Modification of Poly(ethylene terephthalate) Fibre by Polymer Blending with Poly(butylene terephthalate) Fibre: Part III—Simultaneous Melt-blending and Spinning

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The blend fibres prepared from poly(ethylene terephthalate) and 0-10% poly(butylene terephthalate) by simultaneous melt-blending and spinning show no transesterification. The crystalline orientation function of the blend fibres is same as that of 100% PET fibre. The amorphous orientation function is more influenced by phase stability and is minimum at the boundary of phase segregation. The crystallinity, tenacity and modulus of the blend fibres improve owing to the formation of either tie chains, as in the case of 98/2 PET/PBT blend, or tie molecules, as in the case of 90/10 PET/PBT blend.

Keywords: Melt-blending, Poly(butylene terephthalate), Poly(ethylene terephthalate), Polymer blending, Spinning

1 Introduction
The properties of poly(ethylene terephthalate) [PET] fibre can be improved by blending it with a small amount of poly(butylene terephthalate) [PBT]. These polymers are compatible because of the lesser difference in solubility parameter and a larger composition range for stability. In general, the morphological structure of the parent polymer can be modified to a significant extent by blending it with a small amount of second compatible polymer. The final properties of the blend will be determined by the properties of pure polymers, geometrical arrangement of the phases, their morphology, the extent of their interpenetration and the nature of interface. Addition of 2% PBT in PET increases melt viscosity and decreases the activation energy due to entanglement. The melting behaviour of isothermally crystallized samples shows that the crystallization behaviour of PET in the blend is governed by the mobility of PBT.

In an earlier study, it was observed that the blend fibres prepared from PET and 3% PBT by sequential melt-blending and spinning show higher birefringence, initial modulus, sonic modulus and tenacity. In this work, the blend fibres have been prepared from PET and 0-10% PBT by simultaneous melt-blending and spinning and their characteristics have been studied.

2 Materials and Methods
2.1 Preparation of Fibres
The polymers chosen for the present study were all commercial grades of PET and PBT. The characteristics of the chips have been reported earlier. The amount of PBT was restricted to maximum 10%, where the polymers are expected to be compatible. The blend compositions were 100/0, 98/2, 96/4, 94/6, 92/8 and 90/10 PET/PBT, where the first number represents PET and the second one PBT weight %.

The fibres were prepared in a laboratory-scale melt-spinning unit having a static mixer with parts for mixing by its internal geometric design. The static mixer was used for the homogenization of the melt. The chips were dried under vacuum at 70°C for 12 h. The spinning temperature was kept at 275°C under nitrogen atmosphere. The fibres were collected at 50 m/min. The as-spun material was drawn in a laboratory-scale stretching unit to 4.22 × at 110°C. The drawn fibres were given a thermal treatment at 70°C for 30 min. PBT fibre was prepared in a similar way.
2.2 Thermal Experiments

Thermal experiments for the undrawn fibres 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 X-ray Diffraction Studies

X-ray diffraction pattern of the powdered samples using CuKα radiation was used to measure the crystallinity of the fibres. X-ray diffraction pattern of the as-spun material of different blends was used as standard amorphous pattern for crystallinity determination.

X-ray diffraction photographs of oriented fibres were obtained by means of a flat-plate camera with CuKα radiation. Crystalline orientation function (f₀) was calculated from (100) and (010) reflections for PET, using Farrow and Bagley's equation:

\[
\sin \phi = \cos \theta \cdot \sin X_e
\]

\[
f_0 = (90° - \phi)/90°
\]

where \( \phi \) is the angle between fibre axis and crystal axis; \( \theta \), the Bragg's angle; and \( X_e \), a half angle in a half width of the reflection curve.

