Elastomers Used in the Rubber Lining Industry

In Chapter 5, a general outline of base rubbers was given. In this chapter, more details about the rubbers most frequently used in the lining industry are given.

6.1 Neoprene Rubber

Commercial types of Neoprene rubber undergo changes on storage. From a practical stand point these changes result in a reduction of processibility, an increase in rate of cure, a reduction in processing safety and changes in plasticity. The effects vary considerably from one Neoprene type to another and among the general purpose types, Neoprene W has by far the least tendency to change on storage. The changes are the result of chemical reactions, and therefore are influenced markedly by the temperature of storage, elevated temperatures accelerating the phenomenon and reduced temperatures retarding them. Oxidation plays a major role in the changes that are observed to accompany the extended ageing of raw uncompounded Neoprene. Two types of oxidation occur; chain scission and creation of additional centres of reactivity. Chain scission reduces the average polymer chain length and results in a softer polymer, having a low potentiality for the development of tensile strength. In the raw polymer, the creation of additional centres of reactivity induces the formation of additional crosslinks with a consequent increase in nerve and toughness. In compounded stock, such increased number of reactive centres due to oxidation, accelerates curing at both processing and curing temperatures.

During processing for increasing the molecular break down of Neoprene, peptisers are used. The most effective peptisers are guanidines such as di-o-tolyl guanidines and dithiocarbamates such as piperidinium pentamethylene dithiocarbamate [1]. Aromatic mercaptans which are widely used in peptising natural rubber (NR) will also peptise Neoprene rubber but exert a strong retarding action on the rate of cure. Neoprene type W having greater stability resists both mechanical break down and chemical peptisation. Murray and Thompson [2] have made an extensive study of processing problems with Neoprene. They recognise that Neoprene is capable of existing in three distinct phases which depend on the temperature.

Below 71 °C it exists in what is called the elastic phase. In this phase Neoprene coheres tightly so that strong running bands are obtainable on a mixing mill.
Tank Lining Guide

Between approximately 71 °C to 93 °C it exists in a ‘granular phase’. In this condition Neoprene loses cohesion to it but tends to stick tightly to the mill rolls.

Above 93 °C the Neoprene enters a plastic phase in which it is very soft and has only weak cohesion to itself, showing very little tendency to stick to the mill rolls and has almost no nerve.

A clear apprehension of this three phase cycle in Neoprene gives a good clue to proper processing of all types of Neoprene stocks, while warming in the mill and sheeting in either the mill or the calender. Some small scale manufacturers are skilled to produce fine sheeting from the mixing mill alternatively from a calendering machine. See Figure 6.1 for an example of sheeting from a mixing mill of size 41 cm x 107 cm.

![Figure 6.1 Sheeting from a rubber mixing mill](image)

Processing in a range from 71 °C to 93 °C, where Neoprene exists in the granular phase should be avoided as far as possible. Best dispersions are obtained when fillers are incorporated when the elastic phase is below 71 °C. Fine calendering of high quality stocks having minimum calender shrinkage and carefully controlled thickness of 1 mm which is to be doubled up to the required thickness say of 3 mm, 4 mm, 5 mm or 6 mm in a special device is required for lining application. This is carried out in the plastic phase above 93 °C. However most sheetings where careful control of thickness is not required, is best carried out at temperatures where elastic phase prevails. Crystallisation that takes place in Neoprene at a temperature considerably higher than in natural rubber sometimes influences the processing of Neoprene stocks. This phenomenon may result in a marked stiffening and loss of tack in an uncured compound as a consequence of exposure at room temperature for several days. This effect, which is readily reversible with heat, is off set in order to enable lining applications where thickness building and laminating are involved.
The unique character of Neoprene vulcanisation is that rubber accelerators as a class are not effective. As a matter of fact several have measurable retarding effects and it has to be understood that mercaptobenzothiazole is an extremely potent retarder in Neoprene vulcanisation. Salicylic acid is a fast accelerator leading many a times to scorching or premature vulcanisation at higher dose levels [3].

Sodium acetate is an efficient retarder for Neoprene compounds. It is selectively preferred for mercaptobenzothiazole or benzothiazyl disulfide since its retarding effect does not persist at normal curing temperatures.

Neoprene is resistant to non oxidising mineral acids at elevated temperatures, to concentrated sodium hydroxide and to animal and vegetable oils. It is weather resistant and ozone resistant. The ozone resistance of Neoprene is well deployed in lining of equipment in the cell houses in caustic soda industry where ozone environment prevails. Its good elongation at low operational temperatures, at -46 °C and its excellent abrasion and tear resistance make it an ideal candidate for tanks lining in chemical industry. Special compounding makes Neoprene more resistant to water and a variety of aqueous solutions. Properly compounded it is self-extinguishing when exposed to flame.

### 6.1.1 Compounding Neoprene for tank lining application

Lining with Neoprene sheets requires excellent building tack. G type Neoprenes are quite tacky, with red lead (lead tetroxide – Pb₃O₄) curing system insuring a good resistance to water. At times blends of G and W types of Neoprene are used to balance the level of building tack and to eliminate possible handling and processing problems. The G types differ from W types in that the former are interpolymerised with sulfur and contain a thiuram disulfide stabiliser. The two classes are distinguished easily by their colour – the G types are amber while W types are either creamy white or silver grey. A typical blend can be 80 parts of G type and 20 parts of W type Neoprene. The selection of fillers to control tack is important because some compounding ingredients such as clay tend to produce a dry stock. Silica fillers help to retain good tack in Neoprene. Tackifiers such as coumarone-indene resins are used in compounding Neoprene for increased tack. Oils and waxes which bloom out during vulcanisation and even during storage of unvulcanised stock should be avoided. Swabbing the dry Neoprene sheet surface with toluene provides instant tack for application.

Red lead is an ingredient generally used in all Neoprene compounds for tank linings for good water and chemical resistance. But it should not be used in compounds of Neoprene designed for contact with food or potable water. Tubes or pipes for conveying potable water are made of ethylene-propylene diene terpolymer (EPDM) rubbers.

While calendering the Neoprene stock it must be prewarmed uniformly before being fed into the calender rolls. Stock temperature will change as the quantity of the stock at the nip varies. This causes fluctuation in viscosity of the stock and in roll pressure leading to rough sheet with differing thickness. Roll temperature in calendering must be accurately
controlled. The processing behaviour of Neoprene at the calender or mill is temperature sensitive and varies from one compound to the other. Generally the temperature differentials of the calender rolls for Neoprene calendering are:

- Top roll - 90 °C
- Middle roll - 85 °C
- Bottom roll - 35 °C/40 °C

Air blisters can be avoided easily in thinner sheets that can be plied up to the required thickness, rather than one step calendering of a thicker sheet that induce formation of air blisters during calendering.

Shrinkage can cause premature failure of the lining. The place to minimise shrinkage is at the calender or at the warming/sheeting mill. High temperature processing reduces shrinkage.

