CHAPTER 1

INTRODUCTION
Polymer modification and blending of elastomers have attained a prominent place in the field of polymer technology, as it is realized that synthesis of new elastomers are not always necessary for applications requiring specific properties. It can be met by modification of existing polymers or by blending of suitable elastomers. So chemical modification and polymer blending have become a growing stimulation for research in the field of rubber chemistry and technology since the last few decades. Modification is attained by the incorporation of reactive functional groups on to the polymer chains. Functionalization of polymers results in new materials with wide spectrum of properties not available in parent polymer. Chemical modification of polymer backbone, grafting on to polymer chains, inter chain reactions and the formation of interpenetrating networks are the subject of many reviews. Modification carried out on synthetic elastomers often result in enhanced properties as compared to original elastomers, where as chemical modification on naturally occurring polymers are generally accompanied by a loss in their basic characteristics. The first commercial carboxylated elastomer butadiene-styrene- acrylic acid terpolymer latex was introduced in 1949 by Goodrich under the trade name HYCAR 1571. Carboxylated nitrile rubber lattices find extensive use in leather-based products, oil resistant seals, gaskets, paper coatings and textile applications. The good abrasion resistance of carboxylated styrene butadiene rubber (SBR) enables it to find application in tyre tread compounds. Bromobutyl rubber, a modified form of butyl rubber (IIR) was first introduced commercially by BF Goodrich in 1955. The combination of low air permeability, good aging properties and better compatibility with natural rubber (NR) makes bromobutyl rubber an ideal choice for tyre industry. Successful materials prepared by modification of natural rubber that have got a lot of commercial applications include cyclised rubber, chlorinated rubber, hydrochlorinated
rubber, epoxidized and grafted natural rubber. In these products the degree of
modification is extensive and the products no longer possess the high elasticity of the raw
material.

Polymer blending is another important route for developing polymer materials
with tailor made physical properties. Blending of thermoplastics is of recent origin,
whereas elastomer blends have been used in rubber industry since long time especially in
tyre and mechanical goods. Blends of nitrile rubber (NBR) and poly vinyl chloride (PVC)
have became commercially significant for use in hose, wire and cable industry. \(^7\) Thermoplastic NR prepared by blending NR with plastics like, polyethylene and
polypropylene and blends of NR with ethylene propylene rubber (EPDM) are materials
that have been widely used in cable insulators, auto bumpers, hoses and gaskets. \(^9,10\)

1.1. ELASTOMERS

Elastomers form a special class of polymeric materials characterized by a unique
combination of useful properties such as elasticity, flexibility, toughness and
impermeability. They are macromolecular substances capable of passing, under the effect
of vulcanization from a predominantly plastic state to a predominantly elastic state. \(^11,13\)

Generally elastomers are classified as commodity or general purpose elastomers
[such as NR, styrene butadiene rubber (SBR), isoprene rubber (IR) etc.], high volume
speciality elastomers [such as ethylene propylene rubber (EPM, EPDM), Chloroprene
rubber (CR), acrylonitrile butadiene rubber (NBR) ] and low volume speciality
elastomers [such as polyurethane (PU, AU, EU), silicone (VMQ, FMQ), fluorocarbon
(FKM, FPM, FFKM), polyacrylate (ACM,AEM), epichlorohydrin (ECO),
chlorosulphonated elastomer (CSM) etc].

Elastomers may also be classified in groups, according to different aspects
including chemical saturation of the polymer chain, oil resistance, flame resistance and
service performance. \(^14\) According to the chemical saturation of polymer chain of the
basic rubber, classification is as in Table. 1.1
Table 1.1

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>Ozone resistance</th>
<th>Excellent</th>
<th>Good/Very good</th>
<th>Fair</th>
<th>Poor</th>
</tr>
</thead>
<tbody>
<tr>
<td>With saturated backbone</td>
<td>Ozone resistance</td>
<td>Excellent</td>
<td>Good/Very good</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>ACM, AEM, CSM, EPDM, EPM</td>
<td>IIR, HNBR</td>
<td>CR</td>
<td>BR, IR, NBR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FPM, FFKM, VMQ, FMQ,</td>
<td></td>
<td>NR, SBR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECO, AU, EU</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Elastomers that exhibit high resistance to ozone and weather are characterized by a saturated backbone. Elastomers with highly unsaturated backbone like NR and polybutadiene (BR) are not inherently ozone resistant. Therefore antiozonents and protective waxes are added during compounding to improve the ozone resistance. CR though highly unsaturated, like NR, show fair ozone resistance due to the presence of chlorine atom which reduces the reactivity of double bonds to oxidizing agents including oxygen and ozone.

Elastomers having polar groups in the polymer chain show resistance to mineral oils. Table 1.2 shows grouping of most common elastomers based on their oil and ozone resistance.
<table>
<thead>
<tr>
<th>Elastomers</th>
<th>Non oil resistant</th>
<th>Oil resistant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone resistance</td>
<td>Excellent</td>
<td>Good/Very good</td>
</tr>
<tr>
<td>EPM</td>
<td>IIR</td>
<td>BR, IR</td>
</tr>
</tbody>
</table>
| EPDM | NR, SBR | FPM, FFKM, VMQ, FMQ, ECO, AU/EU |}

Halogen containing polymers like, perfluorocarbon rubbers (FFKM), fluorocarbon rubbers (FPM), chloroprene rubber (CR), chlorosulphonated rubber (CSM), CO and epichlorohydrin rubber (ECO) are inherently flame resistant and flame resistance improves as the polymer halogen content increases. Halogen free elastomers are not flame resistant unless they contain a high concentration of flame-retardants.
1.1. A. Natural Rubber

NR remains the best choice of elastomer for many applications that require low heat build up such as, in large tyres, carcasses of passenger car tyres, vibration dampers, springs, engine mountings and bearings. Other products like, hoses, conveyor belts, gaskets, seals, rollers, rubberized fabrics, elastic bands, latex foams, adhesives, pharmaceutical and medical products also consume a major part of NR.

It is the most widely used naturally occurring elastomer which is a homopolymer of isoprene having a cis 1,4 configuration as in Figure 1.1 and available in a variety of types and grades including latex, technically specified grades, sheets, crepes, etc.¹⁵

NR vulcanizates have high tensile strength over a wide hardness range due to its "strain induced crystallization".¹⁶ It has the highest resilience (except BR) which is responsible for its very low heat build up. It shows very low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue.

\[
\text{CH}_2 \quad \text{C = CH} \quad \text{CH}_2 \quad \text{CH}_3
\]

\[\text{Figure 1.1.}\]

As an unsaturated elastomer, NR vulcanizates are susceptible to attack by atmospheric oxygen and ozone and hence its heat and weather resistance is very poor. It is not resistant to petroleum-based oils and fuels, as it contains no polar groups, but can be used with a wide range of organic and inorganic chemicals such as, non-petroleum based automotive break fluids, silicone oils and greases, glycols, alcohols, water and non-oxidizing aqueous solutions of acids, alkalies and salts.
The properties of NR can be improved either by chemically modifying or blending with speciality elastomers.

1.1.B.Hydrogenated nitrile rubber (HNBR)

HNBR as designated by ASTM D1418 was first commercialized in 1984 by Zeon Corporation (Nippon Zeon Co. Ltd., Japan) under the trade name Zetpol. Later the same year Bayer also announced the commercialization of their new HNBR under the trade name Therban. Tomac is another commercial grade by Polysar International S.A, Switzerland. This family of elastomer has been manufactured by the hydrogenation of diene containing polymers, by a well-known and established reaction process, which starts with an emulsion polymerized acrylonitrile butadiene copolymer (NBR). The NBR base polymer is dissolved in a pre selected solvent. Then through the addition of a particular catalyst in combination with a pre determined pressure and temperature undergoes a selective hydrogenation process producing a highly saturated nitrile elastomer.\textsuperscript{17,18} Recently a bimetallic complex catalyst for hydrogenation of nitrile rubber is reported by D.M Yue and coworkers.\textsuperscript{19} A new commercial grade trade named as Thortan is reported by DSM Nv, a Dutch Co., based on a new technology which reduces the production cost of HNBR.\textsuperscript{20} Hydrogenation of NBR latex is also reported.\textsuperscript{21} The structure of HNBR is as shown in figure 1.2. The subscript (x-z) after the initial ethylene unit shows the variation in the ethylene unit concentration as a function of degree of hydrogenation of the butadiene units.

\[
\left[ -(CH_2-CH_2-CH_2-CH_2^-)_{(x-z)}(-CH_2-CH^-)_y(CH_2-CH=CH-CH_2)_z^- \right]_n \quad C≡N
\]

\textbf{Figure 1.2}
Through control of this reaction many different grades of HNBR are currently produced. The available grades vary in hydrogenation level, acrylonitrile content, and Mooney viscosity and are given Table 1.3(a).

