

Lecture 4

**Elastomers: Styrene Butadiene
Rubber(SBR), Poly Butadiene,
Nitrile Rubber**

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ELASTOMERS: STYRENE BUTADIENE RUBBER (SBR), POLY BUTADIENE, NITRILE RUBBER

Elastomers are used in wide variety of industrial, medical and household products and major portion of elastomers consumption goes into tyres next largest product sector is latex goods. There are two major types of elastomers; natural rubber a product of tropical tree *Hevea brasiliensis* is and synthetic rubber- a family of materials derived from petrochemical feed stocks [[Chemistry & industry 5, August 1996, p.574](#)]. Major producers of natural rubber are natural rubber producing country are Thailand, Indonesia and Malaysia, Africa, Latin America, Brazil, Cambodia, Nigeria, Sri Lanka, Thailand, India.

Demand for natural is estimated to have been around 10.9 million tones in 2011 out of which around 45 percent was from Asia. About 92percent of natural rubber is produced from Asian countries. The demand for natural rubber globally is projected to grow by 3-4percent through 2013 [[Chemical weekly, Jan'17, 2012](#)].

Synthetic rubbers have slowly replaced natural rubbers and have undergone various developments for applications in automotives, chemical industry, energy generation, sports, aerospace industry etc.

NATURAL AND SYNTHETIC RUBBER

- 1525 Elastic ball reported by Mexico tribal people
- 1735 First scientific study of rubber by Charles de la Condamine
- 1820 First planting of rubber in India at Travancore
- 1832 Rosburg factory was set up for rubber goods with non –vulcanized rubber
- 145 R.W Thomson invented the Pneumatic tire
- 1902 First commercial plantation
- 1910 First large scale commercial production of butadiene rubber
- 1914-18 Methyl isoprene rubber in Germany
- 1930 Organic polysulphide rubber
- 1931 Neoprene production started
- 1932 First synthetic rubber plant in USSR

1933 BUNA-S made in USSR
 1936 First automatic tyre factory (Dunlop) in India
 1963 First synthetic rubber plant in India
 1976 First nitrile rubber by Synthetics Chemicals
 1978 First polybutadiene plant in India by IPCL
 Petro based synthetic rubber 20 percent India, 80 percent in developed countries.
 Annual growth rate 7 percent

NATURAL RUBBER

Christopher Columbus voyage to Haiti 1496

Tree: Cau-achu Weeping wood

Priestley (1770), Rubber Rub-off

1839 Vulcanising of Rubber

1840 Henry Wickham smuggled 70,000 Hevea tree seed to England planted at London.

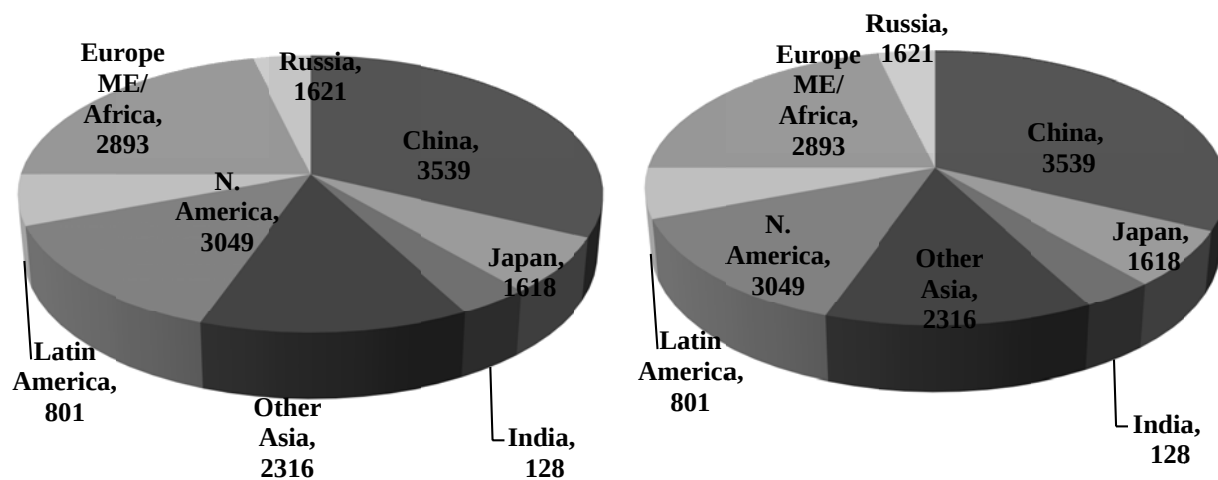
SYNTHETIC RUBBER

With the availability of petrochemical feedstocks there has been tremendous increase in the production of synthetic rubber. World synthetic rubber market and its production is given in [Figure M-VIII 4.1](#) and [Figure M-VIII 4.2](#) respectively. Synthetic rubber may be classified as general purpose rubber, specialty rubbers, thermoplastic rubber or liquid processing rubber (eg. silicon rubber, liquid polysulphide rubber). Classification of synthetic rubber is given in **M-VIII 1.4**. Forecast of synthetic rubber and natural rubber consumption in India is given in [Table M-VIII 4.3](#).

