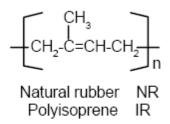
Natural Rubber (NR):

Natural rubber is the prototype of all elastomers. It is extracted in the form of latex from the bark of the Hevea tree. The rubber is collected from the latex in a series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety of grades based on purity (color and presence of extraneous matter), viscosity, viscosity stability, oxidation resistance, and rate of cure. Modified natural rubbers are also available, with treatment usually performed at the latex stage. These include:

- 1. epoxidized natural rubber (ENR).
- 2. deproteinized natural rubber (DNR).
- 3.
- 4. process oils have been incorporated.
- 5. Heveaplus MG rubber- natural rub ber with grafted poly(methyl methacrylate) side chains.
- 6. thermoplastic natural rubber (TNR) blends of natural rubber and polypropylene.

The natural rubber polymer is nearly 100% cis-1,4 polyisoprene with M_w ranging from 1 to 2.5 x 10⁶. Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. Low temperature crystallization causes stiffening, but is easily reversed by warming. Crystallization gives natural rubber high tensile strength and resistance to cutting, tearing, and abrasion.



Like other high polymers, natural rubber can be pictured as a tangle of randomly oriented sinuous polymer chains. The "length" of these chains is a function of their thermodynamic behavior and is determined as the statistically most probable distance between each end. This chain length reflects the preferred configuration of the individual polymer molecule. The application of force to a rubber sample effectively changes the chain length. When the force is removed, the chain tries to regain its preferred configuration. In simple terms, this can be compared to the compression or extension of a spring. This effect is the basis of rubber's elasticity.

Elasticity is one of the fundamentally important properties of natural rubber. Rubber is unique in the extent to which it can be distorted, and the rapidity and degree to which it recovers to its original shape and dimensions. It is, however, not perfectly elastic. The rapid recovery is not complete. Part of the distortion is recovered more slowly and part is retained. The extent of this permanent distortion, called permanent set, depends upon the rate and duration of the applied force. The slower the force, and the longer it is maintained, the greater is the permanent set. Because of rubber's elasticity, however, the permanent set may not be complete even after long periods of applied force. This quality is of obvious value in gaskets and seals.

The rubber's polymer network allows elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched. The elastic nature of this network also accounts for the exceptional resilience of cured rubber products. This resilience means less kinetic energy is lost as heat during repeated stress deformation. Products made from natural rubber are less likely than most other elastomers to fail from excessive heat buildup or fatigue when exposed to severe dynamic conditions. This has secured the place of natural rubber as the preferred sidewall elastomer in radial tires.

As already noted, the rubber polymer network was originally an impediment to rubber processing. Mixing additives with a tough, elastic piece of raw rubber was a substantial challenge. The solution came with the discovery of its thermoplastic behavior. High shear and heat turn the rubber soft and plastic through a combination of extension, disentanglement, and oxidative cleavage of polymer chains. In this state it is considerably more receptive to the incorporation of additives so that the rubber's natural attributes can be modified and optimized as desired. The commercial utility of natural rubber has in fact grown from the ease with which its useful properties can be changed or improved by compounding techniques.

Another important and almost unique quality of uncured natural rubber compounds is building tack. When two fresh surfaces of milled rubber are pressed together they bond into a single piece. This facilitates the building of composite articles from separate components. In tire manufacture, for example, the separate pieces of uncured tire are held together solely by building tack. During cure they fuse into a single unit.

Natural rubber is used in the carcass of passenger car cross-ply tires for its building tack, ply adhesion, and good tear resistance. It is also used in the sidewalls of radial ply tires for its fatigue resistance and low heat buildup. In tires for commercial and industrial vehicles, natural rubber content increases with tire size. Almost 100% natural rubber is used in the large truck and earthmover tires which require low heat buildup and maximum cut resistance. Natural rubber is also used in industrial goods, such as hoses, conveyor belts, and rubberized fabrics; engineering products, for resilient load bearing and shock or vibration absorption components; and latex products such as gloves, and adhesives.

Styrene-Butadiene Rubber (SBR):

SBR polymers are widely produced by both emulsion and solution polymerization. Emulsion polymerization is carried out either hot, at about 50°C, or cold, at about 5°C, depending upon the initiating system. SBR made in emulsion usually contains about 23% styrene randomly dispersed with butadiene in the polymer chains. SBR made in solution contains about the same amount of styrene, but both random and block copolymers can be made. Block styrene is thermoplastic and at processing temperatures helps to soften and smooth out the elastomer. Both cold emulsion SBR and solution SBR are offered in oil-extended versions. These have up to 50% petroleum base oil on polymer weight incorporated within the polymer network. Oil extension of SBR improves processing characteristics, primarily allowing easier mixing, without sacrificing physical properties.

