1. Reinforcement

Fillers are widely used to enhance the performance related properties of rubbers and other polymeric materials. Rubbers produced by crosslinking of amorphous elastomers are soft and weak. Reinforcement of rubbers with fillers or “hard domains” can increase stiffness and resistance to fracture. Reinforcements are discrete inclusions used to improve the performance characteristics of a material. They can be continuous (fibre, filament or tape) or discontinuous in form (whisker, flake or particle). In addition to the modification of mechanical properties such as stiffness and resistance to fracture, a filler can also modify the electrical, thermal and fatigue properties as well as cost of elastomeric materials.

1.1 Reinforcement of rubbers with particulate fillers

In thermoset rubber technology the most important class of reinforcing hard domains are the particulate fillers whereas with thermoplastic elastomers, self reinforcement is provided by thermodynamic phase separation of hard domains. Particulate fillers can increase the strength of vulcanized rubbers. The elastomers reinforced with particulate fillers can maintain almost the same flexibility as that of the unfilled. The improvement in modulus and other physical properties achieved for elastomeric vulcanizates through particulate fillers is more pronounced with non-crystallizing rubbers.

The basic parameters of the filler particles, responsible for reinforcement, are particle size, surface area, specific surface activity/chemical composition and structure/porosity.
1.1.1 Particle size / surface area

Filler particle size is the most important property which influences reinforcement. The principal requirement for rubber reinforcement is sufficiently small domain size, less than about 1 μm. Sufficiently small filler can give good reinforcement, even when matrix/domain bonding is poor. (eg, graphitized or fluorinated carbon black). However, if domain size is greater than about a micron, reinforcement is absent or minimal regardless of domain shape, and even if bonding between the matrix and domain is quite strong. The most important single factor which determines the degree of reinforcement is the development of a large polymer-filler interface. It can be provided only by particles of colloidal dimensions. Spherical particles of 1 μm in diameter have a specific surface area of 6 m²/cm³. This constitutes approximately the lower limit for significant reinforcement. The upper limit of useful specific surface area is of the order of 300-400 m²/cm³ and it is decided based on considerations of dispersibility and processability of the unvulcanized mix and serious loss of rubbery characteristics of the composite. Many effects of filler in rubber are surface area dependent.

The surface area of particulate solid is related to its particle size. If all the particles are considered spheres of the same size, the surface area \( A_s \) per gram of a filler is given by Equation 1.1

\[
A_s = \frac{6}{d\rho}
\]

Eq.1.1

where \( d \) is the diameter and \( \rho \) the density of the filler particle.

In reality particles have a distribution of size and are usually far from being spherical. Different fillers of the same particle size may not impart the same reinforcement, eg: carbon black and silica. The shape of particle also may be different for different fillers; viz; spheroidal, cubic/prismatic, tubular, flaky or elongated. Non-spherical particles can impart better reinforcement.
1.1.2 Specific surface activity / chemical composition

The nature of the filler surface may be varying in a chemical sense, having different chemical groups, e.g.: hydroxyl or metal oxide in white fillers and carbonyl, quinone, lactone etc. in carbon black. In a physical sense they may be different in adsorptive capacity and in energy of adsorption, e.g.: polar rubbers showing dipole interaction with filler surface groups.

Chemical surface groups on fillers play an important role in their effect on rate of cure, with many vulcanizing systems. Physical adsorption activity of the filler surface is of greater importance than its chemical nature. Carbon black which loses the active sites on heat treatment exhibits poor mechanical properties. Strong chemical bonding between filler and polymer does not lead to desirable vulcanizate strength properties, but causes high moduli.

1.1.3 Structure and aggregation/porosity

'Structure' is a measure of aggregation of primary particles resulting in deviation from the spherical shape leading to lower packing density and higher void volume. Aggregates can be of different shape such as (a) spherical (b) ellipsoidal (c) linear and (d) branched. High structure carbon exhibits high oil absorption.

In the case of inorganic or mineral fillers, differences in particle geometry depending on the crystal form of each mineral can be observed. Crystals with almost identical dimensions in the three directions will result in isometric particles. Higher anisometry as in the case of platelets, rod shape etc when used in rubber results in high modulus.

Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain-like filler structure or cluster, generally termed as 'secondary structure' or filler network. Such a network has a significant effect on the properties of filled rubber. Filler networking is determined by the attractive
potential 'Sr' between the aggregates in rubber as well as by their distance. Wang et al\textsuperscript{10} studied the effect of distance between filler aggregates on the dynamic mechanical properties of vulcanizates, using fillers of different 'Sr' values. Morphological characterization of fillers was made by many workers\textsuperscript{11,12}. Tables 1.1 and 1.2 show the

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
\textbf{Processing properties} & \textbf{Decreasing particle size} & \textbf{Increasing structure} \\
\hline
Loading capacity & Decreases & Decreases \\
Incorporation time & Increases & Increases \\
Oil extension potential & Little & Increases \\
Dispersibility & Decreases & Increases \\
Mill bagging & Increases & \\
Viscosity & & \\
Scorch time & Decreases & Decreases \\
Extrusion shrinkage & & \\
Extrusion smoothness & Increases & Increases \\
Extrusion rate & Decreases & Little effect \\
\hline
\end{tabular}
\caption{Effect of particle size and structure on processing characteristics}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
\textbf{Vulcanize properties} & \textbf{Decreasing particle size} & \textbf{Increasing structure} \\
\hline
Rate of cure & Decreases & Little effect \\
Tensile strength & Increases & Decreases \\
Modulus & Increases to maximum and then decreases & Increases \\
Hardness & Increases & \\
Elongation & Decreases to minimum and then increases & Decreases \\
Abrasion resistance & Increases & Increases \\
Tear resistance & & Little effect \\
Cut growth resistance & & Decreases \\
Flex resistance & & \\
Resilience & Decreases & Little effect \\
Heat build-up & Increases & Increases slightly \\
Compression set & Little effect & Little effect \\
Electrical conductivity & Increases & Little effect \\
\hline
\end{tabular}
\caption{Effect of particle size and structure on vulcanize properties}
\end{table}

various effects of filler particle size and structure on rubber compound processing and vulcanize properties\textsuperscript{13}. 
For effective reinforcement, specific surface activity and structure are necessary. High structure without surface activity does not result in high reinforcement. 

Porosity can be seen with many particulate fillers. Filler porosity can affect the vulcanizate properties. However, its effect on reinforcement is secondary. In the case of carbon black, porosity results in higher viscosity and higher electrical conductivity.

1.2 Particulate fillers

Particulate fillers used in rubber industry in general can be classified as “Black” and “Non black”, depending on their origin, the former being mostly produced from petroleum feed stock and the latter from mineral sources. The most important particulate fillers being used in rubber industry are carbon black and silica. Silicates, clays, whiting (calcium carbonate) and other mineral fillers are used extensively where a high degree of reinforcement is not essential.

1.2.1 Carbon black

Carbon black was introduced as a reinforcing filler in elastomers during 1917-1929. It is a colloidal form of elemental carbon. It owes its reinforcing character to its colloidal morphology (the size and shape of the ultimate units) and to its surface properties. The primary units of carbon black are aggregates. Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lampblack and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. The predominant purpose of furnace type carbon blacks in elastomers, is the reinforcement they impart to the vulcanizates.

Carbon black is characterized based on its surface area, particle size, structure and tinting strength. Surface area is usually determined by iodine adsorption, nitrogen adsorption or cetyl trimethyl ammonium bromide (CTAB) adsorption. Structure refers to
the bulkiness of the carbon black aggregate. Bulkiness is associated with large average number of particles per aggregate. Structure is measured by dibutyl phthalate (DBP) absorption (ASTM D-2414) method. Tinting strength is a measure of the amount of carbon per aggregate and is measured by optical means \(^ {17-20}\). Elastomer reinforcement of carbon black is dependent on these properties. Dispersion of carbon black in the

Table 1.3 Specifications of different carbon blacks

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Lamp</th>
<th>Channel</th>
<th>Furnace</th>
<th>Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle size (nm)</td>
<td>100-150</td>
<td>1-3</td>
<td>14-80</td>
<td>240-320</td>
</tr>
<tr>
<td>Surface area (N(_2)) (m(^2)/g)</td>
<td>20-95</td>
<td>100-1125</td>
<td>27-145</td>
<td>7-11</td>
</tr>
<tr>
<td>Oil absorption (ml/g)</td>
<td>1.05-1.65</td>
<td>1.0-6.0</td>
<td>0.67-1.55</td>
<td>0.32-0.47</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>0.4-0.9</td>
<td>3.5-16.0</td>
<td>0.3-2.8</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0-0.16</td>
<td>0-0.1</td>
<td>0.1-1.0</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>Sulphur, ppm</td>
<td></td>
<td>0.0-0.1</td>
<td>0.5-1.5</td>
<td>10</td>
</tr>
<tr>
<td>pH</td>
<td>3-7</td>
<td>3-6</td>
<td>5.0-9.5</td>
<td>7-9</td>
</tr>
</tbody>
</table>

Table 1.4 Properties of furnace blacks

<table>
<thead>
<tr>
<th>Black</th>
<th>Name</th>
<th>Surface area (m(^2)/g)</th>
<th>Average particle size (nm)</th>
<th>DBP absorption (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>Type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N110</td>
<td>SAF Super abrasion furnace</td>
<td>140</td>
<td>20-25</td>
<td>1.13</td>
</tr>
<tr>
<td>N220</td>
<td>ISAF Intermediate super abrasion furnace</td>
<td>120</td>
<td>24-33</td>
<td>1.14</td>
</tr>
<tr>
<td>N330</td>
<td>HAF High abrasion furnace</td>
<td>80</td>
<td>28-36</td>
<td>1.02</td>
</tr>
<tr>
<td>N550</td>
<td>FEF Fast extrusion furnace</td>
<td>45</td>
<td>39-55</td>
<td>1.21</td>
</tr>
<tr>
<td>N660</td>
<td>GPF General purpose furnace</td>
<td>37</td>
<td>50-60</td>
<td>0.91</td>
</tr>
<tr>
<td>N774</td>
<td>SRF Semi-reinforcing furnace</td>
<td>28</td>
<td>70-96</td>
<td>0.70</td>
</tr>
</tbody>
</table>

elastomer also influences the extent of reinforcement. A typical range of specifications of the four different carbon blacks are given in Table 1.3.

