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Effects of Annealing on Structure and Properties of TLCP/PEN/PET Ternary Blend Fibers

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Abstract: Thermotropic liquid crystalline polymer (TLCP)/poly(ethylene 2,6-naphthalate) (PEN)/poly(ethylene terephthalate) (PET) ternary blends were prepared by melt blending, and were melt-spun to fibers at various spinning speeds in an effort to improve fiber performance and processability. Structure and property relationship of TLCP/PEN/PET ternary blend fibers and effects of annealing on those were investigated. The mechanical properties of ternary blend fibers could be significantly improved by annealing, which were attributed to the development of more ordered crystallites and the formation of more perfect crystalline structures. TLCP/PEN/PET ternary blend fibers that annealed at 180 °C for 2 h, exhibited the highest values of tensile strength and modulus. The double melting behaviors observed in the annealed ternary blend fibers depended on annealing temperature and time, which might be caused by different lamellae thickness distribution as a result of the melting-reorganization process during the DSC scans.

Keywords: thermotropic liquid crystalline polymer, poly(ethylene 2,6-naphthalate), poly(ethylene terephthalate), melt spinning, annealing.

Introduction

In recent years, melt blending of thermotropic liquid crystalline polymers (TLCPs) with conventional thermoplastics has attracted great attention because of the improvement of the strength and modulus of polymer composites.[1-9] TLCPs have been used for high performance engineering plastics due to their high strength and modulus, excellent thermal endurance and chemical stability.[10-13] They consist of rigid molecular chains, and exist as ordered domains in LC state. TLCPs that have a relatively low melt viscosity can be oriented to form fibrils under elongational flow in melt processing, and the oriented fibrous structures are developed in the extruded TLCPs. Due to the rigid rod-like molecules of TLCPs, they exhibit the high strength and stiffness, which develop into the highly ordered structures and result in self-reinforcing characteristics.[14,15]

Blending of poly(ethylene terephthalate) (PET) with poly (ethylene 2,6-naphthalate) (PEN) has attracted increasing interest from industrial fields to scientific, because of the improved properties that combines the excellent properties of PEN with the economical efficiency of PET.[16-22] Transesterification reactions occurred between PEN and PET during melt blending, leading to the formation of block copolymers first, and then of random copolymers, which enhances the miscibility of the blend systems.[20-23] The melt blend fibers with TLCP and conventional polyester resins produced by conventional melt spinning can be utilized for the high strength and modulus fibers. The melt spinning is the most economical method for producing the synthetic fibers, and provides the technique for obtaining various kinds of polymer structures. In general, the high performance polymers are high cost and difficult to process. It is important to improve the processability without the decrease in mechanical properties at lower cost. Although melt spinning is the most effective fiber-forming process for polymers, the present research and development work may yet achieve super-fibers having higher performance and characteristics with lower cost.

In this research, TLCP/PEN/PET ternary blends were prepared by melt blending, and were melt spun into fibers at various spinning speeds in an effort to improve fiber performance and processability. The structure and properties of ternary blend fibers were analyzed by using wide-angle X-ray

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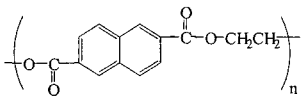
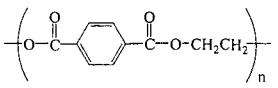
diffraction (WAXD), differential scanning calorimetry (DSC), tensile testing, and thermal shrinkage measurement. In order to investigate the effects of annealing on structure and properties of ternary blend fibers, those were annealed at various temperatures and for different time periods.

