16

Rubber

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INTRODUCTION

The word "rubber" immediately brings to mind materials that are highly flexible and will snap back to their original shape after being stretched. In this chapter a variety of materials are discussed that possess this odd characteristics. There will also be a discussion on the mechanism of this "elastic retractive force." Originally, rubber meant the gum collected from a tree growing in Brazil. The term "rubber" was coined for this material by the English chemist Joseph Priestley, who noted that it was effective for removing pencil marks from paper. Today, in addition to Priestley's natural product, many synthetic materials are made that possess these characteristics and many other properties. The common features of these materials are that they are made up of long-chain molecules that are amorphous (not crystalline), and the chains are above their glass transition temperature at room temperature.

Rubber products appear everywhere in modern society from tires to biomedical products. The development of synthetic rubber began out of the need for countries to establish independence from natural products that grew only in tropical climates. In times of conflict the natural product might not be available, and its loss would seriously threaten national security. Synthetic rubber, then, became a strategic concern during World Wars I and II.[1] Beyond the security issue, the need for materials with better performance also provided a strong impetus for the development of new rubbery materials. In particular, improvements in oil resistance, high-temperature stability, and oxidation and ozone resistance were needed.[2] Research today is driven to develop materials with even better performance in these areas. In the 1980s and 1990s tires with lower rolling resistance were demanded by car manufacturers to improve fuel economy. This was accomplished, in part, by developing functional tread polymers which chemically bond to fillers resulting in a dramatic reduction in the hysteresis (energy loss) of the tire tread. These new functional polymers will be discussed in this chapter.

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TABLE 16.1 Synthetic Rubber Production by Type, 2003

Type	Description	Capacity (Metric Tons)
SBR-solid	Styrene/butadiene rubber	2,635,000
BR	Butadiene rubber	2,018,000
IR	Isoprene rubber	258,000
CR	Chloroprene (or neoprene)	244,000
EPDM	Ethylene/propylene terpolymer	883,000
NBR	Nitrile or acrylonitrile/butadiene rubber	303,000
Others		1,025,000
Total		7,366,000

Source: *Worldwide Rubber Statistics 2004*, International Institute of Synthetic Rubber Producers, Inc., by permission.

TABLE 16.2 Worldwide Rubber Consumption Forecast, 2008 (Metric Tons)

Total new rubber	19,442,000
Natural	9,042,000
Total synthetic	10,400,000
SBR	4,114,000
Nitrile	424,000
Polybutadiene	2,572,000
EPDM	1,048,000
Other Synthetics	2,242,000
% Natural	46.5
% Synthetic	53.5

Source: *Worldwide Rubber Statistics 2004*, International Institute of Synthetic Rubber Producers, Inc., by permission.

The worldwide demand for rubber was estimated to be 19.4 million metric tons for 2008,[3] excluding latex materials. Of this demand, 54 percent is synthetic rubber of various kinds. Rubber has been classified by use into general purpose and specialty.

The major general purpose rubbers are natural rubber, styrene–butadiene rubber, butadiene rubber, isoprene rubber, and ethylene–propylene rubber. These rubbers are used in tires, mechanical goods, and similar applications. Specialty elastomers provide unique properties such as oil resistance or extreme heat stability. Although this differentiation is rather arbitrary, it tends also to classify the polymers according to volumes used. Styrene–butadiene rubber, butadiene rubber, and ethylene–propylene rubber account for 78 percent of all synthetic rubber consumed.

The 2003 synthetic rubber capacity by type is presented in Table 16.1, and Table 16.2 lists the worldwide rubber consumption forecast by type for 2008.

RUBBER CONCEPTS

Several key principles (outlined below) greatly help in understanding the performance of elastomeric materials. This outline should present these concepts well enough for use in the following discussions of specific polymer types. However, the reader should consult the references for a more complete understanding of these principles. The concepts are classified as those that relate to polymer structure, those that relate directly to physical properties, and those that relate to the use of the material, as listed below.

1. Polymer structure:
   (a) Macrostructure
      - Molecular weight
      - Molecular weight distribution
      - Branching
   (b) Microstructure
   (c) Network structure

2. Rubber properties:
   (a) Elasticity—the retractive force
   (b) Glass transition temperature
   (c) Crystallinity

3. Rubber use:
   (a) Compounding
   (b) Processing

POLYMER STRUCTURE

Macrostructure

Molecular Weight.   The single most important property of any polymer is the size or length of the molecule. The polymerization process consists of combining many of the simple monomer molecules into the polymer chain. Most of the monomers used to produce rubbers are either gases or low-viscosity liquids under normal conditions; upon polymerization they form liquids whose viscosity increases to extremely high values as the chain length is increased. At very low chain length, this increase is linear with molecular weight until the chains are long enough to become entangled. Above the entanglement molecular weight, the viscosity increases to the 3.4–3.5th power of molecular weight increase.[4] In addition to viscosity, a great many other physical properties of any polymer depend upon the molecular weight.[5]

Molecular Weight Distribution.   A given polymer sample is composed of many polymer chains, which in most cases are not of the same length. This variability can be a result of the synthesis process or of possible random scission and cross-linking that can occur upon processing. For economic reasons, it is not possible to separate the various polymer chains by length prior to use; so it is important to characterize this distribution in order to describe the polymer and understand its performance. As with any distribution, no single number is a totally satisfactory descriptor.

The commonly used molecular weight parameters are the number, weight, and z average molecular weight, which are defined, respectively, as:[6]

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$
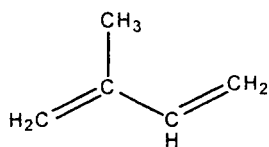
$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

where N_i is the number of moles of species i, and M_i is the molecular weight of species i.

Although there are many different statistical ways to describe any population, the above parameters have been widely used because they are readily understood in physical terms, and they can be measured directly in the laboratory.[7] A fourth parameter, the dispersion index, frequently is used to characterize the breadth of the distribution. This parameter is simply the ratio of the weight to the number average molecular weight, with 1.0 being the lowest possible number (i.e., all chains of exactly the same length). Typical values for commercial polymers are in the 2–5 range, with those under 2 considered relatively narrow and those over 2.5 considered broad in distribution. The measurement of these molecular weight averages once was a time-consuming task, but with the development of gel permeation chromatography (GPC), also referred to as size exclusion chromatography, the measurement of these distributions has become commonplace.[8] Units are even available that automatically sample polymerization reactors, process the sample, and perform all necessary calculations to provide data for process control. These units can have multiple detectors, thereby providing compositional distribution as a function of molecular weight.
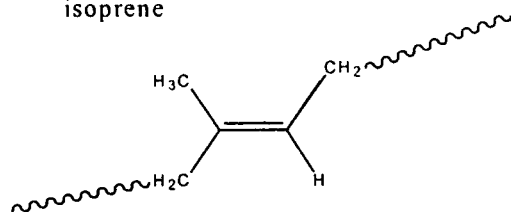
Branching.   The concept of a polymer chain implies two ends per chain. However, because of the nature of the process used to form the polymer, the chain may contain one or more branch points, resulting in multiple ends per chain. These chain ends can have an adverse effect on polymer performance. Branching, molecular weight, and molecular weight distribution have been shown to affect processability as well.[9] The optimum macrostructure often represents a compromise between processing and ultimate performance. Branching can also be measured using the GPC technique with special detectors.
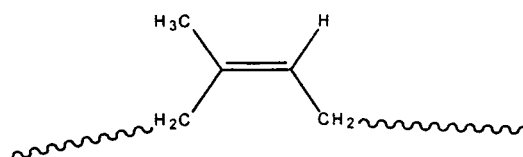
Microstructure

In the formation of elastomers from diolefin monomers such as butadiene or isoprene, there are a number of possible structures. Since the control of these structures is critical in obtaining optimum properties, this area has received great attention from the synthesis chemist. The possible polyisoprene structures are:
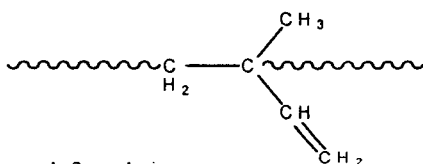
chain mobility, polymer composition also defines the solubility parameter of the polymer, which is a critical property relative to the type of solvents in which the polymer is soluble, the ability of the polymer to accept and hold oil, and the relative compatibility of the polymer with other polymers.[11] Basically, these properties all involve polymer–solvent
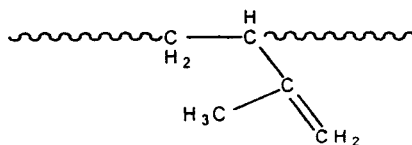

isoprene

trans-l,4 polyisoprene

cis-l,4 polyisoprene

l,2 polyisoprene

3,4 polyisoprene

For butadiene (no methyl group) the 3,4 form does not exist. The 1,2 addition is referred to as *vinyl addition*.

The polymer in natural rubber (from the *Hevea brasiliensis* tree) is pure *cis* polyisoprene; gutta percha and balata are composed of the *trans* isomer.

Many of the commercial synthetic elastomers are synthesized from more than one monomer, such as styrene–butadiene and ethylene–propylene rubbers. The properties of the resultant polymer depend on the ratio of the two monomers in the polymer and upon the distribution of the monomers within the chain.

If the monomers are uniformly distributed within the polymer chain, the ratio of monomers will define the flexibility of the polymer chain.[10] Because many properties depend on this chain mobility, polymer composition is carefully controlled. In addition to

interaction, with the difference being the increasing molecular weight of the solvent.

In addition to the relative ratio of the monomers, the arrangement of the units in the chain is important. This arrangement is referred to as the copolymer *sequence distribution*. In the previous discussion, the assumption was made that the comonomer units were well mixed in the polymer chain. If this is not the case, parts of the chain can reflect properties of the corresponding homopolymer. It is thus possible to produce polymers that have significantly different properties in different parts of the polymer chain. A most dramatic example of this can be found in styrene–butadiene–styrene or styrene–isoprene–styrene thermoplastic elastomers. The properties of these unique materials will be discussed in the section "Thermoplastic Elastomers."

Network Structure

A critical requirement for obtaining engineering properties from a rubbery material is its existence in a network structure. Charles Goodyear's discovery of vulcanization changed natural rubber from a material that became sticky when hot and brittle when cold into a material that could be used over a wide range of conditions. Basically, he had found a way to chemically connect the individual polymer chains into a three-dimensional network. Chains that previously could flow past one another under stress now had only limited extensibility, which allowed for the support of considerable stress and retraction upon release of the stress. The terms "vulcanization," "rubber cure," and "cross-linking" all refer to the same general phenomenon.

For most rubber systems the network is formed after the polymer is compounded and molded into the desired final shape. Once cross-linked, the material no longer can be processed. If cross-linking occurs prior to compounding or molding, the material is referred to as *gelled*, and it cannot be used. Most rubber is used in a compounded and cured form. There is an optimum *cross-link density* for many failure properties such as tensile strength and tear which will be discussed in the next section.

The one general class of polymers that fall outside this concept is the thermoplastic elastomers, which will also be discussed later.

