

Melt Spinning and Annealing of Poly(ethylene terephthalate)/*p*-Hydroxybenzoate Liquid Crystalline Polymer

Yun Hyuk Bang,¹ Sun Hee Lee,² Ik Hyun Kwon,¹ Hyun Hok Cho²

¹*R&D Center for Fiber and Textile, Hyosung Corporation, Hoge-Dong, Dongan-Ku, Anyang-Si, Kouggi-Do 431-080, South Korea*

²*Department of Textile Engineering, Pusan National University, Jangjeon-Dong, Geumjeong-gü, Busan 609-735, South Korea*

Received 30 March 2004; accepted 23 May 2004

DOI 10.1002/app.21065

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(ethylene terephthalate)/*p*-hydroxybenzoate (PET/PHB) copolymer materials have relatively low melt viscosity because of the 60 mol % PHB material having a value that is lower by approximately two orders of magnitude than the value for PET homopolymer. The structure development during melt spinning and thermal treatment (annealing) of liquid crystalline copolyesters, with a rigid backbone structure, were analyzed through the density, birefringence, X-ray diffraction, DSC, dynamic viscoelasticity, and tensile testing. As the take-up velocity increased, the birefringence of PET/PHB as-spun fiber increased, which

indicated that it directly influenced the initial modulus and specific stress. The lateral packing of PHB molecular chain in a copolymer was shown to be loosened in the course of thermal treatment. The thermal treatment slightly increased the crystal orientation factor, whereas total molecular orientation was decreased by annealing. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1265–1278, 2004

Key words: PET/PHB copolymers; high take-up velocity; annealing; microstructure; mechanical properties

INTRODUCTION

To control the anisotropic solution or melt obtained from anisotropic polymer is a very important factor in the preparation of a high-strength fiber. During fiber formation, the liquid crystal domain of such polymer solutions of melts easily orientates by shear or elongational flow. In addition, an anisotropic polymer becomes a high crystalline solid by way of the cooling process and consequently forms a high-strength fiber with high orientation and crystallinity.

Recently, research on the synthesis of thermotropic liquid crystalline polymers, to lower a melting point by varying the suitable chemical structures without reduction of liquid crystalline properties, has been conducted by a number of investigators.^{1–3} In the case of the first liquid crystalline polymer developed by Jackson,¹ through reacting poly(ethylene terephthalate) (PET) with *p*-acetoxybenzoic acid (ABA),⁴ the copolymer containing more than 30% of ABA showed liquid crystalline behavior. Moreover, in particular, Eastman Kodak commercialized such copolymers composed of PET/ABA = 40/60 and 20/80 that

showed excellent mechanical properties as well as easy processability, which was corroborated by many researchers.^{5,6} Muramatsu and Krigbaum^{7,8} reported the following result from research on the orientation behavior of liquid crystalline fiber: if capillary L/D of the spinneret was >49.44 , orientation of the fiber was still successful, even when a spin-draw ratio was much lower.

Wu and Hsu⁹ proposed a normal or cybotactic nematic structure model on which the hard segment was oriented first, followed by a soft segment (called a spacer), as drawing the liquid crystalline polymer. In addition, many extensive investigations were conducted that focused on the physical and mechanical property changes—including viscosity, strength, and modulus—that depended on polymer composition and draw ratio using the soft polymers, blended with thermotropic liquid crystalline polymers, to improve processability as well as mechanical strength.^{10–15} However, to date scant research has been reported concerning the property changes using the thermotropic liquid crystalline fiber spun at high take-up velocity.

Results of only several studies have been published concerning structural analysis of liquid crystalline copolymer, which shows a structure between a three-dimensionally organized crystal and nonorganized isotropic liquid. In particular, the position and inten-

Correspondence to: S. Lee (sunny6798@hanmail.net).

TABLE I
Crystal Systems and Lattice Constants of PHB Homopolymer

Phase	Crystal system	Lattice constant	Condition	Author
Phase I	Orthorhombic	$a = 7.47\text{--}7.62 \text{ \AA}$ $b = 5.67\text{--}5.7 \text{ \AA}$ $c = 12.5\text{--}12.55 \text{ \AA}$	High molecular weight	Blackwell ¹⁶ Geiss ¹⁷
Phase II	Orthorhombic	$a = 11.06\text{--}11.12 \text{ \AA}$ $b = 3.77\text{--}3.78 \text{ \AA}$ $c = 12.89\text{--}12.9 \text{ \AA}$	Low molecular weight	Lieser ¹⁸
Phase III	Hexagonal	$a = 9.13\text{--}9.24 \text{ \AA}$ $b = 5.28\text{--}5.3 \text{ \AA}$ $c = 12.49\text{--}12.5 \text{ \AA}$	Anneal treatment near 340°C	Blackwell ¹⁶ Hanna ¹⁹

sity of meridional WAXD reflections were calculated for a liquid crystalline polyester with a random sequence distribution by Blackwell et al.¹⁶ to elucidate the dependency of composition, length of monomeric repeating unit, and chain distribution block on its structure. However, there are still many difficulties in transferring an irregularly chain distributed structure of liquid crystalline copolyester into a three-dimensional structure containing regular crystal lattice. Because the crystal structure of liquid crystalline copolyester is very complicated and a crystal structure of *p*-hydroxybenzoate (PHB) homopolymer is a prerequisite to understand their copolymer structures, most researchers have obtained the partial—but still controversial—results with respect to only the PHB part. Because of the recent results, the crystal structure of PHB is shown to be an orthorhombic structure without thermal treatment, but transformed to a hexagonal

structure after thermal treatment at high temperature, as detailed in Table I.^{16–19} Therefore, in this work, we report the effect of take-up velocity on structure formation and property changes of fiber that has been melt-spun, copolymerized at 40 mol % of PET with 60 mol % of PHB, and present a detailed analysis of the crystal structure of fiber developed at various thermal-treatment temperatures and times. In addition, we also propose the possible relationship between a microstructure and mechanical properties of fiber after thermal treatment.