Experimental

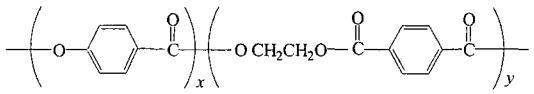
Materials. Poly(ethylene 2,6-naphthalate) (PEN) with an intrinsic viscosity of 0.93 dL/g and poly(ethylene terephthalate) (PET) with an intrinsic viscosity of 1.07 dL/g were supplied by Hyo Sung Co. in Korea. Thermotropic liquid crystalline polymer (TLCP) used in this research was based on 80 mol% poly(*p*-hydroxybenzoate) (PHB) and 20 mol% PET, and was purchased from Unitika Co. in Japan. These chemical structures were as follows:



Poly(ethylene 2,6-naphthalate)



Poly(ethylene terephthalate)



Poly(*p*-hydroxy benzoate) / poly(ethylene terephthalate)

Preparation of TLCP/PEN/PET Ternary Blend Fibers. All the materials were dried at 120 °C in vacuo for at least 12 h to minimize the effect of moisture before being used. TLCP/PEN/PET ternary blends were prepared by melt blending in Haake Rheometer equipped with twin screw. The predetermined blending composition and sample codes were shown in Table I. The temperature of heating zones from hooper to die were set to 270, 285, 285, and 275 °C, respectively, and screw speed was fixed at 15 rpm. All the materials to be spun were pre-dried at 110 °C for 5 h in vacuo, and then pre-crystallized at 150 °C for 10 h in vacuo. Mixed polymer chips were melt spun in the extruder with 4 holes spinneret having a diameter of 0.5 mm, and output rate was controlled as 5 g/min per hole. In order to investigate the effects of annealing on the structure and properties of TLCP/PEN/PET ternary blend fibers, annealing process was performed at various temperatures and for different time periods.

Characterizations. Tensile properties of TLCP/PEN/PET ternary blend fibers were measured by using an Instron tensile tester (UTM Instron 4465) equipped with standard fiber grips at room temperature in accordance with ASTM-D638. The gauge length was 20 mm, and the crosshead speed was 5 mm/min. The thermal shrinkage of ternary blend fibers was measured as a function of temperature without the applied tension for 30 minutes in the heating oven according to ASTM-D2259. Thermal behavior of TLCP/PEN/PET ternary blend fibers were investigated by DSC (TA instrument 2010) under nitrogen in the temperature range from 40 to 300 °C with scanning rates of 5, 10, 20, 30, 40, and 50 °C/min, respectively. The calorimeter was calibrated using indium and zinc, and the melting point (T_m) was given as the peak of the melting endotherm. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a Rigaku Denki X-ray diffractometer using Ni-filtered CuKα X-rays ($\lambda = 0.1542$ nm). The scanning 2θ angle covered a range between 5 and 40° with a step scanning of 0.05°. The degree of crystallinity (X_c) was calculated by means of the curve fitting procedure given by Blundell and Osborn.[24] Broad Gaussian peaks were used to describe the amorphous halo, and the crystalline peaks were fitted with Gaussian functions.

Table I. Composition of TLCP/PEN/PET Ternary Blend Fibers

Sample Codes	TLCP (wt%)	PEN (wt%)	PET (wt%)
NT	0	50	50
NT-7.5	7.5	46.25	46.25
NT-10	10	45	45

Results and Discussion

The changes of tensile strength and modulus of TLCP/PEN/PET ternary blend fibers (NT-series) on spinning speed were shown in Figure 1. For all of NT-series, tensile strength and modulus were increased with spinning speed, which were attributed to the development of more ordered structures with uniform and continuous PHB domains which have been distributed well. These results indicated that the molecular orientation and mechanical properties of NT-series was significantly enhanced at higher spinning speed. Generally, molecular orientation and degree of crystallization increase with spinning speed, and fibers change from unoriented yarns to fully oriented yarns.[25] It could be also seen that the crystallinity of NT-series or the number of crystallites was increased, which led to the improvements in tensile strength and modulus of NT-series. In order to investigate the effects of annealing on structures and properties of TLCP/PEN/PET ternary blend fibers, those were annealed at various temperatures and for different time periods. Tensile strength and modulus of the annealed ternary blend fibers were shown in Figure 2. In ternary blend system, annealing process was required because each component in ternary blend was difficult to crystallize. In general, annealing process is one of the methods to improve the performance of as-spun fibers, and results in the improvements of the mechanical properties and thermal stability. The annealed NT-7.5 and NT-10 exhibited better tensile strength and modulus than those of NT-7.5 and NT-10. It indicated that tensile strength and modulus of the annealed NT-7.5 and NT-10 could be improved by annealing. As shown in Table II, annealing process resulted in the

