Chapter III

Chemistry of Materials
3.1 Introduction:

Raw rubber as such is very week and hence, needs to be compounded with various fillers, vulcanizing agents for making it stronger and suitable for the end application. Several compounding ingredients like fillers, Vulcanizing agents, Actvators, Accelerators, Anti degradants etc., are added to the raw rubber to obtain specific characteristic properties necessary to sustain the conditions of the end application. Compounding of rubber therefore, plays a crucial part in analyzing the rubber’s end properties and performance. It covers a wide spectrum of science and technology underlined, which is adopted not only to minimize the malfunctions, if any; but also contributes to enhance the existing performance of each individual rubber. It is therefore evident that the final performance of the rubber at the assigned end application is influenced to a great extent on the Compounding conditions, ingredients and Kinetics involved. This chapter deals with chemistry of various raw polymers, chemicals and materials, their vulcanization mechanisms etc.

Study was carried out on the following polymers.

1. Acrylonitrile Butadiene Rubber – [NBR]
2. Hydrogenated Acrylonitrile Butadiene Rubber – [HNBR]
3. Ethylene Propylene Diene Monomer Rubber [EPDM]

3.2 Acrylonitrile Butadiene Rubber – [NBR]

Acrylonitrile rubber (NBR), also called nitrile-butadiene rubber, is an oil-resistant synthetic rubber produced from a copolymer of Acrylonitrile and Butadiene. Nitrile rubber, like styrene-butadiene rubber and other synthetic elastomers (elastic polymers), was a product of research that took place during and between the two world wars. A group of acrylonitrile-butadiene copolymers, given the name Buna N, was patented in 1934 by German chemists Erich Konrad and Eduard Tschunkur, working for IG Farben. Buna N was produced in the United States during World War II as GR-N (Government Rubber-Nitrile), and subsequently the group of acrylonitrile-butadiene elastomers became known as nitrile rubber.
In the production of NBR, Acrylonitrile (CH\textsubscript{2}=CHCN) and Butadiene (CH\textsubscript{2}=CH-CH=CH\textsubscript{2}) are emulsified in water and then polymerized (their single-unit molecules are linked into large, multiple-unit molecules) through the action of free-radical initiators.

Acrylonitrile content varies in commercial products from 18% to 48%. As the nitrile content increases, resistance to petroleum base oils and hydrocarbon fuels increases, but low temperature flexibility decreases. Due to its excellent resistance to petroleum products, and serviceability over a temperature range of -65°·F to +275°·F (-54°·C to +135°·C), Nitrile is the most widely used elastomer in the seal industry today. Most military rubber specifications for fuel and oil resistant O-rings demand nitrile base compounds. In order to obtain good low temperature properties with nitrile compounding, it is almost always necessary to sacrifice some high temperature fuel and oil resistance. Nitrile compounds are superior to most elastomers with regard to compression set or cold flow, tear and abrasion resistance. Inherently, they do not possess good resistance to ozone, sunlight or weather, but this can be substantially improved through compounding. However, since ozone and weather resistance are not always built in, seals from nitrile bases should not be stored near electric motors or other equipment which may generate ozone or in direct sunlight.

**Producers:**

The worldwide production of NBR and HNBR is about 320 kilo tones. Nippon Zeon is the largest worldwide manufacturer with about 22% of the capacity, including the sole capacity for HNBR and has plants all over the world. Goodyear (18%), Uniroyal (15%) and Bayer (17%) are all major producers of nitrile elastomers. There is always an increasing trend in Production as well as demand.

**3.2.1 Structure and synthesis of NBR**

NBR is a copolymer of 1, 3 -butadiene and acrylonitrile (ACN) (see Fig. 3.1). The co-polymer can be largely linear to highly branch depending on the conditions of polymerization. NBR containing 8 to 27 wt% of ACN is available. NBR is used for its resistance to various organic oils, fuels and chemicals in seals, gaskets and hose. NBR containing higher amounts of ACN is more resistant to fluids but has a higher Tg. Virtually all nitrile elastomers are manufactured by emulsion polymerization technique.
The primary step in the process includes polymerization into a latex form, coagulation of the latex into a wet crumb and then drying into a final product.

![Chemical structure of NBR Rubber](image)

**Fig. 3.1** Chemical structure of NBR Rubber

### 3.2.2 Grades of Nitrile Rubber:

The amount of acrylonitrile present in the final co-polymer varies from 15 to 50 percent. According to the content of Acrylonitrile present in the polymer, it is classified as Low nitrile content NBR, Medium Nitrile content NBR Rubber and High Nitrile NBR Rubber.

**Table 3.1** Category of NBR and its Nitrile content

<table>
<thead>
<tr>
<th>S.No</th>
<th>Grade</th>
<th>% of ACN content</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low nitrile content NBR rubber</td>
<td>15 to 20</td>
<td>Industrial goods, aircraft components</td>
</tr>
<tr>
<td>2</td>
<td>Medium nitrile content NBR rubber</td>
<td>21 to 30</td>
<td>Oil seals, packing seals, gaskets</td>
</tr>
<tr>
<td>3</td>
<td>High nitrile content NBR rubber</td>
<td>31 to 45</td>
<td>Automotive parts and Fuel hoses</td>
</tr>
</tbody>
</table>

With increasing acrylonitrile content the rubber shows higher strength, greater resistance to swelling by hydrocarbon oils and lower permeability to gases. At the same time, the rubber becomes less flexible at lower temperatures owing to the higher glass transition temperature of poly acrylonitrile (i.e., the temperature below which the molecules are locked into a rigid, glassy state). Nitrile rubber is mostly used where high oil resistance is required, as in automotive seals, gaskets or other items subject to contact...
with hot oils. So, it becomes a challenging job for a technologist to get very good low temperature resistance without compromising on oil resistance properties. As these two properties are of contradictory in nature due to the plastic characteristics of acrylonitrile part in NBR rubber having more polar group which is contributing to more plastic characteristics. As the acrylonitrile content increases in the polymeric chain, the rubber will become rigid approaching plastic characteristics and its Tg will be shifting to higher side and hence the low temperature properties will decrease.

