CHAPTER 5
MIXING, BOUND RUBBER AND RHEOLOGICAL CHARACTERIZATION OF NR-SILICA COMPOSITES

5.1 Introduction
Manufacturing of rubber products involves mixing of various ingredients into rubber usually followed by a few further processing operations such as extrusion, calendering etc. and the final curing. Mixing involves energy consumption. The production sector always looks for energy efficient processing operations. Mixing and processability of rubber compounds are hence important for a product manufacturer. Processability of rubber compounds, especially filled compounds, generally depends upon their rheological properties. Carbon black and silica are the two important reinforcing fillers being used by the rubber industry. Unlike carbon black, silica has many mixing and processing problems due to its surface polarity and the resulting filler-filler networking which ultimately results in stiff and viscous rubber compounds which are difficult to handle. To overcome the problems with silica and to bridge the technological gap between silica and carbon black, conventionally silane coupling agents are used in silica compounds.

In the present chapter a processability study of silica in NR in the presence of different modifiers such as silane and ENR was conducted in comparison with carbon black. The composites thus produced were also evaluated for bound rubber.

5.2 Experimental
5.2.1 Materials
Natural rubber (ISNR-5) and epoxidised natural rubber (ENR50) were obtained from the Rubber Research Institute of India. Silica (Ultrasil VN3) and silane coupling agent (bis (3-triethoxysilyl propyl) tetrasulphide (TESPT) “Si 69”) were products of Degussa A.G. Germany, and carbon black (ISAF-N220) of Phillips Carbon Black Ltd., India.
5.2.2 Mixing of rubber-filler composites

Various composites of rubber with silica or carbon black were prepared in a Haake Rheocord (Model, Rheocord 90). Natural rubber alone or in combination with ENR50 having similar viscosity \((M_L(1+4), 73)\) was either premasticated or blended in the Rheocord at 40 °C, 60 rpm for 5 minutes. The resultant rubber was used for further mixing with silica and carbon black. The conditions of premastication/blending and the respective data generated are given in Table 5.1.

Table 5.1 Mastication/Blending data (Rheocord)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Blending parameters</th>
<th>Final Mooney viscosity, (M_L(1+4), 100^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Init. temp. °C</td>
<td>Final temp. °C</td>
</tr>
<tr>
<td>NR(100)</td>
<td>40</td>
<td>143</td>
</tr>
<tr>
<td>NR/ENR(95/5)</td>
<td>40</td>
<td>141</td>
</tr>
<tr>
<td>NR/ENR(90/10)</td>
<td>40</td>
<td>140</td>
</tr>
<tr>
<td>NR/ENR(85/15)</td>
<td>40</td>
<td>139</td>
</tr>
</tbody>
</table>

The rubber or rubber blend thus made was used further for making the rubber-filler composites. The formulations of the rubber-filler composites made, mixing conditions and mixing data generated are given in Table 5.2.

Table 5.2 Filler mixing studies (Rheocord)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixing parameters</th>
<th>Final Mooney viscosity, (M_L(1+4), 100^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (initial) °C</td>
<td>Temp. (final) °C</td>
</tr>
<tr>
<td>NR/Silica (100/50)</td>
<td>40</td>
<td>130</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/1/50)</td>
<td>40</td>
<td>126</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/2/50)</td>
<td>40</td>
<td>122</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/3/50)</td>
<td>40</td>
<td>114</td>
</tr>
<tr>
<td>NR/ENR/Silica(95/5/50)</td>
<td>40</td>
<td>111</td>
</tr>
<tr>
<td>NR/ENR/Silica(90/10/50)</td>
<td>40</td>
<td>112</td>
</tr>
<tr>
<td>NR/ENR/Silica(85/15/50)</td>
<td>40</td>
<td>109</td>
</tr>
<tr>
<td>NR/ISAF(100/50)</td>
<td>40</td>
<td>116</td>
</tr>
</tbody>
</table>
5.2.3 Testing of samples

Mastication/blending of the gum rubber and mixing of the rubber-filler composites were made in the Haake Rheocord. The viscosity of the masticated/blended gum rubber and the composites made from it was determined using a Mooney viscometer model Shimadzu SMV 202. Rheological characterization of the gum rubber and filled composites was made using a capillary rheometer attached to a Universal Testing Machine model Zwick 1474. Rubber – filler composites were also evaluated for bound rubber by swelling in toluene.