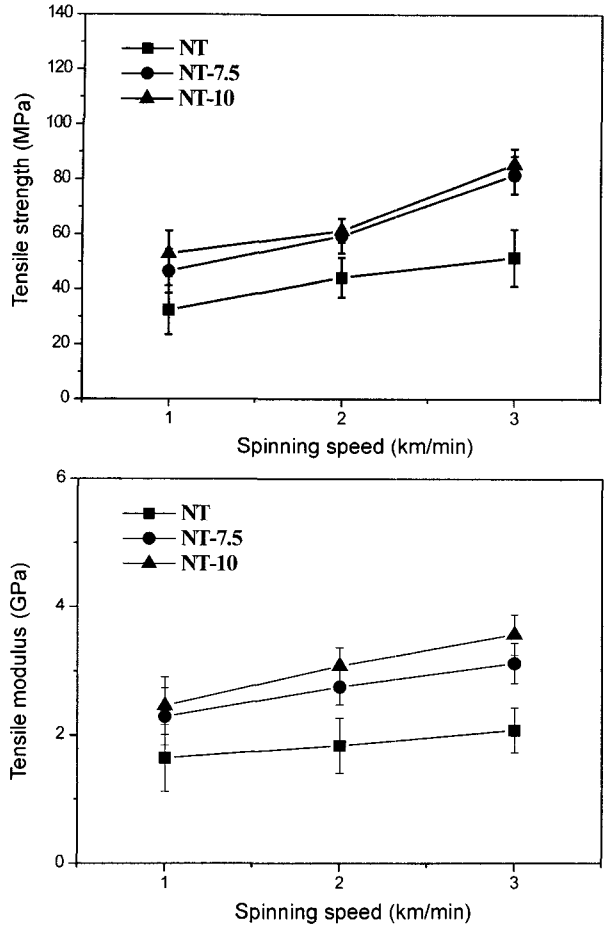


Figure 1. Tensile strength and modulus of TLCP/PEN/PET ternary blend fibers as a function of spinning speed.

