

A Novel TLCP Blended with PET and PC Matrices

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SYNOPSIS

This investigation focused on the potential of improving the performance of poly(ethylene terephthalate) (PET) and polycarbonate (PC) fibers by incorporating a novel thermotropic liquid crystalline copolymer (TLCP). The degree of mechanical enhancement obtained in the fibers incorporating 20 wt % TLCP depended upon the chosen matrix material and the processing conditions. The PET matrix systems did not exhibit any modulus improvements until after posttreatment of the fibers. Following posttreatment, the blends exhibited a modulus of 24 GPa, an increase of 40% compared to the PET control fiber. The PC systems exhibited a 1 GPa modulus increase in the as-spun fiber blends, but improvement was negligible after fiber posttreatment. The morphologies of the as-spun and posttreated fibers suggest that different mechanisms of reinforcement are occurring depending upon the matrix material selected. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The reinforcement of poly(ethylene terephthalate) (PET) by blending with thermotropic liquid crystalline copolymers (TLCPs) has been attempted by several researchers.¹⁻⁹ In some cases, the strength and moduli of the PET blends have been found to follow a linear rule mixture, leading to substantial increases in material strength and stiffness.⁴ The degree of improvement obtained is highly dependent on the processing history of the blends.⁷ Studies that subject the melt to a large elongational flow field typically exhibit the greatest property enhancements. However, regardless of processing technique, significant increases in modulus and strength are typically not observed until concentrations in excess of 20 wt % liquid crystalline polymers (LCP) are incorporated into the blends. At these concentrations, matrix embrittlement is often observed due to incompatibility between blend components. The incorporation of as little as 10 wt % LCP usually reduces the elongation of the matrix material dramatically.

The studies conducted thus far in the area of thermoplastic/TLCP blends have focused on improving the properties of extruded or injection-molded PET. The modulus of extruded or injection-molded PET is relatively low and tends to fall within the 2–3 GPa range. It was reasonable therefore to attempt to increase the strength and stiffness of PET by incorporating a high-performance TLCP. Unfortunately, due to the nature of these processing techniques, posttreatment or postdrawing of the blends after solidification was not a primary consideration. Investigators typically were not concerned with the low elongation to break and matrix embrittlement induced by blending with an LCP. However, the mechanical properties of PET can be significantly improved by posttreatment after solidification. Drawing of PET induces crystallization and orientation of the thermoplastic, resulting in a substantial increase in mechanical performance. The tensile modulus of high molecular weight PET fibers can attain values in the range of 14–17 GPa just by carrying out cold- and/or hot-drawing posttreatments. The moduli of blended systems, containing 10–20 wt % TLCP, typically do not exceed 5–12 GPa. Furthermore, the ultimate strength of neat PET fibers after posttreatment is approximately 1100 MPa, which is significantly greater than PET/TLCP blends incorporating up to 70 wt % of the TLCP

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Vectra. Thus, if processed correctly, the stiffness and ultimate strength of neat PET easily exceeds that of low to moderately concentrated blend systems that cannot be posttreated.

If the compatibility between PET and a TLCP reinforcement material could be sufficiently increased to permit postdrawing, the mechanical properties of these blend systems should increase dramatically. Improved stiffness, strength, and toughness would be expected, since the properties of the PET matrix would increase by an order of magnitude. A better matrix material would improve the efficiency of the reinforcement phase since less TLCP would be needed to obtain moderate stiffness values. Enhanced compatibility could also result in better adhesion between the polymers along with greater processing flexibility. In addition to the melt techniques of extrusion and injection molding, processes requiring solid-state drawing such as biaxially oriented film formation and fiber spinning could be performed.

In a previous study, the possibility of improving upon the properties of neat PET fibers by incorporating novel TLCP block copolymers was investigated.¹⁰ One particular blend system exhibited a 40% increase in fiber modulus without causing matrix embrittlement. Even at a concentration of 20 wt % TLCP, the blended fibers could still be easily posttreated using conventional fiber-processing methods. However, the mechanism of reinforcement provided by the block copolymer was unclear. The as-spun fibers did not exhibit any significant property improvements despite fibrillation of the LCP phase. Increases in mechanical and thermal performance were observed only after posttreatment, indicating that a modification of the PET matrix material had occurred rather than a true mechanical reinforcement by the LCP phase. Partial miscibility or interaction between the copolymer and the PET matrix was also considered a possibility since all of the LCP could not be accounted for by scanning electron or optical microscopy.

The objective of this study was to determine whether the LCP modified the PET matrix phase or provided true mechanical reinforcement of the fiber. Since the block copolymer was specifically engineered to be compatible with PET, a model system using a polycarbonate matrix has been designed to elucidate the mechanism of property enhancement. Fiber compositions containing 20 wt % TLCP are compared. The fibers are prepared by melt extrusion followed by cold drawing. In the PET systems, the fibers are also hot drawn to maximize performance.

The fibers are tested for tensile performance and dimensional instability.

EXPERIMENTAL

Materials

The fiber-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 2.04 (dL/g). The PET was blended as received without further purification.

The polycarbonate (PC) used in this study is sold under the trade name Merlon M-50 (H) and was kindly provided by the Bayer Corp. A glass transition of 143°C was determined by differential scanning calorimetry using a heating rate of 20°C/min. The pellets exhibited an inherent viscosity of 0.55 (dL/g) as measured at a concentration of 0.25% in dioxane at 30°C. The PC was also blended as received without further purification.

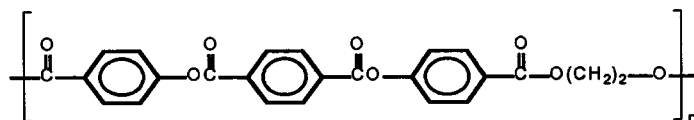
The TLCP used in this study was a novel block copolymer kindly synthesized by Drs. Lenz and Kantor's group at the University of Massachusetts, Amherst.¹¹ The LCP is a segmented block copolymer consisting of rigid-rod, diad, and flexible coil segments. Figure 1 shows a schematic of the general structures incorporated into the block copolymer. The mesogenic segments consists of six poly(dimethylene-4,4'-terephthaloyl dioxydibenzoate) (Triad2) units. The flexible coil segment is composed of seven poly(butylene terephthalate) (PBT) units. Furthermore, due to the reaction scheme chosen to synthesize these copolymers, tetramethylene-4,4'-dioxydibenzoate (Diad4) sequences are incorporated between the rigid-rod and flexible coil segments. These diads are known to be mesogenic.¹²

The block copolymer, shown in Figure 2, has been designated Triad2 (2 : 6 : 7), corresponding to the 2 Diad4 units connecting Triad2 and PBT blocks having segment lengths of 6 and 7 units, respectively. The amount of material available for blending and property determination was limited; thus, the mechanical properties of the neat copolymer could not be determined.