Table M-VIII 4.1: Synthetic and Natural rubber consumption scenario

India	2005	2010	2015
Capacity	85	113	-
Consumption	233	406	613
Oversupply/ (Shortage)	(148)	(293)	-

Source: IISRP (2011) TSRC Corporation



Capacity (2011) by Region (15,965 kmta)

Consumption (2011) by Region (14,540 mta)

Figure M-VIII 4.1: World Synthetic Rubbers Market by Region

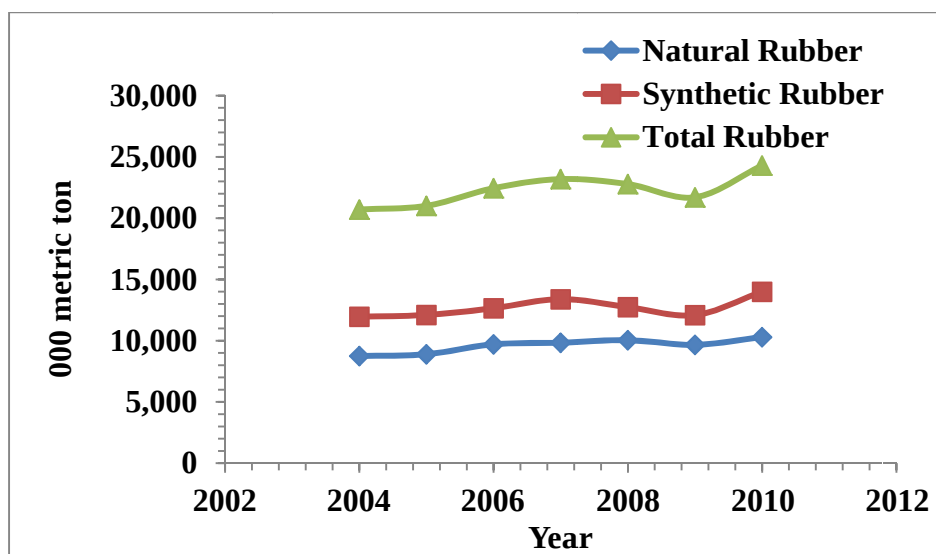


Figure M-VIII 4.2: World Rubber Production

Sources: International Rubber Study Group

Table M-VIII 4.3: Indian Consumption of Synthetic Rubber (SR) and Natural Rubber (NR) Forecast

Unit: 000' metric ton

	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
NR, Tyre Sector	661	680	772	783	850	897	950	1010	1046	1093	1152
NR, Non-Tire Sector	283	284	295	308	329	342	358	383	397	414	447
Sub-total	944	964	1017	1091	1179	1239	1308	1393	1443	1507	1599
SR, Tyre Sector	145	143	156	164	166	178	189	210	214	221	248
SR, Non-Tire Sector	261	285	342	414	452	513	570	625	636	661	687
Sub-total	406	428	498	578	618	691	759	835	850	882	935
Total of Rubber Consumption	1350	1392	1515	1669	1797	1930	2067	2228	2293	2389	2534

Source: IRSG (December) TSRC Corporation 2011

STYRENE BUTADIENE RUBBER (SBR)

Styrene butadiene rubber is most widely used elastomer in the world. SBR is used for both tire and non-tire application. Styrene butadiene rubber known as Buna-S was first prepared by I.G. Farbenindustrie in Germany. There has been significant development in the process technology of styrene butadiene rubber manufacture. Amongst the various processes, emulsion polymerisation of SBR is most commonly used. The cold process of emulsion polymerisation process has replaced the hot polymerisation process. In India, first SBR manufacture was started by Synthetic and Chemicals, Bareilly in 1963, however, the unit has been closed presently. Although butadiene is recovered from cracker plant, it can be also made from ethanol route. Styrene is made from ethyl benzene by alkylation of benzene with ethylene which can be also recovered from FCC gases.

