POLYBLEND FIBERS OF POLY(ETHYLENE TEREPTHALATE) AND A BLOCK COPOLY(ESTER-ETHER)

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Synopsis

Poly(ethylene terephthalate) (PET) was mixed with a block copoly(ester-ether) (PEE) and spun into fine fibers by a melt process. The blend fibers were drawn in water at 92°C and annealed at 200°C in silicone. The microstructure of the blend fibers was investigated by means of WAXS, DTA, microscopy, density measurement, and tensile experiments. In all fibers, PET was distributed as continuous fine fibrils in the matrix of PEE. The diameter of a PET fibril was almost in proportion to the PET content and of the order of 0.1 micron. The matrix PEE was in unoriented state due to the annealing above its Tm. Tensile properties of the blend fibers were rather tough and elastic because of the cooperation of the elastmeric PEE with highly oriented and crystallized PET. These structure and tensile properties were compared with those of natural wool. The formation of copolyester due to an interesterification between PET and PEE was disclaimed by means of WAXS and DTA experiments: The reflections of both components were clearly distinguished in their x-ray scattering diagrams and the melting peaks of PET and PEE were separately observed in their DTA traces.

INTRODUCTION

In a previous paper¹, we revealed that in some bicomponent blend fibers (1) the minor component polymer was usually distributed as rather long and thin fibrils floating in the matrix of the major component and (2) the fibrils entangled mutually and run parallel to the fiber axis.

This microstructure of the bicomponent blend fibers is quite resemble to that of natural wool in which many microfibrils of about 70 Å in diameter are surrounded by matrix materials and packed in hexagonal arrays being about 100 Å apart²). Furthermore, the microfibrils of wool are made up of highly oriented crystalline polypeptide material, while the matrix being constructed with randomly oriented amorphous polypeptides. This complicated microstructure results in the superior properties of wool, such as the excellent recovery from strain and the dimensional stability.

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These facts lead us to an idea; we can possibly produce a fiber having the structure and properties similar to those of natural wool by adopting a proper pair of linear polymers. From this point of view, in the present study a rigid crystalline polyester, poly(ethylene terephthalate) (PET), was subjected to blend with a thermoplastic elastomer, a block copoly(ester-ether) (PEE), whose chemical structure is illustrated in Figure 1 together with that of PET. PET is a well-known fiber forming crystalline polymer with some excellent physical properties, while PEE behaves as an elastomer even at rather low temperature because of its low Tg and poor crystallizability³⁻⁵).

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Fig. 1. The chemical structure of polymers examined: poly(ester-ether) (top) and poly(ethylene terephthalate) (bottom)
EXPERIMENTAL

Materials

Both PET and PEE were kindly supplied by Toyo Spinning Co. in the form of pellet and used without further purification. The intrinsic viscosity of the PET, determined for the dilute phenol-1,1,2,2-tetrachloroethane solution, was 0.63 dl/g, while the inherent viscosity of the PEE (Pelprene P-70B) measured for a 0.2 g/dl 1,1,2,2-tetrachloroethane solution was 1.947 dl/g. Table 1 gives some basic characteristics of these polymers.

Three blends of different compositions, as well as each of the parent polymers, were subjected to melt spinning. Before blending both polymer pellets were dried in a vacuum oven at 95°C for 4 h and at 130°C for more than 4 h. These dried pellets were mixed in a bottle by tumbling.

Melt Spinning

Melt spinning was performed by using a laboratory extruder equipped with a spinneret having 12 nozzles of 0.5 mm diameter. Spinning temperature was controlled at three different portions of the instrument, i.e., the feeding and the metering sections of the extruder barrel and the spinneret. The molten polymer stream emerged downward through the spinneret nozzles was cooled in the atmosphere to room temperature and then wound up on a bobbin. Take-up speed was kept constant at 5.5 m/min throughout the spinning experiments.