 $\left[(CH_2-CH=CH-CH_2)_{5} + (CH-CH_2)_{n} \right]_{n}$ Styrene-butadiene rubber SBR

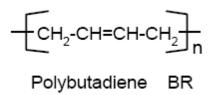
SBR was originally produced by the hot emulsion method, and was characterized as more difficult to mill, mix, or calender than natural rubber, as well as being deficient in building tack, and having relatively poor inherent physical properties. Processability and physical properties were found to be greatly improved by the addition of process oil and reinforcing agents. "Cold" SBR generally has a higher average molecular weight and narrower molecular weight distribution. It thereby offers better abrasion and wear resistance plus greater tensile and modulus than "hot" SBR. Since higher molecular weight can make cold SBR more difficult to process, it is commonly offered in oil-extended form. Solution SBRs can be tailored in polymer structure and properties to a much greater degree than their emulsion counterparts. The random copolymers offer narrower molecular weight distribution, low chain branching, and lighter color than emulsion SBR. They are comparable in tensile, modulus, and elongation, but offer lower heat buildup, better flex, and higher resilience. Certain grades of solution SBR even address the polymer's characteristic lack of building tack, although it is still inferior to that of natural rubber.

The processing of SBR compounds in general is similar to that of natural rubber in the procedures and additives used. SBR is typically compounded with better abrasion, crack initiation, and heat resistance than natural rubber. SBR extrusions are smoother and maintain their shape better than those of natural rubber.

SBR was originally developed as a general purpose elastomer and it still retains this distinction. It is the largest volume and most widely used elastomer worldwide. Its single largest application is in passenger car tires, particularly in tread compounds for superior traction and treadwear. Substantial quantities are also used in footwear, foamed products, wire and cable jacketing, belting, hoses, and mechanical goods.

Polybutadiene Rubber (BR):

This elastomer was originally made by emulsion polymerization, generally with poor results. It was difficult to process and did not extrude well. Polybutadiene became commercially successful only after it was made by solution polymerization using stereospecific Ziegler-Natta catalysts. This provided a polymer with greater than 90% cis-1,4polybutadiene configuration. This structure hardens at much lower temperatures (with Tg of -100°C) than natural rubber and most other commercial elastomers. This gives better low temperature flexibility and higher resilience at ambient temperatures than most elastomers. Greater resilience means less heat buildup as well under continuous dynamic deformation. This high-cis BR was also found to possess superior abrasion resistance and a great tolerance for high levels of extender oil and carbon black. High-cis BR was originally blended with natural rubber simply to improve the latter's processing properties, but it was found that the BR conferred many of its desirable properties to the blend. The same was found to be true in blends with SBR.



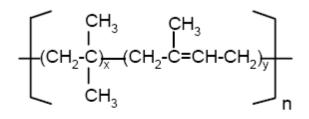
By selection of catalyst and control of processing conditions, polybutadienes are now sold with various distributions of each isomer within the polymer chain, and with varying levels of chain linearity, molecular weight and molecular weight distribution. Each combination of chemical properties is designed to enhance one or more of BR's primary attributes.

The largest volume use of polybutadiene is in passenger car tires, primarily in blends with SBR or natural rubber to improve hysteresis (resistance to heat buildup), abrasion resistance, and cut growth resistance of tire treads. The type of BR used depends on which properties are most important to the particular compound. Polybutadiene is also used for improved durability and abrasion and crack resistance in tire sidewalls and carcasses, as well as in elastomer blends for belting. High. BRs are also used in the manufacture of high impact polystyrene.

Butyl Rubber (IIR):

Butyl rubber is the common name for the copolymer of isobutylene and 1 to 3% isoprene produced by cold $(-100^{\circ}C)$ cationic solution polymerization. Isoprene provides the unsaturation required for

vulcanization. Most of butyl rubber's distinguishing characteristics are a result of its low level of chemical unsaturation. The essentially saturated hydrocarbon backbone of the IIR polymer will effectively repel water and polar liquids but show an affinity for aliphatic and some cyclic hydrocarbons. Products of butyl rubber will therefore be swollen by hydrocarbon solvents and oils, but show resistance to moisture, mineral acids, polar oxygenated solvents, synthetic hydraulic fluids, vegetable oils, and ester-type plasticizers. It is likewise highly resistant to the diffusion or solution of gas molecules. Air impermeability is the primary property of commercial utility. The low level of chemical unsaturation also imparts high resistance to ozone. Sulfur-cured butyl rubber has relatively poor thermal stability, softening with prolonged exposure at temperatures above 150oC because the low unsaturation prevents oxidative crosslinking. Curing with phenol-formaldehyde resins instead of sulfur, however, provides products with very high heat resistance, the property responsible for a large market in tire-curing bladders.



