tetramer radicals. Because the reactivity of tetramer radical would be lower than radical monomer [16], this tetramer radicals probably reacts first with the resin radicals to form initial Py/MEKF-R copolymer species. Typical chain growth mechanism takes place.

CONCLUSIONS

During the PPy formation on ITO electrode, which was followed by UV-Visible measurements, the maximum absorbance around 450 nm, attributable to the formation of polarons, disappeared in the presence of MEKF-R. This result supports the occurrence of a reaction between polarons and the radicals of MEKF-R. Even though the conductivity of the copolymer is lower than that of PPy, the switching property between oxidized and reduced forms of the copolymer films is not reduced. Insoluble products are probably due to crosslinking of the formed polymers by overoxidation. The formed smooth Py/MEKF-R copolymer films adhere to the surface of Pt electrode much better than PPy film produced under similar conditions. This property of the copolymer, beside reversible electrochemical behavior, might give some advantages during the application of conductive PPy. Furthermore, by changing the ratio of Py/MEKF-R, copolymers with conductivity in between PPy homopolymer and MEKF-R could be synthesized.

REFERENCES

importance in selection of polymer and its processing conditions [1].
Studies on the rheological behavior and the extrusion characteristics of polymer melts have been reported by White and Tokita [2] and
White [3-4]. Several studies on the rheological characteristics of short fiber reinforced polymer composites were reported [5-8]. Setua
studied the rheological behavior of short silk fiber filled elastomer composites and confirmed the pseudoplastic nature of the composites
[9]. Murty et al. studied the rheology of short jute fiber filled natural rubber composites [10] and found that the viscosity–shear rates
relationship was similar to that found in other fiber filled polymer melts. Crowson et al. reported the rheology of short glass fiber rein-
forced thermoplastics and concluded that the fibers orient along the flow direction in a convergent flow and at 90° to the flow direction in a divergent flow [11-12]. Many studies on the dependence of the die swell on the L/D (length to diameter) ratio of the capillary have been reported [13-17]. Kutty et al. reported the rheological characteristics of short aramid fiber reinforced thermoplastic polyurethane and found that the pseudoplastic behavior of the melt decreases with increased temperature [18]. Rheological behavior of short sisal fiber reinforced natural rubber composite was studied by Vargehse et al. [19]. Rheolo-
gical properties of short polyester fiber polyurethane elastomer com-
posite with and without bonding agent were reported by Suhara et al.
[20-21]. The present article reports the results of the studies on the rheology of short Nylon-6 fiber reinforced Styrene Butadiene rubber
containing an epoxy resin bonding agent. The fiber loading was varied
from 0 to 30 phr.

EXPERIMENTAL

Materials

Styrene butadiene rubber (synaprene 1502) was obtained from Syn-
thetics and Chemicals Ltd., Bareilly. Nylon-6 fiber with an outer dia-
meter of 20 μm was obtained from SRF Ltd., Madras. It was chopped
to approximately 6 mm in length. Zinc oxide (ZnO) was obtained from
M/s Meta Zinc Ltd., Bombay. Stearic acid was procured from Godrej
Soap (Pvt.) Ltd., Bombay, India. Epoxy resin (LAPOX, A31) and hard-
eener (LAPOX K30) were obtained from Cibatul Limited, Gujarat, India.

Processing

Formulation of mixes is given in Table 1. These mixes were prepared
as per ASTM D 3182 (1989) on a laboratory size two roll mixing mill.

<table>
<thead>
<tr>
<th>TABLE 1 Composition of Mixes (Parts by Weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredient</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>NBR</td>
</tr>
<tr>
<td>Nylon</td>
</tr>
<tr>
<td>Epoxy resin*</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>Stearic acid</td>
</tr>
</tbody>
</table>

*Epoxy resin formed by 1:0.5 equivalent combination of Epoxy resin and amine-based hardener, respectively.

The compounding temperature was kept below 90°C by passing water
through the mill rolls.