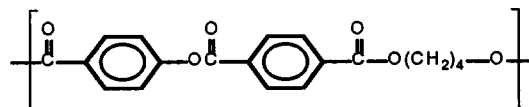
Thermal Characterization

The transition temperatures of the neat materials and the blends were measured calorimetrically using a TA Instruments 9900 differential scanning calorimeter. Temperature calibration was performed using an indium standard. Samples of approximately

Triad2 Mesogenic Block



Diad4 Unit



PBT Flexible Block

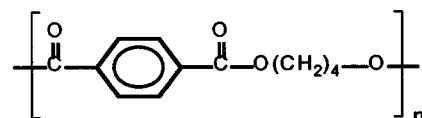


Figure 1 Structural moieties incorporated into the TLCP alternating block copolymer.

10 mg were initially heated in a nitrogen atmosphere from 30 to 300°C at a heating rate of 20°C/min, followed by quenching with liquid nitrogen. Samples were then reheated to 300°C at a heating rate of 20°C/min. The reported transitions are the maximum peak temperatures observed during the second heating run.

Fiber Formation

Powders of the thermotropic polyesters and the respective matrix material were tumble mixed for 24 h. The amount of block copolymer used in the extruded blends was 20% by weight. The mixed polymer powders were then compression-molded 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 microns and vacuum-dried at 120°C for a minimum of 24 h. Compression molding followed by grinding was convenient for obtaining particles that effectively fed into the miniextruder.

Once thoroughly dried, the blends were extruded and spun into fibers. Extrusion was carried out with a $\frac{1}{4}$ in. Randcastle single-screw miniextruder. The miniextruder 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, respectively. The temperature of the die zone was also set at 280°C for both the PET and the PC blends. The ability to obtain a uniform melt without die swell was the main criteria for determining the die temperature. The screw speed was held constant at 30 rpm, corresponding to an extrusion rate of 1.5 g/min 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 a 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 either 75 or 225 m/min was used for all systems. The stretch ratio for each system was determined as the ratio between the die and the

Block Copolymer

Copolymer Structure

Triad2 (2:6:7)

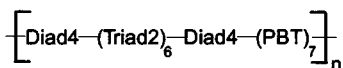


Figure 2 Triad2 (2 : 6 : 7) alternating block copolymer chemical structure.

drawn extrudate cross sections (A_0/A_f). The round-hole capillary die had a diameter of 1575 μm and an aspect ratio of 10. Fiber diameters were determined by optical microscopy.

A two-step posttreatment process was performed on the PET blends immediately following the spinning process. The heat treatment of PET fibers is an important processing stage that determines the ultimate properties of the material. Postdrawing 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, whereas 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 of 3.5.

Hot drawing of the PET systems 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 fiber. The total draw ratio was calculated as the ratio between the as-spun and final posttreated fiber cross-sectional areas. All samples were collected and tested at the maximum draw ratio unless otherwise specified.

Since PC is an amorphous material, the fibers could not be hot-drawn; thus, the posttreatment of the PC fibers consisted of a single drawing step performed at 85°C. The cold drawing of the PC and PET systems were performed in an identical manner. The final draw ratio obtained for the PC systems was approximately 2. Pertinent fiber processing information is summarized in Table I.

Tensile Testing

Tensile tests were performed on an Instron 1113 tensile tester connected to a personal computer. Specimens were affixed with an adhesive onto paper tabs to facilitate mounting and alignment. Fiber diameters were measured using an Olympus microscope equipped with a calibrated scale accurate to ± 0.5 microns. A minimum of five diameter measurements per fiber 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 fiber 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 found to be approximately 2%. 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%.

Thermal Instability

Shrinkage experiments were performed by placing the fibers in a convection oven preheated to the desired temperature for 15 min. The preheat temperatures were 190 and 130°C for the PET and the PC systems, respectively. Prior to heating, the fibers 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 fibers 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 fibers were reconditioned for 1 h and the resultant dimensional changes determined. The free shrinkage was computed as

Table I Fiber Processing Results

	Spun Diameter (μm)		Stretch Ratio		Drawn	Draw Ratio
	75 m/min	225 m/min	75 m/min	225 m/min	Diameter (μm) 75 m/min	
PET	86	64	335	600	38	5.1
20% Triad2 (2 : 6 : 7)/PET	84	60	350	680	36	5.5
PC	74	40	450	1520	57	1.7
20% Triad2 (2 : 6 : 7)/PC	82	42	370	1400	56	2.1

