Thermotropic liquid-crystalline polymers with flexible moieties blended with poly(ethylene terephthalate)

Scott L. Joslin*, Reiner Giesa† and Richard J. Farris‡
Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA
(Received 9 January 1993; revised 10 March 1994)

Several novel thermotropic liquid-crystalline polymers (TLCPs) were blended with poly(ethylene terephthalate) (PET) and spun into fibres in an effort to improve fibre performance and processability. The TLCPs were screened to determine the optimal molecular architecture for fibre enhancement and compatibilty. At concentrations up to 20 wt%, blends of the block copolymers PME-*b*-PET and PME-*b*-PBT (PME = poly(ethoxy 1,4-phenylene terephthalate), PBT = poly(butylene terephthalate)) with PET showed minor improvements in modulus. Another TLCP, PBEM (poly(butoxyethoxy 1,4-phenylene terephthalate)), proved to be an excellent processing aid for PET, since it reduced the melt viscosity of PET by approximately 75% at a concentration of only 2.5 wt%. The third class of TLCP investigated was a 'Random Copolymer' system. At a concentration of only 5 wt%, this blend exhibited a 50% modulus improvement (25 GPa) and an equivalent ultimate strength (1100 MPa) compared to neat PET fibres. SEM experiments exposed TLCP fibrils uniformly dispersed within the PET matrix with aspect ratios ranging between 20 and 200. The thermal stability of these fibres was similar to the PET control.

(Keywords: blends; poly(ethylene terephthalate) fibres; thermotropic liquid-crystalline polymers)

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibres are used in a variety of applications including textiles, tyre cord and composites. Depending upon the final application, the properties of the fibre can be tailored by adjusting processing parameters such as molecular weight, spinning speed, draw ratio and drawing temperature. However, the demand for higher-performance PET is continually increasing owing to more stringent product requirements. Recently, the production of PET fibre with greater moduli, strength and dimensional stability has been the subject of intense research[1-5]. These studies have focused on structurally modifying PET fibres by mechanical and/or thermal treatments. Another approach that has not received much attention would be to blend PET with a high-performance thermotropic liquid-crystalline polymer (TLCP).

TLCPs offer a range of potential benefits such as high strength and stiffness, low viscosity and low thermal expansion. Several investigators have been able to improve the stiffness and dimensional stability of extruded and injection-moulded articles simply by incorporating low concentrations of a TLCP material. These performance enhancements have been attributed to *in situ* reinforcement of the engineering thermoplastic matrices by an oriented TLCP phase[6-10]. The moduli of the extruded and injection-moulded systems, containing 10 to 20 wt% TLCP, were typically reported to be in the range of 5 to 12 GPa. This stiffness increase is considerable since the modulus of amorphous PET is only about 2 GPa. However, these modulus values are not sufficient to improve upon the mechanical performance of PET fibres. The tensile modulus of high-molecular-weight PET fibres can attain values in the range of 14–17 GPa just by carrying out cold and/or hot drawing post-treatments. Therefore, in order to apply the concept of *in situ* reinforcement successfully to PET fibre spinning, the TLCP material must demonstrate the ability to reinforce a high-performance matrix material. If successful, PET fibres blended with a TLCP could have greater mechanical performance and thermal stability than currently obtainable with neat PET. Furthermore, owing to their low melt viscosity, TLCPs may function as a processing aid[11-13] permitting higher-molecular-weight PET to be processed.

A potential disadvantage associated with blending commercial TLCPs with engineering thermoplastics is that the majority of the thermoplastics investigated have been found to be incompatible with TLCP reinforcing agents. This incompatibility has resulted in matrix embrittlement, skin–core morphologies and poor interfacial adhesion between the blend components at low to moderate TLCP loading levels[14-16]. PET embrittlement by the addition of a TLCP would be catastrophic since PET fibres must undergo significant drawing to attain maximum performance. Thus in order for this approach

---

* Present address: Motorola Corp, 1500 Gateway Blvd, Boynton Beach, FL 33426-8292, USA

† Present address. Materials Dept, University of California, Santa Barbara, CA 93106, USA

‡ To whom correspondence should be addressed

0032-3861/94/20/4303-10

to be successful, the TLCP must improve the performance of PET fibres at low concentrations without embrittlement. This would allow post-treatment of the fibres and maximize cost effectiveness, since the expensive TLCP would be used in small quantities.

The objective of this study was to determine if properties superior to those of neat PET fibres could be achieved by blending with novel liquid-crystalline polyesters. The following TLCP architectures have been investigated: (1) mesogenic copolymers containing either alternating or random flexible units and (2) rigid rods with flexible side groups. The incorporation of flexible units into the TLCPs should promote compatibility between the PET and the TLCPs. Compatibility for this study is defined as a post-treatable fibre with enhanced performance characteristics. Miscibility is not desired since a two-phase morphology is regarded as necessary in order to obtain the processing and mechanical benefits associated with TLCPs.

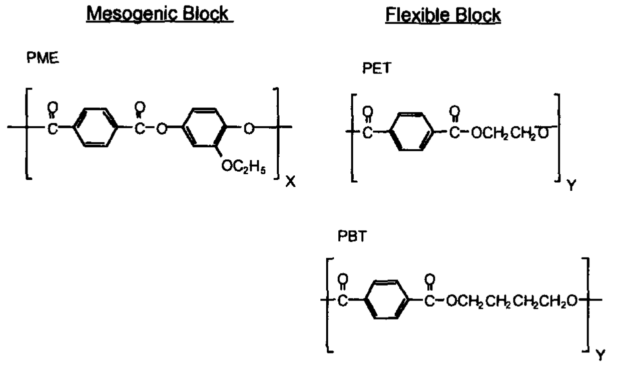
Owing to a limited amount of the TLCPs, a screening procedure has been developed to determine if a blend system exhibits desirable characteristics. Systems containing low to moderate concentrations of TLCP are commercially appealing because the synthesis of TLCPs is typically quite costly. Thus evaluations focused on compositions varying from 5 to 20 wt% TLCP. Fibres were prepared by melt extrusion followed by cold and hot drawing. Fibre performance was evaluated based on tensile properties, dimensional instability (shrinkage) and the development of shrinkage stresses.

EXPERIMENTAL

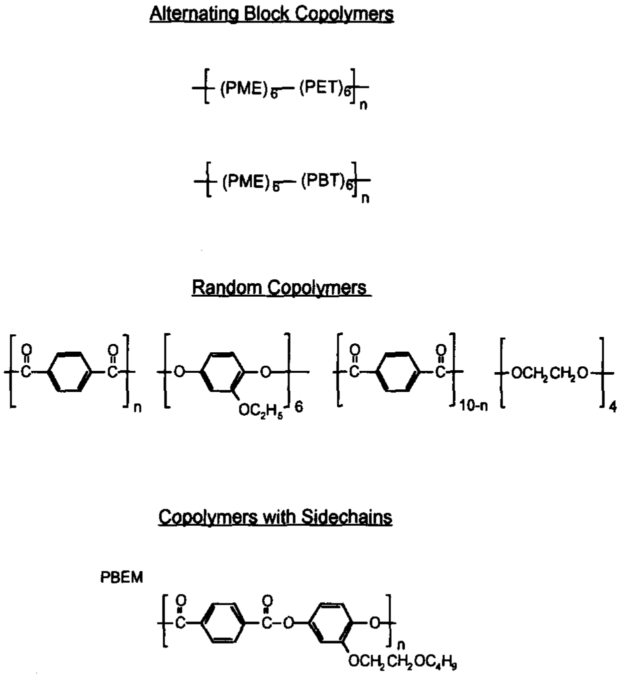
Materials

The thermotropic LCPs used in this study are a group of novel polymers developed at the University of Massachusetts, Amherst. Their synthesis and characterization are the subjects of separate publications[17]. The polymers have been specifically designed in an effort to enhance compatibility between the TLCPs and PET. The following structural approaches have been investigated: (1) block copolymers consisting of rigid-rod and flexible-coil segments and (2) a copolymer composed of a rigid-rod backbone with flexible oligomers as side chains.