### 3.2.3 Vulcanization of NBR:

Unsaturated rubbers like NBR are mostly cured with sulphur based curing system. Two forms of sulphur are used in industry for the vulcanization: soluble and insoluble. The molecular structure of soluble sulphur comprises an eight membered ring, crystalline in nature. Sometimes, in compounds containing high level of sulphur, a phenomenon called “sulphur bloom” is observed. It appears as an off-white powdery coating on the surface of the uncured compound due to migration from the bulk compound when the limit of solubility is exceeded. Consequently, to avoid the blooming insoluble sulphur is used. In fact, this is a crystalline, polymeric form of sulphur and is insoluble in solvents and elastomers. However, insoluble form of sulphur transforms in the soluble form above 120 °C. Thus, the mixing temperature must be kept below 120 °C. Sulphur vulcanization occurs by the formation of polysulfide linkages between rubber chains. However, usually much of the sulphur is not involved in cross-links but there is the formation of dangling sulphur fragments and cyclic sulphides. As a consequence, the network formed is unstable and has poor aging resistance.

![Elastomer + S8](image)

**Fig. 3.2** Sulphur vulcanization of Rubbers

To increase the rate and efficiency of sulphur cross-linking, accelerators are normally added. These materials also known as sulphur donors are used to replace part of the elemental sulphur in order to produce Vulcanizates with few sulphur atoms per cross-link
(mono- and di-sulphidic linkages). These are organic chemicals and are classified in five main groups: guanidines, thiazoles, dithiocarbamates, xanthates and thiurams.

Generally, for certain rubber compounds like thick articles and multiple processing based products, delayed beginning of vulcanization is desirable. This permits forming operations to be accomplished before curing starts. Premature vulcanization is known as “scorch”. The five accelerator groups have different effects on the curing process; consequently, a combination of them is usually employed to achieve the desired scorch resistance and cure rate.

The level and the kind of cross links are based on

1. Sulphur content,
2. Accelerator type,
3. Sulphur/accelerator ratio and
4. Cure time.

High sulphur/accelerator ratio and long cure time increase the number of mono sulphidic linkages, consequently improving heat stability, set resistance and reversion resistance property of the final vulcanized product. These properties impart greater stability of C-S bonds compared to S-S bonds. On the other hand, compounds containing high number of poly sulphidic linkages show better tensile strength and fatigue cracking resistance. This behaviour depends on the ability of S-S bonds to break reversibly.

3.2.4 Application / Uses

Oil resistance property of NBR fetches the rubber a wide range of applications i.e. fuel hoses, gaskets, rollers; oil seals, O-rings, gaskets, oil field parts and diaphragms etc. Gloves pump stators, belts, wire and cable insulation, hose tubes/covers, rolls, sound insulating gaskets, footwear/shoe products and miscellaneous molded rubber goods are some of the minor applications. Nitrile rubber is also used for modification of plastics, adhesives coatings and friction materials. The rolls for spreading ink in printing and hoses for oil products are other prominent applications. NBR when employed in textiles improves the finish and waterproofing properties of woven and non-woven fabrics.
Sophisticated and developed form of NBR fetches better resistance to thermal and oxidative deterioration and low temperature flexibility. This Advanced form of NBR is termed as Hydrogenated Acrylonitrile Butadiene Rubber (HNBR).

### 3.3 Hydrogenated NBR:

HNBR has been the fastest growing specialty elastomer in the last decade. With its excellent cost-performance balance for the most demanding of applications; HNBR is the ideal choice for applications which require excellent physical properties, along with good oil, heat and/or chemical resistance. HNBR was first developed in the late ‘70s and early 80’s. Though commercial production did not begin until 1984, there were numerous companies looking at the feasibility of producing this type of elastomer.

HNBR Rubber is a new class of chemically modified NBR Rubber. Hydrogenation of NBR leads to the elimination/reduction of unsaturation part of NBR main chain (butadiene part) which improves the heat / thermal resistance, weather, ozone & oxidation resistance properties of NBR polymers. It’s highly saturated main chain provides good resistance against thermal oxidation and chemical attack. It is a saturated rubber containing no halogen, used for high temperature O-Ring application because of its excellent oil resistance due to its polarity, high temperature stability and also good weather, ozone resistance characteristics. HNBR is widely known for its physical strength and retention of properties even after long-term exposure to heat, oil and chemicals. Compounding techniques allow HNBR to be used over a broad temperature range, -40° to 165 °C, over long periods of time with minimal degradation. For low-temperature performance, low ACN grades are selected; high-temperature performance can be obtained by using highly saturated HNBR grades with white fillers. As a group, HNBR elastomers have excellent resistance to common automotive fluids (e.g. engine oil, coolant, fuel, etc.) and many industrial chemicals. Like NBR, fluid and chemical resistance improves as the ACN content is increased. However, its suitability under high temperature and steam application was not studied and hence this study also taken up in this project. HNBR is already in use in various high temperature applications in the automotive, oil drilling & nuclear power plant sectors. Hydrogenated nitrile rubber provides excellent all round performance at a compound cost between Nitrile and Fluoroelastomer.
3.3.1 Producers of HNBR:

The following 3 companies produce HNBR:

1. Bayer Corporation,
2. Zeon Corporation,
3. Polysar,
4. Lanxess.

Of these three, Zeon Corporation was the first to commercialize HNBR in March 1984 with Bayer and Polysar very close behind. Zeon Corporation’s initial manufacturing site was in Takaoka, Japan. The other initial manufacturing site was Polysar’s in Orange, Texas. However, Polysar eventually sold that business to Bayer Corporation (now Lanxess) who now owns and operates that facility.

3.3.2 Vulcanization of HNBR

HNBR elastomers are either peroxide cured or sulphur cured. Laboratory observations of sulfur/sulfur-donor and peroxide cured HNBR compounds indicate that peroxide curing provides better compression set and heat resistance. Because HNBR has fewer highly reactive alkyl position hydrogen versus other diene-based elastomers, such as NBR and SBR, it is necessary to add 50-100 % more peroxide in order to produce excellent curing characteristics. In case of peroxide curing, the Peroxides decompose during vulcanization because of the increased temperature, forming free radicals which lead to the formation of carbon - carbon cross-links in the polymeric chains as depicted in below mentioned Fig. 3.4.

![Chemical structure of hydrogenated nitrile rubber](image-url)
Many kinds of peroxides are available for curing HNBR. However, it is important to select one that is the most suitable based on the process and cure temperature that will be utilized to produce the finished parts. Since peroxides have different molecular weights and decomposition temperatures, it is imperative to select the correct one based on the criteria noted above or one can greatly affect the processability and cost-effectiveness of producing the finished goods in question. As in all peroxide cured material, vulcanization in the presence of oxygen causes reversion and thus leaves a sticky surface on the cured part. Therefore, one must take care when using pressure less cures and purge the autoclave prior to pressuring up for curing.

In case of sulphur / sulphur donor based cure system, when compared to SBR or NBR, the curing speed tends to be slower; therefore, to increase the curing speed a secondary accelerator should be employed in combination with the primary accelerator. When long curing times are required thiazole based (MBTS) or sulfonamide-based (CBS, OBTS) primary accelerators are used. To accelerate the curing process, a small quantity of guanidine-based (DPG) or thiuram-based (TMTM) secondary accelerator is used in combination with the primary accelerator. Even when using a thiuram-based (TMTD, TETD) primary accelerator, the addition of a thiazole based (MBT) secondary accelerator will shorten the time required for curing. The use of di thio carbamate (ZEDC) as the primary accelerator is undesirable since the scorch time will be shortened.

HNBR is widely known for its physical strength and retention of properties even after long-term exposure to heat, oil and chemicals. Depending on filler selection and loading, HNBR compounds typically have tensile strengths of 20 – 31 MPa when measured at 23 °C. Compounding techniques allow for HNBR to be used over a broad temperature range, -40° to 165 °C, with minimal degradation over long periods of time. For low-temperature
performance, low ACN grades should be used; high-temperature performance can be obtained by using highly saturated HNBR grades with white fillers. As a group, HNBR elastomers have excellent resistance to common automotive fluids (e.g., engine oil, coolant, fuel, etc.) and many industrial chemicals. Like in NBR, fluid and chemical resistance increases as the ACN content is increased.

### 3.3.3 Applications

The unique properties attributed to HNBR have resulted in wide adoption of HNBR in automotive, industrial and assorted, performance-demanding applications. On a volume basis, the automotive market is the largest consumer, using HNBR for a host of dynamic and static seals, hoses and belts. HNBR has also been widely employed in industrial sealing for oil field exploration and processing as well as rolls for steel and paper mills. Common uses of HNBR include A/C seals and hoses, Engine seals, grommets, and gaskets. Fuel system seals and hoses, Serpentine (multi-V) belts, Suspension seals, Synchronous (timing) belts, Transmission system bonded piston seals, Blow-out preventers, Chevron seals, Heat exchanger gaskets, Oil field packers, Paper mill rolls, Rotary shaft seals, Steel mill rolls, Hi-performance shoe soles etc.

### 3.4 Ethylene Propylene Diene Monomer [EPDM] Rubber

EPDM rubber (Ethylene propylene diene monomer (M-class) rubber), a type of synthetic rubber, is an elastomer which is used for wide range of applications. The E refers to ethylene, P to propylene, D to diene and M refers to its classification in ASTM standard D-1418. The M class includes rubbers having a saturated chain of the polymethylene type. Dienes used in the manufacture of EPDM rubbers are di cyclopentadiene (DCPD), ethylidene norbornene (ENB) and vinyl norbornene (VNB). EPDM rubber is closely related to ethylene propylene rubber (ethylene propylene rubber is a co-polymer of ethylene and propylene whereas EPDM rubber is a terpolymer of ethylene, propylene and a diene-component).

