

열방성 액정고분자 강화 폴리에스터 블렌드 섬유의 특성

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Characterization of TLCP Reinforced Polyester Blend Fibers

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1. Introduction

Due to the potential application to ultra-high strength fibers and excellent properties such as high mechanical properties, excellent thermal endurance and chemical stability, thermotropic liquid crystal polymers (TLCPs) are attractive in recent years [1, 2]. Furthermore, the melt blends of TLCPs and conventional thermoplastics have been extensively investigated because of their easy processing and high performance [3-6]. Since high performance polymers generally has high melt viscosity, introduction of the relatively low viscosity components may be one of the more effective techniques to improve processability through the decrement of melt viscosity in melt processing. The orientation of the domains of TLCPs can easily achieved in the elongational flow during processing, and TLCPs can be developed into the highly ordered structures, resulting in the self-reinforcing characteristics [7, 8]. These characteristics of TLCPs make it possible to utilize for high performance fibers through the conventional spinning, and TLCPs and their blends could be produced as high performance and functional materials by conventional processing. It is very important to improve the processability without the decrease in mechanical properties at lower cost because high performance fibers are high cost and difficult to process. In this research, ternary blend fibers (TBFs) based on melt blends of poly(ethylene 2,6-naphthalate) (PEN), poly(ethylene terephthalate) (PET), and TLCP were prepared by melt blending and spinning to achieve the higher performance fiber and processability. Fiber property and structure of TBFs were analyzed by wide-angle X-ray diffraction (WAXD), birefringence, density, and tensile testing, and structure-property relationship of TBFs were also investigated.

2. Experimental

2.1. Materials and Preparation

The conventional thermoplastics used in this research were PEN with an intrinsic viscosity of 0.93 dL/g and PET with an intrinsic viscosity of 1.07 dL/g, and were supplied by Hyo Sung Co. in Korea. 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. All the materials were dried at 120°C *in vacuo* for 12 hours to minimize the effect of moisture before being used. TLCP/PEN/PET ternary blends were prepared by melt blending in a Haake Rheometer equipped with twin screw. The predetermined compositions of TLCP/PEN/PET ternary blends were 7.5/46.25/46.25 and 10/45/45 in weight ratio, respectively. The temperatures of heating zones from hopper to die were set to 270, 285, 285, and 275 °C, respectively, and screw speed was fixed at 15 rpm. All

ternary blends to be spun were pre-dried at 110°C for 5 hours *in vacuo*, and then pre-crystallized at 150°C for 10 hours *in vacuo*. The prepared ternary blends 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. Melt spinning was carried out at the spinning speed range of 0.5~3.5 km/min. Annealing process of the prepared ternary blend fibers was performed at 180°C for 2 hours, because that was the optimum annealing condition in our previous research [9]. In this article, TBFs denote the prepared ternary blend fibers based on PEN, PET, and TLCP, and the symbols of 7.5 and 10 stand for the weight percentage (wt%) of TLCP added, respectively.

2.2. Characterization

Mechanical properties of TBFs were measured at room temperature by using an Instron model 4465 tensile testing machine equipped with standard fiber grips according to ASTM-D638. The gauge length was 20 mm, and the crosshead speed was 5 mm/min. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a Rigaku Denki X-ray diffractometer using Ni-filtered CuK α X-rays ($\lambda=0.1542\text{nm}$). The diffracting intensities were recorded every 0.05° from 2 scans in the range 5~40°. Apparent crystal size, interplanar spacing, and the number of repeating unit of crystal in TBFs were calculated by using the Scherrer equation and Bragg equation [10]. Birefringence of TBFs was measured using a Nikon polarizing microscope equipped with the tilting compensator K (Wild Leitz Ltd., Germany). Density of TBFs was measured at 25°C by using a density gradient column filled with carbon tetrachloride and *n*-heptane.

