

# Structure and Property Relationship of Thermotropic Liquid Crystal Polymer and Polyester Composite Fibers

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**ABSTRACT:** Poly(ethylene 2,6-naphthalate) (PEN) and poly(ethylene terephthalate) (PET) composite fibers reinforced with a thermotropic liquid crystal polymer (TLCP) were prepared by the melt blending and spinning process to achieve high performance fibers with improved processability. Polymer composite fibers consisting of cheap polyester and small quantity of expensive TLCP are of interest from an economic point of view and from an industrial perspective. The increase in the birefringence and density of the TLCP/PEN/PET composite fibers with the spinning speed was attributable to the enhancement of the molecular orientation and effective packing between chains in the TLCP/PEN/

PET composite fibers. Annealing process resulted in the formation of more ordered and perfect crystalline structure and higher crystallinity, improving the mechanical properties of the TLCP/PEN/PET composite fibers. The increase in the crystallite size and the degree of chain extension with increasing spinning speed resulted in the gradual increment of the long period for the TLCP/PEN/PET composite fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2211–2219, 2006

**Key words:** composites; fibers; liquid crystalline polymer (LCP); melt spinning; poly(ethylene 2,6-naphthalate) (PEN); poly(ethylene terephthalate)

## INTRODUCTION

As various industries have been developed rapidly, there has been a great interest in a wide range of applications of high performance polymers and fibers as advanced industrial materials. Moreover, polymer composites with high mechanical strength and good processability have been extensively investigated not only for scientific interest but also from an industrial perspective, because of their interesting properties and potential applications as well as their growing industrial importance. In particular, the melt blends based on poly(ethylene 2,6-naphthalate) (PEN) and poly(ethylene terephthalate) (PET) has been attractive because of significant improvement of their performance by combining the excellent properties of PEN with the economical efficiency of PET.<sup>1–6</sup>

For the past two decades, thermotropic liquid crystal polymers (TLCPs) have attracted a great deal of interest from fields ranging from the industrial to the scientific because of their excellent mechanical properties and thermal stability, resulting in their application as higher performance engineering plastics and fibers.<sup>6–8</sup> However, despite this advantage and exten-

sive research into TLCP, its application is limited because of the high cost of the monomer. For this reason, much research and development in TLCP processing has been carried out to reduce the costs by employing melt blending with a less expensive material. The melt blending of polymers is an effective method for enhancing the specific properties of each component. In particular, the melt blends consisting of cheaper commodity polyester and a small mass of the expensive TLCP are of interest from an economic point of view. Furthermore, thermoplastic polymer melt blends are easier to process, and the reinforcement effect of the polymer matrix and the reduction in melt viscosity leads to the formation of fine fibrils, even with small concentration of TLCP. Therefore, the melt blends of TLCPs and thermoplastic polymers have been one of the extensive scientific and engineering research fields because of their potential application for high performance polymers.<sup>9–20</sup>

As high performance polymers commonly involve high costs and are difficult to process, it is very important to reduce their processing costs without losing any of their mechanical properties. Because of its low melt viscosity, the incorporation of small concentration of TLCP can effectively reduce the melt viscosity of polymer blends, thereby enhancing their processability.<sup>20–22</sup> In general, the TLCP can be oriented to form fibrils during the melt processing, and then developed into high oriented fibrillar structure, leading to the reinforcement effect of the polymer matrix and

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easier processing. These characteristics make it possible for the TLCP to be utilized in high performance fibers with conventional melt spinning. The melt spinning is the most effective and economical method for producing the synthetic fibers, which provides the means for obtaining various kinds of polymer structures.<sup>23</sup> Therefore, the polyester composite fibers reinforced with a small mass of TLCP produced by conventional melt blending and spinning process have the higher possibility to be used practically in the advance industrial fibers that demand high performance and low cost, from an economic point of view and an industrial perspective. The structure and property relations of TLCP and their blends must be developed that predict the thermal, rheological, and mechanical properties of polymer composites, to facilitate the development of TLCP-reinforced polymer composites.

Although many studies on the fundamental aspects of fiber formation and on the structural development during melt spinning have been carried out, little research and development into low-cost and high-performance composite fibers has been performed. In this research, TLCP/PEN/PET composite fibers were prepared by melt blending and spinning process to improve fiber performance with good processability and even lower processing cost. The objective of this research is to facilitate synergistic effects, especially to produce high performance industrial fibers that have optimized combination of excellent properties of TLCP with high performance of PEN/PET composites. Effect of incorporating TLCP on the structure and fiber properties of the polyester composite fibers was investigated, and the structure and property relationship of the TLCP/PEN/PET composite fibers is discussed.

## EXPERIMENTAL

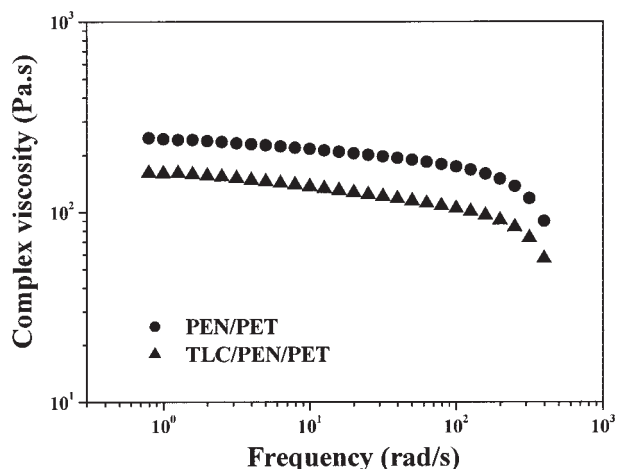
### Materials and preparation of TLCP/PEN/PET composite fibers