Carbon blacks have reactive organic groups on the surface that cause affinity to rubber\(^ {21}\). Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance and better overall technological properties. Details of a range of furnace blacks generally used for rubber reinforcement are given in Table 1.4.
1.2.2 Non-black fillers

Non-black fillers include a range of inorganic materials with a variety of particle shapes and sizes. It is available in a broad range of sizes from about 10 to 0.015 microns. These fillers can broadly be classified as:

a) Fillers used to reduce cost
b) Semi-reinforcing filler
c) Reinforcing filler

Earlier non-black fillers used were mainly naturally occurring minerals or by-products of manufacturing such as clay, whiting, barytes, zinc oxide, zinc sulphide, blanc-fixe, mica, asbestos, kieselguhr, magnesium carbonate, iron oxide, litharge etc. They were used in rubber to reduce tack, increase hardness, improve durability and reduce cost. Other important non-black fillers being used in the elastomer industry are aluminium hydrate, aluminium oxide and titanium dioxide.

The need for more reinforcing non-black fillers in many rubber applications led to the introduction of calcium carbonate, calcium silicates, hydrated silicas and fumed silicas between 1940 and 1960. These were characterized by very small particle size much smaller than the natural products and similar to the reinforcing carbon blacks. Since then a lot of developments and refinements in hydrated silicas and fumed silicas have taken place resulting in a number of grades for specific applications.

1.2.2.1 Silica

Different forms of silica are commercially available for various industrial applications. Important natural varieties are silica (amorphous), silica (crystalline), silica diatomaceous (fossil origin) and silica (microcrystalline). Types of synthetic silica are precipitated, pyrogenic, aerogels and hydrogels. Of these varieties, precipitated silica and pyrogenic (fumed) silica are being used for elastomer reinforcement.
a) Production and Characterization

Precipitated silica is produced by acidification of alkalisilicate solutions under controlled conditions. Colloidal pyrogenic silica is produced by reaction of silicon tetrachloride at high temperatures with water.

\[
\text{SiCl}_4 + \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}
\]

The reaction products are quenched immediately after coming out of the burner. Pyrogenic silica is too active and expensive. Precipitated silicas are silicon dioxide containing about 10-14% water, with particle size in the range 1-40 nm. They are reinforcing fillers giving composites of high tensile strength, tear resistance, abrasion resistance and hardness. It is being used in the manufacture of translucent and coloured products, shoe soling, tyres and other mechanical rubber goods. Fumed or pyrogenic silica is silicon dioxide containing less than 2% combined water. These silicas are highly reinforcing fillers of very small particle size, giving high tensile strength, tear resistance and abrasion resistance particularly to silicone rubbers.

Characterization of silica filler is also based on particle size and specific surface area. Surface area measurement is usually done by nitrogen adsorption (BET) method. Also pH, chemical composition and oil absorption are specified. The smallest physically observable primary particle for precipitated silica is about 15-20 µm and for fumed silica it is about 15µm in size. The surface forces of the small primary particles are so high that many particles conglomerate to form the so-called secondary particles. Usually the shear forces generated during rubber mixing is not sufficient enough to disperse primary filler particles in the rubber.

The secondary particles of silica fillers form further agglomerates. They form chain-like structures, the so-called tertiary structures. Though the tertiary structures are also relatively stable, they get more or less shattered by the shear forces during mixing. The higher the shear force, the better the dispersion.
b) Chemistry of silica

(1) Silica which is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure. Particle size usually ranges from 1-30 nm and the surface area from 20-300 m²/g.

(2) Surface silanol concentration (silanol groups – Si-O-H) influence the degree of hydration. Water content can affect processing and vulcanization. Absorbed water can decrease cure time, tensile strength and also abrasion resistance.

(3) Silanol types fall into three categories – isolated, geminal (two-OH groups on the same silicon atom), and vicinal (-OH on adjacent silicon atoms). Isolated hydroxyls exist predominantly on dehydrated silicas, pyrogenic silica and to a lesser extent on precipitated silica. Vicinal hydroxyls are stronger adsorption sites and hence, have stronger reinforcement effect than the isolated hydroxyls.

(4) Surface acidity is controlled by the hydroxyl groups on the surface of the silica and is intermediate between those of P-OH and B-OH. This intrinsic acidity can
influence vulcanization. The rubber filler interaction is affected by these sites. A general silica structure is depicted in Fig. 1.1.

Silicas have strongly polar surface groups, mostly hydroxyl groups bound to silicon. The reactivity of the surface causes foreign substances to be adsorbed on the filler surface. With increasing water content the dispersion time of colloidal silica into the rubber gets prolonged.

The filler also adsorbs organic compounds, particularly basic ones: eg diphenyl guanidine (DPG), diortho tolyl guanidine (DOTG). Therefore, a larger amount of the same has to be added to compensate for the loss due to adsorption by silica. Accelerator adsorption by the filler will be lower, if it already contains water.

c) Activators for silica fillers

Silica fillers can, not only interact with water and accelerators, but also with polymers. With increasing filler content and consequent increasing filler activity the viscosity of the compound increases, thus making processing difficult. To the extent that filler-polymer interaction is reduced, compound viscosity can be reduced. Materials that get adsorbed stronger on the filler than the rubber, can soften the mixtures and could be processed more easily. Additives of this type are DPG, DOTG, hydroxyl containing compounds like glycols, glycerol etc. and materials with basic nitrogen like triethanolamine and secondary amines. Such additives are technically termed as ‘filler-activators’ since they act not only to improve processing, but also to reduce accelerator adsorption. In addition to this the glycols, triethanolamine etc. also cause breakdown of the ‘tertiary filler structure’ thus making dispersion more effective. With highly active silicas by the addition of small amounts of activators an increased viscosity may be observed because of better filler dispersion, and lower viscosity could be achieved with further addition of activator, after passing through a viscosity maximum.
Carbon blacks have reactive organic groups on its surface that cause affinity to rubber\textsuperscript{21}. These reactive sites are missing in light coloured fillers. There are other group of filler activators such as silanes\textsuperscript{26-36}, titanates and zirconates\textsuperscript{37-39} and others which can make the filler more reactive.

In general, silicas produce relatively greater reinforcement in more polar elastomers such as acrylonitrile – butadiene rubber (NBR) and polychloroprene rubber (CR) than in non-polar polymers such as styrene butadiene rubber (SBR) and natural rubber (NR). The lack of reinforcement properties of silica in NR and SBR can be corrected through the use of silane coupling agents. An essential prerequisite for a coupling agent is that the molecule is bifunctional, i.e., capable of reacting chemically with both silica and either directly or indirectly with the polymer via participation in the vulcanization reaction or sulphur crosslinking process\textsuperscript{3}.

1.3 Filler surface activity

The surface activity is related to different chemical groups on the surface of fillers such as carboxyl, quinone, phenol and lactone in the case of carbon black and hydroxyl, metal oxide etc in the case of silica. The surface chemical groups play an important role in their reinforcing ability for elastomers\textsuperscript{21}. Surface energy of filler particles play much greater role with regard to the mechanical properties of the filled elastomers. The surface free energy $\gamma_s$ of a solid has two components viz; dispersive component (London or non-specific) $\gamma_s^d$ and specific component (including polar, acid–base, hydrogen bonding etc.) $\gamma_s^{sp}$, which can be expressed as,

$$\gamma_s = \gamma_s^d + \gamma_s^{sp}$$

Rubber-filler interaction depends on the surface energies of the two. It is the two components of the surface energy of the filler which describes its distribution in the rubber. $\gamma_s^d$ is high for carbon black, while $\gamma_s^{sp}$ is high for silica. This implies that the
former can disperse easily in rubber, the latter leads to high filler-filler interaction which in turn will lead to filler agglomeration and therefore poor dispersion in the rubber matrix. To overcome these difficulties, filler surface is to be modified. Surface energies of a series of carbon blacks and the interaction between carbon black and elastomers were estimated by Wang and Wolff\textsuperscript{40}. Inverse gas chromatography (IGC) is one of the important tools for the investigation of filler surface energies\textsuperscript{41,42}.

1.4 Filler surface modification

The surface activity of a filler has influence on the reinforcement of rubber. Several methods are being used to modify the filler surface.

1.4.1 Carbon black – surface modification and characterization

1.4.1.1 Modifications

\textit{a) Heat treatment}

Heat treatment in an inert atmosphere alters the physico-chemical characteristics of carbon black. The chemical nature of surface is modified at a temperature below 1000°C, whereas the physical nature of the surface gets modified around 1000-1500°C\textsuperscript{43-46}. A drastic change in surface energy\textsuperscript{40} and a change in the crystalline property\textsuperscript{47} are the major physical changes of heat treatment. Heat treatment or graphitisation leads to a major reduction in both dispersive component ($\gamma_s^d$) and specific component ($\gamma_s^p$) of the surface energy\textsuperscript{40}.

\textit{b) Surface grafting}

Surface grafting of various organic molecules including polymers on to carbon black surface has been studied extensively\textsuperscript{18}. Several techniques are being adopted for the grafting of polymers on to carbon black, of which the important ones are

- Grafting on to carbon by chain termination / or chain transfer of a growing polymer radical\textsuperscript{49-51}. Polymer grafted to carbon is only less than 10%.
Grafting through copolymerisation of the small molecules already grafted on the black \(^{49,50}\); most favourable process.

- Grafting by direct reaction of the carbon black surface and functionalised polymer \(^{49,52,53}\).

Dannenberg \(^{54}\) observed that elastomer grafted carbon black did not improve the reinforcing property of the vulcanizate. However, Papier \(^{55}\) and Wolff et al \(^{56}\), observed superior reinforcing properties in the case of polyisoprene grafted channel black and silane modified carbon black. The result of grafting on to carbon black surface caused surface deactivation hence, filler-filler interaction decreased drastically \(^{57,58}\).

**c) Plasma treatment**

Plasma treatment is an effective means to modify carbon black surface \(^{59-61}\) and the modification is fairly uniform over the whole surface. Wang \(^{62,63}\) reported that significant changes in surface chemistry occurred on air and ammonia plasma treatment of graphitised black. Air plasma treatment results in the formation of oxygen containing groups \(^{64}\) and ammonia plasma treatment results in nitrogen containing groups \(^{65}\).