In addition to proper compounding of the elastomeric lining it is important that the tank is designed and fabricated so that the lining can be applied without formation of air pockets between the lining and the metal surface. Air pockets promote permeation of the liquids media leading to damage of the metal surface at the place and resulting in total lining failure.

The metal surface of the tank/vessel to be lined with Neoprene should be either sand or shot blasted and cleaned with a solvent to make the surface free from any grease or oil. One coat of Neoprene based primer is applied over which one coat of isocyanate bonding agent is applied and allowed to dry. A top coat of Neoprene based tie-cement is then applied and the lining with Neoprene sheet is done. The tie-coat will have a solid content of about 25%. The drying time for the prime coat can be four hours and for the other coats the drying time can be one hour between coats [4]. The drying time given here is only indicative as it depends on the type of solvent or the mixture of solvents. Normally longer drying time is given for the prime coat as the prime coat film thickness is more than that of the subsequent coats. In essence the coatings should be thoroughly dried before the lining sheet is applied to avoid blister formation during vulcanisation caused by rapid evaporation of residual solvent in the coating. The lining is applied very carefully without stretching of the sheet. All the air must be rolled out from beneath the lining with a knurled roller. In other words, the metal surface of the tank must be free of any pits and rough welds. Welded corners should be radiused and should not be square.

The lined tanks are cured \textit{in situ} to achieve good adhesion with metal. Neoprene linings can be cured with air, steam or hot water. Many curing cycles for Neoprene are adopted depending upon the compound type, size and shape of the equipment.

Typical curing cycles for Neoprene linings are given in Table 6.1.
Table 6.1   Typical curing cycles for Neoprene linings

<table>
<thead>
<tr>
<th>Curing medium</th>
<th>Temperature</th>
<th>Time of cure (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>70 °C</td>
<td>96</td>
</tr>
<tr>
<td>Air</td>
<td>100 °C</td>
<td>24</td>
</tr>
<tr>
<td>Air</td>
<td>121 °C</td>
<td>8</td>
</tr>
<tr>
<td>Air</td>
<td>141 °C</td>
<td>4</td>
</tr>
<tr>
<td>Open stream in autoclave</td>
<td>120 °C at 2 kg/cm² pressure</td>
<td>6</td>
</tr>
<tr>
<td>Hot water</td>
<td>98 °C</td>
<td>48</td>
</tr>
</tbody>
</table>

In autoclave curing best results can be obtained with high pressure and curing temperatures, i.e., at 3 to 4 kg/cm² pressure and 134 °C to 144 °C temperature. The usual procedure followed is to subject the rubber lined vessel to air pressure of about 2 kg/cm² at the beginning of the cure cycle which ensures good contact between metal and rubber and then introduce steam and raise pressure and temperature to complete the cure. Typical cure cycles for ebonite and soft rubber are represented in the curves as shown in Figures 6.2a and 6.2b.

Figure 6.2a Autoclave curing cycle for soft rubber lining

Figure 6.2b Autoclave curing cycle for ebonite lining
At the completion of the cure cycle, and during the cooling process, air is again applied so that the pressure on the lining is maintained to prevent distortion or shrinkage. Fast cooling will create stresses on the adhesive bond, leading to failure due to debonding.

### 6.2 Hypalon Rubbers

This elastomer is manufactured by DuPont de Nemours and Co. Inc., Wilmington, DE, USA. This has outstanding resistance to ozone and generally is more resistant to acids than Neoprenes. It is attacked by esters and ketones. It is applied in tanks which handle corrosive sodium hypochlorite and in drying towers in caustic soda plants, where sulfuric acid is handled and in electroplating service, where chromic acid is used. The temperature range where this rubber can be used is −5 °C to 125 °C. While compounding Hypalon rubber, the fillers largely used are clay and barytes rather than any reinforcing fillers like carbon blacks. The non black fillers do not leach out and discolour the acid medium as the black fillers do. Furthermore, vulcanisates which contain barytes tend to exhibit a somewhat better resistance to volume swell than do compounds containing carbon black. Whiting cannot be used in Hypalon lining for acid service.

The chemical name for Hypalon is chlorosulfonated polyethylene and it has excellent resistance to heat, ozone and oxidising chemicals and has good abrasion resistance. It can be compounded for outstanding resistance to oxidising chemicals, such as sodium hypochlorite solutions in sulfuric acid saturated with chlorine and concentrated phosphoric acid. It is one of the few synthetic rubbers that can be mixed in any colour without loss in mechanical properties.

The uncured Hypalon compound behaves much like a thermoplastic resin. It is tough and nervy at room temperature, but its viscosity is reduced rapidly as it is warmed by working on a two roll mill. By contrast Neoprene is not as tough as Hypalon at lower temperatures.

### 6.2.1 Compounding Hypalon for tank lining

Hypalon does not break down during mastication in the sense that natural rubber and Neoprene do. These rubbers undergo an irreversible chemical change (i.e., a reduction in molecular weight) when they are worked in the mixing mill.

The reduction of toughness that occurs as Hypalon is milled is strictly temperature sensitive and is temporary and reversible. Compounds of Hypalon can be reworked in the calender or mill without significant change in processing behaviour as long as a scorch free accelerating system is used. The processing operation with any one production stock is consistent from batch to batch if the best temperatures in rolls are determined and maintained. The thermoplasticity of raw or compounded Hypalon disappears with vulcanisation and hence does not reappear in the cured finished sheets. Because of thermo plasticity and lack of breakdown, Hypalon compounds tend to be dry and non tacky at room temperatures, but prewarmed stock gives good flow, knitting and ply adhesion during the lining operations.
The selection of plasticisers for use in a Hypalon compound as in any other compounds depends upon such factors as compatibility, processing requirements, cost and the ease of application of lining and curing. Petroleum oils are used because of low cost. Paraffinic waxes are effective but they must be used sparingly; if used in excess, they bloom to the surface making application impossible. Solvents like trichloroethylene, xylene or toluene will have to be used on the surface to freshen the same. Polyethylene glycol is very effective at low processing temperatures. Aromatic oils are compatible with Hypalon, improving tack of the calendered sheets during application of the lining. Even though resin and tackifiers can be used in Hypalon compounds, still noticeable increase in tackiness will not occur when the stock is cold. Generally it can be observed in Hypalon stock that chemical resistance is decreased when the level of resins and plasticisers is increased.

