

Polymer Science

Introduction to Fibre Science and Rubber Technology B. Rubber Technology

Natural and Synthetic Rubber

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Natural Rubber

Introduction

The natural rubber (NR) presently used by industry is obtained by tapping the sap known as 'Latex', from the large forest tree *Hevea Brasiliensis*, which occurs in the southern equatorial region of America. By the end of eighteenth century the properties of rubber as obtained from the Hevea tree available at that time entirely in the forest of Amazon valley, were known throughout Europe. The Europeans found that by systematically tapping the tree, the latex can be extracted regularly. With the development of plantation in the Far East, it was found that latex could be preserved by adding ammonia to it immediately after it is collected. This marked the beginning of our commercial latex technology. Presently apart from Brazil, vast plantations are in existence in India, Malaysia, Indonesia, Sri Lanka, Vietnam, Cambodia and Liberia.

Tapping is usually done by shaving about one or two millimeters thickness of bark with each cut, usually in the early morning hours, after which latex flows for several hours and gets collected in cups mounted on each tree. The cut is made with special knife or gouge, sloping from left to right at about 20-30° from the horizontal. The content of each latex cup is transferred to five-gallon containers and transported to storage tanks at bulking station.

The latex may either be concentrated to about 60% dry rubber content (DRC), usually by centrifuging or evaporation, or alternatively coagulated or dried. The two approaches lead to two distinct branches of rubber technology, namely latex technology and dry rubber technology.

Latex Technology

Latex technology is a highly specialized field that is not too familiar to most polymer chemists and even many rubber compounders. The art and science of handling latex problems is more intricate than regular rubber compounding and requires a good background in colloidal systems. While latex differs in physical form from dry rubber, the properties of the latex polymer differ only slightly from its dry rubber counterpart. Unlike the dry rubber, which must be masticated (mechanically sheared) before use, the latex polymer need not be broken down for application, thus retaining its original high molecular weight which results in higher modulus products. Other advantages enjoyed by applications involving latex are, lower machinery costs and lower power consumption, since the latex does not have to be further processed into dry form and compounding materials may be simply stirred into the latex using conventional liquid mixing equipment.

Composition of Rubber Latex

The natural product, which is exuded as a milky liquid by the Hevea tree, is a colloidal solution of rubber particles in water; the particle diameters range between 0.05 μ and 5 μ. It is a cytoplasmic system containing rubber and non-rubber particles dispersed in aqueous serum phase.

Freshly tapped Hevea latex has a pH of 6.5 to 7.1 and density 0.98 g/cm³. The total solids of fresh field latex vary typically from 30 to 40 wt % depending on clone, weather, stimulation, age of the tree, method of tapping, tapping frequency and other factors. The dry rubber content is primarily cis-1,4,- poly isoprene, $-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-$



The non-rubber portion is made up of various substances such as sugars, proteins, lipids, amino acids and soluble salts of calcium, magnesium, potassium and copper. The solid phase typically contains 96% rubber hydrocarbon, 1 wt % protein and 3 wt % lipids with traces of metal salts.

Stabilization of Rubber Latex

Though fresh rubber latex is nearly neutral and the rubber particles are stabilized by an adsorbed layer of protein and phospholipids, but on exposure to air the latex rapidly develops acidity and within 12 to 24 hours spontaneous coagulation sets in (at an approximate pH of 5). The latex has therefore, to be preserved immediately after collection against rise in acidity by bacterial putrefaction. As already mentioned, ammonia has long been used as preservative of latex owing to certain advantages including the ease of its removal by blowing air or reaction with formaldehyde. Other preservatives such as sodium pentachlorophenate, sodium salt of ethylene diamine tetraacetic acid, boric acid or zinc alkyl dithiocarbamates, may be used with smaller amount of ammonia. This is known as low ammonia latex and has the advantages of lower cost and elimination of the need to deammoniate the latex before processing into products.

Concentration of Rubber Latex

The ammonia preserved field latex which is known as normal (un-concentrated) latex is not suitable for commercial use as it contains considerable amount of non-rubber constituents which are detrimental to the quality of products and also contains too much water which is costly for transportation. The latex is, therefore, concentrated to about 60% rubber solids before leaving the plantation. This concentration process is carried out either by centrifuging, creaming, electrodecantation or evaporation.

The first two processes make use of increasing the gravitational force of the rubber particles, by applying centrifugal force on the former or by adding a creaming agent like sodium alginate, gum tragacanth etc. in the latter process. Both these processes of concentration result in a decrease of non-rubber content, the centrifuging process being superior in this respect.

The concentrated latex obtained by electrodecantation process which utilizes the negative charge on the tiny rubber particles, is similar in composition to the centrifuged latex; however cost economics does not favour this process to be exploited on commercial scale.

The evaporated latex contains all the non-rubber constituents present in the original normal latex. It contains a small amount of ammonia. Because of its high stability, evaporated latex is useful in compounding heavily loaded mixes, hydraulic cement etc.

The centrifuged latex is most widely used in industry. Latex concentrate constitutes slightly more than 8% of the global natural rubber supply, and about 90% of this is centrifuge concentrated. The term 'latex' mentioned anywhere in this text now onwards will mean the ammonia preserved centrifuged latex. Principal outlets for natural rubber latex are foam rubber, dipped goods and adhesives.

Latex Compounding

In latex technology, concentrated latex is first blended with the various additives as required for different applications. The blending of different additives is known as latex compounding. Latex compounding involves not only the addition of the proper chemicals to

obtain optimum physical properties in the finished product but also the proper control of colloidal properties which enable the latex to be transformed from the liquid state into finished product.

Viscosity control in the latex is very important. The particle size of the latex has a great effect on viscosity. Large particles generally result in low viscosity. Dilution with water is the most common way to reduce viscosity. Certain chemicals such as trisodium phosphate, sodium dinaphthyl methane disulfonate are effective viscosity reducers.

Thickening Agents

Thickening may be accomplished with either colloidal or solution thickeners. Small particle size materials such as colloidal silica will thicken latex when added to it. Solutions of such materials as alpha protein, starch, glue, gelatin, casein, sodium polyacrylates and poly (vinyl methyl ether) will also thicken latex.

Wetting Agents

Sometimes the addition of a wetting agent to latex mix is necessary for successful impregnation of fabric or fibres with latex. Sulfonated oils have been found to be effective in assisting complete penetration between textile fibres without any danger of destabilizing the latex.

Vulcanizing Agents

Curing or vulcanization, which involves the chemical reaction of the rubber with sulphur in presence of an activator (such as zinc oxide) and accelerator, manifests itself in an increase in strength and elasticity of the rubber and an enhancement of its resistance to ageing. Vulcanization of latex may be effected by either of the two ways; i) The rubber may be vulcanized after it has been shaped and dried, or ii) The latex may be completely vulcanized in the fluid state so that it deposits elastic films of vulcanized rubber on drying. The latter process, however, does not yield products of high quality and is resorted to only in the production of cheaper articles, e.g. toy balloons.

The problem of scorching or premature vulcanization is rarely encountered in practical latex work and hence ultra accelerators such as zinc diethyl dithiocarbamate (ZDC) alone or in combination with zinc salts of mercaptobenzothiazole (ZMBT), tetramethyl thiuram disulphide (TMTD), polyamines and guanidines are used. The latter two also function as gel sensitizers, or secondary gelling agents, in the preparation of foam rubber. The doses of the vulcanizing ingredients are adjusted according to the requirements of the end products. Thus only small amount of sulphur and accelerator (0.5-1.0 phr) with little or no zinc oxide are required in the production of the transparent articles, whereas in case of latex foams the doses are quite high.

Antioxidants

Because of the great surface area exposure of most latex products, protection against oxidation is very important. Many applications involve light colored products, which must not darken with age or on exposure to light. Non-staining antioxidants such as hindered phenols (styrenated phenols) must be used. Where staining can be tolerated, amine derivatives such as phenylene diamines, phenyl beta-naphthylamine, ketone-amine condensates may be used. These have good heat stability and are also effective against copper contamination, which cause rapid degradation of rubber.

Fillers

Fillers may be added to latex to reduce the cost of rubber articles, to prevent spreading mixes leaking through the fabric, to increase the viscosity of the compound or to modify the properties of the rubber. Most of the non black fillers such as china clay, mica powder, whiting (calcium carbonate), Lithopone, Blanc Fixe (barium sulphate) may be used in latex compounds. Carbon black does not reinforce latex in the manner that it does dry rubber, and is used only in small amounts in latex for color, as are various other dyes and pigments.

Softeners

In applications like toy balloons, softeners are added to soften them so that they may be easily inflated. Softening agents in general used are liquid paraffin, paraffin wax and stearic acid.

Dispersing Agents

The particle size of solid materials added to latex must usually be made as small as possible to ensure intimate contact with the rubber particles. Solid materials are usually added to latex as dispersion. The material to be added is mixed with dispersing agents in deionized water and ground to a small particle size in a ball mill or attritor. In these devices stones or other hard pebble-sized materials are made to tumble and mix with chemicals reducing them to very small size.

The selection and amount of dispersing agent is determined by the physical properties of the material to be dispersed. The functions of these agents are to wet the powder, to prevent or reduce frothing and to obviate re-aggregation of the particles. The concentration of dispersing agents rarely exceeds 2% except in special circumstances. None of the common materials such as gelatin, casein, glue or soap such as ammonium oleate possesses all the requisite properties and hence it is necessary to use mixtures of two or more of them. When putrefiable dispersing agents such as casein, glue and gelatin are used, a small amount of bactericide, such as 0.01% sodium trichlorophenate may be added.

Non putrifiable proprietary dispersing agents such as Dipersol F conc. of Indian Explosives Ltd. based on sodium salt of methylenebis [naphthalenesulfonic acid] are also available which are highly efficient dispersing agents with little foaming tendency during milling. Time, equipment and labour can often be saved by dispersing together (in the correct proportion) all the water insoluble ingredients required for a particular compound including sulphur, zinc oxide, accelerator, antioxidant, color and fillers. Mixed dispersion having excellent storage stability against reaggregation and settling can be prepared by using the following formula and method:

Mixed total solids	-	100 parts
Dispersal F conc.	-	4 parts
Deionized water	-	96 parts

The mixed ingredients are dispersed by ball milling for at least 48 hours.

Emulsifying Agents

As in the case of dispersions, deionized water should also be used for the preparation of emulsion of water immiscible liquids to be used in latex compounds. An emulsion is defined as a system in which a liquid is colloiddally dispersed in another liquid. The emulsions use in for latex should be the 'oil-in-water' type in which water is the continuous phase.

Simple equipment for the preparation of emulsion consists of a tank and a high-speed stirrer. Very fine and stable emulsions can be prepared by using a homogenizer. In a homogenizer, the liquid mixed with the required amount of water and emulsifying agent is forced through fine orifice under high pressure (1000-5000 psi); the liquid mix is thus subjected to a high shearing force which breaks down the particles to the required size.