The conventional thermoplastic polymers used were the PEN with an intrinsic viscosity of 0.93 dL/g, and the PET with an intrinsic viscosity of 1.07 dL/g, supplied by the Hyosung Corp., Korea. The TLCP used was a flexible semiaromatic copolyester synthesized from poly(*p*-hydroxybenzoate) (PHB) and PET with a molar ratio of 80 : 20, purchased from the Unitika Co. Ltd., Japan. According to the supplier, the TLCP has an intrinsic viscosity of 0.55 dL/g, determined at 30°C in a phenol/tetrachloroethane (50 : 50, v/v) mixture. The glass transition temperature and melting temperature of TLCP were 79 and 286°C, respectively. All the materials were dried at 120°C in vacuo for at least 24 h before use, to minimize the effect of moisture. The polyester composites reinforced with a TLCP were

prepared by a melt blending process in a Haake rheometer (Haake GmbH, Germany) equipped with a twin screw. For the fabrication of TLCP/PEN/PET composites, the temperatures of the heating zones from the hopper to the die were set to 270, 285, 285, and 275°C, respectively, and the screw speed was fixed at 20 rpm. The predetermined blend compositions of the PEN/PET and the TLCP/PEN/PET composites were 75 : 25 and 10 : 67.5 : 22.5 by weight ratio, respectively. All the materials to be melt-spun were predried at 110°C in vacuo for 5 h. Blended polymer chips were melt-spun in the extruder that had a four-hole spinneret with a diameter of 0.5 mm, and the output rate was controlled at 5 g/min per hole. Melt spinning was carried out with spinning speeds in the range of 0.5–2.5 km/min. To investigate the effect of annealing on the structure and properties of the TLCP/PEN/PET composite fibers, we performed the annealing process at 180°C for 2 h in the heating oven at a fixed length, which was determined to be the optimum annealing condition from our previous research.<sup>15,16</sup>

### Characterizations

The complex viscosities of the PEN/PET composite fibers and the TLCP/PEN/PET composite fibers as a function of angular frequency were measured at 280°C using an advanced rheometric expansion system (ARES, Rheometric Scientific, Inc.) on which a 25-mm diameter parallel-plate was mounted. The plate gap was set at 1 mm, and the applied strain level was 10% in the frequency range of 0.05–450 rad/s. The birefringence ( $\Delta n$ ) of the TLCP/PEN/PET composite fibers was measured using a Nikon polarizing microscope equipped with a K tilting compensator (Wild Leitz Ltd., Germany). The density of the TLCP/PEN/PET composite fibers was measured at 25°C with a density gradient column filled with carbon tetrachloride and *n*-heptane. The WAXD analysis were performed using a Rigaku Denki X-ray diffractometer with Ni-filtered Cu K $\alpha$  X-rays ( $\lambda = 0.1542$  nm). The diffracting intensities were recorded at steps of  $2\theta = 0.05^\circ$  over the range of  $5^\circ < 2\theta < 40^\circ$ . The degree of crystallinity was calculated with a curve-fitting procedure suggested by Blundell and Osborn.<sup>24</sup> Broad Gaussian peaks were used to fit the amorphous halo, and the crystalline peaks were fitted to Gaussian functions. Synchrotron small angle X-ray scattering (SAXS) measurements were performed at the SAXS beamline facility of the Pohang Accelerator Laboratory (PAL) in Korea. The X-ray wavelength used was 0.1542 nm, and the beam size at the focal point was less than 1 mm<sup>2</sup>, focused by platinum-coated silicon premirror through a double crystal monochromator. The mechanical properties of the TLCP/PEN/PET composite fibers were measured at room temperature using an Instron 4465 tensile



**Figure 1** Complex viscosities of the PEN/PET composite fiber and TLC/PEN/PET composite fiber as a function of angular frequency.

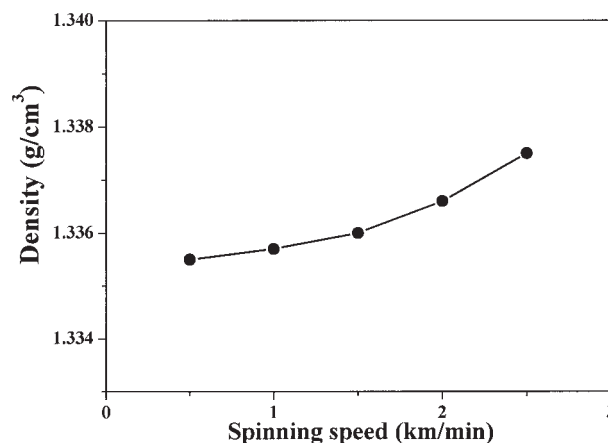
testing machine equipped with standard fiber grips, according to the procedures in the ASTM D 638 standard. The gauge length was set to 20 mm, and the crosshead speed was set to 5 mm/min. The results represented the averages over at least 10 individual measurements. The morphologies of the TLC/PEN/PET composite fibers were observed with a Hitachi SEM S-4200 scanning electron microscope. The measured TLC/PEN/PET composite fibers were broken in liquid nitrogen, and then the fracture surfaces were sputter-coated in vacuo with gold before scanning to prevent charging in the electron beam. For the observation of TLC fibrils, the TLC/PEN/PET composite fibers were treated with an *o*-chlorophenol solution at 55°C for 2 h to dissolve the polymer matrix from the TLC/PEN/PET composite fibers. The thermal behaviors of the TLC/PEN/PET composite fibers was investigated using a TA Instrument 2010 differential scanning calorimeter (DSC) under nitrogen atmosphere in the temperature range of 60–300°C with a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed using a TA Instrument 2960 TGA in the temperature range 30–800°C with a heating rate of 10°C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

