Modification of the Processing Window of a Thermotropic Liquid Crystalline Polymer by Blending with Another Thermotropic Liquid Crystalline Polymer

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ABSTRACT: This paper is concerned with properties and processing performance of two thermotropic liquid crystalline polymers (TLCPs) produced by DuPont (HX6000 and HX8000) with widely varying melting points and blends of these two TLCPs. This work was carried out in an effort to develop a TLCP suitable for generating poly(ethylene terephthalate) (PET) composites in which the melting point of the TLCP was higher than the processing temperature of PET. Strands of the neat TLCPs and a 50/50 wt %TLCP-TLCP blend were spun and tested for their tensile properties. It was determined that the moduli of the HX8000, HX6000, and HX6000-HX8000 blend strands were 47.1, 70, and 38.5 GPa, respectfully. Monofilaments of PET-HX6000-HX8000 (50/ 25/25 wt %) were spun with the use of a novel dual extruder process. The strands had moduli as high as 28 GPa, exceeding predictions made using the rule of mixtures and tensile strengths around 275 MPa. The strands were then uniaxially compression molded at 270°C. It was found that after compression molding, the modulus dropped from 28 GPa to roughly 12 GPa due to the loss of molecular orientation in the TLCP phase. However, this represents an improvement over the use of HX8000. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2209-2218, 1999

Key words: thermotropic liquid crystalline polymer; composite; polymer blends; fiber spinning; dual extruder

INTRODUCTION

The use of thermotropic liquid crystalline polymers (TLCPs) to reinforce commodity thermoplastics has attracted considerable interest since the mid to late 1980s.^{1–5} One reason for this interest has been due to the fact that when blends of a thermoplastic and a TLCP are subjected to extensional deformation, the TLCP phase is deformed into fibrils. These TLCP fibrils are found to provide mechanical reinforcement to the matrix, producing lightweight, wholly thermoplastic composites. Because the reinforcing fibrils are formed during the melt processing step, Kiss³ called the resulting materials in situ composites.

There are several reasons that TLCPs are potentially viable alternatives to traditional reinforcing materials like glass fiber. One significant reason is their combination of low-density and high mechanical properties. It has been shown that neat TLCPs can possess moduli of up to 100 GPa and strengths of 1 GPa and greater when they are highly oriented, while having densities of only around 1.4 g/cm³.^{6–9} These properties are competitive with other forms of reinforcement, such as glass fiber, which has a tensile modulus of

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Figure 1 Schematic of the dual extrusion processing scheme.

69 to 83 GPa, a tensile strength from 1.72 to over 2.07 GPa, and a density of 2.52 to 2.61 g/cm³.^{10–13} Therefore, if the full reinforcing potential of the TLCP is realized, it would be possible to produce wholly thermoplastic composites, which would have mechanical properties matching or exceeding those obtained with glass and even aramid fiber reinforcement. Other important reasons cited for using TLCPs as reinforcement rather than glass fiber are as follows.

- 1. The composite melt requires less energy;
- 2. There is less wear on the processing equipment;
- 3. The ability to use compatibilization to provide interfacial adhesion between the two phases;
- 4. Their recycling potential.¹⁴

Therefore, TLCPs possess several key features that make them a possible alternative to more conventional reinforcing materials.

However, one problem in producing *in situ* composites are the high temperatures at which many TLCPs need to be processed. Lin and Winter^{15,16} have shown that for Vectra A900, it is

necessary to take it up to temperatures of 320 to 330°C to remove all high melting crystallites. Likewise, many TLCPs, such as Xydar, have melting temperatures well in excess of 300°C.^{17,18} With such high melting temperatures, these materials can only be combined with select engineering thermoplastics, such as polyphenylene sulfide, polysulfone, and polyetheretherketone. Therefore, finding methods of overcoming this limitation are essential for being able to blend TLCPs with high melt processing temperatures with lower melting thermoplastics, such as polypropylene (PP) and poly(ethylene terephthalate) (PET).