Two alternating block copolymers have been investigated[17]. These systems have poly(ethoxy 1,4-phenylene terephthalate) (PME) mesogenic units with either poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) flexible segments incorporated into the main chain. *Scheme 1* shows the rigid-rod and flexible segments used in these block copolymers. The oxyethylene substituents incorporated into the mesogenic unit should lead to polar interactions with the ester linkages of the matrix polymer, promoting compatibility. The PET or PBT flexible segments in the main chain should also enhance compatibility with the PET matrix.



Scheme 1



Scheme 2

The flexible PBT units are not identical in architecture to the matrix polymer, but PBT is miscible with PET[18]. Furthermore, the PBT block may also act as a nucleating agent for the PET matrix, since PBT and PET do not co-crystallize[19]. Thus flexible PBT segments should be a suitable candidate for attaining compatibility with a PET matrix. Ultimately it is hoped that compatibility can be improved by incorporating a flexible block in the main chain, whether it be PET or PBT. *Scheme 2* shows the polymer designations and structures selected to blend with PET for this investigation.

A random block copolymer has also been investigated. The copolymer was prepared by the reaction of oxyethylene-substituted hydroquinone, ethylene glycol and terephthaloyl chloride[20]. The copolymer incorporated a 60:40 ratio of oxyethylene-substituted hydroquinone to ethylene glycol. This polymer has flexible side groups and PET moieties randomly distributed along the polymer backbone in an effort to achieve compatibility with the PET matrix. Here, we call it 'Random Copolymer'.

The final polymer, PBEM, has a rigid backbone composed of poly(1,4-phenylene terephthalate) with butoxyethoxy flexible side groups. As in the previous polymers, the flexible side substituents should lead to polar interaction with the ester linkages of the PET matrix. The length of the side substituent was increased since flexible moieties were not incorporated into the main chain.

The amount of material available for blending and property determination was limited to approximately 7 g for each polymer, and thus the mechanical properties of the neat copolymers could not be determined.

The fibre-grade PET used in this study was kindly provided by the Akzo Corp. The material had a reported melting transition of 273°C and an inherent viscosity of $\eta = 2.04\,\mathrm{dl\,g^{-1}}$. The PET was blended as received without further purification.

Fibre formation

Powders of the thermotropic polyesters and PET were tumble mixed for 24 h. The amounts of block copolymer used in the blends were 5, 10 and 20% by weight. The mixed polymer powders were then compression moulded using a Carver laboratory press at 270°C for 1 min. The compressed sample was consequently ground in an analytical mill to a particle size less than 1000 μm, sieved, and vacuum dried at 120°C for a minimum of 24 h. Compression moulding followed by grinding was a convenient procedure for obtaining particles that fed effectively into the mini-extruder.

Once thoroughly dried, the blends were extruded and spun into fibres. Extrusion was carried out with a quarter-inch (~6.3 mm) Randcastle single-screw mini-extruder. The mini-extruder has four temperature zones, which may be varied independently. The feeding, compression and melting sections, zones one, two and three respectively, were set at 220, 260 and 280°C. The temperature of the die zone was varied to observe the effects on fibre spinning. The ability to obtain a uniform melt without die swell was the main criterion for determining the die temperature. The screw speed was held constant at 30 rev min^{-1} corresponding to a flow rate of 1.5 g min^{-1} and a polymer residence time of 2–4 min within the extruder. The residence time in the extruder was kept to a minimum in order to reduce the possibility of transesterification reaction between the blend components.

Upon exiting the die of the extruder, the polymer was stretched using a custom-built take-up device. A take-up speed of 75 m min^{-1} was used for all systems, which corresponds to approximate stretch ratios of 250 to 400. The stretch ratio of each system was determined as the ratio between the die and the stretched extrudate cross-sections (A_0/A_f). The capillary die had a diameter of 1575 μm and an aspect ratio of 10. Fibre diameters were determined by optical microscopy.

A two-step post-treatment process was performed immediately following the spinning process. The heat treatment of PET fibres is an important processing stage that determines the ultimate properties of the material. Post-drawing was accomplished using a continuous process between optoelectronically monitored feed and take-up spools. Cold drawing was performed at 85°C using a standard laboratory hot plate. The speed of the feed spool was kept constant at 5 m min^{-1} while the speed of the take-up winder was continuously monitored and increased until a stable neck was observed. For neat PET this occurred at a draw ratio (*DR*) of 3.5.

Hot drawing was accomplished using a similar procedure at a temperature of 205°C. The maximum draw ratio was determined by slowly increasing the speed of the take-up spool until excessive filament breakage occurred. The speed of the take-up spool was then decreased until drawing could proceed for at least 2 min without filament breakage. For neat PET this corresponded to a maximum hot draw ratio of 1.5 and a total draw ratio of 5 for the fibre. The total draw ratio was calculated as the ratio between the as-spun and final post-treated fibre cross-sectional areas. All samples were collected and tested at the maximum draw ratio unless otherwise specified.

Tensile testing

Tensile tests were performed on an Instron 1113 tensile tester connected to a personal computer. Specimens were affixed to paper tabs with an adhesive in order to facilitate mounting and alignment. Fibre diameters were measured using an Olympus microscope equipped with a calibrated scale accurate to ±0.5 μm. A minimum of five diameter measurements per fibre were obtained. The applied strain rate was 10% elongation per minute, with an initial gauge length of 50 mm. A 550 g Toyo TI550 load cell was used to measure the fibre load. The Young's modulus was determined from the best linear fit through the initial region of the stress–strain curve. Instrument compliance was measured and the apparent modulus was found to be approximately 2% lower than the true modulus. Samples that exhibited grip failure were omitted from the tenacity and ultimate elongation results. Each tensile property was averaged over nine tests and performed at ambient conditions in the laboratory. Standard deviations ranged from 5 to 10%.

Rheological measurements

Steady-state shear flow measurements were performed on a Rheometrics Mechanical Spectrometer (RMS-800) using a parallel-plate geometry. The platens had a radius of 12 mm and a separation distance of 1 mm. Temperatures between 270 and 290°C were investigated at a shear rate of 1 rad s^{-1}. Experiments were performed on ground powders prior to extrusion. All test samples were dried under vacuum at 130°C for 24 h and then fabricated into 24 mm diameter discs by compression moulding at 275°C. Samples were equilibrated at each temperature for 2 min prior to measurements and kept under a continuous dry nitrogen purge.

Thermal characterization

The transition temperatures of the liquid-crystalline block copolymers were measured calorimetrically using a TA Instruments 9900 differential scanning calorimeter. Temperature calibration was performed using an indium standard. Samples of approximately 10 mg were initially heated in a nitrogen atmosphere from 30 to 300°C at a heating rate of 20°C min^{-1}, followed by quenching with liquid nitrogen. Samples were then reheated to 300°C at a heating rate of 20°C min^{-1}. The reported transitions are the maximum peak temperatures observed during the second heating run.