EXPERIMENTAL

Material and spinning conditions

The copolyester, composed of PET/PHB = 40/60 mol % (Japan Unitika), which contains a flexible segment in the main chain (which decreases its melting point through partial reduction of rigidity and crystallinity of liquid crystalline polymer), was melt-spun under a total distance of 3.3 m from the nozzle (diameter = 0.5 μm) to the winder, at a take-up velocity of 0.5–4

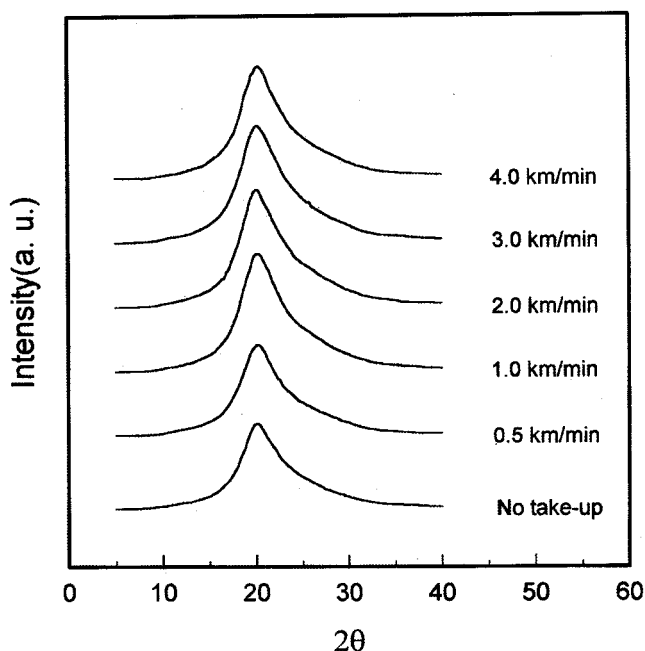


Figure 1 Wide-angle X-ray equatorial scans of PET/PHB filaments with take-up velocity.

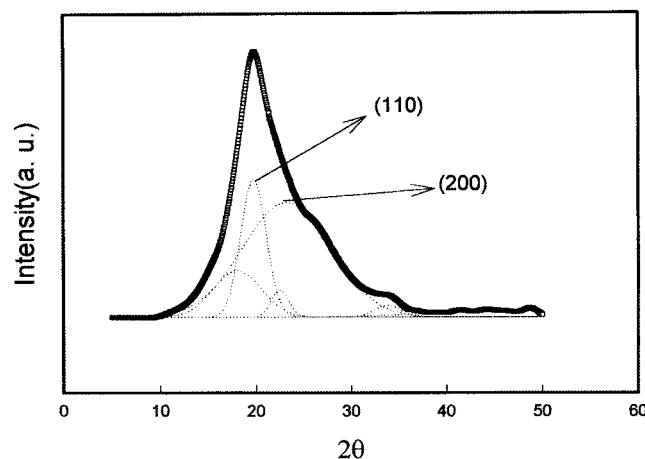


Figure 2 X-ray scattering patterns resolved into individual intensities of fiber treated under the following conditions: take-up velocity = 3 km/min, annealing temperature = 220°C, annealing time = 8 h.

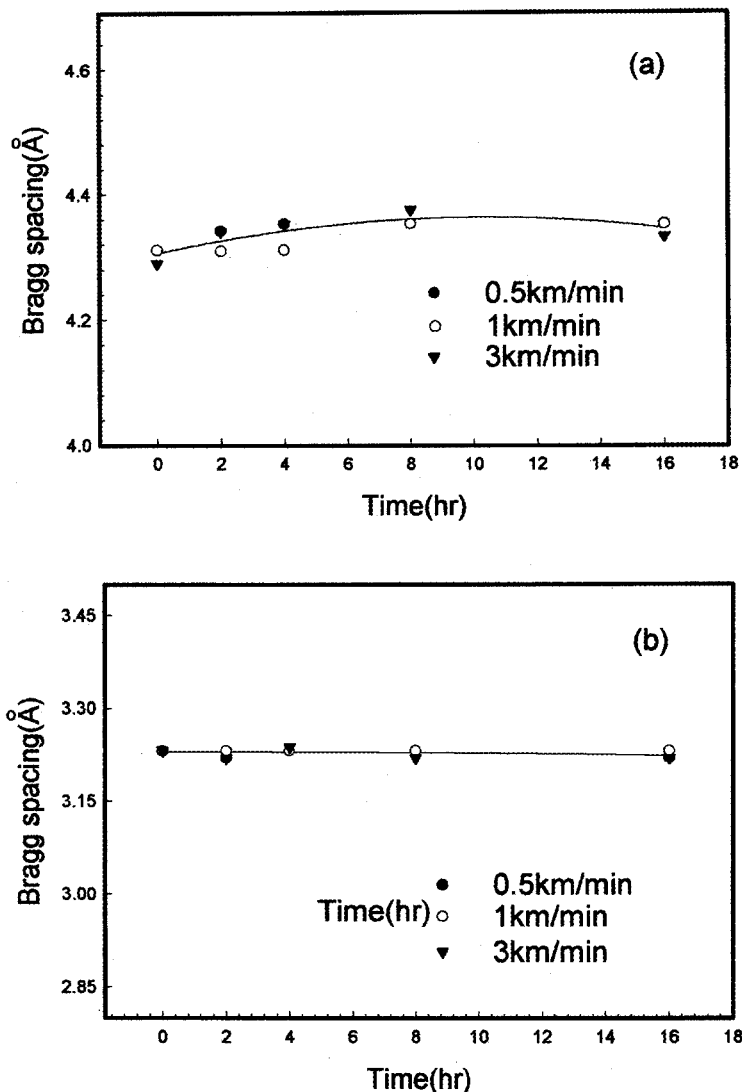


Figure 3 Effects of annealing time on the Bragg spacing for (a) (110) and (b) (004) plane of fiber annealed at 180°C; take-up velocity = 0.5, 1, 3 km/min.

km/min and a mass flow ratio of 7.0 g/min at 260°C, to obtain the fiber.