Various synthetic emulsifying agents are available in the market, but for use with latex, soaps have been found to be quite satisfactory. For getting a satisfactory emulsion, the soap is produced in situ during mixing of the components. In this method, the cationic part of the soap (ammonia, KOH or amine) is dissolved in water and the anionic part (oleic, stearic or rosin acid) is dissolved in the liquid to be emulsified. Soap forms when these solutions are mixed. A method of preparation of a typical 50% emulsion of liquid paraffin is given below:

Liquid paraffin	-	50.0 parts
Oleic acid	-	2.5 parts
Concentrated ammonia solution	-	2.5 parts
Deionized water	-	45.0 parts

The oleic acid is mixed with liquid paraffin and the mixture is added to the water containing concentrated ammonia solution. The two phases are mixed by agitation and a stable emulsion is obtained by passing through a homogenizer.

Stabilizers

The stabilizing system naturally occurring in ammonia preserved latex is adequate to cope with the conditions normally encountered during concentration, transportation and distribution but fails to withstand the more severe conditions met with during compounding and processing, when additional stability must be ensured by the addition of more powerful agents.

Some degree of stabilization may be attained by adding simple materials such as soap and proteins (e.g. casein). Casein is liable to putrefy and impart to latex a high initial viscosity, which may yield products having inferior physical properties. Soaps are convenient to use but their behaviour is not always predictable and they have limited applications. Synthetic stabilizers are now available which are free from the limitations associated with soaps and proteins.

An anionic surface-active agent such as sodium salt of cetyl / oleyl sulphate when present in sufficient quantity, stabilizes latex against heat, fillers and mechanical working. It has no thickening action on latex compounds, does not alter the rate of cure and has no adverse effect on the vulcanizate. It is most effective in alkaline medium and loses its activity in presence of acids and polyvalent ions. It is, therefore, most suitable for the coagulant dipping process. Its efficiency remains unaffected by the increase in temperature.

A non ionic surface active agent such as an ethylene oxide condensate possesses remarkable stabilizing power to protect latex compounds against the effects of mechanical action, acids, polyvalent salts etc. It differs from anionic stabilizers in its method of functioning. It increases the hydration of the stabilizer film at the rubber/water interface and has little or no effect on the charge. Because of the high chemical stability, its use is not recommended in acid coagulant dipping process. However, it loses its activity at elevated temperature and this property is utilized in heat-sensitive compounds. It affords excellent protection to such compounds during storage at room temperature, but on heating it loses this power and gelling (or setting) of rubber particles takes place.

Compounding Criteria

During compounding, it is essential to avoid the addition of any material liable to cause coagulation. As already discussed, the latex compound should be properly stabilized. In general, the addition of water-soluble organic liquids, salts of polyvalent metals and acidic materials are to be avoided. Water-insoluble liquids and solids must be added as emulsions and dispersions respectively, in which the size of the individual particle is of the same order as that of the rubber particles in the latex. Care should be taken to avoid the use of hard water at any stage of latex compounding as it has a destabilizing action on latex.

The containers for the latex may be made from stone, enamelled iron, stainless steel, and wood lined with rubber or gutta-percha. It is preferably thermostatically controlled against changes in atmospheric temperature and is fitted with water jacket. It is equipped with a mechanical stirrer. During the addition of the compounding ingredients, the mix should be stirred slowly but thoroughly. Slow stirring of the latex mix assists in the removal of bubbles and minimizes the formation of a skin, which arises from evaporation of water in the latex. It is important to avoid contact between the stirrer and the container, since latex is readily coagulated by friction.

Processing of Latex Compound

After a suitable latex compound has been prepared, the next step is to get the shape of the article to be made, set the shape and then vulcanize. The different latex processes classified according to the method of shaping are: i) Dipping ii) Casting and Moulding iii) Spreading iv) Spraying v) Foaming

(i). Dipping: A variety of thin rubber articles e.g. toy balloon, teats, gloves etc. can be prepared from latex by dipping process. The process consists essentially of dipping a former in the shape of the article to be made into the compounded latex. The formers may be made from a variety of materials, including metal, glass, lacquered wood and porcelain. The deposited film is dried, vulcanized in circulating hot air, steam or hot water and then stripped from the former. This is known as 'straight' dipping as against coagulant dipping where the former is first coated by dipping into a chemical coagulating agent. The coagulants may be either salt coagulants or acid coagulants. A typical dipping compound suitable for balloons, gloves etc is given in Table 1.

(ii)Casting and Moulding: Casting involves the use of a mould on the inside walls of which the rubber article is formed, the pattern on the inside of the mould determining the ultimate shape of the article. The basic principle of latex casting is to 'set' the compound in the mould followed by subsequent drying, removal from the mould and vulcanizing. Depending on the technique of 'setting' (gelling) inside the mould, two types of moulds are used: i)Plaster of Paris moulds, and ii) Metal moulds. Gelation in plaster mould is brought about by partial absorption of water by the mould material and in a metal mould by using a heat-sensitizing agent.

Both solid and hollow articles can be produced by the process of casting. In the preparation of the solid articles the entire rubber latex content of the mould is gelled and subsequently dried. Non-porous metal moulds are used both for hollow and solid articles whereas the porous plaster moulds are generally used for hollow articles. Hollow articles are produced by forming the required thickness on the inside wall of the mould. With a well-formulated compound, satisfactory wall thickness can be built up in about 5-10 minutes. The plaster mould, together with its deposited latex, is then placed in an oven at 40°-60°C for several hours. When the deposit is consolidated and partially dry, the mould is removed from the oven, allowed to cool and the article is carefully removed. It is then washed, dried and cured

for 30 minutes at 100°C in air. A general formulation of latex compound suitable for casting in plaster of Paris moulds is given in Table 1.

Table 1: Typical formulation of latex compounds for different applications

Ingredients	Dipping Compound (Parts by wt.)	Casting Compound (Part by wt.)	Carpet Backing Compound (Parts by wt.)	Spraying Compound (Parts by wt.)	Foam Compound (Parts by wt.)
60% Centrifuged Latex	167.0	167.0	167.0	167.0	167.0
20% Non ionic stabilizer Solution	1.0	-	-	-	-
20% Anionic Surface active agent	-	3.0	25.0	6.0	-
20% KOH Solution	-	-	1.5	1.0	-
20% Potassium oleate soap solution	-	-	-	-	5.0
50% ZDC dispersion	2.0	2.0	2.0	2.5	2.0
50% Sulphur dispersion	2.0	3.0	3.0	5.0	4.0
40% Zinc oxide dispersion	0.5	4.0	7.5	7.5	10.0
50% ZMBT dispersion	-	-	-	-	2.0
50% Phenolic antioxidant Emulsion	0.5	2.0	2.0	2.0	2.0
20% Ketone-amine Antioxidant dispersion	-	-	-	5.0	2.5
40% DPG dispersion	-	-	-	-	0.6
Sulphonated oil wetting agent	-	-	-	0.75	-
50% Liquid Paraffin Emulsion	3.0	-	-	-	-
50% Filler (China clay) dispersion	-	18.0	150.0	-	20.0
20% Pigment dispersion	-	5.0	As required	-	-
20% Sodium Silicofluoride dispersion	-	-	-	-	5.0
Fast Colour	-	-	-	-	As required
Deionized Water (To adjust viscosity)	As required	As required	As required	As required	As required
Cure	20 mins, 110°C hot air	30 mins, 100°C hot air	100°-120°C hot air	100°-120°C hot air	100°C, Steam

(iii) Spreading: Spreading of latex is used in the manufacture of proofed fabrics, which consists of applying a suitable latex compound on the fabric with the help of a Doctor's Knife. This process has found wide application in the backing of tufted carpets in which the loosely woven piles of wool or jute fibres must be anchored strongly to the base by using a suitable compound. A compound found satisfactory in carpet backing application is given in Table 1.

(iv) Spraying: The adhesive property of latex has been utilized in the spraying process for bonding paper, cloth, leather, fibre etc. Spraying of latex is now days largely used in the manufacture of cushions and mattresses from latex treated coir. Coconut fibres can be bonded by spraying a suitable latex compound to yield latex treated coir, which is a cheap but useful as upholstery material. The process consists of spraying the loose fibres with the latex compound, drying the product, compressing the dried mass in a mould to obtain a desired shape and curing it in an air oven for the permanence of shape. A typical formulation of a latex compound suitable for spraying is given in Table 1.

(v) Foaming: The production of latex foam for mattresses and upholstery is the most important of all the latex processes. Latex foam is a flexible cellular material containing many cells (either open, closed or both) distributed throughout the mass. There are currently two methods of producing latex foam: the Dunlop process and the Talalay process.

In the Dunlop process, sodium silicofluoride is used as the gelling agent. The latex compound is mechanically beaten and / or air blown through it to foam. Then the requisite amount of a dispersion of sodium silicofluoride is added, which in presence of zinc oxide sets the foam into gel in a mould (usually made of aluminium) in which it is poured. The gelled foam is then vulcanized in steam, stripped from the mould, washed and dried. In the compound a secondary gelling agent, Diphenyl guanidine (DPG), is added to reduce the gelling time so that no premature foam collapse may occur. A typical formulation of latex foam is given in Table 1.

In the Talalay process, partially foamed latex is poured into a mould which is sealed and vacuum is applied so that the foam expands to fill the mould completely. The foam is then frozen by cooling the mould to -35°C . Carbon dioxide is then admitted which penetrates the structure and owing to the pH change, causes gelling. The final stage is heating of the mould to vulcanizing temperature to complete the cure. In spite of the high capital cost, this process is currently used because of the excellent quality of the product and the low rejection rate.

Dry Rubber Technology

A variety of coagulation methods are available to prepare the rubber for dry rubber technology processes. Since the properties of the rubber are affected by trace ingredients and by the coagulating agents used, rubbers of different properties are obtained by using the different methods. The major types of raw rubbers are:

(i) Ribbed Smoke Sheet (RSS): It is the sheet of coagulum obtained by vertically inserting aluminum partitions into the coagulation tanks containing the latex and the coagulation is effected by adding acetic acid. The sheet is then passed through a series of mill rolls, the last pair of which are ribbed, giving the surface of rubber a diamond pattern, which shortens the drying time of rubber. The sheet is then dried slowly in a 'smoke house' at a temperature gradient of 43°C - 60°C for about four days. The rubber is dark in color.

(ii) Pale Crepe: This is a premium grade of rubber, for use where lightness of color is important as in white side walls of tires, surgical goods etc. For pale crepe high quality of latex is used and the lightest colors are obtained by removing a colored impurity, β -carotene, by a two stage coagulation process, followed by bleaching the latex with xylyl mercaptan and adding sodium bisulphite to inhibit an enzyme catalyzed darkening process. The coagulum is machined eight or nine times between grooved differential-speed rollers with liberal washing.