3. Results and Discussion

The variations of tensile strength and modulus of TBF (10) before and after annealing process on spinning speed are shown in Figure 1. The increased tensile strength and modulus of TBFs with spinning speeds could be obtained by the development of more ordered structures with the well distributed TLCP domains in TBFs. This result suggested that the molecular orientation and mechanical properties of TBFs were improved by increasing spinning speed. As spinning speed was increased, the development of the fibril structure in TBFs resulted in the enhanced mechanical properties of TBFs. Tensile strength and modulus of TBFs were slightly enhanced with increasing TLCP contents, which suggested that the TLCP might act as a reinforcing agent in the blends, resulting from the dispersion of TLCP in the matrix polymers [11, 12]. Compared with the unannealed TBFs, the annealed TBFs exhibited better tensile strength and modulus, which indicated that tensile strength and modulus of TBFs could be improved by annealing process. The degree of crystallinity of the annealed TBFs was increased with spinning speeds, which suggested that the crystalline structures of TBFs became more perfect by annealing process. The crystallinity of TBFs or the number of crystallites was increased, which led to the improvements in tensile strength and modulus of the annealed TBFs. Compared with the WAXD patterns of the unannealed TBF, the annealed TBFs exhibited three characteristic crystalline peaks attributed to the (010), (-110), and (100) reflections indicating the crystalline structures of PEN and PET components. This result meant that more perfection of crystalline structure of TBFs was enhanced by annealing process. The intensities of diffraction peaks were increased with spinning speeds, which was attributed to the development of more ordered and perfect crystallites. Annealing process resulted in the increased crystallinity and crystal perfection of TBFs. The result of WAXD patterns for the annealed TBFs indicating the development of more ordered and oriented crystalline structure was

also corresponded with the increment of the degree of crystallinity for the annealed TBFs. The structural parameters of TBFs are listed in Table 1. Apparent crystal size, interplanar spacing, and the number of repeating unit of crystal in the annealed TBFs were increased with spinning speeds. It could be seen that the crystals were larger in all dimension when they were formed at higher spinning speed. These variations of structural parameters for the annealed TBFs were similar to the trends in the results of the degree of crystallinity. This result suggested that the increment of apparent crystal size was attributed to the development of larger crystallites and more ordered crystalline structures in the annealed TBFs. Thus, it was found that the higher orientation and the more perfection of crystalline structure favored the crystal growth process in the annealed TBFs. Both density and the degree of crystallinity for TBFs were increased with spinning speed. This was attributed to the improved the packing between chains and more densely packed fiber structure [13], and corresponded well with the increased mechanical properties of TBFs. The birefringence of TBFs was increased with spinning speeds, which indicated that TBFs changed into the more oriented fibers as spinning speed was increased. The increment of the value of birefringence generally represented the development of molecular orientation. As spinning speed was increased, shear stresses were increased, resulting in a higher degree of orientation of the molecules during melt spinning. With increasing spinning speed, molecular orientation of TBFs was promoted and the birefringence was increased. It suggested that the packing of the molecular chains in TBFs might be enhanced due to the development of molecular orientation. The annealed TBFs exhibited the higher birefringence than the unannealed TBFs. This suggested that annealing process resulted in the increment of the molecular orientation and crystallinity of TBFs. The linear relationships between birefringence and mechanical properties of the annealed TBFs were observed, which suggested that molecular orientation represented by birefringence had significantly affected tensile strength and modulus of TBFs.

4. Conclusion

Ternary blend fibers (TBFs) based on melt blends of PEN, PET, and TLCP were prepared to achieve the higher fiber performance and processability. Tensile strength and modulus of TBFs were increased with spinning speed, which was attributed to the development of more ordered and oriented structures. The annealed TBFs exhibited higher tensile strength and modulus than the unannealed TBFs, which suggested that crystallinity and more perfection of crystalline structures were enhanced by annealing process. Apparent crystal size, interplanar spacing, and the number of repeating units of crystal in TBFs were increased with spinning speeds. It suggested that larger crystallites and more ordered crystalline structures were developed in the annealed TBFs with increasing spinning speeds. With increasing spinning speed, molecular orientation of TBFs was promoted and the birefringence was increased, which suggested that the packing of molecular chains in TBFs might be improved because of the development of molecular orientation in TBFs. The increment of molecular orientation and crystallinity during annealing process resulted in the increment of birefringence of the annealed TBFs. The density of TBFs was increased with spinning speeds, which indicated that the crystal packing in TBFs was improved at higher spinning speeds. The molecular orientation was an important factor to determine tensile strength and modulus of TBFs.