**d) Surface oxidation**

Donnet and Voet \(^{66}\) reviewed the processes of surface oxidation of carbon blacks and categorized two important methods of oxidation depending on the nature of the oxidizing agent, gas phase and liquid phase. Oxygen, ozone, air or oxides of nitrogen are basically the gas phase oxidants \(^{57-69}\), whereas nitric acid, aqueous potassium permanganate and bromine water are the liquid phase oxidants \(^{70-72}\). Donnet and Papier \(^{73}\) reported that increase in the duration of oxidation increases the oxide content on the carbon black surface and consequently the hydrophilicity of the black. The effect of surface oxidation on specific area has been extensively studied \(^{74, 75}\). Pores are created on the surface of carbon black during oxidation.
Oxidation of carbon black in liquid phase is characterized by formation of carbon dioxide and oxidised groups on the surface, such as carbonyl, hydroxyl, carboxyl etc.

1.4.1.2 Characterization

Considerable efforts have been devoted to the instrumental analysis of carbon black surface. Infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), atomic force microscopy (AFM), secondary ion mass spectroscopy (SIMS), high resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM) are widely used to investigate the physico-chemical properties of carbon black surface. IR, XPS and STM provide the most useful information.

1.4.2 Silica - surface modification and characterization

The surface of silica is less complex than carbon black. Wagner has made an extensive review on different aspects of silica and silicates. Silica consists of silicon and oxygen, tetrahedrally bound in an imperfect three dimensional structure. The imperfections in the lattice structure leave free silanol groups on the surface. The number of silanols, their distribution and also the conformation of the surface siloxanes depend on the method of preparation and thermal treatment. The distribution and also the close proximity of the hydroxyl groups have an influence on the adsorption and reinforcing properties. Three types of surface silanol groups have been identified; isolated, vicinal and geminal adjacent silicon atoms (two hydroxyls on same silicon atom). In IR spectra, the isolated hydroxyls give a strong band at 3750 cm\(^{-1}\), while the vicinal hydroxyls and the geminal hydroxyl show peaks at 3600 cm\(^{-1}\) and 3500 cm\(^{-1}\) respectively. The –OH concentration may vary between 4.5 to 12.5 per nm\(^2\).

Various modifications have been done to improve the reinforcing ability of the silica which includes heat treatment, polymer grafting on silica surface and chemical modification by heat treatment with modifiers like silane coupling agent.
Heat treatment is the simplest way of modifying the silica surface. The surface hydroxyl groups remain constant up to a temperature of 300°C. At this temperature the adsorbed water molecules are removed and then thermal condensation begins. At temperatures beyond 600-700°C, only 1.5 -OH per nm² is left over. Linger et al had used IGC for characterizing the heat treated silica surface. At infinite dilution, IGC is an ideal tool to characterize the changes in the surface of the silica due to heat treatment.

Silica surface modification by grafting of alkyl chains through esterification has been reported by several workers. Esterification of silica surface by methanol, ethanol and butanol was reported. Donnet et al have reported the characterization of alkyl grafted silica surface using IGC. Grafting of methyl and hexadecyl chains on the surface of silica has been found to decrease the thermodynamic parameters. Esterification results in the reduction of the dispersive component $\gamma_s^d$ of the surface energy. By esterification, the surface heterogeneity of the unmodified silica reduces and hence the filler-filler inter-aggregation diminishes.

### 1.4.2.1 Silanes as silica surface modifier

Varieties of silanes are being used by the polymer industry for improving the interfacial adhesion or bonding of silica with the polymers. Plueddemann gives a detailed account of the use of silanes, in bonding thermoplastic polymers to mineral surfaces. The silane by co-reacting with the polymers modifies the polymer morphology at the interface to improve stress-transfer at the interface.

In silica filled rubber systems, silane modification improves the interfacial adhesion between the two. Silane modified silicas reduces the specific component of surface energy $\gamma_s^s$ and hence improves its compatibility with rubbers. A series of silane coupling agents are available with general formula YRSiX₃, in which Y is the organofunctional radical, R represents the alkyl group and X the silico functional group such as chloro, alkoxy or acetoxy which on hydrolysis get attached to the silica surface.
groups. Silanes generally are of three categories viz; Monofunctional silanes, bifunctional silanes and non-sulphur bearing silanes. Hydrophobation through silanization of silica with a monofunctional silane reduces the filler network, thereby makes the silica more compatible with the rubber matrix. The extent of network reduction depends not only on the degree of hydrophobation (amount of silane) but also on the kind of silane. Alkyl chain length is a factor in determining the reduction of filler network. Examples of few commercially important monosilanes are

1. PTES - Propyl triethoxy silane
2. ETES - Ethyl triethoxy silane
3. OTES - Octyl triethoxy silane
4. HDTES - Hexa decyl triethoxy silane

Considerable reduction in filler networking could be achieved with HDTES treatment.

Bifunctional silanes are used as coupling agent, which chemically binds silica with rubber. The silicofunctional group reacts with the filler surface groups and the organofunctional group with the rubber resulting in rubber-silica bonding, thus results in improved reinforcement. Several silanes with appropriate functionality such as alkoxy silyl groups have been successfully used as coupling agents. Some of the bifunctional silanes of commercial importance are the following.

1. TESPT - Bis (triethoxy silylpropyl) tetrasulphide (Si 69)
2. TESP - Bis (triethoxy silylpropyl) disulphide
3. TESPM- Bis (triethoxy silylpropyl) monosulphide
4. MTMO-Mercapto propyl trimethoxy silane (A 189)
5. Bis (triethoxysilyl ethyl tolylene) polysulphide (Y9194)

It has also been reported that bis (disisopropyl) thiophosphoryl disulphide, a new group of chemical can also be used as coupling agents to bond silica and rubber.
Wang et al. have showed that silane modified silica increases its compatibility with hydrocarbon elastomers, thereby improving filler dispersion, compound processability and vulcanizate technological properties.

1.5 Rubber reinforcement

1.5.1 Reinforcement mechanism

Addition of fillers to rubber has a strong impact on its static and dynamic behavior. Surface interaction between fillers and rubber molecules involves a range of bond energies from relatively weak to very strong. In general, physical adsorption of polymers on filler surface occurs to varying degrees depending on the filler surface and the nature of the polymer segments. In the case of carbon black, the level of physical interaction is high. Although chemical interaction between carbon black and rubber is taking place, it occurs only to a minor extent and is not a necessary condition for reinforcement. Filler, above a critical concentration in rubber matrix, can cause filler-filler interaction, extent of which is determined by both physical or chemical interaction and the distance between filler aggregates in the rubber compound.

When rigid spherical particles are dispersed into a fluid, an increase in viscosity takes place in the case of liquids or a modulus enhancement in the case of polymers, which is known to be due to the hydrodynamic effect.

According to Payne the enhancement of mechanical properties due to the presence of a filler in rubber compounds can be attributed to the additive effects of polymer network, hydrodynamic effect, in-rubber structure and the filler-filler interaction. The dynamic modulus, $G^*$, of a reinforced rubber hence depends both on strain independent parameters such as crosslinking of the matrix, hydrodynamic effect, filler to rubber interaction (in-rubber structure) and the strain dependent filler-filler interaction. The phenomena of stress softening of a filled rubber with strain known as
"Payne effect" arises from filler-filler interaction. A comparison of the reinforcement behavior due to the above 4 factors of carbon black and silica is given in figure 1.2.

**Fig.1.2 Payne effect - carbon black, silica comparison**

**a) Polymer network**

The first component of the 'additive factors' of reinforcement is the strain independent polymer network which results from the proportionality of the modulus ($G_0$) to that of the crosslink density and can be represented using Equation 1.2 as

$$G_0 = v k T$$

Eq.1.2

where $v$ = number of moles of elastically effective network chains per unit volume as a result of vulcanization.

$k$ = Boltzmann constant

$T$ = Temperature (K)

**b) Hydrodynamic effect**

When rigid spherical particles are dispersed into a fluid, whether it be a liquid or an elastomer, an increase in viscosity takes place in the case of the liquid or of the modulus in the case of a polymer. This is generally designated as hydrodynamic effect. The viscosity or modulus increase due to filler addition in liquids and elastomers
respectively due to hydrodynamic effect can be represented by the equations proposed by the Guth-Gold\textsuperscript{102} and Smallwood\textsuperscript{133}.

Guth-Gold equation (Equation 1.3) for viscosity\textsuperscript{102}

\[ \eta = \eta_0 (1 + 2.5\phi + 14.1\phi^2) \]

where \( \eta \) and \( \eta_0 \) are the viscosities of the filled and unfilled system, \( \phi \) is the volume fraction of the filler.

Smallwood\textsuperscript{103} showed that for an elastic material filled with rigid spherical particles the equation for modulus enhancement can be represented as in Equation 1.4.

\[ G = G_0 (1 + 2.5\phi + 14.1\phi^2) \]

where \( G \) and \( G_0 \) are the shear moduli of the filled and unfilled system respectively and \( \phi \) is the volume fraction of the filler. The value of \( G_0 \) is obtained from equation 1.2. The shear modulus can also be replaced by tension elasticity modulus without much change of the equation.

For non spherical particles, Guth introduced a shape factor, \( f \) (the ratio of the longest dimension of the particle to the shortest) and proposed the following equation\textsuperscript{104}

\[ G = G_0 (1 + 0.67 f\phi + 1.62 f^2\phi^2) \]

The equations were derived on the assumption that the medium wets the filler particles, but does not chemically react with the filler surface. The modulus as given in equation 1.4 and 1.5 is independent of applied strain.

c) In-rubber structure

The in-rubber structure can be understood as a combination of the structure of the filler in the in-rubber state and the extent of filler–polymer interaction. The in-rubber structure is, amongst others, a measure for the occluded rubber, which is shielded from deformation and therefore increases the effective filler content leading to a strain-independent contribution to the modulus. The filler-polymer interaction can be
attributed to physical (Van der Waals) as well as chemical linkages or both. In the case of silica-coupling agent system, this interaction is formed by chemical linkages.\textsuperscript{105-108}

d) Filler-filler interaction

Elastic modulus of a filled rubber is strongly dependent on deformation and decreases substantially at higher strains ("Payne effect"). This is attributed to the presence and breakdown of the filler network during dynamic deformation. The sigmoidal decline of the storage modulus at zero amplitude ($G_\infty'$) to a high amplitude plateau $G_\infty'$ was interpreted by Payne as due to the breakage of physical (London and Van der Waals) bonds between filler particles. It was also noted that the value $G_\infty'$ is mostly recoverable upon return to smaller amplitudes and showed that the phenomenon is independent of the polymer, provided enough time is allowed for recovery. When using silica as a reinforcing filler, a high level of elastic modulus and the drop of elastic modulus at higher strain amplitudes prove the existence of a stable filler network formed by silica as is represented in Fig.1.\textsuperscript{2,101,108-111}.