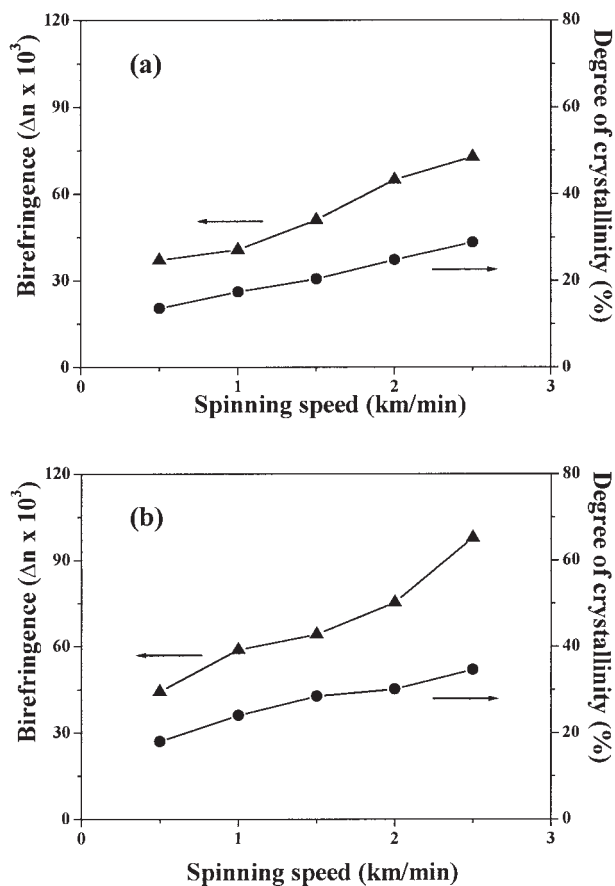
The complex viscosities of the PEN/PET composite fibers and the TLC/PEN/PET composite fibers as a function of frequency are shown in Figure 1. Compared with the PEN/PET composite fibers, the complex viscosity of the TLC/PEN/PET composite fibers was decreased on the addition of TLC at all frequency ranges, indicating the possibility of improving processability and the potential applications for polymer composite fibers reinforced with a TLC. Thus,

the incorporation of small quantity of TLC, because of its relatively low melt viscosity, can reduce the melt viscosity of the PEN/PET composites, thereby enhancing the processability of the TLC/PEN/PET composite fibers. The dependence of the density of the TLC/PEN/PET composite fibers on the spinning speed is shown in Figure 2. The density of the TLC/PEN/PET composite fibers was increased with the spinning speed, which was attributed to the enhancement of the packing between the chains and the development of more densely packed fiber structure in the TLC/PEN/PET composite fibers.<sup>25</sup>

The dependence of the birefringence of the TLC/PEN/PET composite fibers on the spinning speed and annealing is shown in Figure 3. The birefringence of the TLC/PEN/PET composite fibers increased with the spinning speed, indicating that the TLC/PEN/PET composite fibers changed into more oriented fibers by higher spinning speed. An increase in the shear stress with increasing spinning speed resulted in a higher degree of the molecular orientation during melt spinning, and the orientation process increased the crystallinity by orienting molecules.<sup>23,26</sup> The increased birefringence of the TLC/PEN/PET composite fibers at higher spinning speeds may be caused by the stress-induced crystallization.<sup>21,23,26</sup> The growth of crystals with high degree of orientation in the stress-induced crystallization resulted in the higher crystallinity, leading to the development of the molecular orientation and higher birefringence. In addition, the increase in the birefringence of the TLC/PEN/PET composite fibers with increasing spinning speed was attributed to the oriented crystal growth in the TLC/PEN/PET composite fibers, together with the fact that more ordered TLC domains could form preferentially oriented fibrils parallel to the flow direction. The birefringence value of the annealed TLC/PEN/PET composite fibers was higher than that of the unan-



**Figure 2** Effect of spinning speed on the density of TLC/PEN/PET composite fibers.



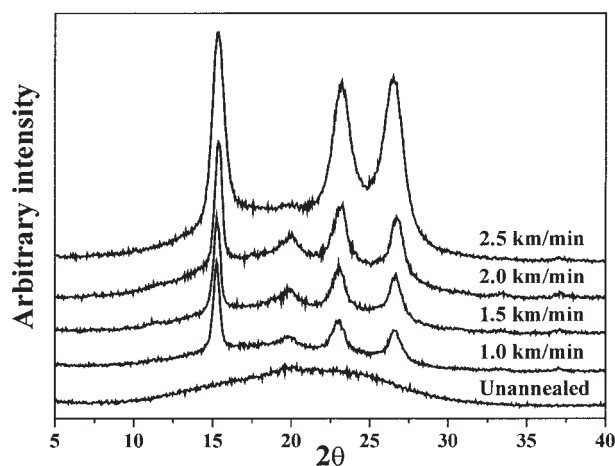
**Figure 3** Changes in the birefringence and the degree of crystallinity of (a) the TLCP/PEN/PET composite fibers and (b) annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.

annealed TLCP/PEN/PET composite fibers, suggesting that annealing process improved the molecular orientation and the crystallinity. As shown in Figure 3, the increase in the degree of crystallinity for the TLCP/PEN/PET composite fibers with increasing spinning speed indicated that more ordered and oriented crystallites were developed in the TLCP/PEN/PET composite fibers with increasing spinning speed. The annealed TLCP/PEN/PET composite fibers exhibited higher degree of crystallinity when compared with the unannealed TLCP/PEN/PET composite fibers. Therefore, the development of more ordered crystalline structures in the annealed TLCP/PEN/PET composite fibers resulted in the increment of the degree of crystallinity for the annealed TLCP/PEN/PET composite fibers by higher spinning speed and annealing process. From the above results, it was expected that the increase in the molecular orientation and the degree of crystallinity will improve the tensile strength and tensile modulus of the TLCP/PEN/PET composite fibers.

