Rheological Properties of Blends of Recycled HDPE and Virgin Polyolefins

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Received: 8th August 2001, Accepted: 20th September, 2001

SUMMARY

This paper investigates the rheological properties for blends of recycled high density polyethylene (HDPE) and virgin polyolefins. It is found that there is an empirical relationship that could relate the Melt Flow Index (MFI) of the virgin component to shear viscosity ratio of the blend across a broad spectrum of MFI values for a variety of polyolefin systems.

INTRODUCTION

This paper presents research outcomes which have been achieved as part of a larger investigation into the behaviour of blends of recycled high density polyethylene with virgin polyolefins. The virgin polyolefins used in these blends include HDPE, linear low density polyethylene (LLDPE), low density polyethylene (LDPE), and polypropylene (PP). The research has been carried out in conjunction with Visy Plastics, a large recycling company based in Australia that principally deals with the recycling of plastic bottles, including HDPE milk bottles. The recycling of these HDPE milk bottles produces the HDPE recyclate that is used in this research.

This particular recycled HDPE is ideal for blow moulding applications, but it is less appropriate for use in injection moulding and some extrusion applications. In order to allow more extensive use of the recycled HDPE, its properties must be modified and improved. This could be done by blending with various virgin polyolefins. For this to succeed, it is important to be able to predict how the properties will vary in the blend.

The research work presented in this paper is aimed at attempting to derive a relationship which could predict the rheological behaviour of a series of polyolefin blends. The research investigation consists of determining Melt Flow Index (MFI) and shear viscosity ratio for a series of polyolefin blends involving recycled HDPE and virgin polyolefins, including HDPE, LLDPE, LDPE and PP.

In previous work by other researchers, conflicting reports on the viscosity of blends of virgin HDPE with virgin HDPE have been found. For instance, blends of two HDPE’s of identical density but with molecular weights differing by a factor of 10 were found to be only partially miscible(1), but other virgin HDPE/HDPE systems have been found to be miscible and that constant shear stress viscosity vs composition follows the log-additivity rule(2,3).

Work by Cho et al(4) on HDPE/LDPE virgin blends shows a log linear relationship between viscosity and shear rate. However, HDPE/LDPE blends of different molecular weights of the components were studied using a capillary rheometer(2), and in most cases, viscosity
plotted against composition showed a positive deviation from additivity. Kammer and Socher\(^5\) also found positive deviations from linearity for viscosity plotted against composition.

Cho et al.\(^4\) also did some work on virgin LLDPE/HDPE systems, and found that the difference between the viscosities of LLDPE and HDPE at the low shear rate is larger than at the high shear rate. The melt viscosities of the LLDPE/HDPE blend do not vary much in the range of shear rates between 10\(^0\) and 10\(^2\) rad/s.\(^4\). The complex melt viscosity for this blend also follows the log additive rule at a given shear rate.\(^4\). It was found that the blend is miscible, especially at high shear rates.

Fujiyama & Kawasaki\(^6\) did work on the rheological properties of HDPE/PP blends and found that MFIs display positive deviation from logarithmic additivity and hence viscosities displayed negative deviations from logarithmic additivity. Their work showed that the flow curves of the blends were located between those of the components and gradually changes from the character of PP to that of HDPE with increasing HDPE content. In the case where the MFI of PP is higher than that of the HDPE, the slope of the flow curve scarcely depends on the composition, and the flow curve shifts in parallel with increasing HDPE content. In the case where the MFI of PP is nearly equal or lower than that of the HDPE, the slope of the flow curve decreases with increasing HDPE content. According to the authors, this means that the non-Newtonian behaviour of the HDPE is weaker than that of PP when compared at the same viscosity level.

Rheological properties of virgin PE/PP systems have also been studied by Noel and Carley\(^7\). They studied the two homopolymers and three blends at 210°C. They found that the two homopolymers had largely linear behaviour, but also found that the blend of 10%PE in PP had a nominal shear stress that was less than that of either homopolymer.

The existence of a relationship between MFI and zero shear viscosity \(\eta_0\) was first indicated by Boenig\(^8\), who showed that for PE the following relationship held:

\[
\log \text{MFI} = \text{const} - \log \eta_0
\]

Alternatively, the relationship between MFI and inherent viscosity was derived by Busse\(^9\), and from this he derived the inverse correlation between MFI and zero-shear viscosity.

