Chapter 3

MECHANICAL AND RHEOLOGICAL EVALUATION OF HDPE/LLDPE BLENDS
Polyethylene blends have become commercially important for optimising the mechanical properties and processability of individual members. Linear low density polyethylene (LLDPE) has better mechanical properties than LDPE. It has a higher tensile strength, elongation at break and also has higher resistance to puncture and tearing. One of the drawbacks of LLDPE is that it has poorer fluidity in the molten state than LDPE. The viscosity of molten LLDPE is about 50% higher than molten LDPE with the same MFI value. As a consequence of the greater viscosity of LLDPE in the molten state it is necessary to carry out processing of the polymer at a higher temperature, using extruder with a modified design. However, the processing problem of LLDPE can be minimised by blending with LDPE or HDPE.

Hence blends of LDPE and LLDPE are now regarded as excellent materials for film manufacture because they combine the processability of LDPE and the good mechanical and environmental cracking resistance of LLDPE. While many studies have been undertaken on LDPE/LLDPE and HDPE/LDPE blends, only very few studies are reported on HDPE/LLDPE blends. However, it is reported that a blend of HDPE and LLDPE exhibited a crystallisation exotherm of a
single peak which indicates that it is a compatible system.  

1. EVALUATION OF MECHANICAL PROPERTIES OF BLENDS OF HDPE AND LLDPE

Experimental

HDPE was blended with two selected grades of LLDPE such that one of them had a higher melt viscosity than HDPE (LLDPE 1) while the other had a lower melt viscosity (LLDPE 2). The polymer blends were prepared in the weight ratios 80/20, 60/40, 40/60 and 20/80. The appropriate constituents in the form of pellets were accurately weighed and then tumbled to achieve a good mix. These blends were then extruded in a laboratory extruder having a screw length to diameter (L/D) of 20:1 attached to a Brabender plasticorder at a die temperature of 220°C and pelletised. This process was repeated again for better homogeneity.

Sheets of 120x120x3 mm size were prepared at 200°C by compression moulding. Test specimens for tensile tests were cut from the moulded sheets with dimensions according to the standard specifications.

Tensile stress-strain data were obtained at 25°C and 50% relative humidity as per the ASTM standard D-638.
Dumbbell specimens (ASTM type IV) were tested in the Zwick UTM at a constant crosshead speed of 50 mm/min.

Results and Discussion

The tensile stress-strain behaviour of the HDPE/LLDPE 1 blends is shown in Fig.3.1. LLDPE has a lower yield stress than HDPE, but a much higher elongation at break. The very high elongation at break of LLDPE 1 is due to its stable necking behaviour. In the case of LLDPE 1, an increase in the neck occurs as a result of the transfer of material from the wider part of the specimen, while in the case of HDPE it occurs by deformation of the already transformed material. The necking behaviour of HDPE and LLDPE 1 is schematically shown in Fig.3.2. The tensile properties of the blends vary smoothly between those of the parent polymers. The obvious effects of adding LLDPE to the blends are to lower the yield stress and increase the elongation at break. The strain hardening during plastic flow is similar for both the polymers and the blends.

Fig.3.3 shows the stress-strain curves of HDPE/LLDPE 2 blends. LLDPE 2 has a lower yield stress and elongation at break than HDPE. Obviously, the low
FIG. 3.1  STRESS-STRAIN BEHAVIOUR OF HDPE/LDPE 1 BLENDS.
FIG. 3.2 SCHEMATIC DIAGRAM OF THE NECKING BEHAVIOUR OF HDPE AND LLDPE 1.
FIG. 3.3 STRESS-STRAIN BEHAVIOUR OF HDPE/LLDPE 2 BLENDS.
molecular weight sample cannot support a stable neck. However, in this case also the properties of the blends vary smoothly between those of the parent polymers, HDPE and LLDPE 2.