Annealing conditions

Thermal treatment was carried out for 2 to 16 h from 180 to 200°C, at 20°C intervals, under a vacuum condition without tension.

Measurements

Birefringence (Δn) values were calculated through the following equation with retardation (r), obtained from use of a cross-polarized microscope, equipped with a GIP filter and a sernarmont compensator under cross-polarization, and fiber diameter (d), measured by a Zeiss optical microscope (Zeiss, Oberkochen, Germany).

$$r = (n_1 - n_2) \times d = \Delta n \times d$$

Density was measured with a density-gradient column (Shibayama, Tokyo, Japan) filled with carbon tetrachloride ($d = 1.59$) and n -heptane ($d = 0.68$) at 23°C.

Wide-angle X-ray scattering(WAXS) measurements were carried out using Ni-filtered and graphite-monochromated Cu-K α radiation (30 kV and 15 mA) at room temperature by a Rigaku D/MAX-III-A diffractometer (Rigaku, Tokyo, Japan), to obtain the WAXS profiles of polymer chip, fiber, and the milled fiber powder. The degree of crystal orientation of spun fiber was calculated from meridional direction X-ray diffraction data and the apparent crystalline size was calculated by use of the Scherrer equation.

Dynamic viscoelastic behavior of the high speed spun fibers was measured using a DDV-III Auto Rheo-

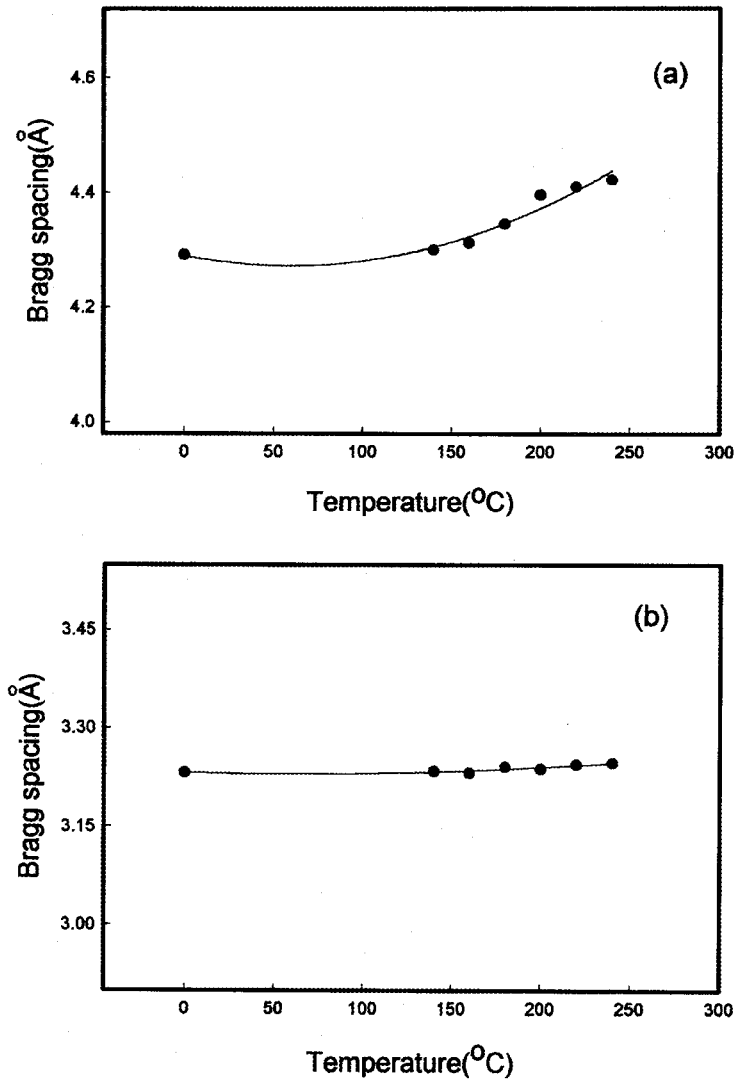


Figure 4 Effects of annealing temperature on the Bragg spacing for (a) (110) and (b) (004) of fiber annealed for 8 h; take-up velocity = 3 km/min.

vibron (Orientec, Tokyo, Japan) at 110 Hz, from 20 to 150°C, at a heating rate of 2°C/min with liquid nitrogen purging.

Specimens were sealed in aluminum pans under dry nitrogen and then heated in a Shimadzu DSC-50 differential scanning calorimeter (Shimadzu, Kyoto, Japan) at the heating rate of 10°C/min. The thermal contraction through thermal stress of specimens was also measured by a Shimadzu thermomechanical analyzer under initial weight of 5 g at the same heating conditions as for DSC measurement.

Tensile properties were measured with 20-mm-long fiber specimens using a Textechno Fafegraph-M (Herbert Stein GmbH, Mönchengladbach, Germany), operated at 10 mm/min.