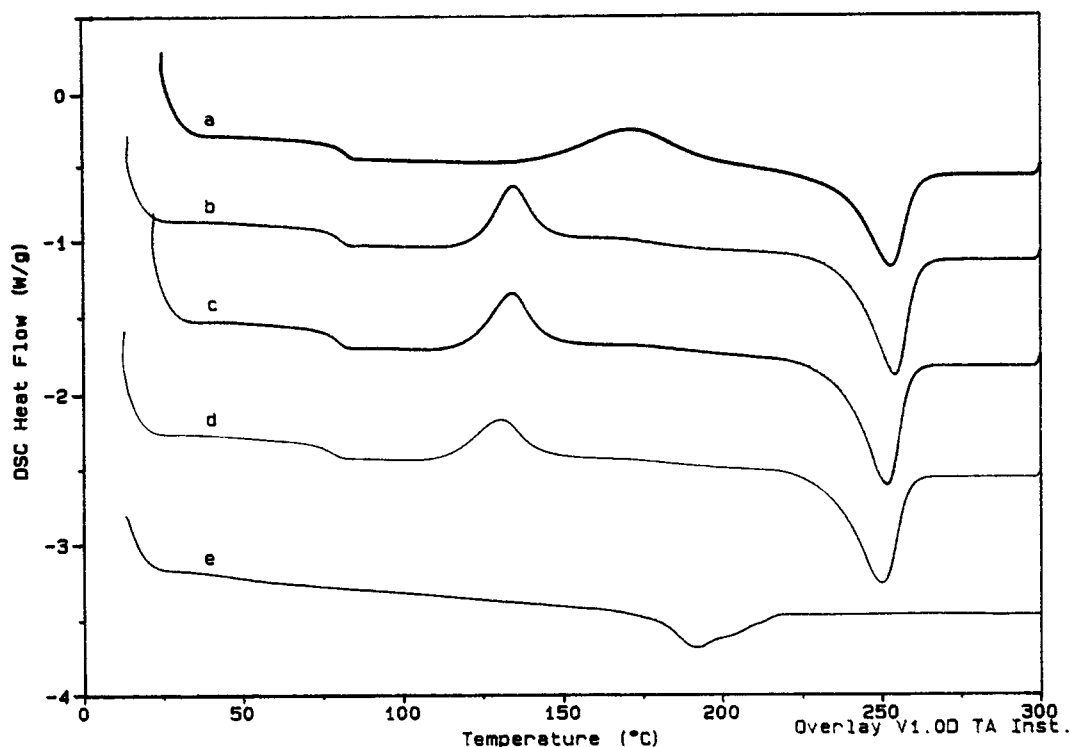


Figure 3 DSC second heating scans: (a) neat PET; (b) 5% Triad2 (2 : 6 : 7)/PET; (c) 10% Triad2 (2 : 6 : 7)/PET; (d) 20% Triad2 (2 : 6 : 7)/PET; (e) neat Triad2 (2 : 6 : 7).

$$[\%] = (L_0 - L_1) / L_1 \times 100.$$

Shrinkage values were averaged over five measurements.

Morphology

The morphology of the blends was investigated by optical microscopy (OM) and scanning electron microscopy (SEM). The as-spun PET fibers were sol-

vent-etched using a 60/40 *para*-chlorophenol tetrachloroethane mixture to remove the PET matrix phase. The solvent mixture was slowly dropped onto the fibers at 5 mL per min for approximately 1 min. The PC samples were prepared in an analogous manner except that the etching solvent was methylene chloride. All SEM samples were mounted on aluminum 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 was used for observing the blends before and after processing.

Table II Numerical Data Determined from DSC Measurements of PET Blend Systems

	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PET	82.4	171.2	23	252.8	29
5% Triad2 (2 : 6 : 7)	81.5	134.5	16	253.9	37
10% Triad2 (2 : 6 : 7)	80.1	134.3	17	251.5	41
20% Triad2 (2 : 6 : 7)	77.6	130.7	18	249.8	46
Triad2 (2 : 6 : 7)				193	17

RESULTS AND DISCUSSION

Thermal Characteristics

The DSC traces of the PET blends and the pure components are shown in Figure 3. As discussed in the Experimental section, these are second heating scans, 20°C/min, performed after a liquid nitrogen quench from 300°C. The relevant numerical data from the DSC measurements are collected in Table II. The enthalpies of fusion and crystallization for the blends are normalized to the PET content.

The heating trace of the neat, as-supplied PET sample (curve a) is characterized by a well-defined glass transition at 82°C (T_g). An exothermic cold crystallization peak (T_c) and melting endotherm (T_m) are also visible at 171 and 253°C, respectively. A comparison of the heat of crystallization (ΔH_c) and the heat of fusion (ΔH_m) suggests that the PET did not crystallize to a significant extent during the liquid nitrogen quench.

The DSC scan of the neat Triad2 (2 : 6 : 7) (curve e) shows an endothermic peak at 193°C (T_m). Following this transition, the material is triphasic, i.e., it exhibits isotropic, nematic, and crystalline characteristics. At higher temperatures, the nematic dyad moieties becomes isotropic and the copolymer develops a biphasic morphology that remains until the onset of degradation at 336°C (see Figs. 4 and 5). The absence of a cold crystallization peak indicates that all of the crystallization occurred during the liquid nitrogen quench. Furthermore, the lack of a well-defined glass transition and a small heat of fusion are common characteristics of thermotropic liquid crystalline polymers.^{13,14}

Curves b–d in Figure 3 are the DSC traces for the PET–LCP blends. Surprisingly, the melting endotherm of the LCP minor component could not be observed in any of the systems; however, the addition of small amounts of LCP does have a profound effect on the thermal behavior of the blends. All the blends exhibit a glass transition, but the temperature of this transition is dependent upon the concentration

of LCP incorporated into the blend. As the concentration of LCP was increased from 0 to 20%, the T_g 's decreased from 83°C for neat PET to 77°C for the 20% blend. This result suggests that some interaction between the blend components may have occurred. It is also interesting to note that the temperature of the transition was reduced, indicating that the glass transition of Triad2 (2 : 6 : 7) is lower than that of neat PET. This is not unreasonable since the block copolymer contains a significant amount of PBT, which typically exhibits a T_g around 55°C and is miscible with PET.

The addition of Triad2 (2 : 6 : 7) also affects the cold crystallization temperature of PET. In all the blended systems, PET undergoes cold crystallization approximately 35°C lower than does the neat PET. Although this phenomenon does not exhibit any clear concentration dependence, the 20% system does exhibit the greatest temperature reduction in PET cold crystallization. The enthalpies of crystallization, normalized to the PET content, were essentially independent of Triad2 content but a slight reduction was observed for all the blends. Conversely, the heat of fusion is seen to dramatically increase with Triad2 (2 : 6 : 7) content. This is an indication that the extent or degree of PET crystallinity was significantly increased by the addition of Triad2 (2 : 6 : 7). Assuming that the enthalpy of fusion of 100% crystalline PET is of 140 J/g,^{15,16} the degree of crystallinity increased from 21% for neat PET to approximately 32% for the 20% Triad2

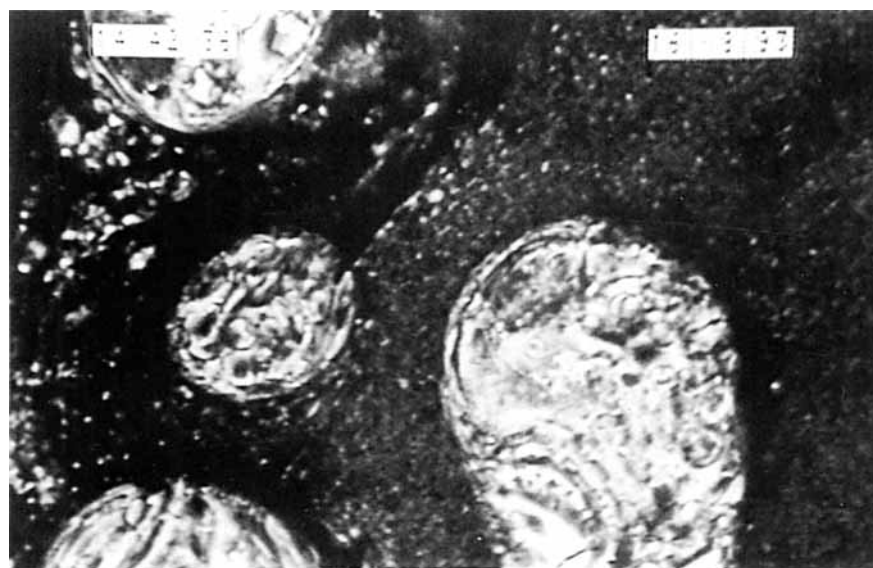


Figure 4 The 20% Triad2 (2 : 6 : 7)/PET blend powder observed prior to extrusion with an optical microscope equipped with a hot stage. The blend was magnified 100 times, heated to 200°C, and observed with crossed polarizers.