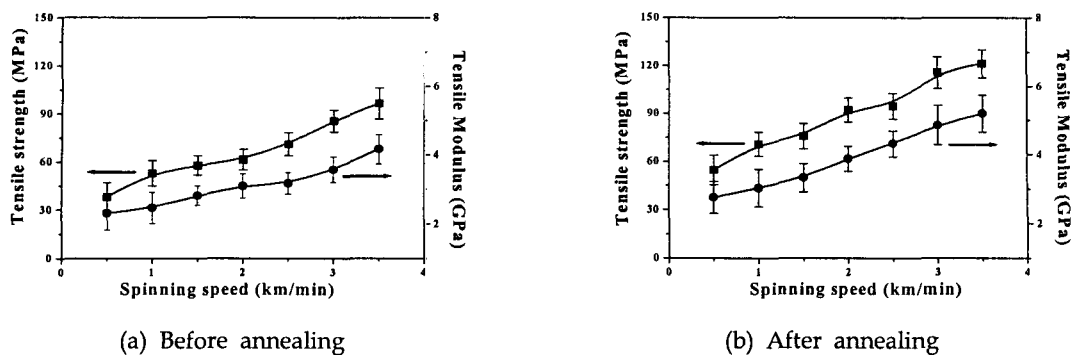


Figure 1. Tensile strength and modulus of TBF (10).

Table 1. Structural parameters of TBFs

Sample codes	Spinning speed	Apparent crystal size (Å)			Interplanar spacing (Å)			Number of repeating unit of crystal		
		(010)	(-110)	(100)	(010)	(-110)	(100)	(010)	(-110)	(100)
TBF (7.5)	1km/min	30.7	42.3	29.7	5.64	3.82	3.30	5.4	10.1	9.0
	2km/min	33.9	44.7	46.1	5.77	3.88	3.34	5.9	11.5	13.8
	3km/min	38.4	53.8	47.2	5.82	3.90	3.35	6.6	13.8	14.1
TBF (10)	1km/min	30.2	41.9	29.8	5.64	3.82	3.30	5.4	10.9	9.0
	2km/min	38.9	48.9	40.9	5.73	3.85	3.32	6.8	12.7	12.3
	3km/min	39.9	55.7	42.9	5.77	3.90	3.34	6.9	14.3	12.8

5. References

1. R. E. Bretas and D. G. Baird, *Polymer*, **24**, 5233(1992).
2. W. C. Lee and T. DiBenedetto, *Polymer*, **34**, 684(1993).
3. S. H. Kim, S. W. Kang, J. K. park, and Y. H. Park, *J. Appl. Polym. Sci.*, **70**, 1065(1998).
4. S. H. Kim and S. W. Kang, *Fibers and Polymers*, **1**, 83(1998).
5. J. G. Lee and S. H. Kim, *J. Korean Fiber Soc.*, **34**, 877(1997).
6. J. K. Park, B. J. Jeong, and S. H. Kim, *Polymer(Korea)*, **24**, 113(2000).
7. L. C. Saywer and M. Jaffe, *J. Mater. Sci.*, **21**, 1897(1986).
8. B. Bassett and A. F. Yee, *Polym. Compos.*, **11**, 10(1990).
9. J. Y. Kim, E. S. Seo, S. H. Kim and T. Kikutani, *Macromol. Res.*, **11**, 62(2003).
10. L. E. Alexander, *X-Ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969.
11. W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2043(1976).
12. A. Siegmann, A. Dagam, and S. Kenig, *Polymer*, **26**, 1325(1985).
13. W. Zhang, T. M. Nicholson, G. R. Davies, and I. M. Ward, *Polymer*, **37**, 2653(1996).