Structure and Properties of Blend Fibers from Poly(ethylene terephthalate) and Liquid Crystalline Polymer

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ABSTRACT: The structure and properties of the as-spun fibers of poly(ethylene terephthalate) (PET) blends with a thermotropic liquid crystalline polymer (LCP), Vectra A900, were studied in detail. The DSC results indicate that the LCP component may act as a nucleating agent promoting the crystallization of the PET matrix from the glassy state but which inhibits its crystallization from the melt due to the existence of an LCP supercooled mesophase. The effect of the drawdown ratio on the orientation of the as-spun blend fibers is highly composition-dependent, which is mainly associated with the formation of LCP fibrils during melt spinning. The modulus of the as-spun blend fibers has a significant increase as the content of LCP reaches 10%, while the tensile strength has a slightly decreasing tendency. The mechanical properties of the as-spun blend fibers could be well improved by heat treatment because of a striking increase in the crystallinity of the PET matrix. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 217–224, 1997

INTRODUCTION

Blending of conventional thermoplastics with thermotropic liquid crystalline polymers (LCPs) has attracted much attention over last decade. As is well known, LCPs, existing as ordered domains in the liquid crystalline state, usually exhibit a considerably low melt viscosity and could preferentially be oriented to form fibrils under an elongational flow as encountered in the ordinary melt-processing techniques. Therefore, it has been considered as a promising way to achieve an *in situ* composite coined by Kiss[1] via simply blending the thermoplastics with the LCP components, which offered many advantages over that of fabricating the composites with short glass fiber reinforcement.

Extensive studies have been conducted for various blend systems containing LCPs,[2] among them many concerned with poly(ethylene terephthalate) (PET) blend systems.[3–15] The effect of processing conditions on the morphology and properties of the blends was predominantly investigated for injection molding, while more recently efforts were also put on making *in situ* composite fibers via melt spinning.[6–7,9,14,15] Both Zhuang et al.[6] and Mehta and Deopura[14] reported the effects of the LCP component on the crystallization behavior as well as on the mechanical properties of PET blends containing a thermotropic copolyester of PET and hydroxybenzoic acid (HBA). Mithal et al.[9] and Li et al.[7] performed similar studies for the blends with a copolyester of 6-hydroxy-2-naphthoic acid (HNA) and HBA (Vectra A900). To further enhance the mechanical properties of the as-spun blend fibers by posttreatment after solidification, Joslin et al.[15] dealt with PET blends with a thermotropic block copolymer. An increase of 40% in the modulus compared to the PET control fiber was achieved. However, of the studies conducted thus far, only a few involved heat treatment.[9]

In this article, the crystallization behavior of the as-spun blend fibers as well as the effect of processing conditions including heat treatment on

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Table I Composition of the PET/LCP Blends

Sample Code	PET (Wt %)	LCP (Wt %)
PET/5LCP	95	5
PET/10LCP	90	10
PET/15LCP	85	15
PET/20LCP	80	20
PET/30LCP	70	30

their structures and mechanical properties was studied in detail. The morphological characteristics were also examined.

EXPERIMENTAL

Materials

The LCP used was Vectra A900, which is a random copolyester containing 73 mol % HBA and 27 mol % HNA produced by the Hoechst Celanese Co. PET with an intrinsic viscosity of 1.0 dL/g was supplied by the Toyobo Co.