5.3 Results and Discussion
5.3.1 Mixing
5.3.1.1 Mixing of filler in rubber

Compared to carbon black, silica causes many mixing problems. Silica aggregates are comparable to those of carbon blacks, but have a relatively higher structure. This structure accounts for a higher reinforcing power than carbon black. Because of its high specific component of surface energy ($\gamma_{sp}$), silica has a stronger tendency to agglomerate, and is difficult to disperse in rubber and rapidly reagglomerates after mixing. To obtain a high dispersion with silica, higher shear stress is required. High shear stress can be obtained when the viscosity of the mass is high, which can be achieved by high filler loading and by use of high viscosity polymers and lower mixing temperature. Silica possess very strong filler-filler interaction. When no coupling agent is used, the compounds show very high viscosity. The handling of such silica-filled compounds is very difficult. When hydrophobing occurs, the surfaces of the silica particles are covered with the coupling agents and filler-filler interactions get reduced, thus leading to low viscosity. High viscosity, generates high shear stresses and consequent excessive energy dissipation in the compound, which will lead to substantial
rise in compound temperature. Boonstra and Medalia suggested that the total filled volume should include not only the filler but also the rubber that is occluded within the agglomerates. During the dispersive mixing stage, these agglomerates are broken down, the amount of occluded rubber decreases, and thus the filled volume decreases, leading to lower viscosity. The bound rubber molecules on the silica surface have more freedom of movement. As a result, hysteresis and heat build-up of silica filled vulcanizates are lower than the corresponding carbon black filled vulcanizates.

A plot of mixing torque versus mixing time shows normally an exponential drop, after the addition of the last ingredients, to some limiting value \( P_\infty \). Such data can be fitted by the following equation:

\[
\ln \frac{P_t - P_\infty}{P_0 - P_\infty} = -Kt
\]

where \( P_0 \), \( P_t \), and \( P_\infty \) represent the torque values just after the addition of the last ingredients, at time \( t \) and the limiting torque after infinitely long mixing. The total change in torque \( (P_0 - P_\infty) \) can be taken as a measure of the initial volume of occluded rubber and \( P_t - P_\infty \) is proportional to the volume of occluded rubber at time \( t \). The constant \( 'K' \) represents the rate at which the filler is dispersed. The above equation represents a process obeying first order kinetics.

### 5.3.1.2 Mixing in Haake Rheocord

Mixing studies were conducted using the Haake Rheocord. It is a computer controlled torque rheometer that can be used for mixing and extrusion. The mixing device fitted with banbury type rotors was used for the present study. In this equipment temperature and rotor speed can be varied. It can measure torque and melt temperature. This device has been used for studying processing characteristics such as viscosity, energy consumption etc. Objective of the study was to understand the mixing behavior of silica in natural rubber with and without ENR/silane as modifier and to compare with
carbon black. Premastication of rubber or rubber blends and the mixing of rubber-filler composites were done in the Rheocord. The filled mixes made were NR/Silica, NR/ENR/Silica and NR/Silane/Silica (Three different concentrations each of ENR and silane) and NR/ISAF. Data for premastication/blending of gum rubbers and their viscosities are given in Table 5.1. The rubber-filler composites made, conditions of mixing, mixing data and the composite viscosities are given in Table 5.2. The rheograms of mixing for the rubber-filler composites are displayed in Figs. 5.1 to 5.8.

From the data it is observed that the order of temperature development at the end of the mixing was NR/Silica>NR/Silane/Silica> NR/ENR/Silica. NR/ISAF shows mix temperature in between that of the silane and ENR modified mixes. The temperature developed during mixing and the final mixing torque value can be taken as a measure of the viscosity of the mix. With the addition of ENR and silane, temperature development and viscosity were lower and the former exhibited the lowest value. The final mixing temperatures developed with the ENR modified systems were comparable to that of the carbon black filled and that of the mix with silane at higher concentration. Also the totalized torque value, which can be taken as a measure of the energy consumed for mixing, was the lowest for the ENR modified mix. The highest value of final torque, totalized torque and the temperature developed for the unmodified NR/Silica mix might have resulted from the high viscosity of the mix caused by filler-filler networking. The efficiency of mixing of the filler in rubber was evaluated from the rheograms using Equation 5.1. The mixing efficiency, as given by the slope (-K), is given in Table 5.3. Slope values indicate that in the presence of ENR, efficiency of mixing silica in natural rubber has increased considerably and is in similar trend as that of carbon black in rubber. Though silane at higher concentration also has improved the mixing efficiency, it is not as high as that for the ENR modified mix. The epoxy-silanol interaction or the
1. Torque: 0-250 (Nm)
2. Totalized torque: 0-2000 (Nm-min.)
3. Temperature: 0-200 (°C)