To overcome this need for overlapping melt processing temperatures, a patented dual extruder system, shown schematically in Figure 1, was developed by Sukhadia and coworkers.^{19,20} In this process, the matrix and TLCP are plasticated in separate extruders. The TLCP is then cooled and introduced into the matrix as continuous streams, using a phase distribution system at the tee connecting the two extruders. Immediately following the phase distribution system, the blend is passed through a mixing head containing static mixers to further divide the TLCP into smaller continuous streams. The composite melt leaving the mixing head is then extruded through a capillary die (L/D < 1) and drawn to orient the TLCP. Because the dual extruder process introduces continuous TLCP streams into the matrix, the final composite strands contain TLCP fibrils with essentially infinite aspect ratios, helping maximize the reinforcing potential of the TLCP.

The utility of the dual extruder system in producing in situ composite strands and fibers has been shown in several studies.¹⁹⁻²⁵ Sukhadia and colleagues²⁰ demonstrated the advantages of using this approach in generating strands of PET-Vectra A900 (70/30 wt %) relative to using a single-screw extruder. For blends prepared in a single-screw extruder, it was only possible to reach a tensile modulus of 13.39 (± 0.45) GPa at a draw ratio of 49 (standard deviations given in parentheses). Meanwhile, at the same draw ratio, the dual extruder process yielded strands with a modulus of $18.99 (\pm 0.17)$ GPa. This difference in stiffness was attributed to the morphology of the composite strands. Strands produced using the dual extruder system had no visible skin-core morphology and possessed fibrils with essentially infinite aspect ratios. Meanwhile, the strands prepared in a single-screw extruder did have a skin-core morphology and did not have axially continuous Vectra A900 fibrils in the PET matrix. Another significant factor contributing to the higher stiffness was the ability to spin the strands at a lower temperature than was possible when using just a single extruder.

Still, this processing scheme is limited by the supercooling behavior of the TLCP, that is, by how much the TLCP can be cooled below its melting temperature before its viscosity begins to dramatically rise. It would be desirable to be able to modify the supercooling behavior of the TLCP so that the maximum difference in processing temperature between the TLCP and matrix could be used without encountering either solidification of the TLCP or degradation of the matrix. This would allow the dual extruder process to utilize the supercooling ability of TLCP to its fullest extent.

One possible method of controlling how a TLCP behaves as it is cooled is by blending it with a second TLCP with a lower melting temperature and similar molecular structure. Baird and coworkers^{26,27} used dynamic rheological measurements to study the solidification behavior of copolyesters composed of 60 mol % 4-hydroxybenzoic acid (HBA) and 40 mol % PET and HBA–PET

(80/20 mol %). For these two polymers, HBA-PET (60/40 mol %) had a melting temperature of approximately 250°C, while HBA-PET (80/20 mol %) had a melting temperature roughly 50°C higher, at 300°C. By blending these two copolyesters together, the melt could be cooled to lower temperatures than were possible with HBA-PET (80/20 mol %) before a sudden increase in complex viscosity was observed.

Recently, McLeod and Baird^{28,29} reported similar supercooling behavior when HX6000, with a melting temperature of 332°C, was melt blended with HX8000, with a melting temperature of 272°C. It was found by measuring the complex viscosity of the blends as the melt was cooled that a linear relationship existed between composition and solidification temperature. This was also confirmed using differential scanning calorimetry (DSC), where the onset of crystallization was lowered relative to that of HX6000 as more HX8000 was added to HX6000.

The supercooling behavior of the blends of HX8000 and HX6000 is important because of its potential to be used with the dual extruder process. Neat HX6000 cannot be readily processed with PET because it cannot be cooled to below 300°C before solidifying. Meanwhile, HX8000 can be directly processed with PET but cannot be reheated to melt the PET without substantial losses in the reinforcing ability of the TLCP phase. Therefore, using the dual extruder processing scheme with HX6000-HX8000 blends. the potential exists to produce composite strands that have the greatest possible difference in processing temperature between the TLCP and matrix resins. This is important because it increases the likelihood that properties generated in the spinning step can be retained in any post-processing scheme.

The objective of this work is threefold. First, it needs to be determined how blending HX8000 with HX6000 affects the spinnability of the TLCP melt. Second, it needs to be determined if the TLCP–TLCP blend can be used to produce *in situ* composite strands with PET as the matrix resin. In particular, it needs to be shown that the modification in supercooling behavior observed in rheological cooling scans can be used to produce *in situ* composite strands using the dual extruder processing scheme. Third, the effect that consolidation of the composite strands at high temperatures has on mechanical properties has to be determined. This is necessary to reveal if the potential for post-processing operations exists.