<table>
<thead>
<tr>
<th>% hydrogenation</th>
<th>% ACN content</th>
<th>Mooney Viscosity, ML(1+4)100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>85-99+</td>
<td>17-50</td>
<td>50-150</td>
</tr>
</tbody>
</table>

The grade names of commercialized HNBR, trade named as Zetpol by Nippon Zeon Co.Ltd. are shown in Table 1.3(b)

<table>
<thead>
<tr>
<th>Grade</th>
<th>Bound ACN, %</th>
<th>Iodine value, g/100g</th>
<th>Mooney Viscosity, ML(1+4)100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zetpol 1010</td>
<td>44 ± 2</td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>Zetpol 1020</td>
<td>44 ± 2</td>
<td>24 ± 4</td>
<td>78</td>
</tr>
<tr>
<td>Zetpol 2000</td>
<td>36 ± 2</td>
<td>7 max.</td>
<td>85</td>
</tr>
<tr>
<td>Zetpol 2000 L</td>
<td>36 ± 2</td>
<td>7 max.</td>
<td>65</td>
</tr>
<tr>
<td>Zetpol 2010</td>
<td>36 ± 2</td>
<td>11</td>
<td>85</td>
</tr>
<tr>
<td>Zetpol 2010 L</td>
<td>36 ± 2</td>
<td>11</td>
<td>57 ± 5</td>
</tr>
<tr>
<td>Zetpol 2020</td>
<td>36 ± 2</td>
<td>28</td>
<td>78</td>
</tr>
<tr>
<td>Zetpol 2020 L</td>
<td>36 ± 2</td>
<td>28</td>
<td>57 ± 5</td>
</tr>
<tr>
<td>Zetpol 2030 L</td>
<td>36 ± 2</td>
<td>56 ± 5</td>
<td>57 ± 5</td>
</tr>
<tr>
<td>Zetpol PBZ 123</td>
<td>28 ± 9</td>
<td>24 ± 4</td>
<td>48</td>
</tr>
<tr>
<td>Zetpol PBZ 521</td>
<td>40 ± 2</td>
<td>27</td>
<td>49</td>
</tr>
</tbody>
</table>
HNBR elastomers are very tough, and provide outstanding stress-strain characteristics and abrasion resistance along with an excellent balance of low temperature and fluid balance properties.\textsuperscript{22-24} As the acrylonitrile content increases, oil and fuel resistance improves. As the acrylonitrile content decreases, low temperature properties improve. The static heat resistance of HNBR elastomers depends on the level of saturation within the elastomer. However, as the saturation level decreases, the dynamic heat generated as a result of flexing decreases. So one has to determine the most appropriate saturation level depending on the desired end use in question. There is a convenient wide grouping of Mooney viscosity available which enables a manufacturer to produce a variety of products from HNBR.

Compounding is similar to NBR with some notable exceptions.\textsuperscript{25} Peroxide cure is preferred for fully saturated grades. Both sulphur and peroxide cure are applicable for slightly unsaturated grades. One can use a wide range of carbon blacks, white fillers, antioxidants and processing aids. Most commonly used plasticizer is triisooctyl trimellitate (TOTM), which provides the best balance of high and low temperature performances. Although HNBR elastomer is sulphur curable, most are peroxide cured, because of the enhanced heat and ozone resistance obtained via this cure chemistry.\textsuperscript{25-28} The most common peroxides used are 1,4 bis(t-butylperoxy) di isopropyl-benzene, dicumylperoxide and 2,5, dimethyl-2,5-di-(t-butyl peroxy)hexane. HNBR uses a significantly higher quantity of peroxide commonly use 6-12 phr. Although not used in all cases coagent may play a key role in both the cure chemistry and processability of HNBR compounds. Electron beam irradiation is also used for vulcanization of HNBR compounds.\textsuperscript{29} Both fully and partly hydrogenated grades are reported to be suitable for radiation induced cross linking.\textsuperscript{30}

Largest single use of HNBR is in synchronous timing belts for automotive industry.\textsuperscript{31,32} Other uses\textsuperscript{33} are in power steering, air conditioning, fuel systems and as O-rings, packings, gaskets, oil seals, hoses, drilling pipe protector, fuel hoses, diaphragms intank insulator, etc. It is also used in cable jacketing and in many different industrial, aerospace, oil fields and food contact applications. Very recently, a multifunctional
elastomeric coating based on HNBR for use on rubber compounds has been reported to form tough, high strength coating with good ozone and weather resistance coupled with excellent oil and fuel resistance.34 Blends of HNBR with Nylon35 and other elastomers such as, CR and NBR are also reported.36

1.2.MODIFIED FORMS OF NR

NR can be modified by physical or chemical means and in some cases by a combination of the two.37 Figure 1.3 gives most of the different types of modifications in NR.38,39 Physical methods involves incorporation of additives that do not chemically react with rubber. Examples are oil extension, blending with other polymers, masterbatching, deproteinisation, prevulcanization, etc. NR is deproteinised to reduce water absorption and protein allergy which is effected by either enzymatic hydrolysis40 /radiation process41 or by multiple centrifugation. Deproteinised rubber (DPNR) is used in electrical and medical applications. Prevulcanization is usually done on latex stage.42 Prevulcanized latex (PVNRL) is used for the production of articles by casting or dipping. Superior processing natural rubber (SPNR) is prepared by blending ordinary and vulcanized lattices in 80:20 ratio before coagulation.43 Unfilled and lightly filled compounds made with SPNR give smoother and less swollen extrudates compared to those prepared from regular NR.

1.2.1.Chemical modification of NR

A chemical modification depends on the chemical reactivity of the NR molecule. Being unsaturated, NR is highly reactive and several chemical reactions could be carried out resulting in materials having entirely different properties. Depending on the extent of modification, four classes of products are identified37 as in Table 1.5. Low levels of modification have the object of retaining high elasticity while providing the means for
### Table 1.4. Modification of NR

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incorporation of compounding ingredients</td>
<td>Polymer blends</td>
</tr>
<tr>
<td>Pre-vulcanized latices</td>
<td>NR/SR, NR/plastics</td>
</tr>
<tr>
<td>OENR</td>
<td>TPNR &amp; Impact modified plastics</td>
</tr>
<tr>
<td>Master batches</td>
<td></td>
</tr>
<tr>
<td>Latex stage compounds</td>
<td></td>
</tr>
<tr>
<td>SP rubber</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intermolecular changes</th>
<th>Grafting</th>
<th>Attachment of pendant functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclisation</td>
<td>Styrene</td>
<td>Antioxidant bound</td>
</tr>
<tr>
<td>Cis-trans isomerism</td>
<td>Methyl methacrylate</td>
<td>Epoxidation</td>
</tr>
<tr>
<td>Depolymerisation</td>
<td>Acrylonitrile</td>
<td>Halogenation</td>
</tr>
<tr>
<td>Peptisation</td>
<td>Malic anhydride</td>
<td>Hydrohalogenation</td>
</tr>
<tr>
<td></td>
<td>Acrylamide</td>
<td>Hydrogenation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dichlorocarbene addition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Viscosity stabilization</td>
</tr>
</tbody>
</table>
altering specific properties to make the rubber suitable for particular application or conditions of use. For example, reactive site might be provided for new type of cross-linking for binding antioxidants or other materials or substrates. At moderate degree of modification, physical properties are altered due to the change in glass transition temperature (Tg) and a rubber with new properties is obtained. More drastic modifications leads to non-rubberly resinous or plastic materials. Finally modification only on the surface may be useful for increasing adhesion to other surfaces or protection against hostile environments.

Table 1.5. Classification of modified forms of NR

<table>
<thead>
<tr>
<th>Degree / type of modification</th>
<th>Approximate extent of modification (mole%)</th>
<th>Effect on elastic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slight</td>
<td>&lt; 5</td>
<td>Essentially unchanged</td>
</tr>
<tr>
<td>Intermediate</td>
<td>5 - 25</td>
<td>Modified</td>
</tr>
<tr>
<td>Extensive</td>
<td>&gt; 25</td>
<td>Lost</td>
</tr>
<tr>
<td>Surface</td>
<td>&lt; 1</td>
<td>Bulk unchanged</td>
</tr>
</tbody>
</table>

Chemical modifications can be broadly grouped into
1) Attachment of a pendant functional group
2) Grafting of a different polymer at one or more points along the NR molecule
3) Inter molecular changes without the introduction of a new chemical group
1.2.1.A. Attachment of pendant functional group

1.2.1.A. i. Chlorinated rubber

Chlorinated natural rubber (CNR) is one of the first forms of chemically modified NR which find use in many commercial applications. Chlorination is carried out either in solution or latex stage and the reaction involves substitution and cyclisation along with addition of chlorine. For the industrial preparation, batch and continuous process are now available and in all cases carbon tetrachloride is used as solvent for NR to perform the chlorination. Recently liquid chlorine has been reported to be used instead of carbon tetrachloride. Use of depolymerised NR as starting material is reported to give higher yield of product. Chlorinated rubber of 65% chlorine content is a pale, cream colored thermoplastic powder which is non inflammable and highly resistant to ozone, weather and chemicals up to 100 °C. CNR prepared from latex (CNRL) is characterized by IR, TGA and DTA investigations and is reported to exhibit poorer thermal and thermo-oxidative stabilities than CNR prepared from solution (CNRS). The effect of copper oxide on thermal stability of CNRL has been studied by Yu, et al. The thermal degradation of CNRL in nitrogen atmosphere is a one step dehydrochlorination reaction. In air it degraded with two distinct steps of weight loss. In the first step, the hydrogen chloride is eliminated along with the release of a little amount of carbon dioxide. In the second step, the backbone of CNR is oxidized into carbon dioxide. The presence of copper oxide is shown to reduce the thermal stability by accelerating the dehydrochlorination reaction.