The WAXD profiles of the TLCP/PEN/PET composite fibers fabricated at various spinning speeds are shown in Figure 4. For the unannealed TLCP/PEN/PET

PET composite fibers, no crystalline peaks were observed except for the characteristic peak of the intermolecular packing of the PHB component in TLCP. The quick cooling speed of as-spun fibers during melt spinning process may cause no crystalline peak in the TLCP/PEN/PET composite fibers. In addition, the PEN and the PET were difficult to form the crystalline structure in ternary blend fiber, and the block or random copolymers produced by transesterification reactions may disturb the development of the crystalline structure in the TLCP/PEN/PET composite fibers. In our previous papers,<sup>3-5</sup> it was also reported that during melt blending, transesterification reactions occurred, which first produced block copolymers and then proceeded to form a random copolymers. However, the annealed TLCP/PEN/PET composite fibers exhibited three characteristic crystalline peak, which was attributed to the (010), (-110), and (100) reflections, indicating the crystalline structures of the PEN and PET components. This result means that more perfect crystalline structures in the TLCP/PEN/PET composite fibers were achieved through annealing process. In addition, the intensities of the diffraction peaks increased with the spinning speed, which was attributed to the development of more ordered and perfect crystallites in the annealed TLCP/PEN/PET composite fibers. The WAXD profiles of the annealed TLCP/PEN/PET composite fibers indicating the development of more ordered and oriented crystalline structure also corresponded with the increase in the degree of crystallinity for the annealed TLCP/PEN/PET composite fibers, as shown in Figure 3. The apparent crystallite size ( $L_{hkl}$ ) in the TLCP/PEN/PET composite fibers was calculated with Scherrer's equation<sup>27</sup>:

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$



**Figure 4** WAXD profiles of the annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.



TABLE I  
Structural Parameter of the TLCP/PEN/PET Composite Fibers

Spinning speed (km/min)	Apparent crystallite size, $L_{hkl}$ (Å)			Interplanar spacing, $d$ (Å)			Number of repeating unit per crystal, $N$		
	(010)	(-110)	(100)	(010)	(-110)	(100)	(010)	(-110)	(100)
0.5	19.4	12.4	11.9	5.80	3.86	3.34	3.34	3.21	3.56
1.0	25.4	14.7	13.2	5.77	3.82	3.33	4.40	3.85	3.96
1.5	28.7	19.0	19.5	5.81	3.85	3.36	4.94	4.94	5.80
2.0	31.3	24.9	24.4	5.86	3.88	3.36	5.31	6.42	7.26
2.5	34.3	29.5	28.7	5.77	3.83	3.36	5.94	7.70	8.54

where  $\beta$  is the half-width of the reflection peak,  $\theta$  is the Bragg angle,  $K$  is a correction factor ( $K = 0.9$ ), and  $\lambda$  is the wavelength of the X-ray beam. The interplanar spacing ( $d$ ) and the number of repeat units per crystal ( $N$ ) in the TLCP/PEN/PET composite fibers were calculated with the Bragg equation,  $n\lambda = 2d \sin\theta$ , and  $N = L_{hkl}/d$ , respectively. The apparent crystallite size of the TLCP/PEN/PET composite fibers calculated with Scherrer's equation is shown in Table I. According to the Scherrer's equation,<sup>27</sup> the narrow diffraction peaks in the WAXD profiles are related to crystals that were large in the direction perpendicular to the observed crystal plane, and it suggests that the lateral dimensions of the crystals in the fibers spun at high spinning speeds were relatively well developed.<sup>27</sup> The  $L_{hkl}$  and  $N$  in the annealed TLCP/PEN/PET composite fibers were increased with the spinning speed, suggesting that the crystallites were larger in all dimensions when they were formed at higher spinning speeds, and more perfect crystalline structures were developed in the TLCP/PEN/PET composite fibers. These variations in the structural parameters of the annealed TLCP/PEN/PET composite fibers are similar to the trend observed in the results for the degree of crystallinity for the annealed TLCP/PEN/PET composite fibers. Therefore, the increase in the  $L_{hkl}$  was associated with the development of larger crystallites and more ordered crystalline structures in the annealed TLCP/PEN/PET composite fibers, with increasing spinning speed. From the above results, it was expected that the increase in the crystallinity or the number of crystallites in the TLCP/PEN/PET composite fibers would improve the tensile strength and tensile modulus of the annealed TLCP/PEN/PET composite fibers.

The SAXS profiles of the TLCP/PEN/PET composite fibers fabricated at various spinning speeds are shown in Figure 5. In the case of the unannealed TLCP/PEN/PET composite fibers, only diffuse scattering curve without the scattering maximum ( $q_{\max}$ ) was observed, while the scattering maximum observed in the annealed TLCP/PEN/PET composite fibers shifted to a lower scattering angle with increasing spinning speed. In addition, the scattering inten-

sity of the annealed TLCP/PEN/PET composite fibers increased with increasing spinning speed. The procedure for estimating the morphological parameters from the SAXS profiles of polymers reported by Verma et al.<sup>28,29</sup> involves the use of correlation function to obtain the morphological parameters such as long period, lamellar thickness, and amorphous interlayer thickness. From the Lorentz-corrected SAXS profiles shown in Figure 6, the average long period associated with the lamellar stacks can be calculated using Bragg relation,  $L = 2\pi/q_{\max}$  (where  $q = 4\pi\sin\theta/\lambda$  is the scattering vector and  $\theta$  is the scattering angle). The average long period ( $L$ ) represents the sum of the average thickness of the crystal lamellar thickness ( $l_c$ ) and of the interlamellar amorphous layer thickness ( $l_a$ ). The variations of the morphological parameters for the annealed TLCP/PEN/PET composite fibers are shown in Figure 7. The values of  $L$  and  $l_c$  increased gradually with increasing spinning speed, while the  $l_a$  value decreased. The gradual increase in the  $L$  value of the annealed TLCP/PEN/PET composite fibers with increasing spinning speed may be attributed to both the increase in the crystallite size with the spinning speed and annealing process and the increase in the degree of the chain extension with the spinning speed.