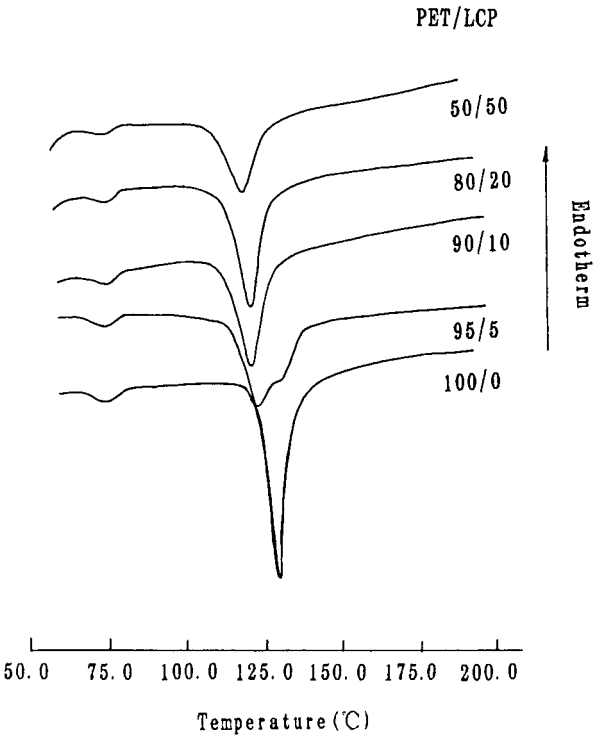


Figure 1 DSC heating curves of PET/LCP as-spun blend fibers.

Spinning

Dry blending was carried out for the predetermined composition shown in Table I. Melt spinning was conducted on a Haake twin-screw extruder at 295–310°C and wound on a bobbin. A spinneret having a diameter of 0.3 mm and an L/D ratio of 10 was used. The drawdown ratios were determined from the as-spun fiber diameters measured by optical microscopy.

Heat Treatment

Heat treatment was carried out in a glass drying apparatus, keeping a vacuum at 0.3 mmHg in the range of temperatures from 160 to 210°C and time from 0.5 to 4.0 h. The as-spun fibers wound on aluminum plates were placed in the apparatus and treated under different conditions.

Characterization

The DSC curves were measured on a Perkin-Elmer DSC-7 calorimeter at heating and cooling

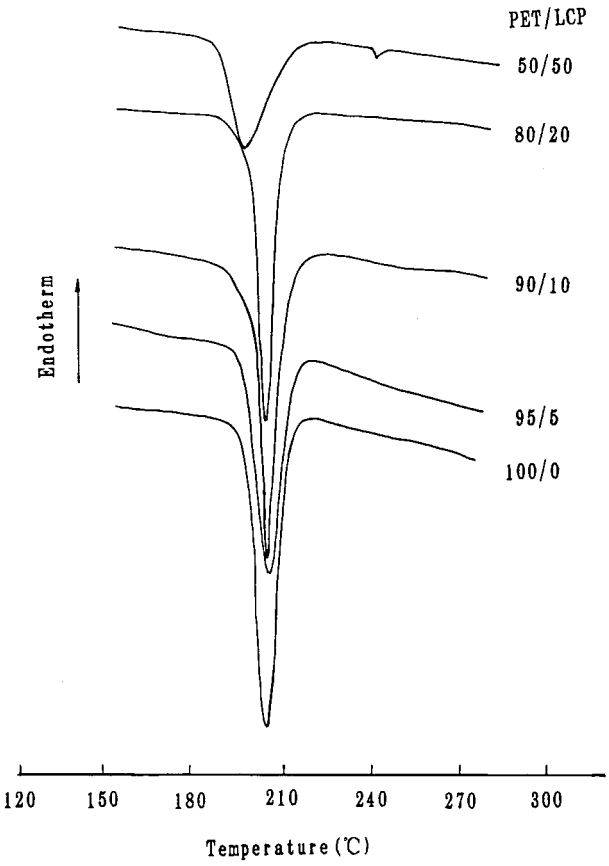


Figure 2 DSC cooling curves of PET/LCP blend as-spun fibers.