CNR is used in anticorrosive and heat resistant paints and coatings, adhesives, printing inks, paper coatings and textile finishes by mixing with an opportune solvent. The composition contains at least 10% of chlorinated rubber with plasticizers and pigments. It is also used to protect wood, steel, cement, etc. from the environmental attacks and has been recommended as traffic paints on roads. Commercial grades are available under several trade names like, Pergut, Alloprene, etc.
1.2.1.A. ii. *Epoxidised NR*

Latex stage epoxidation of NR under controlled conditions gives epoxidised NR (ENR) with improved resistance to hydrocarbons and oils, low air permeability, increased damping and good bonding properties while retaining the high strength properties of NR. Improvement of these properties depends on the degree of epoxidation. Two grades of epoxidised NR, ENR 25 and ENR 50 with 25 and 50 mole percent of epoxidation respectively have attained commercial importance. It is reported that the volume swelling value of ENR 50 in ASTM oils approaches that of medium acrylonitrile NBR and is superior to that of polychloroprene rubber. Another distinctive feature of ENR is the high degree of reinforcement achieved with silica fillers without the addition of silane coupling agent. ENR can be used as cover compound for PVC core conveyor belts. The processing characteristics and physico chemical properties of thioglycolic acid modified low molecular weight ENR (ELMWNR-TGA) and its blend with NR has been reported recently. It is shown that ELMWNR-TGA exhibits lower tensile strength, higher elongation at break but better resistance to solvents and mineral oils.

\[
\text{CH}_2\text{C} = \text{CH}\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_2\text{C} = \text{CH}\text{CH}_2\text{O} \text{CH}_3
\]

*Figure 1.3.*
1.2.1.A. iii. *Constant viscosity and low viscosity NR*

Increase in viscosity of NR during storage under ambient conditions known as storage hardening is caused by the cross linking reaction involving the randomly distributed carbonyl groups present on the main rubber chain and the amino acids present among the non-rubber constituents.\(^5^9\) This can be inhibited by the addition of small amount of hydroxyl amine hydrochloride or hydroxyl amine neutral sulphate to the latex before coagulation. These chemicals effectively block the carbonyl groups and preserve the Mooney viscosity of the rubber. Viscosity stabilized rubber is technically specified and is available in two forms. Indian Standards Natural Rubber, ISNR 5CV and ISNR 5LV as per Indian standards with Mooney viscosity range of 60-65 for CV and 50 ± 5 for LV.

1.2.1.A. iv. *Carbene addition*

Carbenes (>C:) react readily with NR and is facilitated by the use of quaternary ammonium salts as phase transfer catalyst. The latter compounds bring the aqueous reagents into contact with the organic phase containing the polymer.\(^6^0\),\(^6^1\) Treatment of cis poly isoprene in dilute aromatic solvent with dichlorocarbene prepared in situ from ethyltrichloroacetate with sodium methylate gives a white powder. The double bonds are converted into a dichlorocyclopropane rings.\(^6^2\) Similarly reaction of polyisoprene with dibromocarbene formed in situ from bromoform give 70-75 % saturation of polymer double bonds. Carbene derived from the photolytic or thermal decomposition of 3,5 di-tert butyl benzene-1,4 diazoxide was used to introduce a polymer bound hindered phenol antioxidant on to NR.\(^6^3\)
1.2.1.A. v. ENPCAF modification

Ethyl-N-phenylcarbamoylazofonnate (ENPCAF) modified NR shows the influence of bulky polar pendant groups on the physical properties of NR.\textsuperscript{64,65} This modification can be carried out in an intermix or mixing mill at 110 °C on dry rubber. The reaction can also be carried out in latex stage at 30°C using deammoniated latex. The chemical modification results in the formation of hydroester pendant groups and is accompanied by an increase in Tg of the polymer along with high damping properties, improved gas impermeability and solvent resistance. The highly polar group introduced has a dramatic effect on the physical properties as shown by changes in stress relaxation and recovery of peroxide cured NR modified by ENPCAF.\textsuperscript{66}

1.2.1.A. vi. Hydrogenation

Hydrogenation of NR was first reported by Berthalot\textsuperscript{67} and there had been a steady stream of research publications on this subject.\textsuperscript{68-70} By using a reaction of hydrogen at 30-35 atmosphere with a 2% solution of pale crepe rubber in cyclohexane over Nickel-Kiesleguhr catalyst in an autoclave at 200°C -220 °C for 12 hours lead to fully hydrogenated NR. More recently, homogeneous two component system based on a variety of Nickel and Cobalt compounds in combination with tri isobutylaluminium is reported to give complete hydrogenation in solution after 1 hour at 28°C.\textsuperscript{71} Hydrogenation of diene elastomers, their properties and applications are discussed by Singha, et al.\textsuperscript{72} in a recent review. Hydrogenated rubber is colorless and transparent. It is a plastic, elastic waxy solid with the peculiar characteristic of forming threads when stretched. Potential area of application is in cable industry, which would utilize its insulation properties.
1.2.1.A. vii. Hydrohalogenation

NR can be modified with hydrogen fluoride, hydrogen chloride, hydrogen bromide or hydrogen iodide to get the respective rubber hydrohalides. The aim of this modification is same as that of halogenation, to reduce chemical reactivity of NR to oxygen and ozone by addition to the double bond. Bunn and Garner reported that addition of HCl to polyisoprene obey Markownikov’s rule. (Figure 1.4) The rubber hydrochloride is a highly crystalline material. It is unaffected by dilute acids and bases at room temperature. NMR studies by Golub and Heller have established that cyclization reaction also occurs during hydrohalogenation.

\[
\begin{align*}
\text{CH}_2=\text{C}=\text{CH}-\text{CH}_2\cdots \quad + \quad \text{HCl} \quad \rightarrow \quad \text{CH}_2-\text{C}=\text{CH}-\text{CH}_2\cdots \\
\text{CH}_3 & \quad \text{H} \\
\end{align*}
\]

Figure 1.4

1.2.1.B. Grafting

NR can be modified to graft copolymers by polymerizing vinyl monomers either in latex or solution. Methylmethacrylate (MMA), styrene and acrylonitrile are the prominent monomers used for grafting on to NR. Among these polymethylmethacrylate grafted NR (PMMA-g-NR) is the most popular and has been commercialized since mid 1950’s in Malaysia under the trade name Heveaplus MG. Generally grafting can be achieved by two methods viz, by use of chemicals or by irradiation with γ rays. The developments on this topic during the period of 1950-1990 had been recently reviewed by Blackly. In later years, considerable efforts had been made to achieve thermoplastic elastomer characteristics to these graft polymers by controlling the polymerization...
Recently Schneider, et al. reported that styrene and methylmethacrylate can be graft polymerized on NR latex in two step emulsion polymerization and can be used as toughening agent for SAN and polystyrene. Lehrle, et al. reported the effect of using small quantity of vinyl acetate on the efficiency of grafting methylmethacrylate in NR latex using AIBN as initiator. Fukushima, et al. compared the grafting efficiency of styrene on to NR prepared from highly deproteinised latex and high ammonia concentrated latex using t-butyl hydroperoxide / TEPA redox system. The results are favorable towards high ammonia concentrated latex.

Polymethylmethacrylate is a hard plastic and when grafted on to NR, it increases the modulus of rubber depending on the percentage of methylmethacrylate grafted to it. Major use of Heveaplus MG is in adhesives. In automotive industry for applications such as light shield, soft fronts, rear ends, rubbing strips and bumpers, blends of Heveaplus MG49 with NR can be used. It can also function as a compatibilizer in rubber/plastic blends. Styrene grafted NR (SG 50) can find application in micro cellular soleings in place of high styrene resin grade SBR.

