Fibers and Polymers 2002, Vol.3, No.1, 18-23

Structure Development and Dynamic Properties in High-speed Spinning of High Molecular Weight PEN/PET Copolyester Fibers

Sung Joong Kim[1] and Seung Soon Im*

Department of Polymer and Fiber Engineering, College of Engineering, Hanyang University Seoul 133-791, Korea
[1]Kolon Industrial Materials Technology Team, Kumi Plant, Kolon Industrial Inc., Korea
(Received November 29, 2001; Revised February 4, 2002; Accepted February 9, 2002)

Abstract: The structure development and dynamic properties of fibers produced by high-speed spinning of P(EN-ET) random copolymers were investigated. The as-spun fibers were found to remain amorphous up to the spinning speed of 1500 m/min, and subsequent increases in speed resulted in the crystalline domains containing primarily α crystalline modification of PEN. The β modification was not found up to spinning speeds of 4500 m/min. On the other hand, annealing of constrained fibers spun at the 2100 m/min at 180, 200, and 240°C exhibited β-form crystalline structure, while the annealed fibers spun in 600-1500 m/min range exhibited dominantly α-form. However β-form crystals disappeared above the spinning speed of 3000 m/min. With increasing spinning speeds from 600 to 4500 m/min, the storage modulus of as-spun fibers increased continuously and reached a value of about 10.4 Gpa at room temperature. The tan δ curves showed the α-relaxation peak at about 155-165°C, which is considered to correspond to the glass transition. The α-relaxation peaks became smaller and broader, and shift to higher temperatures as the spinning speed increases, meaning that molecular mobility in the amorphous region is restricted by increased crystalline domain.

Keywords: PEN/PET copolymer, High-speed spinning, Annealing, Crystal structure, Dynamic property

Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a relatively well-known engineering polymer that combines the properties of superior chemical resistance, mechanical strength and thermal resistance. Its glass transition temperature, melting temperature and mechanical properties are higher than those of poly(ethylene terephthalate) (PET), because PEN has a naphthalene ring instead of the benzene ring in PET. Therefore the demand of high molecular weight PEN is on the increase especially for the application of industrial textiles, films and various rubber goods.

It has been reported that PEN has two crystal modifications (α- and β-form), depending on the crystallization conditions such as crystallization temperature. α- and β-form crystal structures were determined by Mencik[1] and Zachmann *et al.*[2], respectively. Besides the study of crystal structures of PEN[1,2], numerous studies have been carried out to investigate the morphology, thermal stability, and crystallization kinetics of PEN[3-7].

In spite of these superior properties, PEN homo-polymer shows some drawbacks that may limit its use, namely, its rather high melt viscosity makes fiber spinning and injection molding difficult[8]. Previous studies devoted to explore the solution to these problems, primarily focusing on blending or copolymerization of PEN with PET, PEI, etc.[9-14].

There are some publications on the structure and physical properties of high-speed spun PEN fibers. Jager *et al.*[15] investigated the properties of high-speed spun PEN fibers from the view point of industrial applications. Miyata *et al.*[16] investigated the mechanism of fiber structure formation in the ultra-high-speed melt spinning (up to 9 km/min) of PEN. Nagai *et al.*[17] investigated the structure and properties of high-speed spun PEN fibers and the change of crystal modification during the annealing of PEN fibers under the stress. Wu *et al.*[18] investigated the effect of spinning conditions on the structural and physical properties of the high-molecular weight PEN fibers.

Along with these studies of high-speed spun PEN fibers, there have been relatively fewer experimental studies about the spinning of P(EN-ET) copolymers. It is the purpose of the present article to discuss the effect of high speed spinning and constrained annealing process on the structure development and dynamic properties of P(EN-ET) copolymer fibers.

Experimental

Materials

The raw material used in this study was P(EN-ET) random copolymer with dimethyl terephthalate (DMT) 6 mol%. Intrinsic viscosity (IV) of P(EN-ET) copolymer measured in a mixture of phenol/tetrachloroethane was 0.451 dl/g. The pellets were polymerized additionally in a vacuum dryer to obtain higher molecular weight copolymer with IV of 0.70 dl/g. The fibers were produced using an extruder of 65 mm diameter attached with a metering pump. The spinning temperature profiles of 295, 298, and 300°C were used along the extruder. The spinneret, attached to the exit of the gear pump, had 2.4 mm (Length)×0.8 mm (Diameter) cross-

*Corresponding author: imss007@hanyang.ac.kr

sectional dimensions and 192 holes. A high-speed winder was used to take up fibers at different speeds as throughput 583 g/min. For some series of experiments, the fibers were wound on a square frame and annealed at 180°C, 200°C, 240°C for 3 hours with their lengths constrained.