A quantitative model of the Payne effect, based on filler agglomeration and deagglomeration was proposed by Kraus.\textsuperscript{112}

1.5.2 Physical and chemical interactions at the filler surface

Whether reinforcement requires the formation of chemisorptive or primary valence bonds, anchoring polymer chains to the filler surface is a subject of controversy. Some of the experimental evidences indicate that

1) Chemical bonding at the filler-rubber interface is not a necessary condition for reinforcement.

2) Chemical bonding leads to the unique combination of mechanical properties associated with carbon black reinforcement.
Studies with carbon black shows the existence of chemical bonds or chemisorptive linkages of higher energy than physical adsorption\textsuperscript{3,113}.

Graft formation of polymer with carbon black was reported, through reaction of the functional group of carbon black with rubber during processing and vulcanization\textsuperscript{114}. Such reactions are chemisorption of olefin on carbon black at the vulcanization temperature\textsuperscript{115}, combining with shear induced polymeric free radicals generated during mixing\textsuperscript{116} and by free radical inhibition through quinonic group of carbon black\textsuperscript{117}. When carbon black is heat treated at 2700\textdegree{}C or higher in an inert atmosphere, all surface functional groups are removed, but the morphology remains more or less the same. Heat treated black exhibits lower bound rubber, modulus and abrasion resistance, while keeping the tensile strength almost intact\textsuperscript{118}.

Colloidal silica is a good reinforcing agent, imparting high tensile strength and excellent resistance to tearing\textsuperscript{25}, however in comparison to carbon black, silica is deficient in modulus and resistance to abrasion. By the use of coupling agents with silica, performance enhancement closer to that with carbon black could be achieved. Esterification of silica can deactivate its surface, giving a stress-strain behaviour similar to graphitised carbon black\textsuperscript{119}.

The surface interaction between fillers and rubber molecules involves a range of bond energies from relatively weak Van der Waals force to very strong chemical bonds\textsuperscript{120}. The number of each kind of interaction is difficult to characterize\textsuperscript{121}. In all cases physical adsorption occurs to varying degrees depending on the particular surface and molecular segments. Evidence for chemical bonding at the interface is also conclusively found in certain systems\textsuperscript{122}. The relative contributions of physical and chemical interactions to reinforcement, differ both with the nature of the filler and the elastomer. When physical interaction is high, such as that for carbon black in hydrocarbon rubbers, there is little contribution to reinforcement from chemical bonding,
although this may contribute to other desirable properties. Chemical interaction improves wetting and adhesion, improves dispersion and prevents reflocculation of dispersed particles. Chemical interaction may result in actual bridging of the particle surface to the elastomeric network\textsuperscript{123, 124}.

Adsorption of polymer segments on the filler surface leads to some loss of mobility of the chains. Studies of proton magnetic resonance in carbon black-reinforced rubbers have shown that there is a loss in segmental mobility, but severe restriction of motion is confined to a layer of 5\r{\AA} thick at the surface i.e., a distance of few carbon lengths along the polymer chain\textsuperscript{125}. However, the chains of bound rubber may extent far into the polymer matrix where they freely intermix with unadsorbed rubber molecules. During vulcanization, they become part of the network and becomes undistinguishable from free rubber.

1.5.3 State of the filler in the rubber mix

When carbon black is mixed into rubber, the first step is the penetration of the rubber into the void space. If at this stage considerable rubber-filler interaction occurs, subsequent dispersion is rendered difficult, as bound rubber cements many primary aggregates together. For this reason low-structure, high surface area blacks are difficult to get dispersed uniformly, though incorporation takes place rapidly. High structure blacks are slowly incorporated but easily attain uniform dispersion.

1.5.4 State of rubber in the filled composite

Adsorption of polymer segments on the filler surface must lead to loss of mobility of the chains. Any loss of mobility will affect the physical properties of the rubber. Degree of immobilization is of fundamental importance. Severe restriction of motion is confined to a layer of about 5 \r{\AA} (a few carbon bond length) thick at the surface\textsuperscript{125}. For a black with about 80 m\textsuperscript{2}/g specific surface area, a surface coating of 5\r{\AA} thick roughly represents 2\% of the total rubber. Mobility gradually increases outward
from the filler surface so that a thicker layer estimated at 30 Å finds itself under the influence of the surface layer\textsuperscript{126}. Thus the glass transition temperature (T\textsubscript{g}) of carbon black filled rubbers is raised by about 2-3°C\textsuperscript{110,127}. Substantial immobilization, if occurs, would cause a much larger change\textsuperscript{128}. Somewhat larger changes have been reported for polymers with polar groups along the chain, reinforced with inorganic fillers\textsuperscript{126}. Immobilized rubber and bound rubber are different. The rubber that finds itself in the void space of the filler structure aggregates is called the occluded rubber\textsuperscript{109,129}.

1.5.5 Rubber-filler interaction

Bound rubber

It has been generally accepted that bound rubber provides a valuable information regarding rubber-filler interaction. Several reviews have been published on this topic\textsuperscript{55,130-133}.

The mechanism of formation of bound rubber is not very clear\textsuperscript{134}. Whether bound rubber can be taken as a measure of the surface activity of filler is also not well established\textsuperscript{55,135,136}. Free radical reaction between carbon black and rubber is proposed as a mechanism for chemisorptive adsorption\textsuperscript{137}. Watson et al\textsuperscript{138,139} proposed free radical mechanism for bound rubber formation, based on the fact that common free radical scavengers like thiophenol can reduce bound rubber formation. However Donnet et al could not find any correlation between free electron and reinforcement in carbon black filled natural rubber\textsuperscript{140-142}.

Oxygen containing functional groups on the carbon black surface lowers rubber-filler interaction for unsaturated rubbers\textsuperscript{143}; Gessler\textsuperscript{144} proposed a cationic interaction between polymer double bond and carbon black. Ban et al\textsuperscript{145} attributed physical adsorption for bound rubber formation. Wolff et al\textsuperscript{146} observed that, on high temperature extraction, the extent of insolubilized rubber was low and therefore concluded that the
rubber-filler interaction involved in bound-rubber formation is essentially physical in nature. Gessler holds the view that carbon black aggregates breakdown on milling and the active filler surface thus formed will react with rubber chains which gets activated by mechanical breakdown\textsuperscript{147}.

Rubber-filler interaction also results in the formation of an immobilized layer or rubber shell around the filler. This arises due to the restriction of the molecular mobility of the rubber in the vicinity of the filler surface. Though bound rubber and rubber shell arise from rubber-filler interaction, basic concept for the two are different. Bound rubber refers to the whole molecule in which one or more segments are in contact with filler, whereas in shell rubber, segments rather than molecules are affected by the force field of the filler. Westlinning\textsuperscript{148} and Schoon et al.\textsuperscript{149} reported the formation of about 3-5 nm of rubber layer around the filler surface. Smit et al.\textsuperscript{150} proposed a shell thickness of 2-5 nm on carbon black surface. The studies were elucidated further by NMR\textsuperscript{151}, DSC and DMTA\textsuperscript{152}.

1.5.6 Effect of filler on processability of rubber compounds

The flow characteristics of filled rubber compounds is of prime technological importance. The melt viscosity of rubber mixes increases with decreasing filler particle size and increasing structure. The viscosity of the unfilled polymers is strongly dependant on their molecular weight distribution and chain branching\textsuperscript{153}. The enhancement in viscosity on incorporation of carbon black in rubber is attributed to occlusion of rubber within and between the carbon aggregates\textsuperscript{154} and immobilization of a layer of elastomer at the filler surface\textsuperscript{155}. Changes in the viscosity of rubbers with filler addition for a series of SBR and NR compounds, have been attributed to entanglement or bound rubber formation\textsuperscript{156,157}. 
Physical properties of silicas were reported to affect the viscosity of rubbers. Hewitt reported that compound viscosity is directly related to the surface area of silica. Highly developed filler networks of silicas can give rise to compounds of high viscosities. Silicas and silicates generally cause higher Mooney viscosity in rubber mixes than other fillers of comparable particle size. The difference between types of filler became less pronounced as the average filler particle size is increased. At about 20 nm size silica produces significantly higher viscosity than carbon black of comparable size. However, at about 40 nm size silica and black filled compounds exhibit almost similar viscosity.

Viscosity modification studies of rubbers filled with smaller particle size silica was reported by Dunnom. Use of silane coupling agent in silica filled rubbers is an effective means of reducing viscosity of the compounds. Generally, with rare exceptions, viscosity of high molecular weight rubbers is shear rate dependent. The increase in viscosity caused by the fillers is more prominent at low shear rates. The viscosity of filled rubber compounds at very low shear rates becomes effectively infinite. This phenomenon is due to the secondary filler agglomeration, resulting in the formation of a weak filler network held together by Van der Waals forces. At higher shear rates, the difference between types of fillers get reduced, so that the difference between silica and carbon black get reduced at high shear rates.

1.5.7 Effect of filler on cure behavior and crosslink formation

Fillers (surface groups on fillers) generally tend to accelerate or retard cure. Carbon black can influence the total concentration of chemical crosslinks and the proportion of mono, di and polysulfidic crosslinks and these factors, in turn, can affect the vulcanizate properties. Janacek has reported that for a carbon black filled natural rubber system, crosslink density increased proportionally with the concentration of the carbon black by volume. Studies by Cotton revealed that the chemistry of
carbon black surface plays an important part in the preceding steps of vulcanization and the rate of vulcanization. Maximum torque in a rheograph ($M_H$) can indicate the characteristic effects of the filler.

Bhowmick et al\textsuperscript{171} have studied the effect of addition of HAF black on the kinetics of vulcanization and the changes in the network structure of natural rubber cured with DTDM. Addition of HAF black enhanced the polysulphidic crosslinks as well as total crosslinks. Bhowmick et al\textsuperscript{171} and Porter\textsuperscript{172} have reported that HAF black influenced the chemistry of sulphuration of sulphur cure systems of NR. The observation of Bhowmick et al\textsuperscript{171} indicate that filler surface may catalyze the sulphuration process and the observed increase in crosslink density may be due to increase in covalent crosslinks and merely not due to polymer-filler attachment. Duchacek\textsuperscript{173} reported that HAF black does not alter the mechanism of TMTD accelerated sulphur vulcanization of NR.

