Modification of poly(ethylene terephthalate) fibre by polymer blending with poly(butylene terephthalate) fibre: Part V—Extrusion behaviour

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The properties of 94/6 PET/PBT blend can be improved by increasing the extrusion temperature from 275 to 285°C. At 285°C, the blend shows no transesterification and improves density, crystallinity and heat of fusion. However, the melt viscosity decreases and activation energy increases due to the plasticising action of PBT. On the other hand, at higher extrusion temperature, PET shows minimum degradation. Density, crystallinity and heat of fusion decrease due to the absence of crystal nuclei of PET. Owing to this, melt viscosity decreases and activation energy increases.

Keywords: Extrusion behaviour, Poly(butylene terephthalate), Poly(ethylene terephthalate), Polymer blending

1 Introduction

The blending of two polymers provides a means of improving specific physical and/or mechanical properties. The final properties are, however, determined by the properties of pure polymers, geometrical arrangement of the two phases, their morphology, the extent of interpenetration and the nature of interface. The type of morphology is the dispersion of the two phases created by processing. Several investigators have studied the morphology of two-phase polymer blends at different processing conditions. In the extrusion process, the extrusion temperature influences the stability of the melt and the physical properties of the product. Plochocki reported that the flow behaviour of blends depends strongly on their thermal and shear history.

Significant improvement in the properties of poly(ethylene terephthalate) (PET) can be achieved by blending it with a small percentage of poly(butylene terephthalate) (PBT). Addition of 2-4% PBT improves the structural defects in PET and modifies its properties due to higher entanglement, which leads to the formation of tie chains or tie molecules. Addition of 6% PBT in PET results in inferior mechanical properties and crystallinity which do not improve at higher draw ratios due to the absence of tie chains or tie molecules. The non-isothermal crystallization behaviour of this blend indicates a higher crystallization rate. So, it is of interest to study the effect of different processing parameters for optimizing the properties of the blend containing PET and 6% PBT.

In this work, blended polymer chips have been prepared from PET and 6% PBT at different extrusion temperatures and their characteristics have been studied.

2 Materials and Methods

Commercial grades of PET and PBT in the form of chips were used. The material characteristics of the chips have been reported earlier.

2.1 Preparation of Samples

The polymer blends were prepared by melt mixing PET and PBT in a laboratory-scale single-screw extruder manufactured by Betol Machinery Ltd, England. Before feeding to the extruder PET and PBT chips were manually mixed and dried. The strand obtained from the extruder was cut into chips. Pure PET was also prepared in a similar way. The extrusion conditions are given in Table 1.

2.2 Thermal Experiments

Thermal experiments for the polymers were carried out in a Du Pont's differential scanning
calorimeter (DSC) at a heating rate of 20°C/min under nitrogen atmosphere. The crystallization thermogram was recorded from melt at a cooling rate of 10°C/min.

2.3 Density Experiments

The density of the samples was obtained on a Davenport density gradient column using the density range 1.25-1.40 g/cc. Carbon tetrachloride and xylene were used to prepare the columns. The weight fraction density crystallinity ($X_d$) was calculated as:

\[ X_d = \frac{d_c (d - d_a)}{d (d_c - d_a)} \times 100 \]  

where $d$ is the density of the sample; $d_c$, the density of totally amorphous sample; and $d_a$, the density of totally crystalline sample. $d_c$ and $d_a$ values of the blend sample were calculated using the following relationship proposed by Wlochowicz and Jeziorny:\(^{15}\)

\[ \frac{1}{d_{c,b}} = \frac{w_E}{d_{c,E}} + \frac{w_B}{d_{c,B}} \]  \(\ldots(2)\)

\[ \frac{1}{d_{a,b}} = \frac{w_E}{d_{a,E}} + \frac{w_B}{d_{a,B}} \]  \(\ldots(3)\)

where $d_{c,b}$ and $d_{a,b}$ are the crystalline and amorphous densities of the blend respectively; $w_E$ and $w_B$, the weight fractions of PET and PBT respectively; $d_{c,E}$, the crystalline density of PET; $d_{c,B}$, the crystalline density of PBT; $d_{a,E}$, the amorphous density of PET; and $d_{a,B}$, the amorphous density of PBT. The following values were used for PET and PBT:\(^{16,17}\)

\[ d_{c,E} = 1.455 \text{ g/cc} \quad d_{c,B} = 1.396 \text{ g/cc} \]

\[ d_{a,E} = 1.335 \text{ g/cc} \quad d_{a,B} = 1.280 \text{ g/cc} \]

2.4 Rheological Experiments

An Instron capillary rheometer was used to obtain the rheological data for PET and PET/PBT blend. It is an extrusion type of instrument in which a constant velocity is applied to the fluid. The temperatures used in the experiment were 270, 280 and 290°C. A die with $L/D$ ratio 20:17 and 60° entrance angle was used. The force at different rates of traverse was obtained from the rheometer. It was then converted to shear stress ($\tau_w$) and shear rate ($\dot{\gamma}_w$). End-effect corrections to the shear stress and Rabinowitsch corrections to the shear rates were neglected\(^{18}\). The viscosity was obtained using the following equation:

\[ \eta = \tau_w/\dot{\gamma}_w \]  \(\ldots(4)\)

The activation energy can be calculated according to Arrhenius equation as follows:

\[ \eta = A \cdot \exp \left( \frac{E}{RT} \right) \]  \(\ldots(5)\)

where $R$ is the gas constant; $T$, the absolute temperature; $E$, the activation energy; and $A$, the constant.

