

Special Purpose Elastomers: Synthesis, Structure-Property Relationship, Compounding, Processing and Applications

Deepalekshmi Ponnamma, Cintil Jose Chirayil,
Kishor Kumar Sadasivuni, Lakshmi Priya Somasekharan,
Srinivasarao Yaragalla, Jiji Abraham and Sabu Thomas

Abstract Elastomers are notable as very special class of polymers due to their multifunctional applications. The superior mechanical properties, high flexibility, resilience and good viscoelastic behaviour make this class applicable in a wide range of technology and industry. Depending on the various properties and general applications elastomers are classified in to a number of categories. This particular chapter deals with a very important class of special purpose elastomers. The synthesis, structure, different properties, mode of vulcanization, processing and applications of most of the synthetic elastomers are discussed. Apart from providing a basic understanding about the materials, this chapter can facilitate wide information about the technical details and industrial importance of this class of rubbers.

1 Introduction

Among the various types of polymers, elastomer class has special significance due to their amazing properties like high resilience, high elasticity, viscoelastic properties, mechanical strength and frictional resistance. Their wider availability and low cost make them highly significant in technological applications. Their damping and energy absorption characteristics, resilience, long service life, ability to seal against moisture, heat, and pressure, non-toxic properties, moldability, and variable stiffness are other distinguishable attributes. Most of the elastomers

D. Ponnamma (✉) · C. Jose Chirayil · L. Somasekharan · S. Yaragalla · J. Abraham
S. Thomas
School of Chemical Sciences, Mahatma Gandhi University,
Kottayam 686 560 Kerala, India
e-mail: lekshmi.deepa09@gmail.com

K. K. Sadasivuni
LIMATB Laboratory, Université de Bretagne Sud,
rue St Maudé 56100 Lorient, France

belong to the 'Rubbers'. But there are elastomers showing properties of thermoplastics (thermoplastic elastomers) as well as thermosets. The flexibility of the elastomers are due to their segmental mobility and vulcanization makes cross links among the rubber chains for the recovery. Vulcanised rubbers are widely used in industries especially in tyre applications.

Even though elastomers have tremendous applications, their end use always depends on the selection of a particular matrix. There are several classifications of elastomers, of which the most significant is based on its functional properties. Depending on the end use applications, elastomers are classified into general purpose and special purpose. As the name indicates, the general purpose rubbers include elastomers having general applications. Natural rubber, styrene butadiene rubber (SBR), polybutadiene and polyisoprene rubber, ethylene propylene rubber, isobutylene based rubbers, etc. are known as general purpose elastomers. Those rubbers having specific applications belong to the special purpose category. All such elastomers are synthetic in nature. Butyl rubber, fluoro rubbers, sulphide rubbers, polyurethanes etc. are some of the examples. The specific properties of such elastomers are air impermeability and resistance to heat, aging and ozone in the case of butyl rubber, oil resistance for nitrile rubber, temperature stability for silicone rubber and so on. Comparing to butyl rubber (IIR), its derivatives chlorobutyl and bromobutyl rubber have better heat aging resistance. The main applications of IIR include electric wire, cable, adhesive, construction materials, sealing materials, inner tube, bladder etc. Chloro butyl and bromo butyl rubber are specifically used in inner tubes, inner liners, automotive parts, electric wires and industrial goods.

Special purpose elastomers are again classified into high volume specialty elastomers such as EPDM and polychloroprene and also low volume specialty elastomers such as silicone rubber, polyurethanes and fluoro elastomers. A detailed study about the special purpose elastomers, their mode of synthesis, curing behavior, end use applications etc. has been given in this chapter. Effort has been taken to address all the important factors in manufacturing and applying specialty elastomers in technology and industry. The main types and their significance are narrated hereafter.

2 Types of Rubbers

2.1 *Butyl Rubber*

Poly (isobutene-co-isoprene) rubber generally known as butyl rubber typically contains about 98 % polyisobutylene and 2 % isoprene polymer chains distributed in a random way. The structure is shown in Fig. 1a. It has several unique properties; the most important being the superior gas impermeability and mechanical damping properties. It is the best sealant of all the known rubbers. The major application of butyl rubber in the lining of tyres (low permeability) comes from the

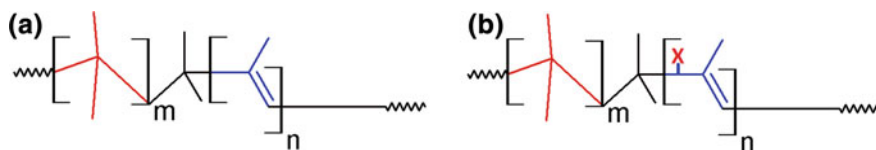


Fig. 1 Chemical structure of (a) butyl rubber ($m = 98 \%$, $n = 2 \%$) (b) Halo (X) butyl rubber

low levels of unsaturation between long poly isobutylene segments. It was formerly used to make the tyre inner tubes, but now incorporating this rubber as inner liners has led to tubeless tyres.

Butyl rubber is produced via a polymerisation process taking place at $-100\text{ }^{\circ}\text{C}$ and thus the process is rather complex [1, 2]. Since the reaction is highly exothermic, control of temperature to lower level (-90 to $-100\text{ }^{\circ}\text{C}$) is necessary particularly to synthesize high molecular weight IIR. In the most common method of polymerization, methyl chloride and boiling liquid ethylene are used as the reaction diluents which can maintain the temperature. Finally the slurry of fine particles of butyl rubber (dispersed in methyl chloride) is formed in the reactor and methyl chloride and unreacted monomers are flashed and stripped overhead by adding steam and hot water, and thus recycled. Zinc or calcium stearate compound is the slurry aid and this along with the antioxidant is introduced into the hot water/polymer slurry to stabilize the polymer and to prevent agglomeration. After screening the polymer from the hot water slurry, it is dried in a series of extrusion dewatering and drying steps [2] to obtain IIR in the final form. Butyl rubber can be produced in bulk by polymerizing in alkane solutions as well.

The allylic halide functionality of the elastomer responds to standard cure accelerators in an anomalous manner, and it is susceptible to isomerization and elimination reactions at elevated temperatures that can detract from end-use performance [3]. So researchers developed halo butyl rubber to make butyl rubber more compatible with other polymers by using substitution of halo group.

2.1.1 Halo Butyl Rubber

Halogenations of poly(isobutylene-co-isoprene) to generate halogenated butyl rubber (XIIR) (Fig. 1b) yields an elastomer that has the air impermeability required for tyre inner liner applications and the cure reactivity required to generate adhesion between the tyre inner liner and its body. There are two kinds of halo butyl rubber; chloro butyl rubber, CIIR and bromo butyl rubber, BIIR. While superior sulfur vulcanization kinetics are known to originate from the exo-allylic bromide structure of bromo poly(isobutylene-co-isoprene), the cure chemistry of this commercially important elastomer is typical to understand [4]. The low level of residual unsaturation in halobutyI rubber XIIR), coupled with the insolubility of crosslinked networks, complicates the structural determination of its vulcanizates [5].

Table 1 Recipe of butyl rubber compounds (*phr* parts per hundred rubbers) [8]

Ingredients	Butyl rubber	Zinc oxide	Stearic acid	Sulphur	MBTS	TMTD	TMQ
phr	100.0	5.0	2.0	1.5	0.5	1.0	1.0

Processing of IIR, CIIR and BIIR by mastication changes the molecular weight distribution of chains between junctions of the polymer network, the coefficient of polydispersity, the share of low-temperature and high-temperature blocks, and their glass transition temperatures. These changes in the structure of rubber depend on both the presence of sulphur and the kind of sulphur (polymeric or mineral) being used during mixing. This suggests that the sequence of rubber compounding and the rubber recipe influence not only the dispersion and the distribution of ingredients (which is well known) but also the structure of the rubber matrix [6]. IIR, CIIR and BIIR must be compounded and chemically cross-linked to yield useful, durable end use products similar to all other rubbers. The vulcanization kinetics or cure-curve is monitored from the evolution of crosslinks, using an Oscillatory Disk Rheometer (ODR). The instrument measures the torque or the shear modulus, as a function of time when the vulcanizate cures, where it is assumed that the modulus is proportional to the evolving concentration of cross-link's. Different grades of this elastomer can be developed according to the processing and property needs, and a range of molecular weights, unsaturation, and cure rates are commercially available. Based on the specificity of applications, the end use attributes and the processing equipment, the right grade can be selected. The selection and ratios of the proper fillers, processing aids, stabilizers, and curatives also play critical roles in compound processing and the end product behaviour [7]. Elemental sulphur and organic accelerators are widely used to cross-link poly (isobutylene-co-isoprene). The low level of unsaturation requires aggressive accelerators such as thiuram or thiocarbamates. The usually used curing agents are given in Table 1.

As illustrated in Fig. 2, the vulcanization reaction starts at the isoprene site with the polysulfidic cross links attached at the allylic positions and displaces the allylic hydrogen. This is the general mechanism involved in the accelerated sulfur vulcanization of butyl rubber. The number of sulfur atoms per cross-link varies between one and four or more. Both the cure rate and cure state (modulus) increase at higher unsaturation rates. The basic steps in the vulcanization reactions are similar in the case of all rubbers even though some important differences remain [9]. The whole vulcanization reaction can be divided into three sub-categories:

1. The scorch delay or induction region, where the accelerator chemistry for the reactions leading to the formation of an active-sulfurating agent is involved.
2. Cure reaction which involves reactions leading to the formation of crosslinks; and
3. Post-crosslinking chemistry involving the reactions that lead to crosslink shortening and crosslink degradation [10] and here the modulus can increase, decrease or remain constant depending upon the specific vulcanization system.