The degradation temperatures in air were also measured using a TA Instruments 951 thermogravimetric analyser. Samples were scanned from room temperature to 600°C at a heating rate of 20°C min^{-1}. The reported degradation temperature corresponds to 0.5% weight loss.

Thermal instability

Shrinkage experiments were performed by placing the fibres in a convection oven preheated to 190°C for 15 min. Prior to heating, the fibres were conditioned for 24 h at 21°C and 68% relative humidity. The sample lengths before and after heating were determined at ambient temperature by straightening the fibres with a small load and measuring the initial (L_0) or final (L_1) length respectively. All samples were approximately 20 cm in length before testing. After removal from the oven, the

Table 1 The thermal characteristics and weight percentage mesogen content for each copolymer (determined by d.s.c., 20°C min^{-1})

	T_m(°C)	LC→LC(°C)	T_d(°C)	Mesogen (wt%)
PME-*b*-PET (6:6)	224	–	300	40
PME-*b*-PBT (6:6)	202	–	334	38
PBEM	236	–	348	67
Rand. Copolym. (6:10:4)	200	267	325	–

fibres were reconditioned at 21°C and 68% relative humidity for 1 h and the resultant dimensional changes determined. The free shrinkage was computed as:

$$\text{shrinkage } (\%) = [(L_0 - L_1)/L_1] \times 100$$

Shrinkage values were averaged over five measurements.

To measure the development of shrinkage stresses, force–temperature experiments were carried out using a TA Instruments thermal mechanical analyser (TMA). This technique applies a constant strain and measures the development of thermal stresses with temperature change. The fibres were placed in the TMA and an initial strain of 0.05% imposed on the samples. The temperature was then increased at 5°C min^{-1} to 190°C and the resultant load monitored. After being held at 190°C for 15 min the fibre was slowly cooled to room temperature and the final shrinkage stresses at 190 and 30°C recorded.

Morphology

The morphology of the blends was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). Fibre cross-sections were prepared by mounting the samples in an epoxy matrix and either fracturing or cryomicrotoming the sample after cooling in liquid nitrogen. All SEM samples were mounted on aluminium stubs, sputtered with gold using an SPE Sputter Coater, and characterized using a JEOL (JSM-35C) scanning electron microscope. An accelerating voltage of 20 kV was used. An Olympus microscope equipped with a Linkam hot stage was used for observing the blends before and after processing.

RESULTS AND DISCUSSION

Thermal behaviour of the TLCPs

The weight percentage rod content and thermal transitions for each of the novel TLCPs are shown in *Table 1*. All of these systems exhibit crystal-to-nematic transitions significantly lower than those of commercially available TLCPs. For instance Vectra®, a TLCP commonly blended with engineering thermoplastics, has a crystal-to-nematic transition at 280°C (ref. 21). Lowering the temperature needed to induce the nematic phase reduces the likelihood of thermal degradation and permits a greater degree of processing flexibility. It is also important that the new TLCPs form anisotropic melts in the temperature range in which PET is melt processed. Many of the processing and mechanical advantages associated with these blends are attributed to the nematic state of the liquid-crystalline component[22–24].

The PBT and PET alternating block copolymers have a single melting transition (T_m) at 202 and 224°C respectively. Above this transition the polymers exhibit a nematic texture until their thermal degradation point. Although these TLCPs have similar chemical structures and rigid-rod contents of approximately 40 wt%, the initial transition points are 22°C different. This behaviour suggests that the non-mesogenic units in these polymers have a significant effect on the thermal behaviour of the block copolymer. This is also apparent when comparing the degradation points of these polymers. The PME-*b*-PET alternating block copolymer had a degradation temperature (T_d) of 300°C in air, which was 34°C lower than for the PME-*b*-PBT system. The large difference is probably due to a higher end-group concentration in the PME-*b*-PET sample since PET should be thermally stable.

Compared to the alternating block copolymers, the PBEM liquid-crystalline polymer has a higher rod content, i.e. 67 wt%. Consequently this material had a higher initial transition (T_m) and degradation temperature (T_d), i.e. 236°C and 348°C respectively. The polymer did not exhibit an isotropic phase prior to decomposition. A large nematic window, approximately 100°C, permits a wide range of processing conditions and applications to be studied. Thus blends can be processed under conditions that are optimum for the matrix component while remaining within the nematic regime of the TLCP.

The Random Copolymer had the lowest initial transition (T_m) at 200°C. Above this transition, optical microscopy revealed a highly birefringent dense nematic thread texture (see *Figure 1a*). This texture was stable until 267°C, when the polymer exhibited a liquid-crystal to liquid-crystal transition (LC→LC). Above this transi-

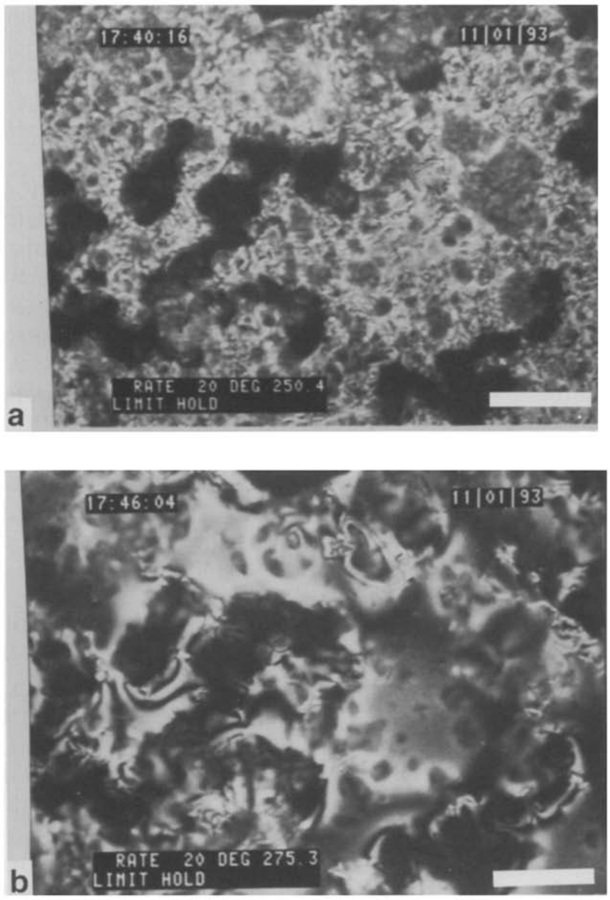


Figure 1 The Random Copolymer dense nematic thread texture (a) following melting at 200°C and (b) following the LC→LC transition at 267°C (scale bars = 0.1 mm)

Table 2 Tensile properties for blends containing 5, 10 and 20 wt% TLCP (take-up speed 75 m min^{-1}, hot drawn at 205°C)

	Modulus (GPa)	Ultimate strength (MPa)	Ultimate strain (%)
PET control	17	1100	9
5% PME-*b*-PET/PET	19	1100	6
10%	20	1000	7
20%	20	700	5
5% PME-*b*-PBT/PET	18	1100	7
10%	19	1100	7
20%	20	920	7
5% PBEM/PET	19	1100	7
10%	18	1000	8
20%	13	600	20
5% Rand. Copolym./PET	25	1100	7

tion the Random Copolymer formed a loose nematic texture as shown in *Figure 1b*. Corresponding to the change in thread texture was a dramatic decrease in the viscosity of the material. Although the decrease in viscosity has not been quantified by rheological measurements, the difference in flow characteristics was clearly apparent under the optical microscope. The Random Copolymer was also thermally stable and did not degrade in air until 325°C (T_d). The complex phase behaviour of this TLCP is not the subject of this study; however, it is known that TLCPs with a similar mesogenic group can exhibit a cybotactic mesophase[25,26].

