Mechanical and structural properties of extruded strands of blends containing a liquid-crystalline polyester with poly(ethylene terephthalate)

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Mechanical and structural properties of extruded strands of blends of a liquid-crystalline copolyester (LCP), containing *p*-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid, with poly(ethylene terephthalate) (PET) were investigated using tensile testing, X-ray diffraction measurements and scanning electron microscopic observation. The extruded strands of the blends consist of a crystalline and oriented LCP phase and an amorphous and unoriented PET phase. The tensile modulus increases almost linearly with increasing LCP content for the strands of the blends of more than 10% LCP content. The LCP component hardly contributes to the improvement of the mechanical tensile properties for the strands of the blends of less than 5% LCP content. The LCP phase tends to form fibrous structures, which orient almost parallel to the direction of extrusion in the blend strands. The fibrils of the LCP component become longer and thinner with increasing extension draw ratio of the blend strands. A relationship between the mechanical tensile properties and the morphology of the LCP phase in the blend strands was discussed.

(Keywords: blend; liquid-crystalline copolyester; poly(ethylene terephthalate); strands; mechanical tensile properties; structure)

INTRODUCTION

Blends of rigid-chain polymers that form thermotropic liquid-crystalline states with conventional thermoplastic flexible-chain polymers such as polystyrene (PS) have recently received considerable attention. In most cases, liquid-crystalline polymers (LCPs) are incompatible with conventional thermoplastic polymers because the melt of the former is in an anisotropic state and that of the latter is in an isotropic one. Moulded or extruded parts obtained from the melt blends of these polymers contain separate phases, composed of each individual polymer[1–6]. The mechanical and structural properties of the blends are mainly dependent upon content and morphology of LCPs. It is well known that nematic LCPs can be easily oriented parallel to the direction of flow in the liquid-crystalline states. This feature of LCPs is almost preserved also in the blended melt containing conventional thermoplastic polymers. Therefore, LCPs are believed to play a role as a reinforcement in moulded or extruded parts of the blends[4]. This is a major reason why the mechanical and structural properties of blends of LCPs with conventional thermoplastic flexible-chain polymers are studied.

Mechanical properties of blends of thermotropic LCPs with conventional thermoplastic polymers have been investigated by many researchers[3–14]. Siegman *et al.* have reported that both elastic modulus and ultimate tensile strength of moulded specimens of blends containing an amorphous polyamide and a liquid-crystalline copolyester based on 2,6-hydroxynaphthoic acid (HNA) and *p*-hydroxybenzoic acid (HBA) increase with increasing LCP content up to 25%[3]. Malik *et al.* have investigated mechanical tensile properties of filaments of blends containing a liquid-crystalline HBA/HNA copolyester with polycarbonate (PC) and have reported that both tensile modulus and ultimate tensile strength of filaments increase initially with increasing LCP content up to 10% and give values much higher than those predicted by the rule of mixing[9]. Crevecoeur *et al.* have studied mechanical tensile properties of moulded specimens of blends of a liquid-crystalline copolyester up to a content of 50% with PS[12]. Their results have shown that the tensile modulus and the strength were not improved for the blend of up to 10% LCP content and begin to increase with increasing LCP content from the 25% LCP blend[12].

The processing conditions and the structures of extruded films of blends prepared from liquid-crystalline HBA/HNA copolyester and poly(ethylene terephthalate) (PET) have been investigated by Ko *et al.*[11]. They have illustrated that the morphology of the LCP in the blends is mainly dependent upon extrusion conditions, blend ratio and viscosity ratio of the component polymers[11]. Jung and Kim have examined the effect of extension draw ratio on mechanical tensile properties of fibres of blends containing a liquid-crystalline 60/40 HBA/PET copolyester with PC, and have concluded that the enhancement of mechanical tensile properties with increasing LCP content is due to high orientation induced by high extension draw ratio[8].

Thermal and structural properties of extruded sheets of blends of a liquid-crystalline HBA/HNA copolyester with PET have been investigated in a previous paper[15].

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We have shown that the LCP phase tends to form spherical or elliptical structures in the blend of 20% LCP content. In this paper, we have investigated mechanical tensile properties and structures of extruded strands of blends prepared from the same component polymers as those reported in the previous paper[15] and have discussed the relationships between mechanical tensile properties and blend ratio or extension draw ratio of the strands.

EXPERIMENTAL

Materials

The LCP used in this work is a commercial polymer, Vectra A950 (Polyplastics Co., Japan), prepared from HBA and HNA. PET is also a commercial product, SA1206 (Unitika Co., Japan). The two-component polymers mixed by a rotor in the form of pellets were dried in a oven at 90°C for 14 h and then 150°C for 4 h. LCP contents in the LCP/PET blends used in this work were 0, 1, 2, 5, 10, 20, 40, 50, 60, 80 and 100 in weight percentage.

Processing

The mixed pelletes of the two-component polymers were melt-blended using a co-rotating twin-screw extruder (Toyoseiki Co.) equipped with a die of 2 mm diameter and 10 mm length ($L/D=5$). The strands of the blends were extruded at 310°C and at an output flow rate of 6 g min^{-1} into a water bath and then were rolled up at various speeds. The extension draw ratio of the strands was obtained from the ratio of the cross-sectional area of the strands to that of the die.