(iii) Comminuted and other 'new process' rubbers: In these cases the coagulum is broken up and then dried. The rubber is then packed in flat bales similar in size to those used for major synthetic rubbers (70-75 lbs) unlike the heavier square bales used with smoke sheet and crepe rubbers.

Properties of raw natural rubber

The better types and grades of natural rubber contain at least 90% of the hydrocarbon cis-1,4 polyisoprene, in admixture with naturally occurring resins, proteins, sugars etc. The raw material of commerce (sheet, crepe etc) comprises a molecular weight mainly in the range of 5,00,000 to 10,00,000 which is very high for its processing.

Hence rubber has to be extensively masticated on a mill or in an internal mixer to break down the molecule to a size that enables them to flow without undue difficulty when processing by extrusion or other shaping operations. The break down occurs more rapidly at either high (120°-140°C) or moderately low (30°-50°C) temperature than it does at temperatures around 100°C. It is now recognized that breakdown at the more elevated temperatures is due to oxidative scission and that at low temperatures due to mechanical ruptures of primary bonds; the free radicals thus produced get stabilized by addition of oxygen.

Because of its highly regular structure, natural rubber is capable of crystallization, which is substantially increased by stretching of the rubber causing molecular alignment. This crystallization has a reinforcing effect giving strong gum stock (unfilled) vulcanizates. It also has a marked influence on many other mechanical properties.

The outstanding strength of natural rubber has maintained its position as the preferred material in many engineering applications. It has a long fatigue life, good creep and stress relaxation resistance and is low cost. Other than for thin sections, it can be used to approximately 100°C and sometimes above. It can maintain flexibility down to -60°C if compounded for the purpose. The low 'hysteresis' (heat generation under dynamic condition) and its natural tack make natural rubber ideal for use in tire building. Its chief disadvantage is its poor oil resistance and its lack of resistance to oxygen and ozone, although these latter disadvantages can be ameliorated by chemical protection. Natural rubber is generally vulcanized using accelerated sulphur system. Peroxides are also occasionally used, particularly where freedom from staining by metals such as copper is important.

Natural rubber is mainly used in passenger tires, primarily for carcasses and white side walls, the remainder of the tire usage is in racing cars, airplanes, heavy duty trucks and buses, tractors and farm vehicles. Besides, it is used in footwear soles, industrial products such as pump coupling, rail pads, bridge bearings, conveyor belts (cover and friction), hoses etc. Some typical NR formulations for use in tire and other industrial products are given in Table 2.

Table 2: Typical NR formulations for use in tire and other industrial products

Ingredient	Truck Trade (normal)	Truck Carcass	Conveyor Belt Cover	Bridge Bearings	Rail Pads
Natural Rubber	100	100	100	100	100
Process Oil	-	-	4	2	3
Pine tar	-	3	-	-	-
Stearic Acid	2.5	2	2	1	2
Zinc Oxide	3.5	5	5	10	5
Antioxidant	2	2	2	1	1
Antiozonant	-	-	-	4	-
ISAF Black	50	-	-	-	-
HAF Black	-	-	45	-	-
FEF Black	-	10	-	-	-
MT Black	-	-	-	35	60
SRF Black	-	15	-	35	-
China Clay	-	-	-	-	20
Paraffin Wax	-	-	1	-	1
Accelerator (CBS)	0.8	0.5	0.5	0.7	1
Sulphur	2	2.5	2.5	2.5	2.5
Cure	15 min @ 158°C	25 min @ 153°C	20 min @ 153°C	20 min @ 140°C	15 min @ 153°C
Tensile strength, psi	4200	3800	4575	3050	2880
% Elongation	620	600	575	520	540
300% Modulus, Psi	1440	900	1650	480	510
Shore-A Hardness	59	50	60	60	66
Crescent Tear, lb/in	650	350	600	-	-

Synthetic Rubber

Introduction

Prior to World War II, developments were being actively pursued in Germany in the production of a polymer as a replacement for the natural rubber i.e. for general-purpose application. Through commercial contacts between German and American manufacturers, much detail of these materials and their manufacture was known in the USA. Hence as a wartime necessity to make up for the deficiency of natural rubber supplies to the allies, large-scale manufacture of the styrene-butadiene polymers with a 25% styrene and 75% butadiene content in USA began.

Since then a series of synthetic elastomers, both general purpose and special purpose came into market. Special purpose rubbers are those produced in much smaller quantities and having a different degree of oil and solvent resistance and / or heat resistance from those in

the general-purpose class, which are produced in large quantities to supplement and replace natural rubber with which they are comparable in non-oil-resistant properties. Initially developed special purpose rubbers are neoprene and acrylonitrile-butadiene rubbers, which remain the workhorses because of their cost and their oil resistance. The market for neoprene rubbers has been much widened by the exploitation of their excellent resistance to ozone and weather, and by their use in fire-resistant application such as cable sheathing and conveyor belting for mines. The largest outlets for nitrile rubbers are in the engineering industries for oil seals, O-rings, gaskets and fuel & oil hoses. Later on chlorosulphonated polyethylene rubbers were developed and established for applications where solvent, chemical, ozone and weathering resistance are required.

Fluorocarbon rubbers, with inferior low temperature properties to the nitrile rubber but superior oil and heat resistance, represent improvements, which have been acceptable in the aircraft and automobile industries. The high price of fluorocarbon rubber and silicone rubbers restricts their widespread use even though silicone rubbers are unique in their wide range of service temperature.

Polyurethane rubbers possess certain outstanding properties. They can have higher tensile strengths than any other rubber, excellent tear and abrasion resistance, and outstanding resistance to ozone, oxygen and aliphatic hydrocarbons.

The thermoplastic elastomers are a unique new class of polymers in which the end use properties of vulcanized elastomers are combined with the processing advantages of thermoplastics. These polymers yield useful articles having true elastomeric properties without compounding or vulcanization.

Hence, it is apparent that rubber compounders have now a wide spectrum of elastomers to choose from, to meet one or more of the requirements for specific end use.

Styrene – Butadiene Rubber (SBR)

SBR is the highest volume and most important general-purpose synthetic rubber in the entire world. Although it was of poor quality in many respects to natural rubber, it has achieved a high market penetration on account of three factors:

- Its low cost
- Its suitability for passenger car tires, particularly because of its good abrasion resistance
- A higher level of product uniformity than that can be achieved with natural rubber.

Composition and Structure: SBR is a copolymer of styrene ($\text{CH}_2 = \text{CH} - \text{C}_6\text{H}_5$) and 1,3-butadiene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$). With the exception of some special grades, typically the styrene content is 23.5% by weight, which corresponds to one styrene to six or seven butadiene molecules per chain. The monomers are randomly arranged in the chain.

Manufacture: SBR can be produced either by emulsion polymerization or by solution polymerization technique.

Emulsion SBR: The monomers, styrene and butadiene taken in the weight ratio of about 1:3, are emulsified in deionized water using soap as emulsifier. The polymerization reaction is carried out at about 50°C ('hot' SBR grades) or at about 4°C ('cold' SBR grade). The chain reaction is initiated by decomposition of peroxide or a peroxy disulfate into free radicals in

case of hot SBR and by a hydroperoxide/ferrous sulphate redox system in case of cold SBR. Dodecyl mercaptan is used as a chain transfer agent or modifier to control the toughness of the product which otherwise may limit its processibility. Typical formulations of hot and cold SBR are given in Table 3.

Table 3: Typical formulations of hot and cold SBR

Ingredient	Hot SBR	Cold SBR
Butadiene	75.0	72.0
Styrene	25.0	28.0
Dodecyl Mercaptan	0.5	0.2
Potassium peroxydisulfate	0.3	-
Diisopropyl benzene hydroperoxide	-	0.08
Ferrous sulphate ($\text{FeSO}_4, 7\text{H}_2\text{O}$)	-	0.14
Potassium pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7$)	-	0.18
Soap Flakes	5.0	-
Rosin Acid Soap	-	4.0
Deionized Water	180.0	180.0

In hot SBR, polymerization is stopped at 70-75% conversion by adding a short stop (0.1 part hydroquinone) whereas in case of cold SBR, it is stopped at 60% conversion to control its molecular weight. After the addition of an antioxidant (1.25 parts of N-phenyl β -naphthylamine), the latex is coagulated by the addition of brine and dilute sulphuric acid. The coagulated crumb is washed, dried and baled for shipment.

The cold SBR has a more linear molecular structure and imparts vulcanizates much improved properties than hot SBR. Other improvements directed towards specific end uses include:

- The development of oil extended SBR in which a rubbery polymer of very high molecular weight is blended with substantial amounts of hydrocarbon oil. This provides a lower cost alternative to a polymer of conventional average molecular weight.
- Preparation of carbon black master batches of regular and oil extended cold SBR. These are of interest to rubber manufacturers having limited mixing capability and those who wish to avoid handling of loose black in factory.

Solution SBR: Several solution SBRs are offered commercially. The random copolymers are rubbery and like emulsion SBR but with several improved properties. The random products have narrower molecular weight distribution, less chain branching, higher cis content, lighter color and less non-rubber constituents than the emulsion SBRs. As a result, they are reported to have better abrasion resistance, better flex, higher resilience and lower heat build-up than the emulsion rubber; tensile, modulus, elongation and cost are comparable.

Polymerization of styrene and butadiene is usually carried out with an alkyl lithium type catalyst in a non-polar solvent. In general, continuous reactor system is used. As the polymerized solution (cement) leaves the last reactor, stopper and stabilizer are added. The cement is steam stripped to get rubber crumb and to recover the solvent; un-reacted monomers are recycled. The rubber crumb is dried on tray or extruder drier.

Properties: Like NR, SBR is an unsaturated hydrocarbon polymer. Hence un-vulcanized compound will dissolve in most hydrocarbon solvents whilst vulcanized stocks will swell extensively. A major difference between SBR and natural rubber is that SBR does not break down to a great extent on mastication. SBR is supplied at a viscosity considered to provide the balance of good filler dispersibility and easy flow in processing equipment. The processing behaviour of SBR, however, is not as good as natural rubber in many other respects. Mill mixing is generally more difficult; it has lower green strength (i.e. inferior mechanical properties in the un-vulcanized state) and does not exhibit the natural tack, which is essential in plying together or otherwise assembling pieces of unvulcanized rubber.