EXPERIMENTAL

Materials

The following two TLCPs produced by DuPont were used in the study: HX6000 and HX8000. HX6000 is a semicrystalline TLCP with no clearly discernible glass transition temperature, two melting endotherms (one at 275.5°C and the second at 331.9°C), and a density of 1.38 g/cm³. A melt temperature of at least 350°C is generally needed for processing. HX8000 is a semicrystalline TLCP with a glass transition temperature of 110°C, two melting endotherms (one at 228.9°C and the second at 271.8°C), and a density of 1.38 g/cm³. To process this TLCP, a melt temperature of at least 290°C is usually required. It is believed that these TLCPs are composed of unspecified ratios of terephthalic acid, 4-hydroxybenzoic acid (HBA), hydroguinone, and hydroguinone derivatives, with HX6000 having a high ratio of HBA. $^{7,18,30-37}$

For spinning the *in situ* composite strands, PT 7067, a grade of PET manufactured by DuPont, was used. It is a high-molecular-weight grade of PET, with a glass transition temperature of 84°C, a melting temperature of 255°C, and a density of $1.33 \text{ g/cm}^{3.38}$

Neat Strand Processing

Neat strands of HX6000, HX8000, HX6000-HX8000 (50/50 wt %), and PT 7067 were spun using a Killion KL-100 extruder with a screw diameter of 1 in. and a L/D = 24. The melt conveying zone was set at 350 to 360°C for HX6000 and HX6000-HX8000 (50/50 wt %) and 330°C for HX8000. Meanwhile, the PT 7067 was processed at a maximum temperature of 280°C. The melt leaving the mixing head was extruded through a capillary die (L/D < 1; diameter = 1.3)mm) and drawn, quenched in a water bath, and collected on a take-up roll. The take-up speed was varied to produce TLCP strands with draw ratios ranging from under 10 to over 40 and draw ratios up to 190 for the PT 7067. Note that all polymers were dried in a vacuum oven set at 110°C for at least 24 h before being processed.

Composite Strand Processing

Composite strands of PT 7067 and HX6000– HX8000 (50/50 wt %) were generated using a patented dual extrusion process, which has been extensively described elsewhere.^{19,20,22} Strands

were spun with two loadings of TLCP, either 20 wt % TLCP or 50 wt % TLCP. The equipment consisted of two Killion KL-100 extruders, each having a screw diameter of 1 in. and a L/D = 24. Regardless of the loading level of TLCP in the composite strands, the HX6000-HX8000 (50/50 wt %) blend was processed in one extruder with the melt conveying zone set at 350 to 360°C, while the PT 7067 was plasticated in the second extruder with the melt conveying zone set at 275 to 285°C. The mass flow rate of the TLCP was precisely metered by using a Zenith gear pump (Model HD-556, 1.725 cm³/rev), with the strand composition determined from the total mass flow rate of the blend and the controlled mass flow rate of the TLCP. After passing through the gear pump, the TLCP stream was cooled to 300°C before being introduced into the PT 7067 using a tee connecting the two extruders. Immediately following the tee, the HX6000-HX8000-PT 7067 blend was passed through a mixing head containing three helical Kenics elements and four Koch elements to further divide the TLCP into smaller continuous streams. The composite melt leaving the mixing head was then extruded through a capillary die (L/D < 1; diameter = 1.8 mm) and drawn to orient the HX6000-HX8000 phase, quenched in a water bath, and collected on a take-up roll. The take-up speed was varied to produce composite strands with draw ratios ranging from under 15 to over 50. Note that the polymer pellets were dried in a vacuum oven set at 110°C for at least 24 h before being processed.

Dynamic Rheological Testing

Rheological measurements were conducted using a Rheometrics RMS-800 with 25-mm-diameter parallel plate tooling. Dynamic oscillatory measurements were carried out using 5% strain and a gap of 1.0 mm. The test specimens were circular disks cut from injection-molded plaques. These were dried in a vacuum oven at 110°C for at least 24 h prior to testing. Each sample was brought to the starting test temperature and held at that temperature until thermal equilibrium was established between the tooling and the melt. This generally took 3–5 min, with the temperature being monitored using a thermocouple located in the center of the bottom plate. For the duration of the tests, each sample was exposed to a continuous nitrogen atmosphere.