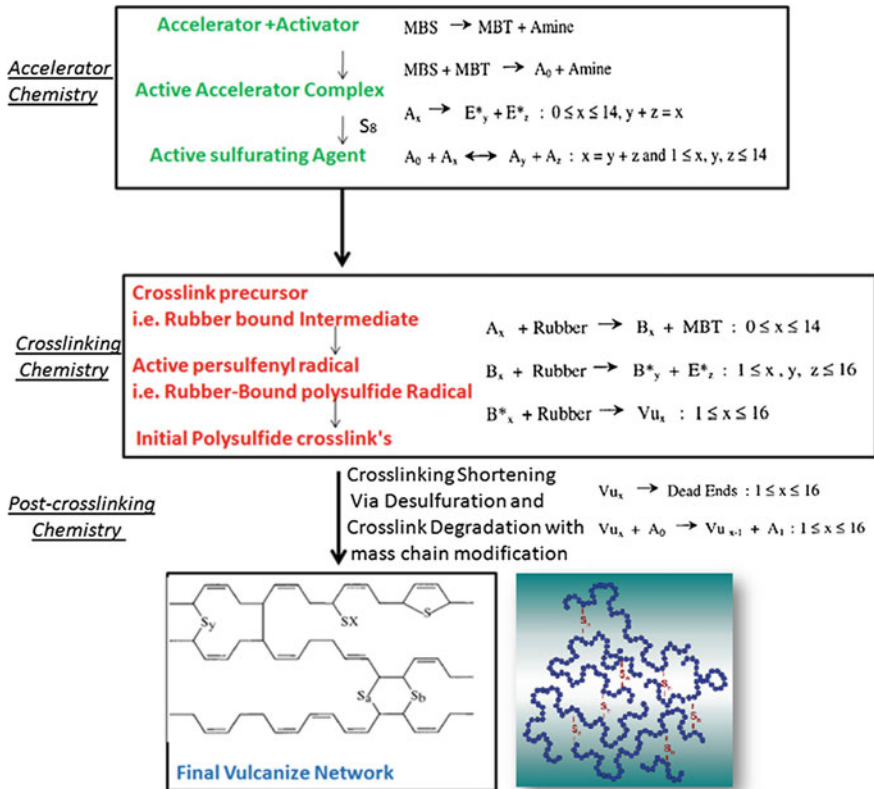


Fig. 2 General mechanism for accelerated sulfur vulcanization for butyl rubber. Mechanism adopted from that of Morrison and Porter [9]

These three vulcanization reaction steps are evidenced from the three main regions of the cure curve [10]. Vulcanization begins with the formation of zinc-free and/or zinc-complexed accelerator species. MBTS formed from the autocatalytic dissociation of MBS act as the precursor in the formation of these accelerator polysulphides. Accelerator polysulphides are subsequently formed by the direct reaction of lower length accelerator polysulphides with sulphur. It has been proposed that these sulfuration reactions proceed by the insertion of sulphur as S8 molecules or, alternatively, that the reactions are sequential, occurring via the insertion of single sulphur atoms [11]. The exact chemical structure of the S_x species and its concentration for x < 8 has not yet been detected. In the absence of zinc, the sulfuration reactions proceed via a radical mechanism whereas in the presence of zinc it proceeds via a polar mechanism. In zinc activated systems sulfuration reactions include a combination of radical and polar mechanisms.

In the case of halobutyl rubber, the halogen atom present in the allylic position causes easier cross-linking than allylic hydrogen alone does as halogen is a better

leaving group in nucleophilic substitution reactions. Zinc oxide is the most common cross-linking agent in this kind of rubbers since it forms very stable carbon–carbon bonds by alkylation reaction through dehydrohalogenation, with zinc chloride by product. In addition to zinc oxide elemental sulfur and organic accelerators are also used to cross-link butyl rubbers. Aggressive accelerators such as thiuram or thiocarbamates are employed whenever low level of unsaturation is required. As already discussed, vulcanization proceeds at the isoprene site with the polysulfidic cross links attached at the allylic positions by displacing the allylic hydrogen. It is important to note that the sulphur cross-links formed are less stable at high temperature. The resin cure systems (commonly using alkyl phenol–formaldehyde derivatives) can eliminate this drawback since it provides carbon–carbon cross-links and thus more stable compounds.

It is generally accepted that the unique cure properties of BIIR originate from the reactivity of allylic bromides [12–15]. However, comparatively little is known about the intrinsic reactivity of the particular allylic bromide functionality found within BIIR, especially at vulcanization temperatures. This is a concern to the technologists, as degradation reactions operate concurrently with the vulcanization process with undesirable consequences as shown in Fig. 3. To facilitate the structural characterization of products arising from BIIR instability, researchers studied the behavior of a model compound and similar approach was used to study the vulcanization of natural rubber [9, 14–16] and poly(butadiene) [16, 17] and the halogenations of isobutylene–isoprene rubber and the ZnO cure of XIIR, in which complications associated with thermal instability were first highlighted [16–18]. The allylic bromide functionality within BIIR undergoes substitution with amine nucleophiles without acceleration of concurrent HBr elimination [5].

Chloro-butyl rubber can be crosslinked upon heating, the reaction being facilitated by the addition of ZnO, ZnCl₂, or zinc dimethyl dithiocarbamate (Zn₂(dmtc)₄) [4, 19]. The most widely accepted theory, as postulated by Baldwin et al. [6] and supported by Kuntz et al. [18] and Vukov [4] postulates a cationic reaction in which ZnCl₂, formed in situ, is responsible for crosslinking as shown in Fig. 3. Stearic acid is frequently added to commercial formulations. It is generally accepted that reactions leading to the formation of ZnCl₂ precede crosslinking, the induction period prior to crosslinking being ascribed to the need to form ZnCl₂ that is considered to act as a catalyst for crosslinking via a cationic mechanism. In ZnO formulations the ZnCl₂ formed may initially result from reaction of ZnO with HCl formed on thermal dissociation of the allylic chlorine [4, 6, 19]. The cationic mechanism as originally proposed by Baldwin et al. [6] also showed the ZnCl₂ initiated cationic reaction to lead to crosslinks without the participation of a conjugated diene butyl precursor. They reported that good co-vulcanization of CIIR with unsaturated rubbers can be effected, although care must be taken in the selection of curatives. Though sulphur and conventional accelerators were included in the formulations, the ability to link CIIR to highly unsaturated rubbers may point to dienes playing a role in the crosslinking process. ZnCl₂ and conjugated

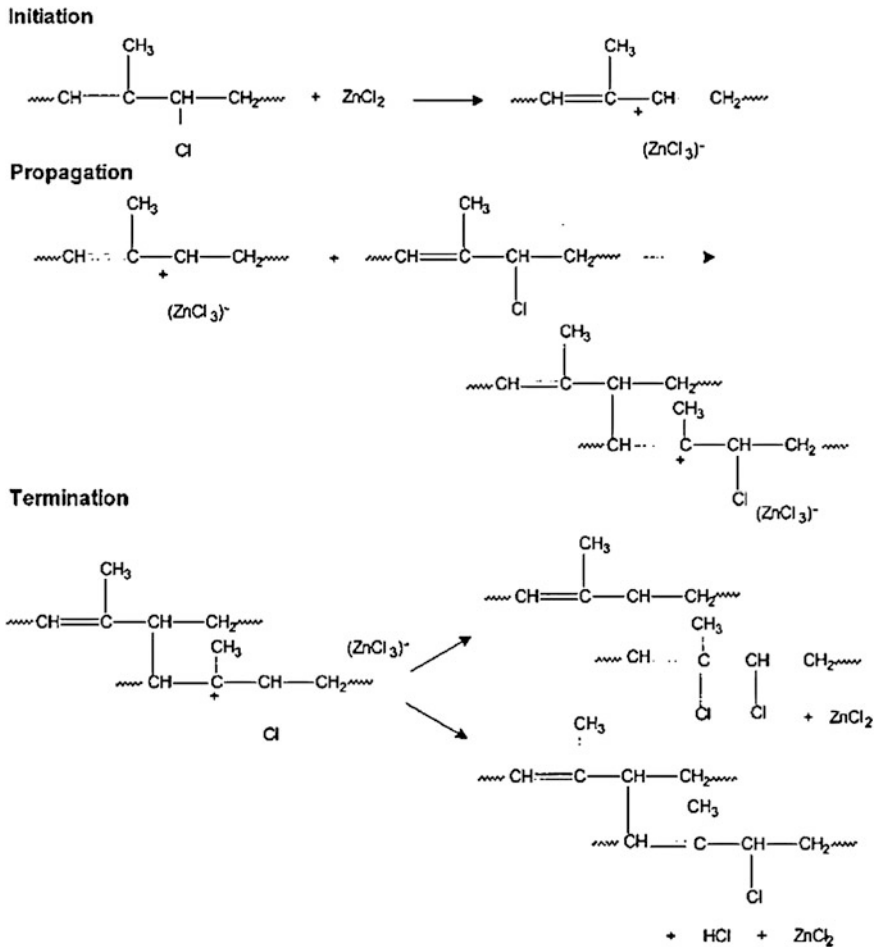


Fig. 3 General mechanism for accelerated sulfur vulcanization for chloro butyl rubber [19]

diene butyl are products of the same reaction, dehydrohalogenation, and separation of their roles in the crosslinking process is not easy.

When the derivatives of butyl rubbers i.e. bromobutyl and chlorobutyl rubbers are considered, the former cures at a faster rate than the latter and has better adhesion to highly unsaturated rubbers. Due to this reason, the volume growth rate of bromobutyl has exceeded that of chlorobutyl in recent decades especially in tyre industry. However, utmost care should be taken while processing the halobutyls as there is a chance for premature dehydrohalogenation. To prevent this problem of premature dehydrohalogenation, stabilizers such as calcium stearate alone (for chlorobutyl) or compounded with epoxidized soybean oil (for bromobutyl) etc. are used.