Measurements

The thermal behavior of the fibers were analyzed using a Perkin-Elmer DSC-7 at a heating rate of 20°C/min in dry nitrogen atmosphere. The fiber birefringence was measured using Karl-Zeis polarizing microscope equipped with Berec compensator. The density(ρ) of the fibers was measured at 23°C in a density gradient column containing carbon tetrachloride and n-hexane. The degree of crystallinity was calculated using the relation:

$$X_w = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \times 100 \quad (1)$$

where ρ_c (1.407 g/cm^3)[1] and ρ_a (1.325 g/cm^3)[19] are densities of 100% crystalline and amorphous phases, respectively. In order to identify the phase behavior in these fibers, a series of WAXD patterns as well as equatorial diffraction profiles were monitored on Bruker wide-angle X-ray diffractometer with 2-D area detector (40 kV, 45 mA, 100 sec exposing time). The dynamic properties were evaluated using a Toyoboldwin rheovibron at a heating rate of 2.0°C/min and frequency of 110 Hz in a length of 30 mm.

Results and Discussions

Thermal Behavior

Figure 1 shows a DSC thermogram for as-spun fibers produced by various spinning speeds. The glass transition was clearly observed at about 120°C for the low speed as-spun yarns. However it became obscure at high speeds. At low spinning speed, the area of the cold crystallization peak located around 210°C is about the same as that of the melting peak. As the spinning speed is increased, the position of the exothermic peak shifts to lower temperatures and begins to broaden. This phenomenon is a typical behavior of melt-spinning process of polyester type polymers. With increasing spinning speed, the molecules that did not crystallize are increasingly oriented before the initial crystallization, allowing cold crystallization to occur easier and shifting the exothermic peak to lower temperatures. In these DSC thermograms, the peak position of endothermic remains constant between 600 m/min to 2100 m/min. Beyond this speed, the melting temperature is found to increase from 254.9°C for 2100 m/min spun fiber to 260.1°C for the fiber spun at 4500 m/min, suggesting that the crystals become larger and more perfect with increasing spinning speed[20].

Figure 2 shows a DSC thermogram of P(EN-ET) fiber (spun at 3000 m/min), which is annealed at different

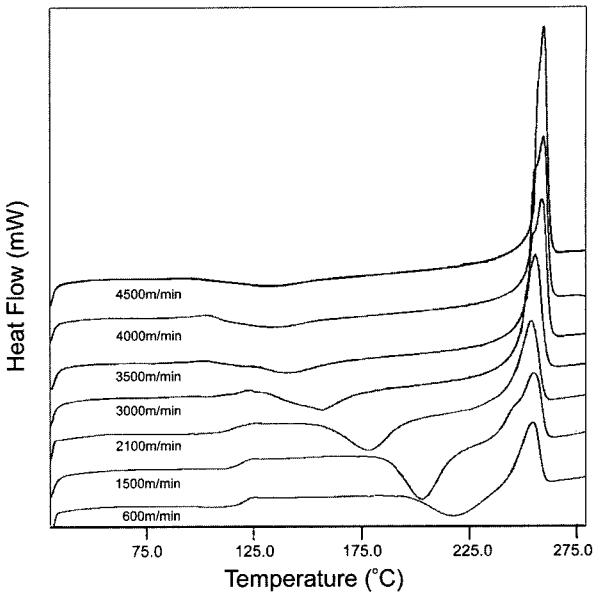

Figure 1. DSC thermogram for as-spun P(EN-ET) fibers obtained under different spinning speeds.