Table II Effect of LCP Content on the Crystallization Behavior of PET in the As-spun Blend Fibers

LCP (Wt %)	T_{g_c} (°C)	X_{g_c} [a] (%)	T_{m_c} (°C)	X_{m_c} [b] (%)
0	128.9	18.2	206.9	34.8
5	123.1	17.4	205.3	32.2
10	120.3	16.7	203.9	34.0
20	120.1	18.3	202.9	34.4
50	118.1	15.8	196.7	31.5

[a] X_{g_c} is the crystallinity of PET in the blends due to cold crystallization.
[b] X_{m_c} is the crystallinity of PET in the blends due to the crystallization from the melt.

rates of 10°C/min under a nitrogen atmosphere for the virgin PET and the as-spun blend fibers. The orientation factor of sonic velocity *Fs* was measured on a SOD-1 sonic velocity measuring instrument for the as-spun blend fibers. The *Fs* values were obtained according to the formula

$$Fs = 1 - Cu^2/C^2$$

where *Cu* and *C* are the sonic velocity of unoriented and oriented samples, respectively. Wide-angle X-ray diffraction patterns were obtained from the cut powders of the as-spun fibers without and with annealing using a *D*/max RB-II X-ray diffractometer.

The phase mophology of the as-spun blend fibers was examined on a CamScan-4 high-resolution scanning electron microscope. The samples were prepared under liquid nitrogen or etched with a 60 wt % solution of propionamide in water for 22 h. Tensile tests were performed on a Model YG-001 tensile tester. The data were averaged for five test samples.

RESULTS AND DISCUSSION

Crystallization Behavior

Figure 1 shows the DSC heating curves of virgin PET and PET/LCP as-spun fibers. It is clearly seen that there are two distinct transitions corresponding to the glass transition T_g and the cold crystallization peak T_{g_c} of virgin PET and the PET in the blends. Either of them shows a T_g at about 75°C, indicating that PET is essentially incompatible with the LCP component. However, a significant drop in T_{g_c} is observed as the content of LCP in the blends reaches 10 wt %. It is believed that the LCP component may act as a nucleating agent, promoting the crystallization of the PET matrix from the glassy state. In contrast, the results from DSC cooling curves (see Fig. 2) show that with increasing the content of LCP the crystallization temperature from the melt, T_{m_c}, for the PET matrix shifts toward the lower temperature region, implying that the crystallization of PET from the melt is inhibited due to the existence of

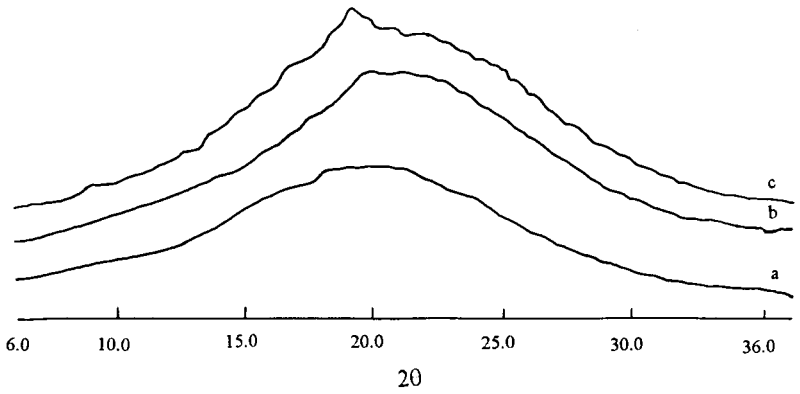


Figure 3 X-ray diffraction curves of PET/LCP as-spun blend fibers with a drawdown ratio of 88.3: (a) PET/5LCP; (b) PET/10LCP; (c) PET/20LCP.

the supercooled LCP mesophase which restricts the mobility of PET chains. A similar phenomenon was observed for the PET as-spun blend fiber containing 10 wt % of a thermotropic PET/PHB copolyester.[14] The data measured are further compared in Table II. It seems that the effect of composition on the T_{g_c} is more pronounced than is that on the T_{m_c}. However, it has only a slight effect on their crystallinity.

Figure 3 presents the wide-angle X-ray diffraction patterns for the as-spun blend fibers with various compositions. In all three cases, a broader diffraction pattern is obtained, manifesting that the as-spun blend fibers possess an amorphous structure in character, which is consistent with the DSC results.