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction patterns of the blends were obtained at room temperature with an X-ray generator (Rigaku Co.) having Ni-filtered Cu Kα radiation and a flat-plate camera. The distance from the sample to the films was about 50 mm and the exposure time was in the range of 2 to 6 h.

Tensile testing

Mechanical tensile properties were investigated using a tensile tester (Tensilon UTM-III-100, Orientec Co.) with a gauge length of 20 mm and a strain rate of 4 mm min^{-1} at room temperature. Average values of more than five measurements were taken for tensile modulus and ultimate tensile strength of the strands of the blends.

Morphological characterization

Morphology of the surfaces fractured by the tensile testing of the strands was observed using a scanning electron microscope (SEM) (model DS-130, Akashi Co.). The fractured surfaces were coated with gold before observation.

RESULTS

Wide-angle X-ray diffraction

Figure 1 shows wide-angle X-ray diffraction patterns of the strands of blends at an extension draw ratio of 80. The diffraction patterns show that the pure PET strand (*Figure 1a*) and the PET component in the blends are amorphous and have unoriented structures. The PET component of the strands of blends at an extension draw ratio of 120, which was the maximum value obtained in this work, has almost the same structure as that of the blends shown in *Figure 1*. On the other hand, the pure LCP strand (*Figure 1b*) exhibits a well oriented fibre

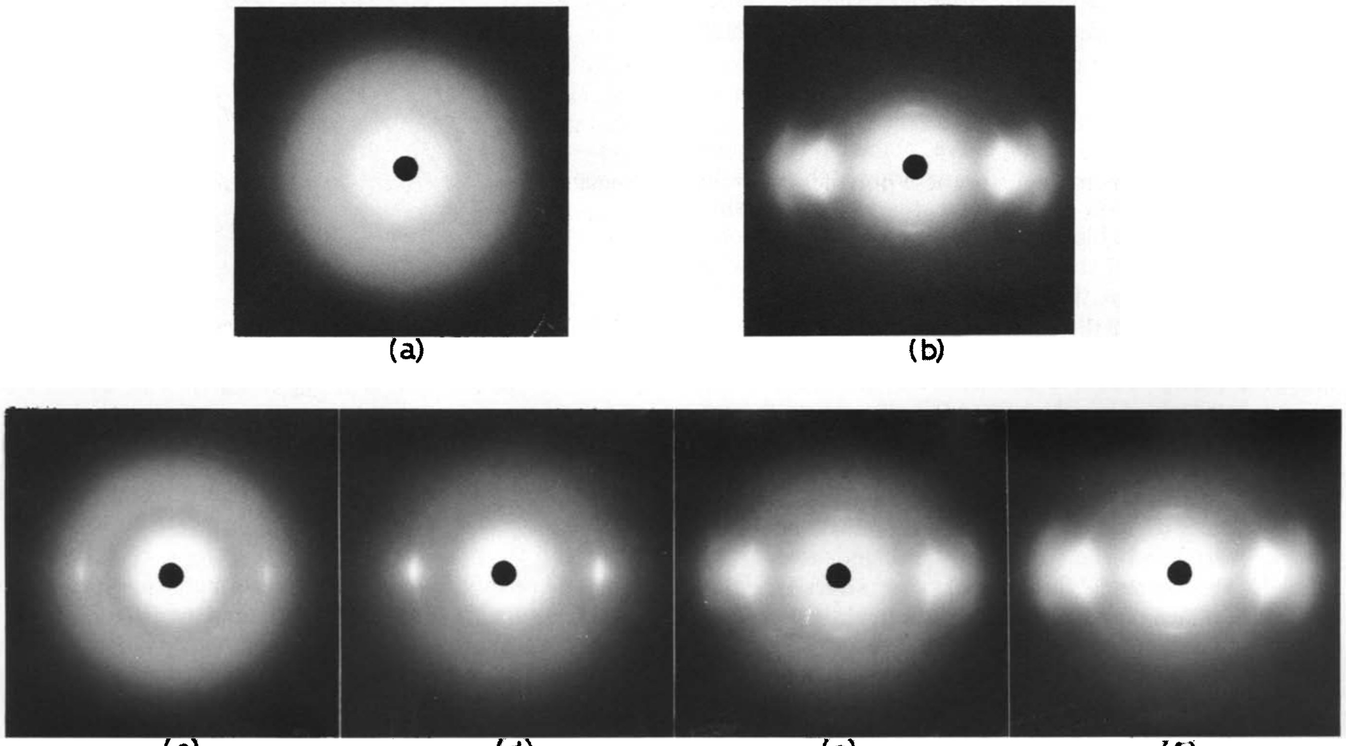


Figure 1 Wide-angle X-ray diffraction patterns of strands of LCP/PET blends at an extension draw ratio of 80. Ratios of LCP/PET are: (a) 0/100, (b) 100/0, (c) 5/95, (d) 20/80, (e) 50/50 and (f) 80/20. The extrusion direction of the strands is vertical