RUBBER PROPERTIES

Elasticity—The Retractive Force

The fact that cross-linked rubber materials can be extended to several times their original length and return to that original length when released is certainly their most striking feature. This is in contrast to crystalline solids and glasses, which cannot normally be extended to more than a fraction of their original length and also to ductile metals which can be extended to large deformations but do not return to the original length after the stress is removed.

There have been both statistical and thermodynamic approaches to solving the problem of rubber elasticity leading to a phenomenological treatment; however, these methods are beyond the scope of this chapter. The important, and most interesting, result of these theories is that rubber elasticity arises from changes in entropy of the network. Rubber molecules are capable of geometric isomerization, examples of which are *cis* and *trans*, just like any other unsaturated organic molecule. Upon stretching the network of chains, no "configurational" changes take place. That is, *cis* is not changed to *trans* and thus there is no configurational contribution to entropy. Elasticity *does not* arise from stretching or deforming covalent bonds either. What does take place are rotations about single bonds in the chain backbone during stretching. It is these "conformational" changes which give rise to the entropy decrease upon stretching. The chains do not like being in a stretched state because there are many conformational states not available to them until the stress is released. The chain ends are held apart at a statistically unfavorable distance, which gives rise to the entropy decrease. The following expression, for extensions >10%, shows that the elastic force, f, is directly proportional to the absolute temperature, or the elastic response of the rubber is entirely governed by the decrease in entropy (S) which it undergoes upon extension.[12] The term ∂L is the change in length of the sample:

$$f = -T \left[\frac{\partial S}{\partial L} \right]_{T,V}$$

This expression was derived for constant temperature and volume experiments.

The shear modulus of the rubber network is related to the molecular weight between cross-link points or M_c. The lower the molecular weight of chains between cross-links (network chains), the higher the cross-link density and the higher the modulus. This is shown in the following expression:

$$G_0 = \frac{\rho R T}{M_c}$$

where G_0 is the elastic shear modulus, ρ is the density, R is the gas constant, and T is

absolute temperature. There is an optimum cross-link density for ultimate strength properties, above which the highly cross-linked network no longer can dissipate strain energy in the form of heat (hysteresis) so all the energy goes into breaking network chains and the material becomes brittle. Below this optimum cross-link level the material simply has too much viscous flow and pulls apart easily. Therefore, the rubber chemist must optimize the state of cure if high strength is desired.

Glass Transition Temperature

In order for a polymer to behave as a rubbery material, it is necessary for the chain to have great mobility. As the temperature is lowered, the ability of the chain segments to move decreases until a temperature is reached where any large-scale motion is prevented. This temperature is referred to as the glass transition temperature (T_g). Below this temperature the rubber becomes a glassy material—hard and brittle. Above this temperature amorphous plastics, such as polystyrene, can exhibit a rubbery character if the molecular weight is sufficiently high. All rubbery materials, then, must have glass transition temperatures below room temperature. For good low-temperature properties, it obviously follows that a low glass transition temperature polymer is required. The control of the glass transition temperature of the polymer is critical for many properties other than low-temperature use. For example, the wet traction and wear of a passenger tire have been shown to greatly depend directly on the polymer glass transition temperature.[13]

Control of this property is possible by controlling the structure of the polymer chain. Monomers with bulky side groups restrict chain mobility and thus raise the glass transition temperature. The composition of copolymers and the ratio of polymer blends often are determined by the desired glass transition temperature of the final product.

The glass transition temperature is usually measured using thermal methods such as differential scanning calorimetry (DSC) which looks at the change in heat capacity when a material goes through its glass transition. Another very useful method is to use dynamic mechanical properties where the polymer is subjected to a temperature sweep in a dynamic mechanical spectrometer from very low temperature ($-120°C$) to well above room temperature ($+100°C$). If the modulus is plotted vs. temperature, there will be a sharp decrease as the polymer warms to above its T_g. There will also be a peak in the energy loss property known as tan delta. The tan delta vs. temperature plot is very useful for predicting tire properties such as rolling resistance and wet traction.

Crystallinity

Polymer chains can exist in spatial arrangements that are orderly enough to allow the chains to form crystalline structures. The existence of strong interchain interactions via polar forces, hydrogen bonding, or ionic groups can facilitate crystallization. The existence of crystallization is very important for many plastics and fibers, but crystallinity cannot be appreciably present in rubbery materials, as the corresponding restriction in chain mobility could preclude the very chain mobility needed for rubbery properties. Rubbery materials must have both their melting temperature (if they have a crystalline point) and their glass transition temperature below the use temperature.

Crystallinity can be reduced by disruption of the order in the chain by copolymerization.[14] For example, both polyethylene and polypropylene are crystalline plastics, whereas ethylene–propylene rubber produced at about a 50:50 ratio is an amorphous elastomer. Compositional excursions much outside this range lead to crystalline materials.[15] For some materials, such as natural rubber, that are close to crystallizing, stretching the chains can align them sufficiently for crystallization to occur. Such polymers can exhibit excellent gum properties and improved strength in the uncured state that greatly facilitate processing.

Attempts have been made with some success to produce other polymers that exhibit this property of natural rubber. Although the melting temperature can be matched by appropriately disrupting the crystallizable structure through controlled introduction of another monomer, an exact match is not possible because the extent of crystallinity and the kinetics of crystallization will differ.

Crystallinity can be measured using the same thermal and dynamic mechanical methods described for measuring T_g however, the melting transition is much sharper than the T_g because it is a first-order transition compared with second-order for the T_g.

RUBBER USE

Compounding

The rubber industry began when Charles Goodyear developed the first useful rubber compound: natural rubber plus sulfur. The concept of mixing materials into rubber to improve performance is still of primary importance today. Without compounding, few rubbers would be of any commercial value. Any given rubber application will have a long list of necessary criteria in addition to cost, encompassing appearance, processing, mechanical, electrical, chemical, and thermal properties. Developing such compounds requires a broad knowledge of material science and chemistry combined with experience. The use of designed experiments can greatly facilitate selecting the optimum compound formulation.

The major components in a compound are curatives, reinforcing agents, fillers, plasticizers, and antidegradants.

Curatives. The function of curatives is to cross-link the polymer chains into a network; the most common ones are the sulfur type for unsaturated rubber and peroxides for saturated polymers. Chemicals called accelerators may be added to control the cure rate in the sulfur system; these materials generally are complex organic chemicals containing sulfur and nitrogen atoms. Stearic acid and zinc oxide usually are added to activate these accelerators. Metal oxides are used to cure halogenated polymers such as polychloroprene or chlorosulfonated polyethylene.

Reinforcing Agents. Carbon black and silica are the most common reinforcing agents. These materials improve properties such as tensile strength and tear strength; also, they increase hardness, stiffness, and density and reduce cost. Almost all rubbers require reinforcement to obtain acceptable use properties. The size of the particles, how they may be interconnected (structure), and the chemical activity of the surface are all critical properties for reinforcing agents. In tire applications, new polymers are currently being developed which contain functional groups that directly interact with carbon black and silica, improving many properties.

Fillers. Fillers are added to reduce cost, increase hardness, and color the compound. Generally they do not provide the dramatic improvement in properties seen with reinforcing agents, but they may have some reinforcing capability. Typical fillers are clays, calcium carbonate, and titanium dioxide.

Plasticizers. These materials are added to reduce the hardness of the compound and can reduce the viscosity of the uncured compound to facilitate processes such as mixing and extruding. The most common materials are petroleum-based oils, esters, and fatty acids. Critical properties of these materials are their compatibility with the rubber and their viscosity. Failure to obtain sufficient compatibility will cause the plasticizer to diffuse out of the compound. The oils are classified as aromatic, naphthenic, or paraffinic according to their components. Aromatic oils will be more compatible with styrene–butadiene rubber than paraffinic oils, whereas the inverse will be true for butyl rubber. The aromatic oils are dark colored and thus cannot be used where color is critical, as in the white sidewall of a tire. The naphthenic and paraffinic oils can be colorless and are referred to as nonstaining.

Antidegradents. This group of chemicals is added to prevent undesirable chemical reactions with the polymer network. The most important are the antioxidants, which trap free radicals and prevent chain scission and cross-linking. Antiozonants are added to prevent ozone attack on the rubber, which can lead to the formation and growth of cracks. Antiozonants function by diffusion of the material to the surface of the rubber, thereby providing a protective film. Certain antioxidants have this characteristic, and waxes also are used for this purpose.

Processing

A wide range of processes are used to convert a bale of rubber into a rubber product such as a tire. The first process generally will be compounding. Typical compounding ingredients were discussed previously. In many compounds more than one rubber may be needed to obtain the performance required. Uncured rubber can be considered as a very high-viscosity liquid; it really is a *viscoelastic* material possessing both liquid and elastic properties. Mixing materials into rubber requires high shear, and the simplest method is a double roll mill in which the rubber is shear-mixed along with the other compounding ingredients in the bite of the mill. Large-scale mixing is most commonly done with a high-shear internal mixer called a Banbury. This mixing is a batch process, although continuous internal mixers also are used.

The compounded rubber stock will be further processed for use. The process could be injection or transfer molding into a hot mold where it is cured. Tire curing bladders are made in this fashion. Extrusion of the rubber stock is used to make hose or tire treads and sidewalls. Another common process is calendaring, in which a fabric is passed through rolls where rubber is squeezed into the fabric to make fabric-reinforced rubber sheets for roofing membranes or body plies for tires. The actual construction of the final product can be quite complex. For example, a tire contains many different rubber components some of which are cord or fabric reinforced. All of the components must be assembled with high precision so that the final cured product can operate smoothly at high speeds and last over 50,000 miles.

NATURAL RUBBER

More than 500 years ago, the people of Central and South America were using a product that they collected from certain trees to make balls and to coat fabric to make it waterproof. This material they called cauchuc, which means "weeping wood." Today we know the tree as the *Hevea brasiliensis* and the material as natural rubber. Although a number of plants produce rubber, the only significant commercial source is the *Hevea* tree. Natural rubber initially had only limited applications because it flowed when hot and had poor strength. In 1839 Charles Goodyear found that when combined with sulfur and heated, the material changed into cured rubber with properties much as we know them today. The development of the pneumatic tire in 1845 combined with the dramatic growth of the automotive industry led to a rapid increase in the demand for natural rubber.

Although the tree was indigenous to Brazil, seeds were taken to England where they were germinated, and the plants were sent to the Far East. Rubber plantations were in existence by the late 1800s, and in the 1920s plantations were begun in West Africa. Because of a leaf blight disease, essentially all natural rubber now comes from plantations in Africa and the Far East rather than Central and South America.[16]

The production process starts with the trees. Over the years considerable biological research has been done to produce trees that grow faster, produce more latex, and are resistant to wind and disease damage. Once such an improved tree has been identified, buds are grafted from the tree onto root stock. All such trees are referred to as clones and will have the same characteristics. It typically takes 6–7 years of growth before a tree is ready for rubber recovery. Peak rubber production is reached at 12–15 years of age. Another major development in improving tree performance has been the use of tree stimulants, which

has resulted in an overall yield increase of 30 percent without adverse effects on the trees.