Fig. 5.1 Mixing curve - NR/Silica (100/50)

Fig. 5.2 Mixing curve - NR/Silane/Silica (100/1/50)
Fig. 5.3 Mixing curve -- NR/Silane/Silica (100/2/50)

Fig. 5.4 Mixing curve -- NR/Silane/Silica (100/3/50)
1. Torque: 0-250 (Nm)
2. Totalised torque: 0-2000 (Nm-min.)
3. Temperature: 0-200 (°C)

**Fig. 5.5** Mixing curve - NR/ENR/Silica(95/5/50)

1. Torque: 0-250 (Nm)
2. Totalised torque: 0-2000 (Nm-min.)
3. Temperature: 0-200 (°C)

**Fig. 5.6** Mixing curve - NR/ENR/Silica(90/10/50)
1. Torque: 0-250 (Nm)
2. Totalised torque: 0-2000 (Nm-min.)
3. Temperature: 0-200 (°C)

Fig. 5.7 Mixing curve - NR/ENR/Silica (90/15/50)

Fig. 5.8 Mixing curve - NR/ISAF (100/50)
hydrogen bonding between the two, might have contributed to improved filler dispersion and lower filler-filler interaction resulting in lower Mooney viscosity and better mixing efficiency.

Table 5.3 Rheocord mixing-Comparison of dispersion efficiency

<table>
<thead>
<tr>
<th>Mix</th>
<th>Slope (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/Silica(100/50)</td>
<td>-0.471</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/1/50)</td>
<td>-0.389</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/2/50)</td>
<td>-0.482</td>
</tr>
<tr>
<td>NR/Silane/Silica(100/3/50)</td>
<td>-0.498</td>
</tr>
<tr>
<td>NR/ENR/Silica(95/5/50)</td>
<td>-0.6182</td>
</tr>
<tr>
<td>NR/ENR/Silica(90/10/50)</td>
<td>-0.59</td>
</tr>
<tr>
<td>NR/ENR/Silica(85/15/50)</td>
<td>-0.696</td>
</tr>
<tr>
<td>NR/ISAF(100/50)</td>
<td>-0.627</td>
</tr>
</tbody>
</table>

5.3.2 Bound Rubber

5.3.2.1 Bound rubber and rubber-filler interaction

Bound rubber is essentially the gel formed in a filler-rubber mix and its estimation is considered to be a practical means of assessing rubber-filler interaction in the uncured state. The gel formed due to polymer-polymer crosslinking is not considered as bound rubber. Bound rubber is generally determined by swelling measurements.

Physical as well as chemical interactions are believed to involve in bound rubber formation. In the case of carbon black, free radical interaction between the filler surface groups and the polymer is proposed as a mechanism for bound rubber formation. Bound rubber is also related to filler surface area and surface activity. High structure black generally exhibits larger rubber-filler interaction. Freshly formed filler surfaces have great adsorption capacity. In the polymer matrix, above a critical concentration \( C_{\text{crit}} \) filler transforms from a disperse to a coherent gel and \( C_{\text{crit}} \) decreases with increasing surface area. The filler-filler aggregates, which get broken down during mixing with
the elastomers may get reformed during the post-mixing period. The trapped rubber in such aggregates can also cause bound rubber. Comparatively higher bound rubber exhibited by black filled NR and SBR can be attributed to the high dispersive component ($\gamma_d$) of the surface energy of carbon black. High bound rubber exhibited by these rubbers is attributed to physical phenomena. Graphitised carbon black (surface groups are lost) exhibits lower bound rubber. Chemical interaction of a filler particle with elastomer can affect the properties of both the uncured mix and the vulcanizate. Covalent bonds between rubber and carbon black contribute to reinforcement, while it is not a necessary condition for bound rubber formation. The bound rubber retained at higher temperature ($>100^\circ$C) is likely to be due to rubber-filler covalent bonds. Polarity of the polymer also contributes to enhanced bound rubber. Polarization of the unsaturated polymers in the presence of polar fillers also contribute to polymer-filler interaction. Bound rubber can be formed even when effective reinforcement is not there as in the case of silica in hydrocarbon rubbers. Important reinforcement properties are considered to be resultant of rubber-filler interaction. Silica exhibits comparatively higher bound rubber with polar polymers like nitrile rubber.

