CHAPTER 4

MELT RHEOLOGICAL BEHAVIOUR OF SBR COMPOSITES FILLED WITH NR PROPHYLACTICS WASTE AND PARTICULATE FILLERS

ABSTRACT

Rheological properties of polymeric materials have paramount importance during their conversion to useful products. This chapter discusses the melt rheological behaviour of styrene butadiene rubber compounds filled with natural rubber prophylactics rejects and selected particulate fillers such as carbon black, silica, and marble powder. All the rubber compounds, irrespective of the composition, prophylactics particle size, mixing conditions and temperature, have showed pseudoplastic behaviour. An increase in the melt viscosity of styrene butadiene rubber compounds has been noted with the increasing loading of prophylactics filler. But this trend has been found to be dependent on the shear rate. The presence of particulate filler has been found to be increasing the viscosity of the rubber compounds only at the highest shear rate while at lower shear rates, a reverse trend has been observed. At the highest shear rate, among the particulate fillers used, the order of increasing the viscosity has been found to be marble powder<silica=black. The general inverse relation between particle size of the filler and viscosity in the case of particulate alone filled elastomer composites has not been observed for the present cases. The influence of particle size of prophylactics filler also has been found to be dependent on the shear rate. At low and intermediate shear rates and at a temperature of 150°C, the compound mixed for 5 minute showed least viscosity but at highest shear rate the curves converge to a point due to ‘spurt’ or sudden combined flow. In the case of samples without particulate fillers, the influence of temperature has been found to have a notable effect on viscosity, only in the case of gum styrene butadiene rubber compounds. In these cases an inverse relation between temperature and viscosity has been observed with some abnormalities in the results at 160 and 170°C. Such abnormalities have not been observed in the case of particulate filled samples at higher
shear rates. Flow behaviour index values have been found to be irregularly decreasing with the loading of prophylactics filler at 150 and 160°C while at 170°C a regular decrease has been observed. Except at 160°C, all the samples filled with particulate fillers have been found to be less pseudoplastic than gum SBR and other prophylactics filled samples. Among the theoretical models studied, Eiler van Dyck equation has been found to be giving closely agreeing values of viscosity to that of experimental values. The variation of ‘m’ and ‘C’ which are characteristic rheological properties have been checked with the composition, particle size of prophylactics, mixing time and temperature of samples. A decrease in the extrudate distortion also has been observed with the addition of prophylactics and particulate fillers to styrene butadiene rubber compounds.
CHAPTER 4
MELT RHEOLOGICAL BEHAVIOUR OF SBR COMPOSITES Filled WITH NR PROPHYLACTICS WASTE AND PARTICULATE FILLERS

Results of this chapter have been communicated to Plast. Rubb. Compos. and Int. Polym. Process.

One of the objectives of polymer blending is the production of a better processing material. Processing of a rubber or elastomer blend involves all operations starting from the initial mastication to the formation of finished material. The knowledge of the rheological behavior of rubber compounds is important than any other properties. In addition to these, careful control of manufacturing processes strongly depends on the appropriate classification of raw materials and their processability characteristics. The complex rheological behaviour of polymer blends has been analysed by various researchers. A number of publications focusing the rheology of various polymer blends are available in the literature. These include the rheological investigations on interacting blend solutions of poly (acrylic acid) with poly (vinyl pyrrolidone) or poly (vinyl alcohol), polyphenylene sulphide/polyamide-66 blends, polypropylene/liquid crystal copolyester, ternary blends based on polypropylene/ethylene propylene rubber/polyethylene and binary blends of LDPE/LLDPE & HDPE/LLDPE.

According to a review by Utracki et al. three types of rheological behaviour are shown by polymer blends. These are the positive deviation behaviour where the blend viscosities are synergistic, the negative deviation behaviour where the blend viscosities are antagonistic, and finally the positive-negative deviation behaviour. The actual behaviour shown by a polymer melt is in fact decided by the composition, morphology and processing conditions.

Rheological characteristics of single polymeric materials as well as polymer blends and especially that of rubber-rubber blends are greatly affected by the presence of fillers.
The filler loading used in most of these studies is in the range of 40 to 60%. The influence of fillers on the rheological behavior of 1,2 polybutadiene rubber has been studied by Bhagawan et al. They observed that the highest viscosity is shown by silica filled samples, while the lowest by clay at all shear rates. Similar studies on silica filled silicone rubber has been studied by Aranguran et al. and also by Li et al., taking zinc oxide and calcium carbonate in addition to black and silica. The greatest yield value and viscosity were observed with calcium carbonate and zinc oxide filled compounds. Recently, the influence of fillers on the compatibility of polymer blends also is reported in the literature. Studies revealed that the compatibilising effect of the filler depends on the change in free energy of mixing between the two polymers.