Whereas natural rubber is crystalline with a T_m of about 50°C, SBR is amorphous due to its molecular irregularity. Natural rubber crystallizes on extension at ambient temperatures to give a good tensile strength even with gum stocks. Gum vulcanizates of SBR on the other hand are weak and it is essential to use reinforcing fillers such as fine carbon blacks to obtain products of high strength. Black reinforced SBR compounds exhibit very good abrasion resistance, superior to corresponding black reinforced NR vulcanizates at temperatures about 14°C. Against this however, the SBR vulcanizates have lower resilience, fatigue resistance and resistance to tearing and cut growth. With their lower un-saturation, SBR also has better heat resistance and better heat ageing qualities. SBR extrusions are smoother and maintain their form better than those of NR.

Compounding: For many uses, blends of SBR and other rubber such as NR or cis-polybutadiene are made. Compounding recipes should be proportioned to balance the requirements for each type of rubber used. All types of SBR use the same basic compounding recipes, as do other un-saturated hydrocarbon polymers. They need sulphur, accelerators, antioxidants (and antiozonants), activators, fillers, and softeners or extenders. SBR requires less sulphur than NR for curing, the usual range being 1.5-2.0 phr. of sulphur based on rubber hydrocarbon. All styrene-butadiene rubbers because of their lower unsaturation, are slower curing than natural rubber and require more acceleration. Zinc stearate (or zinc oxide plus stearic acid) is the most common activator for SBR. Recipes may also contain plasticizers, tackifiers, softeners, waxes, reclaim etc.

Processing of SBR compounds is similar to that of natural (or other) rubber. The ingredients are mixed in internal mixers or on mills, and may then be extruded, calendered, molded and cured in conventional equipment. In general, the rubber, zinc oxide, antioxidant and stearic acid are mixed; then carbon black is added in portions, with the softener or oil. This may be considered as masterbatch. It may be desirable at this point to dump, sheet out and cool the

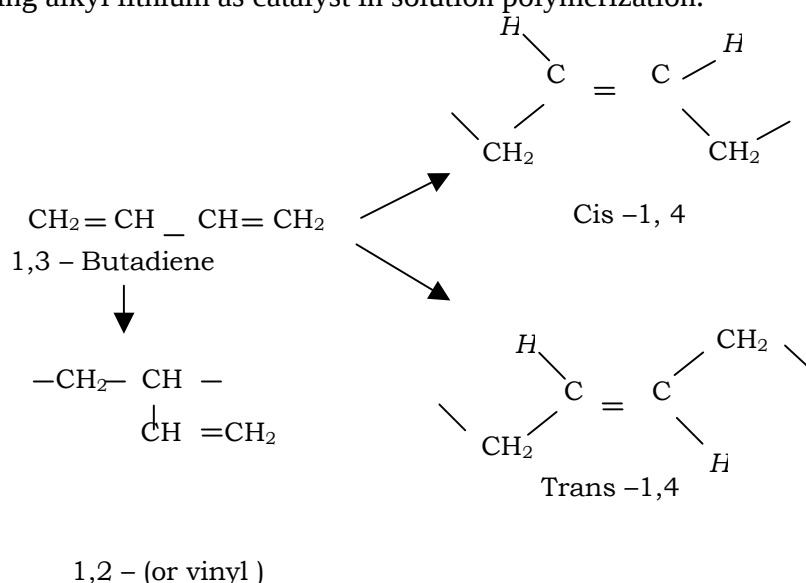
batch. In the second phase, all the ingredients are mixed, with sulphur and accelerator being added last and mixing is continued till sulphur is well dispersed.

Applications: While passenger tires and tire products account for the major portion of SBR consumption, a wide variety of other products are also fabricated from this rubber where its low cost coupled with adequate physical properties lead to its preference over more expensive materials, particularly natural rubber. SBR finds uses in mechanical goods, footwear, belting, hose, tubing, wires and cables, adhesives, latex goods etc.

Polybutadiene

Polybutadiene was first prepared during World War I by metallic sodium catalyzed polymerization of butadiene as a substitute for natural rubber. However, polymer prepared by this method and later by free radical emulsion polymerization technique did not possess the desirable properties for its applications as a useful rubber. With the development of the Ziegler- Natta catalyst systems in the 1950s, it was possible to produce polymers with a controlled stereo regularity, some of which had useful properties as elastomers.

One distinguishing feature of polybutadiene is its microstructure, i.e. the ratio of cis, trans and vinyl configuration. Polymers containing 90-98% of a cis-1,4 structure can be produced by solution polymerization using Zeigler- Natta catalyst systems based on titanium, cobalt or nickel compounds in conjunction with reducing agents such as aluminum alkyls or alkyl halides. Useful rubbers many also be obtained from medium – cis- polybutadiene (44% cis content) using alkyl lithium as catalyst in solution polymerization.



Today commercial polybutadienes are made exclusively by solution polymerization processes employing organometallic catalysts capable of controlled microstructure, molecular weight distribution and branching. Solution polymers are characterized by fairly narrow molecular weight distribution and less branching than emulsion butadiene, which account for some of the major differences in processing and performance.

Manufacture: A polybutadine with high cis content is obtained by using a titanium catalyst containing iodine, e.g., the combinations of trialkyl aluminium compound such as tri-isobutyl aluminium and titanium tetraiodide, or an alkylaluminium, iodine and titanium tetrachloride. Aromatic and aliphatic solvents can be used for high cis-1,4 polymer at 0°-70°C. A typical

polymerization recipe yielding 90% in 2 hours at 50°C is, benzene 85 ml; butadiene 15 ml; (i-C₄H₉)₃ Al 50 mg and TiI₄ 25 mg. The catalyst composition greatly influences activity.

Use of organolithium compounds such as butyl lithium in heptane, produces butadiene polymers in a reproducible manner because of their solubility in hydrocarbon and thermal stability. Alkyl lithium initiation takes place in a homogeneous reaction mixture with a complete absence of termination and other side reactions, thereby giving 'living polymers'. This fact, along with the ability to propagate other monomers and the ability of polar solvents to modify the reactivity and microstructure of polybutadiene, allows a great deal of flexibility that is not offered by free radical, coordination or cationic mechanisms.

Properties: The structure of cis-1,4 polybutadiene is very similar to that of the natural rubber molecule. Both the polymers are unsaturated hydrocarbons but, whereas with natural rubber molecule the double bond is activated by the presence of a methyl group, the polybutadiene molecule, which contains no such group, is generally somewhat less reactive. Further more, since the methyl side group tends to stiffen the polymer chain, the glass transition temperature of polybutadiene (-70° to -100°C) is consequently less than that of natural rubber molecule. This lower T_g has a number of ramifications on the properties of polybutadiene. For example, at room temperature, polybutadiene compounds generally have higher resilience than similar natural rubber compounds. In turn this means that the polybutadiene rubbers have a lower heat build-up and this is important in tire application. On the other hand, these rubbers have poor tear resistance, poor tack and poor tensile strength. For this reason, polybutadiene rubbers are seldom used on their own but more commonly in conjunction with other elastomers. For example, they are blended with natural rubber in the manufacture of truck tires and, widely with SBR in the manufacture of passenger car tires. Their use also improves tread wear.

Processing : Most polybutadiene rubbers possess inherently high resistance in breakdown and poor mill banding characteristics. At temperature below 100° to 110°F the rubber is continuous on the mill rolls, glossy and smooth in appearance, and bands tightly. As the temperature of the stock is increased, the band becomes rough & loose on the mill and loses cohesion so that the milling is poor. It normally displays very little breakdown as a result of intensive mixing. However, polybutadiene can be broken down with certain peptizers such as modified zinc salt of pentachlorothiophenol and diortho-benzamidophenyl disulfide to obtain some improvement in processing.

Blends of cis-polybutadiene and natural rubber were made initially as a means of obtaining improved processing characteristics. It was then noted that polybutadiene rubber conferred many of its desirable properties such as a high tolerance for extender oil, excellent abrasion resistance and outstanding hysteresis properties to the blends, e.g. blends of polybutadiene rubber with clear and oil extended SBR or oil black masterbatch are easily prepared with high tolerance for carbon black and oil levels.

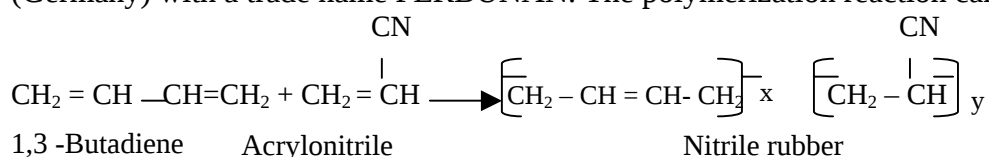
Polybutadiene rubbers are usually vulcanized with sulphur and accelerator whether used alone or in blends. Polybutadiene- natural rubber blends having a useful balance of physical properties can be obtained with a wide range in sulphur levels (1.0 to 2.5 phr) and appropriate accelerator levels (0.6-1.2 phr) to get the best balance in properties.

Applications: Polybutadiene rubber has been primarily used both in passenger and heavy duty trucks tires as blends with natural rubber and SBR taking advantages of its inherently good hysteresis properties, abrasion resistance and crack growth resistance.

Significant amount of polybutadiene is used in footwear and belting compounds as a means of improving abrasion and durability. The outstanding resilience or abrasion resistance of the polymer has been utilized in the manufacture of solid golf balls and high rebound toy balls and shock absorber. Polybutadiene as well as butadiene – styrene rubbers are used extensively as modifier of styrene to make high impact polystyrene.

Nitrile Rubber (NBR)

In the course of work on the copolymerization of 1,3 - butadiene with mono-olefins, Konrad and co-workers (1930) obtained a synthetic rubber based on butadiene and acrylonitrile which when vulcanized had excellent resistance to oil and petrol classifying it as a special purpose rubber. Pilot plant production of Buna N, as this product was first named, started in Germany in 1934 and full-scale production started in 1937 by Farbenfabriken Bayer AG (Germany) with a trade name PERBUNAN. The polymerization reaction can be written as:



The acrylonitrile content of the commercial rubbers ranges from 25 to 50% with 34% being a common and typical value.

Manufacture: Basically, nitrile rubbers are manufactured by emulsion copolymerization of butadiene and acrylonitrile. As the ratio of butadiene to acrylonitrile in the polymer largely controls its properties, the design of the polymerization recipe and the temperature at which this is carried out are important features of nitrile rubber production. The nature and amount of modifiers also influence the properties of the end product.

The early nitrile rubbers were all polymerized at about 25°-50°C and these ‘hot’ polymers contain a degree of branching in the polymer chain known as ‘gel’. By analogy with the developments in the emulsion polymerization of SBR, since early 1950s, an increasing number of nitrile rubbers are being produced by ‘cold’ polymerization at about 5°C. This results in more linear polymers containing little or no gel which are easier to process than ‘hot’ polymers. The dry rubber is obtained by coagulation of emulsion with salts and acids into fine crumbs. The pH of the slurry is adjusted with caustic solution and it is then filtered, washed, denatured and dried.