Fibril structures on the fiber cross section were studied from the cryogenically fractured surplane of the samples, sputtered with gold before viewing, under a

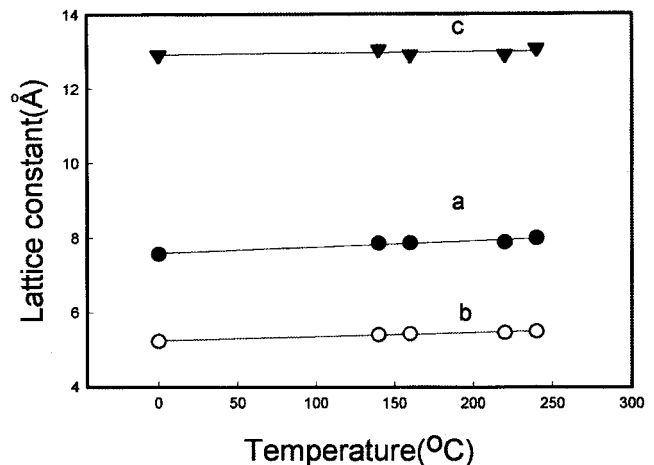


Figure 5 Effects of annealing temperature on the lattice constant of fiber annealed for 8 h; take-up velocity = 3 km/min.

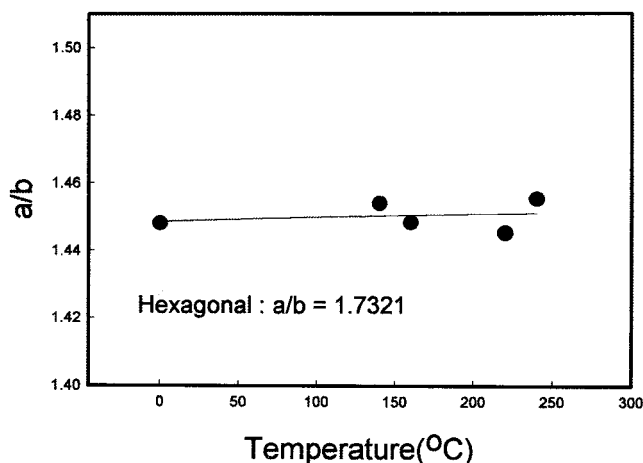


Figure 6 Effects of annealing temperature on the difference between a - and b -axis of fiber annealed for 8 h; take-up velocity = 3 km/min.

JSM 6400 scanning electron microscope (JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Crystal structure changes of PET/PHB fibers with take-up velocity and annealing condition

Figure 1 shows the equatorial WAXD profile of high speed spun PET/PHB fiber. The reflection at $2\theta = 20^\circ$ showed a broad intensity of distribution with a peak shoulder at around 22° . The intensity of fibers spun at speeds up to take-up velocity of 1 km/min was increased slightly but that of fibers spun at a higher take-up velocity did not change at all. On the other hand, we could not observe the expected diffraction peak at $2\theta = 26\text{--}27^\circ$ assigned to the (100) plane of PET.

Figure 2 shows the scattering intensity distributions, separated by each crystal plane from the X-ray diffraction patterns and scattering intensity distribution curves, of liquid crystalline fibers spun at the take-up velocity of 3 km/min after thermal treatment at 220°C for 8 h. Two shoulder peaks appeared on both sides of the central peak at $2\theta = 20^\circ$. Although these peaks did not change with increasing take-up velocity, they became more obvious after thermal treatment. This result confirms that perfect crystallization of rough crystals can occur through such heat treatment, which is frequently used both to improve fiber properties and to identify its structural transformation. We determined five separated peaks from $2\theta = 18^\circ$ to $2\theta = 45.4^\circ$, as shown in Figure 2, and calculated the plane spacing and crystal lattice constant by using diffraction peaks for the (110) plane and the (200) plane of PHB crystal at $2\theta = 19.75$ and 22.0° , respectively, as well as diffraction peak for the (004) plane at $2\theta = 27^\circ$, obtained from the meridional direction X-ray diffrac-

tion experiment of fiber sample, even though several publications on the crystal structure and transformation were still unclear. Because it is almost impossible to obtain clear resolution of diffraction patterns for amorphous regions of liquid crystalline polymers, such as PET/PHB containing a multiphase structure, we also have as yet been unable to achieve a solution to this problem.

Crystal spacing changes of PET/PHB fibers with annealing condition

Figure 3 shows the spacing changes of the (110) plane [Fig. 3(a)] and the (004) plane [Fig. 3(b)] with thermal treatment time of liquid crystalline fibers spun at a take-up velocity of 0.5–3 km/min; considering the error ranges, the spacings of the (110) and (004) planes did not significantly vary. Generally, the crystal transformation of high molecular weight PHB homopolymer occurred at $325\text{--}360^\circ\text{C}$.¹⁹ Over this temperature range, the rigid PHB chains in the fiber and thermally treated homopolymer were well organized to a parallel direction toward the c -axis because of the improvement of free rotation of aromatic ester linkages, although they became more irregular to the perpendicular direction to the c -axis because of axial distortion.¹⁶ We expected that copolyesters containing more than 60 mol % of PET might show a similar trend at even lower temperatures ($\sim 180^\circ\text{C}$) because of the flexible ethylene units, but we could not detect any plane spacing change at that temperature over the course of many hours. This result implies a thermal

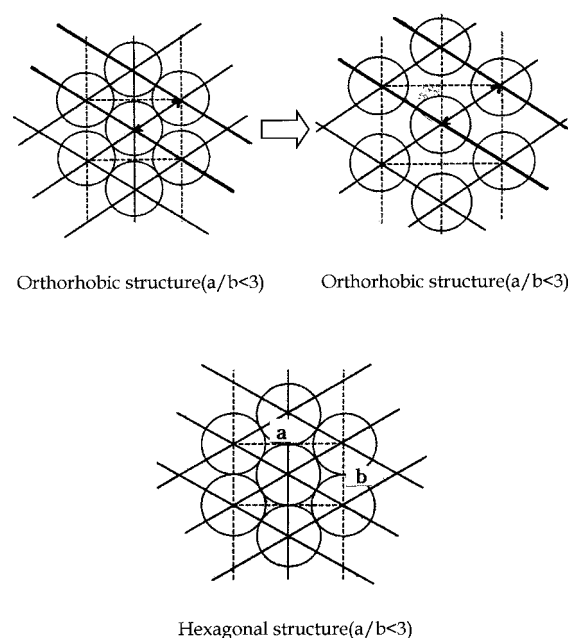


Figure 7 Illustration of the possible means of orthorhombic packing of cylindrical polymer chains.