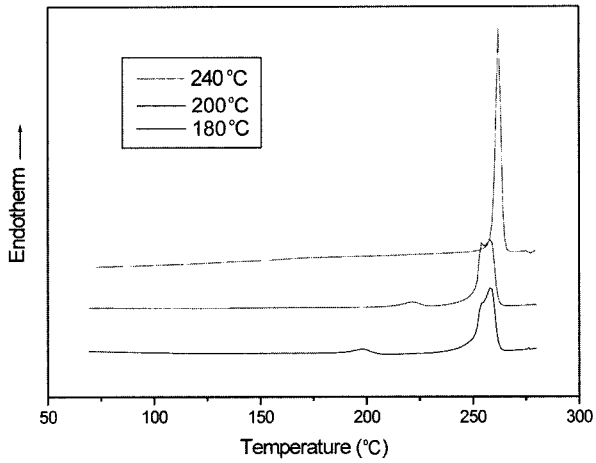

Figure 2. DSC thermogram for P(EN-ET) fibers (spun at 3000 m/min) after annealing at different temperatures.

temperatures. When these fibers were annealed at 180, 200, 240°C for 3 hours with their lengths constrained, the cold crystallization peak disappears from the DSC thermogram as a result of increased crystallinity. When these fibers annealed at 180 and 200°C three melting peaks can be observed, while only one melting peak was observed in the fiber annealed at 240°C. As the annealing temperature increases up to 200°C, low and middle melting peaks shift to higher temperatures and its height increases slightly. In contrast, the highest melting peak, which always appears at the same temperature, reduces in height. Then it is finally

merged to one melting peak and shifts to higher temperature, when fiber was annealed at 240°C. This result is similar to the results of Cheng and Wunderlich[4]. The lowest small melting peak, which appears at 20°C above the annealing temperature, must be attributed to the melting of defective crystals formed during secondary crystallization. The middle melting peak and the highest melting peak resulted from the melting of the crystal grown by isothermal crystallization and recrystallization of the imperfect crystals, respectively. Since the size and perfection of these crystals increase with the increase of annealing temperature, the low and middle melting peaks shift to higher temperature and finally show one melting peak.

The Phase Behavior and Structure Development

Dependence of the density of as-spun and annealed P(EN-ET) fibers on the spinning speed is shown in Figure 3. The density data do not show the significant change in the 600-1500 m/min range and starts to increase linearly from about 1.342 g/cm^3 at 1500 m/min to about 1.357 g/cm^3 at the spinning speed of 4500 m/min. It can be also calculated the degree of crystallinity of these fibers using density data, as

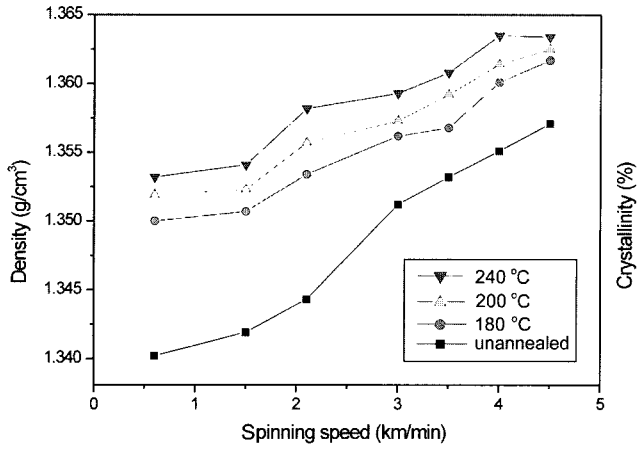

Figure 3. Density and crystallinity of P(EN-ET) fibers obtained under different spinning speeds.

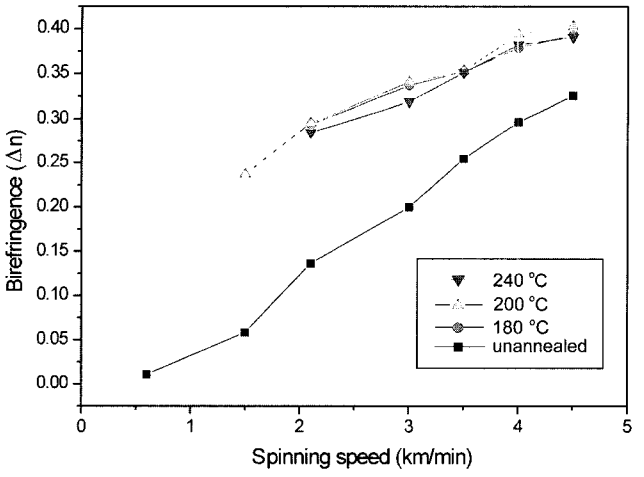

Figure 4. Birefringence of P(EN-ET) fibers obtained under different spinning speeds.