Blends with PME-b-PET and PME-b-PBT block copolymers

Table 2 is a summary of the post-treated fibre tensile properties for blends containing 5, 10 and 20 wt% of the novel TLCPs. The PET control, spun using a die temperature of 280°C, had a modulus of 17 GPa, an ultimate strength of 1100 MPa and 9% strain to break. These are excellent numbers for PET fibres, indicating that the spinning and post-treatment processes were sufficiently optimized.

The tensile properties of the PME-*b*-PBT and PME-*b*-PET blends exhibited only minor differences compared to the PET control. Varying the TLCP concentration from 5 to 20% did not significantly influence the modulus characteristics of either system, although the PME-*b*-PBT system does indicate a gradual improvement in modulus with concentration. At 20 wt% TLCP the strength of the fibres was significantly less than that of neat PET for both systems. However, this was not as disappointing as the modulus observations. The ultimate strength and strain to break are not considered crucial when evaluating these materials as potential reinforcing agents for PET. These properties may be influenced by many factors, such as the number of fibre defects and molecular weight of the TLCPs. Variables such as these are difficult to optimize when screening many different systems with very small quantities of material. Thus the major criterion for determining a system's effectiveness at this juncture is the fibre modulus, since this quantity is less sensitive to processing variables.

Processing of the PME-*b*-PET blends was difficult owing to degradation of the block copolymer. The fibres were processed using a die temperature of 280°C, which is 20°C lower than the degradation point as determined by t.g.a., but gas bubbles were still readily apparent in the fibre during spinning. This degradation may be responsible for the large drop in tensile strength at 20% TLCP concentration for this system. The PME-*b*-PBT block copolymer was processable without visible degradation at all concentrations, but significant modulus or strength improvements were not obtained. However, the 10 and 20% fibre blends were stronger than the corresponding PME-*b*-PET systems. Thus the PBT units increased the thermal stability of the block copolymer without inducing compatibility problems.

Large improvements in mechanical performance were not observed, but processability of the PME-*b*-PBT blends was good and large-scale phase separation was absent. These results indicate that the block copolymer provided some compatibility with the PET matrix, but the incorporation of 50% flexible moieties may have excessively limited the stiffness of the copolymer. In order for an LCP to mechanically improve drawn PET, it should have a modulus significantly greater than 17 GPa. This may require block copolymers to have smaller flexible blocks in order to provide a sufficient modulus for reinforcement of the PET.

Blends with PBEM

Although PBEM has a higher rod content than the alternating block copolymers, it still did not significantly reinforce the PET fibres. At lower loading levels, 5 and 10 wt%, the blends exhibited minor improvements in modulus, 18 and 19 GPA respectively. The strength of the 5% system was equivalent to the PET control, 1100 MPa, but the 10% blend showed a 100 MPa reduction in strength. The 20% blend had a significantly lower modulus and strength, 13 GPa and 600 MPa respectively. As indicated by their high ultimate strain, 20%, these fibres could not be post-treated effectively due to defects and frequent fibre breakage.

Observation of the 20% as-spun PBEM fibre under the optical microscope indicated a skin–core morphology (see *Figure 2a*). Cracks in the liquid-crystalline skin are visible in the fibre at a magnification of 200, but become more apparent when examined under crossed polarizers, as shown in *Figure 2b*. The highly birefringent skin surrounds a less oriented core. The cracks in the skin region may be the result of a large amount of stretching during the spinning process or thermal expansion differences between the components as the fibre cooled. During post-treatment the skin region becomes increasingly damaged, with large sections lost during the hot drawing step. The final post-treated fibre contained a large number of defects due to inefficient drawing, which ultimately resulted in the poor tensile properties.

The development of a skin–core morphology is generally observed when the viscosity ratio of the matrix polymer to the dispersed phase is large[24]. The low-viscosity liquid crystal migrates to the surface, forming an LCP-rich skin region. These observations indicated the PBEM may have potential applications as a processing aid for PET. Blending a low-viscosity LCP with an isotropic polymer often decreases the viscosity of the isotropic polymer. The lower viscosities of these blend systems allow them to be processed more easily than the neat thermoplastic.

The steady shear viscosities for blends containing 2.5, 5 and 10 wt% PBEM show almost a 75% reduction in viscosity compared to the PET control at 270°C (see

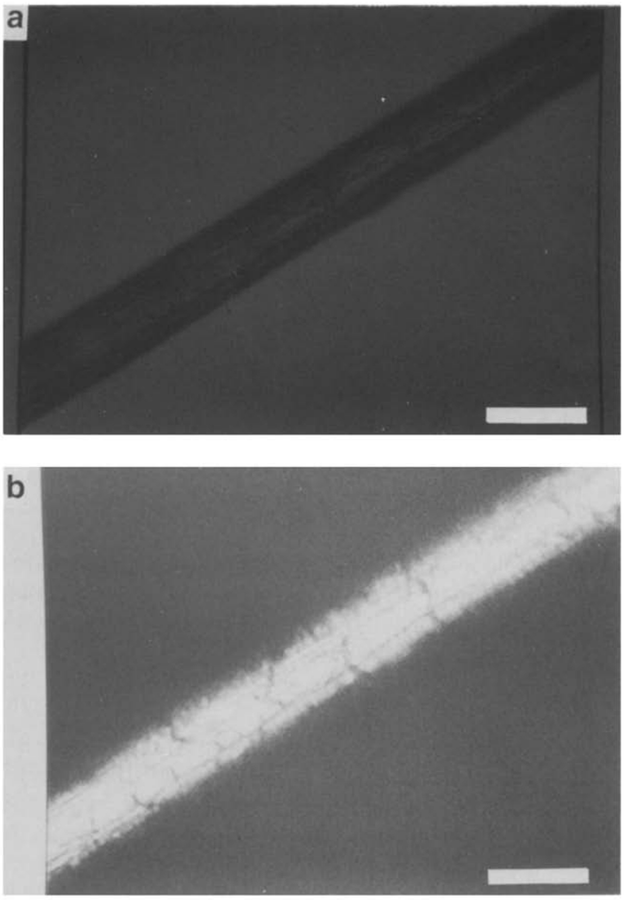


Figure 2 (a) Optical micrograph of the 20% PBEM fibre exhibiting a skin–core morphology and (b) with crossed polarizers (scale bars =0.1 mm)

Figure 3). Viscosity reduction in the blends appears to be independent of TLCP concentration, i.e. the 2.5% blend was just as effective as the 10% blend at lowering the viscosity of the PET. This indicates that the reduction mechanism may be a surface phenomenon, since it is unlikely that a bulk effect would be concentration-independent. Immiscibility of the two components combined with a high viscosity difference could promote the formation of a surface region rich in PBEM reducing the measured viscosity. The extent of the concentration independence is unknown since blends containing less than 2.5 wt% PBEM have not been investigated. This experiment was performed at a shear rate of 1 rad s^{-1}, which is significantly lower than that experienced under practical processing conditions; however, most investigators have observed improved viscosity reduction at higher shear rates[11,27–30].