In the field of recycling, the rheological behaviour of cryoground rubber-natural rubber blends has been observed by Phadke et al. and that of polystyrene-SBR blends by Ciesielska et al. Publication of Reena et al. regarding the rheological and extrudate behaviour of natural rubber/latex reclaim blends also is noteworthy.

This chapter in two parts examines the rheological behavior of SBR/prophylactics systems by using a capillary rheometer. In the first part, the main parameters focused are the variation in viscosity and elastic effects, with respect to shear rate, shear stress, temperature & loading, particle size and mixing time of natural rubber prophylactics waste with SBR. In the second part, the influence of selected particulate fillers such as carbon black, silica and marble powder in SBR mixes with natural rubber prophylactics (size 2) is discussed.

4.1. Results and discussion

PART 1. Influence of Prophylactics Loading, Particle Size, Mixing Time and Temperature

The basic formulation used for the study is given in Table 4.1

4.1.1. Viscosity variation

(a). Influence of prophylactics loading

The variation of log melt viscosity with log shear stress of SBR compound with natural rubber prophylactics waste (S1) loading at different shear rates and at 150°C is presented in Figure 4.1. (The antilog values of viscosity (y-axis) are in Pa-s and that of
shear stress (x-axis) are in Pa).

Table 4.1. Basic formulation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Gum</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TDQ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Prophylactics</td>
<td>0</td>
<td>10(S1)</td>
<td>40(S1)</td>
<td>20(S2)</td>
<td>20(S4)</td>
<td>20(M)</td>
<td>20(M)</td>
<td>20(M)</td>
<td>20(S2)</td>
<td>20(S2)</td>
<td>20(S2)</td>
<td>20(S2)</td>
</tr>
<tr>
<td>Filler</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon, HAF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Marble powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

a - mixing time 10 min, b - mixing time 5 min, c - mixing time 20 min

Figure 4.1. Variation of melt viscosity with shear stress for SBR samples with increasing prophylactics loading
The melt viscosity is found to be decreasing with shear stress and shear rate for all the mixes under study. This observation confirms the pseudoplastic behaviour of the mixes. At zero shear, the polymer chains are extensively entangled and randomly oriented. Under the application of shear, the chains get disentangled and become oriented. Pseudoplasticity results from this behaviour of the polymer chains. In the case of prophylactics filled cases also, pseudoplastic nature is observed. This is because of the orientation of the randomly oriented prophylactics particles under the action of shear with their major axis in the direction of shear. With increasing shearing force, this orientation also is facilitated. Therefore the viscosity drops considerably with increase in shear stress and shear rate. It is reported\textsuperscript{23} that even in a molecular level, such orientation can help the smooth sliding of molecules over each other dissipating less energy than the randomly oriented and entangled molecules. Such a flow of gum SBR in layers is clearly visible from the scanning electron micrograph given in Figure 4.2.

Figure 4.2. SEM photo of gum SBR extrudate

Another observation is that the gum mix exhibits a lower viscosity at lower shear stress and a higher viscosity at higher shear stress. At lowest shear rate of 1.249 s\textsuperscript{-1}, as the concentration of waste prophylactics increases, the melt viscosity increases slightly, which becomes maximum for the mix with 40 phr prophylactics. When the shear rate increases the value of gum becomes comparable to that of prophylactics filled mixes and at higher shear rates, gum remains as one among those with higher viscosities. At the highest shear
rate, instead of gum SBR, the mix with 10 phr prophylactics exhibits the minimum melt viscosity. The slightly increasing trend in the melt viscosity with the addition of prophylactics is expected from the presence of crosslinked particles in an elastomer matrix. The increase in viscosity with the addition of prophylactics at low shear rate indicates the restriction to the flow of the material induced by prophylactics particles. This results from the inability of prophylactics particles to get oriented at low shear rate. The structural build up, as reported earlier by Munstedt, is a possible reason for this. At high shear rates this will be less predominant and therefore such an increasing viscosity behaviour with the addition of prophylactics particles is absent. Figure 4.3 clearly indicates the presence of a structural build up in the composite sample.

Figure 4.3. SEM photo of SBR extrudate with 10 phr prophylactics

The low melt viscosity of SBR compound with 10 phr prophylactics filler at higher shear rates indicates the better mould flow for these samples in a molding process. In such cases, the additional energy consumption for molding will be much less. Such a behaviour is due to the difference in the size of the flow units initially suggested by Mooney and Wolstenholme and later developed by the theory of Nakajima and Collins. At low shear rate, the size of the flow unit must be smaller than the size of the prophylactics particles. In such a case, the prophylactics particles act as flaws and therefore viscosity increases with prophylactics loading at low shear rates. But at high shear rates, the combined flow occurs in which the size of the flow units increases over the size of prophylactics particles. Therefore, no significant effect on the viscosity can be observed with the presence of
prophylactics particles.