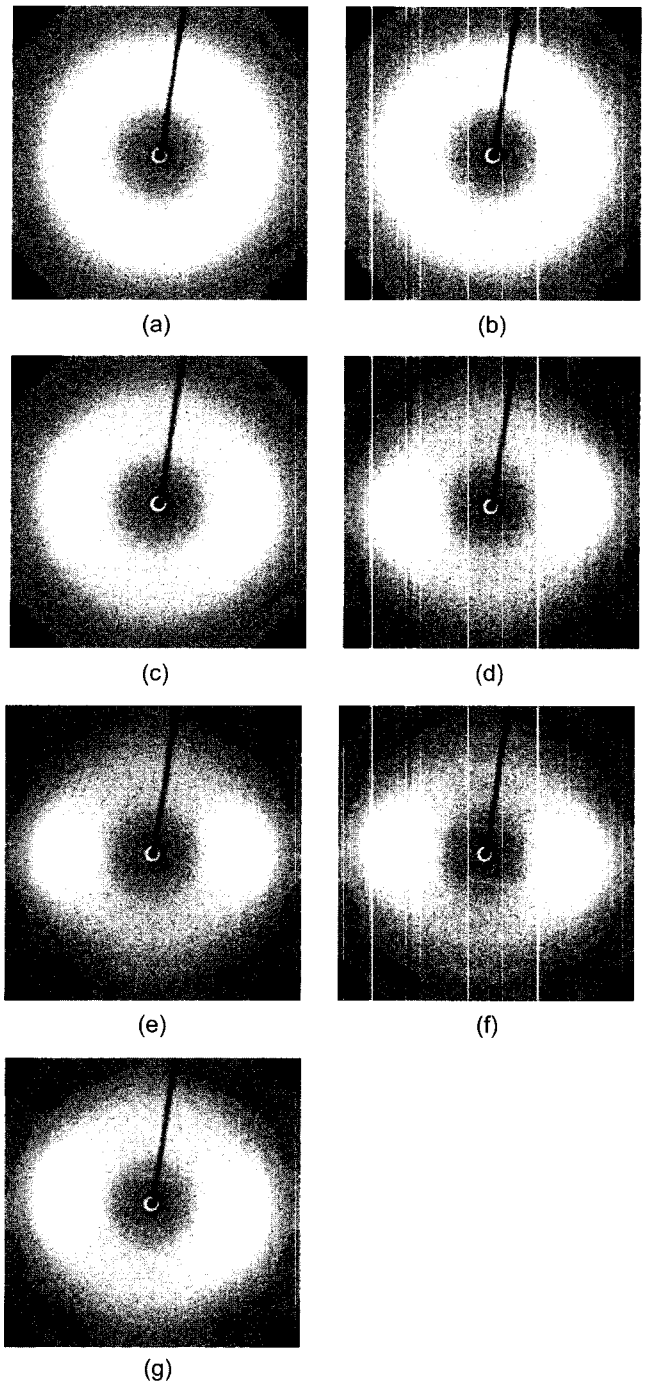

Figure 5. Wide angle X-ray diffraction patterns of as-spun P(EN-ET) fibers (a) 600, (b) 1500, (c) 2100, (d) 3000, (e) 3500, (f) 4000, (g) 4500 m/min.

shown in the Figure 3.

Effect of spinning speed on birefringence of the P(EN-ET) fibers is shown in Figure 4. P(EN-ET) fiber spun at 600 m/min exhibits very low birefringence near "zero", indicating very low levels of orientation at this speed. With an increase in the spinning speed, it begins to increase very linearly. This implies that an intensive development of molecular orientation occurs in the spinning speed range of 600-4000 m/min. After the constrained annealing process, the birefringence increases by about 0.1-0.15, presumably attributed by the increase in a number of crystallites and the crystal growth along the *c*-axis during annealing. The birefringence of annealed fibers spun below 1500 m/min could not be measured owing to their opacity.