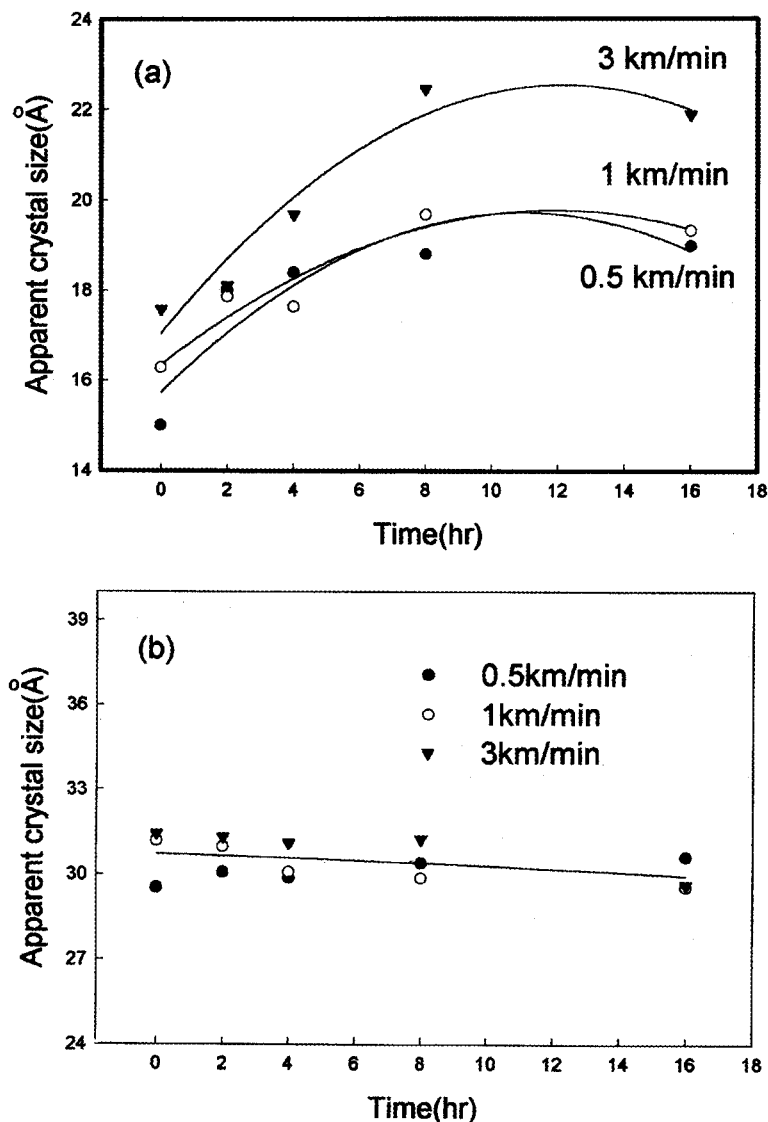


Figure 8 Effects of annealing time on the apparent crystal size for (a) (110) and (b) (004) plane of fiber annealed at 180°C; take-up velocity = 0.5, 1, and 3 km/min.

treatment at 180°C did not seriously affect the conformation and chain interaction of PHB crystals.

Figure 4 shows the spacing changes of the (110) plane [Fig. 4(a)] and the (004) plane [Fig. 4(b)] with thermal treatment temperature of liquid crystalline fibers spun at the take-up velocity of 3 km/min. Although the spacing of (110) planes was increased with thermal treatment over 200°C, that of (004) planes did not vary significantly. This result suggested that the length change occurred in an *a*- or *b*-axis direction, instead of *c*-axis, because the molecular motion of polymer chains in the PHB crystal became more active, thus broadening the space between chains.

Kaito and coworkers²⁰ reported that in the case of liquid crystalline copolyester the distribution of projected repeating units, which were dependent on the conformation of aromatic ester linkages, was spread

out more with thermal treatment and, consequently, the plane spacing was increased in a parallel direction toward the *c*-axis. However, in their work no change of spacing of (004) planes was caused by applying stronger tensile stress to the parallel direction of fiber during the high-speed spinning process.

Figure 5 shows the lattice constant changes of PHB crystal with thermal treatment temperature of liquid crystalline fibers spun at the take-up velocity of 3 km/min. Because most researchers have assumed that the crystal structure of PHB might be an orthorhombic unit cell, in this work we calculated the lattice constant from Bragg angles and Miller indices of the (110), (200), and (004) planes on the basis of the same assumption. The lattice constant of fiber obtained from our experiment was similar with that of high molecular weight PHB homopolymer, except the length of