To monitor the rheology of the supercooled TLCPs, the complex viscosity $(|\eta^*|)$ of the melt

was measured as the TLCP was cooled. An angular frequency (ω) of 10 rad/s was used in each test. The specimen was heated to the starting test temperature, then cooled at a fixed rate of 2.3°C/min. The test was stopped once the torque exceeded 500 g cm.

Mechanical Properties

All of the tensile properties of the individual strands were measured using an Instron Mechanical Tester (model 4204) equipped with a 1 kN load cell. At least 30 strands of each material were tested to determine the relationship between draw ratio and mechanical properties. Ten measurements of the strand diameter were made for each sample to establish both the average and smallest diameter. The gage lengths were approximately 250 mm for all strands, except where noted otherwise, with the fiber ends wrapped in masking tape to help provide uniform gripping of the strands. Because of the difficulty in spinning HX6000 strands with a uniform diameter, strands 40 mm long had to be tested to ensure a fairly consistent diameter for the entire length of the strand. Also, for comparative purposes, both 40 and 250 mm long strands of HX8000 were tested. The crosshead speed was set at 1.27 mm/ min. For calculating the tensile modulus, the average strand diameter was used. Meanwhile, for calculating the tensile strength, the smallest strand diameter was used. This was done because it was the point with the lowest cross-sectional area, so the strands generally failed at this location.

RESULTS AND DISCUSSION

In order to process the TLCPs using the dual extruder processing scheme, the TLCPs needed to be evaluated for their ability to remain molten as they were cooled. This was done by measuring the complex viscosity of the neat TLCPs and the TLCP–TLCP blends as they were cooled at a fixed rate. By doing this, it was possible to determine what the composition of the HX6000–HX8000 blend had to be in order for it to be cooled well under 300°C. This is the temperature above which the PET will undergo rapid degradation.

As shown in the plot of complex viscosity versus temperature (Fig. 2), it was possible to modify the solidification behavior of the HX6000 by melt blending it with HX8000. By adding HX8000, the



Figure 2 Complex viscosity $(|\eta^*|)$ as a function of temperature for polymers cooled at a rate of 2.3°C/min: (\Box) PT 7067, (\blacksquare) HX8000, (\bullet) HX6000–HX8000 (25/75 wt %), (\blacktriangle) HX6000–HX8000 (50/50 wt %), (\blacktriangledown) HX6000–HX8000 (75/25 wt %), and (\blacklozenge) HX6000.

temperature at which the viscosity of the HX6000 began to rise dramatically could be shifted downward with increasing levels of HX8000. Based on these data, it appears that a 50/50 wt % blend of HX6000–HX8000 would be appropriate to use with PET, as the blend remained deformable down to approximately 280°C. This was believed to provide a wide enough processing temperature range (280 to 300°C) in which to combine the TLCP–TLCP blend with PET without having to be concerned with premature solidification of the TLCP stream or degradation of the matrix. Also, over the 280–300°C range, the HX6000–HX8000 (50/50 wt %) blend was less viscous than the PET matrix, which may be important for processing.^{17,39}

Having demonstrated that the HX6000-HX8000 (50/50 wt %) blend possessed the desired supercooling behavior, it was then necessary to spin strands of neat fiber to show the effects of composition and draw ratio on mechanical properties. Strands of HX6000, HX8000, and HX6000-HX8000 (50/50 wt %) were extruded and drawn to determine the spinnability of the three materials. Comparing the spun strands of HX6000-HX8000 (50/50 wt %) to the strands of the neat TLCPs, it was shown that the blend exhibited better spinnability than neat HX6000 by the maximum draw ratio attained and the standard deviations in the draw ratios (Table I). For HX6000, it was observed that it had limited melt strength and fluctuated dramatically in diameter. Specifically, as the HX6000 melt was

Composition	Maximum Draw Ratio
HX6000	28.32 (67.65)
HX6000–HX8000	44.12 (8.28)
(50/50 wt %)	
HX8000	45.84 (10.90)

Table IMaximum Draw Ratiosof the TLCP Strands

 $^{\rm a}$ These draw ratios are based on the average diameters of the strands. Standard deviations are given in parentheses.

drawn, it would not deform uniformly. Rather, it would neck, producing lengths with very small diameters, followed by lengths with very large diameters. This necking phenomenon was so pronounced that a few test samples had draw ratios exceeding 150, while most of the strands had a draw ratios of just over 20. Meanwhile, the neat HX8000 and HX6000-HX8000 (50/50 wt %) strands both showed the capacity to be drawn to draw ratios over 40. Also, the standard deviations throughout the range of draw ratios produced were appreciably lower than what were seen for the HX6000 strands. From this it can be concluded that adding HX8000 to HX6000 improved the spinnability of the TLCP melt by preventing the melt from periodically necking as it was drawn down.