The production process of natural rubber in the tree is not yet fully understood. However, it involves a long series of complex biochemical reactions that do not involve isoprene as a monomer, even though the resulting polymer is 100 percent *cis* 1,4 polyisoprene. Because the tree makes the product, the rubber production process is really one of recovery.

The recovery process starts with tapping of the tree, which involves manually removing thin sections of bark at an angle so that as the latex is exuded from the damaged living latex cells, it will flow down to be collected in a cup. The depth of the cut is critical, as a tool shallow cut will not allow optimum latex yield, and too deep a cut will damage the tree. The damaged latex vessels will seal off after several hours. A preservative is added to the collection cup to prevent coagulation of the latex. The tapper then collects the latex and takes it to a collection station, from which it is shipped to the rubber factory. Additional preservative is added at the collection station to assure stable latex. The latex contains around 30–45 percent rubber. Approximately 3 percent of the solid material is nonrubber materials, consisting primarily of proteins, resins, and sugars.

The latex is processed in one of several ways, depending on the desired final product. If it is going to be used in the final product application in the latex form (such as for dipped goods and adhesives), it will be concentrated to 60 percent or higher solids. The most common process is centrifugation. The latex separates into the high-solids product and a low-solids skim material that contains a much higher percentage of the nonrubbery components; rubber produced from skim is generally of a lower quality because of these impurities. A variety of chemicals can be added to the latex to provide the necessary preservation and mechanical stability. As the final use of the latex will involve destabilizing the rubber particles, care must be taken not to overstabilize the latex concentrate. Being a natural product, the latex tends to change upon aging, a factor that also must be compensated for in the process.

Dry rubber is produced from the latex first by dilution, then by coagulation with organic acids, and finally by formation into sheets or crepe. Rubber smoked sheets are made by working the coagulated sheets between rolls to remove as much of the nonrubbery components as possible, followed by drying for up to a week in a smokehouse. The smoke serves as a fungicide that prevents biological attack of the rubber. To provide a more well-defined uniform product, Technically Specified Rubber (TSR) processes have been developed. These processes involve converting the coagulated rubber into rubber crumb, which is further washed, dried, and baled. Constant-viscosity grades of natural rubber have been developed by chemically reacting the aldehyde groups, which otherwise would lead to cross-linking upon storage. In the pale crepe process the latex is carefully selected for colored bodies (from carotene) and treated with sodium bisulfite to stop enzyme activity. The rubber is extensively washed through rollers to remove serum, as this can lead to yellowing. The wet crepe is dried under carefully controlled temperatures and in the absence of light to assure optimum properties. The previously described processes involve considerable investment and are practical only for plantation operations. Small shareholders may allow their latex to coagulate naturally and sell it to processors. Such a product will vary greatly, depending on the specific history of each rubber slab.[17]

Uses

The largest use of natural rubber is in the manufacture of tires. Over 70 percent of its consumption is in this area. The next largest use is as latex in dipped goods, adhesives, rubber thread, and foam. These uses account for approximately another 10 percent. The remainder is used in a variety of applications such as conveyor belts, hoses, gaskets, footwear, and antivibration devices such as engine mounts.

Because of the high stereoregularity of natural rubber, the units in the polymer chain can form very orderly arrangements, which

result in crystallization upon storage at low temperatures or upon stretching. Stored crystallized rubber may be converted to its original amorphous state by heating. Several crystalline forms are reported, with melting points varying from 14°C to 36°C.[18] Although crystallization upon storage can be a problem to users, the ability to crystallize reversibly upon stretching accounts for many of the unique properties of natural rubber. Specifically, the ability of natural rubber to be used as a gum polymer (unfilled vulcanizate) depends on this property. The crystallites that form act both as filler and as temporary crosslinks, providing high tensile properties.[19] In tire fabrication this property is reflected in natural rubber stocks possessing high green (uncured) strength and excellent building tack. In the final product, strain-induced crystallization provides tear and cracking (cut growth) resistance.

Although many other polymers can crystallize, only natural rubber has been found to have the necessary combination of rate of crystallization, degree of crystallization, and melting point to provide all the properties discussed above. Natural rubber has good flexibility and resilience. In truck and bus tires, it is used extensively with blends of polybutadiene to give the low heat buildup needed as well as wear and cut growth resistance. In passenger tires, natural rubber is used in the sidewalls and carcass areas. These areas require the building tack, ply adhesion, and hot strength properties that it imparts. Synthetic rubber is used almost exclusively in passenger tire treads.

The largest use of natural rubber latex is in the dipped goods area. Products include balloons, surgical and examination gloves, and prophylactics. The rapid spread of AIDS has led to a dramatic increase in the surgical and examination glove market. Latex also is used to make adhesives, rubber thread, and foams. However, natural rubber is being replaced in these two latex areas by urethanes and synthetic rubber latex. Some of the replacement has been driven by skin allergy problems which are caused by the natural proteins in the latex. Although natural rubber latex is

a mature product, research continues on improving its uniformity, stability, and performance.[20]

POLYISOPRENE

Faraday discovered in 1826 that natural rubber was composed of a hydrocarbon with a ratio of five carbons to eight hydrogen atoms; and in 1860, G. Williams isolated isoprene by collecting the distillate from the heating of natural rubber. By 1887, scientists in France, England, and Germany had converted isoprene back into a rubbery material. Because this offered a potential for manufactured "natural" rubber, research was undertaken to find ways to obtain isoprene from sources other than rubber itself.[21]

Monomer Production

The primary source of isoprene today is as a by-product in the production of ethylene via naphtha cracking. A solvent extraction process is employed. Much less isoprene is produced in the crackers than butadiene, so the availability of isoprene is much more limited. Isoprene also may be produced by the catalytic dehydrogenation of amylenes, which are available in C-5 refinery streams. It also can be produced from propylene by a dimerization process, followed by isomerization and steam cracking. A third route involves the use of acetone and acetylene, produced from coal via calcium carbide. The resulting 3-methyl-butyne-3-ol is hydrogenated to methyl butanol and subsequently dehydrogenated to give isoprene. The plants that were built on these last two processes have been shut down, evidently because of the relatively low cost of the extraction route.

Polymer Production Process

The free-radical catalysts were found to produce a product that did not have the tack, green strength, or gum tensile of natural rubber. Whereas natural rubber is an essentially pure *cis*-1,4 structure, the emulsion product was of mixed microstructure. This

precluded the ability of the latter to undergo strain-induced crystallization, which is required to obtain many of the desired natural rubber properties.

In 1955 investigators from the Firestone Tire and Rubber Company and the B. F. Goodrich Company announced the synthesis of polyisoprene with over 90 percent *cis*-1,4 structure. The work at Firestone was based on lithium metal catalysts, whereas the work at Goodrich was the result of using Ziegler–Natta type coordination catalysts.[22,23]

Use

Although considerable interest was generated by these discoveries, their commercial success has been rather limited. The lithium-based polymers were found to produce up to 94 percent *cis*, which still was not high enough to provide the properties of natural rubber. Polymers made with the coordination catalysts have *cis* contents of up to 98 percent, providing products that can more closely serve as replacements for natural rubber than the lithium-based polymers. In comparison with natural rubber, they offer the advantage of a more highly pure rubber (no nonrubber material) and excellent uniformity. For economic reasons, polyisoprene has seen only limited success. Several of the plants built to produce polyisoprene have been either shut down or converted for use to produce other polymers. In terms of synthetic rubber production in 2003, only 258,000 metric tons were produced (excluding centrally planned economy countries, CPEC), which represented only 3 percent of total synthetic rubber production. In comparison, in 2003 natural rubber usage was 7,554,000 metric tons.[24] Evidently because of its strategic importance,

the Former Soviet Union (FSU) continues to rely heavily on polyisoprene.

STYRENE–BUTADIENE RUBBER

The largest-volume synthetic rubber consumed is styrene–butadiene rubber (SBR). In 2003, SBR solid rubber accounted for 41 percent of all synthetic rubber. If SBR latex and carboxylated SBR latex are included, its share increases to 55 percent. The major application of solid SBR is in the automotive and tire industry, accounting for approximately 70 percent of the use. Therefore, SBR has been tightly tied to the tire business.[25]

Initially, SBR was developed as a general purpose alternate material to natural rubber. In the United States the thrust came early in World War II when the U.S. supply of natural rubber was cut off. The basic technology was developed in Germany in the late 1920s, and by 1939 Germany had 175,000 metric tons of capacity in place. The first U.S. production was 230 metric tons in 1941, but by 1945 there were more than 850,000 metric tons of capacity. Basically, in a period of five years the emulsion SBR business as we know it today was put in place. By 1973 U.S. capacity had increased to almost 1,400,000 metric tons, but in 1989 it had contracted to 881,000 tons close to the 1945 capacity.[26]

Monomer Production

The production of butadiene monomer is discussed below in polybutadiene section "Polybutadiene." The largest volume of styrene is produced by the alkylation of benzene with ethylene to give ethyl benzene, which is then dehydrogenated to give styrene.[27]

benzene   ethylene

ethyl benzene

styrene
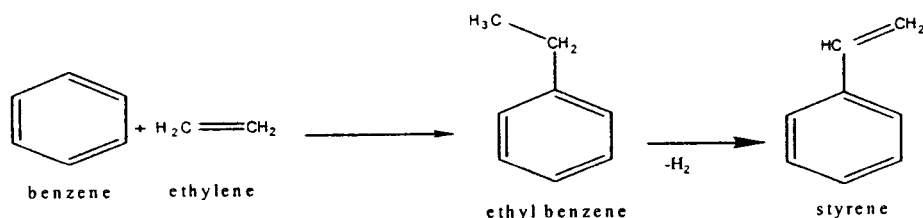
Polymer Production Process

SBR is produced by two different processes: emulsion and solution. The emulsion process involves a free-radical mechanism, whereas solution SBR is based on alkyllithium catalysis.
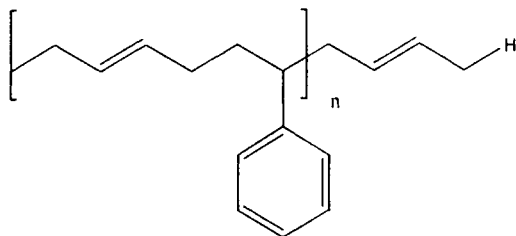

copolymer of butadiene and styrene

Emulsion Process

The formula developed to provide SBR during World War II was standardized, with all rubber plants owned by the U.S. government. The standard recipe is listed below:[28]

Component	Parts by Weight
Butadiene	75
Styrene	25
n-Dodecyl mercaptan	0.5
Potassium peroxydisulfate	0.3
Soap flakes	5.0
Water	180

Initiation occurs through reaction of the persulfate with the mercaptan, as shown below:

$$K_2S_2O_8 + 2RSH \rightarrow 2RS\bullet + KHSO_4$$

$$RS\bullet + M \rightarrow RSM\bullet$$
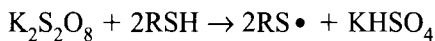
Chain propagation occurs by the growing chain free radical attacking either the butadiene or styrene monomer. The active radical chain can react with mercaptan to form a new mercaptyl radical and a terminated chain. The mercaptyl radical then can initiate an additional chain. The molecular weight of the chain P can be controlled by the concentration of mercaptan via this chain transfer mechanism.

