CHAPTER IV.A
RHEOLOGICAL PROPERTIES – I*

Processing of a composite material involves flow under shear and is determined by the rheological study of the composite. White and Tokita\textsuperscript{1-2} have established a correlation between rheology and processing. Crowson and Folkes\textsuperscript{3} studied the rheology of short glass fiber reinforced thermoplastics and concluded that the fibers in the composite oriented along the flow direction during convergent flow, and that fiber alignment took place only at high shear rates. Several other studies have reported the rheological characteristics of short fiber reinforced polymer melts.\textsuperscript{4-9} This section deals with the rheological characteristics of short polyester fiber - polyurethane elastomer composite with reference to the effect of shear rate, fiber concentration, temperature and the bonding agent on the shear viscosity.

The formulation of the mixes is given in the Table IV .A.1.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mix No.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Adiprene</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>PET fiber</td>
<td>-</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Base Recipe: Zinc stearate 0.5phr, Catur-4 0.35 phr MBTS 4phr and MBT 1 phr

*Results of this section has been published in Polym. Plast. Tech. Engg.36 (3) (1997) 399 - 409
The mixes were prepared using a Brabender Plasticorder and the details were given in Chapter 2.

Rheological studies were carried out using a Monsanto Processability Tester. The investigations were carried out in a shear rate range of 18 - 145 s\(^{-1}\) at different temperatures varying from 90 - 150 °C. A capillary of diameter 1.5 mm and L/D ratio of 20 was used for the study. Determination of fiber breakage after the Brabender mixing was given in Chapter 2.

4.A.1. FIBER BREAKAGE

![Fiber length distribution of mix B after mixing in a Brabender Plasticorder](image)

Figure 4.A.1. Fiber length distribution of mix B after mixing in a Brabender Plasticorder

The average length of fibers used for mixing was approximately 4 mm. Figure 4.A.1 shows the fiber length distribution of mix B after the Brabender mixing. It can be seen from the figure that during mixing the average fiber length is reduced and shows a broad distribution. The maximum is in the range of 1 - 3 mm indicating an extensive fiber breakage.
4.A.2. EFFECT OF SHEAR RATE

Figure 4.A.2. shows the effect of shear rate on the shear viscosity of mixes A - D at 90°C. Because of the instrument constraints the study was limited to a shear rate range of 18 - 145 s⁻¹. In all the cases the viscosity is found to decrease with increase in shear rate, indicating a pseudoplastic nature of the system. Similar patterns are observed at 100, 120 and 150 °C also (Figure 4.A.3 - 4.A.5.).

Figure 4.A.2. Variation of shear viscosity with shear rate of mixes A - D at 90°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)
Figure 4.A.3. Variation of shear viscosity with shear rate of mixes A - D at 100°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

Figure 4.A.4. Variation of shear viscosity with shear rate of mixes A - D at 120°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)
Figure 4.A.5. Variation of shear viscosity with shear rate of mixes A - D at 150°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

4.A.3. EFFECT OF SHEAR STRESS

A log-log plot of shear viscosity versus shear stress of mixes A - D at 120°C is given in Figure 4.A.6. The viscosity shows a linear reduction with shear stress. At 150°C the viscosity of the fiber filled samples registers a steeper reduction at a shear rate range of 18 - 36 s⁻¹ (Figure 4.A.7.). A relatively softer matrix at elevated temperature can facilitate orientation of fibers under shear deformation resulting in a lower shear viscosity.
Figure 4.A.6. Variation of shear viscosity with shear stress of mixes A - D at 120°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

Figure 4.A.7. Shear stress versus shear viscosity at 150°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)
4.A.4. EFFECT OF FIBER LOADING

In the shear rate range studied mix A exhibits the lowest viscosity. Progressive increase in the fiber content from 10 - 30 phr (mixes B - D) causes a rise in viscosity values at a given temperature (Figure 4.A.2). This effect is represented in Figure 4.A.8. as a plot of relative viscosity versus the volume fraction of fiber.

![Graph showing variation of relative viscosity with volume fraction of fiber](image)

Figure 4.A.8. Variation of relative viscosity with volume fraction of fiber at a shear rate of 72.3 s\(^{-1}\) (Series 1: 120°C, 2: 150°C)

The relative viscosity is calculated as the ratio of the viscosity of the fiber filled compound to that of the unfilled one. The relative viscosity values of Figure 4.A.8. correspond to a shear rate of 72.3 s\(^{-1}\) at 120°C and 150°C. The two nonlinear plots in Figure 4.A.8. can be represented by the following equations:
3.8 \(X^2 + 4.6X + 0.99\) \hspace{1cm} (4.A.1)

and

\[2 \times 3 X^2 + 1.04X + 1\] \hspace{1cm} (4.A.2)

at 120 and 150°C, respectively. \(X\) is the volume fraction of fibers. It is observed that the relative viscosity is higher than one at all fiber loadings.