It is interesting to note in Figure 4.1, that the melt viscosity verses shear stress curves present a change in the slope at an earlier shear rate of 4.164 s\(^{-1}\) and later at 124.9 s\(^{-1}\). The slope is higher at both low and high shear rates while it is less at intermediate shear rates. It is interesting to see that most of the curves converge at the higher shear rate. Similar slope changes as noted in Figure 4.1 are reported in the case of natural rubber–cryoground rubber systems also\(^{29}\) at 30s\(^{-1}\). The convergence of the curves at higher shear rates is due to a phenomenon called ‘spurt’\(^{30,31}\) which is a sudden combined flow.

(b). Influence of prophylactics particle size

The effect of particle size of waste prophylactics filler (20 phr loading) on the log viscosity-log shear stress plots at 150\(^0\) C is presented in Figure 4.4.

![Figure 4.4. Variation of melt viscosity with shear stress for SBR samples with increasing prophylactics particle size](image)

For all the particle sizes under study, pseudoplasticity is observed. At the lower shear rate, comparatively higher viscosity is shown by size 2 prophylactics filled samples.
while at intermediate shear rates, values become comparable. At the highest shear rate, large size fillers such as size 4, M and gum compound exhibit highest viscosity while size 2 shows the lowest. Normally, in the case of elastomers filled with particulate fillers, the viscosity is reported to be increasing for smaller particles with larger surface area than larger particles with smaller surface area. But here, such a trend cannot be observed.

(c). Influence of mixing time

SBR mix containing mill-sheeted form of the prophylactics is selected to study the effect of mixing time. The mixing time of the SBR compound containing 20 phr of mill sheeted is varied as 5, 10 and 20 minutes (Figure 4.5).

![Figure 4.5. Variation of melt viscosity with shear stress for SBR samples with increasing mixing time](image)

At low and intermediate shear rates, the compound mixed for 5 min shows the lowest viscosity (at 150°C) while the maximum viscosity is exhibited by the sample when the mixing time is 10 minutes. An intermediate viscosity is shown by the sample mixed for 20 minutes. At the highest shear rate, it is found that the curves converge at a point.
proving the non-dependence of mixing time on the viscosity of the mixes. In these cases also, the variation in viscosity is marginal. Here it should be noted that the viscosity of a rubber matrix filled with crosslinked rubber particles depends on many phenomena such as size distribution of particles and their agglomeration effects in the matrix. The convergence of viscosity values at the highest shear rate to a point can be due to ‘spurt’ or combined flow observed in flowing polymer melts.

(d). Influence of temperature on melt viscosity

The effect of temperature on the melt viscosity of SBR gum compound is presented in Figure 4.6. It is a general observation that as the temperature increases, the melt viscosity decreases at all shear rates. However, some abnormality exists between the mixes at 160 and 170°C.

Figure 4.6. Variation of melt viscosity with shear stress for gum SBR samples at different temperatures
The influence of temperature in SBR compound containing 20 phr size 1 prophylactics filler is shown in Figure 4.7.

![Figure 4.7. Variation of melt viscosity with shear stress for SBR with 20 phr size 1 prophylactics at different temperatures](image)

The melt viscosity is found to be almost unaffected with temperature at most of the shear rates. But at the highest shear rate of 416.4 s\(^{-1}\), similar values are shown by the sample at 160 and 170 °C while higher value is observed at 150 °C. In the case of SBR sample filled with 40 phr size 1 prophylactics filler (Figure 4.8), comparable values are observed at various temperatures given.
Figure 4.8. Variation of melt viscosity with shear stress for SBR with 40 phr size 1 prophylactics at different temperatures

4.1.2. Flow behaviour index

The flow behaviour index (n'), which is a measure of the pseudoplasticity, is presented in Table 4.2. As per the theory, the more the value of n', lesser is the non-Newtonian behaviour (or higher the Newtonian behaviour), the lower the pseudoplasticity.

(a). Influence of prophylactics loading

At 150°C and for a mixing time of 10 min, it can be seen that the presence of prophylactics filler decreases the n' values in an irregular manner, i.e., as the loading of prophylactics filler in SBR increases, the value first decreases at 10 phr and then increases for further loading. So SBR mix with 10 phr prophylactics loading shows the maximum pseudoplasticity (Table 4.2). At 160°C also, the same trend is observable while at 170°C, a regular drop in n' value can be observed with the temperatures studied.
Table 4.2. Flow behaviour index (n') values

<table>
<thead>
<tr>
<th>Mix</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120</td>
</tr>
<tr>
<td>Gum</td>
<td>0.2373</td>
</tr>
<tr>
<td>10 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>40 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr S2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr S4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;c&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr S2+10 black&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ND</td>
</tr>
<tr>
<td>20 phr S2+10 silica&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.2833</td>
</tr>
<tr>
<td>20 phr S2+10 marble powder&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.1724</td>
</tr>
</tbody>
</table>

<sup>a</sup> - mixing time 10 min,  <sup>b</sup> - mixing time 5 min,  <sup>c</sup> - mixing time 20 min

ND- Not determined

(b). Influence of prophylactics particle size

In the case of n' values of SBR mixes at 150 °C with different particle sizes (Table 4.2), the lowest value is obtained for 20 phr size 2 prophylactics filled system which agrees with the its low viscosity value only at highest shear rate 416.4 s⁻¹ (Figure 4.6). The highest n' value is observed for SBR mix with size 4 prophylactics system.