$$P\bullet + RSH \rightarrow PH + RS\bullet$$

$$RS\bullet + M \rightarrow RSM\bullet$$
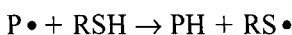
Termination also can occur by the reaction of two free radicals, through either combination or disproportionation reactions.

$$P\bullet + P\bullet \rightarrow P\text{-}P \text{ combination (bimolecular coupling)}$$

$$P\bullet + P\bullet \rightarrow P\text{-}CH=CH_2 + PH \text{ disproportionation (hydrogen-free radical transfer)}$$
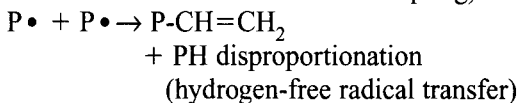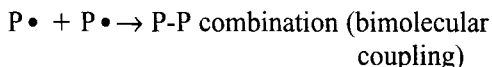
The mercaptyl radical also can react with growing chains, to lead to termination.[29]

Polymerization is initially carried out at 50°C until conversion of 70–75 percent is reached, at which time the polymerization is terminated by the addition of a free-radical scavenger such as hydroquinone. Polymerization beyond this point results in excessive free-radical attack on the polymer chains. Products made under such conditions have poor properties due to excessive branching and gelation. Unreacted butadiene and styrene are removed by flashing and steam stripping. Antioxidant is added to the latex, followed by coagulation with the addition of polyelectrolytes and salt-acid. The coagulated crumb then is washed, dried, baled, wrapped, and packaged for shipment. Because of the soap and other chemicals in the formulation, most emulsion polymers will contain about 7 percent of nonrubber residues. The emulsion process flow sheet is shown in Fig. 16.1.

It was soon discovered that polymers made at lower temperatures had significantly better properties, especially in tire treads. This was mainly because they contained fewer low molecular weight species. A lower temperature process, using "redox" chemistry, was eventually developed. It used peroxides or hydroperoxides with a reducing agent such as a water-soluble transition metal salt which were active even at 0°C.

Mercaptans are also used as chain transfer agents to provide a mechanism for molecular weight control. Commercially these types of polymerization are carried out at 5°C and are referred to as "cold" polymerizations to differentiate them from the previously discussed "hot" systems. A typical formula is listed below.[30]
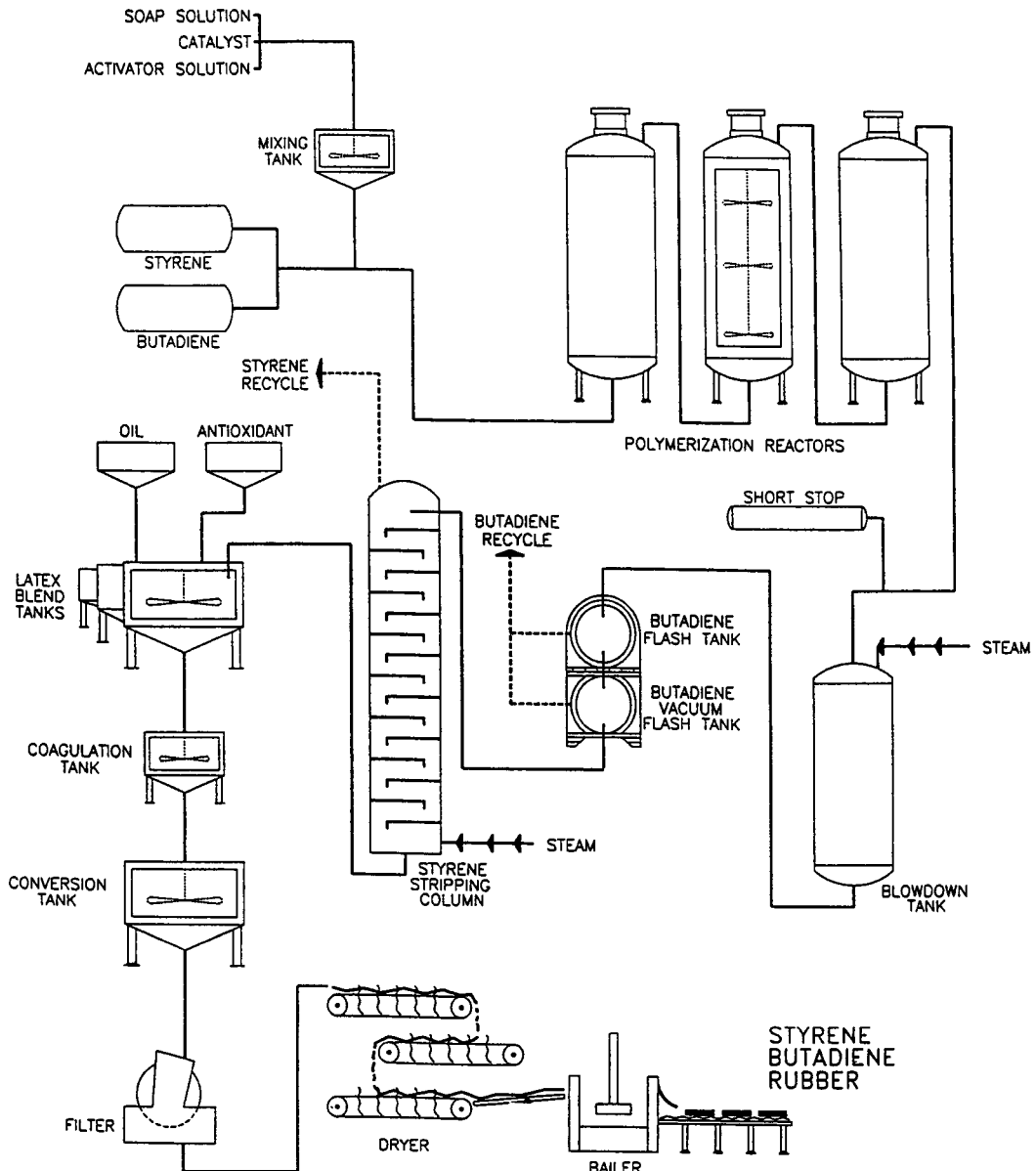
Fig. 16.1. The production of styrene-butadiene rubber. (*Modified by D.F. Graves from a drawing in the Vanderbilt Rubber Handbook, 1990 Edition, Copyright the R.T. Vanderbilt Company, Inc., by permission.*)

Component	Parts by Weight
Butadiene	71
Styrene	29
tert-Dodecyl mercaptan	0.18
p-Methane hydroperoxide	0.08
Ferrous sulfate heptahydrate	0.03
Trisodium phosphate decahydrate	0.50
Tetrasodium ethylenediaminetetraacetate	0.035
Sodium formaldehyde sulfoxylate	0.08
Rosin acid soap	4.5
Water	200

The improved tire wear of cold polymerization SBR led to the very rapid replacement of hot SBR for most applications. This change was relatively easy to make, as all the equipment could be used with the only modification required being the addition of reactor cooling, which is achieved with either the reactor jacket, internal coils, or both.

It later was found that even more improvements could be realized by polymerizing to

very high molecular weights and then adding petroleum-based oils to the latex prior to coagulation. The oil is absorbed by the rubber which, upon coagulation, produces oil-extended polymers. For tread applications, oils of higher aromatic content were preferred because of their excellent compatibility with the rubber. Typically 37.5 parts of oil are added, although grades containing up to 50 parts have been produced. Very high molecular weight polymers thus can be processed without requiring excessive energy to mix them. The oil also allows these tough polymers to be processed without excessive degradation. Carbon black masterbatches also are produced. In this process carbon black is added to the latex prior to coagulation, and the black, along with oil, is incorporated into the latex in the coagulation step. These products offer the user the advantage of not having to handle free black in their mixing operation, and can provide additional compounding volume for manufacturers with limited mixing capacity.

Not all emulsion SBR is converted to dry rubber for use. There is a variety of applications where the latex can be used directly in the final fabrication process. This technology logically grew out of the latex technology developed for natural rubber. For latex applications the particle size distribution can be critical because of its effect on viscosity and performance variables, as when used to provide impact strength in plastics such as ABS.[31] Careful control of the mechanical stability of the latex also is critical, as these systems must destabilize under relatively mild conditions such as those in a coating operation. A number of processes have been developed to control particle size via partial destabilization of the latex. Among the commercial methods are: careful control of a freeze–thaw cycle, controlled shear agitators, high-pressure colloid mills, and the addition of chemicals such as hydrocarbons or glycols.

A special variation of SBR latex containing terpolymerized vinyl pyridine is used in the tire industry to provide adhesion of organic fiber tire cords to rubber stock. The vinyl pyridine SBR latex is combined with resins and coated on the fiber by a dipping process. The adhesive is set by a controlled temperature and tension process to control the shrinkage properties of the cord.

Solution Process

The discovery of the ability of lithium-based catalysts to polymerize isoprene to give a high *cis* 1,4 polyisoprene was rapidly followed by the development of alkyllithium-based polybutadiene. The first commercial plant was built by the Firestone Tire and Rubber Company in 1960. Within a few years the technology was expanded to butadiene–styrene copolymers, with commercial production under way toward the end of the 1960s.

The copolymerization with alkyllithium to produce uniformly random copolymers is more complex for the solution process than for emulsion because of the tendency for the styrene to form blocks. Because of the extremely high rate of reaction of the styryllithium anion with butadiene, the polymerization very heavily favors the incorporation of butadiene units as long as reasonable concentrations of butadiene are present. This observation initially was somewhat confusing because the homopolymerization rate of styrene is seven times that for butadiene. However, the cross-propagation rate is orders of magnitude faster than either, and it therefore dominates the system. For a 30 mole percent styrene charge the initial polymer will be almost pure butadiene until most of the butadiene is polymerized. Typically two-thirds of the styrene charged will be found as a block of polystyrene at the tail end of the polymer chain:
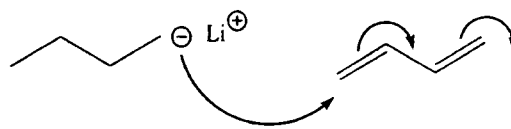
anionic initiation of butadiene by butyllithium

Several methods have been proposed to overcome this problem. In one, the styrene and part of the butadiene are charged initially with butadiene metered at a rate equivalent to its incorporation into the chain. A second approach involves adding both monomers at a relatively slow rate so that the equilibrium monomer concentration reaches a pseudosteady state that will produce polymer at the desired composition.[32] This process can be done in either a batch or a continuous mode.[33]

In addition to these reaction engineering approaches to produce uniformly random copolymer, the chemistry may be changed by the addition of polar agents such as amines and ethers. This action results in bringing the reactivity rates much closer together. The change in chemistry also is reflected in the microstructure of the butadiene portion of the polymer. Whereas in the nonpolar system the vinyl content of the butadiene portion is around 10 percent, in polar systems vinyl contents of 30–40 percent typically are obtained when a 20 percent styrene polymer is randomized. Higher styrene contents require higher modifier levels, resulting in even higher vinyl contents. An added complication with polar modifiers is their ability to react with the growing chain, resulting in undesired termination.