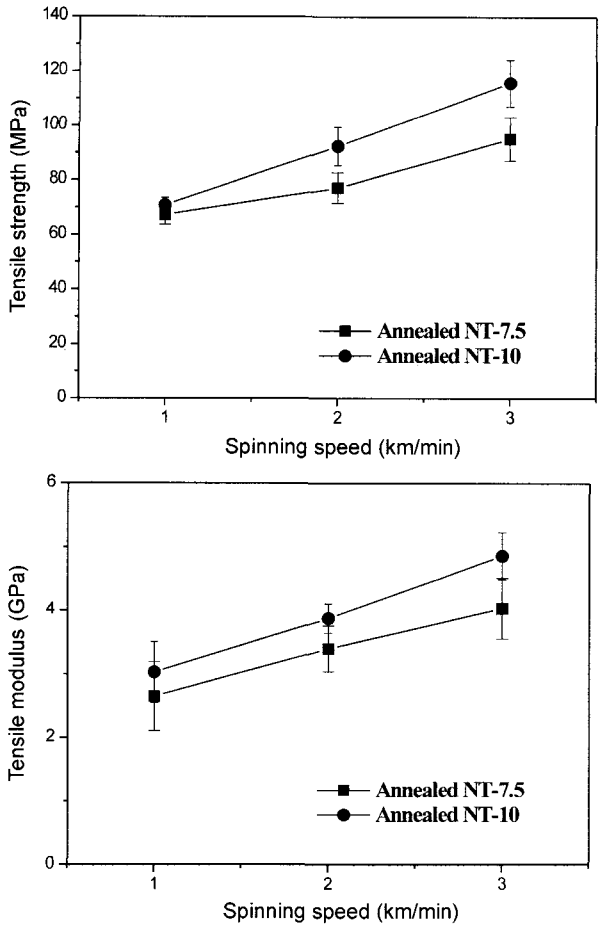


Figure 2. Tensile strength and modulus of TLCP/PEN/PET ternary blend fibers annealed at 180 °C for 2 h as a function of spinning speed.

increment of crystallinity of ternary blend fibers because the amorphous region was crystallized. It suggested that the crystalline structures of NT-7.5 and NT-10 became more perfect by annealing. The effects of annealing temperature and time on tensile strength and modulus of NT-10 were shown in Figures 3 and 4, respectively. Tensile strength and modulus of the annealed NT-10 have the tendency to increase with annealing temperature and then to decrease. At 180 °C, tensile strength and modulus of the annealed NT-10 exhibited the maximum. As shown in Figure 4, tensile strength and modulus of the annealed NT-10 were increased with annealing time. Tensile strength and modulus of the annealed NT-10 exhibited the maximum values at 2 h, and thereafter, were decreased as annealing time was increased. Therefore, the optimum annealing time was 2 h when annealing temperature was 180 °C for NT-10.

Wide-angle X-ray diffraction (WAXD) patterns of TLCP/PEN/PET ternary blend fibers at different spinning speeds were shown in Figure 5. As shown in Figure 5(a), no crystalline trace could be observed in the WAXD patterns of NT. This result indicated that neither PEN nor PET could form a crystalline structure, and another possible reason was that block or random copolymers produced by transesterification reactions may disturb the formation of crystalline structure

Table II. Effect of Annealing on Properties of TLCP/PEN/PET Ternary Blends Fibers

Sample Codes	Before Annealing			After Annealing		
	Tensile Strength (Mpa)	Tensile Modulus (Gpa)	X_c (%)	Tensile Strength (Mpa)	Tensile Modulus (Gpa)	X_c (%)
NT-7.5	81.7	3.1	8.2	95.2	4.0	21.5
NT-10	85.5	3.6	15.1	115.8	4.9	34.6

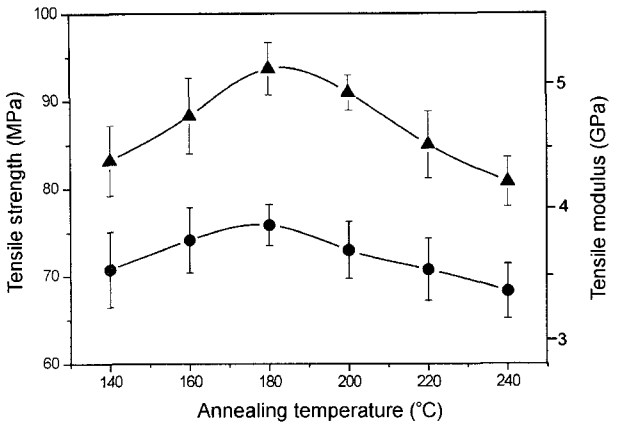


Figure 3. Effect of annealing temperature on mechanical properties of NT-10 annealed for 0.5 h.

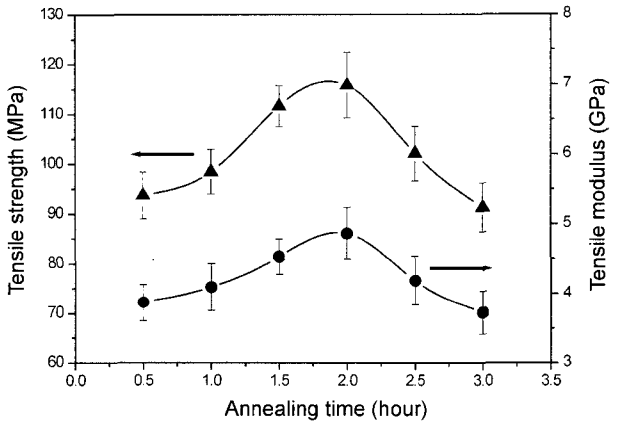


Figure 4. Effect of annealing time on mechanical properties of NT-10 annealed at 180 °C.