Rheological studies were carried out using a capillary rheometer
attached to a Shimadzu Universal testing machine model AG-I
50KN. A capillary of L/D 10 and an angle of entry 90° was used.
The measurements were carried out at various shear rates ranging
from 1.6 s⁻¹ to 831.2 s⁻¹. The temperature difference between different
zones was kept to a minimum. Small strips of composites were placed
inside the barrel and warmed for a minute. Then they were forced
down with a plunger attached to the moving crosshead. The height
of the melt in the barrel before extrusion was kept constant in all runs.
The experiments were carried out at six different shear rates obtained
by moving the cross head at pre-selected speeds (1 to 500 mm/min).
The force corresponding to different plunger speeds was recorded.
The true shear stress was calculated as

\[ \tau_w = \frac{PR}{2L} \]

where \( \tau_w \) is the shear stress of the wall, P is the pressure drop, L is the
length of the capillary, and R is the radius of the capillary.

Apparent shear rate, shear rate at the wall, and viscosity were
calculated using the following equations:

\[ \gamma_a = \frac{32Q}{\pi d^3} \]

\[ \gamma_w = \frac{(3n' + 1)}{4n'} \gamma_a \]

\[ \eta = \frac{\tau_w}{\gamma_w} \]
where: \( \gamma_a \) is the apparent shear rate (s\(^{-1}\)); \( Q \) is the volumetric flow rate (mm\(^3\) s\(^{-1}\)); \( d_c \) is the diameter of the capillary (mm); \( \gamma_w \) is the shear rate at wall (s\(^{-1}\)); \( n' \) is the flow behavior index, and \( \eta \) is the shear viscosity (Pa•s).

\( n' \) was calculated by linear regression from \( \log (\tau_w) \) and \( \log (\gamma_a) \). The extrudates emerging from the capillary were collected with the utmost care to avoid any further deformation and the diameters were measured after a relaxation period of 24 h. The die swell was calculated as the ratio of the diameter of the extrude to that of the capillary (\( d_e/d_c \)).

Relative Viscosity (\( \eta_r \)) was calculated by using the following equation:

\[
\eta_r = \frac{\eta_b}{\eta_0}
\]

where \( \eta_b \) is the viscosity of the mixes with bonding agent and \( \eta_0 \) is the viscosity of the mixes without bonding agent.

Relative Die swell ratio (\( D_r \)) was calculated by using the following equation:

\[
D_r = \frac{D_b}{D_0}
\]

where \( D_b \) is the die swell ratios of the mixes with bonding agent and \( D_0 \) is the die swell ratios of the mixes without bonding agent. Relative Activation energy was calculated by using the following equation:

\[
A_r = \frac{A_b}{A_0}
\]

where \( A_b \) is the activation energies of the mixes with bonding agent and \( A_0 \) is the activation energies of the mixes without bonding agent.

**RESULTS AND DISCUSSION**

**Effect of Shear Rate and Shear Stress on Shear Viscosity**

The variation of shear viscosity with shear rate of the mixes A–D at 80°C, 90°C, and 100°C is shown in Figures 1–3, respectively. In all the cases it is seen that the viscosity decreases almost linearly with shear rate in the shear rate range studied, indicating a pseudoplastic behavior of the composite with epoxy resin as bonding agent. The reduction in viscosity with increasing shear rate may arise from the molecular alignment during flow through the capillary. A similar pattern is also observed in the case of fiber filled mixes. This indicates
that the fibers, although restricting the free flow of the melt, also get aligned in the direction of flow. Similar results in the case of short polyester fiber polyurethane elastomer composite have been reported by Suhara et al. [20-21].

Figures 4-6 shows the variation of shear viscosity with shear stress for mixes A-D. Plots of shear viscosity versus shear stress also show similar patterns; but with marked difference at higher shear stresses. All the plots show significant drop in viscosity at shear stress beyond 1 MPa. As the fiber concentration increases, the point at which the sudden drop occurs shifts to higher shear stress values. For the gum compound it occurs at 1.13 MPa at 80°C whereas for the 30 phr fiber filled sample the corresponding values is 1.67 MPa at the same temperature. The sudden drop at higher shear stress values also indicates a probable plug flow at higher rates of flow. The point of inflection is plotted against the corresponding fiber loading in Figures 7a and 7b at 80 and 90°C, respectively. It is observed that there is a linear relationship between the onset of plug flow and the fiber content at both the temperatures. This is because the melt viscosity increases with increasing fiber content. With high melt viscosity the material slips at the wall and the stress is relieved. The extent of drop is reduced with increasing temperature. This may be because the chances of plug flow are lower when the sample becomes softer at elevated temperature. This is also evident from the fact that the gum compound, with relatively lower viscosity, shows no evidence of plug flow at 100°C.