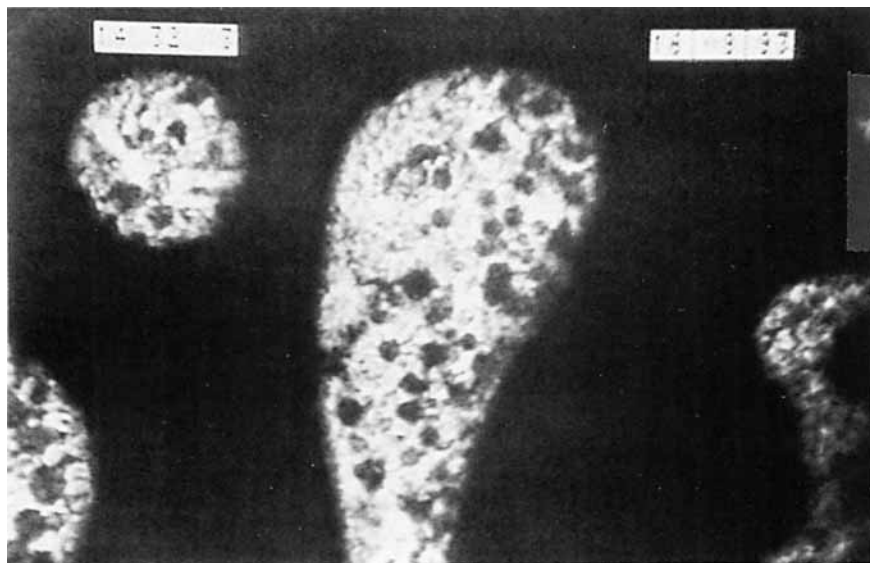


Figure 5 The 20% Triad2 (2 : 6 : 7)/PET blend powder observed prior to extrusion with an optical microscope equipped with a hot stage. The blend was magnified 100 times, heated to 270°C, and observed with crossed polarizers.

(2 : 4 : 6) blend. Other investigators observed similar phenomena in other LCP-random coil systems but typically to a lesser degree than observed here.^{7,17} The increase in crystallinity is often attributed to the LCP performing as a nucleating agent for the PET.

Tensile Performance

The effect of adding 20 wt % Triad2 (2 : 6 : 7) on the Young's modulus of as-spun PET and PC is shown in Figure 6. The controls and the blends were spun using identical temperature profiles, i.e., a die zone temperature of 280°C was used for all sample preparation. Take-up speeds of 75 and 225 m/min were used to determine the effect of elongational flow on mechanical performance.

The modulus of the PET control was essentially independent of the take-up speed and the addition of 20% Triad2 (2 : 6 : 7) to PET does not significantly enhance the mechanical performance of the thermoplastic. A slight increase in modulus, 0.4 GPa, was observed when the take-up speed was increased to 225 m/min, but this was not considered significant.

Adding 20 wt % Triad2 (2 : 6 : 7) to PC improved the modulus of the samples by approximately 1.0 GPa. The degree of enhancement was dependent upon take-up speed with the higher speed, 225 m/min, leading to a greater amount of reinforcement. If the general rule of mixtures is used to estimate the modulus of the neat Triad2 (2 : 6 : 7), a value

of approximately 9 GPa is obtained. This result is comparable to the 13 GPa modulus obtained by Shin and Chung,⁶ although a different flexible spacer group was investigated.

Thus, the incorporation of flexible moieties into the LCP chain may promote interaction between the blend components, but this does not necessarily lead to mechanical reinforcement of the system. For instance, DSC results indicate that some interaction occurs between PET and Triad2 (2 : 6 : 7), but there is no evidence of any substantial mechanical reinforcement. Conversely, the PC blends do exhibit mechanical reinforcement; the incorporation of flexible PBT units into the TLCP chain appears to have severely limited the modulus of the block copolymer. Compared to more rigid TLCPs, the amount of reinforcement observed in the PC blend is not dramatic.¹⁸

After spinning, the fibers were posttreated as described in the Experimental section. Posttreatment was performed on the fibers taken up at 75 m/min. The PET systems were cold and hot drawn, whereas the PC systems were only cold drawn since the T_g of the PC prohibited high-temperature drawing. The mechanical properties of the blends after posttreatment are shown in Figure 7.

The results of the PET blended with 20% Triad2 (2 : 6 : 7) were surprising. After posttreatment, a significant improvement in mechanical performance was observed, i.e., the modulus increased from 17 to 24 GPa compared to the PET control. This was un-