(c). Influence of mixing time

The effect of mixing time on n’ value can also be seen from Table 4.2. The n’ value for the SBR compound with 20 phr M prophylactics filler is lower for samples with mixing time 10 and 20 min compared to that with a mixing time of 5 min.

(d). Influence of temperature

In the case of gum SBR compound, n’ values decrease with increase of temperature from 120 to 170⁰C, except at 160⁰C. Similar reduction in n’ value with temperature is reported in the literature³³. Different mixes show highest n’ value at different temperatures. In the case of gum SBR and the mix with 40 phr S1, the highest n’ value is obtained at 160⁰C, in the case of the mix with 20 phr s1, at 170⁰C, and in the case
of the mix with 20 phr M, the highest value is at 150° C. Similarly SBR gum and the mix show the minimum value with 40 phr s1 at 170° C, 20 phr s1 at 150° C, and for the mix with 20 phr M, at 160° C. Generally it can be understood that the n’ value showed a decreasing trend with temperature except a few cases.

4.1.3. log ζ Vs. log γ plots and ‘m’ & ‘C’ values

It is interesting to check the application of certain mathematical relations in the present cases. The flow rate depends on the nature of the compound being processed and its viscosity, which is shear rate –shear stress dependent. The extrusion rate depends upon changes in viscosity, which may result from changes in shear rates during the extrusion process, and so the slope ‘m’ and ‘y’ intercept ‘C’ of the plots are critical rheological properties. The proposed relation is

\[ \log \zeta = \log \gamma^m + C \]  

(4.1)

A typical plot is given in Figure 4.9

Figure 4.9. Variation of log ζ verses log γ for SBR compounds with increasing prophylactics loading

[Antilog values of shear stress (y axis) are in Pa and that of shear rate (x axis) are in s⁻¹]
Values of ‘m’ and ‘C’ are given in Tables 4.3 and 4.4.

Table 4.3. Effect of composition of ‘m’ and ‘C’ values

<table>
<thead>
<tr>
<th>Mix</th>
<th>m</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>0.2285</td>
<td>6.0119</td>
</tr>
<tr>
<td>10 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.1927</td>
<td>6.0989</td>
</tr>
<tr>
<td>20 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.2038</td>
<td>6.0911</td>
</tr>
<tr>
<td>40 phr S1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.2082</td>
<td>6.0926</td>
</tr>
<tr>
<td>20 phr S2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.1912</td>
<td>6.1299</td>
</tr>
<tr>
<td>20 phr S4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.2211</td>
<td>6.0604</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.2166</td>
<td>6.0612</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.2405</td>
<td>5.9932</td>
</tr>
<tr>
<td>20 phr M&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.2231</td>
<td>6.0358</td>
</tr>
<tr>
<td>20 phr S2+10 black</td>
<td>0.2604</td>
<td>5.9664</td>
</tr>
<tr>
<td>20 phr S2+10 silica</td>
<td>0.2611</td>
<td>6.0317</td>
</tr>
<tr>
<td>20 phr S2+10 marble powder</td>
<td>0.2447</td>
<td>6.0027</td>
</tr>
</tbody>
</table>

<sup>a</sup> - mixing time 10 min, <sup>b</sup> - mixing time 5 min, <sup>c</sup> - mixing time 20 min

Table 4.4. Effect of temperature on ‘m’ and ‘C’ values

<table>
<thead>
<tr>
<th>Mix</th>
<th>120</th>
<th>150</th>
<th>160</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m</td>
<td>C</td>
<td>m</td>
<td>C</td>
</tr>
<tr>
<td>Gum</td>
<td>0.2384</td>
<td>6.0279</td>
<td>0.2285</td>
<td>6.0119</td>
</tr>
<tr>
<td>20 phr S1</td>
<td>ND</td>
<td>ND</td>
<td>0.2038</td>
<td>6.0911</td>
</tr>
<tr>
<td>40 phr S1</td>
<td>ND</td>
<td>ND</td>
<td>0.2082</td>
<td>6.0926</td>
</tr>
<tr>
<td>20 phr M</td>
<td>ND</td>
<td>ND</td>
<td>0.2166</td>
<td>6.0612</td>
</tr>
<tr>
<td>20 phr S2</td>
<td>ND</td>
<td>ND</td>
<td>0.1912</td>
<td>6.1299</td>
</tr>
<tr>
<td>20 phr S2+10 black</td>
<td>ND</td>
<td>ND</td>
<td>0.2604</td>
<td>5.9664</td>
</tr>
<tr>
<td>20 phr S2+10 silica</td>
<td>0.2799</td>
<td>6.0072</td>
<td>0.2611</td>
<td>6.0317</td>
</tr>
<tr>
<td>20 phr S2+10 marble powder</td>
<td>0.1723</td>
<td>6.2333</td>
<td>0.2447</td>
<td>6.0027</td>
</tr>
</tbody>
</table>