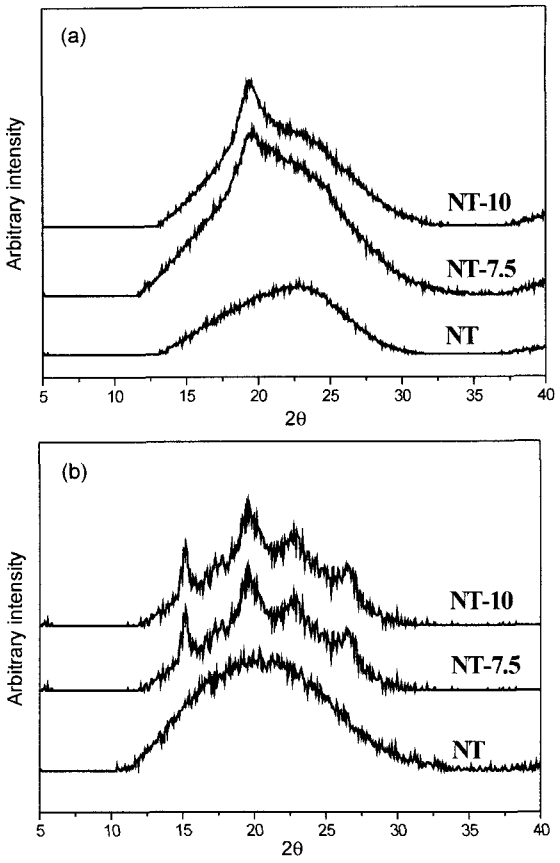


Figure 5. WAXD patterns of TLCP/PEN/PET ternary blend fibers: (a) Before annealing; (b) After annealing.

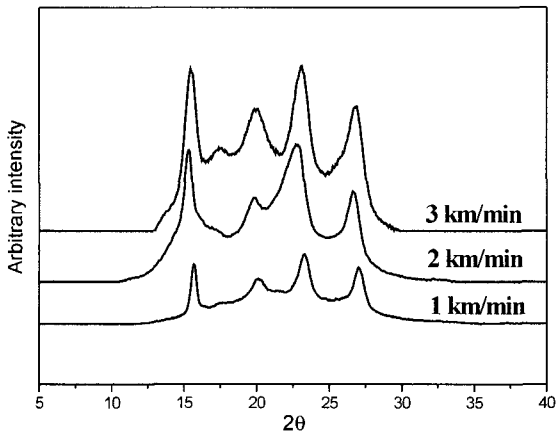


Figure 6. The WAXD patterns of NT-10 annealed at 180 °C with different spinning speeds.

in ternary blend fibers. In our previous paper,[21,22] it was reported that during melt blending, transesterification reactions occurred, and first produced a block copolymer and then proceeded to form a random copolymer. The WAXD patterns of NT-7.5 and NT-10 exhibited one characteristic peak at 2θ of about 19°, which was attributed to the characteristic of the intermolecular packing order of PHB components. However, for the annealed NT-7.5 and NT-10, new crystalline peaks were clearly observed as shown in Figure 5(b), which were attributed to the (010), (-110), and (100) reflections indicating the crystalline structures of PEN and PET components. As shown in Figure 6, the intensity of the characteristic crystalline peaks was increased with spinning speeds. This was attributed to the development of more ordered crystallites and the formation of more perfect crystalline structures in the annealed ternary blend fibers.