The ethylene content varies from 45% to 75% and is subsequently classified into various grades. The higher the ethylene content the higher the loading possibilities of the polymer, better mixing and extrusion. Peroxide curing of these polymers results in higher
crosslink density compared with their amorphous counterpart. The amorphous polymers are also excellent in processing. This is very much influenced by their molecular structure. The dienes, typically comprising from 2.5% up to 12% by weight of the composition, serve as crosslink sites when curing with sulphur and resin with peroxide cures the diene (or third monomer) functions as a coagulant, which provides resistance to unwanted tackiness, creep or flow during end use.

EPDM exhibits satisfactory compatibility with fireproof hydraulic fluids, ketones, hot and cold water and alkalis and unsatisfactory compatibility with most oils, gasoline, kerosene, aromatic and aliphatic hydrocarbons, halogenated solvents and concentrated acids. The main properties of EPDM are its outstanding heat, ozone and weather resistance. The resistance to polar substances and steam are also good. It has excellent electrical insulating properties. It has good resistance to ketones, ordinary diluted acids and alkaline. EPDM exhibits excellent radiation resistance as well as steam resistance properties. Hence, EPDM rubber is widely used in industrial and nuclear sectors.

EPDM can be compounded to meet specific properties to a limit depending first on the EPDM polymers available, then the processing and curing method(s) employed. EPDM rubbers are available in a range of molecular weights (indicated in terms of Mooney viscosity ML (1+4) at 125 °C), varying levels of ethylene, third monomer and oil content.

EPDM rubber is used in seals (for example it is used in cold-room doors since it's an insulator as well as in the face seals of industrial respirators in automotive paint spray environments, where silicone must be avoided). EPDM is also used in glass-run channels, radiators, garden and appliance hose, tubing, pond liners, washers, belts, electrical insulation, vibrators, O-rings, solar panel heat collectors and speaker cone surrounds. It is also used as a medium for water resistance in electrical cable-insulation, roofing membranes (since it does not pollute the run-off rainwater, which is of vital importance for rainwater harvesting), geo membranes, rubber mechanical goods, plastic impact modification, thermoplastic, vulcanizates and many other applications. Colored EPDM granules are mixed with polyurethane binders and troweled or sprayed onto concrete, asphalt, screenings, interlocking brick, wood etc. to create a non-slip, soft, porous safety surface.
for wet-deck areas such as pool decks and as safety surfacing under playground play equipment (designed to help lessen fall injury).

The most common use however is probably in vehicles. It is used in door seals, window seals, trunk seals and sometimes hood seals. Frequently these seals are the source of noise due to movement of the door against the car body and the resulting friction between the EPDM rubber and the mating surface (car painted sheet metal or glass). This can be alleviated using specialty coatings that are applied at the time of manufacture of the weather seal. Such coatings can also greatly increase the chemical resistance of EPDM rubber. Some vehicle manufacturers also recommend a light application of silicone dielectric grease to weather stripping to reduce noise. Other uses in vehicles include cooling system circuit hoses where water pumps, thermostats, EGR valves, EGR coolers, heaters, oil coolers, radiators and degas bottles are connected with EPDM hoses; as well as charge air tubing on turbo charged engines to connect the cold side of the charge air cooler (intercooler) to the intake manifold.

Ethylene-propylene rubbers & elastomers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and general purpose applications. These rubbers are mixed with other compounding ingredients along with various nanofillers as per the formulation given under each type of nanocomposites.

EPR & EPDM rubbers containing no halogen are rated as excellent weather resistant & good thermally stable in nature due to its saturated polymeric chain configuration. EPDM elastomers are nominally rated by O-ring manufacturers for service temperatures of −70 to 300 °F [-55 to 150 °C] in air, with higher temperatures possible with compounding and in certain media. In most cases, the high-temperature continuous service ratings are usually based on adequate performance for 1000 hours in normal (usually fluid) applications. For most applications, such ratings are sufficient. Unfortunately, the true service life of an elastomeric O-ring at elevated temperature is dependent upon many other variables. Though literature survey says that these polymers have limited temperature resistance compared to the actual requirement for the scope of this project work, an attempt has been made to modify the compound characteristics to obtain such
high temperature resistance properties. Rubbers like EPDM, EPR, containing saturated in
the main polymer chain; has been selected as base polymeric materials to start with the
compound development activities to obtain an elastomeric compound which can
withstand high temperature application. Experiments are designed and carried out using
these rubbers as starting materials and scrutinized.

Producers

The worldwide production of EPR and EPDM is approximately 1,150 kilo tones. In the USA the producers are Uniroyal (11 % of worldwide capacity), Exxon Chemical (11 %), DuPont/Dow Elastomers (12 %) and Copolymer/DSM (9%). Western European producers are Exxon Chemical (10 %), DSM (7%) and Degussa-Hüls (5 %). In Japan the producers are Mitsui Petrochemical (8 %) Japan Synthetic Rubber (7 %), DSM/Idemitsu (6 %) and Sumitomo Chemical (5%). There are additional smaller capacities in Brazil (2 %), Korea (2 %) and India (2 %). In addition to these solution plants, Polysar/Bayer (7 %) and Eni Chem (10 %) have suspension plants in the US and Europe, respectively. Additional US capacity (12 % of worldwide capacity) has been announced by Union Carbide using a novel gas phase process.