**Effect of Fiber Content on Shear Viscosity**

The viscosity increases with increase in fiber concentration at all shear rates (Figures 1-3). The presence of fiber restricts the molecular mobility under shear, resulting in higher viscosity. The increase in viscosity on introduction of fiber is temperature dependent and is larger at higher temperatures. The rise in viscosity with fiber concentration decreases at higher shear rates. This means that the effect of fiber on shear viscosity is prominent at lower shear rates only. This is in agreement with earlier observations [7, 18]. All fiber-containing mixes have more or less equal viscosity at higher shear rates, which is higher than that of the gum compound.
FIGURE 5 Shear viscosity versus shear stress at 90°C.

FIGURE 6 Shear viscosity versus shear stress at 100°C.

FIGURE 7 a) Variation of shear stress at the point of inflection with fiber loading at 80°C. b) Variation of shear stress at the point of inflection with fiber loading at 90°C.
Effect of Temperature

The variation of shear viscosity with shear rate for mixes A & D at various temperatures and shear rates is shown in Figures 8 and 9, respectively. The effect of temperature on the viscosity is found to be shear rate dependant. In the case of gum compound, at lower shear rates, the log viscosity drops from 4.94 Pa·s to 4.76 Pa·s as the temperature is changed from 80°C to 100°C, whereas at higher shear rate all the viscosity values tend to merge to a common point. Similar trends are shown by the fiber filled sample. The changed temperature sensitivity of the composite is also reflected in the calculated activation energy values (Table 2).

Activation Energies

The activation energies of mixes A to D are given in Table 2. The activation energies were calculated from Arrhenius plots of viscosity and temperatures at different shear rates. The activation energy of flow is reduced by the introduction of 10 phr fiber but at further increase of fiber concentration to 30 phr the activation energy remains more or less constant. The higher temperature sensitivity of flow of the rubber matrix is reduced in the presence of fibers. Similar trends were reported in the case of short Kevlar fiber reinforced thermoplastic polyurethane by Kutty et al. [18]. The activation energy of gum compound decreases as shear rate increases, indicating that the temperature sensitivity of the gum is also shear dependent and the sensitivity is lesser at higher shear rates. But in the case of fiber filled mixes the activation energy does not vary much with shear rate.

Die Swell

The die swell ratio ($d_v/d_e$) of the gum and fiber filled mixes with bonding agent, at different temperatures and shear rates, is given in

<table>
<thead>
<tr>
<th>Mixes</th>
<th>1.6</th>
<th>16.6</th>
<th>83.1</th>
<th>166.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.06</td>
<td>8.81</td>
<td>6.08</td>
<td>4.61</td>
</tr>
<tr>
<td>B</td>
<td>5.89</td>
<td>5.64</td>
<td>4.29</td>
<td>4.94</td>
</tr>
<tr>
<td>C</td>
<td>4.80</td>
<td>5.45</td>
<td>5.34</td>
<td>5.03</td>
</tr>
<tr>
<td>D</td>
<td>4.20</td>
<td>6.20</td>
<td>4.56</td>
<td>3.03</td>
</tr>
</tbody>
</table>

FIGURE 8 Shear viscosity versus shear rate for Mix A.

FIGURE 9 Shear viscosity versus shear rate for Mix D.
A. Seema and S. K. N. Kutty