Increasing the temperature of the rheometer to 290°C reduced the magnitude of the viscosity difference between the blends and the PET control, but the systems were still concentration-independent. Thus adding a small percentage of PBEM to PET could permit processing at lower temperatures without hurting fibre performance. As shown previously, the tensile properties of the 5 wt% blend were equivalent or slightly improved compared to those of neat PET. Reducing the processing temperature to 270°C or lower would decrease the threat of polymer degradation and save energy. The spinning of higher-molecular-weight PET may also be possible.

Blends with the 'Random Copolymer'

Fibre containing 5% of the Random Copolymer had the best mechanical performance. The post-treated 5% Random Copolymer blend had a 25 GPa modulus, an 1100 MPa ultimate strength, and 7% strain to break. This corresponds to a 50% increase in fibre stiffness with no change in ultimate strength compared to the PET control. The strain to break was decreased slightly from 9 to 7%, but this was not considered significant. A blend containing 10% Random Copolymer was spun but the fibres were intractable during the post-treatment process. Owing to the problems associated with processing the 10% system, a 20% blend was not attempted.

Although the systems became intractable at the higher loading levels, the modulus improvement in the 5% system was impressive. Assuming the fibre contained 95 vol% PET, a rule-of-mixtures relationship would imply that the Random Copolymer has a modulus of approximately 175 GPa. This was surprising and unlikely since it is approximately 25 GPa greater than stiffness values obtained for heat-treated aramid poly(*p*-phenylene terephthalamide) (PPTA) fibres (125 GPa). The modulus of the Random Copolymer should be lower than those of the all-aromatic aramids since flexible moieties were incorporated into the main chain.

Several investigators have shown mechanical reinforcement of extruded or injection-moulded PET using the commercial TLCP Vectra[31–33]. If the Random Copolymer had a modulus of 175 GPa, dramatic improvements in the as-spun moduli would also be expected, since as-spun PET only has a modulus of 2 GPa. The as-spun moduli for fibre blends containing 2, 5, 6, 8 and 10 wt% Random Copolymer are shown in *Figure 4*. These data show a gradual improvement in blend modulus from 2 to 3 GPa as the loading level was increased from 2 to 6%. Above 6% a plateau is observed and the blend moduli remained constant as the LCP concentration was increased to 10%. Thus the Random Copolymer does not appear to mechanically reinforce as-spun PET significantly, particularly when compared to the post-treated samples. These results indicate the Random Copolymer either modified the behaviour of the PET matrix in some fashion or was itself dramatically improved by the post-treatment process. For instance, if the LCP induced an increase in PET orientation or crystallinity during

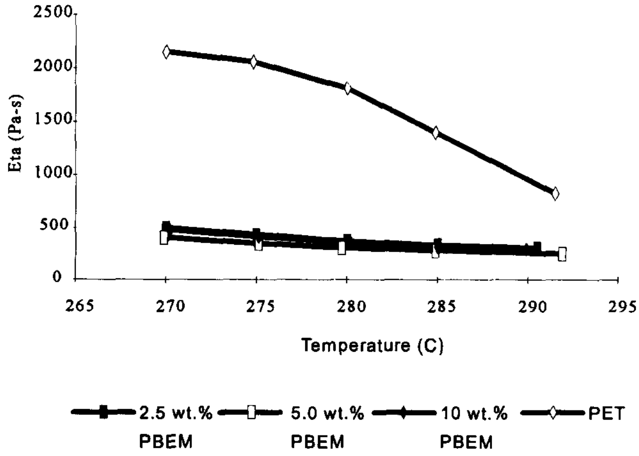


Figure 3 Steady shear viscosities of the PBEM blends as a function of LCP content and temperature (parallel plates, $\omega = 1$ rad s^{-1}, under N_2)

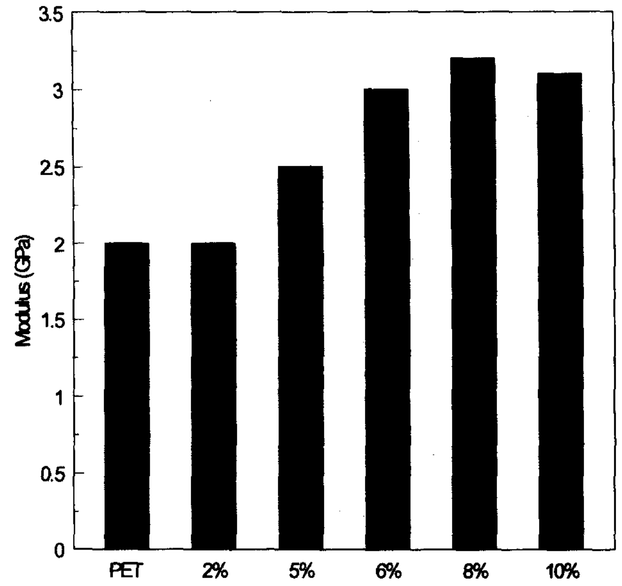


Figure 4 As-spun moduli for the Random Copolymer blends as a function of concentration (die temperature 290°C, take-up speed 75 m min^{-1})

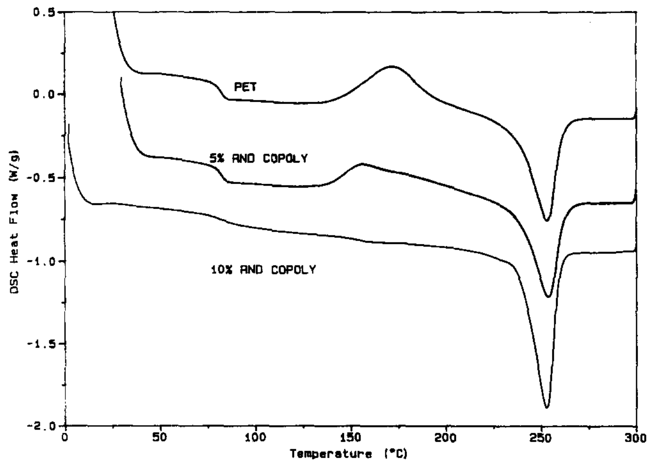


Figure 5 D.s.c. heating scans as a function of Random Copolymer concentration (fibres as-spun, die temperature 290°C, heating rate 20°C min^{-1} after quenching)

post-treatment, an improvement in performance could be obtained strictly on the basis of an enhanced matrix. Conversely if the drawing performed during post-treatment increased the aspect ratio and orientation of the LCP, the improved properties may have permitted mechanical reinforcement of the fibre.

D.s.c. heating scans were performed on the powders prior to extrusion. The samples were heated to 300°C to remove any prior thermal history and quenched with liquid nitrogen. The results of the second heating runs for the 5 and 10% Random Copolymer blends are compared to a PET control in *Figure 5*. *Table 3* gives the relevant numerical data. The heats of fusion and crystallization for the blends have been normalized with respect to PET content.

