

SYNTHETIC RUBBER

Synthetic rubbers (elastomers) are long-chain polymers with special chemical and physical as well as mechanical properties. These materials have chemical stability, high abrasion resistance, strength, and good dimensional stability. Many of these properties are imparted to the original polymer through crosslinking agents and additives. Selected properties of some elastomers are shown in Table 1.

An important property of elastomeric materials is their ability to be stretched at least twice their original length and to return back to nearly their original length when released. Natural rubber is an elastomer constituted of isoprene units. These units are linked in a cis-1,4-configuration that gives natural rubber the outstanding properties of high resilience and strength. Natural rubber occurs as a latex (water emulsion) and is obtained from *Hevea brasiliensis*, a tree that grows in Malaysia, Indonesia, and Brazil.

Charles Goodyear (1839) was the first to discover that the latex could be vulcanized (crosslinked) by heating with sulfur or other agents. Vulcanization of rubber is a chemical reaction by which elastomer chains are linked together. The long chain molecules impart elasticity, and the crosslinks give load supporting strength. Vulcanization of rubber has been reviewed by Hertz, Jr.³⁵ Synthetic rubbers include elastomers that could be crosslinked such as polybutadiene, polyisoprene, and ethylene-propylene-diene terpolymer.

It also includes thermoplastic elastomers that are not crosslinked and are adapted for special purposes such as automobile bumpers and wire and cable coatings. These materials could be scraped and reused.

However, they cannot replace all traditional rubber since they do not have the wide temperature performance range of thermoset rubber.

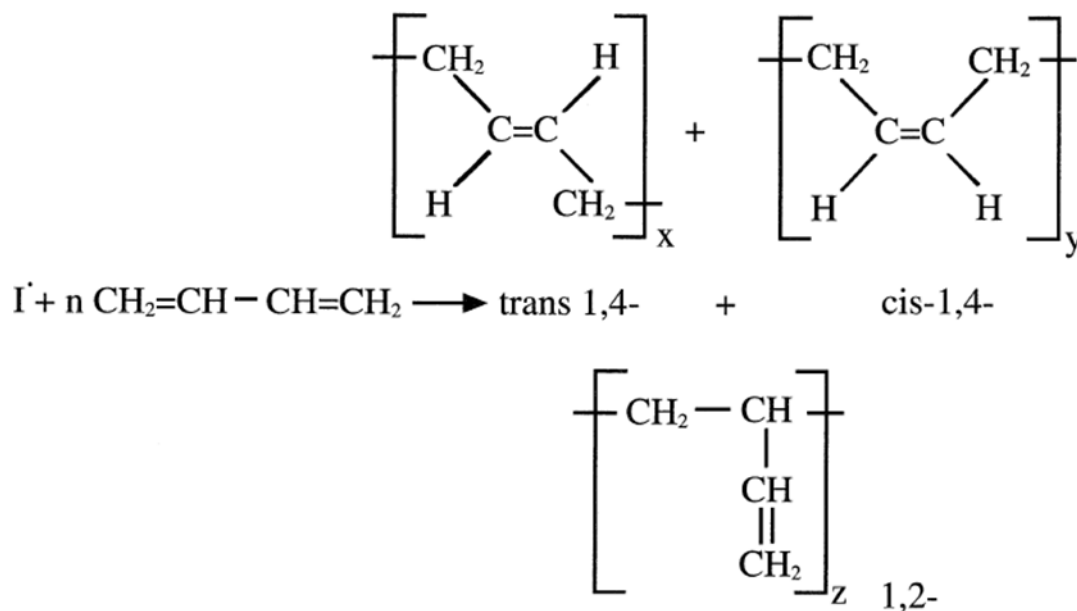
The major use of rubber is for tire production. Non-tire consumption includes hoses, footwear, molded and extruded materials, and plasticizers.

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resis- tance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	–55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	–60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

Table 1 Selected properties of some elastomers.

BUTADIENE POLYMERS AND COPOLYMERS

Butadiene could be polymerized using free radical initiators or ionic or coordination catalysts. When butadiene is polymerized in emulsion using a free radical initiator such as cumene hydroperoxide, a random polymer is obtained with three isomeric configurations, the 1,4-addition configuration dominating:



Polymerization of butadiene using anionic initiators (alkyllithium) in a nonpolar solvent produces a polymer with a high cis configuration. A high cis-polybutadiene is also obtained when coordination catalysts are used.

Properties and Uses of Polybutadiene

cis-1,4-Polybutadiene is characterized by high elasticity, low heat buildup, high abrasion resistance, and resistance to oxidation. However, it has a relatively low mechanical strength. This is improved by incorporating a cis, trans block copolymer or 1,2-(vinyl) block copolymer in the polybutadiene matrix.⁴⁰ Also, a small amount of natural rubber may be mixed with polybutadiene to improve its properties. trans 1,4-Polybutadiene is characterized by a higher glass transition temperature ($T_g = -14^\circ\text{C}$) than the cis form ($T_g = -108^\circ\text{C}$). The polymer has the toughness, resilience, and abrasion resistance of natural rubber ($T_g = -14^\circ\text{C}$).