2.4 Measurement of Birefringence

Birefringence was measured by using Vickers polarizing microscope with a Leitz Wetzler compensator. The amorphous orientation function (f₀) was calculated by using the following equation:

\[
\Delta n = x_c \cdot f_0 \cdot \Delta \nu_0 + (1 - x_c) \cdot f_0 \cdot \Delta \nu_0
\]

where \( \Delta n \) is the birefringence; \( x_c \), the crystallinity; and \( \Delta \nu_0 \) and \( \Delta \nu_0 \) are the intrinsic birefringence of perfectly oriented crystalline and amorphous phases. These values are 0.220 and 0.275 for both PET and PBT fibre and so for the blends.

2.5 Measurement of Mechanical Properties

The load-elongation curve was obtained under standard conditions on an Instron tensile tester (Model 1112) at 100% per minute strain rate. Stress, strain and modulus were calculated. Sonic modulus was measured on a dynamic pulse propagation meter at 5 kHz.

3 Results and Discussion

Figs 1 and 2 show the DSC thermograms of undrawn PET, PBT and blend fibres. The melting temperature \( (T_m) \), crystallization temperature \( (T_c) \), supercooling \( (\Delta T) \), heat of fusion \( (\Delta H_f) \) and heat of crystallization \( (\Delta H_c) \) are given in Table 1. The melting temperature \( (T_m) \) of 100% PET fibre is 265°C.
of 30°C in melting temperature, i.e. 235°C for PET, owing to the presence of comonomers and low molecular weight compounds. Also, the presence of low molecular weight compounds reduces spinnability and stretchability. A high melting temperature as well as a high stretch ratio (4.22 ×) confirms minimum degradation during the process of drying and spinning.

The melting temperature decreases up to 96/4 PET/PBT blend, showing a diluent effect. There is no further decrease in melt temperature. This shows that a small fraction of PBT is miscible. Very small changes in the melting point of the blends indicate that no significant transesterification has taken place. Similar observations were reported by Li and Wong and Herlinger et al. For no transesterification, the melting points of each component, in each molar ratio, are recognizable near each other.

90/10 PET/PBT blend shows two melting peaks referring to independent crystallization of the components. 92/8 PET/PBT blend shows a tendency for phase segregation. 94/6 PET/PBT blend has a low supercooling (ΔT) and high heat of crystallization. It appears that the process of phase segregation is operative during crystallization, giving rise to high nucleation density as a result of PET crystallization. Garg and Mishra reported that PBT provides nucleation sites for the crystallization of PET, which, in turn, results in a much faster crystallization rate for the block copolymer as compared to that of PET.

X-ray crystallinity and birefringence values are given in Table 2. The table shows that X-ray crystallinity is significantly high for 98/2 and 90/10 blend fibres. 98/2 blend shows higher melt viscosity and lower activation energy due to high entanglement density in melt stage, as reported earlier. The entanglement may result in higher crystalline links as changes introduced in the supramolecular structure of a polymer melt may be reflected in the solid state. For 90/10 blend, significant phase segregation has taken place. PBT may be acting as sites for nucleation and crystallization, thereby increasing crystallinity. Crystallinity is low for 94/6 blend, where phase segregation is operative during crystallization or during the process of melt flow in rheological study.

The birefringence values show similar behaviour like that of crystallinity. 94/6 blend has the lowest birefringence value. Crystalline orientation function (Φc) and amorphous orientation function (Φa) are shown in Fig. 3. The crystalline orientation function is nearly constant for all the samples. The amorphous orientation function has a distinct minima for 92/8 blend. In this composition, the second component is not sufficient to crystallize independently. On the other hand, there is a tendency to phase segregate, resulting in a drop in amorphous orientation.