It can be seen that except in the case of the sample with 5 min mixing time, the presence of prophylactics in gum SBR mix decreases the ‘m’ values while ‘C’ values increase slightly. Similarly, as the particle size of the prophylactics increases from size 1 to 4 and M (at same loading of 20 phr), ‘m’ values increase (only one exception is the value of S2 which
is less) while the ‘C’ values decrease slightly. In the case of SBR with 20 phr mill sheeted form, as the mixing time increases from 5 to 10 min, ‘m’ value decreases considerably and for the sample with mixing time 20 min, it slightly increases compared to 10 min sample, but still it is much less than that of the sample mixed for 5 min. ‘C’ value first increases for 10 min sample and then decreases for 20 min sample. It can be suggested here that the interactive effect of SBR with the inclusion can be characterised by changes in ‘C’ while it is more related to particle size of the prophylactics filler.

Table 4.4 gives the effect of temperature on ‘m’ and ‘C’ values. In the case of gum SBR, as the temperature increases, ‘m’ value first shows a decrease at 150°C, an increase at 160°C and finally a drop at 170°C while ‘C’ values show a regular drop up to 160°C and finally a slight increase at 170°C. For SBR mix containing 20 phr S1 prophylactics, value of ‘m’ goes on increasing and that of ‘C’, decreasing with temperature. At a loading of 40 phr S1 prophylactics filler to SBR, the highest ‘m’ value is obtained at 160°C while ‘C’ value is lowest at that temperature. For SBR filled with 20 phr M case also, lowest ‘m’ value is at 160°C while lowest ‘C’ value at 150°C.

4.1.4. Theoretical modeling of viscosity

The variation in the melt viscosity of SBR with NR prophylactics loading at different shear rates is compared with different previously established mathematical models. These are Einstein, Mooney, Guth, Kerner, Sato-Furukawa, Eiler van Dyck, Bills, Brinkman and Narkis models. The terms used in this section are the following. \( \eta \) - viscosity, \( V_f \) - volume fraction of filler, S- crowding factor, \( \nu \) - Poisons ratio, suffixes c and m denote composite and gum matrix. The equations are given below.

1. Einstein equation

Einstein has proposed an equation for the viscosity of the composite assuming perfect bonding between the phases.

\[
\eta_c = \eta_m (1 + 2.5 V_f)
\]  

(4.2)

2. Mooney equation

This equation considers the interaction of strain fields around particles while it agrees with Einstein’s equation at low volume fraction of the filler, it can represent the data at higher volume fractions as well.
3. Guth equation

Guth\textsuperscript{36} modified Einstein equation by considering the particle interactions also.

\[ \eta_c = \eta_m \exp \left( \frac{2.5 \, V_f}{1 - S \, V_f} \right) \]  

(4.3)

4. Kerner equation

The equation derived by Kerner\textsuperscript{37} assumes spherical particles.

\[ \eta_c = \eta_m \left\{ 1 + \frac{V_f}{V_m} \left( \frac{15 (1 - v_m)}{8 - 10 v_m} \right) \right\} \]  

(4.5)

5. Sato-Furukawa equation

The weak adhesion between matrix and filler is best represented in the literature\textsuperscript{38} by Sato-Furukawa equation

\[ \eta_c = \eta_m \left[ 1 + \frac{y^2}{2(1-y)} \right] \left[ 1 - \frac{y^3 T}{3} \left( \frac{1+y-y^2}{1-y+y^2} \right) \right] - \left\{ \frac{y^2 T}{3(1-y)} \right\} \left[ \frac{1+y-y^2}{1-y+y^2} \right] \]  

(4.6)

where \( y \) is a filler concentration variable equal to \( V_f ^{1/3} \) and \( T \) is a constant characterising the filler-matrix adhesion. If the adhesion is perfect \( T=0 \), and if it is weak, \( T=1 \).

6. Eiler van Dyck equation\textsuperscript{39}

\[ \eta_c = \eta_m \left[ 1 + \frac{k \, V_f}{1 - S' \, V_f} \right] \]  

(4.7)

where \( k = 1.25 \) and \( S' = 1.20 \)

7. Bills equation\textsuperscript{40}

\[ \eta_c = \eta_m \exp \left( \frac{A \, V_f}{1 - B \, V_f} \right) \]  

(4.8)
where \( A = 2.5 \) and \( B = -6.4 \times 10^{-3} T + 2.51 \) where \( T \) is the test temperature.