Processing aids are used in Hypalon compounds to minimise sticking to calender rolls. Microcrystalline waxes are effective release agents and are widely used because of their good solubility. A polyethylene glycol such as Carbowax 4000 is useful at temperatures below 77 °C. Low molecular weight polyethylene such as a C₆ polyethylene are effective at temperatures above 77 °C, but when added on a cold mill it can actually aggravate sticking. It is good to use small amounts of several process aids to help release over a range of temperatures without exceeding the compatibility of any individual processing aid. In compounds containing litharge, stearic acid and stearates should be avoided because they may tend to promote scorch. Blends of naphthenic and aromatic plasticisers give easier processing compounds than aromatic oils alone. Large amounts of aromatic oils tend to make the Hypalon compound sticky. Naphthenic oils are compatible in amounts up to 15 to 20 phr. Reinforcing fillers such as silica and fast extrusion furnace (FEF) carbon blacks are used to increase the green strength of highly plasticised compounds. Such stocks are some times soft and become tender when hot, though they may not be sticky. Three to five parts of cis-4-polybutadiene or EPDM rubber may be added to such stocks resulting in more body and improved release. It is not necessary to add a cure pack for these polymers as they are in small quantities. When used in such small levels they do not seriously affect cure rate or vulcanisate properties. Polybutadiene will give some reduction in scorch time.

The Mooney viscosity and the cure rate of Hypalon compounds do not change appreciably under typical storage conditions. Temperature is a factor as mentioned earlier because of thermoplasticity. Because of longer heat exposure mill mixed compounds are likely to be scorchier than those mixed in internal mixers. A typical mixing time for a normal batch is approximately 25 minutes depending upon the types and amounts of fillers and plasticisers. Fillers should be added as soon as smooth blend is formed. Since Hypalon does not break down, no time should be spent working the polymer alone. After mixing, the stock should be cooled as quickly as possible.

Mixed stocks should not be stored in conditions of high humidity. Because moisture absorbed by Hypalon compounds under high humid condition acts as an accelerator
causing an increase in mooney viscosity and subsequent scorching. Mixed compounds of Hypalon should be used as quickly as possible. Unaccelerated stock can be stored for a comfortable period in accordance with production schedule and when final calendering is scheduled the accelerators can be added. The calendering temperatures can be between 60 °C to 93 °C. Uneven roll speeds are preferred and the top roll is usually hotter than the middle roll. Cool calendering obviously helps to eliminate trapped air. Higher temperature produce smooth surfaces with the upper temperature limits dictated by the tendency of the hot sheet to sag and distort, as it leaves from the bottom roll of the calender. Stock fed to the calender should have almost the temperature of middle roll. Temperature variation in feed stock causes uneven gage and a rough surface.

Division strips, caulking strips and end rings used for fixing filter grids on the Hypalon lined filter drums for sulfamic acid slurries are extruded from Hypalon compounds. The extrusion temperature condition are maintained as follows:

<table>
<thead>
<tr>
<th>Screw</th>
<th>Cool (atmospheric temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed area</td>
<td>50 °C</td>
</tr>
<tr>
<td>Barrel</td>
<td>60 °C</td>
</tr>
<tr>
<td>Head and die</td>
<td>93 °C – 107 °C</td>
</tr>
</tbody>
</table>

Extrusion of Hypalon tends to be soft when hot. The die correction for the profiles for accommodating shrinkage and swelling of the stock should be done based on a few trials. As soon as the correct profile comes out of the die, it should be thoroughly cooled in a cooling tank with soapy water.

Hypalon lined tanks are used for best possible resistance to oxidising acids. The litharge curing systems can be used for black or non black compounds. However, for minimising the absorption of hydrochloric acid, a low level, i.e., less than 10 phr of litharge should be used. For minimum absorption of water, the optimum amount is 20 phr. An epoxy curing system is best suited for wet chlorine environment for the tank lining. This gives good building tack also. However, it becomes weaker than litharge in taking up the hydrochloric acid, generated during cure. This limits the over all uses of the epoxy cure. However the epoxy cure has to be considered when conditions warrant its use. A level of 15 phr of epoxy resin is good enough to replace of 25 phr of litharge.

The curing system based on magnesia would be used to provide resistance against concentrated sulfuric acid and other drying agents. If there is a possibility where the lining is exposed to 30% hydrochloric acid, magnesia should not be used.

The litharge cures are safe and provide scorch free cures. Therefore they are generally preferred in designing compounds for lining. The dosage of dipentamethyline thiuram hexasulfide (Dupont’s Tetrone A-DPTH) in a litharge cured stocks can be varied from 1.5 to 2 phr and 0.5 phr of benzothiozyl disulfide can be added for additional safety. Carbon blacks are added for aiding calendering. But when the sheets are cool, they become tough. Medium thermal carbon blacks with some clay will alleviate this problem. Epoxy resin
cured stock gives handling advantages over litharge cured stocks. It is safer from the point of view of shelf life, pliability, tack and gives better cured adhesion with the metal surface. It is slower curing than litharge and so preferred for thicker lining.

During processing of Hypalon compounds for tank lining application it should be kept in mind that the total heat cycle (the heat history of the stock) must be kept to a minimum. It is to say that at the optimum or more practical temperatures of the exposure time of the stock should be minimum at each stage of processing starting from mixing. In the mixing operation, more than in any other operation, the heat exposure or heat life of the stock is more. The following mixing tips can be helpful:

- Use a short mixing cycle as far as possible
- Do not prolong the time after mixing litharge and acceleration
- Cool the mixed stock as quickly as possible.

Mill mixing should be completed in 30 minutes. Properly compounded stock may have a Mooney viscosity of about 30 to 35 (MS 1 + 4 at 121 °C; MS: Mooney viscosity with a small rotor).

Mixing mill temperature can be 85 °C to 90 °C. In Banbury mixing the cycle will be 5 minutes. Dumping should be done before the temperature goes up to 110 °C, especially if a litharge cure is used. From a scorch safety point of view, masterbatches of litharge can be used, such as 10% EPDM with 90% litharge.

Calendering of Hypalon stock is a tricky job. The shelf life for the mixed stock before calendering preferably should be kept to a maximum of 24 hours and a minimum of 12 hours. Such resting period for the compounded stock leads to successful calendering resulting in smoother sheets. The good finish of the calendered Hypalon sheets depends upon the total loading in it and the calendering temperatures. In general a 30% volume loading will result in smooth calendering and the sheet is released smoothly from the rolls.

The suggested temperatures of the calender rolls are:

- Top roll 60 °C
- Middle roll 55 °C
- Bottom roll Room temperature

Low molecular weight polyethylene such as a CPE6 is often used at 3 to 5 phr levels to provide safer stocks and to prevent sticking on roll surface when roll temperatures are at times increased slightly to get smoother and tacky sheets enabling plying up to the required lining thickness. Hot calendering also reduces cured shrinkage. Hypalon is less tacky than Neoprene and so it is advisable when plying up the sheets to augment tack by using temperature that can be tolerated and yet avoiding sticking to the rolls. It should be noted however that uncured Hypalon sheets soften considerably during cure at high temperatures causing plies to knit better and form a satisfactory cured lining.
**Tank Lining Guide**

For adhering the Hypalon sheet to the metal surface, invariably a tie-gum or tie-solution in toluene can be used over the isocynate coat (i.e., Chemlok 205) for better integrated bond with the metal. The technique of application of Hypalon lining is almost same as that of Neoprene. The curing in autoclave, in open steam or hot water is also similar to that of Neoprene.