The relative viscosity at 150°C is lower than that at 120°C up to a fiber volume fraction of 0.140, after which the trend is reversed. This indicates that for a given melt viscosity a high melt temperature requires higher fiber loading up to the cross over point after which the reverse holds good. That is, for a given volume fraction of fiber the relative viscosity is higher at higher melt temperature. This is because of the lower melt viscosity of the matrix at higher temperature. The existence of such a cross over point indicates that a critical fiber loading is required for a

![Figure 4.A.9. Variation of critical fiber loading with shear rate](image)

Figure 4.A.9. Variation of critical fiber loading with shear rate
better fiber - fiber interaction. At fiber loading lower than the critical value of the cross over point the fiber - fiber interaction is limited. When the fiber content is above the critical value the entanglement of the fibers occurs, leading to a more effective restraining of the matrix.

The critical fiber loading calculated from the plots of relative viscosity versus volume fraction of fiber at different shear rates is given in Figure 4.A.9. as a function of the corresponding shear rates. The critical fiber loading shows only a marginal increase at high shear rates.

4.A.5. ACTIVATION ENERGY

Activation energies of the composites calculated from the semi logarithmic Arrhenius plot of viscosity and temperature. In the Arrhenius equation, viscosity is related to absolute temperature by the following equation

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

(4.A.3)

where \( A \) is a constant characteristic of the polymer, \( E \) is the activation energy and \( R \) is the universal gas constant. From the slopes of the plots activation energies were calculated. Activation energy calculated at different shear rates are given in the Table IV.A.2.

In the shear rate and temperature range studied activation energy of the melt flow is not much affected by the presence of fibers, that is, the temperature sensitivity of the polyurethane elastomer is not much affected by the incorporation of fibers. Similarly the increase of shear rate also does not change the temperature sensitivity of the gum compound.
Table IV.A.2. Activation energies of the composites at different shear rates.

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Activation Energy, kcal.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shear rate s⁻¹</td>
</tr>
<tr>
<td></td>
<td>18.06</td>
</tr>
<tr>
<td>A</td>
<td>5.72</td>
</tr>
<tr>
<td>B</td>
<td>6.01</td>
</tr>
<tr>
<td>C</td>
<td>5.32</td>
</tr>
<tr>
<td>D</td>
<td>4.29</td>
</tr>
</tbody>
</table>

4.A.6. FLOW BEHAVIOUR INDEX

Figure 4.A.10. Flow behaviour indices of mixes at different temperatures (Series 1: 90°C, 2: 100°C, 3: 120°C, 4: 150°C)

Flow behaviour indices, n', of mixes A - D at different temperatures are shown in Figure 4.A.10. For mix A, the n' increases as the temperature increases from 90°C to 150°C.
This indicates that the matrix becomes more Newtonian as the temperature increases. Mixes B - D show not much change with the increase of temperature. Flow behaviour indices of the fiber filled mixes are less than that of the gum compound. This may be due to the lower flowability of the fiber filled samples.5,7

REFERENCES

CHAPTER IV.B
RHEOLOGICAL PROPERTIES – II*

The rheological behaviour of polymer melts provides the choice of processing conditions and influences the morphology and mechanical properties of the final product. The effect of interfacial bond on the rheological characteristics were studied by many workers. In this section rheological characteristics of the composites with different bonding agents are evaluated in detail.

The formulation of the mixes is given in the Table IV.B.1. The mixes were prepared in a Haake Rheomix and the details were given in Chapter 2. Rheological studies were carried out using Monsanto Processability tester. A capillary of diameter 1.5 mm and L/D = 30 was used. The measurements were carried out at different shear rates ranging from 61 s⁻¹ to 608 s⁻¹ and at a temperature range of 100-160 °C.

4.B.1 EFFECT OF SHEAR RATE AND SHEAR STRESS

Figure 4.B.1 represents plot of log (viscosity) versus log (shear rate) at 120 °C of the composites with and without bonding agents. It is evident from the figure that for all the mixes viscosity decreases with the increase of shear rate indicating a pseudoplastic nature. Similar results have been reported earlier. Over the whole shear rate range studied, the viscosity of the mix C1, containing bonding agent based on PPG and MDI shows a marginal decrease in viscosity than that of mix C, with no bonding agent.

**Table IV.B.1. Formulation of the mixes**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Mix No.</th>
<th>C</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adiprene</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>PET fiber</td>
<td></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Zinc stearate</td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Caytur-4</td>
<td></td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>MBTS</td>
<td></td>
<td>4</td>
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<td>4</td>
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</tr>
<tr>
<td>MBT</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPG</td>
<td></td>
<td>-</td>
<td>4.44</td>
<td>-</td>
<td>2.22</td>
</tr>
<tr>
<td>GL</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.99</td>
<td>0.07</td>
</tr>
<tr>
<td>MDI</td>
<td></td>
<td>-</td>
<td>0.56</td>
<td>4.01</td>
<td>0.56</td>
</tr>
</tbody>
</table>

MBTS = Dibenzothiazyldisulphide; MBT = 2-mercaptobenzothiazole; PPG=polypropyleneglycol ; GL=glycerol; MDI= 4,4'-diphenylmethanediisocyanate.