The effects of annealing temperature (T_a) and time (t_a) on thermal behavior of TLCP/PEN/PET ternary blend fibers melt-spun at 1 km/min were shown in Figures 7~9. For the annealed ternary blend fibers, double melting peaks were observed when annealing temperature was lower than 200 °C. As annealing temperature was increased, the lower melting

peak (T_{m1}) shifted to higher temperature, but the higher melting peak (T_{m2}) remained almost constant and independent of annealing temperature. When annealing temperature was 200 °C, double melting peaks of the annealed NT-7.5 merged into a single melting peak. It indicated that annealing temperature have influenced on melting behavior of the annealed ternary blend fibers. In almost semicrystalline polymers in addition to copolymers and blends, multiple melting peaks have been observed during DSC scans. Many investigations on the origin of the multiple melting behavior in semicrystalline polymers have been performed.[26-29] Various factors such as the change in morphology, orientation effects, the presence of more than one crystal modification, and melting-recrystallization-remelting process occurring during DSC scans have influences on the multiple melting behaviors. In DSC thermograms of the annealed NT-7.5 shown in Figure 7, it was observed that with increasing annealing temperature within the annealing temperature range (140~200 °C), the lower melting peak shifted to higher temperatures, and the height ratio of the lower and higher melting peaks changed with annealing temperature. However, T_{m2} remained almost constant, and it finally overlapped by the lower melting peak of annealing temperature above a certain critical value. The perfection of the crystalline of T_{m1} was increased during annealing process, and T_{m1} shifted to higher temperature, and hence, was observed in the form of only a single peak. The perfection of the crystalline of T_{m1} was increased with annealing time, which was confirmed by the fact that T_{m1} also shifted to the higher temperature direction with annealing time as shown in Figure 8. The relatively imperfect crystals would be formed at the lower crystallization, and would melt at a lower temperature. As shown in Figure 9, the position of the higher melting peak is independent of the heating rate, while the lower melting peak shifts gradually toward higher temperature with heating rate. The annealing temperature and time have affected the melting behavior of TLCP/PEN/PET ternary blend fibers. Wu *et al.*[30] reported that the observed higher melting temperature peak is independent of annealing temperature for the cold-crystallized samples, and suggested that it could result from the melt, recrystallization, and subsequent remelts of the crystalline species with a lower melting point. The melting-recrystallization-remelting mechanism proposed that original imperfect, thin crystals or lamellae in the polymers could melt and recrystallize to form crystals of better perfection during DSC scans. In the WAXD patterns of NT-series shown in Figure 5(a), no apparent crystalline diffraction peaks except for the characteristic peaks of PHB was observed before annealing process. However, for the annealed NT-7.5 and NT-10, the new crystalline diffraction peaks appeared after annealing process, but the position of diffraction peaks was unchanged with annealing temperature and time as shown in Figures 10 and 11. This result suggested that the double melting behavior was attributed to different lamellae thickness, not to different structure. There-

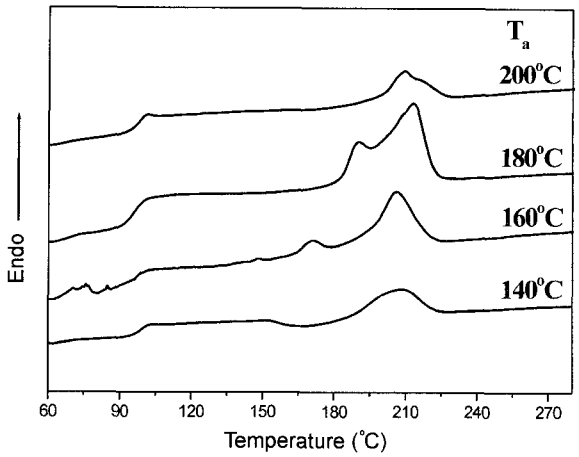


Figure 7. DSC thermograms of NT-7.5 annealed for 0.5 h at different annealing temperatures.