### 6.3 Butyl rubber

Butyl rubber was developed by the research department of Standard Oil Company [4], New Jersey in the 1930s which later became a constituent of the Exxon Corporation.

Butyl rubbers are copolymers of isobutylene and isoprene. Like natural rubber, butyl rubber too does not break down on mastication or during the normal mixing process. The compound viscosity is controlled by selection of raw polymer grade, carbon black type and loading and oil type and loading. Relatively high loadings of paraffinic or naphthenic oils are employed for typical butyl applications such as tubes, etc., but such heavy loadings are not advisable in lining compounds.

Butyl rubber like Hypalon, Neoprene or nitrile rubber is a speciality polymer which can be compounded for a soft, deformable elastic vulcanisate similar to the other elastomers, but having certain distinctive characteristics, like low permeability to all gases and resistance to ageing and ozone cracking. Butyl has poor oil resistance and medium low temperature flexibility.

Halogenated butyl rubbers called halobutyls such as chlorobutyl rubber (CIIR) and bromobutyl rubbers are later developments. Zinc oxide is a vulcanising agent with low levels of sulfur for halobutyls and stearic acid. Sulphenamides accelerate vulcanisation of halobutyls. Bromobutyl shows higher cure reactivity than CIIR. Both bromobutyl (BIIR) and CIIR will cure with zinc oxide, but only BIIR will cure with sulfur alone, no zinc oxide or accelerator being necessary. BIIR can be cured with 0.5 phr of sulfur, 1.3 phr of dibenzothiazyl disulfide and 1 phr of stearic acid. Sulfur levels as low as 0.5 phr will give a rapid cure.

Zinc dithiocarbamate can be used in small quantities (0.25–0.75 phr) with zinc oxide cures used in heat resistant and improve compression set.

The tensile strength of pure gum butyl compound is the highest. As the filler loading increases, the tensile strength falls. In practical formulations 50 to100 phr of general purpose furnace black or fast extrusion furnace black (FEF) is added and 100–150 phr of mineral fillers such as hard clay, talc or silicas are added. Higher levels of carbon blacks make the lining sheets unsuitable at times for spark testing at higher voltage, as at this voltage the rubber is burnt due to excessive carbon. If high loadings of carbon blacks are unavoidable, the spark testing voltage has to be reduced. The recommended plasticisers are highly saturated hydrocarbon oils and waxes. The maximum level of ozone resistance is achieved when low unsaturated grades of butyl are vulcanised to the highest state of cure. In general plasticisers reduce ozone resistance.
Elastomers Used in the Rubber Lining Industry

Butyl vulcanisates are not serviceable in continuous contacts with hydrocarbon oils and solvents as swelling is more. Butyl is resistant to vegetable and animal oils. Strong acids and bases do not attack butyl neither do strong oxidising agents or reducing solutions. Concentrated nitric acid or sulfuric acid however, cause degradation to a level less than natural or Neoprene rubbers. In compounding for minimum swell, the factors of highest importance are high filler loadings high reinforcement and maximum state of cure. If butyl sheets are compounded for resistance to mineral acids, chemically sensitive fillers like calcium carbonate should be avoided. To protect the non black butyl compounds from sunlight, it is necessary to use adequate loadings of high opacity pigments such as titanium dioxide.

For zinc oxide at, for example, levels of 15 to 45 phr, good filler dispersion is essential for better dimensional stability in calendered sheets. Butyl sheets are used in storage tanks, digesters and other large equipment handling phosphoric acid, hydrochloric acid and sulfuric acid very effectively in fertiliser and chlor-alkali plants. When high temperatures are encountered, carbon bricks or acid resistant bricks are lined over the rubber lining.

Butyl rubber is used in specialty application such as reservoir or canal linings, tank linings, pharmaceuticals and sealing caulks. The low unsaturation and low permeability of the rubber molecule contribute to the chemical inertness of the butyl rubber.

In Europe exhaust gas from chimneys in power plants was desulphurised in scrubbers and other equipment using butyl rubber lining for more than 25 years [5]. Service lives of butyl rubber lining of more than 15 years have been reported. Many countries like USA, Japan, Austria, Netherlands, Denmark, Finland and England followed the procedure of applying butyls or halobutyl in the flue gas desulphurisation plants. Using the wet scrubbing process for separation of phases in lime stone or calcium hydroxide suspension more than 150 plants of this kind have been rubber lined with butyl and were in operation throughout Europe.

In many cases of scrubber lining in situ self-curing butyl rubber linings are used which is curable in 15 to 20 days time at atmospheric temperature. In some other cases pre-vulcanised butyl or bromobutyl rubber sheets are applied using contact adhesives based on isocynates. The tie coat between the bonding adhesive and the lining is made from CIIR that has good compatibility with the lining and the bonding agent and good adhesion strength. Butyls or halobutyls meet the following rubber lining functions in scrubbers such as:

- Low diffusion and permeation
- Resistance to acids and salts
- High abrasion resistance
- Thermal resistance at a maximum temperatures of 90 °C
- Oxidation resistance
- Low ageing
- Ease of application
Coal fired power plants have soft butyl linings in their plants and equipment which give a service life of about 15 to 20 years. In this case either pre-vulcanised or self-curing butyl lining of 4 mm thickness with a durometer hardness of 55 A has been used. In lignite based power stations, bromobutyl gives a life of 10 years. Operating times in many plants are increased, leading to changes in the condition of the linings. Rubber lining swells, become embrittle, develop cracks and increases the layer thickness. If embrittlement predominates, in other words deterioration of the mechanical properties like elongation and tensile strength occurs, the rubber lining is not able to cope up with the mechanical stress caused by suspension or sludges as the case may be. When such situations are noticed, relining is to be done after removing the old lining.

In vulcanising butyl rubbers, sulfur vulcanisation is generally used with higher accelerator levels as in the case of EPDM. Unlike EPDM, this elastomer has sufficient chain regularity to permit crystallisation on stretching so it can exhibit high gum strength. Butyl rubber has a $T_g$ of $-72 \, ^\circ C$. It shows a low resilience at room temperature with a high hysteresis loss. It is therefore a useful damping rubber. Butyl rubber cannot be blended with high unsaturation rubbers in sulfur vulcanisation.

6.4 EPDM Rubber

EPDM rubbers are amorphous polymers. Like any other non crystallising polymeric materials, the mechanical properties of the unfilled EPDM rubbers are very poor and as a result, addition of reinforcing fillers becomes important for giving strength to this rubber. In general special physical properties of high values are not required in the case of EPDM rubber compounds since their application areas are critical chemical and acid environments and water and gas systems. Usually easy processing, semi reinforcing carbon blacks are used in EPDM compounds. Its low density enables use of high loadings of extender oils and inert and semi reinforcing fillers from the point of view of economic consideration. EPDM rubbers have high esteem in process industries handling nitric acid and chromic acid corrosive environment in small concentration at around 5% in application such as electroplating industry. Another variety of oil extended EPDM is available in the market.