Orientation of As-spun Fibers

Figure 4 shows the effect of the drawdown ratio on the orientation of the as-spun fibers with various compositions. Comparing the composition of PET/5LCP with virgin PET, the former has a higher *Fs* value than has the latter due to the addition of LCP having a higher sonic modulus; with increasing drawdown ratio, the *Fs* values of these two types of samples monotonically increase in a similar manner. As the content of LCP reaches 10 wt %, the effect of the drawdown ratio on the orientation is more remarkable. It is considered that the ordered domains of the nematic phase could preferentially form highly oriented fibrils

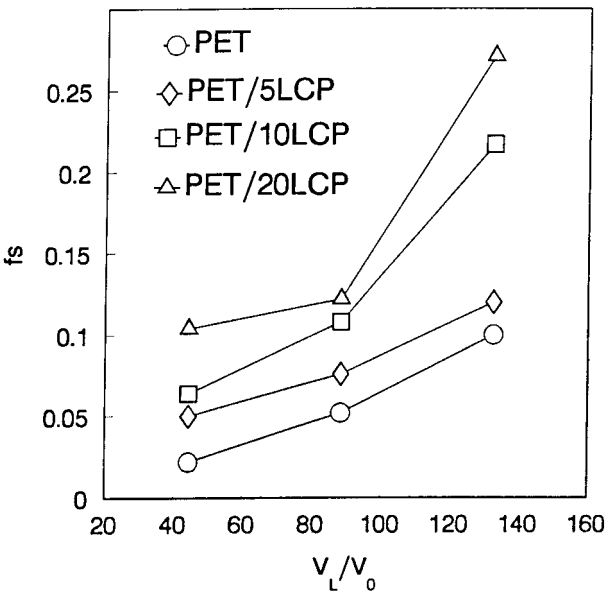


Figure 4 The relation between orientation and drawdown ratio of the as-spun blend fibers.

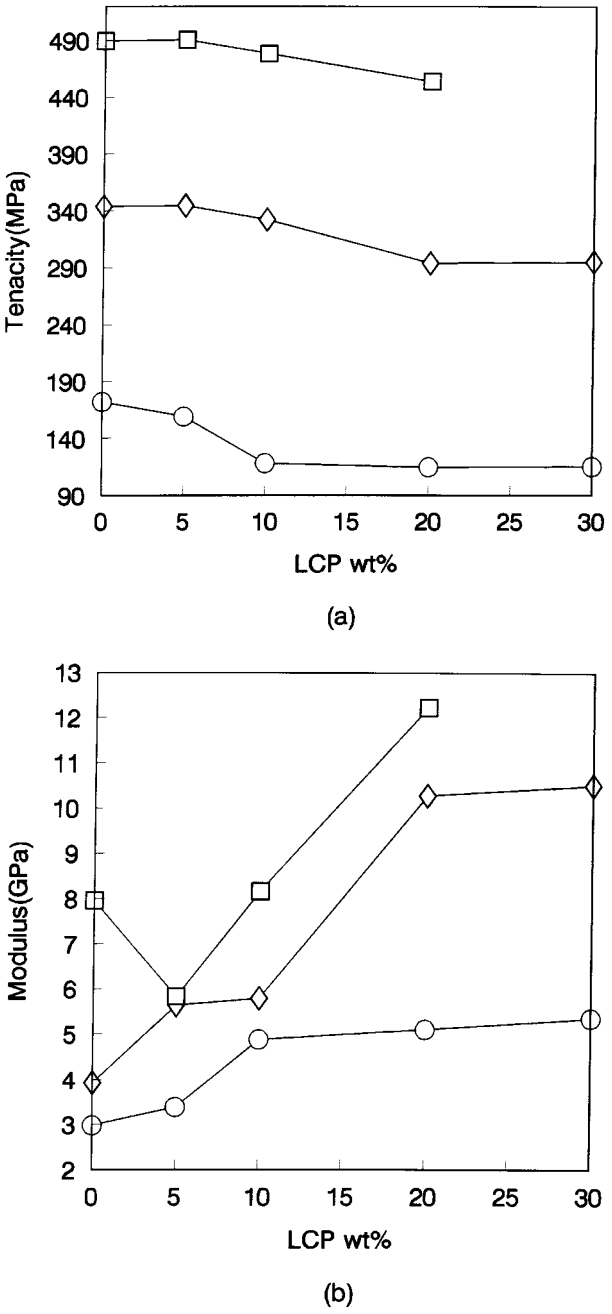
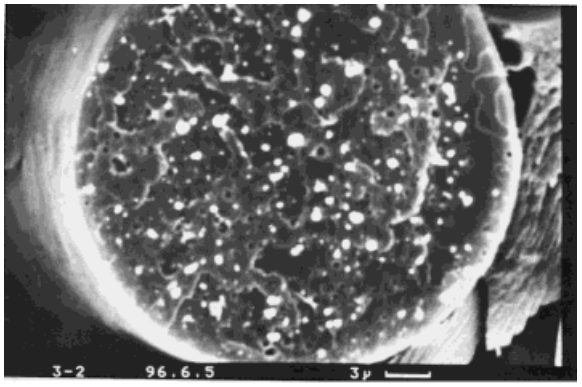