Properties: Acrylonitrile imparts very good hydrocarbon oil and petrol resistance to the polymer. As a general rule, raising the acrylonitrile level increases the compatibility with polar plastics such as PVC, slightly increases tensile strength, hardness and abrasion resistance and also enables easier processing; however, in the process, low temperature flexibility and resilience properties deteriorate. At temperatures up to 100°C or with special compounding up to 120°C, nitrile rubber provides an economic material having a high resistance to aliphatic hydrocarbon oils and fuels. It has limited weathering resistance and poor aromatic oil resistance. It can generally be used down to about –30°C, but special grades can operate at still lower temperatures.

Generally NBR possesses better heat resistance than neoprene, but like natural rubber, is subject to ozone cracking. Products with low compression set properties can be made. The physical properties of nitrile rubbers are good when the rubbers are compounded with carbon black of suitable type, mainly the semi reinforcing type though unfilled vulcanizates have very low tensile strength.

In general NBR is compounded along lines similar to those practiced with natural rubber and SBR. The rubbers may be vulcanized by the conventional accelerated sulphur systems and also by peroxides. The use of tetramethyl thiuram disulphide without sulphur or tetramethyl thiuram monosulphide with sulphur generally produces vulcanizates with the lower compression set properties. A tetramethyl thiuram monosulphide – sulphur cure is an excellent general-purpose system. Another widely used general-purpose cure system is 1.5 MBTS/ 1.5 sulphur; for improved ageing 3 MBTS / 0.5 sulphur is recommended. When NBR is blended with PVC, products with improved resistance to ozone and weathering, gloss, bright colors, abrasion & oil resistance, and flame resistance are obtained when used alongwith suitable plasticizers.

Applications: Polymers with high acrylonitrile content are used where the utmost oil resistance is required such as oil well parts, fuel cell liners, fuel hose and other applications requiring resistance to aromatic fuels, oils and solvents. The medium grades are used in applications where the oil is of lower aromatic content such as in petrol hose and seals. The low and medium low acrylonitrile grades are used in case where low temperature flexibility is of greater importance than oil resistance.

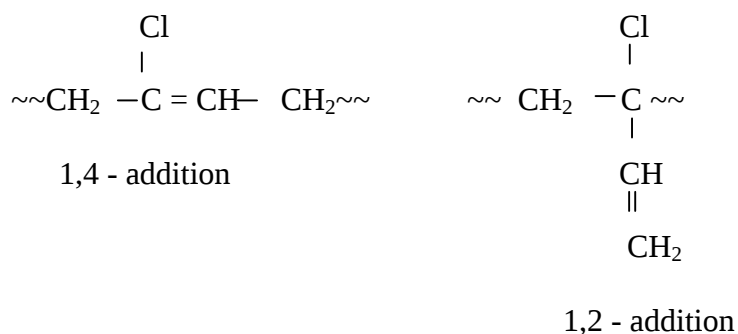
Neoprene Rubber (CR)

Neoprene is the generic name for chloroprene polymers (2-chloro-1,3 butadiene) manufactured since 1931 by E.I. DuPont de Nemours and company. Today these materials are amongst the leading special purpose rubbers (i.e. non tire rubbers).

The solid neoprenes are classified as general purpose, adhesive or specialty types. General purpose types are used in a variety of elastomeric applications – particularly molded and extruded goods, hose, belts, wire and cable, heels and soles, tires, coated fabrics and gaskets. The adhesive types are adaptable to the manufacture of quick setting and high bond strength adhesives. Specialty types have unique properties such as exceptionally low viscosity, high oil resistance or extreme toughness. These properties make specialty neoprenes useful in unusual applications: for example, crepe soles, prosthetic applications, high solids cements for protective coatings in tanks and turbines. Neoprenes are also available in latex form, which like dry rubbers may be classified as general purpose and specialty types.

Manufacture: Neoprene rubbers are manufactured by polymerizing 2-chloro-1,3 butadiene by free radical emulsion polymerization technique at 40°C using an initiator such as potassium persulphate, emulsifiers, modifiers such as dodecyl mercaptan and stabilizers. A sulfur- modified grade such as Neoprene GN is the oldest general-purpose neoprene still produced today. The manufacturing process for neoprene GN is typical of a commercial emulsion polymerization system. A solution of sulfur and rosin in chloroprene is emulsified with an aqueous solution of caustic soda and the sodium salt of naphthalene sulfonic acid-formaldehyde condensation product. The sodium rosin soap emulsifier is formed in situ; the condensation product is used to stabilize the latex till it is subsequently acidified for polymer isolation. The polymer chain is built up through the addition of the monomer units, of which approximately 98% add in the 1,4 - positions. About 1.5% additions in 1,2 - positions are

utilized in the vulcanization process since in this arrangement the chlorine atom is both tertiary and allylic. Accordingly, it is strongly activated and thus becomes a curing site on the polymer chain.



Properties: Since neoprene predominantly consists of 1,4 - trans unit, both the raw and cured polymer crystallize, particularly upon stretching. Neoprene vulcanizates give high tensile strength owing to stress induced crystallization. Crystallization rate is reduced by modification of the polymers' molecular structure and / or incorporation of a second monomer in the polymerization reaction. The commercial polymers have a Tg of about -43°C and a Tm of about 45°C so that at usual ambient temperatures the rubber exhibits a measure of crystallinity.

The close structural similarities between neoprene and the natural rubber molecule are apparent. However, whilst the methyl group activates the double bond in the polyisoprene molecule, the chlorine atom exerts opposite effect in neoprene. Thus the polymer is less liable to oxygen and ozone attack. The chlorine atom has two other positive impacts on the polymer properties. Firstly, the polymer shows improved resistance to oil compared with all hydrocarbon rubbers and these rubbers also have a measure of resistance to burning which may further be improved by use of fire retardants. These features together with a somewhat better heat resistance than the diene hydrocarbon rubbers have resulted in the extensive use of these rubbers over many years.

Pure gum vulcanizates of CR, like those of natural rubber show high levels of tensile strength. However, to provide optimum processing characteristics, hardness and durability, the majority of the neoprene compounds contain fillers. This rubber in general has a good balance of mechanical properties and fatigue resistance second only to natural rubber, but with superior chemical, oil and heat resistance. Hence, It is widely used in general engineering applications. It is suitable for use with mineral oils and greases, dilute acids and alkalis, but are unsuitable in contact with fuels. It has generally poorer set and creep than natural rubber.

It is less resistant than natural rubber to low temperature stiffening but can be compounded to give improved low temperature resistance. It has good ozone resistance. Service in air is satisfactory up to 85°-90°C with suitable antioxidant. Neoprene vulcanizates show a high level of resistance to flex cracking. The resilience of a pure gum neoprene vulcanizate is less than that of a similar natural rubber compound. However, increase in filler loading has lesser influence on the consequent decrease in resilience, as a result of which, the resilience of most practical neoprene is above than that of natural rubber with similar filler loading.

Compounding of Neoprene: Neoprene products require certain engineering properties usually associated with strength or working environment. Raw neoprene is converted to these products by mixing selected ingredients into the neoprene and curing the resulting compound.

Metal oxides are essential in vulcanizate curing systems, the best system being a combination of magnesium oxide and zinc oxide. This combined metal oxide system provides the most desirable relation of process safety to rate and state of cure combined with vulcanizate quality and age resistance. Neoprene may be vulcanized with sulphur, but metal oxides must also be present. The reaction is much slower than that of natural rubber or copolymers of butadiene. Cross-linking with sulphur probably occurs at the double bonds in the linear polymer chain rather than at the allylic position. Though it is impossible to designate a base compound meeting all requirements, a starting formula for general purpose neoprene's could be, neoprene 100/ antioxidant 2/ magnesium oxide 1-4/ zinc oxide 5/ accelerator and / or curing agent 0-3. In all operations it is important to avoid pre-cure or scorching as a result of too much heat history. This means short mixing cycles at the minimum possible temperatures. Accordingly, mixing cycles call for processing aids, stabilizers, antioxidants, magnesia, fillers with softeners, and finally, zinc oxide with accelerators and / or curing agents.

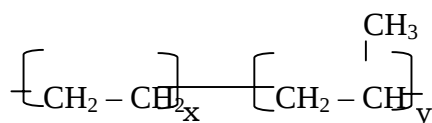
Applications: Application and end products of polychloroprene are probably much more than any other specialty synthetic rubber. Some of the more important uses are in adhesives, transport sector, wire and cable, construction, hose and belting.

There are hundreds of different kinds of neoprene-based adhesives available for use in shoes, aircraft, automobiles, furniture, building products and industrial components. In the automotive field, neoprene is used to make window gaskets, V-belts, sponge door gaskets, wire jackets, molded seals, motor mounts etc. In aviation, it is used in mountings, wire and cable, gaskets, deicers, seals etc. In railroads, it is used in track mounting, car body mountings, air brake hose, flexible car connectors etc. In wire and cable, jackets for electrical conductors are one of the oldest uses. In construction, neoprene is used in highway joint seals, bridge mounts, pipe gaskets, high-rise window wall seals and roof coatings. All types of hoses including industrial and automotive, garden, oil suction, fire, gasoline curb pump, oil delivery and air hoses are made from neoprene. Neoprene's heat and flex resistance make it an excellent choice for making V-belts, transmission belts, conveyor belts and escalator handrails.

Ethylene- Propylene Rubber

Ethylene – propylene rubber was first introduced in the United States, in limited commercial quantities in 1962. Though full-scale commercial production only began in 1963, ethylene-propylene rubber is one of the fastest growing polymers today because of its certain unique properties. These poly olefins are produced in two main types: the standard binary copolymers (EPM) and unsaturated ternary copolymers (EPDM).

A fully saturated copolymer of ethylene and propylene (EPM) is having the following structure:



EPM copolymer (x/y = 50/50 to 65/35).

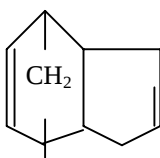
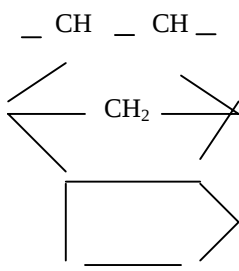
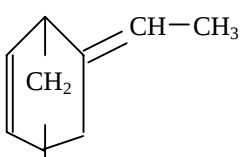
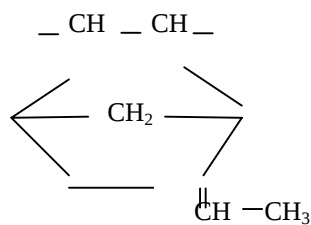
Because of their saturated structure, the raw polymer could not be vulcanized using accelerated sulphur systems and the less convenient peroxide curing systems were required causing reluctance for the wholehearted acceptance by the rubber processors. Besides, peroxide curing systems are much more liable to premature vulcanization (scorch) than accelerated sulphur systems which can lead to high scrap generation.