Attempts to modify NR latex particle to produce NR interpenetrating networks was made by Hoursten, et al. Recently Subramanian, et al. reported NR latex seeded emulsion polymerization of a highly hydrophobic monomer, vinyl neo-deaconates, under carefully controlled conditions. The DSC studies of the particles so formed shows a 5°C rise in Tg of the NR indicating the formation of a relatively homogeneous semi interpenetrating network or graft microphase.

1.2.1.C. Intramolecular changes

1.2.1.C.i. Liquid NR (LNR)

Liquid NR is prepared either by thermal or by chemical depolymerization of NR. In thermal depolymerization, rubber with 0.2 to 0.6 phr peptizer is first masticated to a Mooney viscosity of 25-30 and depolymerized by heating to 220°C -240°C under stirring
for 3-7 h. LNR with viscosity average molecular weight (Mv) in the range of 5000 – 20000 has been reported to be produced by this method. Chemical depolymerization is carried out in the latex stage by a redox reaction involving phenylhydrazine and air. The mechanism of depolymerization involves the oxidation of phenyl hydrazine by air to give phenyl radical which through addition or transfer reaction initiates the formation of hydroperoxides. These peroxides lead by chain breakage to liquid NR with molecular weight range 6,000 – 20,000 depending on the quantity of reagent used. The low molecular weight NR has been found to have similar properties with NR, for example affinity for ingredients during compounding, chemical behavior and service life performance.

Liquid NR is used in elastic moulds, printing industry, as binder in grinding wheels, as reactive plasticizer and as bulk viscosity modifier in rubber compounds. Carboxy terminated liquid NR (CTNR) is reported as an adhesive in bonding rubber to rigid and non-rigid substrates.

1.2.1.C.ii. Cyclised NR

Cyclised NR is a resinous material, obtained by treating NR with acidic reagents like, sulphuric acid, p-toluene sulphon acid and by Lewis acids like, SnCl₄, TiCl₄, BF₃, and FeCl₃. Cyclisation could be done in solid, solution or latex stage. Cyclised NR is found to have increased softening point, density and refractive index than NR. The preparation of cyclised NR latex on commercial scale was well established as early as 1947. It is used in soling compounds as on heating it changes to a hard thermoplastic material.

1.3. POLYMER BLENDS

Developments of polymeric materials have been driven by the desire to make better products at minimum cost. Polymer blending technique is quite attractive based on the fact that, already existing polymers can be used and the costly development of new
polymers via co-polymerization or by polymerization of new monomers can be avoided to achieve the requirement more rapidly and economically. As there is no generally accepted definition for polymer blends, they are generally considered as physical mixtures of two or more polymers. Normal methods of obtaining polymer blends are dry blending, solution blending, latex blending, etc. In these cases, no chemical bonds exist between the component polymers forming the blend.

1.3. 1. Reasons for blending

The flexibility associated with blending of elastomers is such that it can be carried out to suit the requirements of both producer and user. The user related advantages are as follows. Developing materials with a full set of desired properties, improving a specific property like, high temperature, oil, ozone resistance etc. and adjusting requirements at lower cost.

The producer related advantages are as follows. Better processability, more uniformity and less scrap rejects, product tailorability to specific customer needs, better customer satisfaction, quick formulation changes, plant flexibility and high productivity and increased economy.

1.3. 2. Preparation of elastomer blends.

Corish\textsuperscript{106} has reviewed the general techniques for preparing elastomer blends namely, latex, solution and dry blending. A brief description of blending technology is given below.

1.3. 2. i) Latex blending.

Angrove\textsuperscript{107} has reviewed latex blending, giving particular attention to processing, properties and economics. This technique has the potential for fine dispersion of the
components, as the particles in the latex are very fine and well dispersed. Blends of NR/BR have been investigated by Blackly.\textsuperscript{108} Blends of BR/SBR and BR/NR prepared by latex blending, reported to give a homogeneous dispersion of carbon black.\textsuperscript{109} However, latex blending does not provide any cost advantage, since coagulation, removal of water and drying are cost intensive process.

1.3. 2. ii) Solution blending

This technique gives coarser particles because the low solution viscosity promotes rapid coalescence. Walters and Keyte\textsuperscript{110} indicate greater heterogeneity (for NR/SBR blend) in solution mixed blends as did Livingstone Rongone.\textsuperscript{111} Shunda, et al.\textsuperscript{112} prepared a satisfactory blend of NR/BR by this technique. However, the drying process needs adequate amount of energy that makes it costly.

Combination of solution and latex blending is also used for master batching.\textsuperscript{108} In the Columbian hydro dispersion process, the elastomer blend is kept in solution and the black is dispersed in solution, which transfers into the solution quite rapidly and produces a master batch. In the reverse process, the black dispersed in a solvent is blended with latex so as to provide a good dispersion.

1.3. 2. iii) Dry blending

This technique is applied for the preparation of most of the elastomer blends by using a mill, Banbury or extruder. This is because the process is economical and facilitates the incorporation of compounding ingredients in one operation. Again, blending is facilitated by mastication, which not only reduces viscosity but under proper conditions provides opportunity for reaction (block or graft polymerization) and covalcanization. While Evans and Patridge\textsuperscript{113} suggest that incorporation of all the ingredients in single step is desirable, Shunda\textsuperscript{112} suggests that multi mixing provides better dispersion. Avgeropolos, et.al carried out extensive mixing studies on EPDM/BR blends.\textsuperscript{114}
These methods may be further divided into two general categories as pre blending\textsuperscript{115} and phase mixing\textsuperscript{116,117}. In the first case, the compounding ingredients are generally added to the premixed elastomers. In the phase mix, an attempt is made to control the specific location of filler and curing agents. This is generally accomplished by the preparation of separate master batches which are then blended mechanically\textsuperscript{118,119}.

In addition to these a number of special mixing techniques have been developed to control more precisely the different aspects of the overall homogeneity, phase morphology, filler distribution and interfacial interaction of the different components of elastomer blends. Hindemarch and Gale\textsuperscript{120} developed a Cavity Transfer Mixer (CTM), designed to improve blending efficiency through better flow patterns which enhances distributive mixing in blends like NR/EPDM and SBR/BR. Coran and coworkers\textsuperscript{121-122} have applied dynamic vulcanization technique to enhance properties of EPDM/NR and ACR/NBR blends.

1.3.3. Factors affecting properties of elastomer blends

During the last few years, considerable research and development has been occurred in the area of polymer blends. The importance of elastomeric blends has lead to extensive literature on this subject including several reviews\textsuperscript{106,123-125} and many patents\textsuperscript{126-128}. Very recent reviews by Roland\textsuperscript{129} and Dhuryodhan Mankaraj\textsuperscript{130} summarize the different aspects of elastomer blends. Antony, et al. have reviewed blends of self cross-linking elastomers\textsuperscript{131}. These studies revealed that the properties of polymer blends depend on many factors like,

- Blend ratio\textsuperscript{132-137}
- Properties of component polymers\textsuperscript{138-139}
- Viscosity of component polymers\textsuperscript{140-142}
- Morphology\textsuperscript{145-148}
- Compatibility or miscibility between polymers\textsuperscript{149-150} and
- Interaction between the components during blending\textsuperscript{151-152}
Unlike plastics, elastomers contain a large number of compounding ingredients and the problems related to these materials also have to be taken care of. Based on this, factors affecting properties of elastomeric blends are:

- Interfacial adhesion / cross linking\textsuperscript{153-156}
- Distribution of filler between elastomers\textsuperscript{157-163}
- Distribution of cross links between elastomers\textsuperscript{164}
- Distribution of other non-reactive ingredients between elastomers\textsuperscript{165-170}

While true miscibility may not be required for good rubber properties, adhesion between the polymer phases is necessary and the respective interfacial energies are important. Shershnev\textsuperscript{154} has summarized the importance and requirement of co-vulcanization of the component elastomeric blends. Co-vulcanization was defined in terms of a single network structure including cross-linked macromolecules of both polymers. They should be vulcanized to similar level with cross-linking across the micro domain interfaces.

The distribution of filler particles between the separate phases of an elastomeric blend is affected by a number of factors like, unsaturation, viscosity, polarity, etc. Carbon black has the tendency to migrate to the more unsaturated polymer. Butadiene has the highest affinity for carbon black and the affinity of carbon black follows the order BR > SBR > CR > NBR > NR > EPDM > CIIR > IIR. These findings are in agreement with that of Sircar and Lamend\textsuperscript{156}. Cotton and Murphy\textsuperscript{158,159} have applied GC technique to quantify carbon black phase distribution in blends of SBR with NR and NBR. In all instances there is a preferential location of carbon black in the SBR phase, which also supports the above study.