Silica/silicates contain substantial amounts of combined oxygen in the form of silanol (Si-OH) and siloxane (Si-O-Si) which retard sulphur vulcanization\textsuperscript{174}. The silanol groups can interact with elastomers, curatives and can also form hydrogen bonding. Effect of these interactions can affect compound properties such as viscosity, scorch time, cure rate and cure efficiency and also the vulcanizate properties. Retardation of vulcanization was earlier attributed to the adsorption of curatives by the silica surface\textsuperscript{175}. Later studies claim that retardation is due to a deactivation mechanism involving interaction of the filler with the zinc-accelerator-sulphur complex\textsuperscript{43}. Addition of activators such as triethanolamine (TEA), diethylene glycol (DEG) and polyethylene glycol are used to reduce the adverse effects of silanol groups\textsuperscript{174}. 
1.5.8 Effect of filler on vulcanizate properties

1.5.8.1 Failure properties

Strong rubber-filler bonding improves modulus at high elongation, tensile strength, tear strength and hysteresis. Strong rubber-filler bonding permits bridging of infinite number of rubber chain through carbon black and is the main reason for improvement of the physical properties of vulcanizates. Development of high strength is on account of the ability of the rubber to dissipate strain energy near the tip of the growing crack by viscoelastic processes. Addition of a filler introduces additional mechanisms by which strain energy is dissipated. Inclusion of particles in a viscoelastic medium increases hysteresis. Loss of segmental mobility in the polymer matrix resulting from interaction with the filler will increase hysteresis. Motions of filler particles, chain slippage or breakage and dewetting at high strains can also enhance hysteresis. The dispersed filler particles: in addition to providing energy dissipation, also serve to deflect or arrest growing cracks, thereby delaying the onset of catastrophic failure.

The increase in tearing energy for carbon black filled rubbers is due to the increases in the threshold tearing energy (\( T_0 \)), which may be due to micro deviations in tear. Tear deviation in carbon black reinforced systems may be due to creation of barriers in the tear path.

Tensile strength has a positive cependence on surface area of carbon black. The effect of structure and loading have been studied by Kraus. With reinforcing blacks, in tensile strength measurements the effective loading of filler, that is the carbon black plus the occluded rubber is taken in to account. In accordance with Kraus’s observation, at a fixed loading a low structure black gives a higher tensile strength and higher elongation than a high structure black of the same surface area, as at this loading low-structure
blacks are near the maximum of both properties and high-structure blacks are to the right of the maximum. The loading at which the tensile strength is a maximum, increases somewhat with increasing particle size\textsuperscript{3}, likely to be due to the lower effectiveness of the occluded rubber.

The increase in ultimate properties with increased effective loading up to the maximum is likely to be due to increased tear deviation. To be effective, tear deviation must take place during the initial stages of the growth of the random flaws\textsuperscript{3}. Cut growth and fatigue are two important failure properties which occur on cyclic deformation. The fatigue life increases with structure level and decreases with specific surface area\textsuperscript{182}.

Natural rubber and other strain crystallizing elastomers display more complex behavior in their response to filler reinforcement\textsuperscript{183}. When crystallinity develops as a result of deformation, the crystallites assume the role of reinforcing fillers and the gum vulcanizates exhibit good tensile strength. In real practical applications, such as in tires the strain rate and temperature encountered are such that crystallization cannot occur. Hence, reinforcement is important in NR just like that is required for SBR or SBR-BR blends\textsuperscript{3}.

Wear or abrasion are important properties which get modified by reinforcement. Wear rate is related to filler surface area and structure. Colloidal silicas, even when compounded with bonding agents do not equal carbon black in wear reinforcing capability\textsuperscript{184}. For off the road tires, blends of silica and carbon black provide improved cut growth resistance\textsuperscript{185}.

1.5.8.2 Dynamic mechanical properties

a) Dynamic mechanical behavior of rubbers

Rubber is a viscoelastic material: as it deforms, a fraction of the energy is stored elastically, and the remainder is dissipated as heat in a hysteric manner. This behavior can be mathematically expressed as given below.
When a linear viscoelastic material is subjected to a sinusoidal shear deformation \( \gamma \) of angular frequency \( \omega \), can be related by equation,

\[
\gamma(t) = \gamma_0 \sin (\omega t) \quad \text{Eq. 1.6}
\]

Where \( \gamma_0 \) is maximum strain and \( 't' \) is time; the shear stress response \( \sigma \) is also sinusoidal, but out of phase with the strain

\[
\sigma(t) = \sigma_0 \sin (\omega t + \delta) \quad \text{Eq. 1.7}
\]

where \( \sigma_0 \) is the maximum stress. The strain lags behind the stress by a phase angle \( \delta \). A vector method of representing the dependence of \( \gamma \) and \( \sigma \) on \( \omega t \) is shown in Fig.1.3.

Equation for shear stress can be written as

\[
\sigma(t) = (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t. \quad \text{Eq 1.8}
\]

Shear stress consists of two components; one in phase with the strain \( (\sigma_0 \cos \delta) \); the other \( 90^\circ \) out of phase \( (\sigma_0 \sin \delta) \).

The relation between stress and strain can be put into a form

\[
\sigma(t) = \gamma_0 [G' \sin \omega t + G'' \cos \omega t] \quad \text{Eq. 1.9}
\]

in which

\[
G' = \sigma_0 / \gamma_0 (\cos \delta) \quad \text{Eq. 1.10}
\]

\[
G'' = \sigma_0 / \gamma_0 (\sin \delta) \quad \text{Eq. 1.11}
\]

Fig.1.3 Plot of sinusoidal deformation - viscoelastic material
The component of the stress $G'\gamma_0$ is in phase with the oscillatory strain; the component $G''\gamma_0$ is $90^\circ$ out of phase.

A complex representation of the shear modulus ($G^*$) can be written as follows.

$$G^* = G' + iG''$$  \hspace{1cm} \text{Eq.1.12}

where $G'$ is called the real part of the shear modulus and $G''$ the imaginary part or loss modulus. Thus when a rubber sample is subjected to dynamic mechanical analysis, the $G'$ (storage modulus) is the measure of energy (elastic) stored and recovered in cyclic deformation, $G''$ (loss modulus) is a measure of energy dissipated as heat. The tangent of the phase angle (loss tangent) is the ratio of $G''$ to $G'$,

$$\tan \delta = \frac{G''}{G'}$$  \hspace{1cm} \text{Eq. 1.13}

$G'$ and $G''$ are frequency and temperature dependent. A typical frequency-dependence of the dynamic moduli (storage, $G'$ and loss, $G''$) for a viscoelastic material like rubber is shown in Fig. 1.4. The variations of the modulus with frequency can be

![Graph showing typical variation of $G'$ and $G''$ with frequency of unvulcanized viscoelastic material](image)
explained on the basis of segmental and chain movements in the rubber molecule. At low frequencies of deformation, all changes of the molecular conformation are possible within one cycle of deformation and there is almost no loss of energy. This part of the frequency-modulus plot is termed as the 'terminal zone'. The next zone corresponding to the variation of the modulus with immediate higher frequency is the rubber zone (plateau zone). At this zone with one cycle of deformation the entanglements cannot straighten out and therefore acts as 'time dependent' cross links. G' reaches a plateau, which can be related to the entanglement density. All other movements are still possible and elastic behaviour takes place at these frequencies. In the rubber plateau region there is a minimum in G". After the rubber plateau, at still higher frequencies there is another transition called glass transition where both G' and G" are increasing. Chain segments between the entanglements are not able to follow the applied deformation any further. This causes another phase shift resulting in the glassy zone. The frequency is so high that only local chain movements can occur. The value of G' equals the glass modulus, while G" decreases slightly. At every transition zone energy is dissipated which causes a peak in G".\(^{186}\)

b) **Dynamic mechanical properties of filled rubbers**

Enhancement of mechanical properties due to the presence of a filler in rubber compounds can be attributed due to various factors such as polymer network, hydrodynamic effect of filler in rubber, in-rubber structure and filler-filler interaction. The ultimate properties exhibited by the reinforced rubber hence will be resultant of the combined effects of these aspects. The extent of these effects vary from filler to filler and their characteristics.

Dynamic mechanical properties of carbon black filled rubbers has been reported by many researchers\(^{187-190}\) and reviewed by Medalia\(^{110}\). The general observations made
from the earlier studies are that the incorporation of carbon black in different types of rubbers results in an increase in storage and loss moduli, $G'$ and $G''$ and an increase in hysteresis, $\tan \delta$. Dynamic storage modulus of filled rubbers is strain dependent. This is due to filler networking. At a lower strain, filler secondary agglomeration remains intact and the large modulus is caused by the elastic response of this network. As the amplitude of deformation is increased, disruption of the agglomeration network causes the $G'$ to fall ("Payne effect") until a new plateau value is approached, where the network gets disrupted. A sigmoidal drop of modulus occur with strain as is shown in Fig. 1.2. The second plateau value (modulus) has been explained satisfactorily with Equation 1.14 with a correction of filler concentration for the occluded rubber. Dynamic modulus at moderate strain amplitude is a function of primary filler structure. Modulus of the secondary agglomeration network must increase with density of filler-to-filler contacts.

Silica filled rubber exhibit specific differences in its dynamic mechanical properties with that of carbon black, because of the specific characteristics of silica. Blume has reported that the amount of silanol groups on the silica surface has an influence on the dynamic stiffness, $G^*$ at 60 °C. Silanol groups will also lead to filler network. Silica filled rubber exhibits larger Payne effect or strain dependent drop in modulus than the carbon black filled.

The effect of temperature dependence of $\tan \delta$ for reinforced rubber compounds is the result of the characteristics of reinforcing fillers to form a filler network. A comparison of the $\tan \delta$ values at different temperatures for silica filled and carbon black filled rubber is given in Fig. 1.5. Silica filled exhibited lower $\tan \delta$ at lower
Fig. 1.5 Typical variations of tan δ with temperature for a silica (○) and carbon black (●) filled rubber

![Graph showing typical variations of tan δ with temperature for silica and carbon black filled rubber.](image)

In the rubbery state at temperatures beyond 20 °C, the tan δ and hysteresis is still higher for carbon black. Replacement of carbon black with silica in tyre compounds, therefore results in a decrease of tan δ at higher temperatures and thereby results in a reduction of rolling resistance. The use of silica also does not adversely affect the ice and wet grip, as the tan δ values at very low temperatures of both are comparable.