In spite of these complications, all recent U.S. expansions or announced plants for SBR have been for solution polymers. The ability to better design the polymer structure and produce special functional polymers (described below) accounts for most of this shift.

Functional Solution SBR

The driving force toward functional solution SBR is its improved hysteresis properties for passenger tire treads. The fact that anionic SBR has a much more narrow molecular weight distribution compared with emulsion gives it lower hysteresis. However, the big advantage is the relatively stable growing chain ends which can be chemically modified to improve interaction with carbon black and silica in tire compounds.[34] This modification can lead to a dramatic reduction in rolling resistance, which is critical for automotive manufacturers who must meet government-mandated fuel economy targets. The most active functional end-groups contain either organotin or certain amines. Termination with tin

"live SBR"

tin-coupled SBR

carbon black

quinone functionality on CB surface
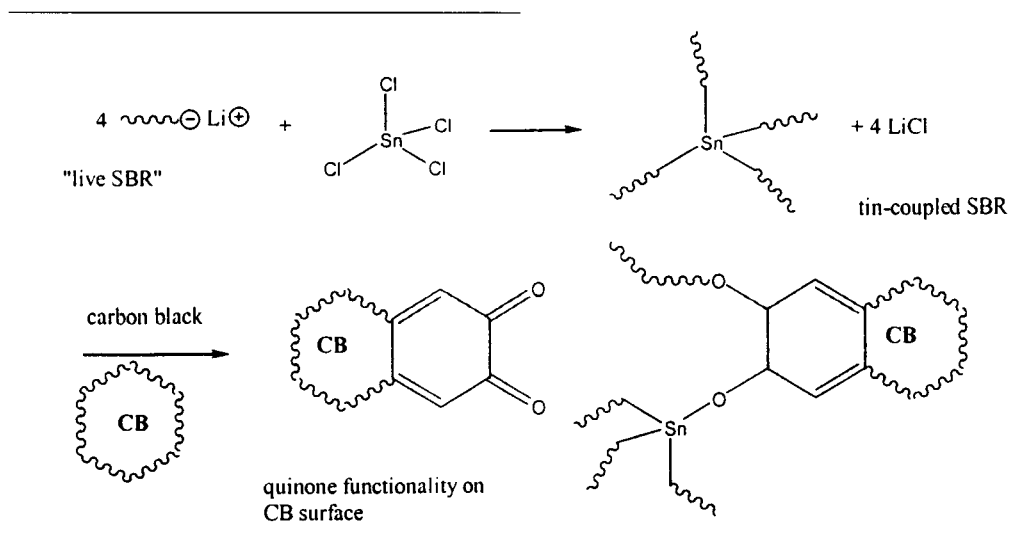
tetrachloride is the easiest and most popular method which generates a four-armed star polymer. The polymer–tin bonds break down during mixing of the compound and both lower the compound viscosity and create active sites for reaction with carbon black surfaces. The creation of this "carbon-bound rubber" effectively prevents the carbon black from agglomerating on a microscale to form hysteretic, three-dimensional networks. The breaking of these networks during the deformation of a tire tread is a major source of rolling resistance. Polymers with amine end-groups also show good activity with carbon black. Termination with silane esters is usually used to obtain interaction with silica fillers producing the same decrease in hysteresis. There have recently been efforts to make functional anionic initiators, some of which could be used to make low hysteresis rubber.[35] However, the main use for such polymers have been in adhesives and other nontire applications. One study comparing an emulsion polymer, its solution counterpart, and a chemically modified version of the solution polymer showed a 23 percent hysteresis reduction in going from emulsion to solution and an additional 15 percent reduction for the chemically modified polymer, to provide an overall reduction of 38 percent.[36] To date, this type of chemical modification is only possible using anionic techniques.

POLYBUTADIENE (BR)

Next to SBR, polybutadiene is the largest volume synthetic rubber produced. Consumption was approximately 2,018,000 metric tons in 2003.[37]

Monomer Production

Butadiene monomer can be produced by a number of different processes. The dominant method of production is as a by-product from the steam cracking of naphtha to produce ethylene. The butadiene is recovered from the C-4 fractions by extractive distil-lation.[38] "On-purpose" butadiene is generally produced by dehydrogenation or oxidative dehydrogenation of four-carbon hydrocarbons.[39,40]

Polymer Production Process

Polybutadiene is usually produced by alkali metal, and transition metal coordination solution processes. Most production is based on the solution processes because of the ability to obtain preferred microstructures by these routes.

Alkali-metal-based polymerization (usually organolithium) produces a product with about 36 percent *cis*, 54 percent *trans*, and 10 percent vinyl. The polymerization process is conducted in an aliphatic hydrocarbon under an inert atmosphere in either a batch or a continuous mode. Because of the characteristics of this polymerization system, polymers of extremely narrow molecular weight distribution and low gel can be produced.[41] The narrowest distribution is produced via batch polymerization. Coupled (star branched) and end-functional polybutadienes are possible using organolithium technology due to the living anion on the chain end which is available for further reactions. Upon the addition of polar agents, such as ethers or amines, the organolithium initiators can produce polybutadienes with vinyl contents up to 100 percent.[42] The vinyl content can be controlled by the ratio of modifier to catalyst and the polymerization temperature, with lower temperatures favoring increased vinyl formation. Even with high vinyl contents such polymers do not crystallize because of the atactic nature of the vinyl units. High *cis* polybutadiene is produced via solution processes using Ziegler–Natta type transition metal catalysts. The major commercial catalysts of this type are based on titanium, cobalt, nickel, and neodymium.[43] Typically the transition metal is used in the form of a soluble metal salt, which can react with an organoaluminum or organoaluminum halide as a reducing agent to give the active species. Because of the active nature of transition metals, the polymer solutions are treated to deactivate or remove such materials
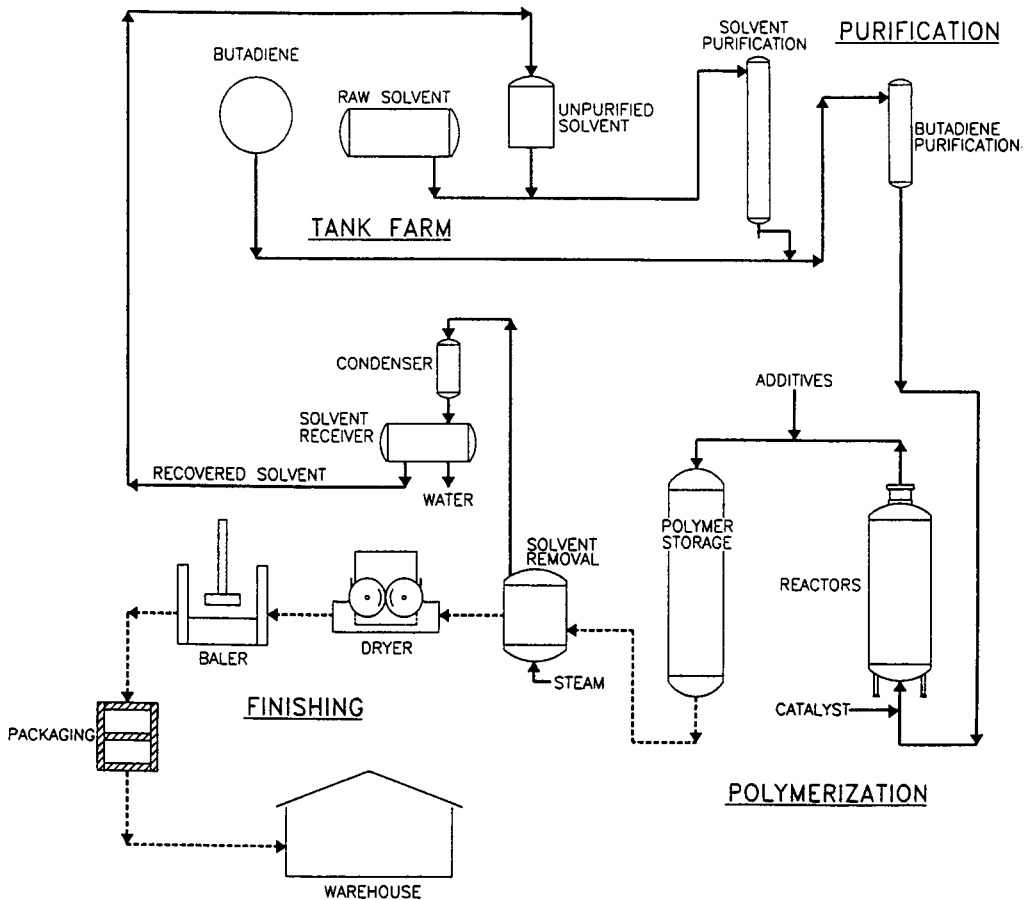
Fig. 16.2. Flow diagram for a typical solution process for the manufacture of polybutadiene. (*Courtesy of Firestone Polymers, Akron, Ohio.*)

from the final product. All of these catalysts produce products with 90 percent or higher *cis* content. The neodymium system is reported to produce the highest *cis* (98–99%) with the most linear chain structure.[44] The highest branched *cis* BR is produced with the Co system with Ni giving intermediate branching.

All the solution processes require high efficiency in recovering the solvent. The most widely used process consists of termination of the polymerization and the addition of antioxidant to the polymer solution. The solution may be treated to remove catalyst residue and then transferred into an agitated steam stripping vessel in which unreacted monomer and solvent are flashed off, leaving the rubber as a crumb slurry in water. The water–crumb slurry then is dewatered and dried. The recovered monomer/solvent is recirculated to a series of distillation columns to recover monomer and purify the solvent. As both the anionic and the coordination catalyst systems are highly sensitive to impurities such as water, the purification system is very critical for satisfactory process control (Fig. 16.2).

Uses

The major use for polybutadiene is in tires, with over 70 percent of the polymer produced used by the tire industry. Cured polybutadiene has excellent low-temperature properties, high resiliency, and good abrasion resistance due to its low glass transition temperature. However, this same fundamental property also leads to very poor wet skid resistance. For this reason, polybutadiene is blended with other polymers such as natural rubber and

SBR for use in tread compounds. In general, polybutadiene is a poorer-processing polymer than SBR, but this is generally not a problem as it is blended with other polymers in use. The very high *cis* polymers have the potential for strain-induced crystallization, which can lead to improved green strength and increased cut growth resistance in the cured product. High *cis* polybutadiene is reported to have a melting point of 6°C.[45]

The other major use for polybutadiene is as an impact modifier in plastics, in particular high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene resin (ABS). In the HIPS application the rubber is dissolved in the styrene monomer, which is then polymerized via a free-radical mechanism. A complex series of phase changes occurs, resulting in small rubber particles containing even smaller polystyrene particles being incorporated into a polystyrene matrix. The rubber is added to increase impact strength. Because of the unique morphology that is formed, low levels of rubber (typically around 7%) provide rubbery particles having a volume fraction of 30–40 percent. This morphology leads to high impact at very low rubber levels, providing good stiffness and hardness.[46]

There is also a fairly large market for high *cis* BR in solid core golf balls. In this application, the polymer is compounded with zinc acrylate and the mixture is cured with peroxide.[47] This produces an ionically cross-linked compound that has outstanding resilience. The covers are also ionomers with superior cut resistance. In the last few years the golf ball market has been shifting away from the traditional wound ball to these new solid core balls that use polybutadiene.