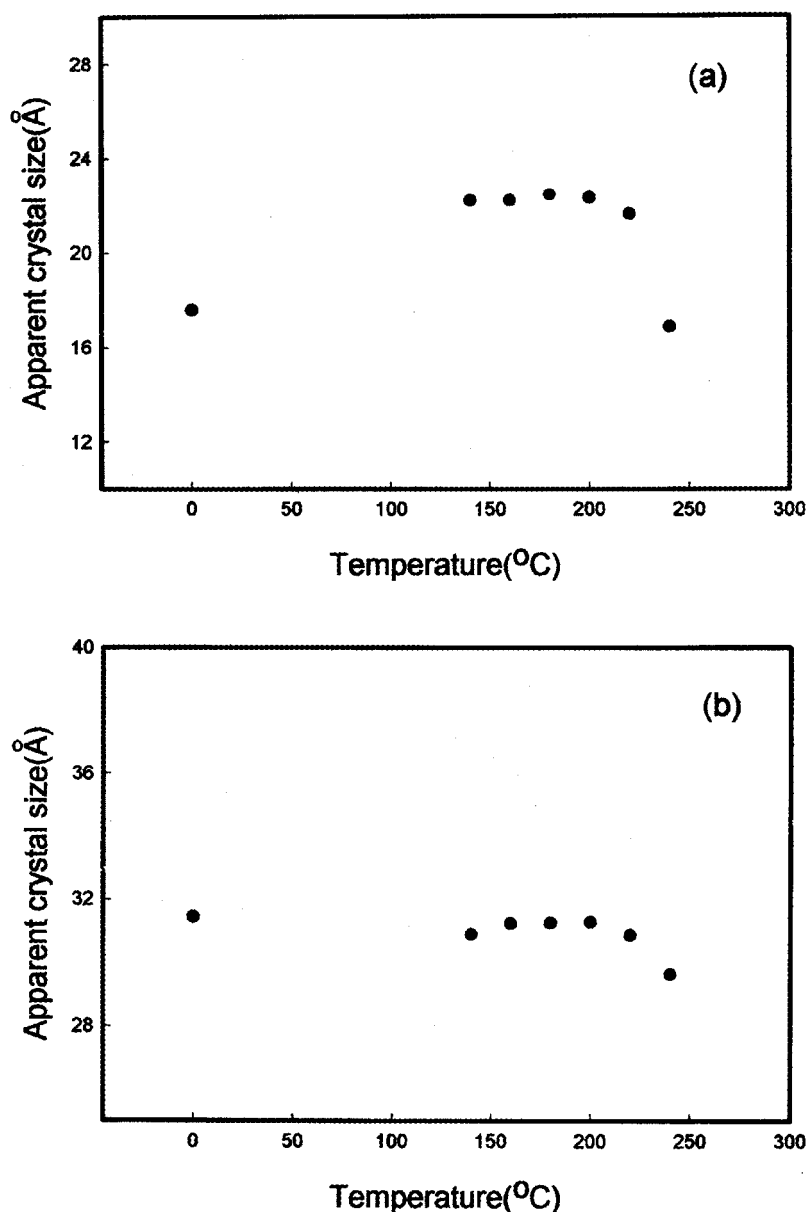


Figure 9 Effects of annealing temperature on the apparent crystal size for (a) (110) and (b) (004) plane of fiber annealed for 8 h; take-up velocity = 3 km/min.

the b - and c -axes. The slight decrease in length of the b -axis and increase of the length of the c -axis was believed to be caused by a high-speed spinning process, which would promote the compact packing of polymer chains. In addition, the crystal structure of PHB is an orthorhombic unit cell because $a/b \neq 3$.

With increasing heat treatment temperature, the length of a - and b -axes slightly increased but that of the c -axis did not change. The lack of change in the a/b value, even at elevated heat treatment temperature as shown in Figure 6, was attributed to the simultaneous increase of the length of both a - and b -axes. The main chain of PHB showed a cylindrical structure through an easier rotation of aromatic ester linkages. Changes

of the orthorhombic unit cell with heat treatment, estimated on the basis of the results as shown in Figure 3–6, are schematically represented in Figure 7. Spacing of the cylinder to direction of the b -axis became wider with heat treatment at 240°C for up to 8 h, but we could not detect any strong thermal transition such as crystal transition.

Apparent crystal size changes of PET/PHB fibers with annealing condition

Figure 8 shows the apparent crystal sizes of the (110) plane [Fig. 8(a)] and the (004) plane [Fig. 8(b)] with thermal treatment time of liquid crystalline fibers

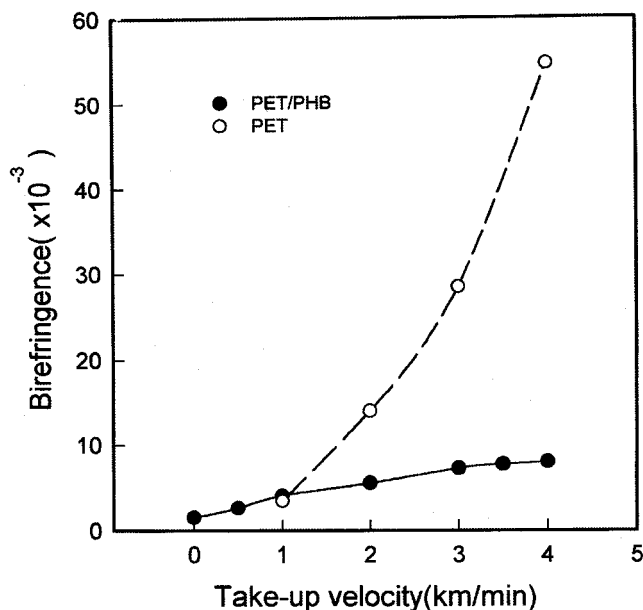


Figure 10 Birefringence of PET/PHB and PET fibers with take-up velocity.

spun at the take-up velocity of 0.5–3 km/min. Whereas the crystal size of the (110) plane was increased with thermal treatment time up to 8 h, and nearly constant after that time, that of the (004) plane showed no change at all. This phenomenon implied that upon thermal treatment at 180°C the crystal grows only in a vertical direction to the crystal axis through rearrangement of polymer chains having the same direction. In addition the increase of apparent crystal size with take-up velocity suggests that both higher orientation and more perfect crystal in the fiber may be more favorable to crystal formation and growth.⁵

Figure 9 shows the apparent crystal sizes of the (110) plane [Fig. 9(a)] and the (004) plane [Fig. 9(b)] with thermal treatment temperature of liquid crystalline fiber spun at the take-up velocity of 3 km/min. The crystal sizes increased with temperature up to 200°C and decreased over that temperature, as a result of the melting of some imperfect crystals.