5.3.2.2 Bound rubber in ammonia atmosphere

Bound rubber in ammonia atmosphere is usually determined to assess the extent of rubber-filler physical bonding. Ammonia is known to cleave physical linkages between silica and rubber. Silica-ammonia interaction is stronger than silica-rubber interaction. For the carbon black filled rubbers, especially with hydrocarbon rubbers, stronger interaction with filler occurs, which cannot be easily broken down by ammonia and consequently the reduction in bound rubber in ammonia atmosphere is not very high. In the case of silica filled systems considerable reduction in bound rubber occurs, in ammonia atmosphere and it can be attributed to the weak silica-polymer interaction. Moreover, the swelling of silica filled vulcanizates in ammonia atmosphere was found...
larger than those of the carbon black filled vulcanizates, which also indicates the weakening of silica – rubber interaction \(^{22}\).

5.3.2.3 Observations on bound rubber

The eight rubber-filler composites given in Table 5.2 were analyzed for bound rubber. Bound rubber values for all the three series of silica filled compounds viz; NR/Silica, NR/ENR/Silica and NR/Silane/Silica (with 3 different ENR and silane concentrations) and NR/ISAF are given in Table 5.4.

Table 5.4 Bound rubber data (Rubber–Filler mix)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bound rubber(%)</th>
<th>Bound rubber(%) (ammonia atmosphere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/Silica(100/50)</td>
<td>33.1</td>
<td>9.01</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/1)</td>
<td>35.98</td>
<td>20.9</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/2)</td>
<td>36.07</td>
<td>19.38</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/3)</td>
<td>34.38</td>
<td>22.19</td>
</tr>
<tr>
<td>NR/ENR/Silica (95/5/50)</td>
<td>28.52</td>
<td>21.59</td>
</tr>
<tr>
<td>NR/ENR/Silica (90/10/50)</td>
<td>32.93</td>
<td>25.18</td>
</tr>
<tr>
<td>NR/ENR/Silica (85/15/50)</td>
<td>32.62</td>
<td>25.74</td>
</tr>
<tr>
<td>NR/ISAF (100/50)</td>
<td>33.55</td>
<td>27.7</td>
</tr>
</tbody>
</table>

The values are found to be in the range of 28 to 36%. Bound rubber in a limited range shows that both the silica filled and carbon black filled mixes give almost the same level of networking either due to filler-filler or filler-rubber interaction. The polar surface groups on silica can interact with NR through dipole-dipole interaction\(^{23}\). Bound rubber values of the corresponding samples measured in ammonia atmosphere were interesting. The lowest bound rubber value retained was for the NR/Silica system. This clearly shows that the bound rubber originated from the rubber–filler interaction in the NR/Silica system could be weakened by ammonia, whereas in the case of NR/ISAF the bonding is stronger, and was not much affected by ammonia. Both ENR and silane modified systems retained high bound rubber values even in the ammonia medium. The silane modified system exhibited a bound rubber in the range of about 20 to 22%
whereas with the ENR modified system it was in the range of about 22 to 25.7. The better interaction of silica with rubber in the silane modified mix can be due to the silanol-ethoxy interaction which provided the silica with a hydrocarbon entity which then might have interacted with the polymer chains through better dispersion entanglement or through its sulphur entity. In the case of ENR modified systems, during mixing, a preferential adsorption of ENR over the silica surface might have taken place through the epoxy-silanol interaction and/or hydrogen bonding. The ENR modified silica, would have dispersed well in the rest of the hydrocarbon matrix thus giving the possibility of better rubber–filler binding. The silanol-epoxy interaction might be stronger than the silanol-ammonia interaction thus giving better retention of bound rubber in the ammonia modified swelling for the ENR containing samples.