Because the draw ratios of the neat HX6000 strands possessed diameters that fluctuated over such a wide range, it was necessary to test them differently than the HX8000 and HX6000– HX8000 strands. Rather than testing 250 mm lengths of fiber, only 40 mm lengths were used. This allowed portions of fiber to be tested, which had a fairly uniform diameter. However, because the fiber length was so short, it was necessary to determine if the difference in strand length would have an effect on the measured mechanical properties. To do this, both short and long HX8000 strands were tested to quantify the effect that strand length may have had on the measurements of modulus.

Comparing the results of testing both short strand lengths ($\sim 40 \text{ mm}$) and long strand lengths ($\sim 250 \text{ mm}$) of HX8000 demonstrated that the strand length had to be considered in the measurements of the tensile modulus. For the short strands, the maximum tensile modulus was 37.1 GPa, while when 250-mm strands with draw ratios over 40 were tested, the tensile modulus was 47.1 GPa (Fig. 3). The value of 47.1 GPa closely matches the maximum stiffness of 47 GPa reported by Krishnaswamy and Baird²⁴ for meltspun HX8000 fiber. Meanwhile, the short HX6000 strands had a maximum tensile modulus of 70.0 GPa. Based on the effect of strand length on the modulus for HX8000, 70.0 GPa should be taken as a conservative value. Specifically, if it was possible to test longer HX6000 strands, it is likely the maximum measured tensile modulus would be slightly higher than 70.0 GPa.

After testing the neat TLCPs, the tensile properties of the strands of HX6000-HX8000 (50/50 wt %) were evaluated to determine how their tensile properties compared to those of the neat resins. For the HX6000-HX8000 (50/50 wt %) blend, it was found that a modulus of only 38.5 GPa could be reached (Fig. 4), even for strands with draw ratios in excess of 50. This is lower than expected for two reasons. First, using the rule of mixtures to predict the modulus of the blend, it was calculated that a much higher modulus of 67 GPa should have been reached. Second, 38.5 GPa is lower than the values for either neat HX8000, at 47.1 GPa, or neat HX6000, at an extrapolated stiffness of 87 GPa. This is surprising because it would not be anticipated that the TLCP-TLCP blend would be of lower stiffness than that of either homopolymer. Hence, although blending the two TLCPs together did achieve the desired goals of improving supercooling behavior and spinnability, the stiffness of the strands was lower than desired.

Tensile testing was also performed to determine the effect of composition on strength. As



Figure 3 The tensile modulus of neat HX8000 strands versus the strand lengths of draw ratio: (■) 40 and (●) 250 mm.



Figure 4 Tensile modulus versus the draw ratio for HX6000−HX8000 (50/50 wt %) strands: (■) experimental data.

shown in Figure 5, the HX6000–HX8000 blend strands had a tensile strength between those of the two neat polymers. In particular, at high draw ratios the tensile strength was about 650 MPa for HX6000 and about 840 MPa for HX8000. This tensile strength for HX8000 matches that found by Krishnaswamy and Baird²⁴ for melt-spun HX8000 fibers. Meanwhile, the HX6000–HX8000 blend had a tensile strength of approximately 720 MPa. From these results, it can be concluded that melt blending the TLCPs did not have an adverse impact on the strength of the strands.