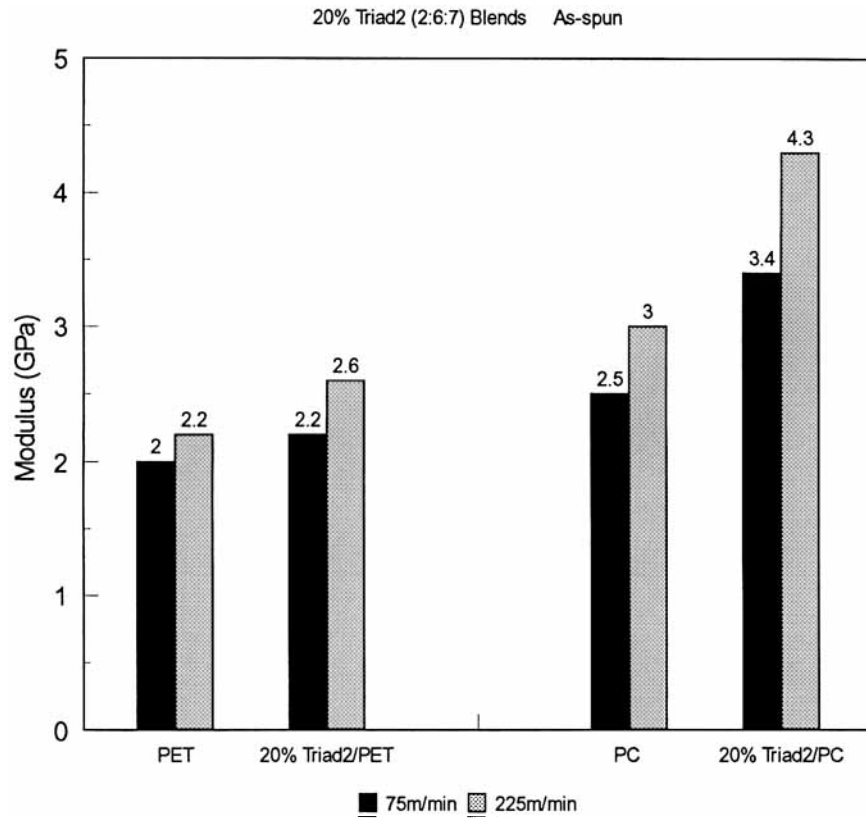


Figure 6 As-spun fiber modulus values for the Triad2 (2 : 6 : 7) blends and controls.

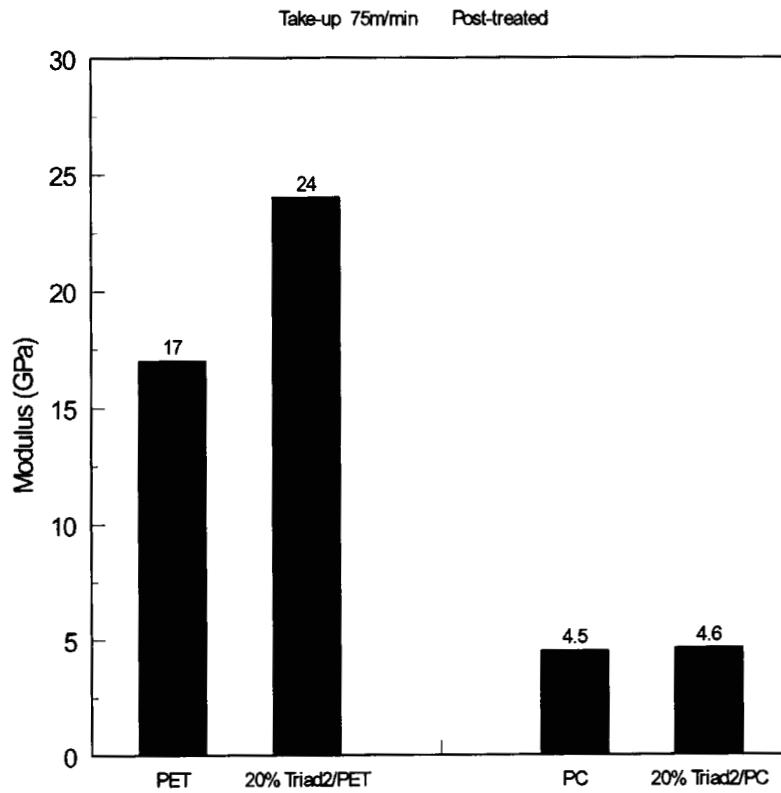


Figure 7 Posttreated modulus values for the control and 20% Triad2 (2 : 6 : 7) fiber blends.

expected since mechanical reinforcement was not observed in the as-spun PET blend. Furthermore, the posttreated PC systems did not exhibit any significant differences in mechanical performance. The PC control and the 20% Triad2 blend had moduli of approximately 4.5 GPa. Thus, the modulus enhancement observed in the as-spun PC blend was not improved upon by postdrawing.

The addition of the Triad2 (2 : 6 : 7) block copolymer appears to have dramatically different effects depending upon the selected matrix polymer. In the PET blend, fiber enhancement was not observed until after posttreatment, whereas in the PC blend system, postdrawing negated the as-spun fiber modulus increases. This result suggests that different mechanisms of reinforcement may be responsible for the improvements observed in the respective matrix materials. For instance, the DSC results indicate that the Triad2 could be modifying the PET matrix by influencing the fiber's crystallization behavior. Since PET crystallization is not induced until the posttreatment step, performance improvements would not manifest until after this processing stage. Conversely, in the as-spun PC blend system, the LCP may provide true mechanical reinforcement analogous to conventional fiber-reinforced composites. Subsequently, a significant increase in the mechanical performance of the PC matrix material, due

to induced orientation during the postdrawing process, could effectively negate any modulus enhancements obtained in the as-spun fibers. This would be particularly likely if the modulus of the Triad2 (2 : 6 : 7) block copolymer was only on the order of 10 GPa.

Another possibility is that the posttreatment process improves the mechanical performance of the Triad2 (2 : 6 : 7) block copolymer. However, this is thought to be unlikely since the effect should be identical for both matrices and not material-dependent.

Dimensional Instability of the Triad2 (2 : 6 : 7) Blends

Free-shrinkage experiments were performed on the posttreated fibers. The tests were performed as described in the Experimental section, but the maximum temperature for each system varied depending upon the matrix polymer. The PET systems were heated to 190°C, whereas the PC systems experienced only a maximum temperature of 115°C. It was hoped that by incorporating a thermotropic LCP the thermal stability of the matrix polymer could be improved. The results are shown in Figure 8.