Fig. 4 General applications of Poly (isobutylene-co-isoprene) and Halo Poly (isobutylene-co-isoprene rubbers)

2.1.2 Properties and Applications

One of the main important applications of butyl rubber based compounds is in the fabrication of tyre inner tubes. This is attributed to its excellent impermeability/air retention and good flex properties. Another important property of this rubber is that it is blood compatible. This feature makes it applicable in biomedical fields such as in fabricating artificial joint materials. This rubber is not toxic and so it is widely used in all chewing gum. IIR and XIIR is used in a wide range of applications, such as inner tubes, tyre liners, curing bladders, air springs, drug cap sealants, gas pipe coating and gaskets, military attires, air conditioner hoses, cable insulations, jacketing, roof membranes and sporting goods [20–22]. Butyl Rubbers are also useful as sorbent materials for the removal of oil and polycyclic aromatic hydrocarbons from seawater [22–24].

The derivative rubbers such as chloro and bromo butyls also have great significance in various fields of technology and industry. The main advantage of such halo butyl rubber is in improving the property of air impermeability. The major contribution of such rubbers is in the development of tyre inner liners. Halobutyls help in the development of more durable tubeless tyres with the air retaining inner liner chemically bonded to the body of the tyre. In short the unique combination of properties of butyl rubbers such as excellent impermeability, good flexing, good weather ability, co-vulcanization with highly unsaturated rubbers (in the case of halobutyl) makes it a preferred material for industry. General Applications of poly (isobutylene-co-isoprene) and halo poly (isobutylene-co-isoprene) are shown in Fig. 4.

2.2 Nitrile Rubber

Nitrile-butadiene rubber (NBR) commonly known as nitrile rubber is an oil-resistant synthetic rubber which is produced from the copolymers, unsaturated acrylonitrile and butadiene. Nitrile rubber (NBR) is considered as the workhorse of the industrial and automotive rubber products industries because of its good elongation properties, good to excellent compression set resistance, adequate resilience and tensile strength but poor flame and steam resistance. Generally NBR can be classified into 5 categories they are hot NBR, cold NBR, cross linked hot NBR, carboxylated nitrile (XNBR), bound antioxidant NBR.

2.2.1 Synthesis of Nitrile Rubber

Nitrile rubber can be prepared by the random polymerization of acrylonitrile with butadiene in the presence of free radical catalyst. Emulsifier/soap, monomers, catalyst, are introduced into the reaction vessel. As a result of polymerization a latex is obtained which is coagulated by using various materials (e.g. calcium chloride, aluminum sulfate). The amount of acrylonitrile present in the final copolymer varies from 15 to 50 % [1, 25].

2.2.2 Structure Property Relationship

Chemical structure of NBR and SBR are almost similar. Replacement of benzene ring of SBR gives NBR. Presence of this cyanogens group provides polarity to NBR rubber. As a result of this oil, heat, air permeability resistance, electrical conductivity properties of vulcanizates get enhanced. Nitrile monomer gives permeation resistance properties to a wide variety of solvents and chemicals. NBR is resistant to hydrocarbon oils, fats and solvents, because of the polar nature of acrylonitrile. Oil resistance means ability of the vulcanized rubber to resist the changes in its physical properties such as modulus, tensile strength, abrasion resistance, and dimensions when it is in contact with oil and fat. The butadiene part is responsible for the softness, flexibility of the rubber and butadiene component is involved in vulcanization process, thereby enhancing the elasticity of rubber.

ACN level, the major reason behind the polarity of the NBR rubber determines properties, of the nitrile rubber. NBR with higher acrylonitrile content has high processability cure rate with sulfur cure system, oil/fuel resistance, compatibility with polar polymers, air/gas impermeability, tensile strength, abrasion resistance, heat-aging. Lower ACN content provides improved cure rate with peroxide cure system, compression set, resilience, hysteresis, low temperature flexibility. There are some more characteristics which determines the properties of nitrile rubber. They are mooney plasticity and gel content. Normally mooney viscosity ranges from 30 to 95. Gel content ranges of nitrile rubber are 0–80 %. Permanent gel content leads to lowering in tensile strength, percent of elongation and abrasion

resistance. Non permanent gels have improved green strength, reduced surface tack and poor mould characteristics [2]. Modification of nitrile rubber by carboxyl group improves abrasion resistance. Blends of NBR and PVC have much improved ozone resistance and improved flame retardant properties [6, 26].

2.2.3 Compounding and Processing

Pure NBR is not useful for applications. In order to get a wide variety of properties nitrile rubber should be compounded. Higher acrylonitrile NBR rubber can be chosen when high resistance applications but they have poorer low temperature properties. Lower acrylonitrile rubbers are used when low temperature and dynamic properties are important but they are poorer in oil and fuel resistance. Commonly used activators are zinc oxide at 3–5 phr level and stearic acid at 1–2 phr level. These activators are used along with sulphur curing system. With peroxide curing system cynurate (Tac) is the activator. Incorporation of different kinds of accelerators such as TMTD, TMTM, DOTG and NPV/C improve cure rate, tensile properties, resistance to oil, aging properties [27]. Antioxidants can be used in order to improve the thermal stability of all nitrile compounds. Ozone resistance of nitrile rubber can be improved by blending it with materials such as poly(vinyl chloride), chlorosulphonated polyethylene, chlorinated polyethylene, epichlorohydrin and ethylene propylene terpolymers.

For the better properties of nitrile rubber, it is reinforced with fillers. Most commonly used filler is carbon black. Many studies have been reported on the effect of different types of carbon black on the properties of nitrile rubber elastomer. Carbon black can reduce the total quality cost of nitrile compounds while improving or maintaining key properties [4, 28]. Recently for non black applications fillers like nanoclay, organosilicates, calcium carbonates are widely used [3, 5, 29]. The tribological properties of GO/NBR under dry sliding and water-lubricated condition have been reported [8, 30].

In order to get better low temperature properties and to improve processability plasticizers are used. Commonly used plasticizers are ester types, aromatic oils and polar derivatives. In summary nitrile compounds can be compounded with vulcanization system, fillers, activators, antioxidants, plasticizers etc. The processing of nitrile rubber includes mixing, extrusion, pre-forming to required shape and vulcanization. Mode of mixing of nitrile rubber is either by two roll mill or by internal mixing equipment. Mooney viscosity values of nitrile rubber determine how the material will process. Compounds can be processed by extrusion, calendaring or moulding by injection or compression.

2.2.4 Applications of NBR

Because of its oil and fuel resistant characteristics nitrile rubber finds its greatest market in applications where these characteristics are necessary. Applications of

nitrile rubber include in the field of molded and extruded parts for the automotive, chemical, mining, home construction, printing rolls and paper industry, conveyor belts for construction and mining industry, industrial and military footwear, gasoline and oil hoses, bulk fuel transfer hose, chemical transfer hose, industrial air hose, food handling, dairy and creamery hose, seals and gaskets, brakes and friction pads, foam lines for thermal isolation. NBR is also employed in textiles, where its application to woven and nonwoven fabrics improves the finish and water proofing properties. It can be used to prepare non-latex gloves for the healthcare industry. It has special application in agriculture, in rice dehusking rollers, where they give much longer life and greater dehusking capacity than any other polymers. NBR finds enormous uses in roll covers, hydraulic hoses, conveyor belts, oil field packers, plumbing appliances etc.

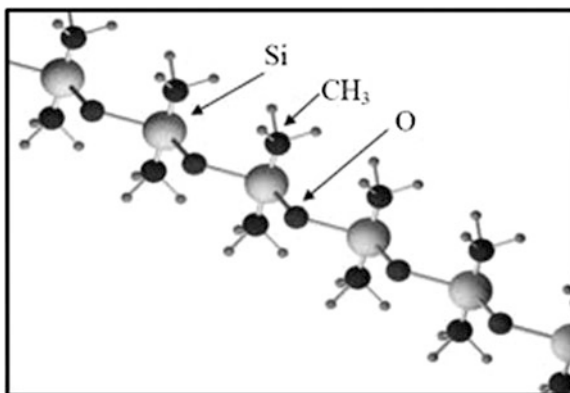
2.3 Silicone Rubber

Silicone rubber is an elastomer composed of silicone-itself a polymer-containing silicon atoms along with carbon, hydrogen, and oxygen. Major use of silicone rubbers is in industry, and there are multiple formulations. Silicone rubbers contains one or two part polymers, and contains fillers to improve properties or reduce cost. Silicone rubber is non-reactive and stable. It is resistant to extreme environments and temperatures from -55 to $+300$ °C, at the same time it is able to maintain its useful properties. Major applications of silicone rubber include automotive applications, food storage products, electronics, medical devices etc. The high permeability of silicone rubber has been attributed to the flexibility of the siloxane linkages in the polymer [31]. Silicone rubber offers good resistance to extreme temperatures, being able to operate normally from -55 to $+300$ °C. At the extreme temperatures, the tensile strength and tear strength and compression set can be far superior to conventional rubbers although still low relative to other materials. Silicone rubber has a very low tensile strength compared to organic rubbers. So care is needed in designing products to withstand even low imposed loads. It is also very sensitive to fatigue from cyclic loading. Silicone rubber coated composite membranes are commonly utilized in industrial membrane based separation processes such as gas separation [32], removal of organic vapors from air [31], pervaporation of various organic species [33] including aroma compounds [34], olefin separation [35] etc.

2.3.1 Structure and Properties of Silicone Rubber

Silicone rubber is a thermoset elastomer having a backbone made up of alternating silicon and oxygen atoms (Fig. 5). The key properties of silicone rubber are its good temperature stability, excellent electrical conductivity, available in medical quality grades and it is easy to give color. Silicone (i.e., polysiloxane)-containing

Fig. 5 Molecular structure of silicone rubber



materials are one of the most widely used polymers in adhesives, coatings and rubber materials in the electronic circuits of microelectronic devices. The important properties of polyorganosiloxanes, which are used in preparing silicone rubber compositions, include excellent weather and thermal stability, low-temperature flexibility, and curability [36].