Examining the effect of draw ratio on the mechanical properties of the composite strands, it was clear that the HX6000, HX8000, and HX6000-HX8000 (50/50 wt %) composite strands showed the same general behavior. For each of the TLCPs, the tensile strength displayed a sharp improvement as the draw ratio was increased, eventually reaching a maximum once the draw ratio reached roughly 75 to 100. Meanwhile, although the draw ratio needed to maximize the tensile modulus differed for each of the TLCPs, each set of strands showed a similar increase in modulus to some asymptotic maximum. This behavior is commonly observed with melt-spun TLCPs and has been recognized as being due to increased molecular orientation from the extensional deformation encountered in fiber and strand spinning.^{8,40} Specifically, it has been noted that no post-drawing process is needed when spinning TLCP fibers and strands because the chain orientation developed in the spinning process is retained in the final strands.

For the sake of comparison to the properties of the TLCPs and composite strands, the tensile modulus and strength were found for PT 7067. Strands of melt-spun PT 7067 were found to have a stiffness of approximately 2.24 GPa and a tensile strength of around 51.4 MPa, irrespective of the draw ratio. Compared to the PET, all of the TLCPs had much higher strengths and moduli. Thus, the potential exists that adding TLCP to the PET could produce composite strands with both improved strength and modulus relative to that of the neat matrix polymer.

Having demonstrated that the HX6000-HX8000 (50/50 wt %) melt was spinnable, the dual extruder processing scheme was used to combine HX6000-HX8000 (50/50 wt %) with PT 7067. This was done at two different loading levels, one with 20 wt % TLCP, and a second with 50 wt % TLCP. In both cases, it was found that composite strands could be extruded and spun to draw ratios in excess of 40. In particular, PT 7067-HX6000-HX8000 (80/10/10 wt %) strands were spun with a draw ratio of $74.32 \ (\pm 17.56)$, while the highest draw ratio attained with PT 7067-HX6000-HX8000 (50/25/25 wt %) strands was $61.99 (\pm 17.03)$. Therefore, it was proven that it was possible to produce in situ composite strands containing a high melting TLCP, satisfying one of the objectives of this work.

The relationship between draw ratio and modulus for HX6000-HX8000-PT 7067 (25/25/50 wt %) composite strands is shown in Figure 6. Consistently, the moduli of the composite strands displayed a positive deviation from rule of mixtures



Figure 5 Tensile strength versus the draw ratio: (\blacksquare) HX6000, (\bullet) HX6000–HX8000 (50/50 wt %), and (\blacktriangle) HX8000.



Figure 6 Tensile modulus versus the draw ratio of PT 7067–HX6000–HX8000 (50/25/25 wt %) strands: (■) experimental data and (—) rule of mixtures prediction.

predictions. For each of the draw ratios produced, the tensile modulus was approximately 25 to 28 GPa, versus a maximum modulus of 20 GPa, predicted using the rule of mixtures. Using the rule of mixtures to back calculate a tensile modulus for the TLCP fibrils, it was found that for the composite strand to have a modulus of 28.3 GPa, the fibrils would have had a modulus of 55.5 GPa. This is nearly 20 GPa over the highest stiffness determined for the neat HX8000–HX6000 strands and approaches the theoretical modulus of 67 GPa predicted for the HX8000–HX6000 blend.

It should be recognized that this positive deviation from the rule of mixtures prediction qualitatively matches the observations of Krishnaswamy and Baird,²⁴ as well as Robertson et al.²¹ for TLCP-matrix in situ composite fibers produced using the dual extruder system. For example, Robertson and colleagues²¹ spun fibers of PP-Vectra B950 (50/50 wt %) to draw ratios over 200. It was found that at these high draw ratios, they possessed tensile moduli of 44 GPa. What made this result striking is that by using the rule of mixtures, the modulus of the TLCP phase was back-calculated to be around 100 GPa. This is much greater than the 75 GPa usually obtained when neat Vectra B950 is spun, showing that the dual extruder processing scheme created a synergistic reinforcing effect. One explanation given by the authors for this behavior was that by using the dual extruder system, perhaps it was possible to orient the TLCP more effectively. In

particular, Yee et al.⁴¹ extrapolated a modulus of 110 GPa for a Vectra B950 sample having complete molecular orientation. Therefore, the polypropylene (PP) matrix may have served as an insulator, allowing the Vectra B950 fibrils to be drawn further and oriented prior to solidification more than is possible when neat Vectra B950 fiber is drawn.