ETHYLENE–PROPYLENE RUBBER

There are two general types of polymers based on ethylene and propylene: ethylene–propylene rubber (EPM) and ethylene–propylene terpolymer (EPDM). EPM accounts for approximately 20 percent of the polyolefin rubber produced. Comprising a totally saturated polymer, these materials require free-radical sources to cross-link. EPDM was developed to overcome this cure limitation. For EPDM a small amount (less than 15%) of a nonconjugated diene is terpolymerized into the polymer. One of the olefinic groups is incorporated into the chain, leaving its other unsaturated site free for vulcanization. This ensures that the polymer backbone remains saturated, with corresponding stability, while still providing the reactive side group necessary for conventional cure systems. The nonconjugated dienes used commercially are ethylidene norbornene, 1,4 hexadiene, and dicyclopentadiene. The selection of the termonomer is made on the basis of the reactivity of the termonomer, both in polymerization and in vulcanization. The estimated 2003 worldwide consumption (excluding CPEQ) was 883,000 metric tons.

Monomer Production

Ethylene and propylene are produced primarily by the cracking of naphtha. They also are available from the fractionation of natural gas. Ethylidene norbornene is produced by reacting butadiene with cyclopentadiene. 1,4 Hexadiene is produced from butadiene and ethylene. Dicyclopentadiene is obtained as a by-product from the cracking of heavy feedstocks to produce ethylene.

Polymer Production

There are two processes used to produce EPM/EPDM: solution and suspension. In either case a Ziegler–Natta type catalyst is used (aluminum alkyl or aluminum alkyl chlorides and a transition metal salt). The most generally used transition metal is vanadium in the form of the tetrachloride or the oxytrichloride.[48] The solution process is similar to that used for other solution polymers. The polymer cement can be finished by stream stripping and drying of the resulting crumb.[49]

In the suspension process, the polymer is suspended in the monomer propylene. This process offers the advantages of being able to operate at higher solids owing to the lower viscosity of a suspension compared with a solution at comparable solids. Other advantages are simple heat removal by the evaporative cooling of the propylene, more uniform

reactor temperature profile, and ease of production of high molecular weight or semi-crystalline polymers.[50]

A specially developed titanium-based catalyst has been used in the suspension process for EPM and EPDM where the termonomer is low-boiling. The advantages claimed, in addition to those characteristic of the suspension process, are better structural control and high catalyst efficiency, resulting in a high-purity product without requiring catalyst removal.[51]

The polymer composition for both EPM and EPDM is usually in the 40/60 to 60/40 ethylene/propylene ratio. Outside these ranges, the polymer will start to crystallize because of either polyethylene or polypropylene blocks.

Use

EPM/EPDM polymers exhibit outstanding resistance to heat, ozone, oxidation, weathering, and aging due to the saturated backbone. They have low density, are miscible with aliphatic and naphthenic oils, and maintain acceptable properties at high filler loadings. They are used in single-ply roofing, wire and cable, automotive parts, impact modification of polypropylene, and viscosity index additives for automotive oils. They also can be used in producing thermoplastic olefin elastomers by blending with polypropylene, which may be partially grafted or cross-linked by dynamic vulcanization. These "polymer alloys" will be discussed in the section "Thermoplastic Elastomers." Although at one time EPDM was expected to become the major polymer for tires, this market has not materialized for a variety of processing and performance reasons.[52]

The halogenated products improve the mixing and cure compatibility with the more common unsaturated rubbers such as natural or styrene–butadiene rubber.
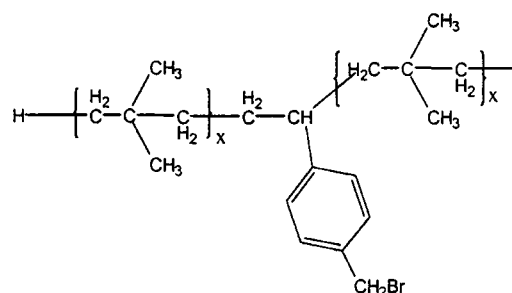
Monomer Production

Isobutylene is obtained as a by-product from petroleum and natural gas plants. The monomer must be highly purified to assure high molecular weight.

Production Process

Butyl rubber is produced at very low temperature (below −90°C) to control the rapid exotherm, and to provide high molecular weight. The process consists of charging isobutylene along with isoprene (2–4%) with an inert diluent such as methyl chloride to a reactor to which a Friedel–Crafts catalyst is added. The polymerization is very rapid, and the polymer forms in a crumb or slurry in the diluent. Heat is removed via the reactor jacket. The slurry is steam-stripped to remove all volatiles. The catalyst is neutralized, and antioxidants are added to the slurry prior to drying.[53] The halogenated derivatives are produced by the direct addition of the halogen to a solution of the isobutylene–isoprene polymer.

During the last 10 years another type of butyl rubber was developed which is derived from a copolymer of isobutylene and p-methylstyrene.[54] They are subsequently brominated to varying degrees producing different grades of the elastomer. Bromination occurs selectively on the methyl group of the p-methylstyrene providing reactive benzylic bromine functionality, which can be used for grafting and curing reactions.

BUTYL RUBBER

Butyl rubber is one of the older synthetic rubbers, having been developed in 1937. Because of the saturated nature of a polyolefin elastomer, the commercial polymer is actually a copolymer of isobutylene and isoprene. The isoprene is added to provide cure sites. In addition, halogenated (bromo or chloro) derivatives are available.

brominated poly(-isobutylene-p-methylstyrene)

Properties and Use

The most important characteristics of butyl rubber are its low permeability to air and its thermal stability. These properties account for its major uses in inner tubes, tire inner liners, and tire curing bladders. Because of the poor compatibility of butyl with other rubbers (with respect to both solubility and cure), the halobutyls are preferred. The brominated *p*-methylstyrene-containing butyl rubbers are used in a number of grafting reactions for tire applications and adhesives. Other uses for butyl rubber are automotive mechanical parts (due to the high damping characteristics of butyl), mastics, and sealants.[55]

NITRILE RUBBER

Nitrile rubber was invented at about the same time as SBR in the German program to find substitutes for natural rubber.[56] These rubbers are copolymers of acrylonitrile–butadiene, containing from 15 to 40 percent acrylonitrile. The major applications for this material are in areas requiring oil and solvent resistance. The estimated worldwide consumption in 2003 was 303,000 metric tons.[57]

Monomer Production

The production of butadiene is discussed in the diene section "Polybutadiene." Although several routes have been developed to produce acrylonitrile, almost all now is produced by the catalytic fluidized-bed ammoxidation of propylene.

Polymer Production

The polymerization process parallels the emulsion process used for styrene–butadiene rubber. Either a hot or a cold process can be used, with the cold polymerization providing the same improved processing and vulcanizate properties as seen in SBR. Polymerizations are carried to 70–80 percent conversion and terminated to avoid gel formation. The latex must be stripped to remove unreacted butadiene and acrylonitrile.
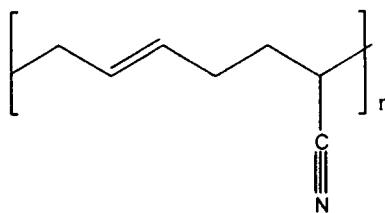
butadiene-acrylonitrile copolymer

Properties and Use

As the acrylonitrile content increases in the polymer chain, the properties change predictably. The glass transition temperature increases approximately 1.5°C for each percent increase in acrylonitrile. Properties such as hysteresis loss, resilience, and low-temperature flexibility will correspondingly change. The oil resistance increases with increased acrylonitrile content, as does the compatibility with polar plastics such as PVC. The major market for nitrile rubber is in the automotive area because of its solvent and oil resistance. Major end uses are for hoses, fuel lines, O-rings, gaskets, and seals. In blends with PVC and ABS, nitrile rubber acts as an impact modifier. Some nitrile rubber is sold in latex form for the production of grease-resistant tapes, gasketing material, and abrasive papers. Latex also is used to produce solvent-resistant gloves.[58]

HYDROGENATED NITRILE RUBBER

During the last 15 years several companies have developed hydrogenated grades of nitrile rubber to both improve its thermal stability and solvent resistance. Although the hydrogenation of a polydiene backbone was done as early as the 1920s, real commercial products with acrylonitrile were not introduced until the mid-1980s.[59]

Hydrogenated NBR (HNBR) is produced by first making an emulsion-polymerized NBR using standard techniques. It then must be dissolved in a solvent and hydrogenated using a noble metal catalyst at a precise temperature and pressure.[60] Almost all the butadiene units become saturated to produce an ethylene–butadiene–acrylonitrile terpolymer.

These "post-polymerization" reactions are very expensive so HNBRs usually command a premium price. HNBR is usually cured with peroxides, similar to ethylene–propylene elastomers, because it has no unsaturation for a conventional sulfur cure system.

Uses

HNBR has many uses in the oil-field, including down hole packers and blow-out preventers, because of its outstanding oil resistance and thermal stability. For the same reasons, it has also found uses in various automotive seals, O-rings, timing belts, and gaskets. Resistance to gasoline and aging make HNBR ideal for fuel-line hose, fuel-pump and fuel-injection components, diaphragms, as well as emission-control systems.

CHLOROPRENE RUBBER

Chloroprene rubber (Neoprene—trade name of DuPont) was one of the earliest synthetic rubbers, first commercialized in 1932. It has a wide range of useful properties but has not become a true general purpose synthetic rubber, probably because of its cost. It does possess properties superior to those of a number of general purpose polymers, such as oil, ozone, and heat resistance; but for these properties other specialized polymers excel. Polychloroprene thus is positioned between the general purpose elastomers and the specialty rubbers.

Monomer Production

Chloroprene monomer production starts with the catalytic conversion of acetylene to monovinylacetylene, which is purified and subsequently reacts with aqueous hydrogen chloride solution containing cuprous chloride and ammonium chloride to give chloroprene.[61]

Production Process

Polychloroprene is produced by using an emulsion process. Two general types of processes are used: sulfur modified and

unmodified. In the sulfur modified process, sulfur is dissolved in monomer and is incorporated into the polymer chain. Upon the addition of thiuram disulfide-type materials and under alkaline conditions, some of the sulfur bonds are evidently cleaved to give the soluble polymer. In the unmodified process chain transfer agents are used. If neither the sulfur modified nor the chain transfer system is used, the resulting polymer is a gelled tough material. Typical polymerization systems consist of rosin acid soap emulsifier and persulfate catalyst. Conversions of 80–90 percent are obtained. Polymerizations are run at around 40°C. For the modified polymer, the thiuram disulfide is added after polymerization, and the latex is aged to allow the peptization (chain scission) reaction to occur. Acidification stops the peptization reaction. The latex is vacuum-stripped and coagulated using a cold drum dryer process. The coagulated rubber is washed and dried.