Processes

Even though EPM and EPDM elastomers have been available for more than 30 years, the technology for these products, both their production and their application is still under development. The most widely used process is a solution polymerization, in which the polymer is produced in a hydrocarbon solvent. EPM and EPDM rubbers are produced in continuous processes. Slurry polymerization is conducted in liquid propylene. Special reactor designs with multiple feeding locations to achieve special molecular structures have been developed. Gas-phase polymerization of EPDM is possible as an extension of the ubiquitous gas-phase processes for polyethylene and polypropylene.

3.4.1 Structure of EPDM

EPM and EPDM as manufactured today are rubbers based on the early work of Natta and co-workers [7]. Generically an EPM contains 60 mol % of ethylene, 40 mol % of propylene. Analogous EPDM polymer contains in addition, 1.5 mol % of non-conjugated
diene such as ethylidene norbornene or dicyclopentadiene. The co-monomers are statistically distributed along the molecular chain as shown in Fig. 3.5.

![Chemical structure of EPDM](image)

**Fig. 3.5** Chemical structure of Ethylene Propylene Diene Monomer [EPDM] Rubber

The following are termonomers which are present in sidegroups of polymeric chains.

![Termonomers for EPDM](image)

**Fig. 3.6** Termonomers for EPDM

### 3.4.2 Properties of EPDM

EPM is a saturated synthetic elastomer since it does not contain any unsaturation. It is inherently resistant to degradation by heat, light, oxygen, and, in particular, ozone. EPDM which contains pendant unsaturation is only slightly less stable to ageing than EPM. The properties of EPM copolymers are dependent on the relative content of ethylene units in the copolymer chain and the variation in the co-monomer composition of different chains. EPM and EPDM polymers with greater than 60 mol% ethylene are increasingly crystalline and are tough. The resistance to heat and ageing of EPM/EPDM is much better than that of SBR and NR. EPM/EPDM vulcanizates have an excellent resistance to inorganic or highly polar fluids, such as dilute acids, alkalis and alcohol. However the resistance to aliphatic, aromatic or chlorinated hydrocarbons is very poor. The electrical-insulating and dielectric properties of the pure EPM/EPDM are extraordinary.
but in compounding they are strongly dependent on the choice of compounding ingredients. Among the synthetic elastomers, EPM and EPDM are the fastest growing elastomers due to their excellent ozone resistance in comparison to the diene elastomers. This growth still comes from replacement of these commodity rubbers by virtue of their better ozone and thermal resistance. Another facet of the growth is that EPDM rubber can be extended with fillers and plasticizers to an extremely high level in comparison with the other elastomers and still maintain excellent Processability and properties in end use articles.

3.5 Liquid NBR

Nipol NBR liquids are copolymers of butadiene and acrylonitrile of medium acrylonitrile content. The outstanding characteristic is their liquid state, provided by very low molecular weight. Nipol NBR liquids can be used in blends with other Nipol polymers, imparting flow and knitting to molded goods, roll covering compounds and extrusions while allowing the development of a compound which is essentially free of extractable or volatile components. Nipol liquid polymers are compatible in all ratios with solid Nipol, however, their major use is in quantities of 5 to 15 parts, either substituted for an equivalent amount of solid polymer or added as a polymeric plasticizer or softener. At the lower level, five parts or so, its effect on the state of cure is minimal, but at higher levels, additional sulfur or accelerator may be necessary if high modulus or low compression set is required. Generally, 0.5 parts of additional sulfur per 10 parts of liquid Nipol rubber is satisfactory.

3.6 Processing Aids

Processing aids are the ingredients added to a rubber compound to facilitate smooth processing operations, such as mixing, calendaring, extrusion and molding. These materials react chemically to breakdown natural rubber and high Mooney viscosity synthetic elastomers chain and soften the rubber for easier processing or increasing the building tack after mixing. Examples of processing aids are fatty acids, metal salts of fatty acid and other fatty acid derivative, low molecular weight polymers and hydrocarbon oils and peptizer.
Among the fatty acids normally used is stearic acid which acts as a plasticizer and aids in dispersion of carbon black and other fillers. It also minimizes the tendency of rubber compound stick to the mill roll. Zinc laureate, stearate and lead oleate have also been used to soften rubber and improve its processing characteristics. Peptizers such as pentachlorothiophenol and phenylhydrazine which serve as either oxidation catalysts or radical acceptors are essential in removal of free radicals formed during the initial mixing of the elastomer. This is very important as it prevents the polymer from recombining and allowing a consequent drop in polymer molecular weight and thus the reduction in compound viscosity. Process aids are additives that lower viscosity and thus enable a rubber compound to be fabricated with less energy. They also increase melt stability so that the rate of processing can be improved. There are two general kinds of process aids: chemical peptizers and physical plasticizers.

Chemical peptizers typically added at 1 to 3 phr, reduce molecular weight by increasing oxidative chain scission. Examples include sulfonic acid and pentachlorothiophenol, which are commonly used in natural rubber. Excess peptizer must be avoided because it results in reduced vulcanized strength of rubber compound.

Physical plasticizers soften a compound by reducing entanglements and decreasing internal friction. The entanglement plateau modulus [indicative of entanglement density] depends on the concentration of rubber in a rubber / plasticizer mixture to a power of 2.0 to 2.3. Addition of physical plasticizer also improves low temperature flexibility. The good physical plasticizer must be compatible with the rubber compound. The bad compatible plasticizer will bleed from compound. Common plasticizers include oils, fatty acids, esters, pine tar, liquid polymers and resin.