Drawing

As-spun fibers thus prepared were drawn in water at 92°C with a conventional drawing instrument which was made up of a drawing bath and two pairs of rollers: One pair to feed the as-spun fiber at a constant rate and the second pair, moving at several times of the linear velocity of the first pair, to draw the fiber. Draw ratios were determined by adjusting the velocity of the second pair. Drawn fibers were wound on a bobbin again and allowed to stand at room temperature for around three weeks in order to relax the internal stress of the fibers induced in the course of drawing, because immediately after the drawing the drawn fibers tended to retract due to the elastic properties of PEE.

Tensile Properties

Tensile experiments were run at room temperature by using an Instron type tensile tester, Shinkoh Model TOM 200D. Gauge length was 50 mm and cross-head speed was 400%/min.

Elastic Recovery

In measurements of recovery, the program of application and removal of stress is of important. In the present study, we adopted a most simple technique: Each fiber was stretched in a tensile tester at the extension rate of 400%/min to the desired level of strain and then unloaded at the same rate. Based on this stress-strain curve of loading and unloading, the elastic recovery was easily calculated as the ratio of elastic extension to total extension.

Density

Density of fibers was measured at 30°C by using a N-heptane-carbone tetrachloride density gradient column. The positions of five calibrated glass floats and specimens were observed after 24 h at which time they settled at their equilibrium positions.

Wide Angle X-ray Diffraction

Wide Angle X-ray Scattering (WAXS) patterns were obtained with a JEOL instrument Model DX-GE-7E to estimate the orientation degree of the crystalline phase of the fibers.

Differential Thermal Analysis

DTA thermograms were obtained by using a Shimadzu Micro-DTA instrument Model DT-2B. Heating rate was 10°C/min. A standard technique was employed.

Microscopy

PEE component can be dissolved out from these blend fibers with 1,1,2,2-tetrachloroethane (TCE) leaving PET component as a residue. A small bundle of fibers was spread on a glass slide, etched with some drops of TCE, and then subjected to the microscopic observations.

Annealing

The highly drawn fibers mounted in a laboratory drawing equipment were allowed to stand in a silicone oil bath at 200°C for 10 min in order to disorder the PEE matrix. The fibers thus annealed were freely cooled in the atmosphere to room temperature, washed in a large amount of equi-weight mixture of toluene and methanol, and dried in an oven at 60°C.
Table 1. Properties of Polymers Examined

<table>
<thead>
<tr>
<th>Property</th>
<th>PET</th>
<th>PEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity, dl/g</td>
<td>0.63</td>
<td>1.947</td>
</tr>
<tr>
<td>density, g/cm³</td>
<td>1.385</td>
<td>1.174</td>
</tr>
<tr>
<td>Tₘ, °C</td>
<td>253</td>
<td>187</td>
</tr>
<tr>
<td>Tₑ, °C</td>
<td>67</td>
<td>-40</td>
</tr>
</tbody>
</table>

a) intrinsic viscosity measured for dilute phenol-tetrachloroethane solutions.
b) inherent viscosity determined for a 0.2 g/dl tetrachloroethane solution.

RESULTS AND DISCUSSION

Spinning and Drawing

The DTA curve traced in Figure 2 shows only an endothermic peak at 187 °C corresponding to the melting point of PEE. This seems that PEE is stable up to 300 °C. In actual melt processing, however, polymer should be held at an elevated temperature for a prolonged period of time. Then it is very dangerous to argue the thermal stability only by the DTA experiments. Therefore PEE was melt spun into fiber within the temperature range from 200 °C to 280 °C.

It was found that PEE can be spun smoothly even at 280 °C. The fibers prepared in this way were subjected to the drawing and the tensile experiments. The maximum draw ratio and the tenacity of the as-spun fibers were plotted against the spinning temperature in Figure 3, showing no significant change in the properties up to 270 °C. It must be noticed that a sudden decrease in tenacity was observed for the fiber spun at 280 °C. On the other hand, the component of this series of blends, PET, has to be melt-spun at 270 °C at least. From these facts it was confirmed that PEE and its blend have to be spun at 270 °C. The optimum spinning temperatures for both blend and unblended polymers were determined experimentally and summarized in Table 2.