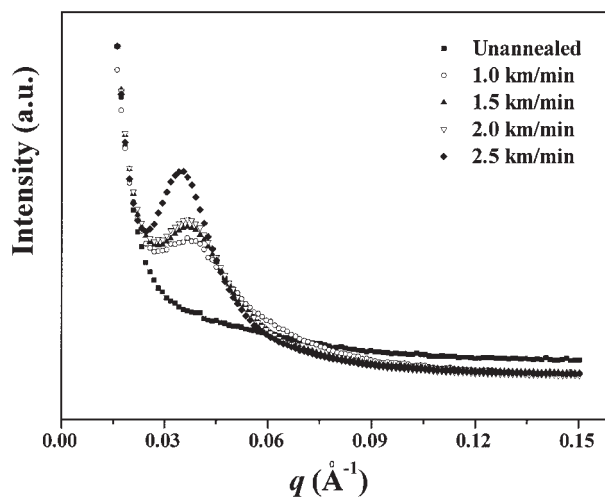
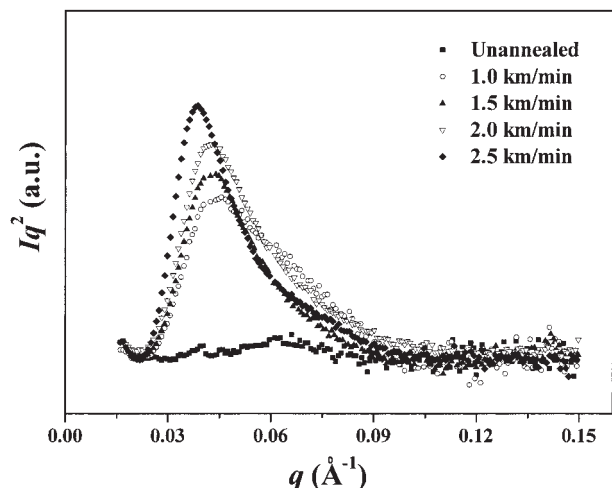
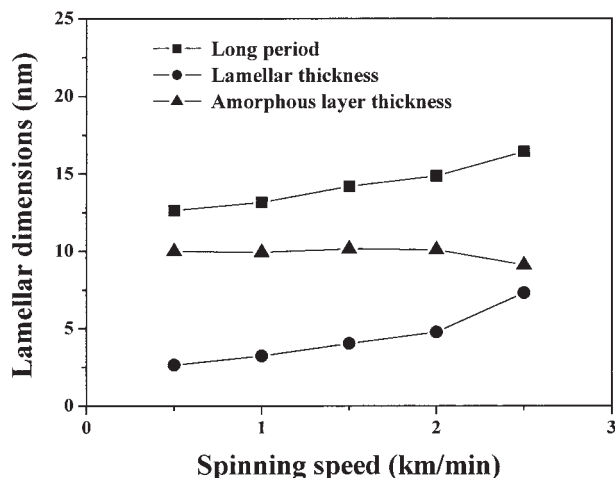


Figure 5 SAXS profiles of the annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.



**Figure 6** Lorentz-corrected SAXS profiles of the annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.

The tensile strength and tensile modulus of the PEN/PET composite fibers and the TLCP/PEN/PET composite fibers fabricated at the melt-spinning speed of 1 km/min are shown in Table II. The tensile strength and tensile modulus of the TLCP/PEN/PET composite fibers were higher than that of the PEN/PET composite fibers, indicating that the incorporation of TLCP into the polymer matrix increased the mechanical properties of polyester composite fiber because of the reinforcement effect of the polymer matrix by TLCP. In addition, the tensile strength and modulus of the PEN/PET composite fibers and the TLCP/PEN/PET composite fibers were increased by annealing. In general, annealing process is one of the effective methods to improve the properties of as-spun fibers such as strength, modulus, and thermal

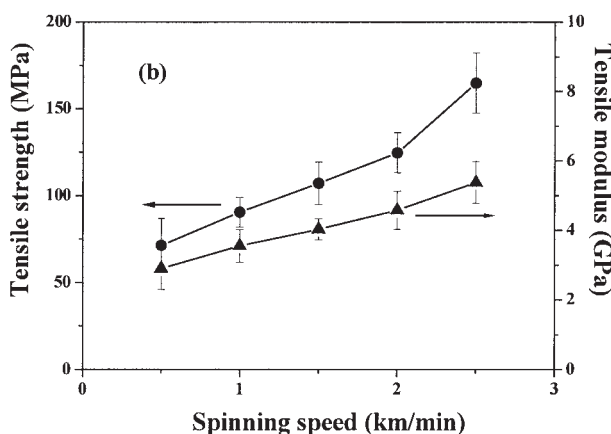
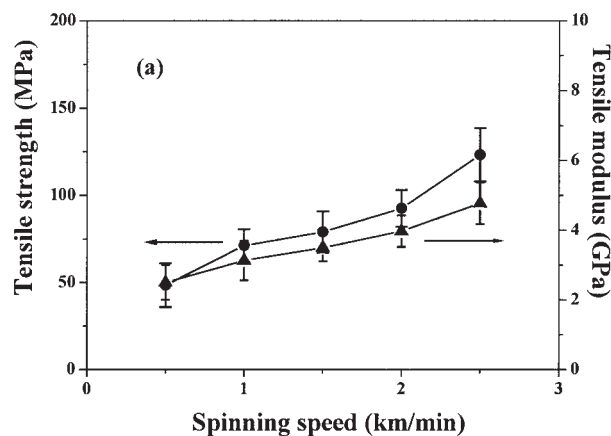


**Figure 7** Morphological parameters of the annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.

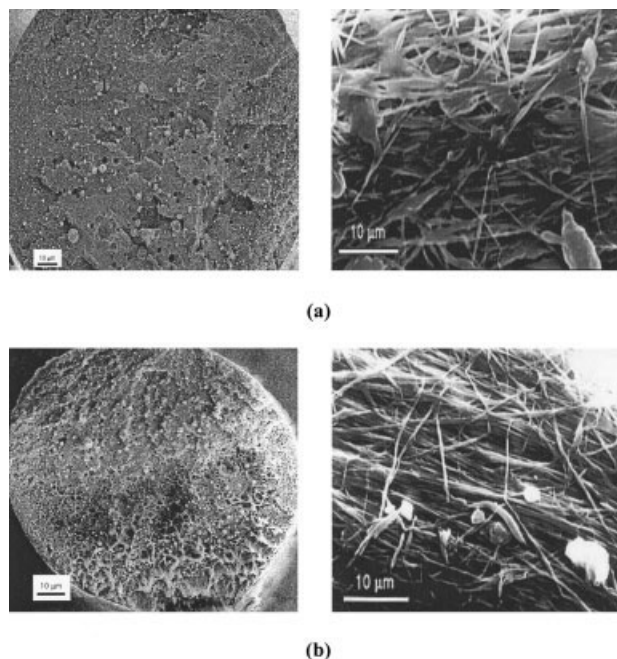
**TABLE II**  
Tensile Strength and Modulus of the Polyester Composite Fibers