These may be used for low hardness compounds in areas where impact abrasion is predominant. EPDM is at times referred as ‘crackless rubber’ since it has high tear resistance. For producing high hardness compounds blends with natural rubber, styrene-butadiene rubber (SBR) and high styrene resins are recommended.

General curing system for EPDM rubbers will be a thiazole (mercaptobenzothiazole or dibenzothiazole disulfide) accelerator with a thiram and/or a dithiocarbamate. For high heat exposure condition in a process industry, sulfur donor types like tetra methyl thiuram disulfide may replace a larger part or all of the sulfur.

The main chains of the EPDM molecule have no double bonds and thus EPDM does not deteriorate due to molecular scission even after prolonged exposure to sunlight and high
Elastomers Used in the Rubber Lining Industry

Ozone concentration. Commercial grades of EPDM rubbers contain a maximum of 15 double bonds per 1000 carbon atoms in contrast to butyl rubbers, or styrene butadiene copolymers with 150–200 double bonds per 1000 carbon atoms in the main chain. Thus ozone, resistance to heat and other atmospheric exposure hazards such as UV radiation and humidity are excellent. Because of its molecular structure and if suitably compounded, EPDM compounds are resistant to weathering of all kinds.

Although EPDM do not possess the excellent low air permeability of butyl rubbers they have good low temperature properties, ageing and better processibility. The many commercial grades available are differing in polymerisation processes such as solution or emulsion polymerisation, Mooney viscosity, molecular weight distribution and the ratio of ethylene and propylene. Because of the absence of double bonds in the main molecules, peroxide cures are used for curing and the cured products excel in heat resistance. Peroxides cures can be adopted if the application requires resistance to temperature of 150–175 °C and a very low compression set in tank flanges. Because of their excellent electrical insulation properties and high dielectric strength, EPDM is the preferred rubber lining compound in electroplating tanks in steel industry. It is flexible above –50 °C. EPDM is resistant to polar solvents such as alcohol, glycol, ketone and phosphate ester, acids, alkalies, salts and fats.

However EPDM does not possess resistance to hydrocarbon oils and solvents. EPDM grades are suitable for use in pipe system in drinking water application. The combined effects of heat resistance and low compression set increase the service life of EPDM compounds. Most EPDM grades conform to several international approvals and regulations for use in drinking water application, such as the Water Regulation Advisory Scheme of the UK (WRAS; www.wras.co.uk), The German Technical and Scientific Association on Gas and Water (DVGW; www.dvgw.de) and the Food and Drug Administration of USA (FDA; www.fda.gov and www.epa.gov).

EPDM’s specific gravity is the lowest of all synthetic elastomers enabling it to admix with large quantity of inert fillers. Copolymer of ethylene and propylene monomers (EPM)/ethylene propylene terpolymer (EPT) rubber belongs to this category and stands for ethylene propylene terpolymer. EPDM has the skeleton structure of a methylene linkage. Various commercial grades of the rubbers are available based on processibility and curing characteristics. EPDM rolls are used in printing industry since they are highly resistant to ester plasticisers. In general, the mixing behaviour of EPDM rubber or EPM/EPT rubbers is excellent and very much comparable when compared with butyl or Neoprene or Hypalon rubbers. The aim of mastication is to reduce the Mooney viscosity of the rubber to aid further processing. Since most grades of EPDM rubbers are set at low Mooney levels, additional reduction of viscosity may not be needed and further reduction due to mechanical breakdown is also not very marked. EPDM has the advantage of minimum fluctuation in the viscosity of the compound enabling it to be easier for pre warming operation prior to sheeting. The low Mooney viscosity enables saving of energy in internal mixers.
Addition of 2 to 5 phr of alkyl-phenol resins improve tackiness of EPDM stocks. In blends with other synthetic rubbers such as SBR, the co-curability is an important factor while designing the overall curing system while compounding. The important factors to be considered here is to synchronise the curing speed between two polymers, using studies in oscillating disk rheometer charts. However, blends with styrene-butadiene rubber do not have as much acid resistance as 100% EPDM.

EPDM has a very low unsaturation which is sufficient enough for sulfur vulcanisation and low enough to reduce oxidative degradation. Because of its irregular chain structure, EPDM is amorphous and shows no crystallisation, unlike natural, Neoprene or butyl rubbers, on stretching. Hence, it exhibits poor strength and requires carbon black reinforcement. At higher ethylene contents say at > 60% the elastomer is semi crystalline and exhibits controllable green strength and crystallisation on stretching. A higher proportion of accelerator is to be used because of low unsaturation. It has good low temperature behaviour the glass transition temperature (T_g) being –60 °C and good resilience.

### 6.5 Silicone Rubbers

These rubbers are based on atoms of silicon chains rather than carbon atoms. Their unique structure is responsible for their extreme temperature properties. The most common types of silicone rubbers are specifically polysiloxanes. The Si-O-Si bonds can rotate much more freely than the C-C bond or the C-O bond. So the silicone chain is much more flexible and less affected by temperature. Silicone rubber is vulcanised by the action of peroxides which crosslink the chains by abstracting hydrogen atoms from the methyl side groups, allowing the resulting free radicals to couple into a crosslink. Some varieties of polysiloxanes contain some vinyl methyl siloxane units, which permit sulfur vulcanisation at the double bonds.

Siloxanes are soft and weak rubbers even with fillers like silica. Carbon black fillers do not work well. Silica fillers give a tensile strength of about 5–8 MPa. However the fillers offer excellent resistance to stiffening at very low temperatures, as well as softening at elevated temperatures thus retaining their properties, because of the great flexibility of the polymer chain. However, these silicone rubbers cannot be stable at 250 °C for longer time more than three months as they tend to degrade. For chemical plant lining applications silicone rubber is not suitable.

The main chemical routes for vulcanisation of silicone elastomers are 1) Elevated temperatures cures and 2) Room temperature vulcanisation mechanisms. Organic peroxide cures are used in elevated temperature cures. Since the organic peroxides are inhibited by most carbon blacks, non black reinforcing fillers such as precipitated silicas, titanium dioxide and zinc oxide are used. Room temperature vulcanisation is normally used with low consistency silicone elastomers.
Elastomers Used in the Rubber Lining Industry

The uses of silicone elastomers are varied. Many grades are available for specific uses like for high tensile strength, toughness and low compression set properties. Silicone rubber is the chosen rubber for high temperature applications in the engineering industry. It has excellent weather and thermal stability, ozone and oxidation resistance and extreme low temperature flexibility. It is more permeable to gases than natural rubber. Silicone rubber retains its rubber like properties and dielectric (preventing flow of elasticity) characteristics over extreme temperatures. It is extremely inert. It remains relatively unaffected by long exposure to water, ozone and ultraviolet light. Silicone rubber has high thermal conductivity and 1 – 1.5 times more than that of resinous or organic rubber. This property is important in application where heat dissipation is required. The silicone rubbers are capable of working through and after fire. The total decomposition of the polymer leaves a brittle silica ash an excellent dielectric on its own. Conventional organic rubbers decompose to form conductive carbon deposits with no insulation properties. Manufactured from quartz and oil, silicone rubbers are unique among elastomeric materials due to the properties inherent in their chemical structure.