Ashida\textsuperscript{160} found that when HAF black is added to a pre blend of BR/IR, the black concentration is initially greater in the IR phase, but with the time of mixing, it gradually decreases to a level lower than that in BR. The effect of carbon black loading in 50/50 blend of NR/SBR was studied by I.aminday\textsuperscript{168} and found that the anomaly of modulus
observed is due to the early crystallization of NR inside the matrix. Manna, Tripady and De\textsuperscript{161} have carried out in depth study on carbon black – rubber interactions, particularly using polar rubbers such as, ENR and oxidized carbon black. They suggest that both primary covalent bond and secondary bonds (H-bonding, dipole-dipole interaction, and dispersion type Vander Wall bonds) exist between carbon black and rubber, which break down under dynamic stress. Klupel, Schuster and Schafer\textsuperscript{162} have analyzed carbon black distribution in elastomer blends by measuring increase in loss modulus maxima in the glass transition region. They found that in EPDM/BR/N550 compound, carbon black is preferentially located in BR phase and in NR/SBR/N530 blend, black concentration is higher in SBR phase.

The factors affecting the migration of crosslinking ingredients are the difference in cure rate, solubility and diffusion of these ingredients by the components of the blend. Differential distribution of vulcanizing agents such as, sulphur, accelerator and ultra accelerator in sulphur cure system and peroxide as well as coagents in peroxide cure systems happens in elastomer blends, particularly when the two elastomers differ in the concentration of reaction sites such as, degree of unsaturation and polarity.\textsuperscript{171} This is because sulphur and most of the accelerators are polar in nature and are likely to partition preferably into polar phase. Common accelerators and sulphur are more soluble in highly unsaturated elastomers as compared to lightly unsaturated elastomers. Hence, curatives migrate from the low unsaturated elastomer to highly unsaturated ones. This type of migration is accelerated by higher curative reaction rates in higher diene elastomers. In blends of NR and NBR,\textsuperscript{170} polar accelerators like, TMTD preferably migrate to NBR phase and the practical consequence of this problem is that the blend components will be either uncured or overcured. This problem can be solved by selecting a proper mixing schedule, masterbatching, or by using curatives that have almost the same rate of diffusion and cross linking independent of rubber polarity.\textsuperscript{172,173}

The possibility of uneven distribution of cross links between the phases of a vulcanized blend has long been seen as a potential cause for poor physical properties within the blends of highly unsaturated elastomers such as NR with elastomers containing
only low level unsaturation like, EPDM. Recently ‘reactive mixing’ method\textsuperscript{176} has been applied to improve the properties of NR/EPDM blends which is similar in nature to that described by Hopper\textsuperscript{175} in which a functionality -(alkylphenol monosulphide, caprolactum or morpholino )- derived from the sulphur donor is bound to EPDM via a sulphur linkage.

Covulcanization at the phase interphase of a rubber blend is important to provide mechanical compatibility and improved performance. This is best achieved if the cure rates are similar in both phases. Covulcanization is difficult in blends of saturated elastomer like, EPDM with high diene elastomers. It is better achieved by using fast accelerators such as, thiuram di and tetra sulphides. The interfacial bonds are largely monosulphidic at the initial stage, maturing to polysulphidic as the vulcanization progresses. Yoshimura and Fujimoto\textsuperscript{176} showed that separate dynamic mechanical peak observed at initial stage, merged on continued vulcanization to give a single peak characteristic of compatible blend. Numerous efforts have been made to improve the cross link density of EPDM phase in elastomer blends.\textsuperscript{177} Use of modified forms of EPDM when blended with NR is shown to give better modulus and tensile strength than unmodified EPDM/NR blends.\textsuperscript{178,179}

In normal rubber vulcanizates, the concentration of the plasticizer is not very high and does not much affect the properties of the blends. However, when substantial quantities of plasticizer are used, the distribution of this ingredient can affect the properties of the rubber blends.\textsuperscript{166,169} The relative solubility and diffusivity can be estimated using the empirical model given by Mangaraj, Pfau and Luttinger.\textsuperscript{165} Goonetilleke and Billingham\textsuperscript{166} have measured solubility and diffusivity of a series of phenolic antioxidants in NR and polyethylene. They found that where as solubility depended largely on the additive size, polymer- antioxidant interaction and melting point of the antioxidant, diffusivity depended largely on the size of the additive molecule and its polarity. Greater polarity and smaller size gave higher diffusivity.
1.3. 4. Thermodynamic criteria of miscibility

The term miscibility can be explained in terms of thermodynamics. The thermodynamic relation connecting the free energy, enthalpy and entropy is

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \] ............................ (1)

Where \( \Delta H_{\text{mix}} \), the change in enthalpy, \( \Delta S_{\text{mix}} \), the change in entropy and \( T \), the absolute temperature. For miscibility \( \Delta G_{\text{mix}} \) must be negative and satisfy the additional requirement

\[ \delta^2 (\Delta G_{\text{mix}}) \frac{(\Phi_1)^2}{\delta (\Phi_1)^2} > 0 \] ........................................ (2)

which ensures stability against phase segregation. The volume fraction \( \Phi_1 \) of component is employed here, but any other measure of mixture concentration could be used. The thermodynamic treatment of the phase behavior of mixtures became more useful when specific models for the enthalpic and entropic terms are used. The simplest model, which introduces most important elements needed for polymer blends, is that developed by Flory Huggins originally for the treatment of polymer solutions.\textsuperscript{180,181} It assumes that the only contribution to the entropy of mixing is combinatorial in origin and approximately by

\[ \Delta S_{\text{mix}} = -R(V_A + V_B) \left[ (\Phi_A/V_A) \ln \Phi_A + (\Phi_B/V_B) \ln \Phi_B \right] \] ..................(3)

For mixing a volume \( V_A \) with volume \( V_B \) of polymer blend. Here \( \Phi \) refers to the volume fraction of \( i \) in the mixture and \( V_i \) is the molar volume of \( i \) which is simply related to molecular weight and density by \( M_i / \rho_i \). For simplicity, each component is assumed to be monodisperse, as more complex expressions result when polydispersity is considered.\textsuperscript{182}
The Flory-Huggins treatment assumes the heat of mixing follows a Van Laar type relation.

\[ \Delta H_{\text{mix}} = (V_A + V_B)B \Phi_A \Phi_B \] ...........................(4)

where \( B \) is an interaction energy for mixing segments of the two components and can be alternatively expressed as \( \chi \) parameter. \( \Delta H_{\text{mix}} \) does not depend on polymer molecular weight, where \( \Delta S_{\text{mix}} \) does. Thus for a fixed mass or volume of a blend, the combinatorial entropy of mixing becomes progressively smaller as the molecular weights of the components increase, and becomes zero as they approach infinity. Endothermic mixing, the case when \( B > 0 \), does not favor miscibility. Thus for mixing, the favorable entropic contribution must be large enough to yield a negative free-energy of mixing, but as molecular weights are increased, a point is reached where this fundamental requirement can no longer be satisfied and phase separation occurs. On the other hand, for the exothermic mixing, \( B < 0 \), the Flory-Huggins theory predicts that all the conditions for miscibility are satisfied no matter how large are the molecular weights. Thus as the most simple rule, miscibility of high molecular weight polymers is only assured when mixing is exothermic.

1.3.5. Compatibilization

There are several hundreds of report about polymer – polymer miscibility which emphasis that miscibility is limited to a specific set of conditions, while immiscibility dominates.\(^1\) Only a very few polymers form truly miscible blends.\(^2\)-\(^4\) Examples are poly (phenylene oxide)/polystyrene (PPO/PS), poly vinyl chloride (PVC)/polymeric plasticizer, etc. Besides these, there are a few polymer blends, which are found to be compatible in solution. These include cellulose nitrate/ poly(vinylacetate), cellulose nitrate/poly(methyl methacrylate) and cellulose benzoate/polystyrene blends. The rest of the blends, which are either partially miscible or immiscible, may undergo micro or macrophase separation leading to hexaphase polymer blends.
So far only few elastomer blends are reported to be truly miscible.\textsuperscript{186-188} In elastomer blends, immiscibility is the general observation and miscibility is only an exception. The properties of miscible blends are an additive average of the properties of components, while those of immiscible polymers, a combination of the properties of the components is observed. Most of the high molecular weight polymer blends are immiscible. Generally, immiscible blends are preferred to miscible blends as it is possible to tailor the properties of component polymers, when they are not miscible. The immiscible blends often exhibit high interfacial tension, which leads to poor degree of dispersion of the phases and lack of phase stability, that is phase coarsening or stratification.

Figure 1.5(a) shows the narrow interface between two immiscible homopolymers of infinite molecular weight.\textsuperscript{189} The interfacial density profiles of the two homopolymers through the interface region is shown in Figure 1.5(b). The number of contact points between two different polymers is less in the case of sharp profile and hence the enthalpic or interaction energy contribution to the total free energy is minimized.