The neat PET and PC fibers exhibited free shrinkage's of 10 and 15%, respectively. The PET

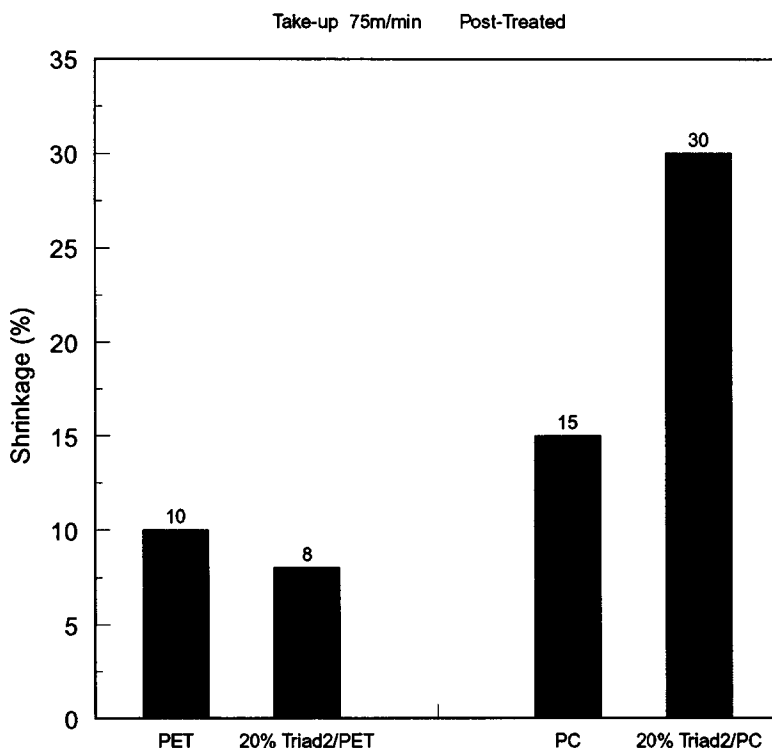


Figure 8 Dimensional instability of the control and 20% Triad2 (2 : 6 : 7) fiber blends.

fiber shrinks significantly less than does the PC due to the large extent of crystallinity in the fiber.¹⁹ The free shrinkage of the blend fibers are significantly different. The addition of 20% Triad2 (2 : 6 : 7) to PET slightly improved the free-shrinkage behavior of the fiber from 10 to 8%. However, the PC blend system exhibited 30% shrinkage, which was double the amount of the neat PC fiber. Thus, the ability of Triad2 to alter thermal behavior also appears to be dependent upon the selected matrix material.

Although the addition of the Triad2 (2 : 6 : 7) block copolymer did not reduce the free shrinkage of the PC matrix, the results offer further evidence that different reinforcement mechanisms are responsible for fiber improvements. If the degree of crystallinity in PET were improved through matrix modification, the amount of free shrinkage experienced by the fiber would be expected to decrease. In the case of true mechanical reinforcement, the Triad2 block copolymer would have to essentially anchor the PC matrix in place in order to reduce shrinkage. This phenomenon has been observed by Nicolais and co-workers²⁰ in polystyrene systems blended with the TLCP Vectra. The dramatic increase in shrinkage for the PC blend fiber indicates that the dimensional instability of the Triad2 block copolymer may be significantly greater than that of the PC matrix material. This result was unfortunate

but reasonable since a significant portion of PBT was incorporated into the block copolymer. Debonding and voiding during the drawing process would also contribute to a lack of mechanical reinforcement and the observed shrinkage increase.

Morphology of the Triad2 (2 : 6 : 7) Blends

To elucidate the geometry of the Triad2 phase within the respective matrices, the as-spun fibers were solvent-etched and observed using optical and scanning electron microscopy. The PET systems were etched using a 60/40 mixture of *para*-chlorophenol to tetrachloroethane, while methylene chloride was used for the PC systems. Figures 9 and 10 are optical micrographs of the remaining residue after etching the PET and PC as-spun fibers, respectively. The presence of Triad2 fibrils are clearly evident in both blend systems; however, the number of fibrils and their aspect ratios were dramatically different. Figures 11 and 12 are SEM micrographs of the etched fibers. Figure 11 shows a single Triad2 fibril oriented along the PET fiber axis, whereas Figure 12 reveals a tremendous quantity of Triad2 fibrils oriented along the fiber direction. The diameters of the fibrils in the PET system ranged from 1 to 1.5 μm with aspect ratios varying from 25 to 160. These aspect ratios are considerably smaller than those observed

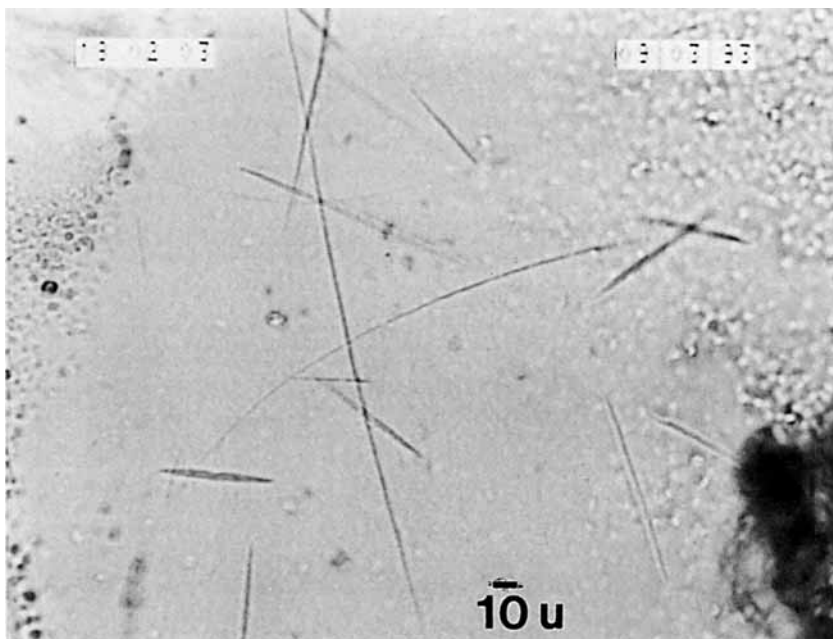


Figure 9 Etched 20% Triad2 (2 : 6 : 7)/PET as-spun fiber magnified 500 times using optical microscopy. Micrograph depicts fibrils of the Triad2 (2 : 6 : 7) phase with various aspect ratios.