SBR is made by emulsion polymerisation at 50°C. Initiation occurs through reaction of potassium peroxydisulphate with n-dodecyl mercaptan. Chain propagation occurs by the growing chain free radical of mercaptyl attaching either butadiene or styrene. The reaction is terminated at 60-75 percent of completion. Unreacted butadiene and styrene were recovered. Antioxidant is added followed by coagulation, washing and drying. It is used as elastomer, emulsion and solution. Used in tyres and tyre-related product, mechanical goods, automotive uses, adhesive, shoe products.

STYRENE BUTADIENE STYRENE RUBBER(SBR)

SBR is a hard rubber which is uses for soles of shoes, tire treads and other places where durability is important. It is a type of copolymer called a block copolymer. Its backbone chain is made of three segments- first segment polystyrene, second polybutadiene and third polystyrene. Polystyrene is tough hard plastic and this gives SBS its durability [[file:/A:/Poly\(styrene-butadiene-styrene\).htm](file:/A:/Poly(styrene-butadiene-styrene).htm)]. Process flow diagram of SBR Manufacture is given in Figure M-VIII 4.2

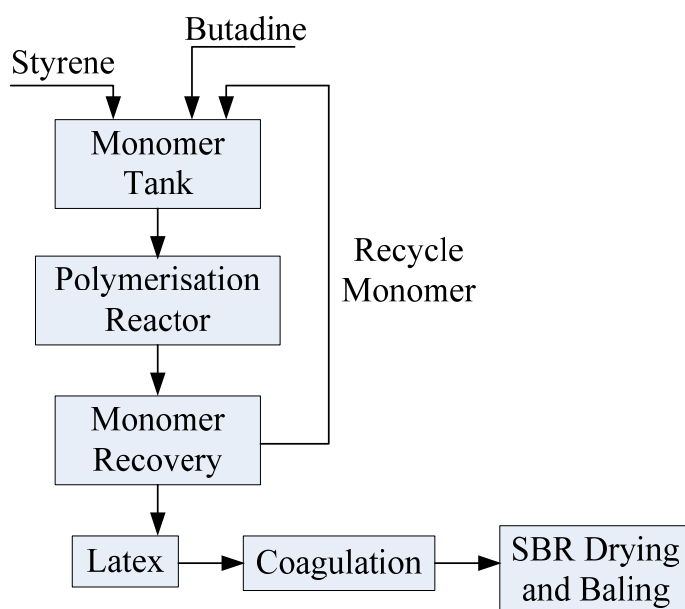


Figure M-VIII 4.2: Process flow Diagram of SBR Manufacture

POLYBUTADIENE

Stream of steam cracker is major source of butadiene. Other routes for butadiene manufacture are

- Catalytic dehydrogenation of butenes
- Catalytic dehydrogenation of butane

With the availability of butadiene from cracker plant, manufacture of polybutadiene has increased significantly in recent years.

Polybutadiene is made by free radical emulsions, alkali methyl solution and transition metal coordination solution processes. Most processes are based on solution process. Large volume use of polybutadiene rubber has been primarily in blend with other polymers. Blend with SBR or natural rubber has improved crack resistance. Cracking and abrasion resistance is very good.

It is characterized with high abrasion and crack resistance, better resistance to heat degradation and blowouts, good hysteresis properties, large scale use in tyre tread, modification of plastics, conveyor & V-belts, sports goods, foot wear material, 90 percent in tyre industry.

POLYISOBUTYLENE (BUTYL RUBBER)

Polyisobutylene is gas impermeable and because of this property it is used for making ballon. Polyisobutylene is made by polymerization of isobutylene. Isobutylene can be recovered from C₄ stream from steam cracker and FCC. Other route for isobutylene are: dehydrogenation of isobutene n-butane isomerisation in gas phase using platinum catalysts

Butyl rubber is made by slurry polymerisation. The polymerisation is carried out in slurry of monomer in methyl chloride using an aluminium chloride catalyst at -100 to -90 °C. The rubber is precipitated by adding water and finally washed and dried. Butyl rubber has unique elastomeric qualities, low rate of gas permeability, thermal stability, good ozone and weathering resistance, vibration damping and higher coefficients of friction, chemical and moisture resistance. Used in tubes, tyre inner liner due to low permeability of air, automotive mechanical parts, adhesives, and sealant.

NITRILE RUBBER

Acrylonitrile Butadiene copolymers are commonly known as nitrile rubber. Nitrile rubbers are available in many grades varying in acrylonitrile content. Increase in acrylonitrile improves resistance to fuels and oil, tensile strength and modulus, processing behavior, heat resistance; increases abrasion resistance and hardness, permeability resistance to gas diffusion; decreases low temperature flexibility, resilience and elasticity, plasticizer compatibility [Patel, 1991]. A broad range of properties can be obtained from properly compounded nitrile rubber.