Sample codes	Before annealing		After annealing	
	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)
PEN/PET	32.5	2.2	40.6	2.6
TLCP/PEN/PET	71.1	3.1	90.5	3.6

stability. The dependence of the tensile strength and tensile modulus of the TLCP/PEN/PET composite fibers on the spinning speed before and after annealing is shown in Figure 8. The tensile strength and modulus of the TLCP/PEN/PET composite fibers were increased with increasing spinning speed. This result suggested that more ordered and oriented structures with well-distributed TLCP having high aspect ratio were developed in the TLCP/PEN/PET composite fibers. In general, the molecular orientation and the



**Figure 8** Tensile strength and modulus of (a) the TLCP/PEN/PET composite fibers and (b) the annealed TLCP/PEN/PET composite fibers in relation to the spinning speed.

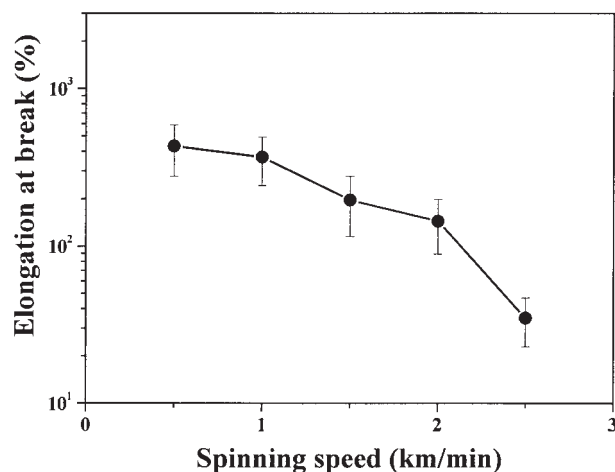


**Figure 9** SEM micrographs of the cross sections of TLCP fibrils prepared by the extraction of the polymer matrix from the TLCP/PEN/PET composite fibers melt-spun at (a) 1.0 km/min and (b) 2.5 km/min.

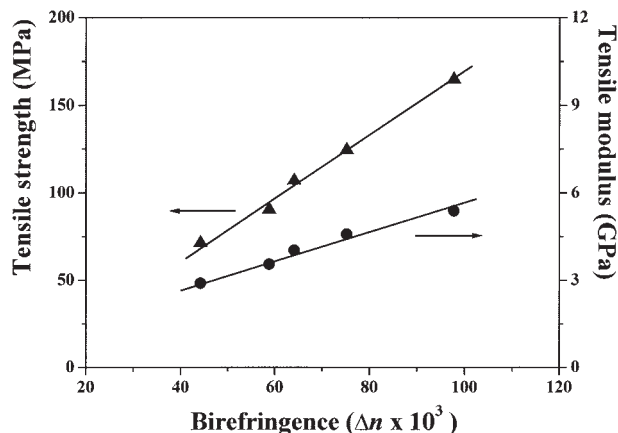
degree of crystallization increase with the spinning speed, and as-spun fibers attains higher chain orientation, i.e., high orientation fibers were prepared by high speed spinning process.<sup>23</sup> The improvement of the tensile modulus of the TLCP/PEN/PET composite fibers with increasing spinning speed may be explained by the existence of the oriented phase of TLCP molecules in the TLCP/PEN/PET composite fibers, possibly as fibrillar structures, together with the result that the birefringence of the TLCP/PEN/PET composite fibers was increased with the spinning, resulting in the increase in the overall orientation. Similar results of the improvement of the mechanical properties by the oriented TLCP fibrillar structure in the polymer composite fibers have also been reported in our previous research.<sup>16</sup> As shown in Figure 9, fibrillar structures of the TLCP/PEN/PET composite fibers with TLCP fibrils of diameters below 1  $\mu\text{m}$  can be observed, despite some beaded or defective fibrils. As the spinning speed was increased, more fine TLCP fibrils were formed in the TLCP/PEN/PET composite fibers and their aspect ratio was increased. The improvement of the mechanical properties of the TLCP/PEN/PET composite fibers was also attributed to the function of the reinforcing agent of TLCP well-dispersed in the polyester matrix.<sup>30,31</sup> Therefore, in the case of the polyester composite fibers reinforced with a TLCP as the minor component, the enhancement of the tensile strength and modulus is caused by the formation of highly elongated TLCP domains parallel to the flow

direction, resulting in the higher molecular orientation and the reinforcement effect of the polymer matrix by TLCP component. In addition, the tensile strength and modulus of the annealed TLCP/PEN/PET composite fibers were improved with increasing spinning speed when compared with the unannealed TLCP/PEN/PET composite fibers, as shown in Figure 8. This result was also related to the results of WAXD and SAXS analysis. In commercial processing, annealing is required to improve fiber performance with respect to parameters such as strength, modulus, and thermal stability. The improvement of the tensile strength and modulus of the annealed TLCP/PEN/PET composite fibers at all spinning speed suggested that the annealing process increased the crystallinity for the TLCP/PEN/PET composite fibers because amorphous region was crystallized and that the crystalline structures of the TLCP/PEN/PET composite fibers became more ordered and perfect by annealing. The dependence of the elongation at break of the TLCP/PEN/PET composite fibers on the spinning speed is shown in Figure 10. The elongation at break of the TLCP/PEN/PET composite fibers decreased with increasing spinning speed, suggesting that lower elongation at break of the TLCP/PEN/PET composite fibers may be attributed to the improvement of the molecular orientation with increasing spinning speed.