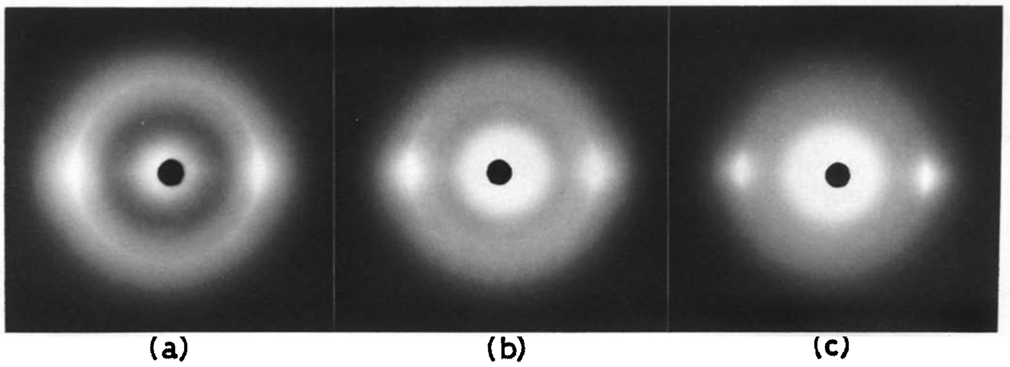


Figure 2 Wide-angle X-ray diffraction patterns of strands of LCP/PET 20/80 blend. Extension draw ratios of the strands are: (a) 10, (b) 25 and (c) 80. The extrusion direction of the strands is vertical

diffraction pattern having equatorial reflections of 0.45 and 0.32 nm and a meridional one of 0.68 nm. The fibre axis is almost parallel to the direction of extrusion. These reflections are strong ones observed in the X-ray diffraction of crystalline HBA/HNA copolyesters[16]. The fibre diffraction pattern shown in *Figure 1b* is also observed in the blends (*Figures 1c–f*) and can be attributed to the LCP component in the blends.

As shown in *Figure 1*, the LCP component in the blends has a highly oriented structure. The degree of orientation of the LCP component, however, was dependent upon extension draw ratio of the strands. *Figure 2* demonstrates wide-angle X-ray diffraction patterns of the strands of 20% LCP content at extension draw ratios of 10, 25 and 80. Orientation of the LCP component becomes higher with increasing extension draw ratio. However, the increase in the degree of orientation tended to level off with extension draw ratios of more than 80.

The results of wide-angle X-ray diffraction patterns for the strands of the LCP/PET blends indicate that the blend strands are composed of oriented structures of the LCP phase and unoriented amorphous ones of the PET phase.

Mechanical tensile properties

Figure 3 shows stress–strain curves of the blend strands at an extension draw ratio of 80. The slope of the straight line starting from the origin increases with increasing LCP content of the blends. In the case of the blend of a given LCP content, this slope tended to increase with increasing extension draw ratio up to about 80. The tensile behaviour of the strands of less than 5% LCP blends was different from that of more than 10% LCP blends. Yielding appeared in the stress–strain curves of the blend strands of less than 5% LCP content, as shown in *Figure 3* for the pure PET strand. After the yield strain, the tensile stress hardly increases with increasing strain up to a value near to breaking of these strands. This tensile behaviour is believed to be, so-called, necking. On the other hand, the strands of the blends with over 10% LCP content exhibit no yield stress in the stress–strain curves. Serrated curves frequently emerged as the behaviour of tensile breaking in the stress–strain curves of the strands of the blends with more than 80% LCP content. This tensile behaviour of breaking has been observed in filaments of other high-performance rigid-rod chain polymers[17].

Figure 4 shows tensile modulus as a function of extension draw ratio of the blend of 20% LCP content.

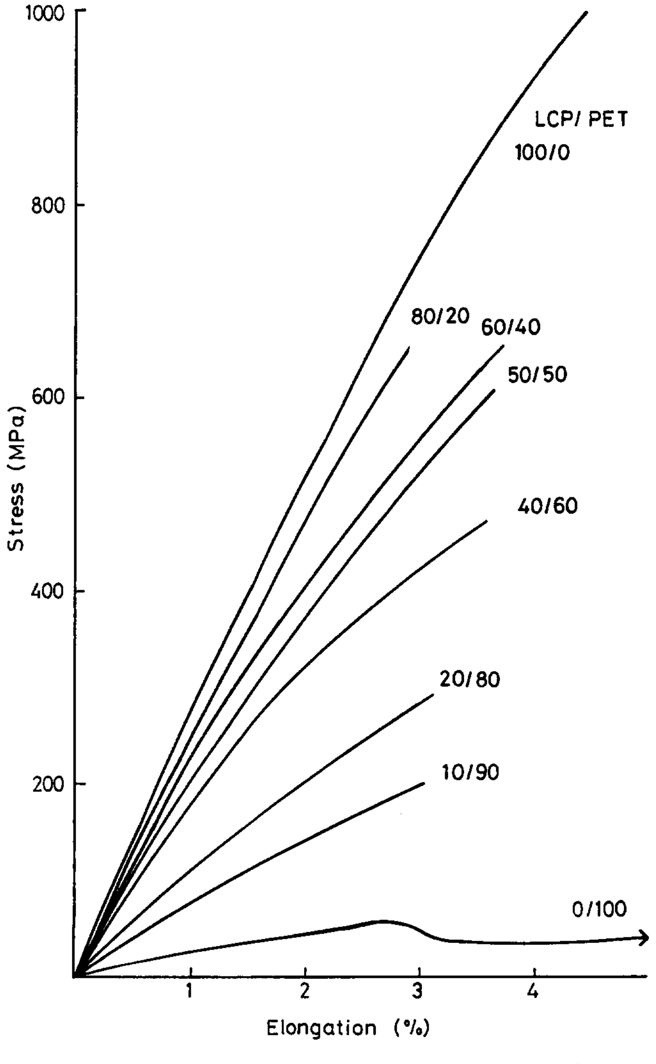


Figure 3 Stress–strain curves of strands of LCP/PET blends at an extension draw ratio of 80. Ratios of LCP/PET are indicated in the figure