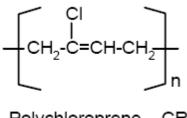
Butyl rubber IIR

The molecular structure of the polyisobutylene chain provides less flexibility and greater delayed elastic response to deformation than most elastomers. This imparts vibration damping and shock-absorption properties to butyl rubber products.

The unique properties of butyl rubber are used to advantage in tire inner tubes and air cushions (air impermeability), sheet roofing and cable insulation (ozone and weather resistance), tire-curing bladders, hoses for high temperature service, and conveyor belts for hot materials (thermal stability with resin cure).

Neoprene (CR):

Neoprene is the common name for the polymers of chloroprene (2chloro-1,3-butadiene). These are produced by emulsion polymerization. The chloroprene monomer can polymerize in four isomeric forms. Neoprene is typically 88-92% trans, with degree of polymer crystallinity proportional to trans content. Cis addition accounts for 7-12% of the structure and 3,4 addition makes up about 1%. The approximately 1.5% of 1,2 addition is believed to provide the principal sites of vulcanization.



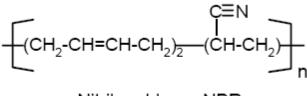
Polychloroprene CR

The high structural regularity (high trans content) of neoprene allows the strain-induced crystallization that results, as for natural rubber, in high tensile strength. The 2-chloro substituent, instead of natural rubber's 2methyl, results in a higher freezing point (poorer low temperature resistance) and alters vulcanization requirements. Neoprenes are generally cured with zinc oxide and magnesium oxide, or lead oxide for enhanced water resistance. The presence of chlorine in the polymer structure improves resistance to oil, weathering, ozone and heat. The improved oxidation resistance is due to the reduced activity of the double bonds caused by the chlorine. Except for low temperature resistance and price, neoprene would be considered nearly as versatile as natural rubber.

There are three types of general purpose neoprenes – G, W, and T types – with selected features modified to offer a range of processing, curing and performance properties. Products are made from neoprene because it offers good building tack, good oil, abrasion, chemical, heat, weather, and flex resistance, and physical toughness. Neoprene is widely used in hoses of all types (water, oil, air, automotive, industrial), wire and cable jacketing, power transmission and conveyor belting, bridge and building bearings, pipe gaskets, footwear, roof coatings, and coated fabrics.

Nitrile Rubber (NBR):

Nitrile rubber is the generic name given to emulsion polymerized copolymers of acrylonitrile and butadiene. Its single most important property is exceptional resistance to attack by most oils and solvents. It also offers better gas impermeability, abrasion resistance, and thermal stability than the general purpose elastomers like natural rubber and SBR. These attributes arise from the highly polar character of acrylonitrite, the content of which determines the polymer's particular balance of Commercial nitrile rubbers available with properties. are acrylonitrile/butadiene ratios ranging from 18:82 to 45:55. As acrylonitrile content increases, oil resistance, solvent resistance, tensile strength, hardness, abrasion resistance, heat resistance, and gas impermeability improve, but compression set resistance, resilience and low temperature flex deteriorate. Selection of the particular grade of NBR needed is generally based on oil resistance vs. low temperature performance. Blends of different grades are common to achieve the desired balance of properties.



Nitrile rubber NBR

Nitrile elastomers do not crystallize when stretched and so require reinforcing fillers to develop optimum tensile strength, abrasion resistance, and tear resistance. They also possess poor building tack. Although nitrile rubbers are broadly oil- and solvent-resistant, they are susceptible to attack by certain strongly polar liquids, to which the nonpolar rubbers, such as SBR or natural rubber, are resistant. Nitrile rubber is poorly compatible with natural rubber, but can be blended in all proportions with SBR. This decreases overall oil resistance, but increases resistance to polar liquids in proportion to the SBR content. Nitrile polymers are increasingly used as additives to plastics to provide elastomeric properties. Blends with polyvinyl chloride are popular for conferring improved abrasion, tensile, tear, and flex properties. Nitrile rubber is used primarily in hoses, tubing, linings, and seals used for the conveyance or retention of oils and solvents.

Polyisoprene (IR):

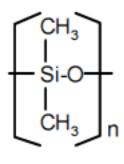
Polyisoprene is made by solution polymerization of isoprene (2 methyl-1,3- butadiene). The isoprene monomer, the structural unit of the natural rubber polymer, can polymerize in four isomeric forms: trans 1,4 addition, cis 1,4 addition, 1,2 addition, leaving a pendant vinyl group, and 3,4 addition. The production of a synthetic analogue to natural rubber was stymied for over 100 years because polymerization of isoprene resulted in mixtures of isomeric forms. In the 1950s, rubber-like elastomers with >90% cis 1,4 isoprene configuration were finally produced using stereospecific catalyts.