6.6 Fluorocarbon Elastomers

These were developed by DuPont and 3M companies in USA during the 1950s. They are the most resistant elastomers to heat, chemicals and many solvents. But they are expensive elastomers. The most common types are copolymers of vinylidene fluoride and hexa fluoro propene. The fluorine atoms give chemical inertness and hydrogen atoms in the methyl group give rubbery properties. Vulcanisation of fluorocarbon elastomers are effected by diamines which cause crosslinks by reacting with the fluorine atoms. These elastomers are generally designed for high temperature use with mechanical properties as secondary considerations. Tensile strengths of 12–15 MPa are generally achievable at ambient temperatures, and they change very little after exposure to high temperatures. Thus these elastomers have an indefinite life at 200 °C and can be heated to 315 °C up to 48 hours. They have poor low temperature properties, reaching a brittle point at –30 °C when compared to nitrile rubber at –40 °C.

Fluorocarbon elastomers are non crystalline polymers exhibiting rubbery properties only when crosslinked. DuPont developed additional types of these elastomers for improved low temperature and chemical resistance properties. Fluorocarbon elastomer compounds show excellent resistance to automotive fuels and oils hydrocarbon solvents, aircraft fuels and oils, hydraulic fluids and chlorinated solvents of certain types. They show excellent resistance to highly aromatic solvents, polar solvents, water and salt solutions, dilute acids, dilute alkaline solutions oxidative environments, amines and methyl alcohol. Hexafluoropropylene containing polymers are not recommended for use in contact with ammonia, strong caustic lye (50%) above 70 °C, and polar solvents like methyl ethyl ketone and low molecular weight esters. Propylene containing fluorocarbon polymers can tolerate strong caustic lye. The thermal degradation temperature of fluorocarbon rubbers is 500 °C.
Gum viscosity of fluorocarbon elastomers is of primary importance in the determination of processibility, as this factor affects vulcanisate properties especially compression set. Gums are available with Mooney viscosity (ML 1+10 at 121 °C; ML: Mooney viscosity with a large rotor) values of 5–160. A Mooney viscosity range of 20–60 is preferred for the optimum combination of flow and physical properties. Higher viscosities can cause excessive heat built up during the mixing operation without a compensatory gain in physical strength and compound viscosity. As in other elastomers it depends on gum viscosity and on filler selection. A preferred range of gum viscosity is MS at 120 °C is 25 – 60.

Fluorocarbon elastomer can be mixed in any conventional mixing equipment and with standard mixing technique. Normally post curing is done at elevated temperatures as it develops maximum physical properties and imparts cure homogeneity. The general post curing system is 24 hours at 200 °C to 250 °C. Most applications of fluorocarbon elastomers are in the transportation areas. Aerospace industry account for a negligible percentage of consumption whereas more than 50% is in the transportation sectors. Segments like petrochemical, industrial pollution control and pneumatic applications are demanding more and more fluorocarbon elastomers.

6.7 Natural Rubber

Natural rubber is essentially polyisoprene (C₅H₈)n. Every fourth bond in the chain is unsaturated and every fourth carbon atom carries a methyl group. It is to the presence of the unsaturated bonds in the chain that natural rubber owes much of its versatility. On stretching, natural rubber displays long range elasticity provided the extension is not too great or the duration of the same is not too long. However, at elongations greater than 200 to 300%, the x-ray diffraction picture of the structured rubber develops the pattern characteristic of an oriented crystalline polymer. If, however, the rubber is stretched very slowly to smaller extension or at high temperatures viscous flow occurs.

The very high extensibility and tensile strength of natural rubber are therefore not entirely due to entanglements of randomly coiled polyisoprene molecules, but also to the formation of crystallites under stress. It is of interest to note that those synthetic rubbers which do not crystalise on stretching have uniformly low tensile strength. The following table gives the stretching crystallisation of elastomers (Table 6.2).
### Table 6.2 The Stretching Crystallisation of Elastomers

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Name</th>
<th>Vulcanising Agent</th>
<th>Stretching Crystallisation</th>
<th>Gum Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber</td>
<td>Cis-1,4-polyisoprene (&gt;99%)</td>
<td>Sulfur</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Styrene-butadiene rubber</td>
<td>Polybutadiene-co-styrene</td>
<td>Sulfur</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Butadiene rubber</td>
<td>Polybutadine cis-1, 4 (&gt;97%)</td>
<td>Sulfur</td>
<td>Fair</td>
<td>Fair</td>
</tr>
<tr>
<td>Isoprene rubber</td>
<td>Cis-1,4 Polyisoprene (&gt;97%)</td>
<td>Sulfur</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>EPDM</td>
<td>Polyethylene-co-propylene-co-diene</td>
<td>Sulfur</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Butyl rubber</td>
<td>Polyisobutylene-co-isoprene</td>
<td>Sulfur</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>Polybutadiene-co-acrylonitrile</td>
<td>Sulfur</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>Polycaprene (mainly trans form)</td>
<td>MgO or ZnO</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Silicones</td>
<td>Polyalkylsiloxane (mainly polydimethylsiloxane)</td>
<td>Peroxides</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Fluorocarbon elastomers</td>
<td>Polyvinylidene fluoride-co-hexa fluoropropene</td>
<td>Diamines</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Polysulfide rubber</td>
<td>Polyalkylene sulfide</td>
<td>Metal oxides</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>Polyurethanes</td>
<td>Di-isocynate</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>Hypalon</td>
<td>Chlorosulfonated polyethylene</td>
<td>Sulfur</td>
<td>Varies with proportions of chlorine and sulfonyl groups</td>
<td>Varies with proportions of chlorine and sulfonyl groups</td>
</tr>
</tbody>
</table>

For the most effective development of rubber-like elasticity, permanent interlocking of the chain molecules at a few points along their length to form a loose three-dimensional network is desirable. The crosslinks should be sufficient in number to ensure a prominence of structure, in other words, a suppression of viscous flow and yet not so numerous as to seriously restrict the internal segment mobility of the polymer chain. A very convenient way of effecting this crosslinking is to react the natural rubber with sulfur. Sulfur linkages are formed between the chain with strengths comparable to those linking the carbon atoms of the polyisoprene chains in the starting material. This process is known as vulcanisation and occurs as a consequence of the presence of highly reactive double bonds in the polyisoprene chains. The effect of vulcanisation is to raise the $T_g$ of the amorphous polymer and to lower the melting point of the crystallites formed on stretching the amorphous material. Table 6.3 shows how the $T_g$ for natural rubber increases with increasing extent of vulcanisation as effected by increased dosage of sulfur.