The tensile behaviour of the HDPE/LLDPE 1 and HDPE/LLDPE 2 suggests that the blends exhibit sufficient compatibility between HDPE and LLDPE in the solid phase, irrespective of the different grades chosen. The ability to co-crystallise may be a strong driving force for the miscibility of these blends.\(^5\)

2. EVALUATION OF THE RHEOLOGICAL PROPERTIES OF HDPE/LLDPE BLENDS USING CAPILLARY RHEOMETER

HDPE/LLDPE blends were prepared in the weight ratios 80/20, 60/40, 40/60 and 20/80 using Brabender plasticorder. For evaluating the rheological characteristics of the blends, a Goettfert capillary viscometer model 1500 with capillary dies of 1 mm diameter and lengths of 10, 20 and 30 mm were used. These three different capillaries were used to evaluate the Bagley end corrections. The Newtonian shear rates used in this study varied from about 20 s\(^{-1}\) to 3500 s\(^{-1}\) and the temperatures employed were 160, 170 and 180°C.
Figs. 3.4 and 3.5 show the variation of apparent viscosity with apparent shear rate of HDPE/LLDPE 1 and HDPE/LLDPE 2 blends. These flow curves are identical indicating their strong non-Newtonian behaviour. The flow curves converge at the high shear rate area, indicating improved compatibility. All the flow curves could be approximated by straight lines and hence described the Ostwald-de Waale power law relation.

Figs. 3.6 and 3.7 show curves of apparent shear viscosity versus composition, obtained by cross plotting the flow curves at a particular shear rate. Also plotted in the figures are viscosities of the blends predicted from viscosities of parent polymers, calculated from simple additivity rules. Conformity to these simple mixing rules is considered to result from miscibility in the melt. In both cases, the experimental values are very close to the predicted values with only minor positive deviation, which have also been shown to imply miscibility. These figures thus suggest that HDPE/LLDPE blends are also compatible in the melt. This is obviously due to the similarities in the structure of HDPE and LLDPE, both possessing regular short branches.
FIG. 3.4 VISCOSITY Vs. SHEAR RATE CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.
FIG. 3.5 VISCOSITY Vs. SHEAR RATE CURVES OF HDPE/LLDPE 2
BLENDs AT 160°C.
FIG. 3.6 VARIATION OF VISCOSITY OF HDPE/LLDPE BLENDS WITH COMPOSITION (SHEAR RATE 57.6 S⁻¹, TEMPERATURE 160°C.).
FIG. 3.7 VARIATION OF VISCOSITY OF HDPE/LLDPE 2 BLENDS WITH COMPOSITION (SHEAR RATE 57.6 S$^{-1}$, TEMPERATURE 160°C)
The flow curves of the blends are replotted in Figs. 3.8 and 3.9 and the power law exponents of the blends calculated from the curves are shown in Table 3.1. It can be observed that LLDPE 1 is more non-Newtonian than HDPE while LLDPE 2 is less non-Newtonian than HDPE. Since structure of HDPE and LLDPE have close similarities, the most important factor contributing to the non-Newtonian behaviour may be the average molecular weight of the polymers. The usual behaviour of the polymers is to become more non-Newtonian with increase in the molecular weight. The power law exponent for the blends also varies smoothly between those of the parent polymers indicating compatibility of the polymers in the melt.

The slope of the log $\eta$ vs. $1/T$ plot is proportional to an apparent energy of activation for viscous flow. Figs. 3.10 and 3.11 are such plots of HDPE/LLDPE 1 and HDPE/LLDPE 2 blends. The activation energies calculated for the various blends are shown in Table 3.1.

The activation energy for flow for low viscosity material is generally smaller than that for high viscosity system. But the behaviour of these blends displays a very interesting phenomenon. LLDPE 1 having a higher viscosity
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1.69

5.6

5.2

4.8

4.4

LOG SHEAR STRESS, Pa

LOG SHEAR RATE, \( \frac{1}{s} \)

\[ \begin{align*}
\Delta & 100 \text{ LLDPE} \\
\bigcirc & 80/20 \text{ LLD/HD} \\
\blacktriangle & 60/40 \text{ LLD/HD} \\
\bigtriangleup & 40/60 \text{ LLD/HD} \\
\blacklozenge & 20/80 \text{ LLD/HD} \\
\bigcirc & 100 \text{ HDPE}
\end{align*} \]

FIG. 3.8 FLOW CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.
FIG.3.9 FLOW CURVES OF HDPE/LLDPE 2 BLENDS AT 160°C.
FIG. 3.10 VISCOSITY VS. 1/T CURVES OF HDPE/LLDPE 1 BLENDS (SHEAR RATE 115.2 S⁻¹).
FIG.3.11 VISCOSITY Vs. 1/T CURVES OF HDPE/LLDPE 2 BLENDS (SHEAR RATE 115.2 S⁻¹).
### Table 3.1 Dependence of non-Newtonian behaviour and activation energy on blend composition