By increasing the average distance of separation of the aggregates from each other the value of \( \Delta G' \) (drop in modulus with strain) and tan δ (thus hysteresis) can be reduced. This can be achieved by prolonged or a two stage mixing technique, or by use of coupling agents as is often done with silicas and mineral fillers. Heat treatment of the mix can also be used to promote carbon black-rubber interaction (eg. butyl rubber). Special varieties of SBR and BR with molecules terminated by reactive end groups have also been found to increase the distance between aggregates. If rubber compounds...
are compared at the same strain, their hysteresis is proportional to their values of $G''$ or $G' \tan \delta$. If they are compared at the same stress, the hysteresis is proportional to $\tan \delta/G'$, whereas at constant energy input, hysteresis is proportional to $\tan \delta$ itself. $G'$ increases with increasing structure, while $\tan \delta$ remains constant.

c) **Relevance of dynamic mechanical analysis in tyre compounds**

Dynamic mechanical properties of a rubber compound could be used for predicting its performance properties in tyres. Abrasion resistance, low temperature flexibility, wet traction, rolling resistance and heat build-up are some of the important properties most relevant for tyre tread compounds. Rolling resistance, is predominantly related to the loss tangent of the bulk polymer at comparatively low frequencies in the plateau region of the storage modulus (region 2 in Fig. 1.4). This low frequency region is in the order of the angular velocity of the rolling tyres. $\tan \delta$ in the glass transition region can give an indication of the wet skid resistance. Higher the Tg, higher the wet

![Diagram](image)

**Fig. 1.6 Typical $\tan \delta$ curve with temperature for a vulcanized tyre tread compound**
skid resistance. Nordsiek related the tan δ values at various temperature to a number of tyre tread properties as given in Fig.1.6. Abrasion resistance also shows a relation to the glass transition temperature. Temperatures of about +30 to +70°C is the usual running temperature of a tyre. Under these temperature conditions the tan δ essentially determines the degree of rolling resistance. Tan δ above 70°C indicates the heat build-up. Thus the choice of the rubber with optimum glass transition temperature (Tg) is an important factor in achieving a compromise between many tyre requirements.

d) Large deformation behaviour of rubber

For viscoelastic materials, stress is not only a function of strain, but also of time. Stress relaxation occurs throughout the experiment. For different strain rates, the stresses attained at any given extension will be higher for higher strain rate. Hysteresis, which is related to stress softening, is more pronounced with filled rubbers. The initial slope of the stress-strain curve of a reinforced vulcanizate will be higher than that of the corresponding gum. Once the effects of secondary agglomeration are overcome, several mechanisms remain which will keep the stress rising faster than the unfilled. Various mechanisms will contribute to this, of which 'strain amplification' is an important phenomenon. Rigid filler do not share in the deformation and hence inclusion of a rigid filler in a soft matrix will cause the average local strain in the matrix to exceed the macroscopic strain. Thus the rubber in the filled vulcanizate finds itself more highly strained and responds with a higher stress. The quantity in parenthesis in the equation is in fact a strain amplification factor which in turn depends on the filler concentration and structure. At higher strains occluded rubber tends to be pulled out of the interstices of the aggregate, diminishing the strain amplification effect. These process causes high elongation at break.
Consideration of rubber on a molecular scale, provides insight into the stress-raising mechanisms. The retractive force ‘F’ of a rubbery network is proportional to the network chain density, v

\[ F \propto \alpha v RT \]

Adsorption of polymer segments at several sites of a filler particle effectively introduces multifunctional crosslinks into the system, thus enhancing the network chain density \(^{207}\).

Several mechanisms have been proposed for stress relaxation of a filled system. On stretching a filled vulcanizate some of the polymer chains linked to the filler particles will get broken thus giving rise to stress-relaxation \(^{208}\). Also at large strains there occurs "dewetting" from the filler surface, which also causes stress relaxation \(^{209}\). Dewetting is delayed to higher elongations as specific surface area and structure of carbon black increases. Hess et al \(^{209}\) observed dewetting stresses of 10 MPa for a furnace black of surface area 30 m\(^2\)/g, while only 1-2 Mpa for graphitised black. Molecular slippage also causes stress relaxation \(^{206}\).

Stress softening \(^{210}\) is another important property associated with filler reinforcement. When a filled rubber is extended to a certain strain, then returned to zero strain and stretched again, the second stress-strain curve lies below the first one, which is resultant of a stress-softening. This phenomenon is known as ‘Mullins effect’. Several mechanisms are proposed for stress softening, viz; incomplete elastic recovery \(^{210}\), progressive breaking or detachment of network chains attached to the filler particles \(^{207}\) and chain slippage of attached polymer segments along the surface \(^{206}\) would have a similar effect.

With carbon black and silicas, the contribution of the filler to the modulus can be described by equation 1. 4, \( E = E_0 (1 + 2.5\phi + 14.1\phi^2) \), in which \( \phi \) is replaced by “f\( \phi \)"
where “f” is an experimentally determined function of strain, temperature and filler surface activity\textsuperscript{211}. The stiffness of rubber vulcanizates is usually expressed as modulus at 300% extension ($\sigma_{300}$), the strain in the region where secondary agglomeration effects have almost disappeared and dewetting has not initiated.

1.5.8.3 Swelling behavior

Uncrosslinked rubber gets dissolved in a good solvent, but a vulcanized or crosslinked sample can only swell. Solvent swelling of rubber is affected by incorporation of filler. In the case of a reinforcing filler, strong rubber-filler interaction will have some effect on the apparent crosslink density of the system. Ratio of the restriction of swelling of the filled rubber vulcanizate to that of the gum rubber is used as a means for evaluating the reinforcing ability of a filler in rubber. Kraus\textsuperscript{212} developed the following expression relating volume fraction of filled rubber in the swollen gel, $V_{rf}$ and volume fraction of gum or unfilled system in swollen gel, $V_{ro}$ as,

$$\frac{V_{ro}}{V_{rf}} = \frac{1 - m\phi}{1 - \phi}$$

Eq.1.15

where $m = 3C (1-V_{ro}) + V_{ro} - 1$, $\phi$ is the volume fraction of the filler and ‘C’ the characteristic parameter of the filler related to the rubber-filler interaction\textsuperscript{213}.

Cunneen-Russell equation (Eq.1.16), which is based on vulcanize swelling parameters, is also used for reinforcement characterization\textsuperscript{214}.

$$V_{ro}/V_{rf} = ae^{-z} + b$$

Eq.1.16

where $V_{ro}$ and $V_{rf}$ are the volume fractions of the rubber in the unfilled and filled vulcanizates respectively after swelling in a solvent to equilibrium, $z$ is the weight fraction of filler in the polymer and $a$ and $b$ are two constants which depend on the filler
activity. High value of ‘a’ and low value of ‘b’ indicates polymer-filler attachment. 

\( V_{r0}/V_{r1} < 1 \) indicates reinforcement.

Paauw et al\textsuperscript{215} and Gajewski et al\textsuperscript{216} reported that chemically modified carbon black increases the apparent crosslink density of the filled rubber vulcanizates. The strong secondary inter-aggregates formed in the case of silica filled vulcanizates play an important role in reducing solvent swelling\textsuperscript{217}.

1.6 **Silica reinforcement of rubbers**

Maximum reinforcement effect of a filler can be achieved through good dispersion and better chemical or physical interaction with the rubber.

1.6.1 **Silica as a filler in rubber – compounding aspects**

Compounding with precipitated silica is quite different from compounding with carbon black; silica has a more reactive surface than carbon black. Carbon black has good affinity with non-polar rubbers, while silica being hydrophilic is incompatible. Silica-to-silica interaction is high, resulting in the formation of large aggregates ultimately impeding the compound flow character. In the case of both carbon black and silica with lower surface area (bigger particle size), viscosity is lower and dynamic properties are better\textsuperscript{218}. Fine particle silica though could reinforce rubber, silica filled compounds exhibits higher viscosity and slower cure.

Some softeners could effectively reduce the viscosity. Natural softeners of vegetable origin, such as tall oil and hydrogenated rosin are effective in reducing viscosity, though its mechanism is not fully understood. Petroleum based aromatic resins are effective in giving smooth extrusion, better tensile strength, tear strength and abrasion resistance. Considerable reduction in viscosity is obtained only with additives that de-agglomerate the silica. Additives such as soluble zinc compounds (e.g. zinc octoate), hexamethylene tetramine (HMT), magnesium Oxide etc. are reported to reduce compound stiffness. Activators such as diethylene glycol (DEG), polyethylene...
glycol(PEG) and triethanolamine(TEA) are used in compounding, which reduces the cure time, compression set and heat build-up and enhances the tensile strength.

Use of silane coupling agents in silica compounding is an important development. Coupling agent bridges the silica filler and rubber, thus enhancing the rubber-filler interaction. Silane coupling agent in silica filled rubbers, could reduce the compound viscosity and enhance the modulus, tensile strength and abrasion resistance.

1.6.2 Silane modification in silica filled rubbers

Organofunctional silanes are being widely used to enhance the bonding properties of glass fibers with various polymers and also to modify siliceous filler surface in rubber and other hydrocarbon polymers. Silane modified silica in elastomers can produce considerable improvement in its failure properties. Use of silane coupling agent as a silica surface modifier has been reviewed by Wagner and Plueddemann. Hewitt describes the reinforcement modification achieved with the use of silane coupling agent in SBR. In NR, with silica/silane combination, properties equivalent to that of carbon black of similar surface area as that of silica could be achieved. By silane modification viscosity reduction of the compound and improvement in tensile strength, modulus, set, heat build-up and abrasion resistance could be achieved. Improved filler dispersion occurs on silane modification. Many researchers have suggested that improved dispersion results in reduced viscosity of rubber matrix. Dannenberg and Cotton reviewed the mechanism for the improved silica reinforcement with silanes and suggested a molecular slippage mechanism. Harwood et al proposed a mechanism based on shell rubber which could account for most of the reinforcement phenomena.