8. **Brinkman equation**

\[
\eta_c = \eta_m (1 - V_f)^{5/2}
\]

(4.9)

9. **Narkis**

\[
\eta_c = \eta_m \left[ \frac{1}{K (1 - V_f^{1/3})} \right]
\]

(4.10)

where \( K \) is the stress concentration factor whose value ranges from 1.4 to 1.7.

**Figure 4.10** represents the comparison of experimental viscosity values with the theoretical values at a shear rate 1.249 s\(^{-1}\). It can be seen from the figure that at 10 phr prophylactics loading, the best agreement is shown by Eiler van Dyck equation and this agreement exits at all the loadings.

**Figure 4.10.** Experimental and theoretical plots for the melt viscosity of SBR compounds at a shear rate of 1.249 s\(^{-1}\).
When Brinkman equation shows negatively deviated values, all other equations give positively deviated values. Among the equations showing positive deviation, better agreement is shown by Sato-Furukawa and then by Einstein equation. The least agreement is shown by Guth equation while all other equations show intermediate values. The same trend is repeated at 20 phr loading of prophylactics also. At 40 phr loading, the only difference noted is that the values given by Guth and Mooney equation are very close. At higher shear rates also, the best agreement between experimental and theoretical values is obtained in the case of Eiler van Dyck model.

4.1.5. Extrudate distortion

Most of the extrudates from capillary rheometer showed visual evidence of surface imperfections. The extrudate appearance can be used to assess the quality of the flow behavior, rupture behavior and to find the shear rate at which flow instability commences. The extrudate distortion shown by gum SBR is the highest (Figure 4.11). In this case, the extrudates appeared like a twisted rope. The extrudate distortion at 120° C becomes high as the shear rate increases. This is clear from Figure 4.11 a-c. Also as the temperature increases, the extrudate distortion is found to be increasing (Figure 4.11 a, d-f). The extrudate distortion is visible in the prophylactics filled sample (10 phr S1) also but to a lesser extent (Figure 4.11 g). This means that the prophylactics particles suppress the distortion and thus they give more uniform extrudates and that the extrudate dimension is less sensitive to shear rate. As the loading of prophylactics increases (Figure 4.11 g-i), still, extrudate distortion is present but it is less predominant. With the increase in the size of prophylactics, no notable change in the extrudate distortion can be observed (Figure 4.11 h, j, k, l). In the case of SBR mix with 20phr M also, extrudate distortion is observable to some extent at 160 and 170° C (Figure 4.11 l, n, o). A low extrudate distortion was noted at the lowest shear rate and at lowest temperature of 150°C (Figure 4.11 l). It is also found that as the mixing time increases in the case of the SBR mix with 20 phr M, extrudate distortion decreases as can be seen from Figure 4.11 p, l, m. The highest extrudate distortion shown by gum SBR is because of its low viscosity compared to the prophylactics particles. The low extrudate distortion in the presence of
prophylactics filler means that there is reasonably good bonding between prophylactics filler particles and SBR.

Figure 4.11. Extrudates of gum and prophylactics filled SBR compounds

Turner and Bickley\(^4\) suggested that the low viscous phase (SBR) in the mix migrates to the surface through a roll mechanism, i.e., a radical flow in addition to longitudinal flow, which gives the extrudates a screw thread appearance. The reduced extrudate distortion also points out the decrease in the melt elasticity with the addition of
prophylactics filler. The presence of crosslinked particles decreases the deformation tendency of the SBR mix and fastens the recovery. The superior efficiency of sulphur crosslinked networks for this is reported in the literature\textsuperscript{33}. The less sensitivity of extrudate distortion to temperature shown by the prophylactics filled mix (40 phr S1) is important in the dimensional stability of extruded profiles because during extrusion neither shear rate/stress nor temperature is constant across the profile.

PART 2. INFLUENCE OF PARTICULATE FILLERS
The recipe used is the same as Table 4.1.

4.1.6. Viscosity variation

The influence of particulate fillers on the rheological properties of molten polymers is both of great scientific and industrial importance. Such fillers are added primarily to strengthen the product and to reduce the cost. Normally, particulate fillers increase the level of viscosity\textsuperscript{44,45} but the extent seems to vary from system to system and decrease with increasing shear rate\textsuperscript{44}. The variation of melt viscosity with shear stress and shear rate for gum SBR and SBR mix with 20 phr size 2 prophylactics filler with and without particulate fillers at 150\textdegree C is presented in Figure 4.12 (The antilog values of viscosity (y axis) are in Pa-s and that of shear stress (x axis) are in Pa). The melt viscosity is found to be decreasing with shear stress and shear rate for all the mixes.