### METHODOLOGY

In this investigation, the recycled HDPE used, called H1 recylcate, was supplied by Visy Plastics Pty Ltd, a dedicated recycling company. This H1 is obtained mostly from recycled milk bottles. The virgin materials used were obtained from Quenos, a company which makes polyolefin resins, and included the following types:

- injection moulding grade HDPE (IM-HDPE)
- film blowing grade HDPE (FB-HDPE)
- injection molding grade LLDPE (IM-LLDPE)
- film blowing grade LLDPE (FB-LLDPE)
- injection moulding grade LDPE (IM-LDPE)
- film blowing grade LDPE (FB-LDPE)
- injection moulding grade IM-PP (IM-PP)
- extrusion grade E-PP (E-PP)

Polymer blending was performed using a single screw Axxon Pacific BX-12 extrusion blender. Rheological testing was performed at Moldflow Pty Ltd. Using a customised capillary rheometer under shear rates that ranged between 9.6-9600s\(^{-1}\), and temperatures in between 160°C and 260°C. MFI was tested on a Ceast Resil MFI tester at 5kg/190°C conditions.

### RESULTS AND DISCUSSION

The viscosity ratio was calculated by dividing the shear viscosity of the recycled HDPE material by the shear viscosity of the blend. At zero volume fraction virgin polyolefin, the viscosity ratio will be equal to unity.

All plots of viscosity ratio Vs composition can be described using standard linear relationships such as the one in equation (1).

\[
\frac{\eta}{\eta_0} = 1 + X\phi
\]

where \(\eta\) is the viscosity of the recycled HDPE and \(\eta_0\) is the viscosity of the blend, while \(\phi\) is the volume fraction of the virgin polyolefin material. The constant X is the gradient of the viscosity ratio plot.

Tables 1 & 2 display the gradient of the viscosity graphs for each of the four shear rates and for different blend systems, averaged across temperature, with a standard deviation.
Next, the viscosity ratio gradient $X$ that describes these viscosity ratio data were each plotted as a function of shear rate for each of the eight blend systems (Figures 1-4).

In these graphs, shear rate was plotted logarithmically. For all eight blend systems, the viscosity ratio gradient $X$ shows an excellent logarithmic fit with shear rate, except for Figure 2, which is linear only within experimental limits.

According to this data, $X$ can be represented by the mathematical equation (2), as follows:

\[ X = A \ln \left( \frac{\gamma}{\gamma_o} \right) + B \]  

(2)  

where $\gamma$ = shear rate in s$^{-1}$  
$\gamma_o$ = 1 s$^{-1}$  
A, B = constants

The final part of the analysis involves plotting the pre- and post-logarithmic constants A and B in the above set of relationships as a function of MFI of the virgin polyolefin homopolymer in logarithmic scale, as shown in Figure 5. The resultant data plots also show good

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Table 1 Gradient of viscosity ratio curve for shear rates 9.6 s$^{-1}$ and 96 s$^{-1}$

<table>
<thead>
<tr>
<th>Virgin component</th>
<th>$X$ at shear 9.6 s$^{-1}$ (x10$^3$)</th>
<th>StD (x10$^3$)</th>
<th>$X$ at shear 96 s$^{-1}$ (x10$^3$)</th>
<th>StD (x10$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM-HDPE</td>
<td>-8.86</td>
<td>0.467</td>
<td>-8.08</td>
<td>0.277</td>
</tr>
<tr>
<td>FB-HDPE</td>
<td>12.12</td>
<td>2.86</td>
<td>8.4</td>
<td>1.694</td>
</tr>
<tr>
<td>IM-LLDPE</td>
<td>-8.54</td>
<td>0.288</td>
<td>-7.84</td>
<td>0.182</td>
</tr>
<tr>
<td>FB-LLDPE</td>
<td>-1.667</td>
<td>0.611</td>
<td>4.5</td>
<td>1.38</td>
</tr>
<tr>
<td>IM-LDPE</td>
<td>-9.02</td>
<td>0.581</td>
<td>-8.46</td>
<td>0.627</td>
</tr>
<tr>
<td>FB-LDPE</td>
<td>-3.85</td>
<td>1.088</td>
<td>-2.3</td>
<td>1.036</td>
</tr>
<tr>
<td>IM-PP</td>
<td>-4.3</td>
<td>0.493</td>
<td>-5.233</td>
<td>0.351</td>
</tr>
<tr>
<td>E-PP</td>
<td>-0.25</td>
<td>1.933</td>
<td>-1.05</td>
<td>0.465</td>
</tr>
</tbody>
</table>

Table 2 Gradient of viscosity ratio curve for shear rates 960 s$^{-1}$ and 9600 s$^{-1}$