\textbf{Figure 1.5.} a) Interface between immiscible polymers and b) interfacial density profile between immiscible polymers.
However, the entropic contribution on the free energy arising from the turning-back entropy of the polymer chain is also smallest for narrow interface, leading to an increase in the total free energy. The interfacial adhesion between the phases is also low and hence immiscible blends usually give poor mechanical properties. The incompatibility or immiscibility between the polymers lead to complex rheological behavior and anisotropy in strength of fabricated articles. The problems associated with the immiscible blends can be alleviated by compatibilizing the blend, either by adding a third component called compatibilizer or by enhancing the interaction of the two component polymers, chemically or mechanically\textsuperscript{190}.

1.3.5. A. Methods of compatibilization

Compatibilization is carried out in non-reactive and reactive mode. In non-reactive mode, an external polymeric material is added whereas in reactive mode, block and graft polymers are formed insitu during mixing of the two components. The essential function of compatibilization is to wet the interface between the two phases. The role of a compatibilizer is to

- Reduce interfacial energy and improve adhesion between phases
- Achieve finer dispersion during mixing and
- Stabilize the fine dispersion against agglomeration during processing and through out the service life.

1.3.5. A.i) Non-reactive compatibilization

Here an external polymeric material, preferably a block copolymer is used.\textsuperscript{191-192} Diblock copolymers are favoured, although in many instances triblock copolymers, random and graft copolymers have also been used. It wets the interface between the two phases which is achieved by spreading at the interphase and mixing with both phases through their component parts which are similar to the phase or the other (Figure 1.6)
Ashaletha and Thomas\textsuperscript{193} have made an in depth study of compatibilization of NR and polystyrene (PS) blends using a graft copolymer of styrene to NR. Reiss and coworkers\textsuperscript{194} had shown that for polyisoprene polystyrene blend, block copolymers provide better compatibilization than graft copolymers and solubilization of compatibilizer by phase taken place when the molecular weight of blend components are comparable or smaller than the molecular weight of the corresponding block in the compatibilizer. Teysie and coworkers\textsuperscript{195} have examined the compatibilizing action of many copolymers concluded that the structure and molecular weight of the copolymer control the efficiency of compatibilization and tapered block copolymers are more effective as compatibilizer than linear block copolymer. Gailand and coworkers\textsuperscript{196} have found that addition of styrene butadiene block copolymers reduce the interfacial tension in PS/BR blends. Coran and Patel\textsuperscript{197} on blending polypropylene with several elastomers found that parameters such as critical surface tension for wetting the interface, critical entanglement spacing, crystallinity and tensile strength of the hard phase determines the mechanical properties of the blend. Leibler, Noolandi and Herg have developed thermodynamic basis\textsuperscript{198} for copolymer compatibilization.

\textbf{Figure. 1.6. Conformation of the copolymer at the blend interface: a) graft, b) di block and c) tri block copolymers extending into the homopolymers}
1.3.5. A.ii) **Reactive compatibilization**

This type of compatibilization is carried out during the blending process by adding a reactive material, either as a blend component or as a reactive third component. The classical example is Du Pont’s production of super tough nylon by blending with maleic anhydride grafted EPDM. Blending nylon with functionalized elastomers have been carried out by several authors and recently by Scott and Macosko. Coran and Patel studied the effect of polyolefins modified by phenolic, triethylenetetramine and chlorine as reactive compatibilizer in polyolefin-nitrile rubber blend and found that the polyolefin-rubber block co-polymer, formed insitu acted as a compatibilizer for this immiscible rubber blend.

1.3.5. A.iili) **Compatibilization by surface activation**

Chemical modification of particle surface aids compatibilization by inducing chemical and physical interaction between the two phases. Mangaraj has reviewed the use of surface activation in scrap tyre recycling.

1.3.5. A.iv) **Compatibilization by cross linking**

Even though most elastomer blends exhibit phase separation, depending on their polarity, there is evidence that co curing may lead to destruction of phase boundary. Contrary to expectations, many elastomer blends, particularly immiscible before vulcanization, develop mechanical homogeneity after vulcanization possibly due to the formation of a block copolymer insitu. Woods and Mass have discussed the occurrence of covulcanization at phase interface of rubber blends and its beneficial effects in blends.
1.3.6. Characterization of elastomer blends

A variety of methods including solubility, spectroscopy, microscopy, thermoanalytical techniques and dynamic mechanical and electrical measurements have been used to characterize elastomer blends. Hess, Herd and Vergl\textsuperscript{125} have made an excellent review on this topic.

1.3.6. i) Microscopy

Phase contrast optical microscopy can be used to differentiate components in gum and lightly colored blends. However, most of elastomer blends contain large volume of fillers and hence they are mostly characterized by electron microscopy. Different methods like swelling\textsuperscript{217}, staining\textsuperscript{213}, etching\textsuperscript{219} and freezing\textsuperscript{220} are used to improve contrast between the phases. Scanning electron microscopy (SEM) is used to characterize surfaces and transmission electron microscopy (TEM) is used to examine morphological features in bulk.

1.3.6. ii) Solution behavior

Solubility of polymers are limited to solvents which have interaction parameter $\chi$ less than 0.4 and two polymers are not miscible unless the difference in their interaction parameter in the same solvent is less than 0.05. Hence, if two polymers are not soluble in a common solvent, they are immiscible. This technique is used for testing miscibility of polymers\textsuperscript{221,222}.

1.3.6. iii) Thermal techniques

Thermo analytical techniques such as, differential scanning calorimetry (DSC), differential thermo gravimetry (DTC) have been used for analysis of polymers. DSC
measures changes in specific heat of systems as a function of temperature. TGA measures weight loss at different temperatures. In the case of miscible blends, it will have a single Tg or Tm whereas immiscible blend will have two Tgs, which may be same or slightly different from Tg of individual components. Compatible blends may have a broad Tg indicating some interaction between the polymers. Sircar, et al. recently reviewed the application of thermal techniques such as DSC, TGA, thermo mechanical analysis (TMA), thermal simulated current (TSC) for determining Tg of elastomers in their blends.

Dynamic mechanical analysis (DMA) provides information on change in internal damping as well as Tg of polymeric materials and their blends. Mazich, et al. have used DMA analysis to study blends of NR with IIR and BIIR.

1.3.7. Processing techniques of elastomers and their blends

By processing we denote the operations that come between the initial mastication of elastomer and the vulcanization of the finished article. The techniques involved are mixing, calendaring, frictioning, extrusion, moulding and combing with textiles or chords. Mixing mill and internal mixers are commonly employed for the preparation of rubber compounds. The shaping operations involve moulding, calendaring and extrusion. Basis of all these process is the flow or viscous deformation of elastomers. The rate of shear occurring in these operations range from $10^1 \text{ s}^{-1}$ to $10^4 \text{ s}^{-1}$. Knowledge of viscosity of compounds over a wide range of shear rate is essential to standardize the conditions for each of these process.

Elastomers are strongly non-Newtonian, that is the rate of shear deformation is not proportional to shear stress except at very low stresses. At any given stress, the shear rate increases with temperature by a factor of roughly 1.3 per degree Celsius. The rate of flow under a fixed stress is time dependent, that is rubber shows thixotropy and this is
very marked in mixes containing reinforcing fillers like, carbon black. All rubbers and mixes show more or less elastic recovery when deforming force is removed.

In mixing a filler with rubber, the surface of every particle should be thoroughly surrounded and wetted by the rubber. The ability of the rubber to flow is important as the surface area involved is enormous and hence low viscosity would be desirable. On the other hand, filler agglomerates have to be broken down, which is favored by a high viscosity and higher stresses are needed to produce broken chain molecules necessary for filler reinforcement. Hence for practical application a right compromise is to be chosen.

Similarly extrusion, calendaring and frictioning involve vigorous working and hence considerable heat generation. The stiffer the mix, greater the heat and hence higher the risk of scorching. So a soft mix is desirable. In calendaring, a soft mix reduces the degree of bending of the bowls and hence adjustments needed to get a uniform gauge. In frictioning, soft mix penetrates more easily to the interstices of the fabric, whereas high viscosity is desirable when calendared sheet is to be wrapped on a fabric liner. Such apparently conflicting requirements may be reconcilable. It is quite possible to have a rubber with low effective viscosity at higher stress and high viscosity at low stresses. A rubber can have an effective viscosity of $2 \times 10^4$ poises at a shear stress of $2 \times 10^6$ dynes cm$^{-2}$ rising to $10^8$ poise when the shear stress falls to $2 \times 10^4$ dynes cm$^{-2}$.