Figure 5 Mechanical properties of PET and PET/LCP as-spun fibers at different drawndown ratios: (○) 44.2; (◇) 88.3; (□) 132.5.

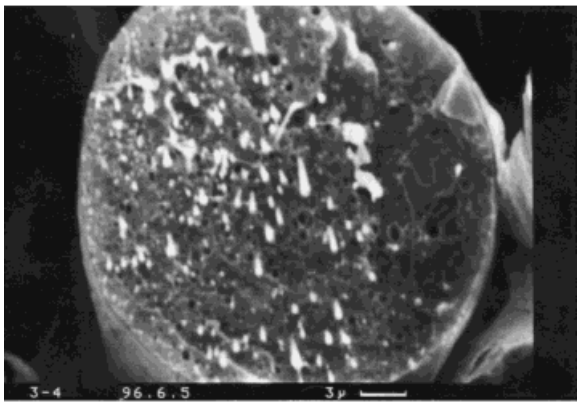
under an elongational flow; the higher drawdown ratio and LCP content, the more fibrils generated and the higher *Fs* values of the as-spun blend fibers achieved.

Mechanical Properties of As-spun Fibers

The mechanical properties of PET and PET/LCP as-spun fibers are compared in Figure 5. It is seen



a



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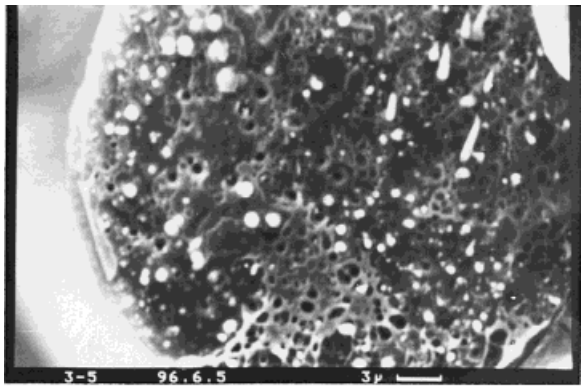
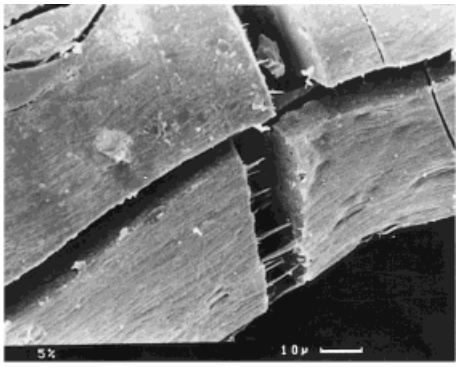