The blends show significant deviations from the PET control. The PET control had a T_g of 82°C while the 5 and 10% blends had T_g values of 83 and 81°C respectively. The T_g values of the blend systems are essentially identical to that of the PET control, indicating either that the Random Copolymer has a similar glass transition temperature or that little or no interaction has occurred between the two materials. However, the most dramatic differences are observed in the cold crystallization and melting transitions. The PET control had a cold crystallization peak at 171°C with a heat of crystallization of 23 J g^{-1}. This transition was shifted down to 157°C in the 5% system and the heat of crystallization was reduced to 16 J g^{-1}. This effect was more pronounced for the 10% system, which did not exhibit any cold crystallization prior to melting. Thus the Random Copolymer was able to induce a significant amount of crystallization during the quench, indicating that it is an efficient nucleating agent for PET. The ability for LCPs to perform as nucleating agents has been observed in several other systems[23]. In addition to the absence of cold crystallization, the 10% system had a heat of fusion of 38 J g^{-1} compared to 29 J g^{-1} for the PET control. Thus the LCP may have also increased the overall amount of PET crystallinity. This is an important observation because an increase in the amount of fibre crystallinity could result in improved performance.

The ability to post-treat the Random Copolymer blends varied depending on the concentration of LCP incorporated. The results are shown in *Figure 6*. The 2% system could be drawn easily but the tensile properties were identical to the PET control except for a 100 MPa

Table 3 Numerical data determined from d.s.c. measurements of PET blend systems (d.s.c., 20°C min^{-1})

	T_g (°C)	T_c (°C)	H_c (J g^{-1})	T_m (°C)	H_m (J g^{-1})
PET	82	171	23	253	29
5% Rand. Copolym.	83	157	16	254	33
10% Rand. Copolym.	81	–	–	253	38

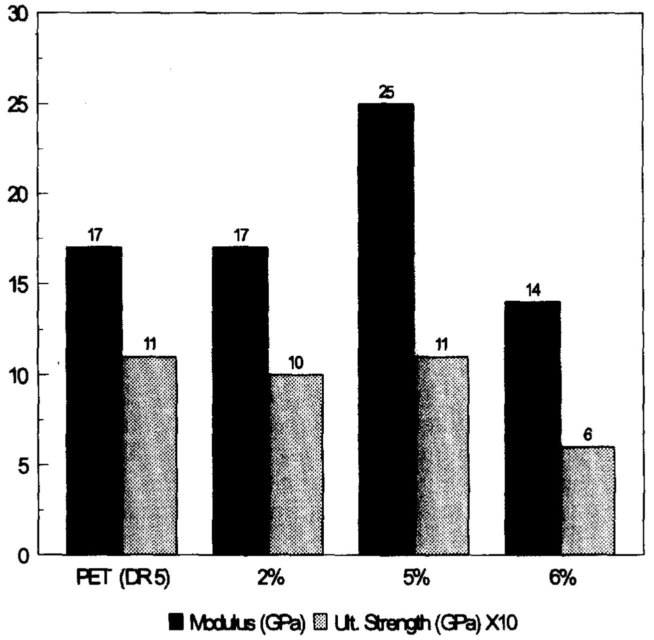


Figure 6 Post-treated tensile performance of the Random Copolymer blends as a function of concentration (take-up speed 75 m min^{-1}, hot drawn at 205°C)

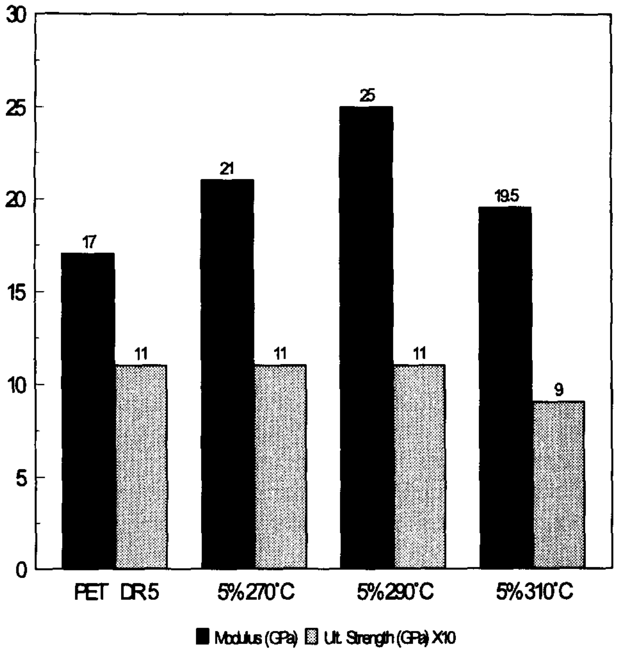


Figure 7 Tensile performance of the 5% Random Copolymer/PET system as a function of the die zone processing temperature (take-up speed 75 m min^{-1})

reduction in strength. The 5% system was also easily drawn, yielding significant enhancement as discussed previously, while the 6% system could only be drawn with difficulty. After cold drawing, the 6% system had a significant number of defects preventing a continuous hot drawing process. These fibres had to be hot drawn by hand and the resultant tensile performance was significantly lower than for the PET control. Results for the 8 and 10% systems are not available since it was not possible to post-treat these blends without fibre breakage.

These results indicate that it is unlikely that the orientation and aspect ratio of the Random Copolymer phase could be improved during drawing steps. If significant deformation of the LCP were possible in the 5% blend, deformation should also occur at higher concentrations, which was clearly not possible. Furthermore the Random Copolymer has shown the ability to affect the crystallization behaviour of PET. Thus it is reasonable to suggest that the LCP could be modifying the PET matrix in the fibres. Increasing the amount of PET crystallinity that develops during drawing could improve the tensile behaviour of the fibre. This phenomenon could also be concentration-dependent since the extent of PET modification could be determined by the amount, the orientation, or the domain size of the copolymer phase within the fibre[34]. Thus a critical LCP loading level may be necessary before modification of the PET is sufficient to improve performance. In addition, higher loading levels could increase the LCP domain size or induce premature crystallization of the PET matrix, preventing efficient drawing behaviour.

Owing to the interesting phase behaviour of the Random Copolymer and the property enhancements obtained with the 5% system, the spinning of this blend was investigated in further detail. An evaluation of three different die zone temperature settings can be seen in *Figure 7*. All of these systems exhibited higher moduli values compared to the PET control, but the fibres spun at 290°C showed the greatest improvement, attaining a modulus of 25 GPa with no decrease in ultimate strength. The fibres spun at 260°C had a modulus of 21 GPa and a strength equivalent to the PET control. The temperature of the die zone for this spinning run was below the liquid-crystal to liquid-crystal transition for the Random Copolymer. Spinning below this temperature obviously has a significant effect on the final fibre properties, but the reason for this is presently unknown. The fibres spun at 310°C had a slightly lower modulus, 19.5 GPa, and a small reduction in ultimate strength. A temperature of 310°C is close to the degradation temperature of the liquid crystal and some degradation of the polymer may have occurred. In addition, at temperatures greater than 300°C chemical reactions such as transesterification can take place very rapidly causing changes in the system.

Thus the processing window for these blends appears to be between 260 and 310°C. Owing to the relatively small quantities of available material, further optimization of the processing conditions was not possible. However, if further process optimization was possible, even greater improvement in fibre performance would be expected.

The effect of increasing draw ratio on mechanical properties was examined for the 5% blend spun at 290°C as seen in *Figure 8*. As the draw ratio was increased, the modulus and ultimate strength improved. The modulus increased from 14 to 25 GPa and the ultimate strength improved from 500 to 1100 MPa. These increases in modulus and strength were accompanied by a corresponding decrease in the ultimate elongation of the fibres from 33 to 7%. The continuous increase in modulus and strength indicates that these fibres have not been excessively drawn. Excessively drawn fibres exhibit increases in stiffness but a corresponding drop in the ultimate strength of the fibre. The decrease in strength is associated with the breaking of the load-bearing tie molecules.