Styrene-Butadiene Rubber (SBR)

Styrene-butadiene rubber (SBR) is the most widely used synthetic rubber. It can be produced by the copolymerization of butadiene ($\approx 75\%$) and styrene ($\approx 25\%$) using free radical initiators. A random copolymer is obtained. The micro structure of the polymer is 60–68% trans, 14–19% cis, and 17–21% 1,2. Wet methods are normally used to characterize polybutadiene polymers and copolymers.

Solid state NMR provides a more convenient way to determine the polymer micro structure. Currently, more SBR is produced by copolymerizing the two monomers with anionic or coordination catalysts. The formed copolymer has better mechanical properties and a narrower molecular weight distribution.

A random copolymer with ordered sequence can also be made in solution using butyllithium, provided that the two monomers are charged slowly. Block copolymers of butadiene and styrene may be produced in solution using coordination or anionic catalysts. Butadiene polymerizes first until it is consumed, then styrene starts to polymerize. SBR produced by coordination catalysts has better tensile strength than that produced by free radical initiators.

The main use of SBR is for tire production. Other uses include footwear, coatings, carpet backing, and adhesives.

NITRILE RUBBER (NBR)

Nitrile rubber is a copolymer of butadiene and acrylonitrile. It has the special property of being resistant to hydrocarbon liquids. The copolymerization occurs in an aqueous emulsion. When free radicals are used, a random copolymer is obtained. Alternating copolymers are produced when a Ziegler-Natta catalyst is employed. Molecular weight can be controlled by adding modifiers and inhibitors. When the polymerization reaches approximately 65%, the reaction mixture is vacuum distilled in presence of steam to recover the monomer.

The ratio of acrylonitrile/butadiene could be adjusted to obtain a polymer with specific properties. Increasing the acrylonitrile ratio increases oil resistance of the rubber, but decreases its plasticizer compatibility.

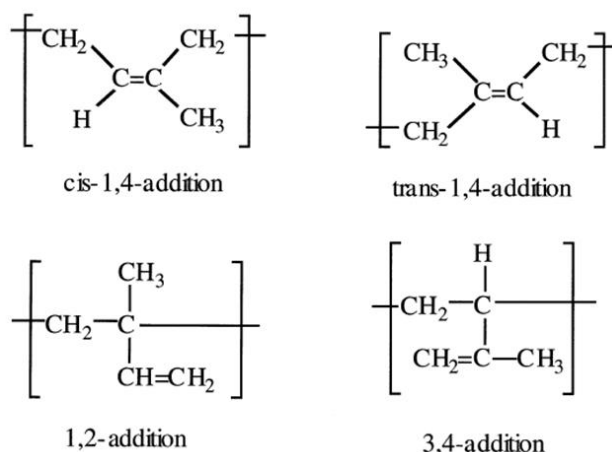
NBR is produced in different grades depending on the end use of the polymer. Low acrylonitrile rubber is flexible at low temperatures and is generally used in gaskets, O-rings, and adhesives. The medium type is used in less flexible articles such as kitchen mats and shoe soles. High acrylonitrile polymers are more rigid and highly resistant to hydrocarbons and oils and are used in fuel tanks and hoses, hydraulic equipment, and gaskets.

POLYISOPRENE

Natural rubber is a stereoregular polymer composed of isoprene units attached in a cis configuration. This arrangement gives the rubber high resilience and strength.

Isoprene can be polymerized using free radical initiators, but a random polymer is obtained. As with butadiene, polymerization of isoprene can produce a mixture of isomers. However, because the isoprene molecule is asymmetrical, the addition can occur in 1,2-, 1,4- and 3,4-positions.

Six tactic forms are possible from both 1,2- and 3,4- addition and two geometrical isomers from 1,4- addition (cis and trans):



Stereoregular polyisoprene is obtained when Ziegler-Natta catalysts or anionic initiators are used. The most important coordination catalyst is α - TiCl_3 cocatalyzed with aluminum alkyls. The polymerization rate and cis content depends upon Al/Ti ratio, which should be greater than one. Lower ratios predominantly produce the trans structure. Figure 1 shows a process for producing cis-polyisoprene by a solution polymerization.