The tensile modulus increases with increasing extension draw ratio up to about 80 and then tends to level off with extension ratio above 80. The relationship between ultimate tensile strength and extension draw ratio was very similar to that demonstrated in *Figure 4* for the same blend strand. The behaviour that the tensile modulus is apt to saturate at high extension draw ratios has been reported in fibres of several liquid-crystalline copolyesters[18,19].

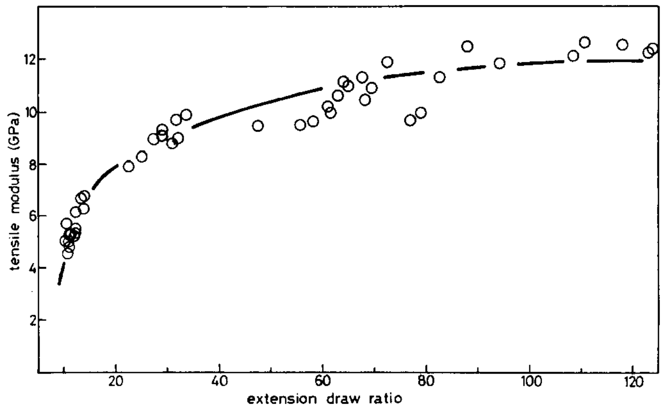


Figure 4 Tensile modulus of strands of LCP/PET 20/80 blend as a function of extension draw ratio

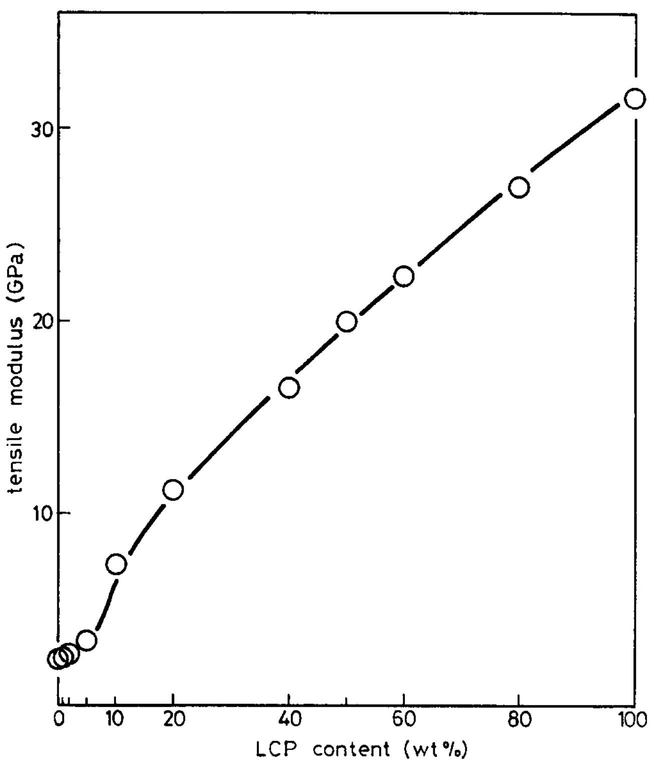


Figure 5 Tensile modulus of strands of LCP/PET blends at an extension draw ratio of 80 as a function of LCP content

Tensile modulus and ultimate tensile strength or yield stress as a function of LCP content are exhibited in *Figures 5* and *6*, respectively, for the blend strands at an extension draw ratio of 80. As shown in *Figure 5*, in the case of the blends with over 10% LCP content, the tensile modulus increases almost linearly with increasing LCP content. The increment in tensile modulus with increasing LCP content, however, is very small for the strands of less than 5% LCP blends. The tensile modulus of the pure PET strand is almost the same value as that of amorphous and unoriented PET reported by Ward *et al.*[20]. As shown in *Figure 6*, the ultimate tensile strength increases with increasing LCP content for more than 10% LCP blends. The strand of the 80% LCP blend, however, indicates that the ultimate tensile strength is nearly equal to that of the 60% LCP blend. If a strand has a defect on which an applied stress concentrates, the ultimate tensile strength of a strand is smaller than that of a strand containing no defects. Many of the defects mentioned above may be involved in the strand of the 80% LCP blend. The yield stress tends to increase with increasing LCP content for the strands of less than 5% LCP blends, but the increment is much smaller than that in ultimate tensile strength for more than 10% LCP blends.