At lower shear rate, an increase in the viscosity can be noted with the addition of prophylactics filler to SBR. The black and marble powder filled mixes exhibit the lower viscosity compared to other samples, and among them, marble powder filled mix presents slightly higher viscosity compared to carbon black. Silica filled samples give higher viscosities at most of the shear rates but at lower shear rates the values are comparable to that of other mixes without particulate fillers. However at the highest shear stress, the behavior becomes more normal, i.e., the SBR/prophylactics mix without particulate filler shows the lowest viscosity, the next higher value by marble powder, which is followed by comparable viscosity values by silica and black.
Figure 4.12. Variation of melt viscosity with shear stress for SBR samples filled with prophylactics and particulate fillers

Figure 4.12 reveals that at the highest shear rate, the silica filled samples show the highest viscosity values and that the drop in viscosity is fast at low and high shear rates. The slope of the plots is higher at both low and high shear rates while it is less at intermediate shear rates. It can be seen that the values tend to converge at a point at higher shear rate. The low viscosity of particulate filled samples compared to prophylactics alone filled samples at low shear rate is in agreement with the observation by Clarke. It is also noticed by Shaheen that addition of a little amount of small particles act as a lubricant to facilitate the rotation of larger particles, leading to a reduction in viscosity. However, at higher shear rates, the relative flow of different layers is checked to a great extent by the filler particles through the formation of adsorbed layers and so the viscosity rises for the particulate filled samples compared to prophylactics alone filled sample.

The observation of lowest viscosity shown by the SBR mix without particulate filler and the increase in viscosity with the addition of particulate fillers at the highest shear rate indicates that at highest shear rates, the particles in the SBR matrix are aligned in the
flow direction subject to the restriction for this imposed by the particulate fillers. Therefore, it is clear from these results that the ability of a filler to contribute to the viscosity depends very much also on the nature and components of the main matrix. The superior reinforcing nature of black in a single elastomer matrix and the comparable behavior shown by black and silica in the case of ENR / NR blends are important to mention here. The highest viscosity values shown by the silica filled mixes can be due to its equal distribution among the SBR and prophylactics phases. This can increase the interfacial thickness, reduce the interlayer slip, which in turn causes an increase in viscosity. This phenomenon shown by silica may also be due to its low density and high absorptive capacity, which causes similar effects of viscosity in filled polybutadiene samples.

Influence of temperature on melt viscosity

The influence of temperature on the viscosity of SBR filled with prophylactics filler in the presence of particulate fillers is presented in Figure 4.13-4.15.

![Figure 4.13. Variation of melt viscosity with shear stress for SBR samples filled with carbon black at different temperatures](image)
Figure 4.14. Variation of melt viscosity with shear stress for SBR samples filled with silica at different temperatures

In the case of black filled samples (Figure 4.13) at lower shear rate, the trend is a bit abnormal while at higher shear rate, the trend is as expected according to the already established viscosity-temperature relations. Figure 4.14 represents the silica filled systems. Upto a shear rate of 4.16 s⁻¹, it is found that the viscosity increases with increase in temperature. But from a shear rate of 12.49 s⁻¹ onwards the trend becomes somewhat similar to that expected from the influence of temperature. Similar inverse relation between viscosity and temperature is shown by marble powder filled samples also (Figure 4.15).
Figure 4.15. Variation of melt viscosity with shear stress for SBR samples filled with marble powder at different temperatures

4.1.7. Flow behavior index

The flow behavior index or $n'$ values of the SBR compounds are presented in Table 4.2. It can be seen that except at 160° C, the $n'$ values of mixes filled with particulate fillers are slightly higher than that of gum SBR mix and that with prophylactics filler alone. At 150° C, black filled sample presents highest $n'$ values among the set. But it fails to give a direct relation with the viscosity data at lower shear rates given in Figure 4.12. It can be seen that a direct correlation between $n'$ and viscosity exists at higher shear rates 124.9 s⁻¹ and 416.4 s⁻¹. At 160° C, the $n'$ of gum SBR mix is found to be decreasing with the addition of prophylactics as well as particulate fillers black and silica. In earlier publications the higher pseudoplasticity of black filled polymer samples was reported compared to other particulate fillers black and silica. But here in the presence of prophylactics, a reverse trend is observed. The black filled samples show the least pseudoplasticity among the fillers at 150° C. The higher $n'$ values is due to the enhanced difficulty for chains to orient
and show pseudoplasticity. This results from the less freedom available to the chains.

4.1.8. log $\tau$ Vs. log $\gamma$ plots and ‘m’ & ‘C’ values

Plots log $\tau$ verses log $\gamma$ of then samples (at 150$^0$ C) are given in Figure 4.16 [Antilog values of shear stress (y axis) are in Pa and that of shear rate (x axis) are in s$^{-1}$] and the values of ‘m’ and ‘C’ are given in Table 4.4.