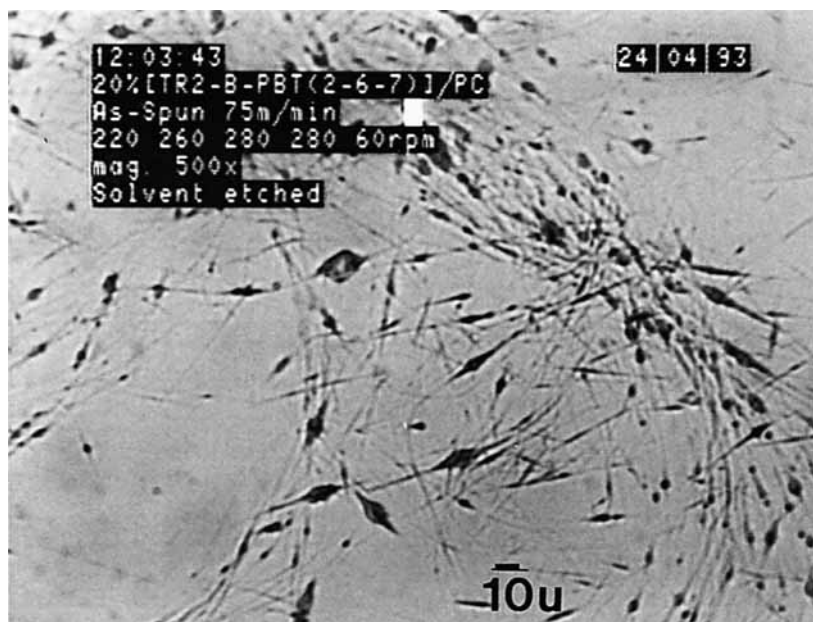


Figure 10 Etched 20% Triad2 (2 : 6 : 7)/PC as-spun fiber magnified 500 times using optical microscopy. Micrograph depicts fibrils of the Triad2 (2 : 6 : 7) phase having high aspect ratios and varying diameters.

in the PC system, which appear to be essentially infinite. The diameters of the fibrils within the PC are very nonuniform and range from 0.2 to 1.0 μm . In addition, the fibrils appear to have formed an infinite network within the PC matrix.

The disparity in the number of fibrils observed in the PET and PC blends indicates that the Triad2 block copolymer may be partially miscible with the PET matrix and/or the geometry of the LCP phase may have been predominately particulate. Partial

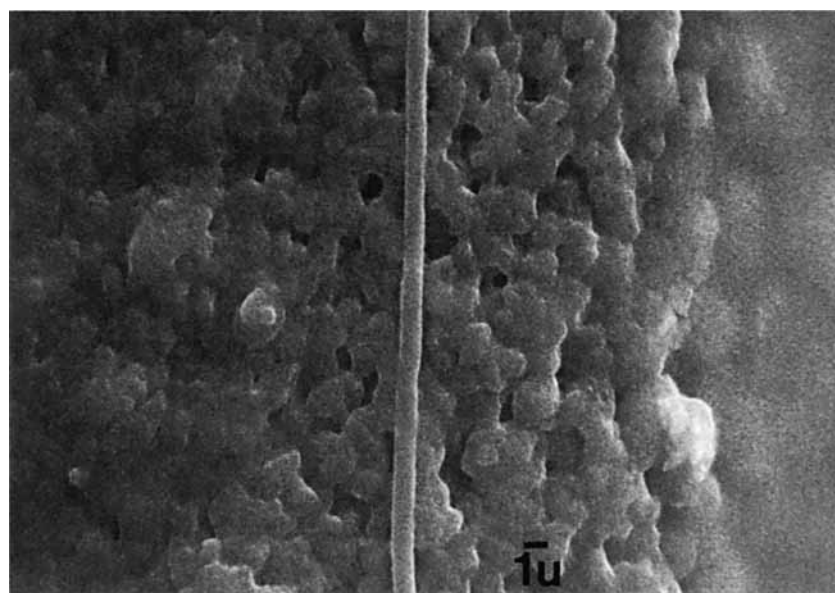


Figure 11 Etched 20% Triad2 (2 : 6 : 7)/PET as-spun fiber magnified 5000 times using scanning electron microscopy. Micrograph depicts a single fibril of the Triad2 (2 : 6 : 7) phase.

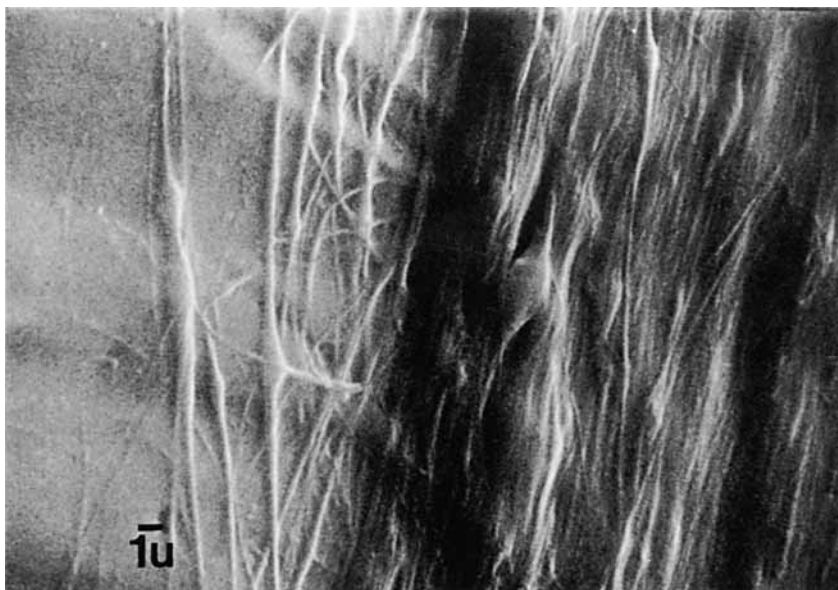


Figure 12 Etched 20% Triad2 (2 : 6 : 7)/PC as-spun fiber magnified 5000 times using scanning electron microscopy. Micrograph depicts fibrils of the Triad2 (2 : 6 : 7) phase having high aspect ratios and varying diameters.

miscibility of the Triad2 with the PET matrix could make fibril generation difficult,⁷ and a particulate morphology would not be readily visible with optical microscopy since particulates would be susceptible to removal during the etching process.

The morphologies of the as-spun fiber blends further indicate that the Triad2 block copolymer performs as a matrix modifier for PET and as a poor reinforcement material for PC. The number of fibrils observed in the PET blend would not be sufficient to improve the mechanical performance of the system as indicated by the tensile results. In addition, all of the Triad2 phase cannot be accounted for at this point, suggesting that some interaction with the PET may have occurred as indicated by the DSC results.

The morphology of the PC system reveals a large number of high-aspect Triad2 fibrils aligned along the direction of the fiber axis. This type of morphology is considered to be ideal for obtaining the maximum reinforcement potential from the Triad2 phase. Indeed, some modulus improvement was observed in the as-spun fibers; however, the increase was moderate at best. Thus, the inherent mechanical properties of the Triad2 do not appear to be extremely high. Furthermore, the estimate of 9 GPa obtained using the simple rule of mixtures is considered a reasonable approximation.