In order to investigate in detail the mechanical tensile properties for the blends with lower LCP content, *Figure 7* illustrates tensile modulus, ultimate tensile strength or yield strength, and elongation for the strands of less than 20% LCP blends. In this figure, the elongation for less than 5% LCP blends and the pure PET corresponds to a strain at a point of the yield strength. *Figure 7* indicates that the tensile modulus and the yield strength of less than 5% LCP blends are very close to those of the pure PET. The elongation at the yield point tends to decrease a little with increasing LCP content. The results of tensile testing mentioned above imply that the LCP component in the LCP/PET blends with less than 5% LCP content hardly contributes to the improvement of the mechanical tensile properties of amorphous and unoriented PET. Wide-angle X-ray diffraction patterns of the strands of less than 5% LCP blends after necking showed that the PET phase in the blends has an oriented structure. Investigation of mechanical tensile properties for the blends containing the PET phase oriented by drawing at room temperature is now in progress.

Structural properties

SEM micrographs of surfaces fractured by tensile

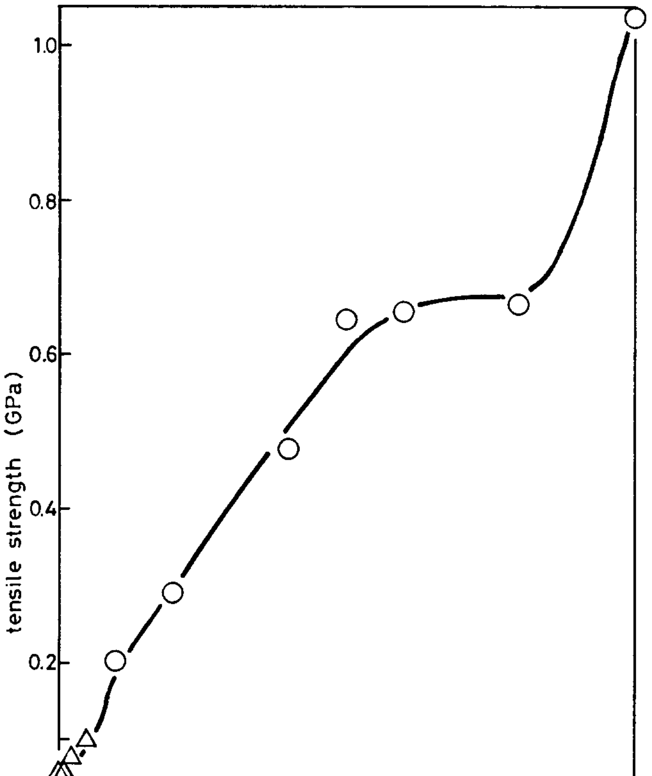


Figure 6 Ultimate tensile strength (○) or yield strength (△) of strands of LCP/PET blends at an extension draw ratio of 80 as a function of LCP content