3 Results and Discussion

Figs 1 and 2 show the DSC melting and crystallization thermograms of PET and PET/PBT blend respectively. The melting temperature ($T_m$), crystallization temperature ($T_c$), supercooling ($\Delta T = T_m - T_c$), heat of fusion ($\Delta H_f$) and heat of crystallization ($\Delta H_c$) for PET and PET/PBT blend are given in Table 2. The table shows that the melting temperature is nearly the same for the PET samples extruded at different temperatures. The melting temperature is sensitive to the oil-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Extrusion temperature, °C</th>
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<tbody>
<tr>
<td></td>
<td>275</td>
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<tr>
<td>Zone temperature, °C</td>
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<tr>
<td></td>
<td>265</td>
</tr>
<tr>
<td></td>
<td>275</td>
</tr>
<tr>
<td>Die temperature, °C</td>
<td>275</td>
</tr>
<tr>
<td>Screw speed, rpm</td>
<td>30</td>
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<tr>
<td>Take-up speed, m/min</td>
<td>75</td>
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</tbody>
</table>

Fig. 1 – DSC melting and crystallization thermograms of PET extruded at (1) 275°C, (2) 280°C, and (3) 285°C.
Table 2 - Thermal properties of PET and PET/PBT blend from DSC melting and crystallization thermograms

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extrusion temp. °C</th>
<th>$T_m$ °C</th>
<th>$T_c$ °C</th>
<th>$\Delta T$ °C</th>
<th>$\Delta H_f$ cal/g</th>
<th>$\Delta H_c$ cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>275</td>
<td>268.5</td>
<td>215.5</td>
<td>53.0</td>
<td>11.3</td>
<td>12.6</td>
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<tr>
<td></td>
<td>280</td>
<td>268.5</td>
<td>214.5</td>
<td>54.0</td>
<td>11.0</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>268.0</td>
<td>210.0</td>
<td>58.0</td>
<td>9.8</td>
<td>11.8</td>
</tr>
<tr>
<td>94/6 PET/PBT</td>
<td>275</td>
<td>266.0</td>
<td>220.0</td>
<td>46.0</td>
<td>7.8</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>266.0</td>
<td>215.5</td>
<td>50.5</td>
<td>8.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>265.0</td>
<td>210.5</td>
<td>54.5</td>
<td>10.8</td>
<td>11.1</td>
</tr>
</tbody>
</table>

$T_m$ - Melting temperature; $T_c$ - Crystallization temperature; $\Delta T$ - Supercooling ($T_m - T_c$); $\Delta H_f$ - Heat of fusion; and $\Delta H_c$ - Heat of crystallization.

Addition of 6% PBT in PET decreases the melting temperature (Table 2), the decrease being only 2.5-3.0°C. This indicates no transesterification during processing. For a small dwell time in extruder, generally no transesterification takes place and the melting point of each component in each molar ratio should be recognizable near each other.

Addition of PBT in PET reduces density, crystallinity, heat of fusion and heat of crystallization when extruded at 275 and 280°C. PBT provides nucleation sites for the crystallization of PET. Higher density of nucleating points, created by PBT and crystal nuclei of PET, inhibits the total crystallinity and heat of fusion. At higher extrusion temperature, the crystallinity and heat of fusion are high. This can be attributed to the limited nucleating points created by PBT and to the absence of crystal nuclei of PET. The heat of crystallization for the blends remains constant.

The melt viscosity of PET and PET/PBT blend at various shear rates is shown in Figs 3-5. The viscosity of PET decreases with increasing extrusion temperature. The melt viscosity is proportional to the entanglement density of the polymer. The viscosity decreases as the entanglement density decreases. At lower extrusion temperature, nascent nuclei are formed due to incipient crystallization. So, the viscosity of the fluid is expected
to be higher due to the formation of temporary
crosslinks.\textsuperscript{21}

High extrusion temperature also favours macromolecular and oxidative degradation under the
influence of oxygen traces present in the inert medium. The decrease in viscosity may be related to
increased degradation at higher extrusion temperature. However, the amount of degradation may
be minimum as there is no change in melting point.\textsuperscript{19}

The presence of PBT in PET lowers the viscosity of the blend as PBT has significantly lower vis-
cosity at these temperatures.\textsuperscript{18} The resultant vis-

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**Table 4 - Activation energy of PET and PET/PBT blend**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Extrusion temp. °C</th>
<th>Activation energy Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>275</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>18.3</td>
</tr>
<tr>
<td>94/6 PET/PBT</td>
<td>275</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>21.2</td>
</tr>
</tbody>
</table>
at 280°C and maximum when extruded at 285°C. A larger entanglement density requires a large change in temperature to cause a small change in viscosity, resulting in a lower activation energy at lower extrusion temperature.

Further, at higher extrusion temperature, presence of PBT in PET increases the activation energy due to the lowering of the viscosity of blend.

4 Conclusions
4.1 Increase in the extrusion temperature of PET from 275 to 285°C shows minimum degradation. Density, crystallinity and heat of fusion decrease owing to limited crystal nuclei of PET. Also, the melt viscosity decreases and the activation energy increases as a result of lower entanglement density.

4.2 94/6 PET/PBT blend on extrusion at 285°C shows no transesterification. Density, crystallinity and heat of fusion increase with increase in extrusion temperature. This can be attributed to the nucleating points created by PBT and to the absence of PET crystal nuclei. Melt viscosity decreases and activation energy increases due to the plasticising action of PBT, the effect being more pronounced at high extrusion temperatures.

References
4 Van Oene H, J Colloid Interface Sci, 40 (1972) 448.