5.3.3 Rheological Studies

5.3.3.1 Rheology of rubber–filler composites

The rheological properties of polymers in the presence of filler depend largely on polymer filler interaction. Guth and Gold utilized Einstein's hydrodynamic concept to explain the increase in viscosity for the filled elastomers over the gum and proposed the following equation.

\[ \frac{\eta_f}{\eta_g} = 1 + 2.5\phi + 16.1\phi^2 \]  

Eq. 5.2

where \( \eta_f \) and \( \eta_g \) are the viscosities of the filled and gum elastomers respectively and \( \phi \) is the volume fraction of filler.

The shear viscosity of polymers is reported to increase significantly with incorporation of carbon black. However, the increase in viscosity is dependent largely on the surface area, structure and surface activity of the filler. Silica, being a highly polar material, the rheological behavior of rubbers filled with it, obviously varies from those filled with carbon black. Many investigations on the rheological
behaviour of carbon black filled $^{33-38}$ and silica filled $^{1,2,39-41}$ elastomers have been reported.

5.3.3.2 Flow behavior of polymeric materials

Viscosity models (Power law model)

The equation derived by Newton for expressing the viscosity of liquid is given by

$$\tau = \eta \gamma$$

Eq. 5.3

where $\tau =$ shear stress

$\gamma =$ shear rate

$\eta =$ proportionality constant known as viscosity

The liquids which follow the above equation are called 'Newtonian liquids'. Polymeric materials deviate considerably from Newtonian behavior and their behaviour is usually represented by the Power law equation given below$^{42}$.

$$\tau = k \gamma^n$$

Eq. 5.4

where $k =$ constant

$n =$ Power law index which is generally $<1$ for polymers

Average apparent viscosity ‘$\eta_a$’ is defined as

$$\eta_a = \tau / \gamma$$

Eq. 5.5

where $\gamma =$ average shear rate over the capillary diameter

$$\eta_a = \tau / \gamma = k \gamma^n / \gamma = k \gamma^{n-1}$$

Eq. 5.6

$$\ln \eta_a = \ln k + (n-1) \ln \gamma$$

Eq. 5.7

The above equation indicates that apparent viscosity of liquids which follows the Power law equation having $n<1$, decreases with increasing shear rate. Such materials are known as 'Pseudoplastic'.

5.3.3.3 Rheological measurements

Processability of NR, NR/ENR blends and its filled composites were characterized by rheological means. Masticated rubber/rubber blends (4 samples) as given in Table 5.1 and rubber-filler composites (8 samples) as given in Table 5.2, made in the Haake Rheocord, were subjected to rheological studies.
The shear stress, shear viscosity and extrudate swell of various experimental composites at different shear rates and temperatures were determined using a capillary rheometer attached to a UTM, model ZWICK 1474. The capillary used was made of tungsten carbide and has an l/d ratio of 30 and an angle of entry of 180°. The sample for testing was placed inside the barrel of the extrusion assembly and forced down the capillary with a plunger attached to the moving crosshead. After a warming up period of 3 minutes the mix was extruded through the capillary at preselected speeds of the crosshead, which varied from 0.5 to 500 mm.min⁻¹. The forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress ($\tau_w$) and shear rate ($\gamma_w$) at the wall respectively, using the following equations involving the geometry of the capillary and the plunger.

$$\tau_w = F/4Ap(l_c/d_c) \quad \text{Eq. 5.8}$$

$$\gamma_w = (3n'^{1}/4n'^{1}+1)32Q/\pi d_c^3 \quad \text{Eq. 5.9}$$

where F is the force applied at a particular shear rate, Ap is the crosssectional area of the plunger, l_c is the length of the capillary, and dc is the diameter of the capillary, Q is the volume flow rate and $n'$ the flow behaviour index. Volume flow rate is calculated from the velocity of the crosshead and the diameter of the plunger. The flow behavior index $n'$ is defined by

$$n' = d (\log \tau_w) / d (\log \gamma_w) \quad \text{Eq. 5.8}$$

The parameter $n'$ is determined by regression analysis of the values of $\tau_w$ and $\gamma_w$ obtained from the experimental data. $\gamma_w$ is the apparent wall shear rate calculated as $32Q/\pi d_c^3$. The shear viscosity $\eta$ was calculated as

$$\eta = \tau_w / \gamma_w \quad \text{Eq. 5.9}$$
Various experimental composites extruded through the capillary were analyzed for shear stress, shear viscosity and extrudate swell.