Nitrile rubber is made by emulsion copolymerisation of butadiene and acrylonitrile at 5°C. The basic steps involved are polymerisation, coagulation, washing and drying. A basic polymerisation recipe in addition to the monomer contains water, stabilizers, emulsifiers, shortstop catalyst activator and electrolytes. Following polymerisation cycle material is transferred to blow down tank in which short stop and antioxidant are added and residual monomers are recovered. Then finally, the latex is concentrated, coagulated, washed, dewatered and finally dried. Nitrile rubber is used in seals; O-rings, gaskets, oil field parts, diaphragm, gloves, belts, wire cable insulation, hosepipes, foot wear shoe products, molded rubber goods.

In the polymerization process the monomer is emulsified in water, a free radical generating catalyst is added and the mixture is agitated. After the polymerization the material from the polymerisation reactor is transferred to blow tank in which short stop and antioxidant are added and the residual monomers are removed. The latex formed is concentrated and coagulated into fine crumbs by addition of salt and acids. This followed by washing, dewatering and drying. The dried crumbs are compacted [Patel, 1991].

Acrylonitrile 18-50 percent, with increase in acrylonitrile resistance to oil, fuel, abrasion and heat increases, higher tensile strength, hardness, gas impermeability.

- Low temperature resistance, resilience, plasticiser compatibility decreases require less sulphur, more accelerators than SBR, highly oil resistant.

Application: Fuel hoses, collapsible containers. Nitrile rubber may be reinforced by phenolic resins and PVC.

- Resistance to ozone, weathering, better gloss, bright colors, high resistance to abrasion and oil.

Process flow diagram of manufacture of Nitrile rubber is given Figure M-VIII

4.2:

POLYISOPRENE

Polyisoprene is one of the most well known natural elastomers derived from the sap of the heavea tree. However, synthetic polyisoprne is made by polymerization of isoprene. Isoprene is recovered from the C5 fraction of naphtha cracker. Isoprene can be also made

Isoprene polymerisation is carried out in an inert hydrocarbon solvent (aliphatic solvents). Basic steps in manufacture of polystyrene are – raw material preparation and purification, polymerisation, catalyst deactivation and removal, solvent recovery, polymer drying. Polymerisation catalysts are either of the coordination (Zeigler) or alkyl lithium types. Coordination catalysts are trialkyl aluminium/titanium tetrachloride. Often polymerisation short stops and anti oxidant is added. The solvent remaining is stripped off.

Poly isoprene has good uncured track, high pure gum tensile strength, high resilience, low hysteresis, good hot tear strength. Tyre market is the major consumer of polyisoprene, a substitute of natural rubber in the tread of truck, aircraft and off the road tyres, for dipped goods, adhesive, extruded thread.

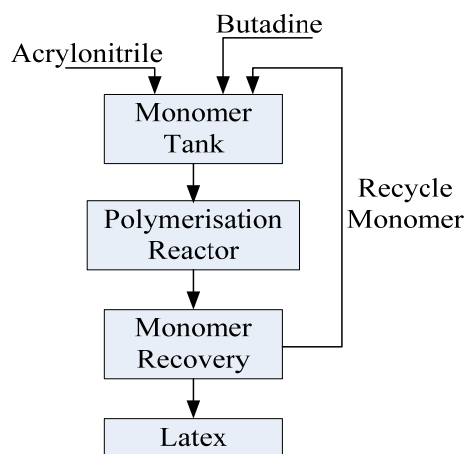


Figure M-VIII 4.2: Process flow diagramme of Acrylonitrile Rubber (Nitrile rubber) Manufacture

NEOPRENE (POLY CHLOROPRENE): [Nadini Chemical journal April 1998, p.21]

Chloroprene is made either via acetylene route or from butadiene. Butadiene process is commonly used.

Acetylene route involves dimerisation of acetylene to monovinyl acetylene followed by reaction of monovinyl acetylene with HCl.

Chloroprene from butadiene involves three steps

- Chlorination of Butadiene: Various steps involved are
- Chlorination of Butadiene- 1,4 dichloro 2-butene and 3,4-dichloro 1-butene
- Isomerisation of 1,4 dichloro 2-butene to 3,4-dichloro 1-butene
- Dehydrochlorination of 3, 4-dichloro 1-butene to chloroprene in presence of caustic soda resulting in formation of chloroprene ($\text{CH}_2\text{CH}=\text{CClCH}_2$)

Polychloroprene is made by emulsion polymerisation process using resin acid soap emulsifier. Polymerisation is carried out at 40 °C in presence of sulphur. Some of the major application of polychloroprene is in adhesives, transportation industry, wire and cable, construction industry, hose and belting.