The silanes which are effective in enhancing the reinforcement have functional groups which can chemically react with both silica and rubber, thus forming a bridge between the two. Many researchers have made studies on the reaction between silanes
and silica filler\textsuperscript{230-232}. Mercaptan, vinyl and methacrylic based silanes were found to be effective in crosslinking with rubber. Wagner reported that silanes are also effective in the case of carbon black filled matrices\textsuperscript{225}. Xue et.al have made studies on the kinetics of the reaction between epoxy group of an epoxy based silane with silanol and alcoholic groups\textsuperscript{233}. Blackshaw have reported that silane can also function as a vulcanizing agent\textsuperscript{234}. Silica filled tyre compounds modified with TESPT exhibited improved technological properties\textsuperscript{235}.

Of the several bifunctional silane coupling agents, a few have attained commercial significance in the rubber industry. TESPT was introduced as a coupling

![Chemical structures](image)

Fig. 1.7 Reaction mechanism of TESPT with silica and rubber
agent in 1970's. The coupling agent TESPT has been covered more extensively in the literature than the other silane coupling agents.\(^3\)

The mechanism of silane coupling agent reinforcement comprises two phases.

(i) **Silanization reaction** in which the coupling agent reacts with silica and

(ii) **Formation of crosslinks** between the modified silica and the polymer.

Probable reaction mechanism of TESPT with silanol groups of silica and rubber through accelerator such as mercaptobenzthiazole disulphide (MBTS) is given in Fig.1.7. Silanization of the silica surface can occur quite readily, though with TESPT systems, the reaction is generally carried out in-situ between 150 and 160°C in an internal mixer. Though excess silanol groups are present on the silica surface and reaction rates are fast, high temperature is generally used because of the steric hindrance around the silyl propyl group in TESPT.

1.6.3 **Silica reinforcement of non-polar rubbers**

Carbon black is the ideal filler for reinforcing hydrocarbon rubbers. Since both are hydrophobic substances, mixing and reinforcement problems do not usually arise when those two are mixed. Precipitated silica, which is of mineral origin, is one of the most promising alternatives to carbon black. However, due to the difference in surface energy, when silica is mixed with the commonly used non-polar olefinic hydrocarbon rubbers, occurrence of filler-filler interaction leads to mixing and reinforcement problems. For overcoming the technical difficulties associated with silica reinforcement of hydrocarbon rubbers, bifunctional organosilanes are generally used.

1.6.3.1 **Natural rubber and its reinforcement**

Cis-polyisoprene, the hydrocarbon component of NR, the structure of which is given below, is fairly widespread in nature, having been identified in about 2000 plant species.\(^{237}\)
Only the species *Hevea brasiliensis* is of any commercial significance. From the tree the rubber is collected in the form of latex by tapping. Rubber is separated from the latex by coagulation usually by acidification. The resultant coagulum is then processed into different marketable forms of NR such as sheet rubber, technically specified rubber and crepe rubber. Most of the natural rubber based products are made from any of these forms. Also certain products are made from concentrated latex\textsuperscript{238}.

The rubber separated from latex contains more than 90% of the hydrocarbon, cis-1,4 – polyisoprene in admixture with naturally occurring resins, proteins, sugars etc. The polyisoprene is having a broader molecular weight distribution with a number average molecular weight of about $5 \times 10^5$.\textsuperscript{239,240}

Most of the latex rubber products can be made from NR latex including medical products. Apart from the conventional rubber products made from dry natural rubber, it finds a few specialized applications. Natural rubber is a versatile and adaptable material which has been successfully used for transport and engineering applications such as automobile tyres, aero tyres, off-shore and aerospace industries, civil engineering, railways, vibration engineering etc. Though natural rubber exhibits very good strength even without reinforcement by filler, excepting a few latex products, most of the rubber products require reinforcement\textsuperscript{241}. The discovery of reinforcement of natural rubber by particulate fillers, is almost a century old.

**1.6.4 Silica reinforcement of polar elastomers**

Generally, silicas produce relatively greater reinforcement in polar elastomers such as NBR and CR than in non-polar elastomers such SBR and NR\textsuperscript{1}. Reinforcement studies of silica in acrylonitrile butadiene rubber of varying acrylonitrile content (NBR) was made by Tan et al\textsuperscript{242} using a series of silica in comparison with carbon black. The
study showed that the changes in viscoelastic properties of the silica-filled compounds can be attributed to improved polymer-filler interaction relative to those of the carbon black filled ones.

Studies conducted by Wang et al\textsuperscript{42} using model compounds revealed that aromatic hydrocarbons exhibit stronger interaction with silica surface than olefins, which may be attributed to the high electron density associated with the conjugated $\pi$ bond system. They have also found that nitriles exhibited the highest interaction with silica probably through the hydrogen bond interaction between the $-$CN group and silanol groups. Based on their study they have proposed the order of interaction of elastomers with silica as NBR$>$ SBR$>$ NR $\geq$ BR$>$ High vinyl-BR$>$ EPR$>$ IIR. Thus as the polarity of the elastomer increases the silica-polymer interaction increases and consequently the filler networking get reduced.

Reinforcement behavior of fumed silica on the reinforcement properties of silicone rubber was studied by Cochrane et al\textsuperscript{243}. In the silica filled silicone rubbers both silica-silica and silica-polymer-silica networking can occur. Increasing the silica loading, surface area and structure increases the level of interactions and hence also the networking. Wang et al\textsuperscript{244} have studied the reinforcement characteristics of in-situ precipitated silica in polydimethyl siloxane (PDMS) elastomers and found that good mechanical properties could be achieved.

1.6.4.1 Acrylonitrile – butadiene rubbers –relevance of reinforcement

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene. Konrade and co-workers\textsuperscript{245} first prepared the polymer. It, when vulcanized, had excellent resistance to oil and petrol. Its commercial production in Germany started in 1937.

Nitrile rubbers are manufactured by emulsion co-polymerisation of butadiene with acrylonitrile. Commercially available nitrile rubbers differ from one another in three respects: acrylonitrile content, polymerization temperature and Mooney viscosity.
Acrylonitrile content has the most profound effect on the properties of a vulcanized nitrile rubber, most important of which is the oil and fuel resistance. NBR possesses generally better heat resistance than polychloroprene rubber. But like NR its ozone resistance is poor. Nitrile rubbers, suitably compounded, have a service temperature range of $-50^\circ$ to $+120^\circ$C.

Unfilled nitrile rubber vulcanisates have very low tensile strength. Carbon black and non-black fillers are used for reinforcement. Silicas or clays are used where non-black compounds are required, but compression set performance is not so good as a black reinforced compound, unless silane-treated silicas are used.

1.7 Epoxidised natural rubber

1.7.1 Preparation and properties

Epoxidised natural rubber (ENR) is a chemically modified form of natural rubber (NR). In the 1930’s German chemists have prepared rubbers with epoxide groups, by reacting peracids with natural rubber in solution. The reaction resulted in a range of secondary products caused by epoxide ring opening reactions. Gelling et al. later optimized the conditions for the preparation of ENR with different levels of epoxidation and to avoid ring opened products. ENR is industrially produced through the latex stage epoxidation of natural rubber using performic acid generated in situ from formic acid-hydrogen peroxide combination. Epoxidised natural rubber has improved oil resistance, gas impermeability and higher damping over NR. In addition to this ENR possesses strain crystallization behavior and hence necessary tensile strength required for many applications. Commercial production of ENR started in Malaysia in 1987. Initially it was thought that ENR, due to its improved oil resistance and air impermeability, could compete with synthetic rubbers such as nitrile, butyl and polychloroprene. However, in reality it could not penetrate much into those areas. Other applications proposed are in vibration damping and in adhesives.
1.7.2 Silica reinforcement of ENR

An important feature imparted to NR by epoxidation is inherent reinforcement with silica even without coupling agent. It has been reported that both 25 and 50 mol percent epoxidised natural rubber exhibit the same properties, when reinforced with silica as with a highly reinforcing black \( ^{249} \). A comparison of properties of the black and silica reinforced ENR vulcanizates is given in Table 1.5.

**Table 1.5 Comparison of Black and Silica-Reinforced ENR Vulcanizates**

<table>
<thead>
<tr>
<th></th>
<th>ENR-25 Black</th>
<th>ENR-25 Silica</th>
<th>ENR-50 Black</th>
<th>ENR-50 Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, IRHD</td>
<td>69</td>
<td>67</td>
<td>73</td>
<td>68</td>
</tr>
<tr>
<td>Modulus at 300%, Mpa</td>
<td>12.4</td>
<td>12.8</td>
<td>13.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td>25.4</td>
<td>21.0</td>
<td>24.5</td>
<td>22.4</td>
</tr>
<tr>
<td>Elongation at break, Mpa</td>
<td>435</td>
<td>405</td>
<td>500</td>
<td>435</td>
</tr>
<tr>
<td>DIN abrasion loss, mm(^3)</td>
<td>272</td>
<td>250</td>
<td>278</td>
<td>289</td>
</tr>
<tr>
<td>Goodrich heat buildup from 100(^\circ)C, (^\circ)C</td>
<td>7</td>
<td>7</td>
<td>23</td>
<td>19</td>
</tr>
</tbody>
</table>

* 50 phr black (N330) or 50 phr silica (HiSil 233).

ENR based tread compounds when reinforced with silica have improved wet grip and reduced rolling resistance, a combination of properties not observed in other general purpose rubbers.

1.7.3 Blending of ENR with other elastomers

Blending or mixing of elastomers is generally undertaken for three main reasons; improvement of the technical properties of the base elastomer, achievement of better processing behavior and lowering of compound cost. Elastomer blends are one class of composite materials which are made by macroscale mixing of high molecular weight elastomers. Unlike many organic liquids, which are fully or partially miscible with each other at room temperature, polymers by virtue of their chain length, are not easily miscible. Walters et.al \( ^{250} \) first demonstrated that elastomer blends are never truly
homogenous and showed discrete areas of each elastomer varying in size from 0.5µm upward, depending on mixing methods, elastomer viscosity etc.

The most widely used method for preparing elastomer blends in industrial operations is mechanical mixing. It was realised that although two high molecular weight polymers may be mutually insoluble, blends can be made with macroscopic homogeneity and useful properties, provided that mechanical mixing is sufficiently intense and that the viscosities after mixing are sufficiently high to prevent gross phase separation. While blending of elastomers it is desirable that the components have similar viscosities for ease of dispersion.