<table>
<thead>
<tr>
<th>Percentage of sulfur</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-65</td>
</tr>
<tr>
<td>0.25</td>
<td>-64</td>
</tr>
<tr>
<td>10.0</td>
<td>-40</td>
</tr>
<tr>
<td>20.0</td>
<td>-24</td>
</tr>
</tbody>
</table>

Crosslinked polymers are to be regarded as giant three-dimensional molecules of indeterminable molecular weight, i.e., varying molecular weight that can be described as molecular weight distribution. Such molecules swell in solvents to an extent that depends on the nature of the swelling solvent and also on the extent of crosslinking. The more crosslinked the molecule is, the less the swelling in a given liquid media. As the number of crosslinks is increased, these polymers, as they are often called hard rubbers or ebonites containing more than 30% sulfur combined with the natural rubber molecules, show progressively less segmented motion of the chains between the crosslinking points. Consequently, they lose their long range of elasticity and resemble ordinary brittle solids in their elastic behaviour. Many of the mechanical products of a high polymer are molecular weight dependent, although the effect may be sidelinied by other factors such as chain orientation and crystallinity. In the case of chemical resistance as judged by the swelling of the polymer in a liquid media over a period of time, the high crosslinking density plays a vital role in providing increased chemical resistance. Natural rubber ebonites exhibit very good protection against acid attack because of their highly crosslinked molecular structure.

The corrosion of metals by non oxidising acids occurs when the metal is able to displace hydrogen ions from the solution. The corrosion effects that arise in the petroleum refining industry are connected with the presence of corrosive sulfur compounds formed by
Elastomers Used in the Rubber Lining Industry

thermal decomposition of sulfur particularly hydrogen sulfide, or of hydrochloric acid produced by the hydrolysis of magnesium and calcium chloride present in the subsurface water. The sulfur compounds are particularly corrosive in petroleum refining at temperature above 260 °C. Chemical corrosion involves so many factors that each case should be considered as a separate problem requiring special treatment. Selection of materials of construction as protective lining on the metal surface should be based on accumulated experience on general principles and on the result of tests designed to simulate the process conditions in the actual plant.

Under these aggressive corroding environments, rubbers play an important role to protect the plant and equipment, facilitating high temperature operations, higher reaction velocities and maintaining equilibrium in a chemical process. Natural rubber as a protective medium is much used in the form of either soft vulcanised rubber, ebonite or semi ebonite which has the disadvantage of higher sulfur content leading to blooming at the surface but with a great advantage for bonding with metal. It is reliable up to about 80 °C to 100 °C. Soft rubber containing less sulfur is often used at temperatures up to about 70 °C. Neoprene has the advantage of being inert to oils and greases when compared with natural rubber. Butyl is used extensively having the great advantage over natural rubber as it will resist oxidising acids, e.g., 5% to 10% nitric acid up to 50 °C. Thiokol (polysulfide rubber) when compared with natural rubber is not highly resistant to chemicals but its resistance to solvents is outstanding.

After the discovery of vulcanisation by Charles Goodyear, it was Nelson Goodyear who patented a process for making ebonite under US Patent 8075 in 1851 [6] by heating the rubber with large proportions of sulfur. The commercial manufacture of hard rubber products started a few years later and thereafter ebonite became an important branch of the rubber industry. Though during the subsequent years, and until today, newer types of hard plastics came into existence to replace hard rubber. The hard rubber industry continued to stay in its position of importance by virtue of its unique characteristics main one being its chemical resistance. The chemical inertness, high strength and good appearance of hard rubber have led to many applications with it. Hard rubber, like soft rubber, is compounded with many ingredients other than sulfur. It may contain varying proportions of fillers incorporated for the purpose of obtaining desirable characteristics. Large proportions of ebonite dust, known as polyisoprenesulfide is manufactured from waste and used as a filler in ebonite compounding. Fully cured ebonite products are not capable of bringing in vulcanisation reaction when mixed with raw rubber. This is indicative of the strong bond which exists between the sulfur atom and the rubber molecule. The study of rubber hydrocarbon’s reaction with sulfur shows that some substitution of sulfur is also taking place in addition to addition reaction. The chemical analysis of fully vulcanised ebonite shows a combined sulfur content of more than 32%. Sulfur obviously reacts with rubber very slowly at room temperature. Vulcanisation of hard rubber is carried out usually at temperature between 130 °C and 160 °C. The commercial period of vulcanisation of hard rubber generally ranges from about 15 minutes to 20 hours or even longer, depending on the composition and dimensions of the product, type of curing process and on the temperature used. The hot water curing
process, which is adopted at client’s site takes as high as 48 hours of curing period. Thick sheets of ebonite require relatively long periods at low temperatures. Heavily loaded and highly accelerated compounds can be cured for a short period at 150 °C to 160 °C.

The hard rubber reaction liberates considerable heat during the curing process. This heat liberated suddenly at an early stage of vulcanisation reaction is accompanied by a vigorous evolution of hydrogen sulfide gas indicating that substitution or decomposition is taking place. At higher temperatures of vulcanisation sulfur combines chemically with rubber at a rapidly increasing rate. If vulcanisation is carried out at 120 °C to 130 °C, the rate of reaction and consequent heat evolution is kept down. This, in conjunction with longer time available for heat flow from the centre of the mass of the compound results in only a moderate internal temperature rise compared with the result of vulcanising at higher temperatures.

In vulcanising thick articles of ebonite such as pipe internals whose wall thicknesses are 2.5 cm to 5 cm, low temperatures and long periods of vulcanisation must be used. Otherwise the material becomes a porous and brittle mass as a result of excessive internal temperature. The general practice in the manufacture of thick articles is to use compounds containing high percentages of hard rubber dust, mineral fillers and reclaimed rubber that reduce the heat evolution during vulcanisation. The use of accelerators should be done with caution in hard rubber vulcanisation especially of thick articles. Their use is, at times, attended with difficulties such as scorching, porous surface, discolouration and brittleness in the final product. Further the slow accelerators for soft natural rubbers will accelerate the hard rubber vulcanisation. An example of this is diphenyl guanidine. Lime and magnesia are frequently used in small percentages to accelerate the vulcanisation of hard rubber. Light calcined magnesia is most commonly used.

Hard rubber dust is used as a common filler in ebonite compounding. It facilitates mixing and reduces excessive shrinkage in the sheetings from the mill or calender. With the use of hard rubber dust, the possibility of blowing or bursting during vulcanisation is greatly reduced. In anticorrosion compounding formulation fillers, such as barytes, whiting and clay, are widely used for greater hardness and toughness and heat resistance as well as for economy.