<table>
<thead>
<tr>
<th>Virgin component</th>
<th>$X$ at shear 960 s$^{-1}$ (x10$^3$)</th>
<th>StD (x10$^3$)</th>
<th>$X$ at shear 9600 s$^{-1}$ (x10$^3$)</th>
<th>StD (x10$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM-HDPE</td>
<td>-6.52</td>
<td>0.383</td>
<td>-4.42</td>
<td>0.683</td>
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<tr>
<td>FB-HDPE</td>
<td>4.85</td>
<td>1.063</td>
<td>2.075</td>
<td>0.403</td>
</tr>
<tr>
<td>IM-LLDPE</td>
<td>-6.14</td>
<td>0.513</td>
<td>-4.02</td>
<td>0.638</td>
</tr>
<tr>
<td>FB-LLDPE</td>
<td>5.9</td>
<td>1.229</td>
<td>2.633</td>
<td>0.929</td>
</tr>
<tr>
<td>IM-LDPE</td>
<td>-7.48</td>
<td>0.597</td>
<td>-6.6</td>
<td>1.134</td>
</tr>
<tr>
<td>FB-LDPE</td>
<td>-2.325</td>
<td>0.854</td>
<td>-1.56</td>
<td>1.034</td>
</tr>
<tr>
<td>IM-PP</td>
<td>-5.5</td>
<td>0.3</td>
<td>-4.867</td>
<td>0.611</td>
</tr>
<tr>
<td>E-PP</td>
<td>-3.225</td>
<td>0.31</td>
<td>-3.85</td>
<td>0.719</td>
</tr>
</tbody>
</table>
Figure 1 Gradient of Viscosity Ratio curve for blends of virgin and recycled HDPE

Figure 2 Gradient of Viscosity ratio curve for blends of virgin LLDPE/recycled HDPE

Figure 3 Gradient of Viscosity Ratio curve for blends of virgin LDPE and recycled HDPE
logarithmic fits, and the variation of constants A and B can be represented by equations (3) and (4).

\[ A = 0.0002 \ln \left( \frac{MFI}{MFI_o} \right) - 0.0003 \]  (3)

and

\[ B = -0.0034 \ln \left( \frac{MFI}{MFI_o} \right) + 0.0027 \]  (4)

This means that an empirical relationship can be derived to relate MFI directly to viscosity ratio for a blend of recycled HDPE and virgin polyolefins, where the virgin polyolefin can have an MFI value anywhere from 0.1 to 100.

Substituting equation (3) and equation (4) into equation (2) gives the viscosity rate gradient, \( X \), as shown in equation (5)

\[ X = \left[ 0.0002 \ln \left( \frac{MFI}{MFI_o} \right) - 0.0003 \right] \ln \left( \frac{\gamma}{\gamma_o} \right) + \left[ -0.0034 \ln \left( \frac{MFI}{MFI_o} \right) + 0.0027 \right] \]  (5)

where MFI = MFI in g/10mins at 5kg/190°C
MFI\(_o\) = 1 g/10mins at 5kg/190°C
And then substituting equation (5) into (1) gives equation (6), below:

\[
\frac{\eta}{\eta_i} = 1 + \left[ 0.0002 \ln \left( \frac{MFI}{MFI_o} \right) - 0.0003 \right] \ln \left( \frac{\gamma}{\gamma_o} \right) \\
+ \left[ -0.0034 \ln \left( \frac{MFI}{MFI_o} \right) + 0.0027 \right] \phi
\]

(6)

where \( \phi \) = volume fraction of virgin polyolefins in recycled HDPE

**CONCLUSIONS**

The research investigation indicates that the relative viscosity of blends of recycled HDPE and virgin polyolefins is a linear function of virgin component volume fraction.

It is also noted that a logarithmic relationship exists between viscosity ratio gradient and shear rate, and that the constants in this logarithmic equation can be determined from another relationship, which is also logarithmic, between the constants and MFI of the virgin polyolefin.

These relations can all be combined into a single empirical equation relating viscosity ratio to MFI of the virgin polyolefin, volume fraction of the virgin polyolefin and shear rate.

In a practical sense, once the manufacturer knows the viscosity behaviour of the recycled resin, then this equation can be used to predict the viscosity behaviour of a of a recycled HDPE/virgin polyolefin blend over a wide variety of shear rates and at any volume fraction of virgin polyolefin. The only other data required is a standard MFI value for the virgin polyolefin.

**ACKNOWLEDGEMENTS**

The authors would like to thank; Visy Plastics for its financial, academic and technical support; Quenos, for its supply of virgin polyolefins; Moldflow Pty Ltd for its technical support

**REFERENCES**