH\overset{O}{\overset{\|}{C}}O\right)_x R-OH$$

This process is based on the very high reactivity of the isocyanate group toward hydrogen present in hydroxyl groups, amines, water, etc, so that the chain extension reaction can proceed to 90% yield or better. Thus when a linear polymer is formed by chain extension of a polyester or polyether of molecular weight 1000–3000, the final polyurethane may have a molecular weight of 100,000 or higher (see URETHANE POLYMERS).

In addition to linear chain extension, excess diisocyanate leads to cross-linking into a network because the diisocyanate groups can also react with the hydrogen atoms of the –NH– groups in the chains. Furthermore, the well-known polyurethane foam rubber can be made by adding water to the mixture because the isocyanate groups react vigorously with water to liberate carbon dioxide gas as follows:

$$—NCO + H_2O \longrightarrow —NH_2 + CO_2$$

The amine groups thus formed can also react vigorously with the isocyanate groups to continue the chain extension and cross-linking reactions. Hence, in the systems there are simultaneous foaming, polymerization, and cross-linking reactions, which produce foam elastomers (or plastics).

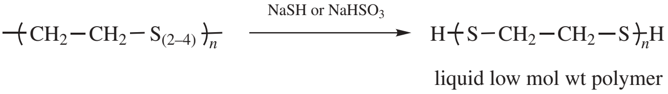
Properties. Polyurethane elastomers generally exhibit good resilience and low temperature properties, excellent abrasion resistance, moderate solvent resistance, and poor hydrolytic stability and poor high temperature resistance. As castable rubber, polyurethanes enjoy a variety of uses, eg, footwear, toys, solid tires, and foam rubber.

9.2. Polysulfides. The polysulfide elastomer, best known under the trade name Thiokol, represents the earliest commercially developed synthetic rubber, developed in 1930 by J. C. Patrick as a highly solvent and age-resistant elastomer (15). It is still considered the most solvent-resistant rubber, but its poor mechanical properties provide a serious disadvantage (see POLYMERS CONTAINING SULFUR).

The polymerization involves the reaction of sodium polysulfide with ethylene dichloride in aqueous media at 70°C for 2–6 h, yielding an aqueous dispersion (latex) of the polysulfide rubber.

$$NaS_{(2-4)}Na + ClCH_2CH_2Cl \longrightarrow \left(CH_2-CH_2-S_{(2-4)} \right)_n$$

It is now generally used in the form of a liquid, low molecular-weight polymer, having reactive end groups obtained by degradation of the base polymer, as follows:



$$-\!\left(\mathrm{CH_2-CH_2-S_{(2-4)}}\right)_n\!- \xrightarrow{\text{NaSH or NaHSO}_3} \underset{\text{liquid low mol wt polymer}}{\mathrm{H}\!\left(\mathrm{S-CH_2-CH_2-S}\right)_n\!\mathrm{H}}$$

The liquid polymer is then compounded with metal oxides or peroxides, as well as fillers (carbon black) and can undergo cold vulcanization, ie, chain extension and cross-linking into a solid matrix. It is largely used as a sealant and gasket material for windows, automobile windshields, etc.

9.3. Thermoplastic Elastomers. These represent a whole class of synthetic elastomers, developed since the 1960s, that are permanently and reversibly thermoplastic, but behave as cross-linked networks at ambient temperature. One of the first was the triblock copolymer of the polystyrene–polybutadiene–polystyrene type (Shell's Kraton) prepared by anionic polymerization with organolithium initiator. The structure and morphology is shown schematically in Figure 3. The incompatibility of the polystyrene and polybutadiene blocks leads to a dispersion of the spherical polystyrene domains (ca 20–30 nm) in the rubbery matrix of polybutadiene. Since each polybutadiene chain is anchored at both ends to a polystyrene domain, a network results. However, at elevated