<table>
<thead>
<tr>
<th>LLDPE (wt. %)</th>
<th>Power law exponent (n)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE/LLDPE 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.65</td>
<td>14.5</td>
</tr>
<tr>
<td>20</td>
<td>0.60</td>
<td>12.5</td>
</tr>
<tr>
<td>40</td>
<td>0.54</td>
<td>10.7</td>
</tr>
<tr>
<td>60</td>
<td>0.48</td>
<td>10.4</td>
</tr>
<tr>
<td>80</td>
<td>0.42</td>
<td>9.7</td>
</tr>
<tr>
<td>100</td>
<td>0.36</td>
<td>8.6</td>
</tr>
<tr>
<td>HDPE/LLDPE 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.65</td>
<td>14.5</td>
</tr>
<tr>
<td>20</td>
<td>0.60</td>
<td>15.1</td>
</tr>
<tr>
<td>40</td>
<td>0.67</td>
<td>16.2</td>
</tr>
<tr>
<td>60</td>
<td>0.68</td>
<td>18.4</td>
</tr>
<tr>
<td>80</td>
<td>0.69</td>
<td>21.0</td>
</tr>
<tr>
<td>100</td>
<td>0.70</td>
<td>22.0</td>
</tr>
</tbody>
</table>
than HDPE, shows a slightly lower activation energy than HDPE and LLDPE 2, which has a much lower viscosity than HDPE and LLDPE 1 shows a higher activation energy. This may imply that LLDPE does possess a certain amount of crystallinity in the melt. The degree of crystallinity may be higher for the lower molecular weight LLDPE due to its increased mobility and ability to pack into ordered regions. Such crystallisation effects have been observed for polypropylene melts.\(^9\)

**Bagley Correction Factor (\(P_c\))**

Bagley correction factor, \(P_c\) for HDPE/LLDPE 1 blends was evaluated from the flow data recorded with three different dies of L/D ratio 10, 20 and 30. Bagley plots, \(\Delta P\) as a function of L/D for HDPE/LLDPE blends at various composition are quite linear (Fig.3.12). This linearity of Bagley plot confirms the absence of slippage at the capillary wall and at the interface boundaries where the slippage is believed\(^10\) to cause curvature in the Bagley plot.

The true shear stress at the wall, \(\tau_w\) was calculated by applying Bagley correction factor. Variation of Bagley correction factor as a function of blend composi-
FIG. 3.12 VARIATION OF PRESSURE DROP, $\Delta P$, WITH L/D RATIO OF THE CAPILLARY FOR HDPE/LLDPE 1 BLENDS (SHEAR RATE 115.2 S$^{-1}$, TEMPERATURE 160 °C).
Table 3.2 Variation of Bagley correction factor with blend composition at various shear rates.

<table>
<thead>
<tr>
<th>Shear rate $S^{-1}$</th>
<th>Blend composition wt % of LLDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 20 40 60 80 100</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4 4.5 5 5.5 5.7 6</td>
</tr>
<tr>
<td>115</td>
<td>4 7.5 8.1 8.7 9.2 10</td>
</tr>
<tr>
<td>575</td>
<td>8 8.9 10.2 11.3 13 14</td>
</tr>
<tr>
<td>1730</td>
<td>9 10 12.1 14.3 16.5 18</td>
</tr>
<tr>
<td>2880</td>
<td>12 14.3 16.8 18.3 20.6 22</td>
</tr>
<tr>
<td>3450</td>
<td>13 15.5 18.6 21.3 23.8 25</td>
</tr>
</tbody>
</table>
tion at various shear rates is shown in Table 3.2. Similarly the Rabinowitsch correction was applied using values of n determined from flow curves, to obtain true shear rate $\dot{\gamma}_w$.

Flow curves in terms of corrected values of shear stress and shear rate for HDPE, LLDPE and HDPE/LLDPE blends at various compositions are shown in Fig.3.13. Flow curves of the blends are in between the flow curves of the pure HDPE and LLDPE.

The power law exponent n obtained from the corrected flow curves (Fig.3.13) are given in Table 3.3.

<table>
<thead>
<tr>
<th>LLDPE (wt %)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power law exponent, n</td>
<td>0.61</td>
<td>0.57</td>
<td>0.50</td>
<td>0.44</td>
<td>0.39</td>
<td>0.28</td>
</tr>
</tbody>
</table>
FIG. 3.13 CORRECTED FLOW CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.
Melt Elasticity

Elasticity of the melt results in the expansion of the polymer on its exit from the die. Variation of extrudate die swell with blend composition at various shear rates is shown in Fig.3.14.