Silicone rubber possesses an extraordinary property that sets it apart from other elastomers its elastic behavior changes only slightly with change in temperature. Silicone rubber has excellent flame resistance. It has a flash point of 750 °C, an ignition temperature of 450 °C. Only very minor amounts of smoke are evolved during combustion. The principal combustion products are carbon dioxide, water, and ash consisting of silicon dioxide. Silicon dioxide is a good dielectric, it finds use in critical sectors to sheathe cables. It also process high oxidation resistance [37].

Silicone rubber is resistant to chemicals and it can be used in applications including contact with dilute acids and alkalis. But its chemical resistance can decrease with increase in temperature and concentration. Its resistance to various oils compares very favorably with that of organic elastomers. Silicone rubber is a highly inert material and will not react with chemicals. Because of its inertness, it is used in many medical applications and in medical implants. During manufacture, heat may be required to cure the silicone into its rubber form. It is carried out in a two stage process. It can also be injection molded. Mechanical properties of silicone rubber are given in Table 2.

Table 2 Mechanical Properties of silicone rubber

Mechanical properties	
Hardness, Shore A	10–90
Tensile strength	11 N/mm ²
Elongation at break	100–1,100 %
Maximum temperature	+300 °C
Minimum temperature	–120 °C

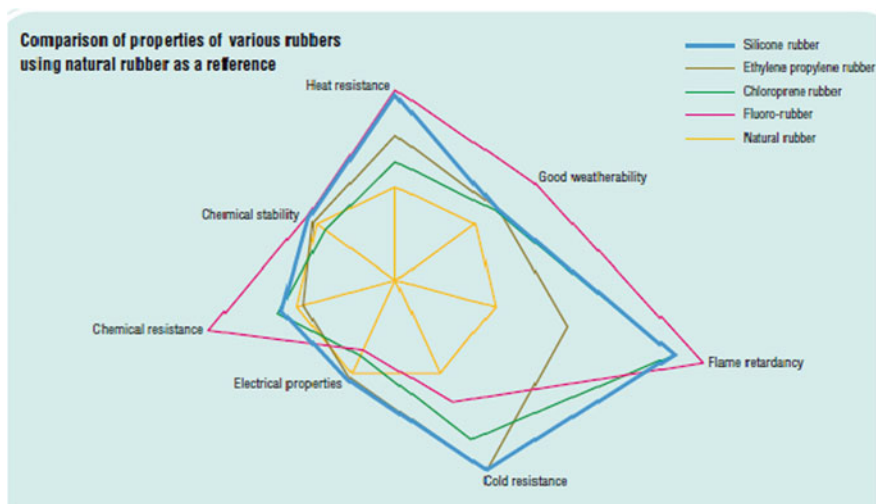


Fig. 6 Comparison of properties of various rubbers using natural rubber as a reference

The siloxane bonds that form the backbone of silicone are highly stable. Compared to organic polymers, these silicone rubbers have higher heat resistance and chemical stability, and better electrical insulation. Silicone molecules are helical and intermolecular force is low. It results in high elasticity, high compressibility, and good resistance to cold temperatures. The methyl groups located on the outside the coil structure can rotate freely. So silicone has distinctive interfacial properties, including water repellency and good repeatability. The tear strength of silicone rubber is generally around 10 kN/m. These products are ideal for moulding large items. Comparisons of various rubbers based on properties are given below (Fig. 6).

Silicone rubber is widely used in many fields due to its high and low temperature resistance, long service life and inertness. But because of the poor mechanical properties, it cannot be used without reinforcement and this deficiency is usually overcome by adding certain reinforcing fillers [38–40], such as carbon black [41–43], fumed nano silica [44], and precipitated silica [45].

2.3.2 Compounding and Processing of Silicone Rubber

Both solid and liquid silicone rubber have a similar basic structure, but different cure and processing methods. High consistency rubber or solid silicone rubber is prepared in large batches and the components are mixed up at high temperatures followed by the addition of a peroxide catalyst. When cross-linking starts the reaction is interrupted before the completion of vulcanization. Then the mildly cross-linked silicone rubber is then rolled out in the form of sheets. Liquid silicone

rubber is a two-component system containing a platinum catalyst (A), a cross-linker, methylhydrogensiloxane (B), and an alcohol inhibitor. The two components are mixed only at the time of processing. Cold runner injection molding equipment is used for processing of liquid silicone rubber. The elastomers long chains cross link during vulcanization and releases a quanta of energy to make it an exothermic reaction. Then it creates bonds in between the long chains and giving rise to a 3- dimensional matrix. As a result the mechanical properties of the rubber are increased. A silicone rubber is prepared from a silicone rubber compound comprising an organopolysiloxane, a reinforcing silica filler, and an organohydrogen polysiloxane by mixing component (C) with components (A) and (B) and heating them at a temperature of at least 100 °C to form the silicone rubber compound, adding an organic peroxide to the compound, and cross linking the compound. The silicone rubber shows a minimal difference in physical properties between primary vulcanization and secondary vulcanization [46].

Liquid silicone rubber has with high thermal conductivity and effective electromagnetic interference (EMI) shielding properties. Silicone-based polymers were prepared by the equilibrium polymerization of cyclic siloxane and end-blockers [47]. Magnesium ferrite nanoparticles with spinel magnetic properties were synthesized by the sol-gel method. A liquid silicone rubber (LSR) nanocomposite was prepared by compounding *a,w*-vinyl poly(dimethyl/methylphenylsiloxane) prepolymer (VPMPs), *a,w*-hydrogen poly(dimethyl/hydrogenmethylsiloxane) prepolymer (HPDHS), catalyst and magnesium ferrite .

Hydrophobic nano silica sol was added into polyvinylmethylsiloxane to prepare reinforced high temperature vulcanized (HTV) silicone rubber [48]. HTV silicone rubber filled with 40 phr hydrophobic nano silica sol showed excellent mechanical and optical properties [48].

There are three different types of crosslinking reactions in silicone rubber (Fig. 7). They are (a) addition curing (where polymer contains vinyl groups and

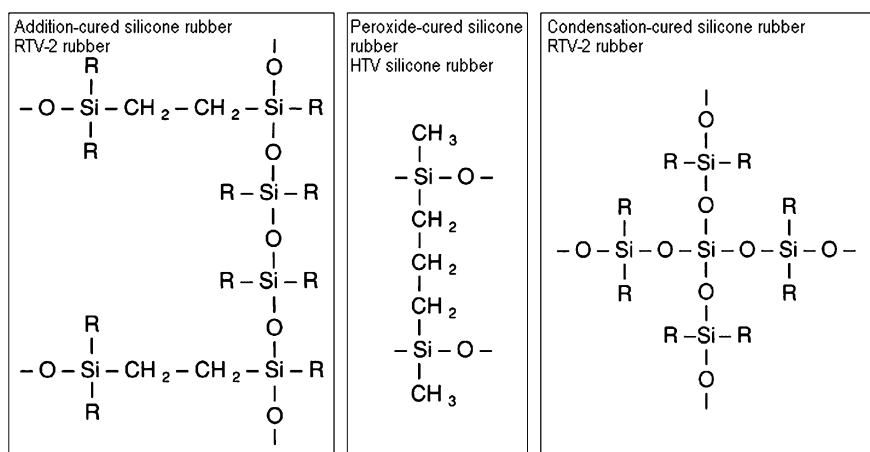


Fig. 7 Three different types of crosslinking reactions in silicone rubber

crosslinking agent contains Si–H groups) (b) peroxide (-initiated) curing (where polymer contains vinyl groups) and (c) condensation curing (between α , ω -dihydroxypolydimethylsiloxanes and silicic acid esters). A platinum catalyst is needed for addition reaction. A tin catalyst is used for condensation curing systems. But, peroxide-initiated curing does not require a catalyst. Addition curing functions by bonding Si–H groups to double bonds. Complexes of platinum or palladium may serve as catalyst and if platinum-olefin complexes are used, curing will take place at normal room temperature. Platinum complexes with nitrogen are used for effecting addition curing at elevated temperatures (e.g. Pt-complexes with pyridine, benzonitrile or benzotriazole). To carry out peroxide curing, it is first necessary to create free radicals. It is possible either with heat or with radiation and different organic peroxides may serve as free-radical generators. Selective crosslinking and superior vulcanizates can be obtained by incorporating vinyl groups into the polymer. Typical catalysts for condensation curing are dibutyltin dilaurate and dibutyltin dioctoate. They function as the catalyst for the reaction between dihydroxypolydimethylsiloxanes and silicic acid esters. The rate of reaction depends on the crosslinking agent, and on the type of catalyst. There is no sulfur used for curing silicone rubbers.

Silicone as an organic polymer is widely used for spacecraft materials which suffered from atomic oxygen (AO) attack [49, 50]. Although the existence of atomic oxygen was known in the early days of space exploration, an awareness of the damaging effects on spacecraft materials was not well-known until the space shuttle began flying missions at much lower altitudes in low earth orbit (LEO). The surface shrinkage of the oxidized silicone leads to cracking of the partially oxidized brittle surface. Such cracks resulted in further exposure to atomic oxygen and ultimately decreased the transmittance of silicone [51–53]. For example, the refractive solar concentrator lenses are fabricated from flexible silicones. Under the radiation of charged particles in space environment, the silicone would be aged, which directly influences the reliability and lifetime of a spacecraft [54, 55].

So a reasonable transmittance of the silicone materials is very important for the solar concentrator lenses in LEO and other space environments. In the traditional silicone rubber industry, the silicone coupling agents are often used to treat inorganic additives, which were used in organic polymers, and change their hydrophilic surfaces into hydrophobic surfaces. This method can enhance the wettability of organic polymers to inorganic additive, and then form chemical bonds between them. Therefore, silicone coupling agents have the capability to develop “molecular bridge” in the interface of organic and inorganic materials. Figure 8 shows the ‘molecular bridge’ mechanism [56].

Silica films were deposited on flexible silicone rubber using solgel method. The surface morphology indicates that the silica sol can easily form a uniform thin film on the surface of silicone rubber pretreated by high concentration coupling agent. After depositing silica films, both AO erosion resistance and optical transmittance of silicone rubber are improved. The procedure for preparing sol–gel coating films is schematically shown in Fig. 9.