3.7 Vulcanization Agent

Vulcanization agents are the main ingredients to cause a chemical reaction, resulting in cross linking of an elastomer molecule. When it is used together with an accelerator and activator at elevated temperatures, thermally stable covalent bonds are formed between the elastomer chains at the carbon – carbon double bonds. Commonly, sulfur is used as vulcanization agent. Sulfur which is suitable for vulcanization has to be at least 99.5 % pure and it must not contain more than 0.5 % ash. There are two types of
sulfur which are cyclic sulfur (S₈) and amorphous sulfur. Other important vulcanization agents are selenium, tellurium, thiuram di sulphides, peroxides, metallic oxides and quinone dioximes.

The famous vulcanization process or the process by which rubber is heated with sulphur to create a network of chemical crosslinks was invented by Charles Goodyear already in 1839. The non-sticky vulcanized product does not harden with cold weather or soften with hot water [much except at very high temperatures]. It is elastic, jumps back into shape when deformed instead of remaining deformed as unvulcanised rubber does and is highly abrasion resistant. The rubber industry had to wait till the first decades of the 20th century before three discoveries greatly improved the quality and durability of rubber: organic accelerators, reinforcing carbon black filler and antioxidants. Inorganic activators/accelerators, like lead oxide, magnesium oxide and calcium oxide, were already added to reduce the vulcanization time.

3.8 Accelerators

Accelerators are ingredients used in compounding to reduce the vulcanization time, by increasing the speed of vulcanization. Accelerators are divided into five classes according to their chemical structure application in the rubber industry.

They are:

a) Sulfonamides – it plays dual role in the vulcanization; provide longer scorch time which avoids premature crosslinking during vulcanization and processing. This would be a good choice when mixing compounds which contain reinforcing furnace black which generate more heat. e.g. N-cyclohexylbenzothiazole-2-sulfenamide (CBS)

b) Thiazoles – thiazoles derivatives are versatile vulcanization accelerator used alone or combine with other accelerator in a compounding formulation. It gives moderate vulcanization rate and scorch time. e.g. 2-mercaptobenzothiazole (MBT)

c) Guanidines – a secondary accelerator which is used with other accelerator of thiazoles class. The thiazoles – guanidine combinations are frequently used for technical goods. e.g N, N’-Diphenylguanidine
d) Dithiocarbamates – vulcanization with dithiocarbamates is faster than with thiurams. It is used as ultra accelerator. e.g: Zinc Dibutylthiocarbamate

e) Thiurams (others than disulfides) – used as ultra-accelerator with normal amount of sulphur. e.g. Tetramethylthiuram disulfide

Table 3.2 Common accelerators used in sulphur vulcanization

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbr.</th>
<th>Structure</th>
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<tbody>
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<td><strong>Benzothiazoles</strong></td>
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<tr>
<td>2-Mercaptobenzothiazoles</td>
<td>MBT</td>
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<tr>
<td>2,2'-Dithiobenzothiazole</td>
<td>MBTS</td>
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<tr>
<td><strong>Benzothiazolesulphenamides</strong></td>
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<td>TBBS</td>
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<tr>
<td><strong>Thiurams</strong></td>
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<td>Tetramethylthiuram disulphide</td>
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<td><strong>Dithiocarbamates</strong></td>
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<tr>
<td>Zinc dimethylthiocarbamate</td>
<td>ZDMC</td>
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</table>
3.9 Activators

ZnO is still generally known as the best activator for sulphur vulcanization.\(^{(2,3)}\)

As mentioned earlier in the previous chapter, there is an increasing potential concern over the environmental and health effects of release of zinc compounds into the atmosphere from rubber and its allied products. A number of papers have been published on the effect of ZnO in the curing of rubber. ZnO is in many vulcanization systems a precursor to zinc-derived accelerators. It reacts with most accelerators to form the highly active zinc salt. Complex formation of the zinc ion with different accelerators is critical to get efficient curing. A preceding reaction with stearic acid forms the hydrocarbon-soluble zinc stearate and liberates water before the onset of crosslinking. Adams and Johnson observed that the crosslink density increases with increasing zinc stearate concentration. The efficiency of crosslinking of natural rubber (NR) and polyisoprene rubber (IR) is largely increased when ZnO is present. Crosslink shortening is catalyzed which leads to reduced reversion. ZnO appears to lead to a small increase in cure time and scorch safety.

In addition to its role as an activator for sulphur vulcanization, inclusion of ZnO is proved to reduce heat-build-up and improves tyre abrasion resistance. ZnO acts as a ‘heat sink’, which accepts frictional energy without a large increase in internal temperature. It has also been found that ZnO improves heat resistance of the vulcanizes and their resistance to the action of dynamic loading. The high thermal conductivity of ZnO helps to dissipate local heat concentrations that might otherwise affect the properties of rubber. The thermal properties of ZnO are particularly beneficial in applications such as rubber vibration mounts, where loading and cyclic stresses would otherwise generate heat and degrade the rubber. ZnO is also needed for bonding rubber to the steel cord of tyres and for bonding between metal and rubber in technical goods. Besides improving the properties of vulcanized rubbers, ZnO also assists the processing of uncured rubbers. ZnO is added to rubber formulations to decrease shrinkage of moulded rubber products and maintain the cleanliness of moulds. This aids productivity by increasing the number of moulding cycles between cleaning. In earlier days zinc compounds were added as filler and to scavenge detrimental reaction products. Use of ZnO as a filler is uneconomic due to its high cost, and hence it is normally replaced by other cheaper active fillers.
(carbon black or silicates). In rubber formulation for other types of vulcanization, e.g. peroxide, ZnO is also often present, although it does not activate peroxides. The role which ZnO can play in a peroxide-cured compound is as an acid acceptor in materials containing acid fillers or a polymer containing halogens. ZnO is also added to improve ageing resistance, possibly by reacting with the acidic by-products of the crosslinking reaction. It is also a crosslinking agent for polymers containing halogen as well as for those containing carboxyl groups.