The relationship between the birefringence and mechanical properties of the TLCP/PEN/PET composite fibers is shown in Figure 11. A linear relationship between the birefringence and mechanical properties of the TLCP/PEN/PET composite fibers was observed. This result suggests that the molecular orientation, as represented by the value of birefringence, has a significant influence on the tensile strength and modulus of the TLCP/PEN/PET composite fibers. Therefore, it can be deduced that the molecular orien-



**Figure 10** Effect of the spinning speed on the elongation at break of the TLCP/PEN/PET composite fibers.



**Figure 11** Relationship between the birefringence and mechanical properties of the TLCP/PEN/PET composite fibers.

tation is a decisive factor in controlling the mechanical properties of the TLCP/PEN/PET composite fibers.

The TGA results of the PEN/PET composite fibers and the TLCP/PEN/PET composite fibers melt-spun at the spinning speed of 1 km/min are shown in Table III. The incorporation of TLCP component has little effect on the glass transition temperature ( $T_g$ ). The thermal degradation temperature ( $T_d$ ) and the residual yield in the TGA at 800°C of the TLCP/PEN/PET composite fibers were higher than those of the PEN/PET composite fibers, and it may be due to high heat resistance exerted by TLCP component. Therefore, the incorporation of TLCP improved the thermal stability of the PEN/PET composite fibers, suggesting that TLCP may act as a thermal stabilizer in the TLCP/PEN/PET composite fibers. The DSC thermograms of the TLCP/PEN/PET composite fibers with the spinning speed are shown in Figure 12. As the spinning speed was increased, the cold crystallization temperatures ( $T_{cc}$ ) of the TLCP/PEN/PET composite fibers shifted to lower temperatures, and then disappeared at the spinning speed of 2.5 km/min. This result was related to the reduction of entropy with preferential orientation during melt spinning, and more oriented chains required lower thermal energy to crystallize, resulting in the occurrence at lower temperature.<sup>32</sup> The decrease in the  $T_{cc}$  and the area of the cold crys-

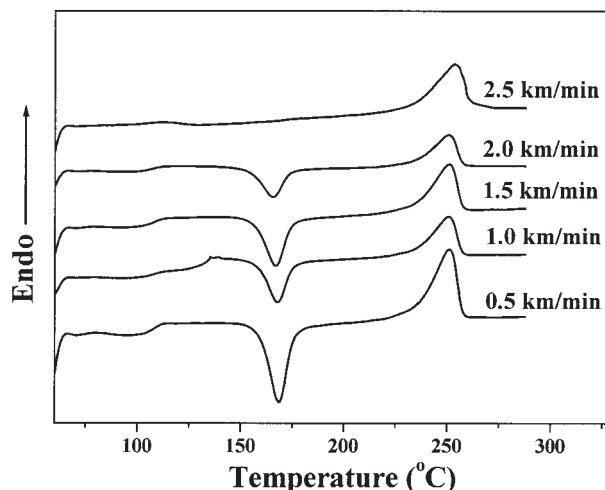
**TABLE III**

**Thermal Behaviors of the Polyester Composite Fibers**

Sample code	$T_g$ (°C)	$T_d$ (°C) <sup>a</sup>	Char yield (%) <sup>b</sup>
PEN/PET	106.2	405.9	24.3
TLCP/PEN/PET	106.4	410.2	27.5

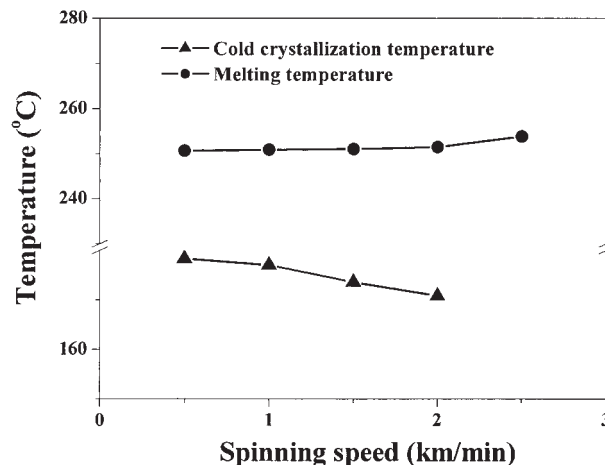
<sup>a</sup> 5% weight loss temperature in TGA at a heating rate of 10°C/min under nitrogen.

<sup>b</sup> Residual yield in TGA at 800°C under a nitrogen atmosphere.



**Figure 12** DSC thermograms of the TLCP/PEN/PET composite fibers in relation to the spinning speed.

tallization peak with increasing spinning speed were attributed to the development of the molecular orientation in the TLCP/PEN/PET composite fibers, together with the fact that the noncrystalline molecules are more oriented with increasing spinning speed before the initial crystallization, leading to easier occurrence of the cold crystallization during the DSC heating scans.<sup>33</sup> As the spinning speed increases, more molecular orientation is occurred in the as-spun fibers prior to solidification, and then increases the crystallinity of the fibers.<sup>33</sup> The variations of the melting and cold crystallization temperatures for the TLCP/PEN/PET composite fibers with the spinning are shown in Figure 13. At the spinning speed of 2.5 km/min, the melting temperature ( $T_m$ ) was increased slightly and the  $T_{cc}$  disappeared. This result was similar to the relation between cold crystallization and melting in



**Figure 13** Variations of the melting and cold crystallization temperatures of the TLCP/PEN/PET composite fibers in relation to the spinning speed.