Fig. 8 The ‘molecular bridge’ in the interface of silicone rubber with silica films by silicon coupling agents [56]

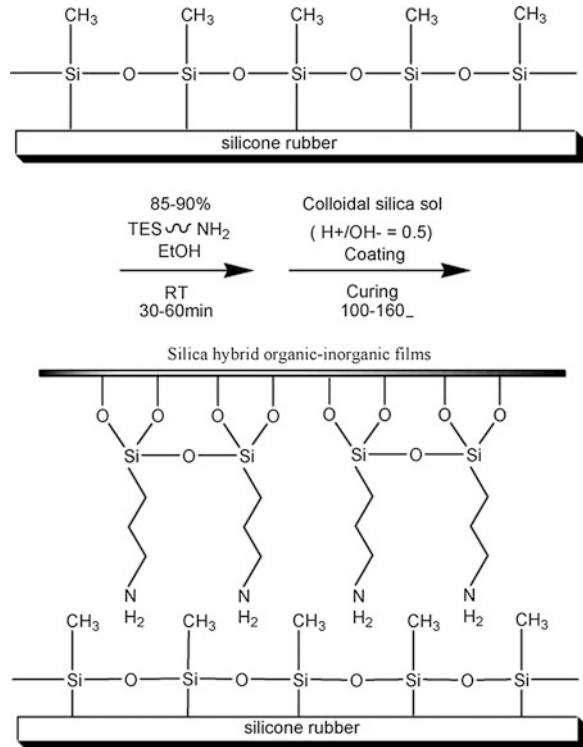
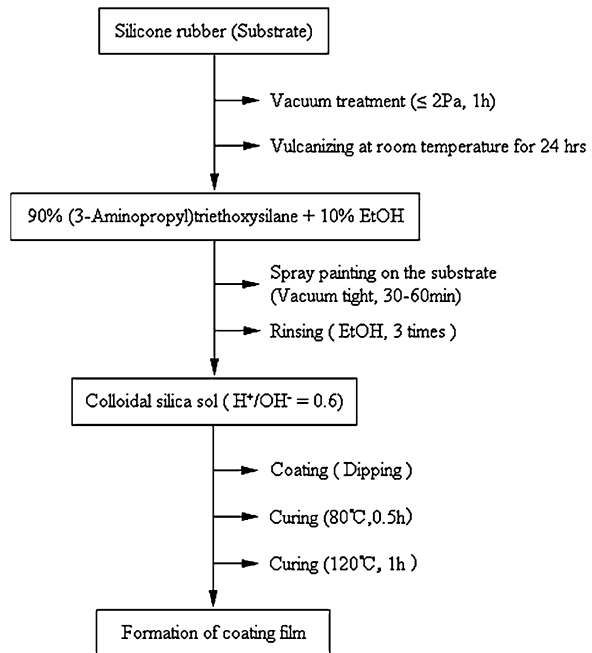


Fig. 9 Preparation process of sol-gel coating films on the silicone rubber substrate [56]



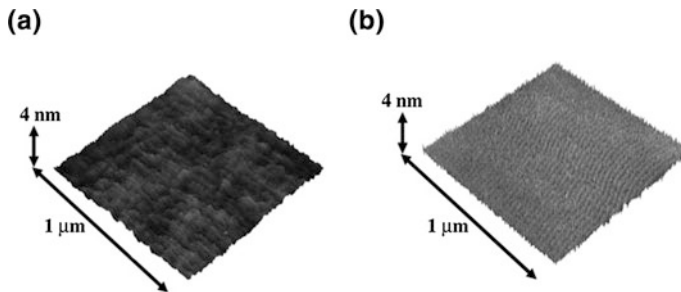


Fig. 10 Surface morphologies of silicone rubber before and after the plasma irradiation [57]. **a** Before plasma exposure. **b** After plasma exposure by Ar/O₂ glow discharge, 5 min

Hino et al. [57] reported that the surface wettability of silicone rubber could be enhanced by Ar, Ar/H₂ and Ar/O₂ plasma irradiations. Silicone rubber is an electrical insulator, so that the charge-exchanged argon atom might have contributed to the enhancement of surface wettability. The mixing of oxygen in an argon plasma significantly increased the wettability, compared to Ar and Ar/H₂ plasmas (Fig. 10). This result suggests that the chemical reactivity to water is enhanced by the reactive oxygen species.

2.3.3 Applications

Silicone rubber is a synthetic compound known for its weatherability and ability to maintain useful properties over a wide range of temperatures. Silicone rubber is a thermal and electrical insulator and is resistant to oxidation, and degradation from ultraviolet radiation. These properties make silicone rubber excellent for electrical insulators and the properties of silicone rubber come from the structure of the polymer and the heat stability and resistance to oxidation and weathering are derived from the strength of the silicone-oxygen bonds. A flexible polymer chain gives low surface energy (hydrophobicity) and low temperature flexibility.

Dimethylsiloxanes can be modified by changing the carbon groups bonded to the silicone. Silicone rubber products include automotive applications to a large variety of applications such as cooking, baking, food storage products, sportswear, footwear, electronics, home repair, hardware, and host of unseen applications. Organic (containing carbon) side groups attached to the silicone atoms allow for crosslinking and tailored applications. The self-healing property of the silicone rubber broadens its application profile to many areas [58].

2.4 Fluoro Elastomers

Fluorinated elastomers have special applications particularly due to their semi-crystalline or totally amorphous nature and the unique combination of relevant

properties. The first fluoro elastomers discovered was polychlorotrifluoroethylene (PCTFE) with low molecular weight and polytetrafluoroethylene (PTFE) with high-molecular weight [59] respectively in 1937 and 1941 and several fluorinated homopolymers came thereafter. These synthetic elastomers have high resistance to oxidation and have excellent hydrolytic stability [60], which is attributed to the low polarizability and the strong electronegativity of the fluorine atom.

2.4.1 Processing and Vulcanization

Similar to other elastomers fluoro elastomers have also must be compounded and vulcanized. The curing (crosslinking) changes both the physical and chemical structure of the material and creates three-dimensional structures capable of exhibiting good mechanical performance. The fluoro elastomer additives allow the easy processing of narrow molecular weight metallocene catalyzed resins with simultaneously improving their optical and mechanical properties. The vulcanization mechanisms of these elastomers are quite similar with that of halobutyl rubber, since both involves halogen elimination step. The elimination of halogen atoms creates crosslinking sites in these elastomers. The mechanism involving in this reaction can be of two types- ionic and radical curing [61–71].

Ionic Curing

In this curing process, a nucleophile initiates a dehydrofluorination reaction which is characterized by the simultaneous elimination of the fluorine atom and an adjacent hydrogen atom. This causes the formation of a double bond in the elastomer backbone. Even though a large number of curatives are useful in fluoro elastomer systems, amine-based ones are most significant. The curing mechanism involved in a vinylidene fluoride (VF_2) site followed by an amine addition is explored by using ^{19}F and ^1H NMR, FT-IR techniques coupled with solid-state curing experiments (where double bonds are formed by dehydrofluorination and nucleophiles are added to the double bond) [65, 72]. The amine curing agents are also used along with MgO [65, 73, 74]. The main advantage of amine based curatives is their capability to enhance rubber-to-metal bonding especially the hexamethylene crosslinks can impart better dynamic properties. Acid acceptors are used in the process of diamine curing, which play a multirole, since these compounds can affect dehydrohalogenation, assist in hydrolysis of the Schiff base and regenerate the free amine from its hydrofluoride. Similar to this system, dihydroxy cure systems were also developed which offers dramatically improved compression-set resistance, excellent heat stability and hydrolytic stability with greatly improved processing safety. Even though amine based curative system is very convenient, it has a disadvantage in finding more reactive base unlike carbamate salts of amines and other Schiff bases [75].

In addition to the amino system discussed so far, bisphenol curative is the other frequently used curing agent via ionic mechanism. The most commonly used compound is bisphenol-bis(hydroxyphenyl hexafluoropropane) [76] due to the processing advantage. Others, like hydroquinone, substituted hydroquinones and 4, 4'-disubstituted bisphenols are also used commercially to lesser extents [77]. The bisphenol does not react with polymer in the absence of accelerators [72]. So an onium (phosphonium, ammonium, etc.) salt in combination with a metal compound is often used as an activator for this curing reaction. The onium salt acts as phase transfer catalyst and determines the phenolate-anion generation during the curing reaction. This is very important as the phenolate-ions are substituted for fluorine atoms at unsaturated carbon atoms leading to crosslinking. The formation of double bonds in the polymer backbone is the rate determining step in this reaction [64]. The quaternary salt catalyst regenerates repeatedly and so its amount in the compound is several times lower than that of the stoichiometric composition. Crosslinking continues up to the use up of bisphenol. Fluoroelastomers containing PAVE are not usually cured with bisphenols [78]. The main drawback of bisphenol cures is the presence of some unsaturation in the vulcanized parts.

Metal compounds are also useful as curatives, where they serve a dual purpose. It absorbs certain gaseous and acidic materials which are involved during curing and also attacks the fluoroelastomers chemically and weakens it. It also provides a long-term aging stability.

Peroxide Curing

Peroxide crosslinking is basically a free radical process. It involves the thermal decomposition of peroxide to provide free radicals which abstract hydrogen from the methylene groups along the polymer chain, and the resultant polymeric radicals interact, directly or through the intermediary of radical traps to form crosslink's. Peroxide crosslinking occurs at specific sites available on the cure site monomer (CSM). The cure-site monomer and curing mechanism was originally developed for an improved low-temperature fluoroelastomer based on vinylidene fluoride (VF₂) and perfluoromethyl vinyl ether (PMVE).