The polymerization produces primarily trans-1,4-polychloroprene. The trans content can be increased somewhat by lowering the polymerization temperature:[62,63]
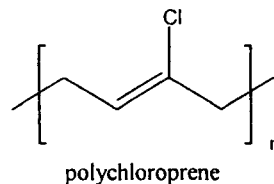
polychloroprene

Properties and Uses

Polychloroprene is stable to oxidation and ozone. It also is flame resistant, and its oil resistance is better than that of general purpose rubbers. Its major disadvantage, other than cost, is relatively poor low-temperature properties. Because of the high stereoregularity, polychloroprene will strain crystallize, giving good tensile to unfilled stocks. At low temperatures the polymer can crystallize, making processing more difficult. Polymer made at lower temperatures will show higher unfilled tensile properties and more rapid crystallization due to the higher trans content (i.e., less disruption of the crystal structure). The major end uses are conveyor belts, V-belts, hoses, and mechanical

goods such as wire insulation, O-rings, and gaskets. It also has found use in single-ply roofing and adhesives.[64]

SILICONE ELASTOMERS

Silicone elastomers represent a rather unique group of polymers in that they consist of alternating silicon–oxygen bonds to form the polymer chain backbone. Side groups off the silicon atoms are selected to provide very specific properties that differentiate one type from another. The most common side group is the dimethyl structure. Replacement of small amounts of the methyl group with vinyl provides sites for cross-linking. Phenyl groups are used to improve low-temperature properties. Fluorosilicones are produced by replacing the methyl with trifluoro-propyl units. The addition of bulky phenyl side groups leads to an increase in the glass transition temperature. However, the disruption caused by such groups leads to the desired reduction or elimination of crystallization, which is critical for low-temperature properties. Such polymers have glass transition temperatures around $-110°C$, which is the range of the lowest T_g carbon-backbone polymers.

Monomer Production

The actual polymerization process involves a ring-opening reaction of dimethyl-substituted cyclic siloxanes. The preparation of the cyclic materials starts with the production of pure silicon via the reduction of quartz with coke in an electric arc furnace. The silicon metal then reacts with methyl chloride to give a mixture of silicones, from which dimethyldichlorosilane is removed by distillation.[65] Subsequent hydrolysis gives the cyclic dimethylsiloxane.

Polymer Production

The polymerization process involves an equilibrium ring-opening reaction carried out in the bulk state, which can be catalyzed by acids or bases:
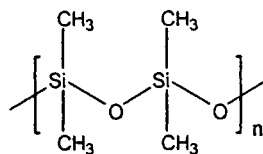
polydimethylsiloxane

Uses

Silicone rubber offers a set of unique properties to the market, which cannot be obtained by other elastomers. The Si–O backbone provides excellent thermal stability and, with no unsaturation in the backbone, outstanding ozone and oxidative stability. The very low glass transition temperature, combined with the absence of low-temperature crystallization, puts silicones among the materials of choice for low-temperature performance. The fluoro-substituted versions provide solvent, fuel, and oil resistance along with the above-mentioned stability advantages inherent with the silicone backbone.
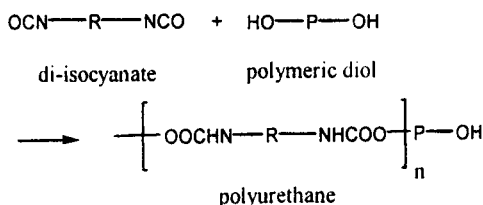
The gum polymer has rather poor tensile properties when cured, but these properties can be greatly improved by the use of silica-reinforcing agents. These systems exhibit some of the greatest improvements in properties by filler addition; and because this improvement is significantly higher for silica than for other reinforcing agents, it is assumed that direct bonding occurs between the silica and the polymer. The silicone materials also may have very low surface energy, which accounts for their nonstick characteristics. Because of the inherent inertness of the materials, they have been widely used for medical purposes within the body. The largest use of silicone is in sealant and adhesive applications.

Several different methods have been developed to cure silicones. Free-radical cures are possible for those polymers containing vinyl groups. The largest-volume process, however, involves room-temperature vulcanizations, which can employ either a one-component or a two-component system. In the one-component system, a cross-linking agent such as methyltriacetoxysilane is used.

With exposure to moisture, hydrolysis of the cross-linking agent leads to the silanol reactive cure site, so such materials must be compounded and stored free of moisture.[66]

POLYURETHANE RUBBER

A wide range of materials is included in this class. The common feature is the use of chain extension reactions to provide products with acceptable commercial properties. The chain extension reaction effectively reduces the actual number of chain ends, thereby eliminating the generally poor properties observed when very low-molecular-weight polymers are cross-linked. The chain extension step involves the reaction of a difunctional polymeric polyol with difunctional organic isocyanates to give the polyurethane:

OCN——R——NCO + HO——P——OH

di-isocyanate   polymeric diol

$$\longrightarrow \quad \left[OOCHN\text{——}R\text{——}NHCOO \right]_n P\text{——}OH$$

polyurethane

The most used polyols have a polyester or a polyether backbone. A wide variety of isocyanates are used, with toluene di-isocyanate, *m*-phenylene di-isocyanate, and hexamethylene di-isocyanate the most common.

Raw Materials

The largest-volume polyether used is obtained from propylene oxide polymerized under basic conditions. Polyester polyols are produced from a number of different materials involving diacids and diols to give the ester linkage. Aliphatic polyesters generally are used for elastomers to impart chain flexibility.

The production of isocyanates is based on the reaction of phosgene with primary amines. Toluene di-isocyanate is the most frequently used di-isocyanate.

Uses

The urethane elastomers are complex-segmented or block polymers. Soft, noncrystalline blocks are provided by the polyether or aliphatic polyester long chains, whereas stiff, hard blocks are produced by the reaction of aromatic di-isocyanates with low-molecular-weight materials such as diols or diamines. The hard blocks can phase-separate to provide a physical rather than a chemical cross-link, similar to those to be discussed for the butadiene–styrene thermoplastic elastomers, although the domain size is much smaller for the polyurethanes. Chemical cross-links can be introduced by using tri-functional materials or by adjusting the stoichiometry to allow additional reactions with the urethane or urea structures to give allophanate or biuret linkages.

Polyurethane rubbers can have high tensile strengths, excellent tear strength, and good abrasion and chemical resistance. The greatest disadvantage is the hydrolytic instability of the urethane linkage. A major use is in automotive bumpers and facias. These materials are made in a reaction injection molding process. Castable urethanes are used to produce solid rubber wheels and printing rolls. Millable urethanes can be processed on conventional rubber equipment. Unsaturation can be introduced to allow the use of conventional rubber cure systems. Cures also are possible by reaction of the active hydrogens with materials such as high molecular weight polyfunctional isocyanates that are nonvolatile at cure temperatures.

Thermoplastic polyurethane elastomers are processed by injection molding and other processes used for thermoplastics. Small gears, seals, and even automotive fender extensions can be produced by this means.

By selecting from the large number of possible reactions and stoichiometry, properties can be tailored to meet a very wide range of applications.[67-69]

MODIFIED POLYETHYLENE RUBBERS

Elastomeric polymers can be produced by the chlorination or chlorosulfonation of polyethylene. Both products start with polyethylene, either in solution or in aqueous suspension, which then is reacted to give the specified

degree of substitution to obtain the desired properties. Sufficient substitution is necessary to disrupt the regularity of the polymer chain, changing it from the crystalline polyethylene plastic into amorphous elastomers.

Chlorinated Polyethylene

The chlorinated products contain around 40 percent chlorine. These materials must be stabilized with metal salts, like other chlorinated elastomers and plastics. Peroxide cross-linking generally is used. Being saturated, the materials have excellent weather and ozone resistance and can be used over a temperature range of $-65-300°F$. The high chlorine content imparts oil resistance and relatively slow rates of burning. Typical applications where this combination of properties is required include hoses for chemical or oil resistance, tubing, and belting. In comparison with plasticized PVC, these materials have better low-temperature properties and do not suffer a loss of plasticizer because none is required.

Chlorosulfonated Polyethylene

Reaction with sulfur dioxide in addition to chlorine introduces cross-linking sites into the polymer chain. Sulfur contents in the range of 1.0–1.5 percent are used, with chlorine contents of 25–40 percent. Curing is accomplished by using metallic oxides, sulfur- bearing organic compounds, and epoxy resins. These materials have outstanding ozone resistance and show little color change upon light exposure. Good resistance to oils, heat, oxidation, weather, and corrosive materials also is exhibited. Applications include pond and pit liners, coated fabrics, light-colored roofing membranes, wire and cable insulation, chemical hose, and belting.[70,71]

THERMOPLASTIC ELASTOMERS (TPE)

This class of elastomeric materials is called "thermoplastic" because they contain thermally reversible cross-links of various types. The types of crosslinks vary from phase-separated polystyrene domains, such as in styrene–butadiene–styrene (SBS) elastomers to ionic cluster cross-links in the ionomers. The beauty of these noncovalent interactions to form cross-links is that when the material is heated, the cross-links are broken. This allows the polymer to flow and be processed, and also recycled. When cooled, the cross-links reform and the material becomes strong again. All TPEs are two-phase systems where there is a soft, rubbery "continuous phase" and a hard "dispersed phase" which does not flow at room temperature. The first two polymers to be discussed are "block copolymers" and "ionomers."

Block Copolymers

A very popular and useful TPE is made from blocks of styrene and butadiene monomers using anionic polymerization techniques, which was described in the solution SBR section above. They are made up of short chains of polystyrene (usually 8000–15,000 MW), followed by a much longer chain of polybutadiene (about 60,000 MW), and capped off by another short chain of polystyrene, hence the name SBS. Similar polymers are prepared using isoprene instead of butadiene (SIS). The differences between SBS and SIS will be discussed later in the subsection "Uses."

block PS segment   polyBd segment   block PS segment
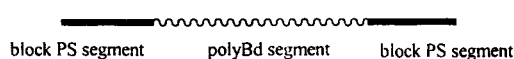
The linear polymers, as shown above, can be built up by the sequential addition of monomer or by coupling the living anionic chains using compounds like dichloro dimethylsilane. Hence, the base polymer would have styrene polymerized first, followed by butadiene, and then addition of the coupling agent. If a multifunctional coupling agent such as silicon tetrachloride is used, a radial block or "star-branched" SBS is formed.