Mooney Viscometer and Wallace plastimeter are commonly used to measure flow properties. But they are operating at a particular temperature and shear rate, which is far less than those typical of modern processing equipments. Studies on viscosity of elastomers, and their compounds as a function of shear rate or shear stress and temperature is of much importance due to its direct dependence on processing methods followed in the rubber industry. These types of measurements are possible with capillary type viscometers.
1.3.8. Processability and rheology of elastomer blends

Miscible blends constitute one phase and are processed like a homopolymer or random copolymer, however, two phase blends have unique processing characteristics. Multiphase blends can exhibit phase segregation and orientation under high shear processing conditions. The degree of orientation depends on many factors including relative viscosities to separate phases, the degree of shear and degree of which dispersed phase is cross linked.

Rheological properties are generally studied from measurement of their viscometric flow behavior. The rheological parameters influencing the processability are viscosity and elasticity as determined by the swell ratio, principal normal stress difference, recoverable shear strain, shear modulus and extrudate characteristics.

The major aspect of the processing step is the flow behavior of elastomers. The influence of fillers and blending of rubbers on flow properties of elastomers has great industrial importance as elastomers are seldom used without fillers and in most cases a blend of elastomers are preferred to achieve a particular end use. Einhorn and Turetzky showed the use of capillary rheometry to characterize elastomeric flow. A number of researchers have investigated the rheology of polymer blends. A comprehensive review on dependence of rheological properties on blend composition has been given by Plochaki. Generally viscosities of blends vary monotonically with blend composition. Several workers have reported the rheological behavior of NR with plastics, ENR with PVC, blends of ethylene propylene diene rubber (EPDM) and bromobutyl rubber (BIIR) and butyl rubber (IIR) as well as many other elastomers, thermoplastic elastomers, composites and elastomer blends.

Several models for viscosity of blends have been applied to polymer blends, from knowledge of their composition. The different blend additivity rules, logarithmic rule, Hashin's upper control rule, Heitmillers inverse additivity rule and sheath-core rule have been used for polymer melts. Agreement between additivity rules and experimental results varies with blends.
Elasticity of polymer melts respond differently to changes in extrusion conditions like, increasing the residence time in the capillary and increasing temperature. The behavior of elastomers is concerned with three functions- the viscosity coefficient $\eta(y)$, principal normal stress coefficient $\psi_1(y)$ and secondary stress coefficient $\psi_2(y)$. The behavior of an elastomer blend is determined not only by dependence of shear stress or shear rate, but also of normal stress on shear stress or shear rate. The die swell of extrudate depends on fundamental properties of the polymers such as, molecular weight and its distribution as well as on flow conditions such as, temperature, shear rate, shear stress and L/D ratio of the capillary. Fillers depending on their concentration and type generally reduce die swell in elastomers.

### 1.3.9 Commercially successful elastomeric blends

Elastomeric products can be generally divided into two categories, tyre and non-tyre products. Non-tyre products include a variety of extruded, calendared and moulded products like, automotive hoses, belts, foot wears, seals, O-rings, roofing materials and numerous other products. Elastomeric blends are being widely used in many products for a long time. Recently, Roger and Waddel have reviewed the past work on the use of blends of butyl (IIR), chlorobutyl (CIIR), bromobutyl (BIIR) and brominated methyl styrene- isobutylene co-polymer (BIMS) with NR and SBR in many tyre and non-tyre applications.

A large number of rubber blends have been patented for tyre application. The earlier patents have been discussed by Baranwal, McDonnel and Andries, Walsh and Higgins as well as by Hess, et al. Pneumatic tyre is a highly engineered product made of several components including chafer, apex, black side wall, white side wall, belts, radial ply, bead and liner. Elastomeric blends used for making them are given in Table 1.5.

Blends of NR or SBR with polybutadiene rubber (BR) are used in tread compounds to achieve better abrasion resistance and wet skid resistance. Levitin and coworkers
showed that 50/50 blends of cis polyisoprene (IR) rubber with methyl styrene butadiene copolymers provide optimum processing and physical properties required for tyre carcass. A ternary blend of IR/NR/BR provide good physical properties for giant tyre treads used for truck and agricultural equipments. Kim and Hammed showed that passenger tyre side wall based on blends of NR and cis-polybutadiene give good resistance to fracture over a wide range of conditions covering rapid as well as slow crack growth, retention ability for longitudinal crack branching, catastrophic rupture resistance and good resistance to slow fatigue crack growth. For black side walls, blending of halobutyl rubbers and EPDM with NR/BR compound increases both dynamic and static ozone resistance as well as resistance to flex strain. Addition of butyl and halobutyl rubber to tyre tread compounds based on NR/SBR or NR/BR blends can lower resilience and improve skid resistance. Addition of bromobutyl rubber to oil extended SBR/carbon black compounds improves tread traction but decreases tread wear in tyre tests. Both rolling resistance and wet grip properties are reported to be improved by partially replacing NR by NBR in NR/BR tyre tread compound.

**Table 1.5. Rubber blends used in typical tyre component formulations**

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber blends</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passenger tyre tread</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Side wall, black</td>
<td>SBR/NR</td>
<td>50/50</td>
</tr>
<tr>
<td>Side wall, white</td>
<td>NR/CIIR/IR</td>
<td>25/55/20</td>
</tr>
<tr>
<td>Body ply (carcass)</td>
<td>NR/BR</td>
<td>70/30</td>
</tr>
<tr>
<td>Inner liner</td>
<td>BIIR/NR</td>
<td>70/30</td>
</tr>
<tr>
<td>Truck tyre</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tread</td>
<td>BR/SBR</td>
<td>50/50</td>
</tr>
<tr>
<td>Carcass</td>
<td>NR/BR</td>
<td>80/20</td>
</tr>
</tbody>
</table>
Blends of NR and SBR are commonly used for foot wear applications.\textsuperscript{270,284,285} (Table 1.6) It consists of a sole cemented to an upper part having the configuration of the foot. They are either injection moulded or calendared, followed by cutting in size and bonding.

Table 1.6. Rubber blends used for foot wear application.

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber blend</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Out sole (Injection moulded)</td>
<td>NR/SBR</td>
<td>50/50</td>
</tr>
<tr>
<td>Boot upper (Injection moulded)</td>
<td>NR/SBR</td>
<td>80/20</td>
</tr>
<tr>
<td>Out sole / Foxing (Calendared)</td>
<td>NR/SBR</td>
<td>80/20</td>
</tr>
<tr>
<td>Out sole (Compression moulded)</td>
<td>NR/SBR</td>
<td>70/30</td>
</tr>
<tr>
<td>Boot lining Gum</td>
<td>NR/SBR/IR</td>
<td>40/20/40</td>
</tr>
<tr>
<td>Heel (High quality)</td>
<td>SBR/BR/IR</td>
<td>30/60/10</td>
</tr>
<tr>
<td>Heel (Standard quality)</td>
<td>SBR/BR/NBR</td>
<td>70/20/10</td>
</tr>
</tbody>
</table>

SBR, NR or IR blends with BR provides bulk of the rubber compounds used in belt applications that is largely used to transport heavy tonnage over long distance. It usually consists of a load bearing component carcass and a protective component called cover. The carcass consists of layers of fabric reinforcement impregnated with rubber. Table 1.7 shows the elastomers used in belt compounds.\textsuperscript{270} NBR and CR are blended to the base rubber to resist oil present in grain or treated coal transport. EPM and chlorosulphonated polyethylene (CSM) rubbers are used for high temperature power transmission belts.\textsuperscript{283}
Table 1.7. Rubber blends used in belt compounds

<table>
<thead>
<tr>
<th>Component</th>
<th>Rubber blend</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction and skirt coat</td>
<td>SBR/NR</td>
<td>80/20</td>
</tr>
<tr>
<td>First grade</td>
<td>SBR/NR</td>
<td>90/10</td>
</tr>
<tr>
<td>Heat resistant</td>
<td>SBR/NR</td>
<td>80/20</td>
</tr>
<tr>
<td>Belt cover</td>
<td>NR/BR</td>
<td>80/20</td>
</tr>
<tr>
<td>First grade</td>
<td>NR/BR</td>
<td>60/20</td>
</tr>
<tr>
<td>Second grade</td>
<td>NR/BR/SBR</td>
<td>80/20</td>
</tr>
<tr>
<td>High temperature</td>
<td>EPDM/CSM</td>
<td>80/20</td>
</tr>
</tbody>
</table>

Nitrile / PVC blends with different flame-retardants are used in applications such as, fire hose roll cover, electrical cover plugs, etc. For covers of rubber hoses, whose main function is to protect carcass from deterioration by environmental conditions, the compounds used are blends of nitrile rubber with PVC or hypalon with polybutadiene rubber. Adhesion of elastomers to wire components in wire reinforced rubber articles such as, steel belted radial tyres, hoses and belting is very important as failure at rubber to wire can cause catastrophic consequences. Croft has studied the use of elastomer blends in wire reinforced hoses to improve rubber to wire adhesion. In cables, blends of EPDM and EVA offer good electrical properties combined with weathering and aging characteristics. Blends of EPDM and NR or blends of nitrile rubber and PVC are used for better ozone resistance. NR or EPDM is blended with PP or HDPE and have been commercialized the production of thermoplastic elastomers.