Two different pathways are developed to increase the efficiency of peroxide cure vulcanization of fluoroelastomers. The first one concerns the increase of the content of hydrogen-containing groups in the copolymer, such as in TFE/P copolymers (tetrafluoro ethylene and propylene). The hydrogen of tertiary carbon atom in propylene units is a little screened (only from one side from fluorocarbon groups the energy of the C-H bond is lowered by the induction effect of CH₃ groups). So, these types of H atom are easily accepted by free radicals with a high yield of polymeric radicals and formation of crosslinks. These polymers are cured by a peroxide co reagent (i.e. radical trap) system. The reaction mechanism of peroxide curing with coagent is well known and described in the literature. These more stable radical intermediates, in turn, abstract halogen (X) atoms from the polymer, generating polymeric radicals. The driving force for such a chain

reaction during propagation is the transfer of an X atom from the electron-poor fluoropolymer to the electron-rich hydrocarbon radical on the radical trap. Among the various peroxides and co reagents, *a,a*-bis(*t*-butyl-peroxy)diisopropyl benzene and triallyl isocyanurate (TAIC) and triallyl cyanurate (TAC) are most suitable [65, 78–81]. Peroxides, in the presence of acid acceptors, act as good vulcanizates. Adding tributyl stannane or triethyl silane also improves curing. It is desirable that the bromomonomers copolymerize to high conversion with minimum chain transfer and inhibition. For good curing performance, aliphatic peroxide, a suitable radical trap, and an inorganic acid acceptor are required. The introduction of iodine-containing fluoroelastomers facilitates the molding process considerably and makes possible injection molding. I/Br-fluoroelastomers combine the properties from iodine as chain end and from Br in the polymer chain.

Other Systems of Radical Curing

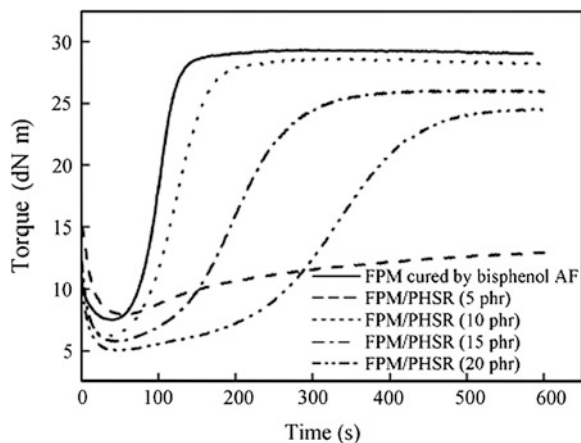
Curing also occurs via certain other mechanisms, other than the exact ionic or radical processes. For instance, although thiol-ene systems have easily led to vulcanize hydrogenated elastomers, this process has been used scarcely to cure fluoroelastomers because of the difficulty in the availability of mercapto side groups. However, an original trifluorovinyl ν -thioacetate monomer (FSAc) was recently used to copolymerize with VDF [82], and the resulting copolymer was hydrolyzed to generate elastomers bearing mercapto lateral groups.

Radiation can also induce curing reactions in fluoroelastomers. Fluorinated polymers containing hydrogen (including VDF-base copolymers) and copolymers of TFE and HFP can be crosslinked with different degrees of effectiveness by high-energy radiation. Several reports have come out explaining the radiation crosslinking of fluoropolymers [83–85] and many articles detail different aspects of this process, recently reported by Logothetis [86] and Forsythe [87, 88]. The mechanism of radiation crosslinking of fluoroelastomers is similar to that proposed for other elastomers: it is a typical radical mechanism closed to peroxide curing. In this way, the total dose for optimum crosslinking can be lowered and the properties of gum can be considerably improved. Doses of 10–15 M rad are sufficient to give excellent properties and the cured parts remain clear and colorless [84]. The advantage of radiation cured materials is that they do not contain any filler or chemical, i.e. any impurity that can be extracted from the vulcanizates which is so important in the semiconductor industry.

Post-curing of Fluoroelastomers

For getting good physical properties researchers follow two step curing process in other words post curing. The first step of this is heating the material at high pressure (compression molding) and in the second step it is heated at atmospheric pressure for long time and it is more applied for chemical curing than for radiation

Fig. 11 Vulcanization curves of the blends at 170 °C [95]



crosslinking [73, 77]. Smith and Perkins [89] observed that the post-curing enhances crosslinking as compared to normal curing process and it was explained by the formation of aromatic rings via Diels–Alder addition. Similarly other works also reported on post-curing [90–92]. They could explain a thermally induced bond-breaking and making process occurring during post-cure. Even though a lot of work has been performed in this area, the true mechanism behind it is not yet understood clearly. Usually the cured parts of this elastomer can be made by curing perfluoroelastomers with a high-energy electron beam followed by a post-cure. The chemical resistance and compression set properties of these materials are excellent, but the tensile properties are lower because of the absence of any reinforcing fillers in it [93].

The curing process of perfluoroolefins containing Br and I atoms [93] and those containing nitrile groups are well established. Vulcanization of perfluoroelastomers with nitrile groups is brought about by the catalytic interaction of tetraphenyltin or silver oxide on the pendant cyano group, thereby creating a triazine crosslinked structure [80, 94].

Self Curing of Fluoroelastomers

Self-vulcanizing blends of phenol hydroxy silicone rubber (PHSR) and a fluoroelastomer (FPM) were fabricated by Wang et al. [95] and they observed smaller S_{\min} values and longer scorch time for FPM/PHSR blends than FPM with the same level of bisphenol curing agent. Figure 11 represents the vulcanization curves of FPM/PHSR obtained from the rheometer at 170 °C. It is clear that the increase of PHSR loading in FPM blends decreased both minimum and maximum torques and increased the scorch time and the optimum cure time except for FPM with 5 phr PHSR.

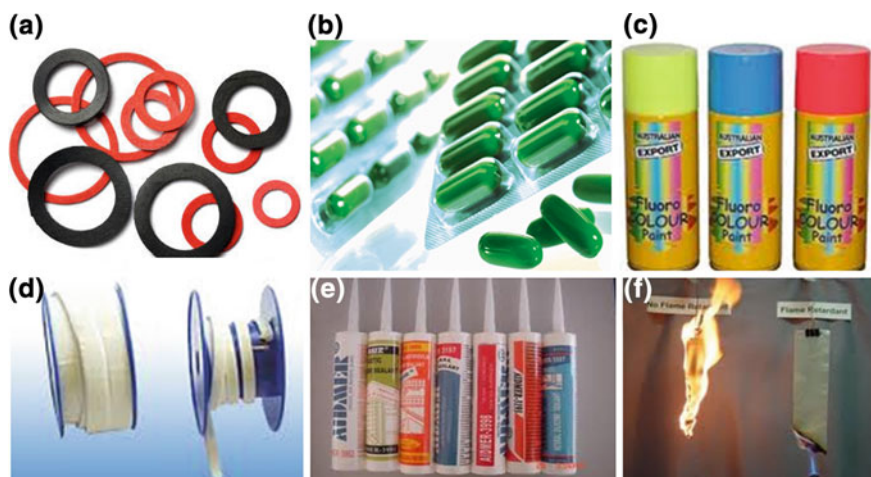


Fig. 12 General applications of poly fluoro-elastomers (a) O-Rings and Gasket (b) Packing (c) Paints (d) Grommets (e) sealants and (f) flame retardants

2.4.2 Properties and Applications

In spite of their high cost (due to the unusual processing of polymerization, cost of purifying the gaseous monomers and small scale production), these polymers have found major applications in modern technologies as given in Fig. 12. These elastomers undergo a wide variety of chemical reactions and operating conditions [62, 65, 93, 96, 97] in these industries. Fluoro elastomers are thermally stable and in general can replace the three commonly used environments, aliphatic hydrocarbons (mineral oil), deionized water, and dry heat. The main characteristics of fluoro elastomers that make them applicable in industries can be summarized by the following points.

1. Outstanding high temperature resistance.
2. Improvements in broad temperature damping characteristics and low-temperature resilience [80].
3. Excellent resistance to fuel, oil, acid and chemicals.
4. Good resistance to gas penetration and radiation and flame retardancy.
5. Stable with thermal, chemical, and UV environments, so used in building industries (paints and coatings resistant to UV).
6. Poor swelling in oils and hydrocarbons, but resistant to heat, ageing, concentrated acids and alkalies.
7. Excellent resistance to heat, fluids, and oxidizing media combined with good physical properties [98–101].
8. Petrochemical and automotive industries, aerospace and aeronautics (use of elastomers as seals, gaskets, making tanks of liquid hydrogen for space

- shuttles), chemical engineering (high-performance membranes) [105], static and dynamic seals, as diaphragms, valve seals, hoses, coated cloth, shaft seals, expansion joints, etc.
9. In optics as core and cladding of optical fibers, for treatment of textiles, stones (especially for old monuments), microelectronics.
 10. Semiconductor processing equipments [106, 107] and to prevent equipment leakage, equipment failure and costly downtime [80].

2.5 Polyurethane Rubber

Polyurethane was invented by Otto Bayer and his coworkers in 1937. Polyurethane is a synthetic elastomer. It is a combination of carbamate links. The carbamate links can be formed by a chemical reaction between isocyanate and alcohol. The polyurethane polymer comes under reactive polymers branch because it is formed by reactive groups such as iso cyanate and alcohol. Most of polyurethane elastomers are based upon segmented block copolymers of the general molecular formulae $(AB)_n$. It contains alternating soft and hard segments [102, 103]. Generally the soft segment consists of polyether or polyester diols, and the hard segment is formed by the reaction products of diisocyanates with a chain extender.