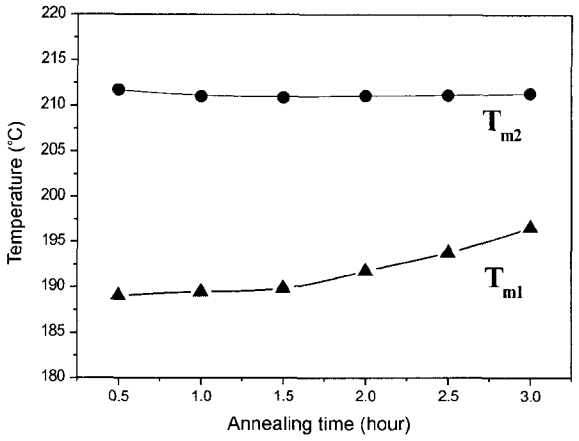


Figure 8. The dependence of the lower and higher melting peaks of NT-7.5 annealed at 180 °C on annealing time.

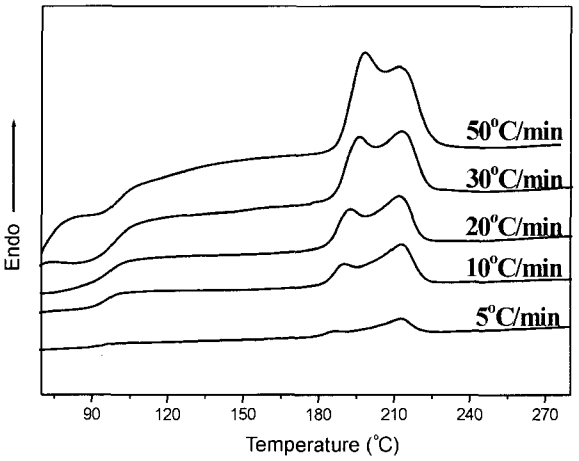


Figure 9. DSC thermograms of the annealed NT-7.5 with different heating rates.

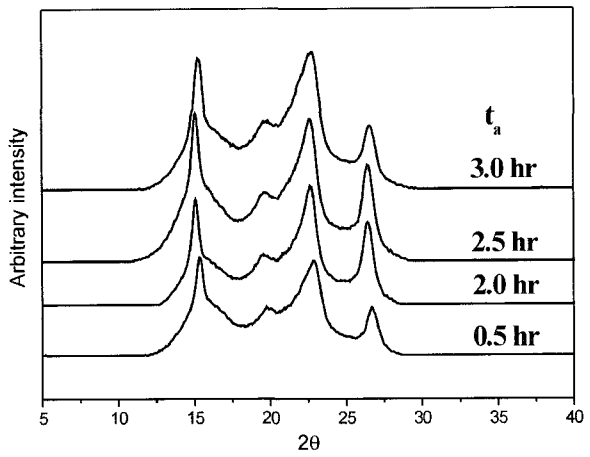


Figure 10. WAXD patterns of the annealed NT-7.5 with different annealing time periods.

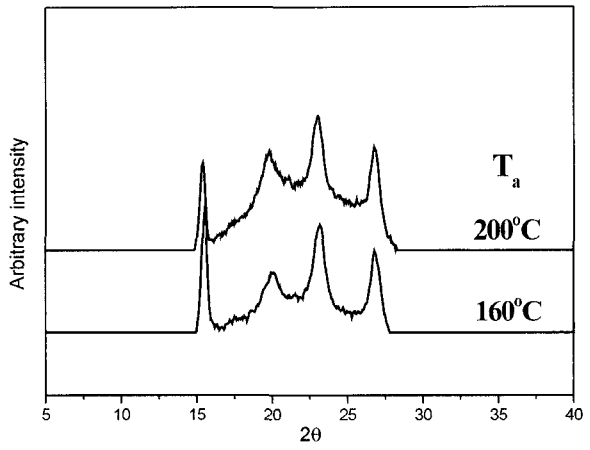


Figure 11. WAXD patterns of the annealed NT-7.5 with different annealing temperatures.

fore, the double melting behaviors of the annealed ternary blend fibers may be resulted from the different lamellae thickness distribution as a consequence of the melting-reorganization process during DSC scans.