![Figure 4.16. Variation of log $\tau$ verses log $\gamma$ for gum and filled SBR compounds](image)

A decrease in ‘m’ and an increase in ‘C’ are observed with the addition of prophylactics filler in gum SBR. Also, with the addition of particulate fillers, an increase in ‘m’ and a decrease in ‘C’ are again observed. But the variations observed are only marginal. The low ‘m’ and high ‘C’ values shown by silica compared to black at 160 and 170$^0$ C, may be due to its uniform distribution among the components of the system. It can be seen that the presence of silica which gives maximum reinforcement in viscosity data fails to give low ‘m’ value but it succeed to present a slightly higher ‘C’ value among the set proving its reinforcing nature.
Table 4.4 gives the effect of temperature on ‘m’ and ‘C’ values. Normally, as the temperature increases, the interface will become strong and so ‘m’ must show a decrease while ‘C’ must show an increase. But for the present case, abnormalities exist. As discussed earlier, even though silica fails to present its reinforcing behaviour in SBR / prophylactics mix at 150°C, it gives a low ‘m’ and a high ‘C’ value compared to black at 160 and 170°C. Among the particulate fillers, silica which gives maximum reinforcement in viscosity data fails to give low ‘m’ value but it presents a slightly higher ‘C’ value among the set. In the case of particulate filler containing samples, ‘m’ values show a regular drop with temperature while ‘C’ values show a regular increase and this is in agreement with the theory. Similar agreement can be seen for black also, but marble powder fails to give such an agreement.

4.1.9. Extrudate distortion

Generally particulate fillers and especially, titanium dioxide\(^5\) is reported to smoothen the surface of the extrudate and delay the extrudate distortion to higher extrusion rates. The influence of particulate fillers on the extrudate distortion can be seen from the Figures 4.17. As the discussions on samples without particulate fillers were already completed in section 4.1.5, discussions here are limited to particulate filled samples only. It is reported\(^2\) that addition of black can reduce the severity of distortion but cannot eliminate it. It can be seen from Figure 4.17 l-v that black is not effective to a satisfactory extent in reducing the extrudate distortion even at low shear rate and low temperature compared to silica. Compared to the behaviour in a single elastomer system, here, black presents an entirely different behaviour. Slightly less extrudate distortion is shown by black filled samples at higher temperatures (Figure 4.17 l, o, p). Silica reduces the extrudate distortion considerably (Figure 4.17 l-v). Even though the increase in elastic distortion with shear rate is still present, the same effect with increasing temperature was only marginal up to 160°C. At 170°C, extrudate distortion is again visible (Figure 4.17 q-v).
(a). SBR gum-4.164 s⁻¹- 120° C  (b). 41.64 s⁻¹  (c). 416.4 s⁻¹  (d). 4.164 s⁻¹-150°C  (e). 160° C  (f). 170° C  
(g). SBR+20 phr S2-4.164 s⁻¹- 150° C  (h). 41.64 s⁻¹  (i). 416.4 s⁻¹  (j). 4.164 s⁻¹-160°C  (k). 170° C  
(l). SBR+20 phr S2+10 phr black-4.164 s⁻¹- 150° C  (m). 41.64 s⁻¹  (n). 416.4 s⁻¹  (o). 4.164 s⁻¹-160°C  (p). 170° C  
(q). SBR+20 phr S2+10 phr silica-4.164 s⁻¹- 120° C  (r). 41.64 s⁻¹  (s). 416.4 s⁻¹  (t). 4.164 s⁻¹-150°C  (u). 160° C  (v). 170° C  
(w). SBR+20 phr S2+10 phr marble powder- 4.164 s⁻¹- 120° C  (x). 41.64 s⁻¹  (y). 416.4 s⁻¹  (z). 4.164 s⁻¹-150° C

Figure 4.17. Extrudates of S2 prophylactics and particulates filled SBR compounds

The presence of marble powder at lower temperature and lower shear rate presents a lower extrudate distortion, as can be seen from Figure 4.17 1-0. The less sensitivity of dependence of elastic distortion on temperature is because of the interpenetration effect of silica in SBR/prophylactics system owing to its uniform distribution among the components. Han⁵⁰ and others⁵¹-⁵³ found that the black surface area and structure are responsible for the considerable extrudate distortion in polymer matrices. Since such a considerable reduction in the extrudate distortion could not be observed here (compared to silica), it means that in SBR/prophylactics system, black is unable to show its identity. Still, some reduction in extrudate distortion noted is due to the decrease in melt elasticity with the addition of black.
4.2. REFERENCES

34. A. Einstein, “Investigation on Theory of Brownian Motion”, Dover, New York, 1956 (English translation)
Chapter 5