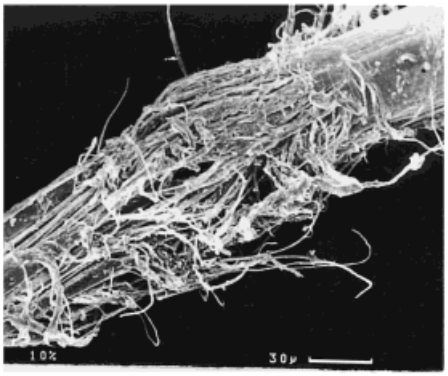
c

Figure 6 SEM micrographs of the as-spun blend fibers with a drawdown ratio of 68: (a) PET/5LCP; (b) PET10LCP; (c) PET/20LCP.

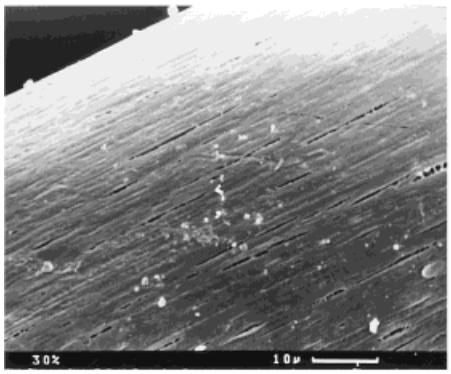
that the effect of the drawdown ratio on the mechanical properties of the as-spun blend fibers is similar to that of the as-spun PET fibers; however, the composition dependence is pronounced. With increasing the content of LCP up to 10 wt %, the initial modulus was markedly enhanced. In the case of PET/20LCP as-spun fiber, it has a modulus about 50% higher than that of the PET as-spun fiber with a drawdown ratio of 132.5. However, the tensile strength shows a slightly decreasing tendency due to a relatively coarse morphology formed as the LCP content increases,



(a)



(b)



(c)

Figure 7 SEM micrographs of PET/LCP as-spun blend fibers: (a) PET/5LCP; (b) PET/10LCP; (c) PET/30LCP (etched surfaces).

which seems different from the results reported by Mithal et al.[9] The reason for this is possibly associated with the different geometry of the spinnerets used in the melt spinning. A conical spinneret used by Mithal et al. is of benefit to generate more fibrils at a high LCP content due to an extensional flow in the conical region. As a result, a better tensile strength of the as-spun blend fibers was achieved.

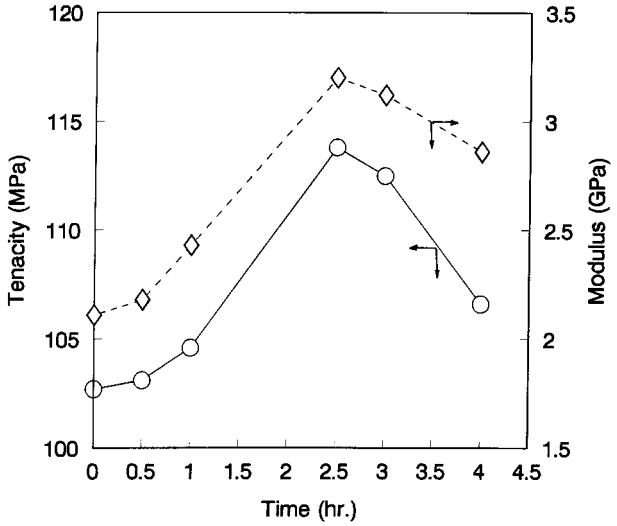


Figure 8 Effect of annealing time at 180°C on the mechanical properties of PET/10LCP as-spun fibers.