As was mentioned in the previous paper, when the mixing of polymers was conducted under unsuitable conditions, and hence, the dispersion state of component polymers was rough, the molten polymer stream emerged through the spinneret nozzle was opaque due to the diffused reflection at the interfacial boundary between both components. This phenomenon was also observed in the present study.

A motionless mixer was combined with the ordinary spinning instrument to improve the dispersion state and to obtain more fine and clear blends. But unfortunately the use of the mixer was not helpful for the fine mixing.

Table 2. Optimum Spinning Temperatures

<table>
<thead>
<tr>
<th>Blending Ratio by Weight</th>
<th>PET</th>
<th>PEE</th>
<th>T₁ (°C)</th>
<th>T₂ (°C)</th>
<th>T₃ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>0.7</td>
<td>210</td>
<td>250</td>
<td>270</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
<td>0.5</td>
<td>210</td>
<td>265</td>
<td>270</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>210</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
<td>0.0</td>
<td>210</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>240</td>
<td>280</td>
<td>285</td>
</tr>
</tbody>
</table>

a) The spinning temperatures were adjusted at the feeding zone, T₁, and the metering zone, T₂, of extruder barrel and at spinneret, T₃.
As seen in Figure 4, the maximum draw ratio of the blend fibers is always smaller than those of the parent polymers. This may be attributed to the rough distribution and caused by the rupture at the boundary between the components.

**Tensile Properties**

The residual elongation of the drawn fibers is plotted against the draw ratio in Figure 5. In both blend and unblended fibers the elongation decreases markedly with increasing draw ratio. The elongation of the PEE fiber is always greater than that of the others. Except for the as-spun fibers, the elongation of the drawn blend fibers is almost similar to that of PET fiber. In other words, the elongation of the blends was governed by PET component.

In Figure 6 the tensile strength of the fibers is shown as a function of draw ratio: The tensile strength increases monotonically with draw ratio in both blend and unblended fibers. Before drawing, the tensile strength of PEE fiber is greater than that of others. This may be attributed to the brittle properties of still unoriented glassy PET. On drawing, the tensile strength of PET increases drastically, as reported by many researchers, while the increase of the tensile strength of PEE fibers is very gradual.

In the present study all samples were drawn at 92 °C because of the high $T_g$ of PET. This temperature is inadequate to the optimal drawing of PEE.

Fig. 4 The variation of the maximum draw ratio of blend fibers with the composition of blend.

Fig. 5 The relation between draw ratio and the residual elongation of blend fibers containing PEE by weight 0 (PET) •, 0.3 ○, 0.5 ⊗, 0.7 ◊, and 1.0 (PEE) ◌.

Fig. 6 The relation between draw ratio and the tensile strength of blend fibers containing PEE by weight 0 (PET) ●, 0.3 ○, 0.5 ⊗, 0.7 ◊, and 1.0 (PEE) ◌.

Sumoto pointed out that the drawing at 40 °C or lower and the subsequent annealing at a temperature above 80 °C resulted in the agglomeration of polyester segments of PEE and thus a more developed internal structure of PEE could be obtained.

The blending of PEE and PET results in the decrease of tensile strength comparing with that of parent PET fibers. This may be obviously illustrated in Figure 7, where the tensile modulus, the tensile strength, and the residual elongation of the most highly drawn fibers are plotted against...
the composition of the blend. We can easily understand that PEE governs the tensile strength and the tensile modulus, while PET restricts the elongation of the resulting fibers. This tensile behavior also implies that the dispersion state is rather rough and the rigid PET is distributed as fine fibrils in the matrix of the elastmeric PEE.

![Image](image_url)

Fig. 7 The variation of the tensile properties of the most highly drawn blend fibers with composition.