The recoverable shear strain calculated from the die swell values is shown in Fig.3.15. Recoverable shear strain increases with increasing shear rates as expected. It also increases with LLDPE content, obviously due to higher elastic nature of LLDPE. The reduction in melt elasticity of LLDPE with addition of HDPE may be advantageously used in processing.11-13

Fig.3.16 shows the apparent shear modulus versus blend composition curves of HDPE/LLDPE blends at various shear rates. The shear modulus decreases with increasing shear rate as expected. It increases and goes to a maximum and thereafter decreases with increasing LLDPE content.

3. RHEOLOGICAL EVALUATION OF BLENDS OF HDPE AND LLDPE USING A TORQUE RHEOMETER

The polymer blends were prepared by melt mixing in a Brabender plasticorder model PL 3S equipped with roller
FIG. 3.14 VARIATION OF EXTRUDATE DIE SWELL WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE BLENDS AT 170°C.
FIG. 3.15 VARIATION OF RECOVERABLE SHEAR STRAIN WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE 1 BLENDS AT 170°C.
FIG. 3.16 VARIATION OF SHEAR MODULUS WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE 1 BLENDS AT 170°C.
mixing heads and a rotor speed of 30 rpm and temperature of 150°C. Rheological measurements in shear flow were also carried out for each blend and pure polymers using the same plasticorder.

Fig. 3.17 shows the equilibrium torque values as a function of blend composition for various rpm of the rotors. The torque values are proportional to the viscosity of the system. The torque increases with increase in LLDPE 1 content and increases with rpm (higher shear rates). The viscosity of the blends are between those of the pure polymers.

Fig. 3.18 shows the variation of torque with blend composition at various temperatures and at a fixed shear rate (rpm). In each case the viscosity decreases with increase in temperature as expected.

The power law relationship between the rotor torque (M) and rotor speed (S) resembles the power law relationship between shear stress and shear rate and hence the slope of the curve log M vs. log S gives the power law index n.
FIG. 3.17 VARIATION OF EQUILIBRIUM TORQUE VALUES WITH BLEND COMPOSITION AT VARIOUS RPM AT 170°C.
FIG. 3.18 VARIATION OF TORQUE WITH BLEND COMPOSITION AT VARIOUS TEMPERATURES (70 RPM).
Fig. 3.19 shows the log M versus log S plot for various composition of the blend. The parallel straight lines in this figure indicate that the power law indices for the parent polymers and their blends are more or less the same.

Fig. 3.20 shows the log torque versus reciprocal of absolute temperature (1/T) for the HDPE/LLDPE 1 blends. The slopes of the linear plots is proportional to the apparent energy of activation, which confirms the Arrhenius type behaviour. This confirms the earlier observation that LLDPE rich blends requires higher energy for processing than HDPE rich blends.

The energy required to plasticize the material was calculated from the torque-time curve at a particular temperature for a specified period of time. The values calculated for the blends and pure polymers at 150°C for 15 minutes are shown in Table 3.4.
FIG. 3.19 VARIATION OF LOG TORQUE WITH LOG RPM FOR HDPE/LLDPE 1 BLENDS.
FIG. 2.20 VARIATION OF LOG TORQUE WITH TEMPERATURE FOR HDPE/LLDPE 1 BLENDS.
Table 3.4: Variation of energy required for plasticization with blend composition

<table>
<thead>
<tr>
<th>Property</th>
<th>Blend composition (wt % of LLDPE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Energy required for plasticization</td>
<td>64</td>
</tr>
<tr>
<td>(kJ)</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

1. HDPE and LLDPE are sufficiently miscible in the solid phase as well as in the melt to take advantage of the attractive properties of both.

2. If the LLDPE used is of sufficiently higher molecular weight to support a stable necking behaviour, it enhances the toughness of HDPE with only slight decrease in yield stress.

3. If the LLDPE added is of low molecular weight, it improves the miscibility of the polymers in the melt. However, the mechanical properties are inferior.

4. Irrespective of the viscosity of LLDPE, it shows a higher activation energy than HDPE. This suggests that under the influence of high stress LLDPE melts may crystallise to a low degree, resulting in enhanced resistance to flow.
REFERENCES


9. D.E. Hanson, F.N. Cogswell, Polymer Rheology and Plastics Processing, Plastics and Rubber Institute, 1975 p. 244.