Activators \(^1\) are ingredients used to activate the accelerator and improve its efficiency. Zinc oxide, Stearic acid and amines are the most widely used activators. In a curing system consisting of sulphur; the presence of zinc oxide and Stearic acid as accelerators usually requires to attain a good cross linking. It can be classified into organic and inorganic activator. Stearic acid is the most popular type of activator used in rubber industry while zinc oxide is common inorganic type activator used in the rubber compounding. Depending on the particle size, full activation of vulcanization is obtained with about 3 – 5 % of zinc oxide. \(^4\)Zinc oxide activates the vulcanization by complexation with the sulfur accelerator system to give a faster cure rate. Fatty Acid is needed to solubilize the zinc to give Zn\(^{2+}\) which can form complex with sulfur and accelerator as shown below:

\[
\text{ZnO} + 2\text{C}_{17}\text{H}_{35}\text{COOH} \rightarrow \text{Zn ( OOC}_{17}\text{H}_{35})_2 + \text{H}_2\text{O}
\]

### 3.10 Antidegradants

Oxygen and ozone can react with elastomers and alter network structure by causing chain scission and/or cross linking. Antidegradants are ingredients used to retard/prevent the deterioration of rubber compound by oxygen, ozone, heat, light, metal catalysis and mechanical flexing. In compounding, Antidegradants are required to facilitate good aging properties to a compound and prolong its service life. In general, the more saturated bond in the main chains of elastomer, the better aging properties.

Antidegradants could be divided into two types; they are

(i) Antioxidants and

(ii) Antiozonants.
Antioxidants are chemicals which extend the life of rubber products by first reacting with polymeric free radicals and stopping propagation of polymer oxidation. Commercially available antioxidants fall in 3 groups: secondary amine, phenolic and phosphates.

Antiozonants are chemicals which diffuse to the surface and react with the ozone before rubber molecules have chance to react with ozone. Chemical protectants are capable of reacting with anti degradants or interfere with the chain of reactions that otherwise would culminate in degradation of rubber. Commonly used antiozonants are paraphenylediamines (PPD) and petroleum waxes. In the selection of Antidegradants, a few factor need to be considerate such as; type of protection require, chemical activity, persistence, discoloration and cost.

3.11 Nano fillers

The nanofillers used in polymers, on a whole can be categorized into four main categories as per their shape:

(i) Spherical or 0-dimensional Nano filler [e.g., silica nanoparticles etc.]
(ii) 1-dimensional rod-like or fiber type nanofiller (e.g., synthetic whiskers, carbon nanotubes, sepiolite etc.)
(iii) 2-dimensional sheet or platelet type nanofiller (e.g., layered silicates such as smectite clays, synthetic mica, graphite etc.) and
(iv) 3-dimensional nanofiller [e.g., polyhedral oligomeric silsesquioxanes (POSS)]

3.11.1 Spherical or zero dimensional nanofillers

The importance and advantages of nanometer-sized particles were shown not only scientifically, but also in various industrial applications. Of these, silica nanoparticles are materials with wide applications since silica is inherently thermally stable. Furthermore, morphology of amorphous silica powders and porous gels is of interest for improving mechanical and electrical properties of substances. SiO₂ nanoparticles are used
to make electronic substrates, thin film substrates, electrical insulators, thermal insulators and humidity sensors. The silica particles play a different role in each of these products. The quality of some of these products is highly dependent on the size and size distribution of the silica particles. It is imperative to have silica particles of a narrow size distribution and a high purity. (5) Silica particles are suitable candidates for application in chemo-mechanical polishing (CMP) because silica can be directly precipitated as mono-dispersed spheres, their narrow size distribution being an important requirement.

Organic/inorganic composite materials have been extensively studied for a long time. Inorganic nanoscale building blocks include nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., TiO$_2$, Al$_2$O$_3$), semiconductors (e.g., PbS, CdS), and so forth, among which SiO$_2$ is viewed very important. Therefore, polymer/silica nanocomposites have attracted substantial academic and industrial interest. In fact, among the numerous inorganic/organic nanocomposites, polymer/silica composites are the most commonly reported in the literature. (6-13)

It is very versatile, since it has been applied in electrical engineering, electronics and consumer goods (6). If dispersed to the scale of 10–50 nm, it can improve the heat distortion temperature (HDT), the modulus and the barrier properties of a polymer matrix. The improvement of properties is mainly due to the creation of hydrogen bond between the hydroxyl groups on the nanosilica surface and soft segment of polymer. Many research efforts have been devoted to the surface modification of silica. (6-13)

The aim is to reduce the high surface energy and the particle-particle interactions. Additionally, filler treatment leads to a better dispersion due to the more probable interactions of a polymer with the modified inorganic particle surface.