It may not be possible to form a detailed picture of the molecular structure of ebonite. Combined sulfur is present partly as crosslinks between neighbouring rubber chains (intermolecular sulfur) and partly as sulfur atoms linked to two carbon atoms in the same chain forming a carbon sulfur ring structure (intra-molecular sulfur). The elastic modulus of ebonite is high, i.e., at high temperature is about 10 times that of a pure gum vulcanisate while its swelling in active swelling liquids is only about one-eighth. The dependence of modulus and swelling on degree of crosslinking would therefore indicate that ebonite is much more densely crosslinked than a soft vulcanisate. The swelling action of a liquid on ebonite is not similar to its swelling action on a soft vulcanised rubber. Although with increasing sulfur content over the range from soft to hard vulcanisates
swelling almost decreases the extent of the decrease depending on the nature of the liquid, being greatest with aliphatic hydrocarbon, slightly less with aromatic hydrocarbons, significantly less with halogen and sulfur compounds and least with polar liquids, such as hydrogen chloride \( \text{H}^+\text{CL}^- \). Consequently the relative swelling capacities of two liquids may be reversed on passing from soft rubber to ebonite. Thus petroleum usually swells soft rubber more than nitrobenzene, but with ebonite, the later provides the greatest swelling.

The swelling time of ebonite is usually greater than (10–15 times) that for soft rubber in the same liquid. Carbon disulfide is an exception since it swells ebonite almost as quickly as soft rubber. Moreover with ebonite there are greater differences between the swelling times of different liquids than with soft rubber.

With soft rubber the swelling time is generally shorter, the less viscous the liquid, but this relationship does not apply to ebonite through which the least viscous liquids like acetone ethyl acetate and petroleum ether, diffuse slowly.

Therefore, although the viscosity of a liquid does influence its rate of penetration into ebonite, the permeability of the ebonite is so greatly increased by absorption of the liquid that its swelling capacity has much more influence on this rate rather than the viscosity itself. It may be useful to understand at this juncture what permeability of a rubber or ebonite is to gases or liquids.

Permeability is a process in which liquid or gas molecules dissolve in the elastomer, on one side of the membrane and diffuse through the other side and there escape out. The solubility of a gas or liquid in a given elastomer is closely related to its tendency to condense and is also related to the interaction between the gas/liquids molecules and the elastomer molecules.

The rate of diffusion in a given elastomer is found to be related chiefly to the size of the liquid/gases molecule. It is observed that the presence of polar group or methyl group in the polymer molecules reduces the permeability to a given liquid/gas. Therefore butyl, Neoprene and nitrile, along with ebonite, have a low value of permeability when compared with natural soft rubber vulcanisates.

Long swelling time and low swelling maximum mean better resistance to the swelling action of the liquid. In general ebonite of a given vulcanisation coefficient resists swelling better if produced by a long cure on a low sulfur package. This procedure also results in a higher elastic modulus (Young’s modulus) at room temperature and in higher yield temperature, in other words, greater resistance to high temperature deformation. The effects on all these properties – modulus, yield temperature, and swelling – imply that the lower temperature and long cured low sulfur ebonite has a more closely knit molecular structure.

Swelling is strongly dependent on the chemical nature of the vulcanised elastomer and the high proportion of combined sulfur in ebonite gives it a much reduced affinity to aliphatic hydrocarbon acids and water.
6.8 Synthetic Ebonites

Some details of synthetic hard rubber (ebonites) are given next.

Fully cured SBR ebonites are brittle on bending through a sharp angle and will fracture more easily than natural hard rubber. Electrical properties of nitrile hard rubbers are inferior to those of SBR and NR hard rubbers. The softening point of nitrile hard rubber is slightly higher and its resistance to petroleum solvents and hydrocarbons is excellent. Polybutadiene hard rubbers have identical properties similar to those of SBR and NR hard rubbers. Chlorobutadiene hard rubbers could not be made and information on ebonites of this rubber is not available. Polysulfide rubbers when compounded with high percentages of sulfur do not yield vulcanisates comparable to hard rubbers.

Isobutylene-isoprene rubbers, the copolymers containing 98% isobutylene and 2% isoprene cannot be made into hard rubbers because of the lack of adequate unsaturation. However a very hard butyl rubber vulcanisate can be obtained by admixture with SBR and high levels of sulfur. The water absorption of NR ebonite is 0.45% to 0.5% at a relative humidity of 97.2%.

The high water absorption values of nitrile ebonite (about 3.3% to 4.5%) could not be anticipated. just because a soft vulcanisate made from similar copolymer absorbs less water than a NR vulcanisate.

Nitrile hard rubbers surpasses all of the other synthetic ebonites in resisting the swelling action of solvents like benzene, gasoline, carbon disulfide, nitrobenzene, petroleum, ether, transformer oils, hydraulic fluid, and so on (Table 6.4).

Reference


Table 6.4  Effect of Acids on Hard Rubbers

<table>
<thead>
<tr>
<th>Acid</th>
<th>Satisfactory effect</th>
<th>Unsatisfactory effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>Natural rubbers</td>
<td>Perbunan</td>
</tr>
<tr>
<td>(12 weeks at 20 °C)</td>
<td>Buna 85</td>
<td>Perbunan extra</td>
</tr>
<tr>
<td></td>
<td>Buna S</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Buna SS</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid dilute</td>
<td>Natural rubber</td>
<td>Perbunan</td>
</tr>
<tr>
<td>(12 weeks at 20 °C)</td>
<td>Buna 85</td>
<td>Perbunan extra</td>
</tr>
<tr>
<td></td>
<td>Buna S</td>
<td></td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>Heavily loaded blends of natural rubber</td>
<td>Perbunan</td>
</tr>
<tr>
<td>(2 weeks at 20 °C)</td>
<td>with Buna 85/Buna SS</td>
<td>Perbunan extra</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Neoprene rubber</td>
<td>Perbunan</td>
</tr>
<tr>
<td>(8 weeks in 32% at 20 °C)</td>
<td>Buna SS</td>
<td>Perbunan extra</td>
</tr>
<tr>
<td>Chlorine gas</td>
<td>Natural rubber</td>
<td>Perbunan</td>
</tr>
<tr>
<td>(4 weeks at 70 °C)</td>
<td>Buna 85</td>
<td>Perbunan extra</td>
</tr>
</tbody>
</table>

Buna 85 is polybutadiene (the number represents Mooney viscosity), molecular weight -80,000. Hard rubber has high softening point and excellent chemical resistance. The coefficient of vulcanisation to the ebonite stage is 39.3. The coefficient of vulcanisation is the number of unit weight of sulfur combined with 100 units by weight of unsaturated hydrocarbons. Buna S is a butadiene styrene copolymer with 70/30 to 68/32 ratio. Buna SS contains a high proportion of styrene. Perbunan are nitrile rubbers.
Tank Lining Guide