The polystyrene is highly insoluble in the polybutadiene so the PS chains cluster together and phase-separate into domains. Since there is much more polybutadiene (PBD) than polystyrene, the PBD becomes the continuous phase containing dispersed particles of PS which act both as cross-links

and reinforcing agents. Every PBD chain is tied to a PS chain on both ends so a very strong cross-linked network is formed. If the PBD is tied to only one PS, then a "diblock" polymer is formed which has very little strength. When this network is heated to above the glass transition of polystyrene (100°C) the PS domains break down and begin to flow, so the polymer can be processed by injection molding or extrusion. Upon cooling to below 100°C, the domains (cross-links) reform and the material becomes strong again. SBS elastomers can have tensile strength as high as conventional thermoset elastomers which may approach 4000 psi.

adhesives because the isoprene segments tend to undergo chain scission during aging instead of cross-linking, which is observed in butadiene polymers. This leads to better retention of adhesion after aging; however, the SIS polymers usually have poorer initial strength compared with SBS. Another high-volume use is in toughening of asphalt compounds for paving, crack sealants, and roofing. The SBS improves rutting and low-temperature performance in paving and crack resistance in roofing applications.[73] SEBS would be the elastomer of choice in many adhesive and asphalt applications because of its superior aging properties; however, its high cost is

polystyrene domains
"hard phase"

polybutadiene
"soft phase"
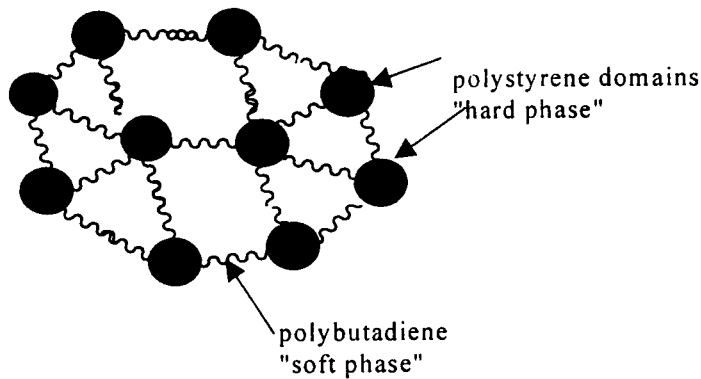
The butadiene blocks can be hydrogenated, as mentioned above with hydrogenated nitrile, to form SEBS polymers having better thermal stability and chemical resistance. The EB stands for ethylene–butylene, which are the structures formed after the butadiene segments have been hydrogenated.

Other block copolymers which are useful are based on polyesters, polyurethanes, and ethylene–propylene. The first two have been discussed in other sections and the ethylene–propylene blocks will be discussed below in the subsection "Metallocene Polymers."
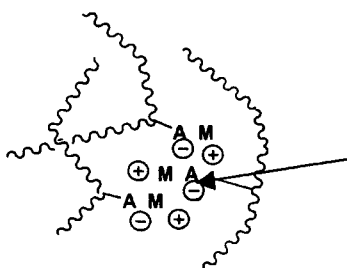
Uses

SBS copolymers are used in a wide variety of applications because of their clarity, toughness, and ease of processing. A major application is hot melt adhesives where they are compounded with hydrocarbon resins and oil.[72] The SIS polymers are very popular in

prohibitive. SBS also is used widely to toughen polystyrene and high-impact polystyrene. This polyblending technique is used to toughen a number of plastics. Various other injection molding and extrusion applications include shoe soles and toys. SBS is limited in use because of its poor high-temperature performance.

Ionomers

Ionomers are copolymers in which a small portion of the repeat units have ionic pendant groups on usually a nonpolar backbone. The ionic groups tend to separate themselves into domains similar to the polystyrene segments in the SBS rubber because they are insoluble in the nonpolar polymer chains. Therefore, these ionic clusters serve as cross-links up to temperatures where they tend to disassociate. Most commercial grades of ionic elastomers are based on ethylene and propylene monomers.

The polymer backbone usually contains sulfonyl or carboxylic acid groups and the metal counterion can be zinc, calcium, sodium, or lithium. The properties are highly dependent on the metal cation because they determine the temperature at which the ion clusters disassociate. The ionic cross-links usually impart outstanding tensile and tear strength properties because these cross-links are very good energy absorbers (hysteretic) due to their mobility. A process known as ion hopping provides one source for absorbing energy.

clusters of ionic groups forming a crosslink

M^+ = metal cation, A^- = anion

Uses

Solid golf balls are a good example of ionic cross-linked materials.[74] The covers are usually lithium or sodium cross-linked plastics but the cores are also a type of ionomer. The cores are high *cis* polybutadiene which is compounded with zinc diacrylate (ZDA) and then peroxide cured. During the curing process, the ZDA grafts to the BR backbone creating a material with a very high cross-link density where the cross-links are clusters of zinc carboxylates with very high resilience. Other applications include heat-sealable food packaging, automotive trim, footwear, foamed sheets (mats), and interlayers for bulletproof glass.

Metallocene Elastomers

Metallocene catalysts are the latest innovations to make a big impact in the polymer industry. They have been used mostly to make new polyolefin plastics, such as very-high-molecular-weight, bullet-proof polyethylene, but they have also been used to make elastomers. The catalysts make very regular "stereospecific" polymers similar to the Ziegler–Natta catalysts.

They are based on various metals. Such as zirconium, complexed with cyclopentadienide anions. This type of compound is called a "zirconocene" and is used with organoaluminum to make highly regular polymers. The catalyst has the ability to flip back and forth from making *atactic* to *isotactic* polypropylene in the same polymerization. The alternating tacticity of the polymer breaks up the crystallinity of the chains and yields an elastomer. Metallocene catalysts are currently very expensive and cannot yet polymerize dienes such as butadiene, so they have only enjoyed limited commercial success in elastomers. However, this is one of the most intense fields of polymer research and many new product breakthroughs are expected in the near future.

Rubber–Plastic Alloys

A discussion on thermoplastic elastomers would not be complete without mentioning the elastomers produced by simply blending rubbers and plastics in an internal mixer using a process known as "dynamic vulcanization." The simplest of these elastomers is based on polypropylene and EPDM rubber. Products are made with various rubber contents (hardness values) by simply mixing the rubber and plastic in a Banbury or an extruder at high temperature while cross-linking the EPDM in situ with a phenolic curing resin or other curing agents such as sulfur or peroxides. The resulting blend processes like polypropylene but is actually an elastomer because of the cross-linked rubber phase which it contains. It can be reprocessed and recycled like other TPEs. The process is described in an excellent review article by S. Abdou-Sabet.[75] Other alloys are based on nylon and NBR to obtain better thermal stability and solvent resistance. Constant improvements are being made in polymer alloys by using different combinations of plastics and rubbers and also new grafting and cross-linking chemistry to achieve properties more like conventional thermoset rubbers.

Uses

The applications for this type of elastomer have been limited because of the melting point

of the plastic phase and poor compression set. For these reasons, alloys probably will never be successful as tire materials but they have many other automotive applications, including instrument panels, cowl vents, body panels, and bumpers. They also are used in appliances, lawn and garden equipment, and as grips on tools.

PLASTICIZED POLYVINYL CHLORIDE

Generally one thinks of polyvinyl chloride as a rigid plastic, which it is, with a glass transition temperature around 85°C. However, the addition of polar chemicals such as dioctyl phthalate can reduce the glass transition temperature below room temperature, producing a rubbery material.

Monomer Production

Vinyl chloride is produced primarily from ethylene, which is converted to ethylene dichloride either by chlorination or oxychlorination. The ethylene dichloride is cracked to give vinyl chloride and hydrogen chloride.

Production Process

Polyvinyl chloride is produced by the free-radical polymerization of vinyl chloride. Bulk, emulsion, solution, and suspension polymerization processes have been used.

The plasticized product can be produced by mixing the polymer and plasticizers at elevated temperatures, also by dry blending in which the plasticizer is absorbed into the resin and then heated. Solution blending is sometimes used, as well as the plastisol process, in which fine polyvinylchloride powder is dispersed in the plasticizer which is relatively stable until it is heated.

Properties and Use

Plasticized polyvinyl chloride can be regarded as the first thermoplastic elastomer, as it is used in an uncross-linked form. Because of the lack of cross-linking, this material exhibits high rates of creep and stress relaxation. As with other thermoplastic elastomers, these disadvantages worsen as the temperature is increased. Although the polymer is saturated, it must be stabilized for use to prevent dehydrochlorination at processing temperatures. Because of the high chlorine content, polyvinyl chloride has excellent flame resistance as well as good electrical properties. Even at high plasticizer levels, these materials have marginal elasticity when compared with most other elastomers. Despite their shortcomings, they are used in many areas where they compete with other rubbers.

One of the larger uses is for wire and cable insulation. The flame resistance makes this the material of choice for residential wiring, extension cords, and so on. Inexpensive garden hose represents another large-volume use. Sports balls can be produced by rotational molding of plastisols. The low fabrication cost allows such products to dominate the lower-price-range market.[76,77]

FLUOROCARBON ELASTOMERS

The fluoroelastomers were developed as specialty materials for high heat applications and solvent resistance. By 2003 there was over 14,800 metric tons of fluoroelastomer capacity worldwide.[78] The elastomers were by-products of Plunkett's 1938 discovery of polytetrafluoroethylene. Copolymers of olefins with vinylidene fluoride were found to be leathery, whereas elastomers were made if tetrafluoroethylene (TFE) or trifluoropropene were used. The first commercial product was produced as a copolymer of vinylidene fluoride and chlorotrifluoroethylene (CTFE) and was called Kel-F. The later, more stable polymers used hexafluoropropene (HFP) with TFE. They were first commercialized by DuPont under the trade name Viton and then a few other companies added their own fluoroelastomers. These elastomers are usually prepared by radical polymerization in emulsion using catalysts such as ammonium persulfate and sometimes with chain transfer agents such as carbon tetrachloride or halogen salts.[79] Caution must be exercised when using these polymerizations because the fluoromonomers can be explosive. They are usually isolated by coagulation and normal rubber drying techniques and sold in the form of pellets, slabs, or rubber crumb.

As a result of being very unreactive, the fluoroelastomers cure very slowly and usually require a high-temperature post-cure. The curatives are designed to remove hydrogen fluoride to generate a cure site which can react with a diamine or bisphenol. They are also cured with organic peroxides. Most fluoroelastomers can be compounded using normal rubber processing equipment such as rubber mills and internal mixers. Processing aids such as dioctyl phthalate or waxes can be used to obtain smoother extrusions and better mold release.
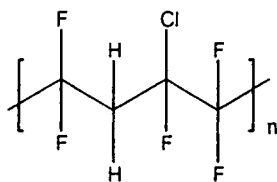
copolymer of TFE with vinylidene fluoride (VF)

Uses

Fluoroelastomers have outstanding heat resistance when cured. Some vulcanizates have almost indefinite service life at temperatures up to 200°C. The perfluoro polymers, such as DuPont's Kalrez, have short-term useage at up to 316°C and extended service as high as 288°C. This polymer is extremely expensive and is only offered in the form of finished parts, usually O-rings, seals, or gaskets. The fluoroelastomers also have excellent solvent and ozone resistance making them ideal for automotive fuel hoses. Although many of the applications involve small seals, O-rings, gaskets, and hose, the single largest applications is flue-duct expansion joints. The polymer's resistance to high temperature and wet acidic flue gases are critical in this application.

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