Properties and Uses of Polyisoprene

Polyisoprene is a synthetic polymer (elastomer) that can be vulcanized by the addition of sulfur. cis-Polyisoprene has properties similar to that of natural rubber. It is characterized by high tensile strength and insensitivity to temperature changes, but it has low abrasion resistance. It is attacked by oxygen and hydrocarbons.

trans-Polyisoprene is similar to Gutta percha, which is produced from the leaves and bark of the sapotacea tree. It has different properties from the cis form and cannot be vulcanized. Few commercial uses are based on trans-polyisoprene.

Important uses of cis-polyisoprene include the production of tires, specialized mechanical products, conveyor belts, footwear, and insulation.

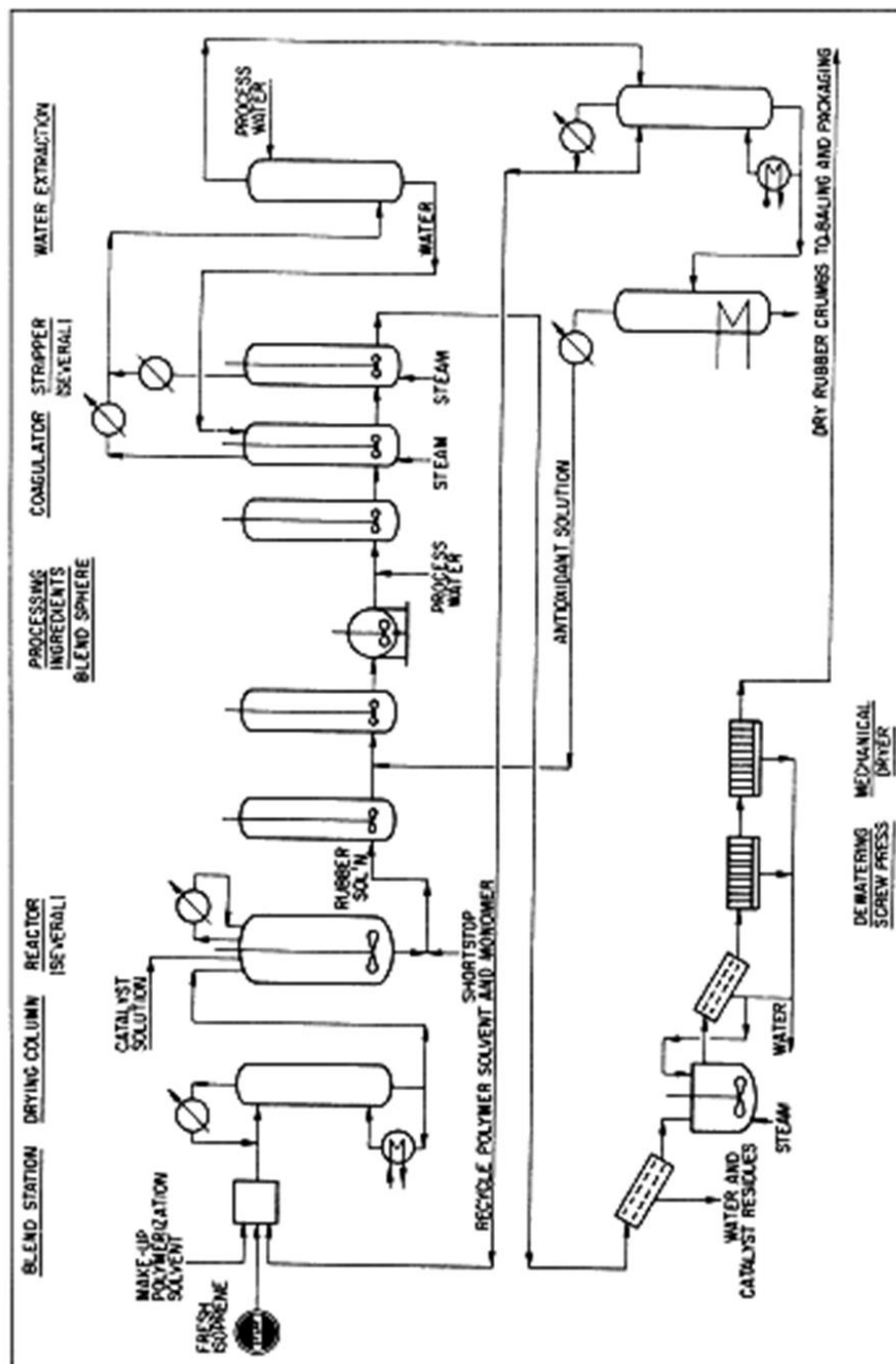


Figure 1 A process for producing 1,4-polyisoprene (>99%) by a continuous solution polymerization.

References

1. Uttam Ray Chaudhuri "Fundamentals of Petroleum and Petrochemical Engineering." University of Calcutta Calcutta, India, 2011.
2. Matar S., Hatch L.F, "Chemistry of PETROCHEMICAL PROCESSES ", 2nd Edition, Gulf Publishing Company, (1994).