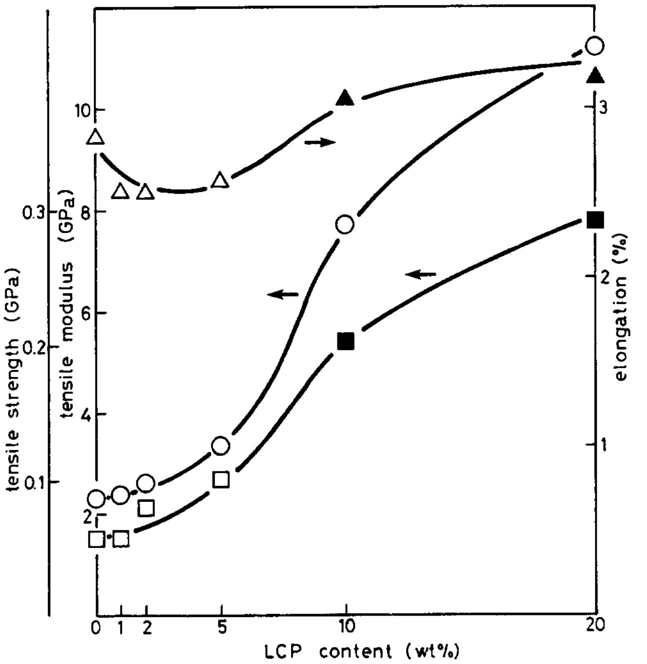
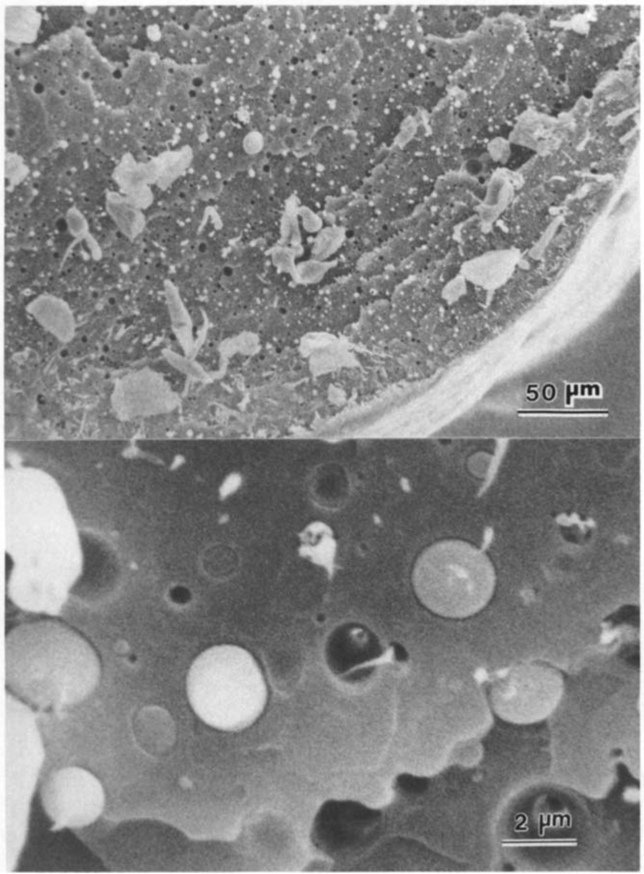
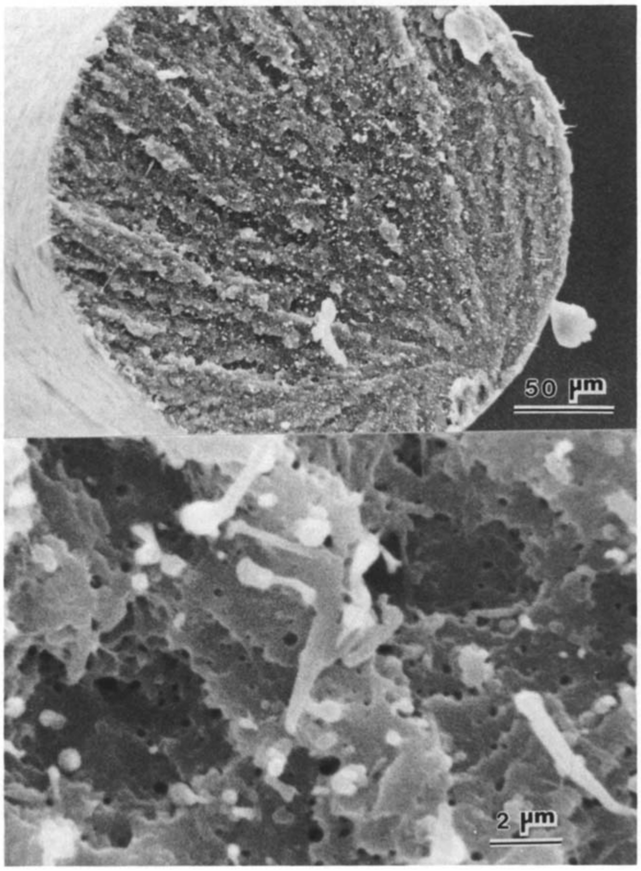


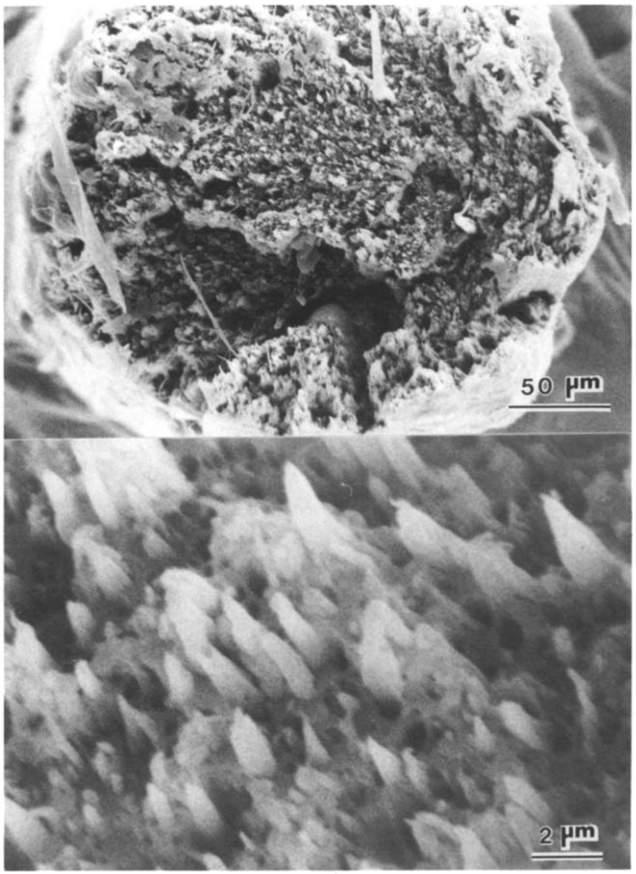
Figure 7 Tensile modulus (○), ultimate tensile strength (■), yield strength (□), elongation at break (▲) and elongation at yielding (△) of strands at an extension draw ratio of 80 as a function of LCP content



(a)



(b)



(c)

Figure 8 SEM micrographs of surfaces fractured with tensile testing for strands of LCP/PET blends. Ratios of LCP/PET are: (a) and (b) 20/80, and (c) 50/50. Extension draw ratios of the strands are: (a) 10, and (b) and (c) 80. The upper and lower pictures of each figure show low- and high-magnification micrographs, respectively