The strengths of the composite strands were also determined, as is shown in Figure 7. As with the tensile modulus data, it appears that it was possible to obtain the maximum mechanical properties at relatively low draw ratios. Also, by adding 50 wt % TLCP, the strengths obtained were four to five times greater than that of neat PT 7067. Even with just 20 wt % TLCP, it was possible to produce composite strands with a average tensile strength of 114.4 (±24.0) MPa, twice that of neat PT 7067. Therefore, in addition to improving modulus, adding HX6000–HX8000 to the PT 7067 resulted in producing strands with higher strengths.

Another point of interest was to determine if the composite strands could be compressionmolded into uniaxially reinforced composites without a reduction in properties. Testing the compression-molded composites, it was observed that consolidation caused a substantial decline in stiffness, as shown in Figure 8. The individual strands possessed a tensile modulus of about 28.4 GPa. However, exposure to 270°C for 4 min caused the stiffness to fall to 11.4 GPa. Although this is still significantly above that of neat PET, it is well below the properties of the individual



Figure 7 Tensile strength versus the draw ratio of PT 7067-HX6000-HX8000 (50/25/25 wt %) strands: (■) experimental data.



Figure 8 The effect of exposure time to 270°C on the tensile modulus of composite strands of PT 7067–HX6000–HX8000 (50/25/25 wt %) strands with a draw ratio of 61.99: (1) individual strands, (2) consolidated strands, (3) consolidation + 5 min, (4) consolidation + 15 min, (5) consolidation + 30 min, and (6) consolidation + 60 min. Note that all consolidation was at 270°C for 4 min, and the additional time represents the exposure to 270°C without the application of pressure.

strands. Therefore, the post-processing options available for these PET-TLCP composite strands may be limited because the full reinforcing potential of the TLCP is not realized.

Still, these properties are significantly better than what would be obtained if neat HX8000 was used as the reinforcing phase. If PET-H8000 composite strands were compression-molded at 270°C, all of the reinforcing ability of the HX8000 would be lost because 270°C is too close to the melting temperature of 272°C for the TLCP. This is further emphasized by the mechanical properties found when nylon 11-HX8000 (65/35 wt %) composite strands were consolidated.²⁴ When these strands were compression-molded into uniaxial composite plaques at 195°C, the mechanical properties dropped from 19.8 GPa for the individual strands to 13.4 GPa. With a 33% decline in stiffness when consolidated at 195°C, it is clear that consolidation at 270°C would cause a complete loss in the reinforcing ability of the HX8000 fibrils.

The results from these tests are also important because they demonstrate that after the initial reduction in properties, continued exposure to 270°C caused no further damage. Specifically, exposing the uniaxially consolidated strands to 270°C for up to 1 h consistently produced composites with tensile moduli of over 9 to 14.3 GPa. This means that if this initial drop in stiffness can be avoided, many post-processing options may be viable for these composites.

One method which may allow a retention of properties through the compression-molding process is to consolidate the strands at a lower temperature. Although this is not an option with PET as the matrix resin, it should be possible with lower melting resins, such as nylon 11 and PP. As stated earlier, the consolidation of nylon 11-HX8000 (65/35 wt %) composite strands at 195°C caused the modulus to drop from 19.8 GPa to 13.4.²⁴ With HX6000 being a stiffer, higher melting TLCP, it is likely that nylon 11-HX8000-HX6000 composite strands would be able to withstand the compression molding step better than nylon 11-HX8000 composite strands. Hence, with the proper matrix resin, it may be possible to exploit the ability to control the cooling behavior of the TLCP melt to produce lightweight, wholly thermoplastic composites with high mechanical properties, which otherwise could not be produced.

CONCLUSIONS

By blending HX8000 with HX6000, it was possible to improve the processability of the TLCP melt by making it more spinnable, as manifested in the ability to produce strands with much smaller fluctuations in diameter than were possible with neat HX6000. Furthermore, it was shown that composite strands of PET-HX6000-HX8000 could be spun with high mechanical properties. This overcame the problems in producing PET-HX6000 composite strands, which were the degradation of the PET as well as the inability to spin HX6000 to high draw ratios. Also, this was an improvement over consolidating PET-HX8000 composite strands, where the HX8000 fibrils would lose their reinforcing ability when taken to 270°C. Although the PET-HX8000-HX6000 strands lost some of their reinforcing ability upon consolidation into uniaxial composites, using lower melting matrix thermoplastics may allow the full reinforcing ability of the TLCP fibrils to be realized.

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