5.3.3.4 Rheological characterisation of the experimental samples

The four premasticated gum rubber/rubber blends given in Table 5.1 and the eight filled composites given in Table 5.2 were subjected to rheological measurements. Each sample, having the same volume of material loaded into the capillary rheometer, was extruded through the capillary at selected shear rates. From the shear force required for each stabilised extrusion at different shear rates, shear stress was calculated. From the shear stress and shear rate data shear viscosity was calculated. The extrudates at different shear rates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured using a binocular stereo microscope. The die swell is expressed as the ratio of the diameter of extrudate to that of the capillary \( \frac{D_e}{D_c} \).

a) Shear viscosity

Processing of most of the rubbers are in the 'non-Newtonian' flow regime. For many polymers the flow is non-Newtonian even at the lowest shear rates attainable \(^{43}\). Rheological properties of the compounds under study are discussed. A comparison of the plot of log viscosity vs log shear rate of the outcome of the rheological experiments of NR and NR/ENR blends given in Table 5.1, carried out at 90\(^\circ\)C and 120\(^\circ\)C are given in Figs. 5.9 and 5.10. Similar behavior was observed at 100\(^\circ\)C and 110\(^\circ\)C. All the samples exhibited pseudoplastic behavior, that is, the viscosity decreased with shear rate. The flow pattern of NR did not change much with substitution of NR with ENR 50 in small quantities upto 15 parts per hundred rubber.

Viscosity of filled rubbers in general increases with decreasing filler particle size and increasing 'structure'. Bound rubber also in certain cases leads to increased viscosity\(^{43}\).
Fig. 5.9 NR/ENR gum blend (Viscosity vs Shear rate) - 90 deg.C

Fig. 5.10 NR/ENR gum blends-(Viscosity vs shear rate)-120 deg.C
Silica filled rubbers generally exhibit high viscosity and therefore their processability is poor as compared to the black filled rubbers\textsuperscript{44}. Derringer \textsuperscript{42} reported that silica filled SBR exhibits higher viscosity, compared to the corresponding ISAF filled, especially at lower shear rates, while at higher shear rates the viscosity margin get reduced. Time and temperature of storage enhances the viscosity of silica filled composites, which is attributed to the formation of filler network or bound rubber\textsuperscript{2}. With annealing, the filler network get stiffened. Schaal et al \textsuperscript{41} reported that ingredients such as CBS or DPG and moisture could reduce the viscosity of silica filled composites. Compared to gum EPDM, silica incorporation considerably raises the compound viscosity especially at lower shear rates\textsuperscript{1}.

Studies on viscosity change with shear rate conducted at 4 different temperatures viz; 90, 100, 110 and 120°C for composites of NR/Silica and the same modified with silane or ENR 50 at 3 different concentrations each, as given in Table 5.3, were made. Results are compared in Figs.5.11 to 5.18. Filled samples also exhibited pseudoplastic behavior. Unmodified silica filled NR exhibited a slight non-linearity in viscosity drop especially at medium to high shear rates which is likely to be due to some filler networking at higher shear rates. Similar observations were noted for silica filled EPDM \textsuperscript{1}. As compared to the unmodified silica composites, a general decrease in viscosity was noted with incorporation of silane and ENR at all ranges of shear rates. The viscosity was found to get reduced to a larger extent with ENR incorporation than with silane. With silane incorporation, the margin of viscosity decrease with that of the unmodified mix got reduced with increase of temperature. This is likely to be due to filler reagglomeration at higher temperatures \textsuperscript{2}. With ENR modification considerable viscosity difference with that of
Fig. 5.11 NR/Silica - Effect of silane (Viscosity vs Shear rate-90 deg.C)

Log shear rate, $S^{-1}$

Fig. 5.12 NR/Silica - Effect of ENR (Viscosity vs Shear rate-90 deg.C)
Fig. 5.13 NR/Silica-Effect of silane (Viscosity vs shear rate) 100 deg.C

Fig. 5.14 NR/Silica-Effect of ENR (Viscosity vs shear rate) 100 deg.C
Fig. 5.15 NR/Silica—Effect of silane (Viscosity vs Shear rate)—110 deg.C

Fig. 5.16 NR/Silica—Effect of ENR (Viscosity vs shear rate)—110 deg.C
Fig. 5.17 NR/Silica - Effect of Silane (Viscosity vs shear rate) - 120 deg.C

Fig. 5.18 NR/Silica - Effect of ENR (Viscosity vs shear rate) - 120 deg.C
the unmodified was retained even at higher temperatures. This indicates that ENR could function also as a process aid for the silica filled NR. Earlier workers have reported that addition of certain ingredients such as glycols and curatives such as CBS, DPG and moisture could reduce the viscosity of silica filled rubbers. Composites filled with stearic acid treated inorganic fillers exhibits lower viscosity. This is attributed to the hydrogen bonding ability of these materials. The tendency for viscosity increase at higher shear rates, also get considerably reduced with ENR incorporation and the viscosity drop became almost linear.