Morphology of As-spun Blend Fibers

Figure 6 presents SEM micrographs of the cross section of the as-spun blend fibers with a draw-down ratio of 68. In the PET/5LCP case, the LCP dispersed phases mainly exist as droplets, but

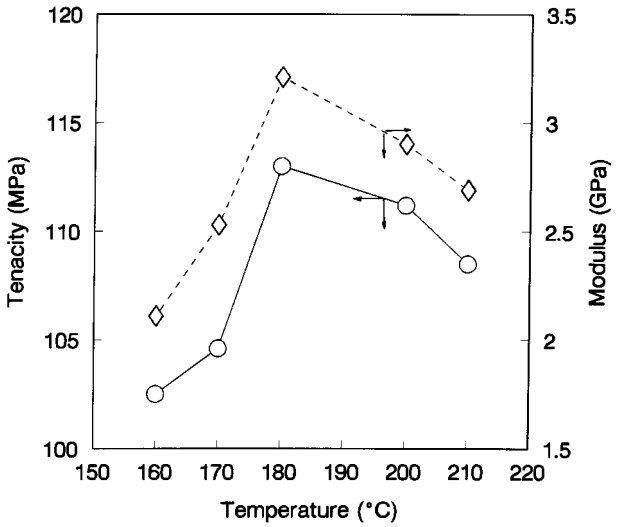


Figure 9 Effect of annealing temperature for 2.5 h on the mechanical properties of PET/10LCP as-spun fibers.

Table III Effect of Heat Treatment on the Mechanical Properties of PET/LCP As-spun Fibers

Sample	Drawdown Ratio (V_L/V_0)[a]	As-spun Fibers		Annealed As-spun Fibers	
		T (MPa)	M (Gpa)	T (MPa)	M (GPa)
PET/5LCP	38.3	69.31	4.32	105.13	5.62
PET/10LCP	38.3	144.88	4.20	158.05	5.65
PET/15LCP	38.3	158.40	4.62	264.00	6.47

[a] V_0 and V_L refer to the velocity at the die exit and the take-up velocity, respectively.

part of which formed fibrils under such spinning conditions. The dimensions of them are in a range from about 0.3 to 1.0 μm. A great number of fibrils with dimensions from 0.3 to 1.2 μm were generated in the PET matrix as the content of LCP reaches 10 wt %; in addition, more and finer fibrils were located at the surface region. Some smooth and round holes embedded in the matrix reflect a weak adhesion at the interfaces. In the PET/20LCP composition, the LCP dispersed phases became rather coarse, indicating a severe coalescence between them. Meanwhile, a sheath layer with more finer fibrils existing is seen. The conclusions mentioned could be further demonstrated by the SEM micrographs taken for the chemically etched samples of PET/5LCP, PET/10LCP, and PET/30LCP as-spun fibers (see Fig. 7). It is more clearly revealed that even in the case of PET/5LCP, some LCP fibrils during melt spinning are still formed; more fibrils were generated as the LCP was increased. A sheath layer was formed in the case of PET/30LCP; consequently, it could not be dissolved by a 60 wt % propionamide solution.

The morphological features mentioned above can generally be explained by Taylor's drop deformation theory.[16] As well known, when the drop viscosity is lower compared with that of suspending fluid, the shear rate required for burst becomes quite large and the drops could be deformed to form fibrils. In this study, the LCP shows a lower viscosity than that of the PET matrix at the shear rates encountered in the spinneret die used; therefore, the LCP fibrils could be formed with a steady shape. Meanwhile, more fibrils would be generated in the sheath layer due to relatively higher shear rates.

Effect of Heat Treatment

In Figures 8 and 9, the effects of annealing time and temperature on the mechanical properties of PET/10LCP as-spun fibers are plotted, respectively. When the samples were annealed at 180°C, both the tensile strength and the initial modulus exhibited a maximum with an optimum time at 2.5 h, whereas an optimum temperature is at 180°C when the annealing time was 2.5 h. The data of the mechanical properties of PET/LCP as-spun fibers with various compositions after heat treatment at 180°C for 2.5 h are listed in Table III. Compared to the control samples, the tensile strength and initial modulus could be enhanced about 10 and 30% for the PET/5LCP sample and 58 and 40% for the PET/15LCP, respectively.