### 3.11.2 One dimensional rod-like or fiber type Nano filler

Sepiolite: Sepiolite is a 2:1 phyllo silicate, where one octahedral sheet is sandwiched between two tetrahedral sheets. The tetrahedral sheets are extended to a considerable distance in the “a” and “b” directions (Fig. 3.7). However, at periodic intervals along the b-axis, the tetrahedral sheets invert and hence sepiolite is also called an “inverted ribbon.” This generates a micro porous structure with a large surface area,
which is responsible for its absorption and adsorption properties and derived applications. Its chemical formula for a half unit cell is given as \[(\text{Si}_{12})(\text{Mg}_8\text{O}_{30}\text{OH})_4(\text{OH}_2)_{48}\text{H}_2\text{O}\]. It contains fine micro pore channels of dimension 0.37×0.16 nm\(^2\) running parallel to the length of the fiber. The parallel piped fibers are bundled together along the c-axis. Thus, micro channels exist along the c-axis and contain free water (zeolite water) molecules attached to the edge of the octahedral layer. Sepiolite, because of its fibrous morphology, high aspect ratio and presence of high density of silanol group, is expected to have a good interaction with the polar groups of rubber chain. Owing to their absorptive properties, sepiolite is used commercially as carriers, fillers, clarifying agents, and for lubricant reclamation.\(^{(14-18)}\)

![Fig.3.7 Structure of Sepiolite](image)

3.11.3 Two dimensional sheet or platelet type nano filler

Clay, organoclay and clay minerals e.g., layered silicates such as Smectite clays, synthetic mica, Graphite etc. The term, clay, is denoted by a particle size range and by certain physical properties. The particle size and properties can vary, depending upon the discipline that is operationally using the term. In geology, the term clay includes all particles that are <2 \(\mu\)m. Clay is often described as a fine grain material that is mainly composed of hydrous alumino silicate minerals.
Clays are composed of two basic building blocks (see Fig. 3.8)

a) Silicon - Oxygen Tetrahedron \((\text{SiO}_4-4)\)

b) Aluminum Octahedral (Gibbsite Sheet) \((\text{AlO}_6-9)\)

Fig. 3.8 (a) Si-Tetrahedron and (b) Al-Octahedral

Smectite clays (e.g., montmorillonite, hectorite, saponite etc.) and related layered silicates have mostly been chosen as the filler in preparing polymer nanocomposite over the years due to the following merits:

- These exhibit rich intercalation chemistry with which compatibilization can be made possible with organic surfactants.
- Clay platelets possess high aspect ratio (length to thickness), high surface area, and high stiffness.
- These occur ubiquitously in nature and can be obtained at low cost.

Montmorillonite (MMT): The most common dioctahedral smectite is montmorillonite, discovered in 1847 in France (Montmorillon). This clay is nowadays the most widely used nanofiller. Common formula of montmorillonite is \((\frac{1}{2}\text{Ca,Na})(\text{Al, Mg, Fe})_4(\text{Si, Al})_8\text{O}_2(\text{OH})_4.n\text{H}_2\text{O}\) (it depends on type of MMT).
Fig 3.9 Structure of Montmorillonite

The model structure (Fig 3.9) consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The MMT layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns. MMT has a very high aspect ratio (e.g. 10–1000); one gram of this clay has a surface area of 800 m². Isomorphous substitutions of Si⁴⁺ for Al³⁺ in the tetrahedral lattice and of Al³⁺ for Mg²⁺ in the octahedral sheet cause an excess of negative charges within the MMT layers. These negative charges are counterbalanced by cations such as Ca²⁺ and Na⁺ situated between the layers. Due to the high hydrophilicity of the clay, water molecules are usually also present between the layers. Stacking of the layers leads to regular van der Waals gaps called interlayers or galleries. There are a number of descriptive terms for MMT. It is mainly based on geographic source, exchangeable cations, production process, and end use application.

This new class of material involves nano-scale dispersion in a polymer matrix, which leads to improved properties over regular composites. Complete dispersion or exfoliation of the clay layers in monomer or polymer may comprise up to three steps similar to dispersion of powders in liquid, described by Parfitt. (19)
The first step is wetting the surface of clay tactoids by monomer or polymer molecules. Secondly, intercalation or infiltration of monomer or polymer takes place, followed by the third step, exfoliation of the clay layers. Thermodynamics control the first and second steps, while mechanical and reaction driving forces determine the extent of the third step. Depending on the strength of interfacial interactions between a polymer matrix and the silicate layers, three types of polymer composites may be formed as shown in Fig. 1.4. In conventional composites, the clay tactoids exist in their original aggregated state with Nano layers stacked face to face and without any polymer intercalation, which results in poor mechanical properties. In the case of intercalated polymer-clay nanocomposite, few molecular layers of polymer penetrate the clay host galleries increasing the d-spacing. Finally, exfoliated polymer\(^{(20)}\) clay Nano composites contain individual Nano layers separated in a continuous polymer matrix by an average distance which depends on the clay loading. Usually, the clay content of an exfoliated nanocomposite is lower than that of an intercalated nanocomposite. Exfoliation is more appealing for enhancement of certain properties of a material because of the high degree of dispersion and maximum interfacial area between polymer and clay.\(^{(21)}\)
3.12 References


18. URL:<http://clays.org/eduresources/EduResourcesWWWLinks.html[cit.2007-06-12]).