In order to investigate the development of orientation and the phase behavior, X-ray diffraction measurements were carried out. Figure 5 shows the WAXD patterns of the as-spun fibers obtained at various spinning speeds. Up to the spinning speed of 1500 m/min, only the fairly broad amorphous halo was observed. With increasing spinning speed, the amorphous halo tends to concentrate on the equator, indicating the development of molecular orientation. However the discrete reflections of crystalline planes are not observed. Figure 6 shows the equatorial intensity profiles of the as-spun fibers. As it can be seen more quantitatively in equatorial scans, the crystalline reflections of (010) and (100) planes of α-form begin to appear beyond 3000 m/min, but the intensity of the peak is relatively small. It is supposed that since the DMT segments in the molecular chains decrease the regularity of the main chain, they do not pack regularly into repeating lattice structure. Furthermore, at 4500 m/min, the crystalline reflections are little decreased, which is consistent with the result of Cakmak and Kim[20]. It is supposed that the crystalline order is significantly reduced at this speed. The crystalline reflections of β-form are not appeared up to 4500 m/min.

Figure 7 shows WAXD patterns of annealed P(EN-ET) fibers spun at various spinning speeds. When these fibers were subjected to constrained annealing process, the WAXD patterns showed increased preferential orientation along the

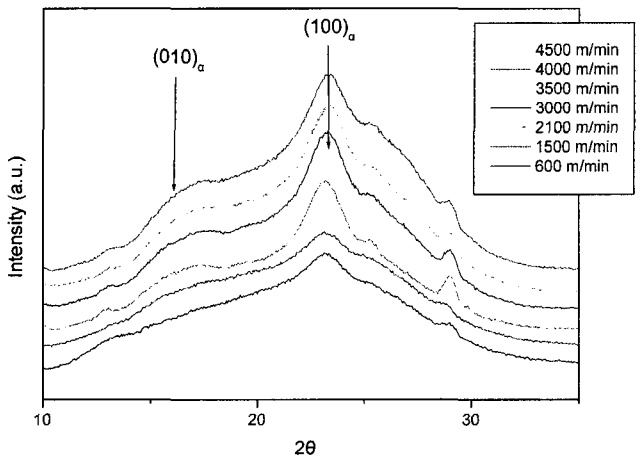

Figure 6. Equatorial wide angle X-ray diffraction profiles of as-spun fibers obtained under different spinning speeds.