Orientation and crystallinity of PET/PHB fibers with take-up velocity and annealing condition

The birefringence of fibers spun at different take-up velocities is shown in Figure 10. Although the degree of birefringence was slightly increased with take-up velocity, the value was much smaller than that of PET fiber. This result implies that it is impossible to obtain a highly oriented PET/PHB thermotropic liquid crystalline fiber by controlling just the take-up velocity.

Figure 11 shows the birefringence changes of liquid crystalline fibers spun at the take-up velocity of 0.5–3

km/min with thermal treatment time [Fig. 11(a)] and temperature [Fig. 11(b)]. The birefringence decreased with thermal treatment time and temperature, and this trend was highly significant for fibers spun at very high take-up velocities.

Figure 12 shows the density of liquid crystalline fibers spun at different take-up velocities: the density of fibers was nearly identical at any take-up velocity. From these two above-mentioned results, the small increase in birefringence with take-up velocity did not affect the structural compactness of the thermotropic liquid crystalline fiber.

Figure 13 shows the density changes of liquid crystalline fibers spun at the take-up velocity of 0.5–3 km/min with thermal treatment time [Fig. 12(a)] and temperature [Fig. 12(b)]. The density increased slightly with thermal treatment time. Because the lattice constant was not substantially increased, as shown in Figure 5, our result did not match with the theory proposed by Blackwell et al.,¹⁶ that the density of PHB was decreased with increasing crystal lattice volume by 13% during the heat treatment at 320°C. Rather, the density would be substantially dependent on crystal size because the density change showed similar trends to apparent crystal size change related to heat treatment time and temperature.

Figure 14 shows the change of degree of orientation of crystalline PHB in liquid crystalline fibers spun at the take-up velocity of 0.5–3 km/min with thermal treatment time. The degree of orientation of fibers increased with increasing thermal treatment time. When the fibers were thermally treated at below 250°C, poorly organized crystals were melted and completely organized crystals acted as crystallizing seeds to induce the crystallization of polymer chains. Therefore, the increase of degree of orientation was caused by the longitudinal rearrangement of poorly organized crystals in the PHB region after melting.

Because this result could be explained by relaxation of polymer chains, except PHB crystals during heat treatment, the greater decrease of birefringence for fibers spun at higher take-up velocities, which improved longitudinal stress of fiber, was also caused by a greater relaxation of polymer chains through increasing latent stress during heat treatment. In particular, the significant decrease of birefringence for fiber treated at 180–200°C was attributed to the melting of PET crystals, like the result obtained by thermal analysis. The more disordered structure of the polymer chains, except PHB crystals, was developed during heat treatment.

Because PET/PHB liquid crystalline polymer crystallizes very slowly, its fiber shows poor crystallinity and it takes extensive time for the completely molten crystalline polymer to recrystallize during spinning at temperatures higher than 260°C.

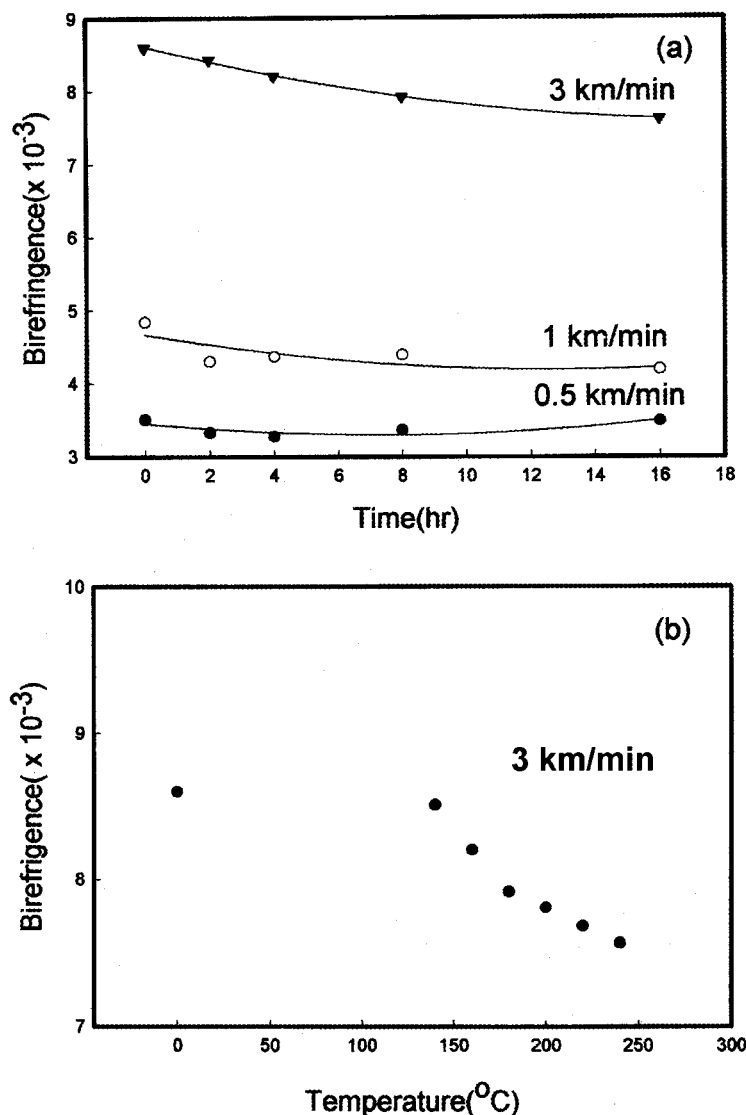


Figure 11 Effects of (a) annealing time and (b) temperature on the birefringence of fiber.