![Figure 4.B.1. Variation of apparent viscosity with shear rate of mixes C - C3 at 120°C (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)](image-url)
The viscosity values of mix C2 suggest a more restrained matrix indicating a better fiber-matrix interaction in the presence of glycerol based bonding agent. With this bonding agent, the resin forms a three dimensional network structure in the matrix and the flow becomes more restricted and the molecular alignment in the flow direction under shear becomes less probable resulting in higher viscosity values. The observed mechanical properties also suggest a better fiber-matrix interaction in the presence of glycerol based bonding agent (Chapter V). As expected, the mix C3 containing both PPG and GL shows viscosity values in between that of mix C1 and C2. The presence of PPG seems to compensate for any restriction to flow due to glycerol and hence the mix C3 shows the viscosity values almost close to that of mix C.

Figure 4.B.2. Variation of apparent viscosity with shear stress of mixes C - C3 at 120°C

A similar pattern of behaviour is observed in Figure 4.B.2 where log (viscosity) is plotted against log (shear stress), at 120°C. The difference between viscosity values of
different mixes seems to be more significant in this figure. This suggests that the log-log plot of viscosity and shear stress will be a better tool to study the effect of interfacial bonding agents on the flow properties.

4.B.2 EFFECT OF TEMPERATURE

In the shear rate range studied, viscosity is found to decrease with increasing temperature (Figure 4.B.3). A similar trend is also observed in the case of composites containing different bonding agents (Figure 4.B.4 - 4.B.6). However, the variation in viscosity with temperature at a given shear rate is found to be different for different mixes.

Figure 4.B.3. Effect of temperature on the variation of apparent viscosity with shear rate of mix C (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)
Figure 4.B.4. Effect of temperature on the variation of apparent viscosity with shear rate for mix C1 (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

Figure 4.B.5. Effect of temperature on the variation of apparent viscosity with shear rate of mix C2 (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)
Figure 4.B.6. Effect of temperature on the variation of apparent viscosity with shear rate of mix C3 (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

Figure 4.B.7. Variation of viscosity of mixes C-C3 with temperature at a shear rate of 61.3 s⁻¹ (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)
Figure 4.B.7 shows a plot of viscosity versus temperature at a shear rate of 61.3 s\(^{-1}\), for different mixes. It shows that beyond a temperature of 140°C, the viscosity of different composites falls very sharply. The fall is less drastic in case of mix C2 containing glycerol based bonding agent when compared to mix C1 and C3. Between temperature 120 °C and 140°C the reduction in viscosity is less significant.

4.B.3 ACTIVATION ENERGY

Activation energies of the composites C and C1 - C3 are calculated from the plots of log (apparent viscosity) versus 1/T (Figure 4.B.8). Table IV.B.2. gives the value of activation energies at three different shear rates.

![Graph showing variation of apparent viscosity with 1/T at a shear rate of 61.3 s\(^{-1}\)](image)

The more or less same values of activation energies of the composites indicate that the temperature sensitivity of the
composites remains unaffected with the rate of shear in the shear rate range studied. Similarly there is not much change in the activation energies of the composites containing different bonding agents. This again shows that the presence of bonding agents also does not alter the temperature sensitivity of the composite.

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Activation energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shear rate s⁻¹</td>
</tr>
<tr>
<td></td>
<td>61.3</td>
</tr>
<tr>
<td>C</td>
<td>15.39</td>
</tr>
<tr>
<td>C1</td>
<td>15.25</td>
</tr>
<tr>
<td>C2</td>
<td>17.43</td>
</tr>
<tr>
<td>C3</td>
<td>18.30</td>
</tr>
</tbody>
</table>

*Table IV.B. 2. Activation energies of the mixes C and C1 - C3*

4.B.4 FLOW BEHAVIOUR INDEX

![Flow behaviour index chart](image)

*Figure 4.B.9. Variation of flow behaviour indices of mixes C - C3 with temperature (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)*
Figure 4.B.9 shows the flow behaviour index, \( n' \), of the composites C and C1 - C3, with and without bonding agents at different temperatures. The magnitude of \( n' \) indicates the extent of non-Newtonian behaviour of the composite. It is clear from the figure that for all the composites \( n' \) increases with the increase of temperature showing that as the temperature increases the melt becomes more Newtonian in nature. Composites with PPG based bonding agent show more or less the same values of \( n' \) as that of the composite without bonding agent where as composites with GL and PPG - GL mixture based bonding agents show lower values of \( n' \). This indicate that the bonding agent formed from GL and PPG - GL with MDI increases the pseudoplasticity of the composite.

REFERENCES