2.5.1 Synthesis of Polyurethane

The polyurethane elastomer can be formed by different combinations of diols and diisocyanates in the presence of various catalysts. So, the exact property of polyurethane depends up on nature of diol and isocyanate and the catalyst. Mehdi Barikani et al. [104] prepared polyester based thermoplastic polyurethanes, and polyether based thermoplastic polyurethane by using polyol and toluene diisocyanate through prepolymer method. In this method they have used ethylene glycol (EG), 1,3-propane diol (PD), 1,4-butane diol (BD), 1,6-hexane diol (HD) and 1,10-decane diol (DID) as chain extenders for getting good thermal properties. They have concluded that polyester based thermo plastic polyurethanes have high tensile strength, and thermal stability than poly ether based thermo plastic polyurethanes. The physical and mechanical properties can be varied which depends up on length of the chain extender. This is due to the fact that if chain length is large then the phase separation will be more.

As we know the conventional polyurethane is insoluble in aqueous media. If we want to increase the solubility of poly urethane, we have to incorporate ionic or nonionic hydrophilic segments in the back bone of polyurethane chain. These kinds of aqueous dispersible polyurethanes are playing crucial role in coatings industry.

2.5.2 Structure–Property Relationship

Generally, the polyurethane contains carbamate (urethane) linkages. This could be formed by the addition reaction between the isocyanate and alcohol. So much work had been carried out to understand the structure- property relationship of polyurethane elastomers. Cooper and his group [105] were the first to report on the structure property relationship in polyurethane elastomer. They have noticed that the hard and soft segments are the cause for the phase separation process. The phase separated hard and soft segments are the main reasons for enhanced properties of thermoplastic polyurethane. Pukánszky et al. reported on the two sets of polyurethanes from polyether and polyester polyols, and 4,4-methylene bis(phenyl isocyanate), 1,4-butanediol is a chain extender [106]. The nature of polyol has strong influence on the structure as well as properties of polyurethane. The polyurethane prepared by polyester polyol shows high T_g . This is due to strong interaction between hard and soft segments in polyester polyurethane. Also the transparency and crosslink distribution in polyester polyurethane is higher than polyether polyurethane. The high transparency and crosslink distribution of polyester polyurethane is due to the formation of smaller dispersed particles of the hard phase. The property of polyurethane can be changed by addition of nano particles such as nano clay, carbon nanotube and graphene etc. Xia Cao et al. reported on the changes in structure- property relationship by the addition of organically modified nanoclay to the polyurethane [107]. The clay nano particles enhance the cell density and reduce size of particle compared to pure polyurethane. Nano clay enhances the glass transition temperature and crosslink density of polyurethane. This is due to the formation of hydrogen bonding between clay and polyurethane [108].

2.5.3 Processing of Polyurethane Rubber

Like natural rubber, polyurethane rubbers can be processed on mills or in internal mixers. A suitable polyurethane rubber is formed from a mixed ester of adipic acid with ethylene glycol and propylene glycol terminated by OH groups and having a molecular weight of approximately 2,000 by reaction with an excess of 4,4-diphenyl methane diisocyanate to form the NCO prepolymer and subsequent reaction with butanediol for chain extension. The polyurethane rubbers are converted into polyurethane rubber mixes by the same methods which are used for natural rubber. For polyurethane rubbers, the cross linking agent may be a diisocyanate, a peroxide or sulphur.

2.5.4 Applications

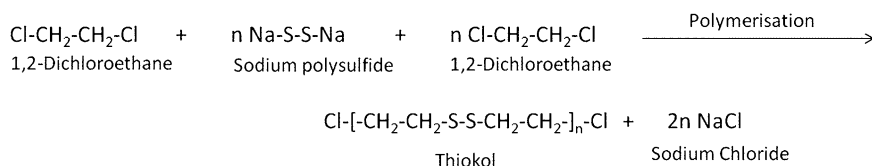
Polyurethane products have tremendous applications in various fields including building construction, furniture, automobile seats, house decorations, filling of spaces and cavities, water vessels, electronic components, adhesives etc.

2.6 Polysulfide Rubber

Among the various synthetic and natural rubbers known to man polysulfide rubbers also come under the class of special purpose rubbers. It was discovered in 1926 by Joseph Cecil Patrick, an American chemist. Like many other prominent inventions in science, polysulfide rubber also is a child of serendipity. Patrick and his companion Mnookin were attempting to synthesise inexpensive antifreeze using ethylene dichloride and sodium polysulfide when they came across a new structure. The substance was like gum with a terrible odour which clogged a sink in the laboratory and none of the solvents they tried could remove it. Their frustration changed to delight when they realized that it was a new substance highly resistant to any kind of solvent. The elastomer became famous under the trade name Thiokol (1929) (after the Greek *theion*, “brimstone” [sulphur] and *kommi*, “gum”). The commercial polysulfide rubbers from Thiokol corporation are trademarked brands Thiokol FA, Thiokol ST and Thiokol LP. The disadvantage due to the bad odour of polysulfide polymers is overcome by the fact that it has become the basis of much advancement in technology. Many construction and aerospace industries are indebted to the technical performance and versatile properties of these polymers.

2.6.1 Synthesis

Polysulfide rubber (Thiokol) is synthesised by the condensation polymerization reaction involving dihalide derivatives of aliphatic hydrocarbons (e.g. 1, 2-dichloroethane) and alkali metal polysulfides (e.g. sodium polysulfide). The products obtained are thiokol and sodium chloride as shown below.



Brief procedure is described here. 40 g NaOH is dissolved in 200 ml distilled water in a round bottomed flask and is placed in a water bath. 15 g sulphur is added to this and refluxed for 30 min. A reddish brown solution is obtained and 500 ml water is added to this. 2 ml dichloromethane is added to this and refluxed for another 45 min till the yellow colored polysulfide rubber is obtained. The contents are cooled at room temperature, washed with water and coagulated with acids.

Thiokol FA has a linear structure with hydroxyl groups at the chain ends, formed by hydrolysis of dichloromethane during polymerisation. Thiokol ST when formed first has a branched structure, after a second treatment some of the disulfide

bonds are cleaved and thiol groups are left at the chain ends. This imparts good processability to the polymer.

2.6.2 Structure and Properties

Polysulfide rubbers typically consist of sulphur–sulphur linkages which connect short sequences of ethylene and the chains are terminated by reactive mercaptan groups that are also used for interlinking. These rubbers can be made into two main categories polytetrasulfides and polydisulfides, which have the general formulas $[-R-S-S-S-S-]_n$ and $[-R-S-S-]_n$ where R is an organic radical. Polysulfide rubbers are produced in both solid and liquid form corresponding respectively to high and low molecular-weight and also as aqueous dispersions, or lattices. The liquids are 100 % polymer itself unadulterated with solvents or diluents whose viscosity ranges from 5 poise to 700 poise. It is formed by the reduction degradation of high- molecular mass polysulfides. It can be converted to elastic rubbers with properties somewhat equal to that of cured solid polysulfides [109].

The high sulphur content and absence of unsaturated bonds in the polymer are the main reasons for the special properties like high resistance to swelling in solvents, fuels and oils; resistance to sunlight, moisture and impermeability to gases. Also the saturated structure is responsible for its excellent resistance to oxidation, weathering and ozone. The thermal properties depend mainly on the polymer structure and in most cases the serviceability range is from -51 to 121 °C. The molecular weight of the solid polymer is of the order of $(200-500) \times 10^3$; a density of $1.27-1.60$ g/cm³ and glass transition point from -23 to -57 °C. The high density and high resistance to hydrocarbon oils of the polymer comes from the high sulphur content, about 80 percent by weight. Conversely the polymer has a tendency to relax and flows under pressure due to the low stability of sulphur–sulphur bonds. Because of its saturation, the polymer does not exhibit high tensile values, the upper maximum limit sometimes being $10.3-12.4$ MPa. It does not possess good abrasion resistance also. Like other synthetic elastomers, polysulfide rubber also requires reinforcing fillers to achieve optimum physical properties. Chemical modification imparts improved flexibility, impact resistance, low shrinkage, less internal strain, better wetting properties and lower moisture absorption to these rubbers. The polysulfide rubbers can be easily broken down to less molecular weight products due to the flexible backbone.

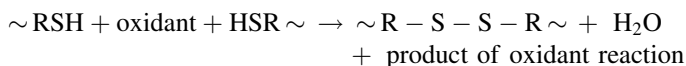
2.6.3 Compounding and Processing

FA and ST grade Thiokols are commonly subjected to compounding. Unlike natural rubber, FA rubber doesn't break down easily by milling process. It has to be softened by using plasticizers like mercaptobenzothiazole disulfide (MBTS) and accelerated by adding diphenylguanidine (DPG). The ratio of MBTS is the key factor determining the extent of plasticization. Plasticization can be started with

very small ratios of MBTS (0.3) and DPG (0.1). By varying the MBTS by 0.05 parts, the adequate amount can be found out. Even if with a small excess, the rubber would end up as a sticky, nonreclaimable mass on the mill. ST grade Thiokol poses no such difficulties in compounding and is used as such.

Carbon blacks (thermal blacks, semireinforcing and fast-extruding furnace blacks are preferred) are commonly used as fillers in polysulfide rubbers. This provides reinforcement, increases tensile strength and compression performance and also reduces the cost of the compound. Other fillers like zinc oxide, TiO_2 and lithopone are also used nowadays. Recently polysulfide sealants are being modified using additives of fullerenes and carbon nanotubes. The chemical, mechanical and adhesive property increased significantly by the strong effect of nanoparticles [110]. Clay is not preferred as it retards vulcanization. Addition of coumarone indene resin can improve the tackiness of the compound. FA grade requires about 10 parts ZnO while ST grade requires 5 parts of zinc peroxide and 1 part of $\text{Ca}(\text{OH})_2$ for curing. Use of stearic acid (1 part) could prevent the sticking of stock on the mill and helps in good dispersion.

Vulcanization of polysulfide rubbers usually proceed through the oxidative polycondensation reaction between oligomer SH groups with transition metal dioxides (MnO_2 , PbO_2) [111]. For vulcanizing polysulfide rubbers, different inorganic oxidants like zinc oxide, p-quinone dioxime, and a mixture of altax and diphenylguanidine (activators) are also used. They oxidise the terminal SH-groups and results in lengthening of macromolecules and the mercapto groups are crosslinked through oxidation polycondensation.