The mutual solution of two materials demands that the free energy of mixing be negative, a situation brought about by exothermic mixing and/or a large entropy of mixing. The mixing of polymers is in general endothermic. Thus for chemically dissimilar polymers, incompatibility is the rule.

Important tools being used for elastomer blend characterisation are microscopy (optical, electron, atomic force), thermal and thermo mechanical devices such as differential scanning calorimetry and dynamic mechanical analysis and spectroscopy (IR, NMR).

Other important aspects determining thermoset elastomer blend properties are curative diffusion and filler migration between component phases. Maiti et. al. have reported on silica distribution studies in NR/ENR blends.

Blending of ENR with rubbers for achieving specific requirements such as with NR for improved adhesion, for air impermeability, in elastic garments for oil resistance and in tyre tread compounds for improved rolling resistance and wet grip are reported.
1.8 Carbon black and silica / silane in the tyre industry

The general concept of “reinforcement with carbon black” is well accepted by the rubber and especially the tyre industry. The newer tailor-made carbon blacks with wide variations in surface area, surface energy and structure can be produced using the furnace production process. Due to its performance, flexibility and cost carbon black has been the dominating filler in the tyre industry. This situation began to change with the introduction of “green tyre” or an eco-friendly tyre. Carbon black offers good abrasion resistance to tyres whereas silica offers better rolling resistance and wet grip. Development of highly dispersible (HD) silica is an advancement in silica production technology, which may lead to its wider use in tyre industry.

The most important requirements of high performance tyres are lower rolling resistance, less tread wear and better wet grip. These properties are popularly represented with a ‘Magic triangle’. Fig.1.8 gives a pictorial representation of the same for the performance comparison of ASTM carbon black and HD-silica in tyre compounds.

![Fig. 1.8 Magic Triangle – comparison of carbon black and silane modified HD -- Silica](image)
However, use of silica / silane by the tire industry though is growing, still have many problems which need to be overcome. Some important limitations are given below.

- Difficult processing
- Poor filler dispersion
- Longer vulcanization time
- Lower abrasion resistance
- Static electricity build-up
- High cost of silane

1.9 Carbon-silica dual phase filler for tyre industry

An ideal filler for tyre tread compounds are those which possess high polymer-filler and low filler-filler interactions. The former ensures higher abrasion resistance and the latter is necessary for lower hysteresis or lower rolling resistance. Based on this objective a new class of filler material ‘carbon-silica dual phase (CSDP)’ filler has been commercialized under the trade name “ECCBLACK” which claims best balance of these properties. These fillers are produced using a special co-fuming technology developed by Cabot Corporation. Instead of containing the typical 90-99 % elemental carbon as in traditional carbon black, the new filler consists of silica phase finely distributed in the carbon phase(about 5% silicon). The main features claimed for the new material are high polymer-filler and low filler-filler interactions.\textsuperscript{262,263}

1.10 Objective and scope of the present work

Annual global industrial rubber consumption, including both natural and synthetic is about 19.5 million tonnes. A major share of this is by the tyre sector.\textsuperscript{264} Rubbers mostly used for tyre manufacture are hydrocarbon based. Carbon black is the ideal filler for reinforcing such rubbers. However, compared to carbon black, precipitated silica in tyres can provide lower rolling resistance and therefore reduced fuel
consumption. Hence, use of precipitated silica as a filler in tyre sector is on the increase either for complete substitution or partial substitution of carbon black. Silica reinforcement has great potential in footwear and other non-tyre sectors also.

Automobile sector aims at tyres with higher wear resistance and lower rolling resistance. This can be achieved mainly through two aspects viz; tyre design and compound design. Development of radial tyres is an advancement in the tyre design for achieving the said goal. With regard to compounding, selection of filler and polymer are important. Silica is known to contribute to lower rolling resistance. Radialization of tyres has led to the usage of larger proportion of NR. In a cross ply tyre the usage of NR is about 40 to 90%, while for a radial tyre it is about 98 to 100%. This has led to a situation where silica reinforcement of NR has become more relevant.

The surface activity and surface energy of the filler play an important role in the reinforcement of polar rubbers such as NBR and CR. Polar elastomers, unlike hydrocarbon elastomers, provide comparatively better rubber-silica interaction and therefore results in improved filler dispersion. In general the vulcanizate properties of silica filled polar rubbers are better than non-polar rubbers. However, the properties of the silica filled polar elastomers could further be enhanced with the use of silane coupling agents. Acrylonitrile butadiene rubber is a typical example of polar elastomer which exhibits comparatively better reinforcement with silica than the hydrocarbon rubbers. It is also reported that when the polymer to be reinforced contains a reactive group, capable of interacting with fillers, the same could modify reinforcement. Polymers such as SBR and NBR when partially functionalized with epoxy functionality, exhibited improved reinforcement with silica. Carbon black and silica also contain functional groups capable of interacting with rubbers.
Coupling agents are known to greatly influence filler dispersion, compound processing properties and failure properties of rubber\textsuperscript{273-275}. Large varieties of coupling agents are being used\textsuperscript{276,277}. Silane coupling agents usually used with rubber are bifunctional. It generally will have silanol reactive groups (ethoxy, methoxy etc.) and a rubber reactive group. For most of the hydrocarbon rubbers sulphide group of the silane will be the rubber reacting entity. With certain other rubbers, silanes having any of the rubber reactive functionality such as chloro, amino, vinyl, methacryl or epoxy group are also used\textsuperscript{273}. Typical rubber-silica reaction product through the silane-coupling agent, TESPT can be illustrated as in Fig. 1.9.

![Rubber-Silica reaction](image)

Fig. 1.9 Rubber-Silica reaction

Viable alternative methods or materials for overcoming the problems associated with the silica reinforcement of rubbers is therefore a current research priority\textsuperscript{278-285}. Recently Varkey et.al have reported the feasibility of using epoxidised natural rubber (ENR) as a reinforcement modifier for silica filled rubbers\textsuperscript{286}. The present thesis describes a detailed study of various aspects of using ENR as reinforcement modifier in silica filled natural rubber and nitrile rubber.
Epoxidised natural rubber, can be considered a bifunctional polymer as it contains two functionalities; viz the epoxy and the double bond. It is already reported that the epoxy group can interact with the silanol groups \(^{271}\). It is also known that the unsaturation in NR can serve as a site for sulphur crosslinking \(^{287}\). The bifunctional structure of ENR is given in Fig.1.10. Moreover ENR is more polar than NR as it contains the epoxy functionality and therefore may get preferentially adsorbed on the silica surface. Therefore, it is likely to function as an interface modifier between rubber and silica or as a silica dispersion modifier. The acid-base interaction between epoxy group and silanol or hydrogen bonding between the two can lead to better rubber-silica interaction. It is reported that ENR can effectively be reinforced with silica even without silane coupling agent \(^{249}\). ENR when used in tyres offer better wet grip and low rolling resistance \(^{249}\). Silane coupling agents being expensive, their widespread use in silica reinforced products of rubber especially in tyres is limited \(^{261}\).

The objective of the present work is to study the effect of using ENR as a silica reinforcement modifier in NR and NBR on its processability and technological properties. These composites were also compared with the corresponding silane modified silica filled and the carbon black filled systems.

To achieve the said objectives the following studies were carried out.

1. NR/ENR blends containing 0-20% ENR were prepared and mixed with silica. The epoxy content of the ENR used was varied from 10 to 60 mole %. Sulphur Vulcanized samples of these composites were compared with the corresponding silica...
filled silane modified and carbon black filled NR. Cure characteristics and compound properties were determined. Vulcanizates were characterized for crosslink density, stress-strain, technological properties and ageing resistance. Scanning electron microscopy was used for characterizing the silica distribution in various systems.

2. **Dynamic mechanical analysis of the sulphur vulcanized silica filled NR modified with ENR of varying epoxy content** was made in comparison with that of silane modified and carbon black filled vulcanizates. Variations in storage modulus, loss modulus and tanδ were determined in the temperature range of -80 to +100°C.

3. **Mixing characteristics and rheological behavior of NR/silica, NR/ENR/silica, NR/silane/silica and NR/carbon black composites** were studied using ‘Haake Rheocord’ and ‘Zwick Capillary Rheometer’ respectively. Mixing parameters such as mixing torque, mixing energy and temperature developed were measured using Haake Rheocord. Processability characteristics such as viscosity variations with temperature and shear rate, at different modifier concentrations in the composites were compared using the capillary rheometer.

4. **Peroxide cured vulcanizates of silica filled NR and its ENR and silane modified compounds** were compared for property variations. Effect of filler loading in those systems were studied. Compound viscosity and vulcanizate properties were determined. Reinforcement characterization of the vulcanizates was made by swelling studies. Selected samples (at 50 phr filler loading) from each series were studied using dynamic mechanical analyzer for the viscoelastic properties and scanning electron microscopy for filler distribution.

5. **Effect of filler loading in sulphur cured vulcanizates of silica filled NR and its ENR and silane modified systems** were studied. Compound and vulcanizate properties were determined. Reinforcement characterization of those systems was made by swelling studies. **Comparison of the selected vulcanizates from each of the series was**
made with respect to stress relaxation, thermogravimetry, differential scanning calorimetry, strain dependent dynamic mechanical analysis and scanning electron microscopy.

6. Sulphur cured silica filled nitrile rubber (NBR) of medium acrylonitrile content and the same modified with ENR50 and silane were compared with carbon black filled. Compounds were tested for cure characteristics and the vulcanizates for technological properties, ageing, swelling resistance and dynamic mechanical properties.
References


49. N.Tsubokawa and T.Endo, Kinou Zainyo, 8, 73, 1988.
60. C.Jones and E.Sammann, Carbon, 28, 1647, 1990.


133. C.M. Blow, Polymer, **14**, 3009, 1973
158. N. Hewitt “Compounding with Non-black fillers”. Educational symposium 4, Meeting of the Rubber Division, ACS, Cleveland, Ohio, October 23-26, 1979.
183. L. Mullins, In "The Chemistry and Physics of Rubber like Substances" (Ed. L. Bateman), Maclarean and Sons Ltd., 1963, Chapter 11, P. 301.
186. D.E. Hall, J.C. Moreland, ACS Rubber Division Meeting, Dallas, Texas, April 4-6, 2000.


248. C.S. Pong (Rubber Research Institute of Malaysia), Indian Patent No. 167854 (29 July, 1986).


284. S. Takashi (Bridgestone Corporation), EP 0661,298 A2 (July 5, 1995).