A comparison of the viscosity variation with shear rate for NR/Silica and its silane and ENR modified systems at particular concentrations with that of carbon black filled at 90 and 120°C are given in Figs.5.19 to 5.20. It can be observed that among the filled samples, the ENR modified system exhibited the lowest viscosity at different shear rates and temperatures.
b) Shear viscosity- Effect of temperature

A comparison of the variation of viscosity with temperature for the silica filled NR, silane modified, ENR modified and carbon black filled systems are compared in Figs. 5.21 to 5.24. The silica filled NR showed a non-linear viscosity relation with temperature, whereas silane modification reduces viscosity linearly with temperature. ENR modified silica filled and black filled NR exhibited a steady viscosity drop with temperature at all shear rates. This indicates that the processability of silica filled NR got considerably improved with ENR addition and is similar to that of the carbon black filled. The dependence of viscosity of various composites on temperature at a shear rate of 854 S\(^{-1}\) is shown in Fig. 5.25, in semi logarithmic Arrhenius plots of \(\eta\) vs \(1/T\). In the Arrhenius equation \(\eta\) is related to absolute temperature \((T)\) by the relation,

\[
\eta = A e^{E/RT}
\]

Eq. 5.10

where \(A\) is a constant characteristic of the polymers, \(E\) is the activation energy of flow, \(T\), is the absolute temperature and \(R\), the universal gas constant.

![Graph showing viscosity variation with shear stress](image)
Fig. 5.21 Effect of temperature on variation of viscosity with shear rate (NRSilica)

Fig. 5.22 Effect of temperature on viscosity (NRSilane/Silica, 100/2/50)
Fig. 5.23 Effect of temperature on viscosity (NR/ENR/Silica, 90/10/50)

Fig. 5.24 Effect of temperature on viscosity (NR/SAF)
Table 5.5 Activation energy of flow (E)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E), Cal.mole⁻¹deg⁻¹ at 854 S⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/Silica (100/50)</td>
<td>1.86</td>
</tr>
<tr>
<td>NR/ENR/Silica (90/10/50)</td>
<td>3.81</td>
</tr>
<tr>
<td>NR/Silane/Silica (100/2/50)</td>
<td>1.96</td>
</tr>
<tr>
<td>NR/ISAF (100/50)</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 5.6 Flow behavior index (n')

<table>
<thead>
<tr>
<th>Sample</th>
<th>n' Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90 °C</td>
</tr>
<tr>
<td>NR/Silica (100/50)</td>
<td>0.239</td>
</tr>
<tr>
<td>NR/ENR/Silica (90/10/50)</td>
<td>0.245</td>
</tr>
<tr>
<td>NR/Silane/Silica (100/2/50)</td>
<td>0.1748</td>
</tr>
<tr>
<td>NR/ISAF (100/50)</td>
<td>0.262</td>
</tr>
</tbody>
</table>

From the slope of the curves, E, the activation energy values were calculated. A comparison of the activation energy of flow for different composites is given in Table 5.5.
Variation of flow behavior with temperature for ENR modified and carbon black filled systems is almost similar. Arrhenius plots and the activation energy values indicate that with temperature rise, considerable viscosity reduction has occurred for the ENR modified and the carbon black filled systems, whereas significant change could not be seen for the silica filled NR and its silane modified. Flow behavior index values for selected composites given in Table 5.6 also indicate that for the ENR modified and the carbon black filled systems pseudoplasticity or reduction in viscosity with shear rate has occurred with temperature rise.

c) Shear stress

Filled composites generally exhibit yield stress for flow to occur. Yield stress generally increases with particle concentration and decreasing particle size. Yield stress usually is attributed to the filler particle network. Dominant networking factors are filler-filler and filler-polymer interactions. Processing aids could lower the yield stress \(^{38,45}\).