Table 3 shows the mechanical properties of the as-spun fibres. The natural draw ratio (NDR), maximum draw ratio (MDR) and yield stress were computed from the stress-strain graph. 98/2 blend fibre shows a higher yield stress. Yield stress is the stress
Table 3—Mechanical Properties of as-spun Blend Fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>NDR</th>
<th>MDR</th>
<th>Yield stress g/d</th>
<th>Sonic modulus g/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>3.45</td>
<td>5.50</td>
<td>0.23</td>
<td>24.6</td>
</tr>
<tr>
<td>98/2</td>
<td>3.30</td>
<td>5.50</td>
<td>0.28</td>
<td>26.1</td>
</tr>
<tr>
<td>96/4</td>
<td>3.45</td>
<td>5.45</td>
<td>0.27</td>
<td>24.0</td>
</tr>
<tr>
<td>94/6</td>
<td>3.45</td>
<td>5.75</td>
<td>0.26</td>
<td>24.0</td>
</tr>
<tr>
<td>92/8</td>
<td>3.55</td>
<td>5.85</td>
<td>0.26</td>
<td>21.2</td>
</tr>
<tr>
<td>90/10</td>
<td>3.30</td>
<td>5.60</td>
<td>0.25</td>
<td>23.2</td>
</tr>
</tbody>
</table>

NDR—Natural draw ratio; and MDR—Maximum draw ratio.

Table 4—Mechanical Properties of Drawn Blend Fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield stress g/d</th>
<th>Breaking stress g/d</th>
<th>Strain %</th>
<th>Initial modulus g/d</th>
<th>Sonic modulus g/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>2.5</td>
<td>5.5</td>
<td>41.0</td>
<td>148</td>
<td>154</td>
</tr>
<tr>
<td>98/2</td>
<td>2.8</td>
<td>5.6</td>
<td>38.5</td>
<td>180</td>
<td>164</td>
</tr>
<tr>
<td>96/4</td>
<td>1.8</td>
<td>5.5</td>
<td>44.0</td>
<td>141</td>
<td>134</td>
</tr>
<tr>
<td>94/6</td>
<td>1.3</td>
<td>4.1</td>
<td>46.0</td>
<td>93</td>
<td>128</td>
</tr>
<tr>
<td>92/8</td>
<td>1.6</td>
<td>4.5</td>
<td>42.0</td>
<td>106</td>
<td>135</td>
</tr>
<tr>
<td>90/10</td>
<td>2.2</td>
<td>4.7</td>
<td>37.0</td>
<td>120</td>
<td>152</td>
</tr>
</tbody>
</table>

required to initiate and propagate plastic deformation. So, this fibre in as-spun state shows a compact structure. Owing to this, NDR is comparatively less and the sonic modulus is high. The yield stress gradually decreases further.

Table 4 shows the mechanical properties of the drawn fibres. 98/2 blend shows higher modulus, breaking stress, yield stress, and low elongation-at-break. The crystalline links or the tie chains as introduced due to entanglement may account for high modulus and strength. Similar type of improvements in the properties of polypropylene blend is reported due to formation of tie chains. 90/10 blend fibre shows high modulus, comparatively high yield strength and low elongation, which may be due to an interconnected structure with PBT crystals acting as tie molecules. 94/6 and 92/8 blend fibres have low breaking stress, yield stress and modulus. Inferior structural development due to partial phase segregation and insufficient amount of the second component for 92/8 blend results in inferior mechanical properties. The absence of tie chains or tie molecules due to PBT crystals results in inferior mechanical properties of 94/6 blend fibre.

4 Conclusions

4.1 The melting temperature decreases to a minimum extent by addition of PBT in PET, indicating no transesterification in simultaneous melt-blending and spinning.

4.2 The crystalline orientation function remains same for all the blend fibres. On the other hand, amorphous orientation function is minimum for 92/8 blend, i.e. the boundary of phase segregation.

4.3 Addition of 2% PBT in PET improves crystallinity, breaking stress, yield stress and modulus due to formation of more number of intercrystalline links or tie chains.

4.4 Addition of 10% PBT in PET improves crystallinity, modulus and yield strength due to interconnected structure with PBT crystals acting as tie molecules.

4.5 Addition of 6% PBT in PET deteriorates structural and mechanical properties due to the absence of tie chains or tie molecules.

References