**Density**

In Figure 8 the density and the specific volume of the blend fibers are shown as functions of the composition. A linear relation found in the plot of the specific volume against the weight fraction suggests that both components are largely segregated even in these blends.

**X-ray Diffraction**

Figure 9 shows the WAXS patterns of drawn and undrawn PEE fibers, indicating that the orientation of the crystalline poly(tetramethylene terephthalate), the hard segment of PEE, increases with an increase of draw ratio. The pattern D, taken for the most highly drawn fiber, seems to be typical of well-developed fiber structure.

The WAXS patterns of the as-spun and the drawn 50/50 blend fibers are shown in Figure 10. The pattern A, obtained for the as-spun fiber, closely resembles that for the as-spun PEE fiber but the diffraction rings are rather diffuse in shape and weak in intensity. No characteristic reflection of PET in the pattern of the as-spun blend suggests that PET component is still in the glassy state as in a usual unblended as-spun PET fiber.

On drawing, PEE component changes to the

![Image](image_url)

Fig. 8. The variation of density and specific volume with the composition of blend fibers.

![Image](image_url)

Fig. 9. The WAXS patterns of PEE fibers drawn by (A) 1x (as-spun), (B) 2.5x, (C) 4x, and (D) 5x.
reflections of both PET and PEE components are clearly and separately observed in the pictures.

**Differential Thermal Analysis**

Kresse\(^8\) studied the melt blending of two different polyesters and found that the ester interchange reaction between both components oriented state. Several sharp arcs from the oriented PET are imposed on the reflections of PEE. Figure 11 represents the patterns of the highly drawn fibers of various compositions. There exist some minor differences with composition but the

**Fig. 10.** The WAXS patterns of the 50/50 blend fibers drawn by (A) 1x (as-spun), (B) 2.5x, (C) 4x, and (D) 5.7x.

**Fig. 11.** The WAXS patterns of the most highly drawn blend fibers containing PEE (A) 1.0 (PEE), (B) 0.7, (C) 0.5, (D) 0.3, and (E) 0 (PET).

**Fig. 12.** The DTA thermograms of the most highly drawn blend fibers containing PEE, from top to bottom, 1.0 (PEE), 0.7, 0.5, 0.3, and 0 (PET).
resulted in the formation of copolyesters. On the other hand, according to Morimoto⁹), DTA is a useful tool for investigating the microstructure of blends, as well as X-ray diffraction.

DTA thermograms of the drawn fibers of PEE, PET, and their blends are shown in Figure 12. Melting peaks for both components are almost independent of the composition and no additional peak can be seen in the figure. This implies that both components distribute roughly in the blends and the interaction at the boundary can be neglected.

Microscopy

The microphotographs shown in Figure 13 represent the residual fibrilar PET aligning along the fiber axis. PEE matrix was dissolved and removed from the drawn fibers by TCE treatment. The thickness of the fibrils seems to be in proportion to the PET fraction in the blend. In other words, as the content of PET is increased, the thickness of the fibrils becomes greater.

Annealing

Both PET and PEE components were oriented in the course of drawing. As was mentioned above, the matrix component in natural wool has a randomly oriented structure. In order to disorient the matrix PEE component, the drawn blend fibers were annealed for 10 min in a silicone oil bath at 200 °C, which is above the melting point of PEE and below that of PET. During this annealing the silicone oil protects the fibers and prevents the molten PEE from mutual adhesion.

After such thermal treatment the oriented PET fibrils were distributed in almost randomly oriented rubbery PEE matrix. We can easily recognize the disorientation of PEE in the WAXS patterns shown in Figure 14 in which several rings from the almost randomly oriented PEE are imposed on the strong spots from the almost

![Fig. 13. The optical microphotographs of the PET fibrils produced in the drawn blend fibers containing PET by weight (A) 0.3, (B) 0.5, and (C) 0.7. (1,200 x)](image)

![Fig. 14. The WAXS patterns of the drawn and annealed blend fibers containing PEE by weight (A) 0.7, (B) 0.5, and (C) 0.3.](image)
fully oriented PET. The reflection intensities of the rings are approximately in proportion to the PEE content and become weaker as the PET content increased.