The effect of high curing temperature on physical properties of blends of BR with NR is discussed by Glanville. The heat stability imparted by cis-BR when blended with NR or SBR is confirmed by Svetlik. Similar improvements in thermal properties are claimed for blends of emulsion BR with NR by Mc Call. Addition of cis-BR is reported to decrease the tensile strength and modulus of NR vulcanizates and increase
the elasticity and abrasion resistance. Flannigan\textsuperscript{293}, commenting on the future consumption of SBR reports that blends with highly saturated EPDM could lead to new applications. The tread wear and wet skid resistance of SBR 1500 series and their blends are dealt with by Kienle.\textsuperscript{294} The hard rubber poly blends of SBR and butyl rubber vulcanized with sulphur have been studied in detail by Meltzer.\textsuperscript{295-296} According to his report, Tg was found to increase with degree of vulcanization and dual or stepwise transition from glassy to rubbery characteristics of polyblends was found in all mixes. Reversion occurred on over cure and the temperature coefficient of vulcanization of SBR/butyl blends was also calculated. Sultan\textsuperscript{297} reported that blends of EPDM with NR, SBR, NBR or CR gave compounds having good ozone resistance, aging and compression set characteristics. Stake\textsuperscript{298} compared laboratory studies of the tyre tread compounds based on SBR/EPDM and SBR/BR/EPDM blends with field performance. Results of the tests of heat aging, groove cracking and abrasion resistance compared with those of SBR and SRR/BR controls indicated that the EPDM blends could be used in treads without antioxidants.

In blends of NR for inner liners of tubeless tyre, two characteristics of butyl rubber, which are particularly advantageous, are its damping properties and impermeability. Blends of chlorobutyl with nitrile rubber are studied in an attempt to develop vulcanizates having the desirable properties of the components at lower cost.\textsuperscript{298,300} EPDM/NBR blends have also been considered for obtaining moderate resistance to oils and ozone combined with an acceptable level of general mechanical properties.\textsuperscript{301} Takenaka reported a blend of fluorosilicone and silicone can be easily bonded using fluorosilicone adhesive, has better processing and technological properties and is cheaper than fluorosilicone itself.\textsuperscript{302} By blending BR with ENR, improvement in wear resistance is reported.\textsuperscript{303-305} Various blends of NBR with PVC and EPDM has been reported to improve ozone resistance.\textsuperscript{306-310} Nagoda and Roland\textsuperscript{311} noted that CR and ENR blends are miscible in all ratios when prepared by solvent casting from carbon tetra chloride. Self-vulcanizing blends of CR and ENR are studied by Alex and coworkers.\textsuperscript{312} Superior processing NR when blended with EPDM shows improvement in properties.\textsuperscript{313} Covulcanized HNBR/EPDM is reported to
exhibit superior thermal and oxidative aging properties.\textsuperscript{314} Blends of silicone rubber with other elastomers enhanced bio compatibility. Medical research Associates Co. has taken several patents\textsuperscript{315} on SEBS block copolymers with silicone for various medical applications. Improved medical grade adhesive has been reported\textsuperscript{316} for the blend of polyisobutylene, IIR and radial styrene block copolymer.

\textbf{I.4. SCOPE OF THE WORK}

NR is the only naturally occurring elastomer, which finds extensive application in many engineering and other fields. Major part of it (nearly 70\%) is consumed in the tyre industry. Mechanical goods like, hoses, conveyor belts, rubber lining, gaskets, seals, rubber rollers, rubberized fabrics, etc. and latex products like dipped goods, foam, carpet backing, elastic threads, adhesives. medical goods, etc. also consume a significant amount of NR. Other uses include footwear, solution adhesives and many engineering products used in dynamic applications such as, springs, anti vibration mountings, bushes, etc. The combination of high tensile strength with a high rebound elasticity, very good low temperature flexibility, excellent dynamic properties and very low heat build up make NR indispensable in several applications despite the availability of a great number of synthetic elastomers. Due to the strain crystallization of NR, which also occurs in vulcanizates, it has a high tensile strength and tear strength in gum vulcanizates, contrary to most type of synthetic elastomers.

However, due to the presence of unsaturation on the backbone of NR, it is highly susceptible to attack by atmospheric ozone and resistance to degradation by heat and oxygen is very poor like all unsaturated elastomers. Also due to the absence of polar groups on the NR, its vulcanizates swell extremely in petroleum fuels. These restrict the application of NR for such products, which has to be come in contact with oils and atmospheric exposure for longer time and for high temperature applications.

Many attempts have been made to improve these properties by chemical modification and by blending with speciality elastomers as discussed earlier. Resistance
to thermo oxidative degradation is an important criterion to be satisfied for rubber products used in outdoor application. It is well known that degradation of rubber is due to its reaction with molecular oxygen. This reaction can be suppressed by reducing the double bonds, or by the introduction of groups that can deactivate the double bonds. The introduction of polar group can bring about the enhancement in resistance to polar solvents and petroleum oils and fuels.

Dichlorocarbene addition to double bond is an attempt to modify elastomers, which attracted much attention earlier. Dichlorocarbene modification has been reported for diene rubbers. However, the products of dichlorocarbene modification have not so far found any good commercial application. Recent studies on dichlorocarbene modification of SBR reported improvement in gum strength, oil resistance and flame resistance.

By dichlorocarbene modification, it is possible to have a reduction in double bonds in the main chain. Introduction of polar functional groups can deactivate the double bonds and also bring about polarity in the molecule as a whole resulting in increased resistance to fuels and oils. As the introducing group contains chlorine atoms, flame retardancy can also be expected to the modified NR. Thus dichlorocarbene modified NR with its unique combination of properties, could find application either alone or in blends with other rubbers or as compatibilizer in blends of NR with polar rubbers. Hence, dichlorocarbene modification is carried out in NR so as to improve the fuel, oil, thermal and flame resistance.

HNBR is the hydrogenated form of nitrile rubber with excellent oil, ozone and thermal aging resistance due to its saturated backbone and the presence of polar acrylonitrile group. Blending of NR with HNBR is expected to improve the properties of NR with respect to oil, ozone and high temperature resistance. However, on thermodynamic conditions these two rubbers are immiscible due to the high difference in their solubility parameter and saturation level. So compatibilization of this blend is essential to alleviate the problems due to immiscibility. The blend can possibly be made miscible by using DCNR as an interface modifier. Due to the presence of chlorine within
the repeat unit of DCNR, there is a possibility of dipolar interaction with the polar units of HNBR. The properties of the blend can also be improved by proper selection of cure system. Mixed cure system and incorporation of fillers may result in blends having good mechanical properties and good aging resistance.

Blends of NR and HNBR would be suitable for applications requiring a combination of good resistance to attack by ozone, better resistance to swelling by oils and fuels and resistance to high temperature, along with good mechanical properties at lower cost.

In this thesis, a detailed work on chemical modification and blending is presented with the following specific objectives:

1. Preparation, characterization and evaluation of dichlorocarbene modified natural rubber.

2. Improvement in resistance to aging of natural rubber by heat, oxygen, ozone, oils, fuel and radiation by blending with hydrogenated nitrile rubber.

3. Evaluation of the role of dichlorocarbene modified natural rubber as an interface modifier in blends of natural rubber and hydrogenated nitrile rubber with reference to the variation in curatives and filler.


The thesis is divided into 8 chapters. The first chapter is introduction, which includes literature survey on elastomers, chemical modification of NR and elastomer blends. The second chapter deals with the materials used and the experimental techniques followed throughout the course of the study. Third chapter contains the results of the preparation, characterization and properties of DCNR and its miscibility with a polar rubber like, HNBR. The fourth chapter discusses the different aspects of blending of NR with HNBR with reference to blend ratio, role of DCNR as an interface modifier, blending methods, type of cure system, fillers, etc., characterization techniques and mechanical properties. The fifth chapter deals with the aging behavior of vulcanizates of
NR/HNBR blends under different conditions such as high temperature, immersion under oils and fuels and exposure to ozone and γ radiation. The sixth chapter focuses on the chemical changes taking place during aging of the blends of NR/HNBR by stress relaxation and solvent swelling methods. The seventh chapter is a comparative study of aging behavior of blends of NR with four speciality elastomers. The eighth chapter discusses the rheological behavior of the blends of NR/HNBR. The summary and conclusion based on the present work is given towards the end of the thesis.
References


39. B. George, R. Alex and N.M. Mathew in “Natural Rubber Agromanagement and Crop processing”, P.J George and C. Kuruvilla Jacob (Eds.), RRRI, India, p-479 (2000).


44. V.H. Fravel, U.S Pat. 2,716,669 (1956).


218. J.D. Moore, Polymer, 12, 473 (1971).

56