Figure 13 is an optical micrograph of a solvent-etched PC blend fiber after posttreatment. The PC

matrix has been completely dissolved away to reveal a dense mat of LCP fibrils. The residue has been magnified 200 times and observed using crossed polarizers. It is immediately obvious that the Triad2 fibrils are highly birefringent and oriented along the fiber direction. There is also an apparent fracture of the Triad2 fibrils across the entire fiber cross section. These fibril fractures are periodic and occur along the fiber axis approximately every centimeter. This observation indicates that fiber postdrawing breaks up the Triad2 fibrils within the matrix. Fracture of the Triad2 phase decreases the fibril aspect ratio and essentially reduces the ability of the LCP to mechanically reinforce the matrix material. This result suggests that it is unlikely that postdrawing improved the mechanical performance of the Triad2 material. Therefore, any modulus enhancement in the posttreated PC blends can be attributed to an improved PC matrix. The drawing procedure effectively orients the PC matrix material but does not increase the performance of the Triad2 phase. After postdrawing, the Triad2 mechanical properties are not sufficient to improve upon the performance of the drawn PC matrix material.

Attempts to distinguish the Triad2 phase within the postdrawn PET fibers were not successful. Due to the high degree of PET crystallinity and the chemical similarity of the two-blend components, a satisfactory sample preparation technique could not be found. However, to dramatically improve upon

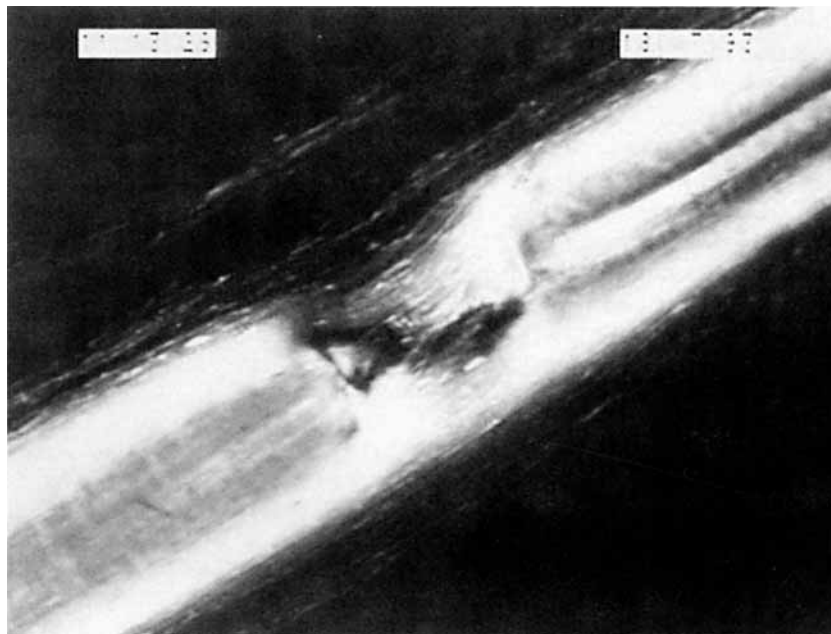


Figure 13 Posttreated 20% Triad2 (2 : 6 : 7)/PC fiber residue that has been solvent-etched and observed using cross-polarized optical microscopy with a magnification of 200 times. The micrograph shows highly birefringent Triad2 (2 : 6 : 7) fibrils fractured after drawing the fiber at 85°C.

the 17 GPa modulus of neat PET, the Triad2 phase would need to have a significantly greater modulus than was apparent in either the PET or PC as-spun systems. Furthermore, if it is assumed that drawing of the PET blends breaks up the Triad2 phase as found in the PC systems, it is unlikely that mechanical reinforcement is responsible for any obtained modulus improvements. Since the PET blends were drawn approximately double that of the PC systems, damage to the Triad2 phase should be even more severe, further indicating that a matrix modification phenomena is probably responsible for the observed modulus enhancements rather than any inherent properties of the Triad2 block copolymer.

CONCLUSIONS

The degree of mechanical enhancement obtained in the fibers incorporating 20 wt % of the Triad2 (2 : 6 : 7) block copolymer depended upon the chosen matrix material and the processing conditions. The PET matrix systems did not exhibit any modulus improvements until after posttreatment of the fibers. Following posttreatment, the blends exhibited a modulus of 24 GPa, an increase of 40% compared to the PET control fiber. The free shrinkage of the

blended PET fiber was also reduced from 10 to 8% after posttreatment. Thus, the dimensional stability of the fiber was improved along with the mechanical performance.

The PC systems exhibited a 1 GPa modulus increase in the as-spun fiber blends, but improvement was negligible after fiber posttreatment. Application of the simple rule of mixtures estimated that the neat Triad2 block copolymer had a modulus of only 9 GPa. The PC blends also indicated that the dimensional stability of the neat Triad2 polymer was poor. Incorporating 20 wt % of Triad2 into the PC matrix essentially doubled the amount of free shrinkage experienced by the fiber at 130°C compared to the PC control.

The morphologies of the as-spun and posttreated fibers suggest that different mechanisms of reinforcement are occurring depending upon the matrix material selected. The as-spun PET fiber blends exhibit some fibril formation, but their low aspect ratios and concentration indicate that true mechanical reinforcement is unlikely. The small amount of the Triad2 phase observed in the fibers also suggests that some interaction between the blend components may have occurred.

The morphology of the as-spun PC blends was ideal for mechanical reinforcement. The Triad2

phase was elongated into fibrils having essentially infinite aspect ratios within the PC matrix. The large number of high aspect ratio fibrils oriented along the fiber axis combined with the absence of significant modulus improvement is further evidence that Triad2 is not a high-performance polymer.

The morphology of the posttreated PC blend indicated that fiber drawing reduces the ability of the Triad2 block copolymer to mechanically reinforce either PC or PET. The posttreatment process periodically fractures the Triad2 fibrils within the matrix material, effectively reducing their aspect ratio. Thus, the modulus enhancement observed in the PET blends is most likely due to a modification of the PET matrix.

Thermal results indicate that the Triad2 block copolymer is capable of modifying the PET matrix phase. DSC results show a 5°C shift in the T_g of PET when blended with Triad2, suggesting that some interaction between components is likely. The addition of Triad2 to PET also dramatically affects the crystallization behavior of PET. The incorporation of Triad2 increases the degree PET crystallinity and decreases the cold crystallization temperature. Thus, the Triad2 performs as an effective nucleating agent for PET. If the nucleating effect also occurs during the drawing process, the enhanced mechanical performance of the PET blends could be attributed to an increase in fiber crystallinity.

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