The structural parameters measured for the as-spun blend fibers after annealing at 180°C for 2.5 h are presented in Table IV. The crystallinity listed is after ΔH normalized per gram of PET. The ΔH^0 of 100% crystalline PET is 140 J/g.[17] These DSC results show a drastic increase in the crystallinity of the PET matrix after annealing. The results of the *Fs* measurements indicate little influence on the orientation of the as-spun blend fibers after annealing. Therefore, it can be con-

Table IV Effect of Heat Treatment on the Structural Parameters of PET/LCP As-spun Fibers

Sample	Drawdown Ratio (V_L/V_0)	As-spun Fibers		Annealed As-spun Fibers	
		X_c (%)	*fs* ($\times 10^2$)	X_c (%)	*fs* ($\times 10^2$)
PET/5LCP	38.3	3.2	4.8	39.8	6.0
PET/10LCP	38.8	4.4	7.2	41.9	8.1
PET/15LCP	38.3	10.5	8.1	42.9	8.5

X_c is the crystallinity measured by DSC, which is calibrated by the weight fraction (ΔH° for 100% crystallized PET is 140 J/g).

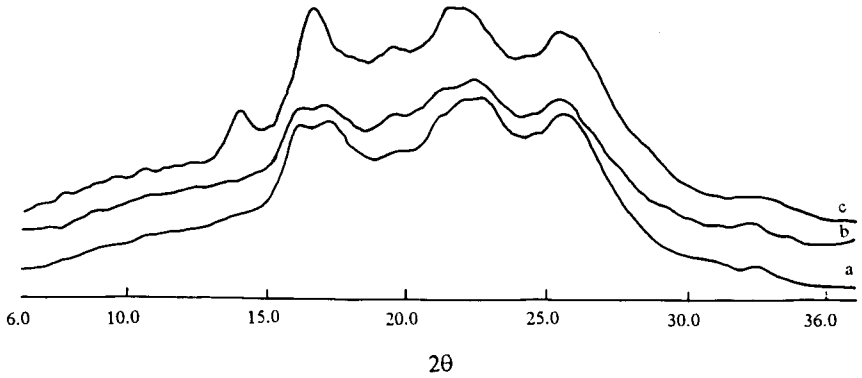


Figure 10 X-ray diffraction curves of PET/LCP as-spun fibers annealed at 180°C for 2.5 h: (a) PET5LCP; (b) PET/10LCP; (c) PET/15LCP.

cluded that the improvement of mechanical properties of the as-spun fiber is associated mainly with a significant increase in crystallinity.

Figure 10 shows wide-angle X-ray diffraction patterns of the annealed PET/LCP as-spun fibers. It evidently proves that in the cases of PET/5LCP and PET/10LCP there are three broader diffraction peaks at 17.5°, 22.4°, and 25.7°, corresponding to the 010, $1\bar{1}0$, and 100 crystal planes of the PET matrix. In the case of PET/15LCP, besides these three peaks, an extra peak at 13.8° appears on the diffraction curve, which presumably is ascribed to the crystallite of the LCP component; moreover, all diffraction peaks became sharper, indicating an increase in crystallinity.

CONCLUSIONS

The PET/LCP *in situ* composite fibers could be formed under the melt-spinning conditions performed. The amount of LCP fibrils generated is governed mainly by composition, which is also a major factor determining the supermolecular structure of the as-spun blend fiber and, in turn, the mechanical properties. The modulus of the as-spun blend fibers is monotonically increased with increasing content of the LCP component but the tensile strength appears as a decreasing tendency at the high LCP contents studied due to a rather coarse morphology formed. The heat treatment is an effective way to enhance the crystallinity of PET and, as a result, to further improve the mechanical properties of the as-spun blend fibers.

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