Dimensional instability

Commercial TLCPs are dimensionally stable and have been used in injection moulding applications where tight

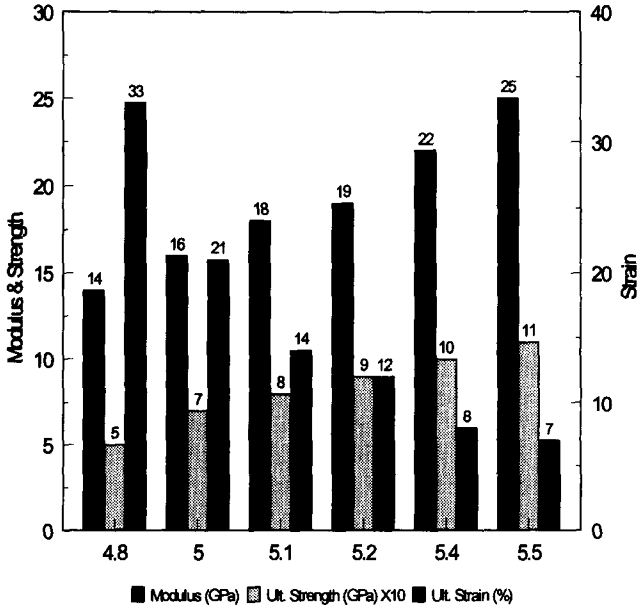


Figure 8 Mechanical performance of the post-treated 5% Random Copolymer/PET system as a function of final draw ratio (die temperature 290°C, take-up speed 75 m min^{-1}, hot drawn at 205°C)

Table 4 Dimensional instability of the post-treated 5% Random Copolymer system as a function of draw ratio (take-up speed of the undrawn fibre, 75 m min^{-1})

Draw ratio	Free shrinkage (%)	Shrinkage stress at 190°C (MPa)	Shrinkage stress at 30°C (MPa)
PET			
5	9	80	45
5% Rand. Copolym.			
4.8	6	25	11
5.0	6	28	13
5.1	8	50	27
5.2	8	70	40
5.4	9	84	45
5.5	10	86	42

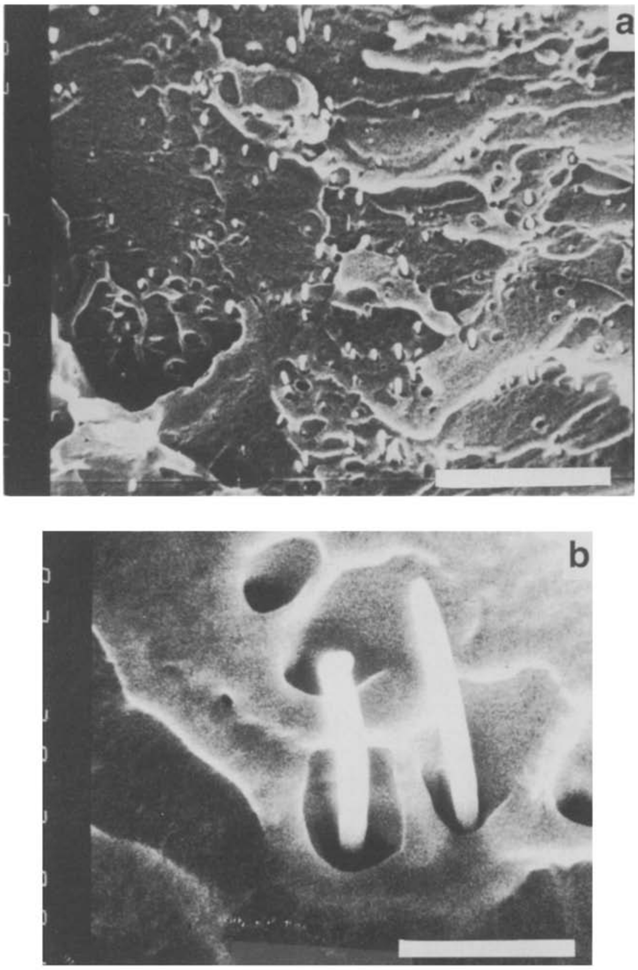


Figure 9 (a) An SEM cross-section of the 5% Random Copolymer as-spun fibre and (b) at greater magnification (die temperature 290°C, take-up speed 75 m min^{-1}; scale bars = 6 μm (a) and 1 μm (b))

tolerances and no part warpage are desired. Nicolais and coworkers[35] have also shown that blending polymeric TLCPs with polystyrene can be very effective in improving the dimensional stability of the thermoplastic. Thus it was hoped that the addition of 5% Random Copolymer to PET would result in fibres with superior dimensional stability compared to neat PET.

The dimensional instabilities of the 5% fibres spun at 290°C were measured using free shrinkage and force temperature experiments. The dimensional instability *versus* draw ratio is shown in *Table 4*. The free shrinkage of the fibres varied from 6 to 10% as the draw ratio was increased. Corresponding to the increase in free shrinkage was an increase in the shrinkage stresses. Comparison of the 5% blend having a draw ratio of 5.4 with the PET control reveals that similar shrinkage stresses result in equivalent dimensional changes. Thus the addition of 5% LCP does not appear to improve or detract from the thermal performance of the fibre.

Morphology

Cross-sections of 5% as-spun fibres, observed using scanning electron microscopy (SEM), showed a distinct two-phase morphology, with the TLCP phase elongated into fibrils as shown in *Figure 9*. The fibrils varied in diameter from 0.2 to 0.4 μm and were uniformly dispersed throughout the PET matrix. The presence of a fibrillated LCP phase indicated that the temperatures selected for processing were reasonable, although they could not be optimized.

Although d.s.c. does not indicate significant interaction between the Random Copolymer and PET, gross incompatibility is also absent. There was no indication of a skin–core morphology and phase separation between the components was limited to sub-micrometre LCP domains. Observation of the fibre cross-section at a higher magnification (*Figure 9b*) did not yield any evidence of adhesion between the phases. This observation could be an artifact of the sample preparation technique. It is well known that cracks tend to propagate along interfaces at liquid-nitrogen temperatures. Many of the fibrils showed evidence of fracture, indicating that the aspect ratio of the fibrils was enough for fractional forces to be significant. This could be the result of thermal expansion differences between the components causing a strong mechanical interaction between the two phases.

A longitudinal fibre cross-section was prepared by mounting a sample in an epoxy matrix and cryomicrotoming at −55°C. Observation of the fibre under the optical microscope at a magnification of 500 times (*Figure 10*) shows the knife cut across the fibre and evidence of elongated fibrils oriented along the fibre axis. Fibrils with

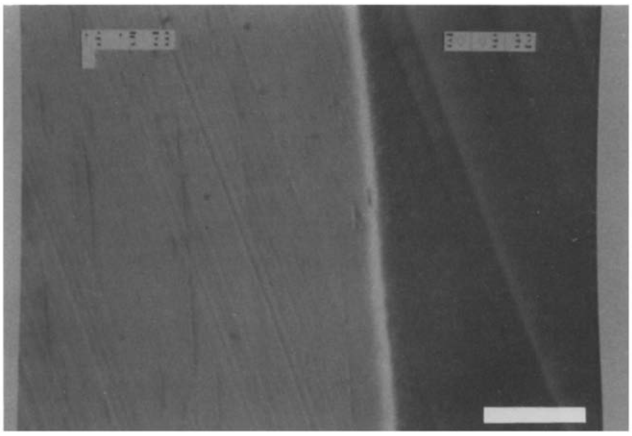


Figure 10 Longitudinal cross-section of the as-spun 5% Random Copolymer fibre observed with optical microscopy (die temperature 290°C, take-up speed 75 m min^{-1}; scale bar = 40 μm)

aspect ratios ranging from 20 to 200 could be easily found assuming a diameter of 0.4 μm. This should be considered a minimum aspect ratio range since the fibre was not cut perfectly horizontally and the maximum observed fibril diameter was assumed.