For a better understanding of the flow behavior of various experimental composites, the plots of log shear stress versus log shear rate were compared. The plots
Fig. 5.27 Variation of shear stress with shear rate (90 deg.C)

Fig. 5.28 Variation of shear stress with shear rate (120 deg.C)
Fig. 5.29 Die swell characteristics (90°C)

Fig. 5.30 Die swell characteristics (120°C)
Table: 5.7 Die swell data (Extrudate), 90 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>De/De (90°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.54 s⁻¹</td>
</tr>
<tr>
<td>NR</td>
<td>1.41</td>
</tr>
<tr>
<td>NR/ENR50 (95/5)</td>
<td>1.21</td>
</tr>
<tr>
<td>NR/ENR50 (90/10)</td>
<td>1.17</td>
</tr>
<tr>
<td>NR/ENR50 (85/15)</td>
<td>1.22</td>
</tr>
<tr>
<td>NR/Silica (100/50)</td>
<td>1.12</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/1)</td>
<td>1.15</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/2)</td>
<td>1.21</td>
</tr>
<tr>
<td>NR/Silica/Silane (100/50/3)</td>
<td>1.38</td>
</tr>
<tr>
<td>NR/ENR/Silica (95/5/50)</td>
<td>1.03</td>
</tr>
<tr>
<td>NR/ENR/Silica (90/10/50)</td>
<td>1.06</td>
</tr>
<tr>
<td>NR/ENR/Silica (85/15/50)</td>
<td>1.03</td>
</tr>
<tr>
<td>NR/ISAF (100/50)</td>
<td>1.18</td>
</tr>
</tbody>
</table>

for gum NR and NR/ENR (90/10) blend are compared in Fig. 5.26. It can be observed that ENR blended NR exhibited slightly higher shear stress than NR alone at lower shear rate and became almost identical at higher shear rates. Similar plots of the selected silica filled and carbon black filled composites at 90 and 120°C are given in Figs. 5.27 and 5.28. ENR modified silica filled composites exhibited lower shear stress, compared to other composites. It is reported that filled systems containing process aids could lower the shear stress indicating better processability. Processing promoters generally improve filler dispersion, flow properties and scorch safety and reduce the energy for
processing. It could be presumed that ENR might have acted also as a processing aid in getting silica better dispersed in NR. At 90°C, black filled composites exhibited higher shear stress, while the corresponding NR/ENR/Silica composite exhibited the lowest shear stress at all shear rates. Under the same temperature condition, incorporation of silane in silica filled NR could not reduce shear stress at lower shear rate, while at higher shear rate, the stress get closer to that of the ENR modified system. At 120°C and at higher shear rates, variations in shear stress among the composites were found to be in the order NR/Silica > NR/Silane/Silica > NR/Black > NR/ENR/Silica.

d) **Die swell:**

Unfilled elastomers generally exhibit higher melt elasticity or higher die swell. Higher molecular weight and broader molecular weight distribution enhances die swell. Decrease in filler particle size and increase in structure reduce die swell.
A comparison of the die swell ($D_v/D_e$) of various extrudates under study at different shear rates at 90°C and 120°C are given in Tables 5.7 and 5.8 respectively and their photographs are given as Fig. 5.29 and 5.30. Unfilled elastomers exhibited the highest swell. Extrudates of gum NR and NR/ENR blends have not shown significant difference.

Among the filled composites, the unmodified and ENR incorporated compounds in general, exhibited lower die swell. Black filled and silane modified silica filled composites exhibited die swell in a narrow range, slightly higher than the other two silica filled systems, most likely to be due to a networking of rubber and filler and the resultant elasticity.

5.4 Conclusions

A comparative processability study of NR/Silica and ENR and silane modified composites was made with that of NR/Carbon black mixes. Mixing behavior of NR/Silica composites improved on incorporation of ENR in limited quantities. Energy requirements for mixing of silica in NR in the presence of ENR was found comparable to that for carbon black. Viscosity values of ENR modified silica filled and carbon black filled systems are almost close. Higher bound rubber values for the ENR modified system indicated better rubber-filler interaction. Larger retention of bound rubber in ammonia medium for the ENR modified system indicates, stronger rubber-filler interaction. Rheological studies showed improved processability of NR/Silica composites with ENR incorporation. ENR modified system exhibited lower die swell as well.
References