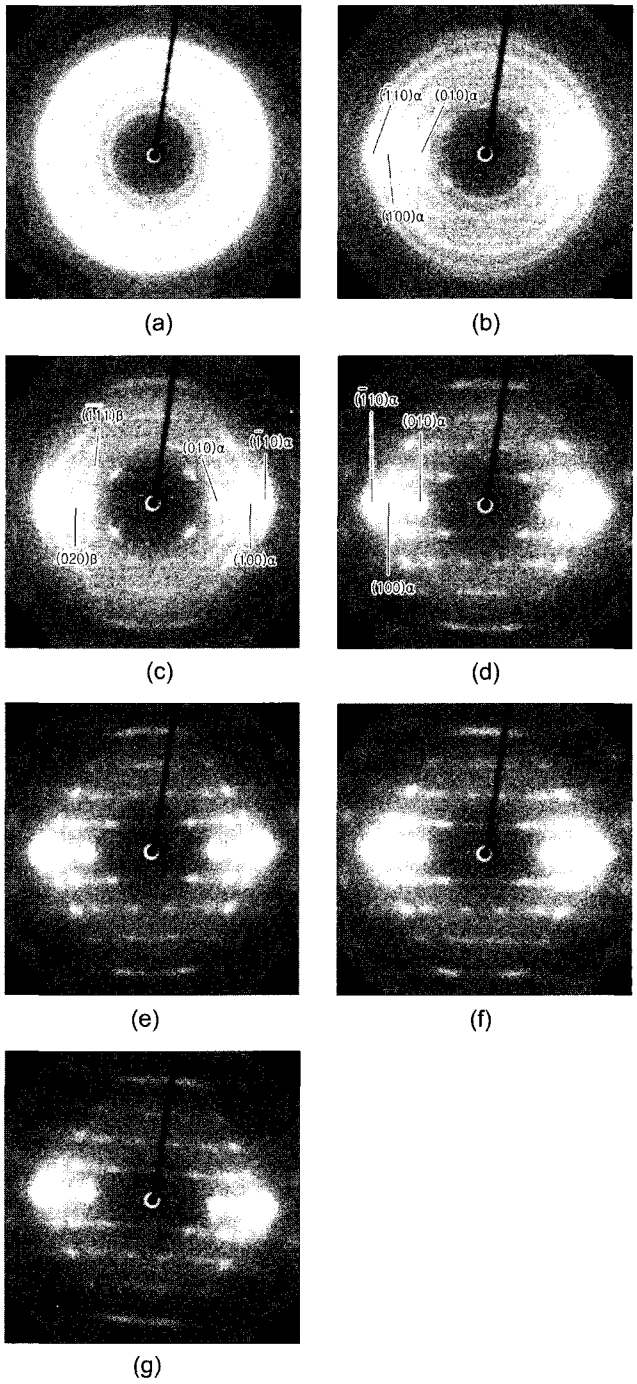

Figure 7. Wide-angle X-ray diffraction of P(EN-ET) fibers annealed at 220. (a) 600, (b) 1500, (c) 2100, (d) 3000, (e) 3500, (f) 4000, (g) 4500 m/min.

fiber axis even in the low spinning speed of 1500 m/min, in which the as-spun fibers did not show any preferential orientation. This result is consistent with the observation in birefringence and density data. The annealed fibers spun at 600-1500 m/min range exhibit dominantly α-form crystal with crystalline reflections of (010), (100), and ($\bar{1}$10) at the equatorial direction. Above the spinning speed of 2100 m/min, the annealed fibers begin to appear the crystalline reflections of (020) and ($\bar{1}\bar{1}$1) plane of β-form crystal. However this β-form crystal peaks disappeared above 3000 m/min completely. Nagai *et al.* reported that the β-form crystals in the as-spun fiber spun at the spinning speed of 5000 m/min transforms to the α-form crystal when the load is applied[17]. In this study, constrained annealed fiber spun at 2100 m/min shows crystalline reflections of β-form crystal, but β-form's peaks are disappeared above the spinning speed of 3000 m/min.

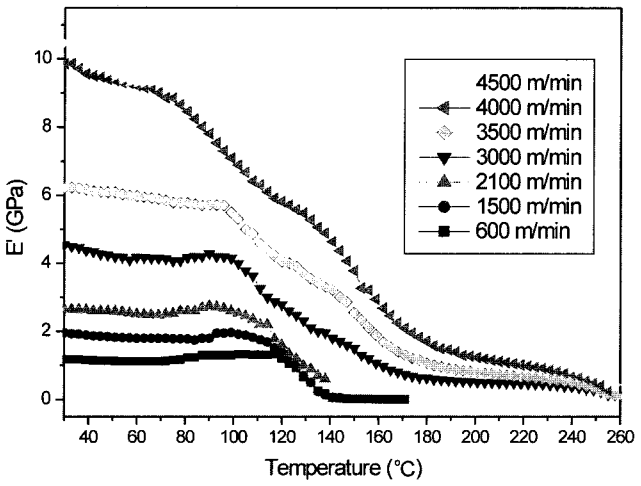

Figure 8. Temperature dependence of storage modulus (E') for P(EN-ET) as-spun fibers obtained under different spinning speeds.

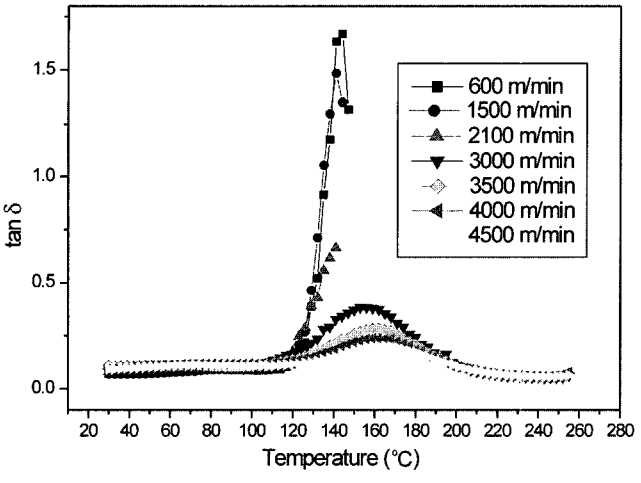

Figure 9. Temperature dependence of tanδ for P(EN-ET) as-spun fibers obtained under different spinning speeds.