Polyisoprene compounds, like those of natural rubber, exhibit good building tack, high tensile strength, good hysteresis, and good hot tensile and hot tear strength. The characteristics which differentiate polyisoprene from natural rubber arise from the former's closely controlled synthesis. Polyisoprene is chemically purer – it does not contain the proteins and fatty acids of its natural counterpart. Molecular weight is lower than natural rubber's. Polyisoprene is therefore easier to process, gives a less variable (although generally slower) cure, is more compatible in blends with EPDM and solution SBR, and provides less green strength (precure) than natural rubber. Polyisoprene is added to SBR compounds to improve tear strength, tensile strength, and resilience while decreasing heat buildup. Blends of polyisoprene and fast curing EPDM combine high ozone resistance with the good tack and cured adhesion uncharacteristic of EPDM alone.

Polyisoprene is typically used in favor of natural rubber in applications requiring consistent cure rates, tight process control, or improved extrusion, molding, and calendering. The synthetic elastomer can be produced with the very low level of branching, high molecular weight, and relatively narrower molecular weight distribution that contributes to lower heat buildup compared to natural rubber. For this reason, certain grades of polyisoprene are used as a alternative to natural rubber in the tread of high service tires (truck, aircraft, off-road) without sacrificing abrasion resistance, groove cracking, rib tearing, cold flex properties, or weathering resistance. Footwear and mechanical goods are also major uses. Because of polyisoprene's high purity and the high tensile strength of its compounds, it is widely used in medical goods and food-contact items. These include baby bottle nipples, milk tubing, and hospital sheeting.

Silicone Rubber:

Because of its unique properties and somewhat higher price compared to the other common elastomers, silicone rubber is usually classed as a specialty elastomer, although it is increasingly used as a costeffective alternative in a variety of applications. Two types of silicone elastomers are available, each providing the same fundamental properties. These are the thermosetting rubbers that are vulcanized with heat, and RTV (room temperature vulcanizing) rubbers.



Silicone MQ

The basic silicone polymer is dimethylpolysiloxane with a backbone of silicon-oxygen linkages and two methyl groups on each silicon. The siliconoxygen backbone provides a high degree of inertness to ozone, oxygen, heat (up to 315°C), UV light, moisture, and general weathering effects, while the methyl substituents confer a high degree of flexibility. The basic polymer properties are modified by replacing minor amounts of the methyl substituents with phenyls and/or vinyls. Phenyl groups improve low temperature flexibility (to as low as -100°C) without sacrificing high temperature properties. Vinyl groups improve compression set resistance and facilitate vulcanization. Of the available silicone elastomers - methyl silicone (MQ), methyl-vinyl silicone (VMQ), methyl-phenyl silicone (PMQ), methyl-phenyl-vinyl silicone (PVMQ), and fluoro-vinyl-methyl silicone (FVMQ) – the methyl-vinyl types are most widely used.

Thermal vulcanization typically uses peroxides to crosslink at the vinyl groups of the high molecular weight solid silicone rubbers. Compounded products offer the attributes noted above plus superior resistance to compression set, excellent biocompatability, vibration damping over a wide temperature range, and thermal ablative properties. The latter enables the silicone rubber to form a thermally insulating surface char on exposure to temperatures up to 5,000°C. The rubber remains elastomeric beneath the char. Silicone elastomers generally offer poorer tensile, tear, and abrasion properties than the more common organic rubbers, but this is routinely improved by reinforcement with fumed silica, which also improves electrical insulation properties.

Room temperature vulcanizing (RTV) silicones are low molecular weight dimethylpolysiloxane liquids with reactive end groups. As with the heat cured polymers, there can be minor substitution of methyl groups with phenyls – for improved low temperature flexibility – or with fluoroalkyl groups – for improved oil and solvent resistance and even broader temperature service. Vulcanization of the RTV silicones is obtained from either a condensation or an addition reaction. Condensation cures can be either moisture independent or moisture dependent.

Solid (thermally cured) rubbers are used in automotive underhood applications, primarily for their heat resistance. Products include ignition cables, coolant and heater hoses, O-rings, and seals. Similar applications are found in aircraft seals, connectors, cushions, and hoses, seals, and gaskets. Long service life plus circuit integrity (from ablative charing) with no toxic gas generation have secured the place of silicone rubber in wire and cable insulation for electric power generation and transmission, for naval shipboard cable of all types, and for appliance wiring. The inherent inertness and biocompatibility of silicone rubbers have enabled their use in food contact and medical products. These include baby bottle nipples, belts and hoses for conveying foods and food ingredients, surgical tubing, subdermal implants, and prosthetic devices.

RTV silicones are used by the automotive, appliance, and aerospace industries for electronic potting compounds and formed-in-place gaskets, to form molds for the manufacture of plastic parts, and widely in construction adhesives, sealants, roof coatings, and glazing.