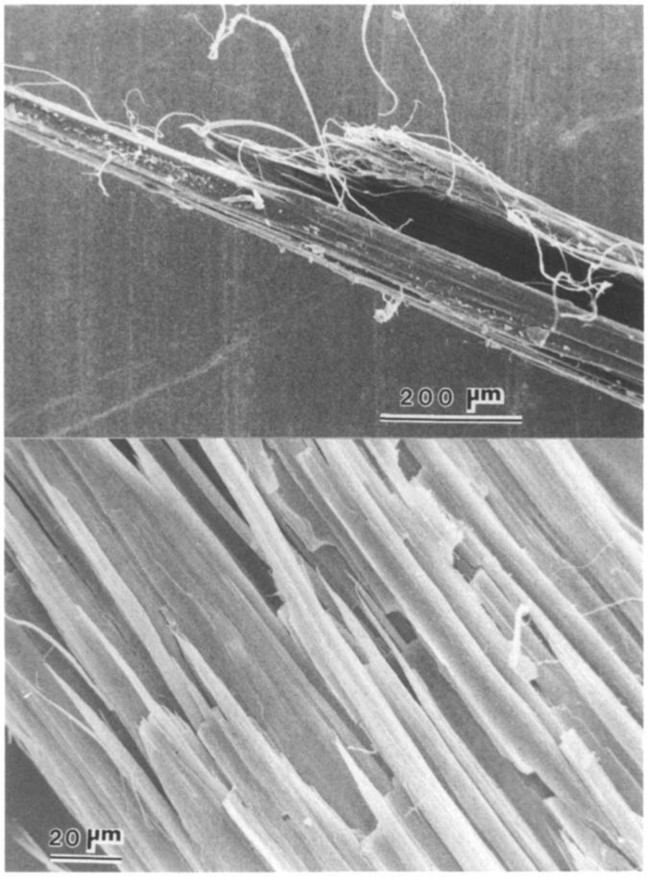


Figure 9 SEM micrograph of a strand of LCP/PET 80/20 blend fractured with tensile testing. The extension draw ratio of the strand is 80. The upper and lower pictures of the figure show low- and high-magnification micrographs, respectively

testing are displayed in *Figure 8* for the strands of the blends with 20% and 50% LCP content. Brittle failure was characteristic of the strands of blends containing LCP content in the range of 10% to 60%. The fracture surfaces shown in *Figure 8* are almost perpendicular to the direction of extrusion. Fibril-like structures of less than 1 μm in diameter are observed in the fracture surfaces in the high-magnification pictures of *Figure 8*. The fracture surfaces of the 20% LCP blend (*Figures 8a* and *8b*) have fewer fibrous structures and are flatter, compared with those of the 50% LCP blend (*Figure 8c*). According to the results of the wide-angle X-ray diffraction patterns described already, the LCP phase in the blends can be believed to form fibrous structures. Therefore, SEM micrographs of the strands of LCP/PET blends indicate that fibrous structures of the LCP phase disperse in a matrix of the amorphous and unoriented PET phase and play a role as a reinforcement. Fibrillization of the LCP phase in the PET matrix is influenced by an extension draw ratio of the strands. As the extension draw ratio increases, the diameter and the orientation of LCP fibrils become smaller and higher, respectively. On the other hand, as the extension draw ratio decreases, the diameter of LCP fibrils becomes larger (*Figure 8a*). In particular, in the case of the strands of blends with low LCP content and small extension draw ratios, a lot of elliptical or spherical structures of the LCP component were observed in the fracture surfaces. Orientation of these strands is very poor, as shown in *Figure 2*. Most LCP component formed elliptical or spherical structures in a sheet of the 20% LCP blend, as reported in a previous paper[15].

Figure 9 shows a SEM micrograph of a strand of the blend with 80% LCP content fractured by tensile testing. As this micrograph indicates that fibrous structures in the strand of the blend are individually broken at separate points, it corresponds to the tensile behaviour of the strand showing a serrated stress–strain curve mentioned in the section on 'Mechanical tensile properties'. Pronounced fibrillization occurred with breaking in tensile testing of the pure LCP strand.

DISCUSSION

The blend strands obtained in this work involve an amorphous and unoriented PET phase as the matrix, and a crystalline and oriented LCP phase as reinforcement. In most cases, the LCP component forms fibrous structures. It is well known that the Tsai–Halpin equation can explain the relationship between modulus and volume fraction of reinforcing species for transversely isotropic composite materials[21]. The equations are[21]:

$$E = E_{\mathrm{m}} \frac{1 + \zeta \eta V_{\mathrm{f}}}{1 + \eta V_{\mathrm{f}}} \qquad (1)$$

with

$$\eta = \frac{E_{\mathrm{f}}/E_{\mathrm{m}} - 1}{E_{\mathrm{f}}/E_{\mathrm{m}} - \zeta} \qquad \zeta = 2(L/D)$$

where E is composite modulus in the fibre direction, E_{m} is modulus of the matrix, E_{f} is modulus of reinforcing fibres, V_{f} is volume fraction of reinforcing fibres, L is length of reinforcing fibres and D is diameter of reinforcing fibres.