**TABLE 3** Die Swell Ratios of Mixes A–D at Different Temperatures

<table>
<thead>
<tr>
<th>Mix</th>
<th>Temperature (°C)</th>
<th>8.6</th>
<th>83.1</th>
<th>83.1</th>
<th>8.3.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>80</td>
<td>1.62</td>
<td>1.35</td>
<td>1.67</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1.41</td>
<td>1.54</td>
<td>1.58</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.19</td>
<td>1.98</td>
<td>1.84</td>
<td>1.98</td>
</tr>
<tr>
<td>B</td>
<td>80</td>
<td>1.11</td>
<td>1.24</td>
<td>1.47</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1.01</td>
<td>1.22</td>
<td>1.49</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.14</td>
<td>1.24</td>
<td>1.43</td>
<td>1.57</td>
</tr>
<tr>
<td>C</td>
<td>80</td>
<td>1.03</td>
<td>1.03</td>
<td>1.15</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.97</td>
<td>1.11</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.94</td>
<td>1.04</td>
<td>1.04</td>
<td>1.08</td>
</tr>
<tr>
<td>D</td>
<td>80</td>
<td>1.05</td>
<td>1.02</td>
<td>1.28</td>
<td>1.25</td>
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<tr>
<td></td>
<td>90</td>
<td>0.92</td>
<td>0.87</td>
<td>1.16</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.90</td>
<td>0.87</td>
<td>1.16</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Table 3. There is much variation in die swell of the gum compound with shear rates. Die swell decreases sharply by the addition of fiber. The reduction in the die swell in the presence of short fibers has been reported earlier [7, 10, 18]. The reduction in die swell with fiber loading may be due to the irreversible orientation of the fibers in the matrix. In the case of fiber filled mixes the die swell remains almost constant with shear rates and temperatures.

**Effect of Bonding Agent**

The effect of bonding agent has been quantified in terms of relative viscosity, defined as the ratio of the viscosity of the mixes with bonding agent to the viscosity of the mixes without bonding agent. Table 4 gives the relative viscosity of mixes at different shear rates and temperatures. The relative viscosity increases with shear rate for fiber containing mixes at all temperatures. In the case of gum compound the relative viscosity increases as shear rate increases up to 83.1 s⁻¹. Afterward it remains more or less constant with increase in shear rates. In general, the relative viscosity increases as fiber concentration increases, the effect being more pronounced at higher temperature. This is due to better fiber matrix adhesion in the presence of bonding agent, forming more restrained matrix. At higher temperature the relative viscosity is less than one for gum compound. This may due to the plasticizing action of the resin in the gum compound.

**Figure 10** Relative activation energy versus shear rate.
A. Seema and S. K. N. Kutty

TABLE 5 Relative Die Swell Ratios at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mix</th>
<th>1.6</th>
<th>16.6</th>
<th>83.1</th>
<th>166.2</th>
<th>332.5</th>
<th>831.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>A</td>
<td>1.20</td>
<td>1.11</td>
<td>1.37</td>
<td>1.37</td>
<td>1.08</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.08</td>
<td>1.20</td>
<td>1.43</td>
<td>1.37</td>
<td>1.31</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.06</td>
<td>1.06</td>
<td>1.08</td>
<td>1.30</td>
<td>1.18</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>1.01</td>
<td>1.06</td>
<td>1.26</td>
<td>1.40</td>
<td>1.35</td>
<td>1.36</td>
</tr>
<tr>
<td>90</td>
<td>A</td>
<td>1.13</td>
<td>1.23</td>
<td>1.26</td>
<td>1.19</td>
<td>1.24</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.07</td>
<td>1.28</td>
<td>1.47</td>
<td>1.37</td>
<td>1.50</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.05</td>
<td>1.21</td>
<td>1.30</td>
<td>1.30</td>
<td>1.19</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>1.11</td>
<td>1.11</td>
<td>1.22</td>
<td>1.10</td>
<td>1.11</td>
<td>1.18</td>
</tr>
</tbody>
</table>

agent. A decreases more or less constant with shear rate for gum and lower fiber loading (10 phr). But A increases sharply with shear rate at higher fiber loading. At higher fiber loading there is more fiber-matrix interfacial interaction, which is strengthened in the presence of bonding agent.

The relative die swell ($D_r$) is greater than one for all the mixes at all shear rates and temperatures (Table 5). The higher die swell in the presence of bonding agent is due to more elastic deformation occurring during the flow. $D_r$ remains more or less constant with respect to shear rate and temperature for all the mixes.

CONCLUSIONS

Short nylon fiber reinforced styrene butadiene rubber composites with epoxy-based bonding agent exhibit pseudoplasticity that decreases with temperature. The shear viscosity is increased in the presence of fibers and the effect is pronounced at lower shear rates. The temperature sensitivity of the gum compound is reduced on introduction of fibers. The temperature sensitivity of the melts is also shear dependent and is lower at higher shear rates. Die swell is reduced in the presence of fibers. Relative viscosity increases with shear rate for composites at all temperatures. Temperature sensitivity of the mixes increases in the presence of bonding agent. Die swell is increased in the presence of bonding resin at all shear rates and temperatures.

REFERENCES