Dynamic Properties

Figure 8 shows the temperature dependence of the storage modulus (E') for the as-spun fibers obtained at different spinning speeds. The E' values over wide temperature range increase with spinning speeds, and E' of as-spun fiber at 4500 m/min reaches 10.4 Gpa at room temperature. In Figure 9, the tan δ curves for as spun fibers show the α-relaxation peak at about 155°C-165°C, which is considered to correspond to the glass transition[21]. However β-relaxation peak, which was reported in 100% PEN fiber, was not found here. The α-relaxation peaks became smaller and broader and shift to higher temperatures as spinning speed increases, indicating that molecular mobility in the amorphous region is restricted by increased crystalline domain.

Conclusion

The structural development and dynamic properties of P(EN-ET) copolymer fibers spun at the spinning speed range of 600 m/min-4500 m/min were investigated. As-spun P(EN-ET) fibers exclusively exhibited the α-form crystal, and the annealed fibers spun in the 600-1500 m/min range exhibited dominantly α-form. At 2100 m/min spinning speed, the annealed fibers began to exhibit β-form crystal and it disappeared above 3000 m/min. The α-relaxation peaks of as-spun fibers were shown at about 155°C-165°C, but β-relaxation peak, which was reported in homo-PEN fiber, was not seen. The α-relaxation peaks became smaller and broader and shift to higher temperatures as spinning speed increases, indicating that molecular mobility in the amorphous region is restricted by increased crystalline domain.

References

1. Z. Mencik, *Chem. Prum.*, **17**, 78 (1967).
2. H. G. Zachmann, D. Wiswe, R. Gehrke, and C. Riekel, *Makromol. Chem. Suppl.*, **12**, 175 (1985).
3. S. J. Kim, J. Y. Nam, Y. M. Lee, and S. S. Im, *Polymer*, **40**, 5623 (1999).
4. S. Z. D. Cheng and B. Wunderlich, *Macromolecules*, **21**, 789 (1988).
5. H. Zhang, A. Rankin, and I. M. Ward, *Polymer*, **37**, 1079 (1996).
6. R. Jakeways, J. L. Klein, and I. M. Ward, *Polymer*, **37**, 3761 (1996).
7. S. Buchnner, D. Wiswe, and H. G. Zachmann, *Polymer*, **30**, 480 (1989).
8. Y. Ülcer and M. Cakmak, *Polymer*, **35**, 5651 (1994).
9. C. S. Cruz, F. J. B. Calleja, H. G. Zachmann, and D. Chen, *J. Mater. Sci.*, **27**, 2161 (1992).
10. X. Lu and A. H. Windle, *Polymer*, **36**, 451 (1995).

11. D. Chen and H. G. Zachmann, *Polymer*, **32**, 1612 (1991).
12. H. W. Jun, S. H. Chae, S. S. Park, H. S. Myung, and S. S. Im, *Polymer*, **40**, 1473 (1999).
13. M. E. Stewart, A. J. Cox, and D. M. Taylor, *Polymer*, **34**, 4060 (1993).
14. J. C. Kim, M. Cakmak, and X. Zhou, *Polymer*, **39**, 4225 (1998).
15. J. Jager, J. A. Juijn, C. J. M. Van Den Heuvel, and R. A. Huijts, *J. Appl. Polym. Sci.*, **57**, 1429 (1995).
16. K. Miyata, T. Kikutani, and N. Okui, *J. Appl. Polym. Sci.*, **65**, 1415 (1997).
17. A. Nagai, Y. Murase, T. Kuroda, M. Matsui, Y. Mitsuishi, and T. Miyamoto, *Sen-i Gakkaishi*, **51**, 478 (1995).
18. G. Wu, Q. Li, and J. A. Cuculo, *Polymer*, **41**, 8139 (2000).
19. I. Ouchi, H. Aoki, S. Shimotsuma, T. Asai, and M. Hosoi, *Proc. 17th Cong. Mater. Res.*, Japan, 217 (1974).
20. M. Cakmak and J. C. Kim, *J. Appl. Polym. Sci.*, **64**, 729 (1997).
21. A. K. Taraiya, A. P. Unwin, and I. M. Ward, *J. Polym. Sci., Part B, Polym. Phys.*, **26**, 817 (1988).