If the aspect ratio, L/D, is infinite, equation (1) yields the following:

$$E = (1 - V_{\mathrm{f}})E_{\mathrm{m}} + V_{\mathrm{f}}E_{\mathrm{f}} \qquad (2)$$

This equation shows the well known rule of mixtures for the modulus of composites. The modulus (E) calculated with equation (1) is plotted against volume fraction of fibres (V_{f}) for three kinds of aspect ratio in *Figure 10*, using $E_{\mathrm{m}} = 2.5$ GPa and $E_{\mathrm{f}} = 33$ GPa obtained in this work. *Figure 10* demonstrates that the relation between E and V_{f} becomes closer to equation (2) with increasing aspect ratio.

The relation between tensile modulus and LCP content was based on the weight fraction of LCP in this work, as shown in *Figure 5*. However, we can obtain a similar curve to that shown in *Figure 5* if the weight fraction of LCP is converted into a volume fraction, because the densities of both LCP and PET used in this work were in the range of 1.33 to 1.40 $\mathrm{g\,cm^{-3}}$. Compared with the theoretical curves displayed in *Figure 10*, the curve shown in *Figure 5* for the blends with over 10% LCP content is slightly different from that based on equation (2). The tensile moduli for the blends with over 10% LCP content are a little higher than those based on the rule of mixtures. On the other hand, the curve for the blends with less than 5% LCP content is similar to that based on equation (1) having smaller aspect ratios. The SEM observation of fractured surfaces for strands at an identical extension draw ratio indicated that the thickness of fibrous structures of the LCP component hardly depends on LCP content in the blends. Moreover, as described in

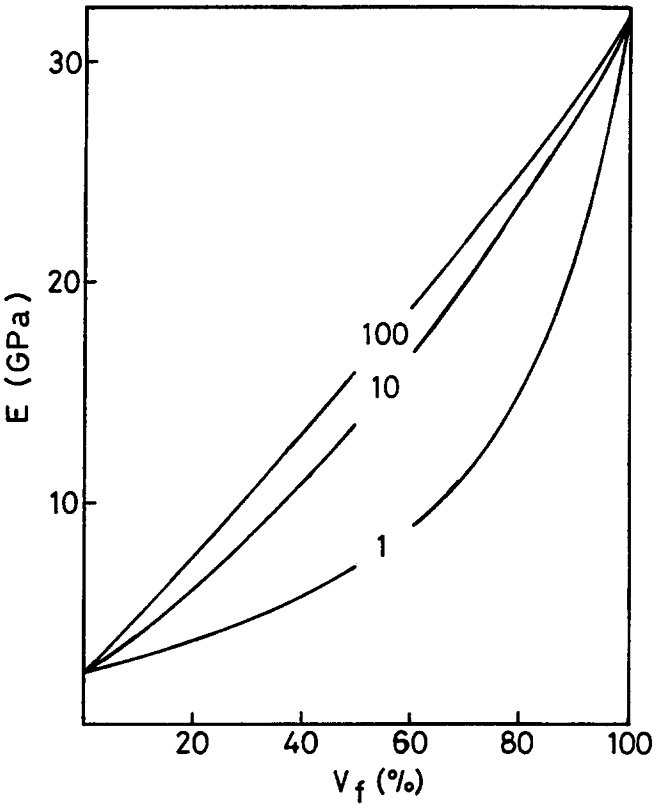


Figure 10 Modulus (E) of fibre-reinforced composite as a function of fibre content (V_f), which is calculated using equation (1). Numbers indicated in the figure show the aspect ratio

the section on 'Structural properties', the blends with lower LCP content have frequently elliptical or spherical structures of the LCP component. Probably, the results mentioned above suggest that the LCP component forms longer fibrils for more than 10% LCP blends and shorter fibrils and elliptical or spherical structures for less than 5% LCP blends. The LCP component in the blends with lower LCP content may be difficult to shape into continuous long fibrils.

In addition to the morphological feature described above, less than 5% LCP blends contain a large amount of continuous PET phase being amorphous and unoriented. Possibly, these cause the strands of these blends to show necking in tensile testing as illustrated in *Figure 3* for the pure PET strand.

As shown in *Figure 6*, the ultimate tensile strength of the strand of the 80% LCP blend is very close to that of the strand of the 60% LCP blend. The result of SEM observation suggests that the PET component in the 80% LCP blend prevents the LCP phase from forming uniform and long fibrous structures and acts as defects at the breaking point in tensile testing. The effective area for tensile stress in the cross section of the strand of the 80% LCP blend may be comparable with that of the 60% LCP blend.

CONCLUSIONS

Extruded strands of blends containing a rigid-chain thermotropic liquid-crystalline copolyester (LCP) with PET consist of a crystalline and oriented LCP phase and an amorphous and unoriented PET phase. Mechanical tensile properties of strands of the blends are dependent upon LCP content and extension draw ratio. These factors also have an effect on morphology of the LCP phase in the blends. The LCP component in the blends shows poor orientation and forms thick fibrils and elliptical or spherical structures for the strands at low extension draw ratios. As the extension draw ratio increases, fibrils of the LCP component become thinner and more uniform. At high extension draw ratios, the LCP component distinctly contributes to the improvement of the tensile modulus and the ultimate tensile strength of the strands of blends with over 10% LCP content. The mechanical tensile properties for the strands of the blends with less than 5% LCP content are close to those for the pure PET strand.

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