The tensile properties of the blend fibers vary drastically by the annealing at 200°C for 10 min as is shown in Figure 15. The tensile strength and the elongation at break are significantly decreased, while the tensile modulus increased slightly after the treatment. This anomalous changes in the properties may also be attributed to the structure of the blend fibers. The annealing at a temperature between the melting points of PET and PEE and above the glass transition point of PET enhances the crystallization of the fibrilar PET, which aligns along the fiber axis and is straightly distributed in the matrix of PEE. On the other hand, the matrix PEE, once oriented in the preceding drawing, must be disoriented as a result of the annealing, because it was conducted above the melting point of PEE. Therefore, the whole tension applied to the fibers should be received by the PET fibrils alone and the fibers break when the PET fibrils are torn off by the tension. Consequently the tensile strength and the elongation at break reduce while the tensile modulus increases as a result of the annealing.

In Table 3 the elastic recovery of the drawn and annealed blend fibers is compared with that of a natural wool, presented by Beste and his coworker. The elastic recovery is defined as the ratio of the elastic extension and the total extension. In the present study the sample fibers were stretched in a tensile tester up to 4 or 12% of their initial length at the extension rate of 400%/min and immediately unloaded at the same rate.

Table 3. Elastic recovery from extension for various drawn and annealed blend fibers

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Extension Level, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEE 0.7 PET 0.3</td>
<td>3 4 5 10 12</td>
</tr>
<tr>
<td>0.5 0.5</td>
<td>79 61</td>
</tr>
<tr>
<td>0.3 0.7</td>
<td>84 67</td>
</tr>
<tr>
<td>Natural Wool a)</td>
<td>84 69 51</td>
</tr>
</tbody>
</table>

a) measured by Beste and Hoffmann.

Table 3 shows that the elastic recovery of these annealed fibers is almost equal to or greater than that of the natural wool. In addition, it must be emphasized that, except for some nylons, the recovery elasticity of these annealed blend fibers is significantly better than those of most commercial synthetic fibers, including the fibers from PET and polyacryls.

CONCLUSIONS

The polyblends comprising PET and PEE could be melt-spun at 270°C into fine fibers by a conventional spinning followed by the hot-drawing by several times in water at 92°C. An annealing in silicone at 200°C for 10 min relaxed perfectly the matrix PEE and facilitated the crystallization of the PET fibrils.

The fibers thus prepared had a very complicated microstructure. A microscopic observation revealed that, in these blend fibers, PET fibrils floated in the matrix of PEE and entangled each other, as was described in the previous paper. It must be noted, however, that PET could form a net-worked fibrils even in the blend containing 70 wt% PET and 30 wt% PEE. The reason why the
major component made the fibrilar net-works is not yet clear. Although poly(tetramethylene terephthalate) sequence in PEE is very similar to that of PET in the chemical structure, the formation of copolyester due to the interesterification between both components during the melt process could not be detected by means of WAXS and DTA techniques: The reflections of PET were clearly distinguished from those of PEE in their WAXS patterns. The endothermic peak temperatures were also independent of their compositions and the height of the melting peaks was almost in proportion to the contents.

This microstructure of the annealed blend fibers has a strong resemblance to that of natural wool, except that the thickness of the fibrils of the fibers prepared in the present study is of the order of 0.1 micron but that of natural wool is about 70 Å.

The tensile strength, tensile modulus, and elongation of these drawn and annealed blend fibers were 40–50 kg/mm² (3.4–4.4 g/d), 300–500 kg/mm², and 35–50%, respectively. These are greater than those of a conventional natural wool: The corresponding values of wool are 1–1.7 g/d, 130–300 kg/mm², and 25–35%, respectively. In addition, the elastic recovery of these blend fibers was almost equal to or greater than that of natural wool.

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