As a consequence, a third monomer, a non-conjugated diene is introduced in the EPM backbone in small quantity (3-8%), which provided crosslink sites for enabling it to be vulcanized with accelerated sulphur vulcanization. Such ethylene- propylene-diene ternary copolymers are designated as EPDM rubber.

The EPDM rubbers, whilst being a hydrocarbon, differ significantly from the diene hydrocarbon rubbers in two principal ways:

- i) The level of un-saturation is much lower, giving the rubber a much better heat, oxygen and ozone resistance.
- ii) The dienes used are such that the double bonds in the polymer are either on a side chain or as part of a ring in the main chain. Hence should the double bond become broken, the main chain will remain substantially intact. Until some years ago dicyclopentadiene (DCPD) was mostly used, but these rubbers are slow curing and therefore, cannot be co-cured with diene rubbers. The recent trend is towards faster curing grades, and most companies now incorporate ethylidene norbornene (ENB) as the third monomer. Some typical dienes used as third monomer in ethylene - propylene rubbers are given in table 4.

Table 4: Typical dienes used in ethylene - propylene rubbers

Monomer	Predominant structure present in the terpolymer
 Dicyclopentadiene (DCPD)	
 Ethylidene norbornene (ENB)	

Manufacture : The monomers ethylene and propylene are copolymerized in solution in hexane using Ziegler-Natta type catalysts such as vanadium oxychloride (VOCl_3) and an alkyl aluminium or an alkyl aluminium halide (e.g. $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$). The ratio in which the

monomers are polymerized does not depend on the ratio in which they are taken for reaction but on the nature of the catalyst. The polymerization is highly exothermic (1100 btu/lb). The heat is constantly removed to maintain the polymerization temperature at 100°F to ensure a product with desired average molecular weight and distribution.

Properties: The ethylene propylene rubbers are predominantly amorphous and non-stereoregular, and therefore, the pure gum vulcanizates show low tensile strength. Whereas butyl elastomers are highly damping at ambient temperatures, the poly olefin elastomers are highly resilient.

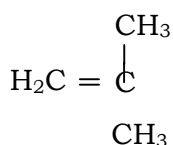
The most striking features amongst the properties of the vulcanizates are the excellent resistance to atmospheric ageing, oxygen and ozone upto 150°C. Probably it is the most water resistant rubber available and the resistance is maintained to high temperatures (upto 180°C in steam for peroxide cures). The highest temperature resistance is achieved by using peroxide cure. It has good resistance to most water based chemicals and vegetable oil based hydraulic oils. However, it has very poor resistance to mineral oils and diester based lubricants.

EPM can be cured with peroxides such as dicumyl peroxide. EPDM, the unsaturated polymers can be cured using sulphur and common rubber accelerators such as tetramethyl thiuram disulphide (TMTDS) activated with mercaptobenzothiazole (MBT). A faster curing can be achieved by activating with a dithiocarbamate such as zinc dibutyl dithiocarbamate (ZDBDC). EPDM compounds generally carry high loading of oils such as paraffinic and naphthenic oils without too much loss in vulcanizate properties. In order to get good properties, the use of reinforcing black or white filler is recommended.

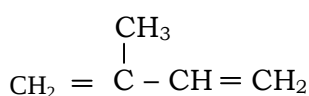
Applications: The 'tire related' end use of EPDM is as an additive to the diene rubber (SBR, natural rubber) compounds in the tire sidewalls and coverstrips to improve their resistance to ozone and weather cracking while under stress and during flexing; EPDM is now almost universally used in this applications. Besides, the unique inherent properties of olefinic elastomers have enabled it for use in cars, domestic and industrial equipment, hose, wire and cable, coated fabrics, linings, footwear, rug underlay, matting pad etc.

Butyl Rubber (IIR)

Butyl rubber has been commercially produced since 1942, and at the present time is a well-established specialty elastomer used in a wide range of applications. Commercial grades of butyl rubber are prepared by copolymerizing isobutylene with small amounts of isoprene at 1-3% of the monomer feed.



Isobutylene



Isoprene

Homopolymer from isobutylene has little use as a rubber because of high cold flow (T_g about -73°C) but the copolymer with isoprene to introduce un-saturation for cross-linking is a useful rubber which is widely used in many special applications.

Manufacture: The monomers are polymerized in solvents such as methyl chloride. The reaction is unique in that it is an extremely rapid cationic polymerization conducted at a low temperature (-100°C) using Friedel-Crafts catalysts such as AlCl₃ or BF₃. The purity of isobutylene is important for acquiring high molecular weight. The n-butene content should be below 0.5% and the isoprene purity should be 95% or more. The methyl chloride solvent and the monomer feed must be carefully dried.

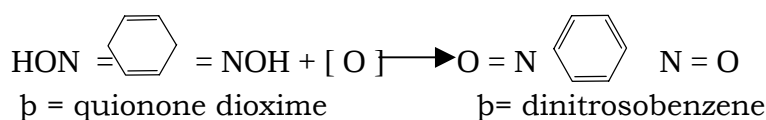
Properties: Owing to the symmetric nature of the isobutylene monomer, the polymer chains have a very regular structure. Hence, butyl elastomers are self-reinforcing with a high pure gum strength (250 Kg/cm²). The abundance of methyl side groups in the chains cause a considerable steric hindrance to elastic movements; although T_g values of around -65°C have been measured, the resilience of vulcanizates at ambient temperatures is very low (about 14% rebound). On the other hand, the densely packed structure of these elastomers causes the gas permeability to be very low, and, because of this, for a long time the main application of butyl rubbers was for inner tubes of pneumatic tires. Mainly as a result of the rather rigid and highly saturated chains, the polymer excels in ozone and weathering characteristics, heat resistance, chemical resistance and abrasion resistance.

Regular butyl rubber is commercially vulcanized by three basic methods. These are accelerated sulphur vulcanization, cross-linking with dioxime and dinitroso related compounds and the resin cure.

As common with more highly unsaturated rubbers, butyl may be crosslinked with sulphur, activated by zinc oxide and organic accelerators. In contrast to the higher unsaturated varieties, however, adequate vulcanization can be achieved with very active thiuram and dithiocarbamate accelerators. Other less active accelerators such as thiazole derivatives can be used as modifiers to improve processing scorch safety. Most curative formulation include the following ranges of ingredients:

Ingredient	Parts by Weight
Butyl Elastomer	100.0
Zinc Oxide	5.0
Sulphur	0.5-2.0
Thiuram or dithiocarbamate accelerator	1.0-3.0
Modifying thiazole accelerator	0.5-1.0

The cross linking of butyl with p-quinone dioxime or p-quinone dioxime dibenzoate proceeds through an oxidation step that forms the active cross linking agent, p-dinitrosobenzene.



The use of PbO_2 as the oxidizing agent results in very rapid vulcanizations, which can produce room temperature cure for cement applications. In dry rubber processing, the dioxime cure is used in butyl based electrical insulation formulation to provide maximum ozone resistance and moisture impermeability. Curing with reactive phenol formaldehyde resins results in vulcanizates with excellent ageing and heat resistant properties.

Chlorobutyl Rubber

The introduction of a small amount of chlorine (1.2 wt.%) in the butyl polymer gives rise to chlorobutyl rubber, which can be blended better with general-purpose rubbers due to increased polarity. Moreover, in addition to the various cure systems acting via double bonds, a variety of new cure systems effective through the allylic chloride can be used in chlorobutyl rubber.

Applications: As already mentioned, the high degree of impermeability to gases makes butyl almost an exclusive choice for use in inner tubes. It is of importance in air barriers for tubeless tires, air cushions, pneumatic springs, accumulator bags, air bellows and the like.

A typical formulation for a butyl rubber passenger tire inner tube is given below:

Ingredients	Parts by weight
Butyl Rubber	100
GPF carbon Black	70
Paraffinic process oil	25
Zinc Oxide	5
Sulphur	2
Tetramethyl thiurum disulphide	1
Mercapto benzothiazole	0.5
Cure	5 minutes @ 177°C or 8 minutes @ 165°C.

The high thermal stability has found widespread use in the expandable bladders of automatic tire curing presses. Another application would be conveyor belting for hot materials handling.

The high level of ozone and weathering resistance enables butyls to be used in rubber sheeting for roofs and water management application. The ozone resistance coupled with moisture resistance of butyl rubber finds utility in high quality electrical insulation. Due to the delayed elastic response to deformation or 'damping', butyl rubber has found wide applications in automotive suspension bumpers and anti-vibration shock absorbing pads in the various machines.

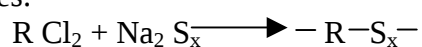
While butyl vulcanizates get highly swelled by hydrocarbon solvents and oils, they are only slightly affected by oxygenated solvents and other polar liquids. This behavior is utilized in elastomeric seals for hydraulic systems using synthetic fluids. The low degree of olefinic unsaturation in the polymer backbone imparts mineral acid resistance to butyl rubber composition. Immersion in 70% H_2SO_4 acid for 13 weeks could hardly affect a butyl compound adversely.

Chlorobutyl is used as innerliners for tubeless tires, tire sidewall components and heat resistant truck inner tubes, hose (steam & automotive), gaskets, conveyor belts, adhesives and sealants, tank linings, tire curing bags, truck cab mounts, aircraft engine mounts, rail pads, bridge bearing pads, pharmaceutical stoppers and appliance parts.

Polysulfide Rubber (TR)

Since the commercial introduction in 1929 of the polysulfide polymers, they have been utilized in specialty applications due to their excellent oil and solvent resistance as well as good ageing properties. Although the original polymers were solid rubbery materials, today the predominant product, discovered some 20 years later, is the mercaptan terminated liquid polymer (LP). It can be transformed in situ from a liquid state into a solid elastomer, even at low temperatures, which makes its use convenient for adhesives, coatings and sealants.

Polysulfide rubbers are produced by the condensation of sodium polysulfide with dichloroalkanes:

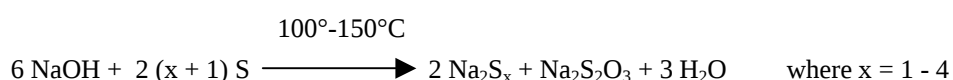


The polymer varies both in characters of R and x and in the length of polysulfide chain. In the year 1929, Thiokol Chemical Corporation, New Jersey first introduced a polysulfide rubber (Thiokol A) based on the reaction product of ethylene dichloride and sodium tetrasulfide. The different polymers produced by the Thiokol Chemical Corporation are given in table 5:

Table 5: Various grades of polysulfide rubbers (Thiokol)

Polymer	Dihalide, R	X	% Sulfur
Thiokol A	ClCH ₂ CH ₂ Cl	4	84
Thiokol B	Cl (CH ₂) ₂ OCH ₂ O (CH ₂) ₂ Cl	4	64
Thiokol FA	ClCH ₂ CH ₂ Cl CH ₂ (OCH ₂ CH ₂ Cl) ₂	2	47
Thiokol ST	CH ₂ (OCH ₂ CH ₂ Cl) ₂ 2% Trichloropropane	2.2	37

Manufacture: The general method of preparation of polysulfides is to add the dihalide slowly to an aqueous solution of sodium polysulfide. Magnesium hydroxide is often employed to facilitate the reaction, which takes 2-6 hours at 70°C. Sodium polysulfide is usually produced directly from sodium hydroxide and sulfur at elevated temperature.