Curing can also be effected with rf current, photocuring or using peroxides. The simplest vulcanizing agents are oxygen in air and molecular sulphur. Vulcanized polysulfide rubbers exhibit inferior mechanical properties when compared to other vulcanized synthetic rubbers.

Conventional mixing and fabricating equipments like two-roll mill or Banbury type internal mixers are used for incorporating fillers, curing agents and additives into the solid rubber. Further processing operations like extruding, calendaring, molding or steam vulcanization could be done in the normal manner but with good factory control than that of general purpose rubbers. Liquid polysulfide rubber compounds use internal mixer, three-roll paint mill, colloid mill or ball mill for mixing. Depending upon the specific characteristics of the end product, the resulting products may be applied by brushing, spraying or casting. Owing to their versatile nature in formation of end products, liquid rubbers are dominating over solid-rubber in application field. Curing of these rubbers can be done over wide temperature ranges. The high popularity of this polymer in a variety of industrial applications lies in the fact that they are able to cure even at room temperature.

2.6.4 Applications

Polysulfide rubbers have high resistance to petroleum solvents, organic solvents (esters, ketones etc.), aromatic fuels, oils, greases, sunlight, ozone and UV rays. Hence they are used as static seals for aircraft, building and marine industries where no other material serves the purpose. When these sealants are chemically modified an enhancement in the inherent properties occurs. Some of them includes modifications with polythio-urethane-urea [112] or with a silyl group [113]. They are also used as binder for rocket fuel, flexible moulds, dental moulding compounds and electrical encapsulations. Polysulfide polymer is absorbed in leather and the cured product is highly resistant to oil and chemicals without loss in pliability and is used for making packing seals, boots and gloves. When polysulfide and rubber are combined, durable roofing materials are produced.

Polysulfide rubbers are also used for applications like gaskets, washers, diaphragms, rubberized fuel storage tanks and various types of oil and gasoline hose where high solvent resistance is required. Another use of these rubbers is in the manufacture of inks, paints and coatings. Care should be taken when they are used on plastics as they will degrade PVC and ABS. *Mostly liquid rubbers are employed in applications that include cold-setting casting* and molding such compounds exhibiting flexibility, low shrinkage and excellent dimensional stability. Liquid polysulfides may also have other industrial applications like coatings, adhesives, modifiers of epoxy resins etc. Polyaniline-thiokol rubber composite coatings when applied on steel surface is very effective in preventing corrosion [114].

2.7 Chlorosulfonated Polyethylene

Chlorosulfonated polyethylene is a synthetic rubber, produced by the controlled treatment of polyethylene in solution by chlorine and sulfur dioxide. Hypalon is a trademark for chlorosulfonated polyethylene (CSPE), noted for its resistance to chemicals, temperature extremes, and ultraviolet light. It was a product of DuPont Performance Elastomers, a subsidiary of DuPont [115].

2.7.1 Structure and Properties

The synthetic chlorosulfonated rubber is obtained by the simultaneous chlorination and chlorosulfonation of polyethylene [116]. This chlorosulfonated polyethylene (CSPE) contains a modified polyethylene chain in its backbone with chloro and sulfonylchloride side groups as shown in Fig. 13. This rubber can also be cross-linked as in the case of all other elastomers for technological applications. The $-\text{SO}_2\text{Cl}$ groups and labile chlorine atoms present in CSPE also participate in the vulcanization process. Such materials are known for their high toughness, weatherability, and resistance to oxidation and oil/solvent and they also exhibit

Fig. 13 Structure of Chlorosulphonated Polyethylene

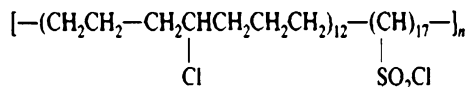
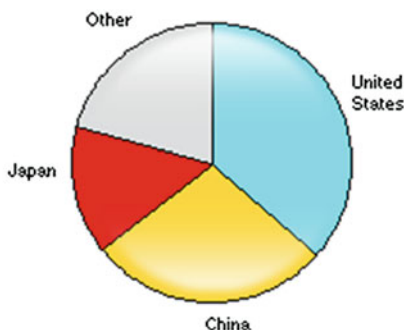


Fig. 14 World consumption of chlorosulfonated polyethylene

World Consumption of Chlorosulfonated Polyethylene—2011



polyethylene properties such as hardness, stiffness and partial crystallinity especially at low-chlorine levels [117].

The density, chlorine content and sulfur content of CSPE are 1.11–1.26 g/cm³, 27–45 % and 0.8–2.2 % respectively. The resistance of CSPE to fire, oil, and microorganisms as well as the surface adhesion behaviour is attributed to the chlorine content in it. Its resistance to ozone, inorganic acids and concentrated alkalis make chlorosulfonated polyethylene superior to other rubbers. On the other hand the increase in chlorine content decreases the low temperature properties. The rubber is impermeable to gas, and has good dielectric properties. Low flammability, excellent green strength, UV resistance and stability are other notable features of CSPE. It exhibits the tensile strength of about 32 MN/m² and a relative elongation of 350–600 % in addition to the good abrasion resistance [118].

The given pie chart (Fig. 14) shows world consumption of chlorosulfonated polyethylene: If we look into the world consumption of chlorosulfonated polyethylene rubber in the year 2011, there is a huge contribution of about 80 % from United States, China and Japan.

2.7.2 Compounding

The common ingredients used for compounding of chlorosulfonated polyethylene are given in Table 3. Magnesia is used as the acid acceptor and the main function of acid acceptor is to act as heat stabilizer to absorb acid byproducts of the curing reaction and to maintain sufficient alkalinity to allow effective curing reactions to proceed. The activator (pentaerythritol) increases the effectiveness of the acid acceptor apparently by solubilizing it in the polymer. Carbon black is the

Table 3 The common ingredients used for compounding of Hypalon

Ingredient	Function	phr
Hypalon-40(35 % Cl)	Polymer	100
Magnesia	Acid acceptor	4
Pentaerythritol	Activator for 2	3
Hard clay	Filler	80
Aromatic oil	Plasticizer	25
Paraffin wax	Process aid	3
Sulphur	Vulcanizing agent	1
Tetra methyl thiuram disulphide	Accelerator for 7	2

preferred filler for CSM vulcanizates because it gives best reinforcement of physical properties and best resistance to chemical degradation, to compression set, and to water absorption. Aromatic petroleum oils are widely used as plasticizers primarily because of their low cost. Paraffin wax and polyethylene glycol are all effective process aids that do not affect scorch safety.

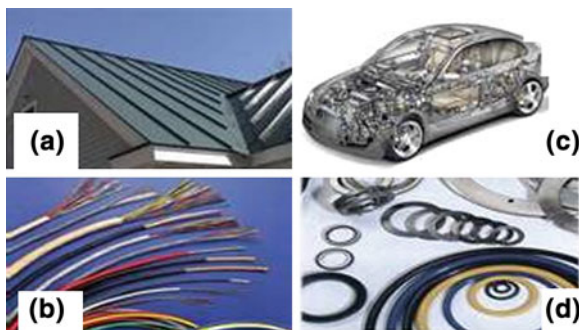
Two types of curing processors are available with CSM elastomers and both are effective regardless of the level of chlorine in the elastomers. Ionic cures of CSM are possible when the acid acceptor is a divalent metal oxide. CSM is also capable of undergoing covalent cross linking, and most applications for CSM make use of this type of curing. Three different systems that are commonly used in covalent cure are sulphur cure, peroxide cure and maleimide cure.

Internal mixing is the most cost efficient volume system for producing well mixed CSM compounds. CSM compounds are successfully processed by compression, transfer or injection molding. Due to the marked thermoplasticity of CSM compounds, multicavity transfer and injection moulds require carefully balanced runner systems and similar flow restrictions for the gates so that uniform filling of all cavities is achieved [119, 120].

2.7.3 Applications

CSPE is highly applicable both in the production of industrial and household goods. It is useful for anticorrosion coatings, insulating cables, automotive hoses, machine parts, floor tiles, magnetic rubber, rubber coated cloth, gaskets, flexible tubes, rolls and linings. It is also used as a film-forming agent in varnishes and paints and as a good adhesive in reinforced concrete. Special applications include escalator handrails, diaphragms, lining for chemical processing equipment, fabricating the inflatable boats and folding kayaks etc. Conductive CSPE composites are also useful in power distribution, audio, and telephone application, as packaging and semi conducting polymeric materials. Image showing applications of chlorosulphonated polyethylene is given in Fig. 15.

Fig. 15 Image showing applications of Chlorosulphonated polyethylene in (a) Construction sector (b) Wire and cable sector (c) Automotive (d) Industrial products sector



3 Conclusion

In the coming years polymer chemists will be able to design new kind of functional elastomers fulfilling specific functions for a definite application. Such new targets are real challenges and should attract the interest of many academic and industrial researchers in this fascinating area. Indeed cure chemistry plays a major role in developing the properties of synthetic elastomers. Each synthetic rubber as discussed has its own applications and by compounding them we can get intended properties for a particular application. Incorporation of nanofillers provides fascinating functional properties to elastomers. The synthesis of new elastomers by direct radical co- or terpolymerization of monomers has been further proved to be a versatile way that offers many opportunities for obtaining wide range of synthetic rubbers. The production and demand of synthetic elastomers are having an increasing market for novel applications. This offers additional chances to a technology that already forms the basis of the commercial production of classes of chemicals which are among the most advanced and successful products. Still there are many challenges in developing new type of elastomers which include the choice of appropriate precursors that would degrade biocompatible compounds. In the rapidly advancing field of tissue engineering, polyurethanes offer numerous opportunities to develop suitable scaffolds. New synthetic protocols such as controlled radical polymerization, atom radical polymerization etc. offer new methodologies for the design of new functional elastomers. Better understanding of the correlation between structure and properties of elastomers is extremely important for the design of new functional materials for various applications.

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