CONCLUSIONS

The objective of this study was to blend PET with novel thermotropic liquid-crystalline polyesters to improve fibre performance and processability. Several specifically tailored TLCP architectures were screened in an effort to determine the optimum molecular architecture necessary for fibre enhancement.

The PME-*b*-PET and PME-*b*-PBT block copolymers did not significantly reinforce the PET fibres, but minor improvements in fibre modulus were apparent in both systems. The fact that only moderate modulus improvements were observed may have been due to the incorporation of 50 wt% moieties into the main chain. This may have limited the moduli of the block copolymers to such an extent that significant reinforcement was not possible at low loading levels. The incorporation of either PET or PBT flexible moieties into the block copolymer did not yield significant differences in tensile performance. This is important because the PME-*b*-PBT copolymer had higher molecular weight, better processability and greater thermal stability.

Although the PBEM material should be stiffer than the block copolymers, the modulus improvement was insignificant. As the PBEM content was increased from 5 to 20 wt% a dramatic skin–core morphology developed, indicating incompatibility between the blend components. Steady shear viscometry at 270°C showed at loading levels as low as 2.5 wt% a 75% reduction in viscosity. Therefore PBEM is an excellent processing aid for PET and could permit processing at lower temperatures, reducing the threat of degradation.

The Random Copolymer system showed improved mechanical properties compared to neat PET fibres. Fibres containing only 5% TLCP exhibited a 50% increase in modulus (25 GPa), while maintaining an ultimate strength of 1100 MPa equivalent to the PET control. The mechanism of reinforcement is unclear, but evidence indicates that the TLCP is modifying the PET matrix. SEM observations of fractured fibre cross-sections revealed that the TCLP phase was elongated into uniformly dispersed fibrils 0.2–0.4 μm in diameter. The spinning temperature and draw ratio dramatically affected mechanical properties and thermal behaviour.

Although the mechanism of improvement is currently unknown, it is obvious that the addition of mesogenic block copolymers can significantly enhance the performance of PET. This is an important accomplishment since PET fibres must undergo extensive drawing in order to attain the necessary performance characteristics. At comparable loading levels, conventional thermotropic LCPs have not exhibited any significant PET reinforcement characteristics. Thus the potential of these materials is high, particularly since the processing conditions could not be optimized due to material constraints. By continuing to modify the molecular architecture and processing of these block copolymers, greater improvements in fibre performance are expected.

ACKNOWLEDGEMENTS

The financial support of this work from Akzo America Inc. is gratefully acknowledged. We are indebted to Drs Lenz and Kantor's group for supplying us with all TLCPs used in this study.

REFERENCES

1 Fakirov, S. and Evstatiev, M. *Polymer* 1990, **31**, 431

2 Ito, M., Miya, H., Watanabe, M. and Kanamoto, T. *J. Appl. Polym. Sci.* 1990, **40**, 543

3 Ito, M. and Takahashi, K. *J. Appl. Polym. Sci.* 1990, **40**, 1257

4 Hotter, J., Cuculo, J. and Tucker, P. *J. Appl. Polym. Sci.* 1991, **43**, 1511

5 Yevstatiyev, M. and Fakirov, S. *Polym. Sci. USSR* 1990, **32**(8), 1619

6 Heino, M. and Seppala, J. *Polym. Bull.* 1993, **30**, 353

7 Ajji, A., Brisson, J. and Qu, Y. *J. Polym. Sci., Polym. Phys. Edn* 1992, **30**, 505

8 Heino, M. and Seppala, J. *J. Appl. Polym. Sci.* 1992, **44**, 2185

9 Kyotani, M., Kaito, A. and Nakayama, K. *Polymer* 1992, **33**(2), 4757

10 Beery, D., Kenig, S. and Siegman, A. *Polym. Eng. Sci.* 1991, **31**(6), 459

11 Hong, S., Kim, B., Hwang, S. and Kim, K. *Polym. Eng. Sci.* 1993, **33**(10), 630

12 Mantia, F., Valenza, A., Paci, M. and Magagnini, P. *Polym. Eng. Sci.* 1990, **30**(1), 7

13 Lee, B. *Polym. Eng. Sci.* 1888, **28**(17), 1107

15 Crevecoeur, G. and Groeninckx, G. *Polym. Eng. Sci.* 1990, **30**(9), 532

16 Bassett, B. R. and Yee, A. F. *Polym. Compos.* 1990, **11**(1), 10

17 Narayan, S., Lenz, R. W. and Kantor, S. W. *ACS Polym. Prepr.* 1993, **34**(2), 668; Ignatious, F., Kantor, S. W. and Lenz, R. W. *ACS Polym. Prepr.* 1993, **34**(2), 586

18 Uracki, L. A., 'Polymer Alloys and Blends: Thermodynamics and Rheology', Oxford University Press, Oxford, 1990, p. 356

19 Olabisi, O., Robeson, L. M. and Shaw, M. T., 'Polymer–Polymer Miscibility', Academic Press, New York, 1979, p. 370

20 Tendolkar, A., Lenz, R. and Kantor, S., to be published

21 Sarlin, J. and Tormala, P. *J. Polym. Sci., Polym. Phys Edn* 1991, **29**, 395

22 Brostow, W. *Polymer* 1990, **31**, 979

23 Dutta, D., Fruitwala, H., Kohli, A. and Weiss, R. *Polym. Eng. Sci.* 1990, **30**(17), 1005

24 Kulichikhin, V. and Plate, N. *Polym. Sci. USSR* 1991, **33**(1), 1

25 De Vries, A. *Mol. Cryst. Liq. Cryst.* 1970, **10**, 219

26 Atkins, E., Thomas, E. and Lenz, R. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 271

27 Mehta, A. and Isayev, A. *Polym. Eng. Sci.* 1991, **31**(13), 971

28 Kohli, A., Chung, N. and Weiss, R. *Polym. Eng. Sci.* 1989, **29**(9), 573

29 Zhuang, P., Kyu, T. and White, J. *Polym. Eng. Sci.* 1988, **28**(17), 1095

30 Blizard, K. and Baird, D. *Polym. Eng. Sci.* 1989, **27**(9), 653

31 Kim, W. and Denn, M. *J. Rheol.* 1992, **36**(8), 1477

32 Golovoy, A., Kozlowski, M. and Narkis, M. *Polym. Eng. Sci.* 1992, **32**(13), 854

33 Siegmann, A., Dagan, A. and Kenig, S. 1985, **26**, 1325

34 Sukhadia, A., Done, D. and Baird, D. *Polym. Eng. Sci.* 1990, **30**(9), 519

35 Apicella, A., Iannelli, P., Nicodemo, L., Nicolais, L., Roviello, A. and Sirigu, A. *Polym. Eng. Sci.* 1986, **26**(9), 600