Uses : Adhesives, transportation industry (Automotive – gaskets, V-belts, shock absorber covers, wire jackets, molded seats, aviation-wire cable, gaskets, seats etc., rail brake hose, track mountings).

CHLORO BUTYL RUBBER

Chlorobutyl rubber is made from isobutylene and 1-3 percent isoprene. Introducing a continuous stream of chlorine gas in a hexane solution of butyl, which is prepared by low temperature copolymerisation of isobutylene, and isoprene in methyl chloride makes Chlorobutyl. Chlorobutyl rubber possesses greater vulcanisation flexibility and tubeless tyres, tyre side wall components, heat resistant truck inner tubes, hose pipes, gaskets, conveyor belts, adhesive, sealants, tyre curing bays, tank lining etc.

SILICON RUBBER (POLYSILOXANES)

Silicon elastomer are made by ring opening reaction caused by action of alkali on monomer acyclic siloxane characterised by exceptional mechanical and electrical performance under extreme temperature condition. Used in aerospace, appliances, electrical industry, construction industry, automotive industry, gaskets sealings, spark plug boots, hose, rubber rolls.

FLURO SILICONE RUBBER (FSR)

FSR is characterized by excellent low temperature flexibility, very good heat resistance, excellent aging characteristics. However, it has poor resistance to aromatic hydrocarbon and common polar solvent.

POLYURETHANE RUBBER

Polyurethane is made by reacting polyisocyanates and polyhydroxyl groups using curing agents. Good abrasion resistance, oil and solvent resistance, oxygen ozone, temperature. Finds wide application in solid tyres for industrial trucks, seals and boots, calendar sheet, potting and sealing of electronic components, general engineering mechanical goods, shoe heels and soles, elastic threads, insulation, mattresses, vibration damping.

ETHYLENE/PROPYLENE RUBBER (EPDM)

EPDM is made by polymerisation of ethylene propylene diene using Ziegler- type catalyst in combination of transition metal halides and metal alkyls. Polymerisation is carried out in a series of two or three vessels. Adding polar material (e.g. water) stops polymerisation. Unpolymerised monomers are recovered and rubber is separated from the solvent by steam flocculation. Rubber floc or crumbs are dewatered and dried. EPDM has outstanding resistance to heat, ozone oxidation, weathering, and aging due to the saturated backbone, low brittle point and glass transition temperature, low density, except aliphatic and naphthenic oils well and maintain acceptable properties at higher filter loading. EPDM are non-tacking, used in single ply roofing, wire and cable installations and automotive parts.

ETHYLENE VINYL ACETATE RUBBER (EVA)

EVA has excellent resistance to heat, ozone and sunlight, moderate resistance to oil and gasoline. It has poor resistance to aromatic and oxygenated solvents, fair process ability.

HYPALON

Hypalon are chlorosulphonated polyethylene and are made by free radical catalysed reaction of chlorinated and SO with polyethylene.

Hypalon is characterised by Ozone resistance, light stability, heat resistance, weather ability, resistance to deterioration by corrosive chemicals and weather ability, resistance to deterioration by corrosive chemicals and good oil resistance, flame resistance, toughness. It finds applications in automotive eat liner coatings, spark plug boots, primary and ignition wire, tarpaulins, hose, conveyor belt, coated fabric.

SPANDEX

Spandex is a polyurethane elastomer which has both urea and urethane linkage and has hard and soft blocks in its repeat structure.

POLYSULPHIDE RUBBER

Polysulphide rubber has out standing resistance to oil, gasoline and solvents, good resistance to weather, ozone and sunlight excellent, impermeability to gases and vapour. It has poor resistance to abrasion, tear, cut growth, low tensile strength.

REFERENCES

1. Chemical Weekly, Jan17,2012
2. Chemistry & Industry 5, August 1996,p. 574
3. file:/A:\Poly(styrene- butadiene-styrene).htm
4. IISRP (2011) TSRC Corporation
5. International Rubber Study Group, 2012
6. Mukhopadhyaya, R., “Recent advances in synthetic rubber and applications”, Chemical industry digest, August 20011
7. Nadini, Chemical Journal, April 1998, p.21
8. Patel, M.M., “Nitrile rubbers”, Chemical engg. Wold vol 24, No12, 1991, p.107