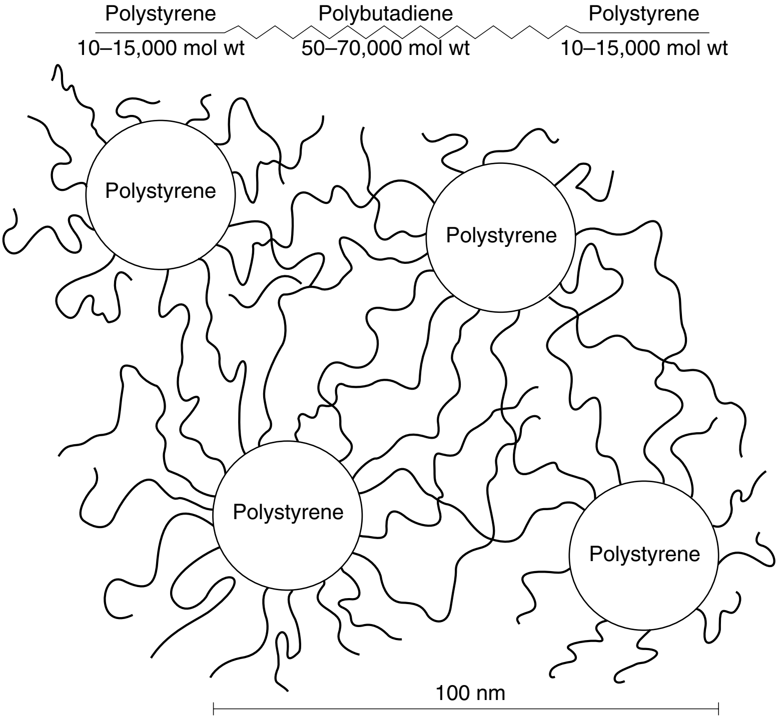


Fig. 3. Morphology of thermoplastic elastomers.

temperatures where the polystyrene softens, the elastomer can be molded like any thermoplastic, yet behaves much like a vulcanized rubber on cooling (see ELASTOMERS, SYNTHETIC–THERMOPLASTIC ELASTOMERS).

The particular type of thermoplastic elastomer (TPE)shown in Figure 3 exhibits excellent tensile strength of 20 MPa (2900 psi) and elongation at break of 800–900%, but high compression set because of distortion of the polystyrene domains under stress. These TPEs are generally transparent because of the small size of the polystyrene domains, but can be colored or pigmented with various fillers. As expected, this type of thermoplastic elastomer is not suitable for use at elevated temperatures (>60°C) or in a solvent environment. Since the advent of these styrenic thermoplastic elastomers, there has been a rapid development of TPEs based on other molecular structures, with a view to extending their use to more severe temperature and solvent environments.

The styrenic triblock copolymers shown in Figure 3 are prepared by anionic "living" polymerization with organolithium initiator, where excellent control can be exercised over the molecular weight of each block or segment in the polymer chain. These methods can only be used with the styrene and diene-type monomers. In order to prepare thermoplastic elastomers based on other molecular structures, suitable chemical reactions must be used for each particular case to obtain alternating blocks of hard and soft segments which can generate the type of morphology shown in Figure 3.

BIBLIOGRAPHY

"Rubber, Synthetic" in *ECT* 1st ed., Vol. **11**, pp. 827–852, by J. D. D'Ianni, the Goodyear Tire & Rubber Co.; "Elastomers, Synthetic" in *ECT* 2nd ed., Vol. **7**, pp. 676–705, by W. M. Saltman, The Goodyear Tire & Rubber Co.; "Elastomers, Synthetic (Survey)" in *ECT* 3rd ed., Vol. 8, pp. 446–459, by J. E. McGrath, Virginia Polytechnic Institute and State University; in *ECT* 4th ed., Vol. 8, pp. 905–923, by Maurice Morton, The University of Akron; "Elastomers, Synthetic, Survey" by Maurice Morton, The University of Akron.

CITED PUBLICATIONS

1. H. Staudinger, *Ber.* **53**, 1073 (1920).
2. J. P. Queslel and J. E. Mark, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **5**, John Wiley & Sons, Inc., New York, 1986, 365–408.
3. R-J. Roe, in Ref. 2, Vol. **7**, 531–544.
4. J. K. Gillham, in Ref. 2, Vol. **4**, 519–524.
5. A. Y. Coran, in Ref. 2, Vol. **17**, 666–698.
6. G. Williams, *Proc. Roy. Soc.* **10**, 516 (1860).
7. G. Bouchardat, *Compt. Rend.* **89**, 1117 (1879).
8. W. A. Tilden, *J. Chem. Soc.* **45**, 411 (1884).
9. Brit. Pat. 24,790 (Oct. 25, 1910), F. E. Matthews and E. H. Strange; C. Harries, *Ann.* **395**, 211 (1913).
10. Ger. Pat. 511,145 (1927), W. Bock and E. Tschunkur (to I. G. Farbenindustrie A.G.); Ger. Pat. 570,980 (Feb. 27, 1933), W. Bock and E. Tschunkur (to I. G. Farbenindustrie A.G.).

11. *Chem. Eng.*, (Apr. 17, 1989).
12. In Ref. 2, Vol. **3**, 288–290.
13. R. S. Bhakuni and co-workers, in Ref. 2, Vol. **16**, 834–861.
14. O. Bayer, E. Mueller, S. Peterson, H. F. Piepenbrink, and E. Windemuth, *Angew. Chem*. **62**, 57 (1960).
15. U.S. Pat. 1,890,191 (1932), C. J. Patrick.

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