Properties: The solid polymers are used almost exclusively in applications where good resistance to solvents is required. This depends on the amount of sulfur in the molecule. Thiokol A is resistant to every type of organic solvent. However, its odour, processing characteristics and mechanical properties are very poor, and the other types which have moderate physical properties and better all-round solvent resistance than neoprene or nitrile rubbers are more widely employed. Curing agents for thiokols are diverse, but it is

customary to use an organic accelerator (e.g. MBTS or TMTD with zinc oxide and stearic acid for Thiokol FA). The thiol terminated polymers (Thiokol ST) can be crosslinked by metal oxides, metal peroxides, inorganic oxidizing agents, peroxides and p-quinonodioxime. Carbon black, usually SRF or FEF in 40-60 phr loading, is essential for adequate strength.

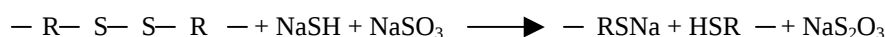
The polysulfide rubbers have very good resistance to oils, fuels, solvents, oxygen and ozone, impermeable to gases but have poor mechanical properties and poor heat resistance. They are however, not recommended for use against strong oxidizing acids in any concentration. They are blended with other synthetic rubbers for improved processing.

Applications: Because of their excellent oil and solvent resistance and impermeability to gases, polysulfides find applications in specialty areas. Thiokol FA is used in the manufacture of rollers for can lacquering, quick drying printing ink application and grain coating of paint on metals. Another major application of Thiokol FA is in solvent hose liner.

Type ST is used in the Gas Metal Diaphragms. Primary use for type A is as flexibilizer for sulfur. 2-5 parts of Thiokol A dissolved in molten sulfur prevents it from crystallization so that it can be used as a mortar for acid pickling tanks, water sewers and oil pipes. Several applications for polysulfide rubber are, as linings and sealants in airplane fuel tanks, concrete fuel storage tank linings, tank car linings, self-sealing aircraft tanks and deicer on wings.

Liquid Polysulfides

A series of liquid thiol terminated polymers (Thiokol LP 2,3,4,31, 32 & 33) are available based on the diethylene formal disulfide structure but containing some branching, and Thiokol LP 205 based on dibuthylene formal disulfide. These low molecular weight polymers are formed by reductive cleavage of disulfide linkage in solid rubber by means of a mixture of sodium hydrosulfide and sodium sulfite. The reaction is carried out in water dispersion and the relative amount of the hydrosulfide and sulfite controls the extent of cleavage and liquid polymers of varying molecular weights can be readily prepared. The sodium hydrosulfide splits a disulfide link to form a thiol and a sodium salt of thiol. The extra sulfur atom is taken up by sodium sulfide.

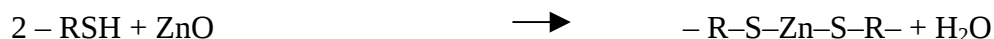
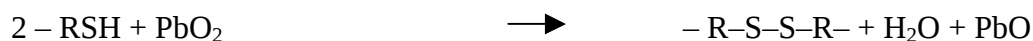


The sodium salt of the polysulfide is converted back to the free thiol on coagulation with acid.

While the commercial liquid polymers contain terminal thiol groups produced by the above method, liquid polymers have been prepared experimentally with terminal alkyl, aryl, hydroxyl, allyl and carboxyl groups. These materials can be produced by using a mixture of dihalide with the appropriate monohalide in the initial reaction with sodium polysulfide. The molecular weight of the product is easily controlled by the mole ratio of monohalide to dihalide. These liquid polymers have molecular weights in the range 600-7500 and viscosities 2.5-1400 poise at 24°C.

The most useful reaction for conversion of the liquid polymers to the high polymer state is that of direct oxidation. This reaction results in a linking of the two thiols to form the polymeric disulfide with liberation of water as a by-product.

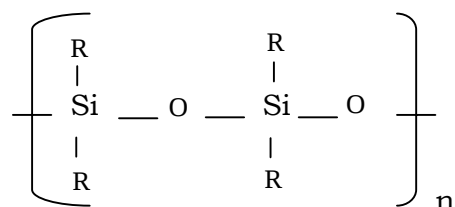
Typical reactions are:



It is customary to incorporate carbon black or white fillers and plasticizers, such as dibutyl phthalate for enhancing properties. They are almost exclusively used in sealing, casting and impregnation applications. Although initially employed as binders for rocket propellants, at present, their largest single use is in the insulating glass industry due to their excellent adhesion to aluminum and glass, and inherent resistance to UV radiation and moisture transmission. They are used as sealants in aircraft industry, marine and construction applications. Other uses include dental molding compound, cold molding compound, formed -in-place gaskets, concrete coatings and bonding, as epoxy flexibilizer for indoor applications and filled molding compounds.

Silicone Rubber (SI)

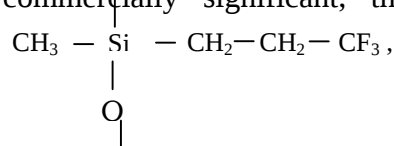
In spite of their high cost silicone, rubbers have established themselves in a variety of applications due to a combination of properties that are quite unique with respect to organic elastomers. These properties are, of course, dependent upon the unusual molecular structure of the polymer, which consists of long chains of alternating silicon and oxygen atoms encased by organic groups. These chains have a large molar volume and very low intermolecular attractive forces. These molecules are unusually flexible and mobile and can coil and uncoil very freely over a relatively wide temperature range. Chemically silicones are polysiloxanes of the general formula:



Where R, in commercially produced polymers, is methyl, phenyl, vinyl or trifluoropropyl group. They are produced by hydrolysis of the appropriate dichlorosilane ($\text{R}_2\text{Si Cl}_2$) to form cyclic tetrasiloxanes which in the presence of suitable catalysts produce the long chain siloxanes.

The first types available were the dimethyl siloxanes, followed shortly by methyl phenyl siloxanes in which the proportion of phenyl was small, imparting the elastomer a lower stiffening temperature than the dimethyl polymer. The newer types of rubber contain an olefinic group usually vinyl, to increase the reactivity of the polymer and provide much faster vulcanization and more elastic vulcanizates. Requirement of vulcanizing agents such as reactive peroxides are less than usual and may also be reinforced with carbon black if desired.

Rubber polymers in which some of the methyl groups had been replaced by groups containing fluorine or nitrile components became available in the 1950s. Although the nitrile-containing polymers failed to become commercially significant, the fluorine-containing polymers,



with their excellent resistance to oils, fuels and solvents have found extensive applications in spite of their high price. The commercial materials usually contain a small amount (about 0.2%) of methyl vinyl siloxane as a cure site monomer, whilst the fluorosilicone component may range from 40% to 90%, the latter figure being more common.

Properties: The molecular weight range of the heat vulcanizable solid polymer is 30,000-10,00,000. The most outstanding property of silicone elastomers is a very broad service temperature range that far exceeds that of any other commercially available rubber. The silicones can be compounded to perform for extended period at -100°C to 315°C under static condition and at -70°C to 315°C under dynamic conditions. At 205°C , the silicone rubber has an estimated useful life of 2 to 5 years, whilst most organics will fail within a few days. Silicone rubber performs unusually well when used as a gasket or O-ring in sealing applications. Over the entire temperature range of -85°C to 260°C , no available elastomer can match its low compression set. The phenyl methyl polysiloxane elastomers have stiffening temperatures some 30° - 40°C lower than the dimethyl polysiloxane.

Silicone rubbers are inert chemically, have no taste or smell, and are, with few exceptions, physiologically acceptable to animal tissue. They are unaffected by atmospheric exposure and do not show ozone cracking. Many types of wires and cables are insulated with silicone rubber, mainly because its excellent electrical properties are maintained at elevated temperatures. The high permeability to gases is utilized medically for making oxygen permeable diaphragms. Its inertness, non-toxicity and biocompatibility are utilized to make medical tubings and surgical implants in human body.

Compounding: The silicone rubbers do not have very good physical properties; in fact they show the lowest pure gum strength of all rubbers. Therefore they have to be reinforced in the same manner as other low strength rubbers. Fumed silica with particle size in the 10-40 nm ranges shows the greatest reinforcing effect. Precipitated and ground silicas with larger particle sizes and correspondingly less reinforcing action are also widely used. Zinc oxide, which imparts tack, titanium dioxide for whiteness, inorganic and organometallic pigments for colouring and ferric oxide for heat stability are among the other compounding ingredients. PTFE at low loading improves its tear resistance.

Cross-linking by organic peroxide takes place in the temperature range 110° - 160°C . Post curing at 200° - 250°C for approximately 24 hours is necessary to remove reaction products and develop the optimum properties, particularly heat resistance.

Applications: The following applications, listed by industry, illustrate the amazing versatility of this unique specialty elastomer:

- i) Aerospace: Aerodynamic balance and control surface scales, airframe opening seals, hot air ducts, dust shields, air & oxygen pressure regulator diaphragm, jet engine starter hose, O-rings, seals and gaskets for lubricating and hydraulic systems, airframe

- and spacecraft body sealants, aircraft and missile wire insulation, missile external and base heating insulation.
- ii) Automotive Industry: Spark plug boots, ignition cable jacket, transmission seals, sealants, hose.
 - iii) Appliances: Oven door and washer-dryer gaskets, seals, gaskets and insulation in steam irons, frying pans, coffee makers etc.
 - iv) Electrical Industry: capacitor bushing, rubber tubing, electrical potting, impregnation and encapsulation, insulation tapes, wires, TV corona shields, nuclear power cable.
 - v) Miscellaneous: Construction sealants for expansion joints, rubber rolls, sponge, prosthetic devices, pharmaceutical stoppers, medical tubing.

Fluorocarbon Elastomers

The best-known fluorocarbon elastomers are those marketed by DuPont under their trade name 'VITON'. VITON-A is a copolymer of vinylidene fluoride and hexafluoropropylene, $\text{CF}_2=\text{CH}_2-\text{CF}(\text{CF}_3)-\text{CH}_2-$,



and can be vulcanized to an elastomer which possesses resistance to chemicals, oils and solvents and to heat which is outstanding in comparison with any other commercial rubber. VITON - B is the terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene having better long term heat resistance, resistance to swelling in oils and resistance to chemical degradation, particularly from oil additives. Both of these grades are of similar importance, holding maximum market share between them. FLOUREL brands of fluorinated rubbers introduced by MMM (USA) are similar in composition possessing similar properties as of VITONS.