The changes of thermal shrinkages of TLCP/PEN/PET ternary blend fibers melt-spun at 1 km/min with temperatures were shown in Figure 12. The values of thermal shrinkage for NT-7.5 and NT-10 were zero or low at temperatures below T_g, while those were increased at temperature above T_g. Generally, shrinkage behavior was related to polymeric structure, and shrinkage was a non-recoverable deformation, which was attributed to the relaxation of oriented molecules in the amorphous regions.[31-33] Thermal shrinkage resulted from the relaxation of oriented amorphous phase into the more random state, and resulted in the removal of residual stresses formed during processing.[28] The amorphous region and crystallinity played dominant roles in the shrinkage behavior. At lower

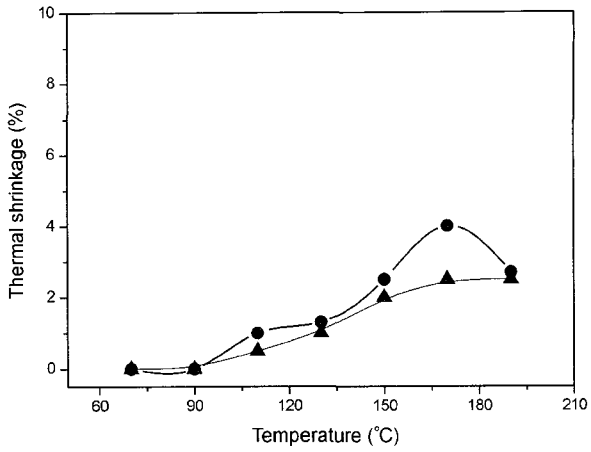


Figure 12. The change of thermal shrinkage for NT-7.5 and NT-10 as a function of temperature.

temperature range, shrinkage is due to the disorientation of the amorphous region. However, at higher temperature range, the disorientation of the oriented non-crystalline chains has been almost completed, and the additional crystallization occurs during thermal shrinkage measurement. Shrinkage behavior mainly depended on the fraction of the oriented amorphous regions at higher temperature range. Masia *et al.*[34] reported that the crystallite formed during stress-induced crystallization in processing has lowered the value of shrinkage. At the temperature below T_g, the values of thermal shrinkage for TLCP/PEN/PET ternary blend fibers little changed due to the restricted molecular motion. However, the values of thermal shrinkage were increased at temperature above T_g. This was attributed the increased molecular motion with temperature.

Conclusions

TLCP/PEN/PET ternary blends were prepared by melt blending, and melt spun to fibers at various spinning speeds to improve fiber performance and processability. Tensile strength and modulus of ternary blend fibers were increased with spinning speeds, which were attributed to the development of more ordered structures with uniform and continuous PHB domains which have been distributed well. Compared with the unannealed NT-7.5 and NT-10, the annealed NT-7.5 and NT-10 exhibited better tensile strength and modulus. This result suggested that annealing resulted in the improvement of mechanical properties, and more enhanced perfection of crystalline structures of ternary blend fibers. Ternary blend fibers that annealed at 180 °C for 2 h, exhibited the highest values of tensile strength and modulus. The stronger diffraction peaks observed with the WAXD patterns were attributed to the development of more ordered crystallites and the formation of more perfect crystalline structures. The annealing temperature and time have affected the melting behavior of the

ternary blend fibers. The double melting behavior of TLCP/PEN/PET ternary blend fibers might be caused by the different lamellae thickness distribution. The values of thermal shrinkage were zero or low at temperatures below T_g due to the restricted molecular motion. Above T_g, thermal shrinkage was increased, which was attributed to the increased molecular mobility with temperature.

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