the high-speed melt spinning of PET fibers.<sup>34</sup> Shimizu et al. reported that in the high-speed melt spinning of PET fibers, the spinning speed at which the thermal behavior of as-spun fibers changed was attributed to higher molecular orientation in the as-spun fibers, and the birefringence value at which this conversion occurred was greater than 0.06.<sup>34</sup> In this study on the melt spinning of the TLCP/PEN/PET composite fibers, the birefringence of the TLCP/PEN/PET composite fibers was  $\sim 0.075$  at the spinning speed of 2.5 km/min. In addition, the  $T_m$  of the TLCP/PEN/PET composite fibers was increased slightly at the spinning speed of 2.5 km/min. This result was attributable to both the increase in the apparent crystallite size and the formation of more perfect crystalline structures with increasing spinning speed and the development of highly ordered crystalline structures in the melt spinning.<sup>33-36</sup>

### CONCLUSIONS

The TLCP/PEN/PET composite fibers were prepared by melt blending and spinning processes to improve fiber performance with good processability. The incorporation of TLCP component into the polymer matrix reduced the complex viscosity of the polyester composites, thereby enhancing their processability. The increase in the birefringence and density of the TLCP/PEN/PET composite fibers with the spinning speed resulted from the improvement of molecular orientation and effective packing between chains. As the spinning speed increased, apparent crystallite size and the number of repeating unit per crystal in the TLCP/PEN/PET composite fibers increased, indicating that larger crystallites and more ordered crystalline structure were developed in the TLCP/PEN/PET composite fibers. The increase in the crystallite size and the degree of chain extension with the spinning speed resulted in the gradual increase in the long period for the TLCP/PEN/PET composite fibers. The improvement of the tensile strength and modulus of the TLCP/PEN/PET composite fibers with increasing spinning speed was attributed to both the reinforcement effect of the polymer matrix by TLCP and the development of more ordered and oriented structures with well-distributed TLCP. The molecular orientation was a critical factor in determining the tensile strength and modulus of the TLCP/PEN/PET composite fibers.

### References

1. Stewart, M. E.; Cox, A. J.; Naylor, D. M. *Polymer* 1993, 34, 4060.
2. Bedia, E. L.; Murakami, S.; Kitade, T.; Kohjiya, S. *Polymer* 2001, 42, 7299.
3. Kim, S. H.; Kang, S. W.; Park, J. K.; Park, Y. H. *J Appl Polym Sci* 1998, 70, 1065.
4. Kim, S. H.; Kang, S. W. *Fibers Polym* 2000, 1, 83.
5. Kim, J. Y.; Kim, O. S.; Kim, S. H.; Jeon, H. Y. *Polym Eng Sci* 2004, 44, 395.
6. Bretas, R. E. S.; Baird, D. G. *Polymer* 1992, 24, 5233.
7. Lee, W. C.; DiBenedetto, T. *Polymer* 1993, 34, 684.
8. Huand, G. H.; Lambla, M. J. *J Polym Sci Part A: Polym Chem* 1995, 33, 97.
9. Kimura, M.; Porter, R. S. *J Polym Sci Part B: Polym Phys* 1984, 22, 1697.
10. Kiss, G. *Polym Eng Sci* 1987, 27, 410.
11. Jung, S. H.; Kim, S. C. *Polym J* 1988, 20, 73.
12. Kim, S. H. In *Thermotropic Liquid Crystal Polymer Reinforced Polyesters*; Scheirs, J.; Long, T. E., Eds.; Wiley Interscience: New York, 2004; Chapter 20.
13. Kim, S. H.; Park, S. W.; Gil, E. S. *J Appl Polym Sci* 1997, 67, 1383.
14. Park, D. S.; Kim, S. H. *J Appl Polym Sci* 2003, 87, 1842.
15. Kim, J. Y.; Seo, E. S.; Kim, S. H.; Kikutani, T. *Macromol Res* 2003, 11, 62.
16. Kim, J. Y.; Kim, S. H.; Kikutani, T. *J Polym Sci Part B: Polym Phys* 2004, 42, 395.
17. Kim, J. Y.; Kang, S. W.; Kim, S. H.; Kim, B. C.; Shim, K. B.; Lee, J. G. *Macromol Res* 2005, 13, 19.
18. Kim, J. Y.; Kim, S. H. *J Polym Sci Part B: Polym Phys*, submitted.
19. Kim, J. Y.; Kim, S. H. *Compos Sci Technol*, submitted.
20. La Mantia, F. P. *Thermotropic Liquid Crystal Polymer Blends*; Technomic: Lancaster, PA, 1993.
21. Bastida, S.; Eguiazaball, J. I.; Nazabal, J. *Polymer* 2001, 42, 1157.
22. He, J.; Bu, W. *Polymer* 1994, 35, 5061.
23. Ziabicki, A.; Kawai, H. *High-Speed Fiber Spinning*; Wiley: New York, 1985.
24. Blundell, D. J.; Osborn, B. N. *Polymer* 1983, 24, 953.
25. Zhang, W.; Nicholson, T. M.; Davies, G. R.; Ward, I. M. *Polymer* 1996, 37, 2653.
26. Hamza, A. A.; Fouda, I. M.; Kabeel, M. A.; Seisa, E. A.; Sharkawy, F. M. *J Polym Sci Part B: Polym Phys* 1998, 36, 555.
27. Alexander, L. E. *X-Ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969.
28. Verma, R.; Marand, H.; Hsiao, B. *Macromolecules* 1996, 29, 7767.
29. Hsiao, B.; Verma, R. *J Synchrotron Radiat* 1997, 5, 23.
30. Jackson, W. J.; Kuhfuss, H. F. *J Polym Sci Part A: Polym Chem* 1976, 14, 2043.
31. Siegmann, A.; Dagam, A.; Kenig, S. *Polymer* 1985, 26, 1325.
32. Cakmak, M.; Kim, J. C. *J Appl Polym Sci* 1997, 64, 729.
33. Meuvel, H. M.; Huisman, R. *J Appl Polym Sci* 1978, 22, 2229.
34. Shimizu, J.; Okui, N.; Kikutani, T. *Sen'I Gakkaishi* 1981, 37, T-135.
35. Wu, G.; Li, Q. C.; Cuculo, J. A. *Polymer* 2000, 41, 8139.
36. Miyata, K.; Kikutani, T.; Okui, N. *J Appl Polym Sci* 1997, 65, 1415.