Manufacture: The vinylidene fluoride based elastomers are in most cases prepared by emulsion polymerization at elevated temperatures and pressures, using as a catalyst system a mixture of a persulfate and a bisulfite, though other redox free radical systems have been successfully employed. Highly fluorinated surfactants, such as ammonium perfluorooctanoate, are most commonly used since it is important to use a dispersing agent which will not enter into the polymerization by a chain transfer reaction.

Properties: The fluorocarbon rubbers range widely in molecular weight. For example VITON-A and AHV have molecular weight from 1×10^5 to 2×10^5 providing a practical processing range of viscosity. Lower molecular weight grades have been produced for special processing requirements, including VITON - LM, a wax like material, having a molecular weight of less than 5000.

The vulcanizates with conventional compounding can range in hardness from 60 IRHD to 95 IRHD. They can be compounded to give tensile strengths up to 200 Kg/cm², with elongation at break in the range of 150-300%, depending on hardness.

The fluorocarbon rubbers have high degree of resistance to heat ageing. Continuous service life of a typical vulcanizate of hardness 75 IRHD is more than 3000 hours at 230°C, 1000 hours at 260°C, 240 hours at 288°C and 48 hours at 315°C.

In general, fluorocarbon rubbers show excellent resistance to oils, fuels, lubricants and most mineral acids. They also resist many aliphatic and aromatic hydrocarbons such as carbon tetrachloride and xylene which act as solvents for other rubbers. They are not so resistant to low molecular weight esters and ethers, ketones and certain amines.

Fluorocarbon rubbers are flame resistant and do not support combustion. They have outstanding resistance to oxidation and are highly resistant to ozone attack. At low temperature, their performance is moderate as can be assessed by their brittle temperature ranging from -40°C to -50°C . These rubbers are useful for low voltage, low frequency insulation where high degree of heat and fluid resistance are necessary.

Converting the thermoplastic, rubbery raw gums of the fluorocarbon elastomers to usable vulcanizates requires primary crosslinking agents such as amines, as well as acid acceptors such as metallic oxides of magnesium, calcium, zinc or lead. The combined effects of these materials promote the removal of hydrogen and halogen to produce the double bonds, which further participate in the crosslinking reactions that produce stable, useful vulcanizates. Most systems can also be sufficiently retarded; salicylic acid or hydroquinone are effective. Some crosslinking agents used are: hexamethylene diamine carbamate (0.75-1.5 phr), ethylene diamine carbamate (0.85-1.25 phr) and N, N' - dicinnamylidene 1,6 hexane-diamine (2-4 phr). They may be cured at 120°C with subsequent oven post cure at 205°C , if long service life in excess of 205°C is required. Fillers such as medium thermal carbon blacks, low hardness talc pigments can be loaded up to 20 parts to achieve smoothness in processing.

Applications : Though maximum consumption of fluorocarbon rubbers is for O-rings, packings and gaskets for aerospace industry, they also find applications in automotive and other mechanical goods. They are used in valve steam seals, heavy duty automatic and pinion seals, crankshaft seals and cylinder liner O-rings for diesel engines. Other uses include seals for diesel engine glow plugs, seals for pilot operated slide valves, protective suiting and flue duct expansion joints. The high price of the fluorocarbon rubbers is a limitation on their use and can only be justified for highly specialized applications as mentioned before.

Thermoplastic Elastomers (TPE)

Thermoplastic elastomers were introduced in the 1960s. They have many properties of rubbers i.e. softness, flexibility and resilience, but in contrast to the conventional rubbers they are processed as thermoplastics. They can be processed on conventional plastics processing equipment such as injection molding machines; their scrap can be usually recycled in contrast with the vulcanized rubbers and have lower processing cost than conventional vulcanizates. Because the melt to solid transition is reversible, some properties of thermoplastic elastomers, e.g. compression set, solvent resistance and the resistance to deformation at high temperatures, are usually not as good as these of the vulcanizates. Applications of thermoplastic elastomers therefore encompass the areas where these properties are less important e.g. footwear, wire insulation, adhesives, polymer blending and not in the areas such as automobile tires.

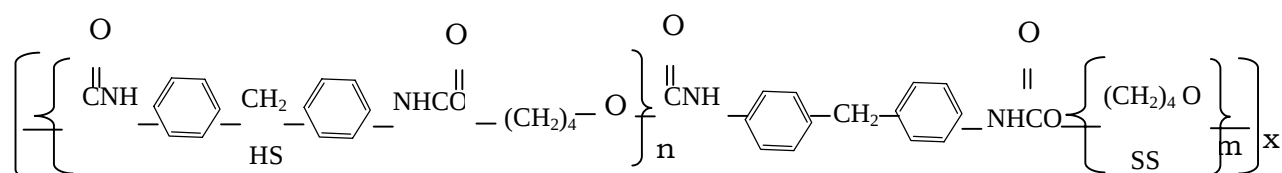
Thermoplastic elastomers are multiphase compositions in which the phases are intimately dispersed. In many cases, the phases are chemically bonded by block or graft copolymerization, in others; a fine dispersion is apparently sufficient. At least one phase consists of a material that is hard at room temperature but fluid upon heating; another phase consists of a softer material that is rubber like at room temperature. A simple structure is an

A-B-A block copolymer where A is a hard phase and B an elastomer, e.g. poly (styrene-b-elastomer-b-styrene).

The typical elastomeric properties of these materials can be attributed to physical cross links resulting from domain formation in the case of triblock or multiblock copolymers having hard and soft segments. The hard segments are so designed that they remain incompatible with the rubber phase, thus forming micro domains which act as physical cross links at service temperatures tying the elastomer chains together in a three dimensional network. At elevated temperatures, these domains lose their strength, enabling the material to flow under the conditions used in thermoplastic processing.

Thermoplastic Polyurethanes

The first commercially available thermoplastic elastomers were polyurethanes (TPUs) formed of long flexible polyether or polyester chains linked by polar polyurethane units which associate into microdomains by hydrogen bonding. These segmented copolymers have the general formula $(AB)_x$, whereas a triblock copolymers has the general formula ABA. Polyurethanes are generally manufactured from an aromatic diisocyanate, an oligomeric diol and a low molecular weight diol. The low molecular weight diol is typically called a chain extender because it links AB segments together. A typical thermoplastic polyurethane based on diphenyl methylene-4,4' diisocyanate (MDI), poly (tetramethylene oxide) and butane diol is given below:



Where $n = 1-5$, $m = 20$ and $x = 20$

Thermoplastic polyurethanes have excellent strength, wear and oil resistance and are used in fibers, footwear, automotive bumpers, snowmobile treads, adhesives, etc and in high performance structural applications. Approximately 15% of the thermoplastic elastomer market is claimed by polyurethanes.

Styrene thermoplastic elastomers

Styrene thermoplastic elastomers were introduced in 1965 by Shell Development Company under the trade name KRATON. These materials are either poly (styrene- b-butadiene-b-styrene) (SBS), poly (styrene-b-isoprene-b-styrene) (SIS), or poly (styrene-b-ethylene butylene-b-styrene) (SEBS) triblock copolymers. The styrene rich domains serve as the hard phase as the T_g for polystyrene is approximately 100°C . The molecular weight polydispersity is low because these triblocks are typically anionically polymerized. The terminal styrene segments reside in glass microdomains which reinforce the elastomeric phase. Approximately 50% of all thermoplastic elastomers produced are SBS, SIS or SEBS triblock copolymer. Their uses include footwear (67%), bitumen modification (14%) to improve low temperature flexibility, thermoplastic modification by blending (6%), adhesives

(9%) and cable insulation and gaskets (4%); these were the approximate share in US market in 1980.

A significant proportion of the present consumption of butadiene-styrene block copolymers is in the form of oil extended grades, typical composition being 45-60 parts of oil per 100 parts elastomers. They serve the dual purpose of improving certain mechanical and rheological properties and improving the cost efficiency of the product.

SBS compounds are generally found in shoe soles and bitumen modification. SIS materials are employed almost exclusively as adhesives whereas SEBS triblocks are used as structural materials. Because the absence of a double bond substantially improves the resistance to UV light and high temperatures, SEBS copolymers are also used in SIS or SBS applications where this resistance is necessary.

Ethylene - propylene copolymers

Ethylene – propylene (EP) copolymers along with other random or block α -olefin copolymers are another major category of thermoplastic elastomers accounting for approximately 30% of the thermoplastic elastomer market. Often these copolymers are blended with another material, usually a homopolymer corresponding to one of the copolymer components, to improve the mechanical properties of both the blend and the homopolymer. Though EP copolymers and copolymer blends cost slightly more, it can offer better performance than triblock copolymers.

Polyether – polyester TPE

Polyether – polyester TPEs have flexible polyether chains, which are crosslinked by crystallization of the polyester groups. Application of such block copolymers based on poly (butylene terephthalate) and poly (tetra methylene oxide) include hose, tubing, sports goods, mechanical goods and automotive components. Their typical polymer properties include relatively high load-bearing capacity; high flex fatigue endurance, good resistance to mechanical abuse, good chemical and weathering resistance and easy and efficient processing. As polar polymers, these rubbers have good oil and petrol resistance as well as a wider service temperature range than many general-purpose rubbers, which make these materials more suitable in applications such as automobile engine parts. About 5% of the thermo plastic elastomer market belongs to copolyesters.

Polyether- polyamide copolymers

Polyether- polyamide block copolymers are the newest TPEs developed and have the

$$\text{HO} \left(\underset{\text{O}=\text{C}}{\text{C}} - \text{PA} - \underset{\text{O}=\text{C}}{\text{C}} - \text{O} - \text{PE} - \text{O} \right)_n \text{H}$$
 schematic structure where PA is the polyamide segment and PE is the polyether segment. Crystallization provides the driving force for phase separation in these materials as well. These materials have especially low chemical permeability and offer good properties at low temperature.

The applications for polyurethanes, copolyesters and copolyamides are substantially different from those of triblock copolymers. The applications for these multiblock copolymers take advantage of their superior abrasion resistance, tear strength and toughness. In the automobile industry these TPEs are used in boots and bearings for joints and some tubing as well as exterior bumpers and some paneling; other industrial uses include industrial hoses, gears and cables.

A very visible consumer product group for TPEs includes sporting goods. Footwear, including ski boots and soccer shoes often contains a substantial fraction of TPE. Athletic shoe soles are an especially major area and application for TPEs. They are also used in skis and tennis racquets. A polyurethane coating is applied to most track and field surfaces.

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