Wissbrun²² reported the above fiber spun at 230 $^{\circ}\text{C}$ showed a clear X-ray diffraction pattern but fiber spun at 280 $^{\circ}\text{C}$ did not show a diffraction pattern at all. However, the crystal structure can be formed through extension of thermal treatment. In addition, a liquid crystalline fiber obtained from copolymer containing more than 60% of PHB forms a PHB-like crystal instead of a PET-like one, and even crystal formed through thermal treatment is easily destroyed by the quenching process. Therefore, there are many difficulties in analyzing the thermal analysis data because of the extremely complicated structure of PET/PHB liquid crystalline fiber. For example, there are some differences that characterize endothermic peaks at 57–75, 152–197, and 230–260 $^{\circ}\text{C}$. Cuculo and Chen⁶ and Menczel and Wunderlich²³ concluded that two peaks at the lower temperature were glass-transition temperatures (T_g 's) of the PET-rich region and the PHB-

rich region, respectively, and the peak at the highest temperature was a melting point (T_m) of the PHB-like crystal region. However, Brostow et al.²⁴ and Joseph et al.⁵ concluded that the second endothermic peak was a T_m of the PET-like crystal region by analyzing thermal analysis data of liquid crystalline copolymers containing various amounts of PHB.

We also discussed our results with respect to the theory proposed by Cuculo and Menczel, given that simultaneous consideration of the polymer property and heat treatment may be more reasonable.

Dynamic viscoelasticity of PET/PHB fibers with take-up velocity

As shown in Figure 15, the temperature dependency on $\tan \delta$ of the PET/PHB fibers at various high take-up velocities was not significant. Whereas the main dis-

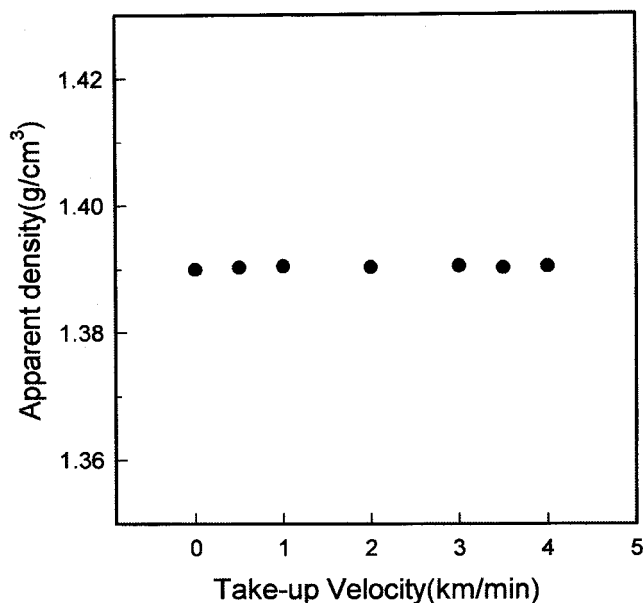


Figure 12 Density of PET/PHB fibers with take-up velocity.

tribution (a) for PET itself was shown at 120–130°C, that for PET/PHB fiber was shown at about 72°C. From this result we determined that, in the case of PET/PHB fiber, molecular chains in the amorphous region were highly disrupted by the diluent effect of rigid PHB chains and, consequently, a molecular motion of amorphous chains occurred at a much lower temperature than PET itself did.

The storage modulus E' of fiber was increased with the take-up velocity, as shown in Figure 16. This phenomenon means the orientation of amorphous chain, which affected the value of E' , was also increased with the take-up velocity, and was well matched with the result of change in birefringence.

Thermal behaviors of PET/PHB fibers with annealing condition

Figure 17 shows the thermal behaviors of liquid crystalline fibers, spun at a take-up velocity of 3 km/min, with thermal treatment time [Fig. 17(a)] and temperature [Fig. 17(b)]. As heat treatment time was increased, the peak around 200°C became sharper and wider, and the peak around 80°C, which was a T_g of the PET-rich region, disappeared. This implies that homogeneously distributed PET-like crystal forms in the course of heat treatment through the reorientation of molecular chains in the PET-rich region.

From the results obtained from different thermal-treatment temperatures, the fibers thermally treated at 140–160°C showed a pattern similar to that of the untreated fibers, except for disappearance of the peak

around 80°C. However, when a fiber was treated at over 180°C the peak around 200°C became sharper and wider and shifted to a higher temperature with thermal-treatment temperature. This trend is similar to that obtained during experiments on thermal-treatment time. Finally, we ascertained that completion of crystallization of the PET-like crystal occurs around 180°C.

Mechanical properties of PET/PHB fibers with take-up velocity

Figure 18 shows stress–strain curves of PET/PHB fibers spun at various take-up velocities, to identify their elongational changes. The shape of curves was identical to that of a typical rigid nematic liquid crystalline polymer. The orientation of amorphous chains in copolymer might be increased with the take-up velocity and, consequently, the strength was also increased but elongation decreased. However, the strength of fiber was not improved with the high take-up velocity, as we had expected.

The birefringence change and initial modulus of fibers had linear relationships with the take-up velocity, as shown in Figure 19. Therefore, the molecular orientation directly affected the mechanical properties of PET/PHB fiber.

Morphology of PET/PHB fibers with take-up velocity

Figure 20 shows the cross-sectional morphologies of PET/PHB fibers spun at different take-up velocities. Fibrillation developed to a better degree with increasing take-up velocity, a result that agreed well with the published data that a fibrillation occurred at the “PHB-rich region” rather than the core part, that is, the “PET-rich region.”²¹

CONCLUSION

An easily processable copolyester, PET/PHB = 40/60 mol %, was melt-spun at different take-up velocities to obtain a fiber with high strength and modulus. The obtained fiber was thermally treated to identify not only the structural morphology but also the mechanical and physical property changes. From the results of above experiments we report the following conclusions.

As the take-up velocity increased, the birefringence of PET/PHB as-spun fiber increased, which indicated that it had a direct influence on the initial modulus and specific stress. The mechanical properties of liquid crystalline fibers were slightly improved with increasing take-up velocity, but it was not the only factor to control their basic properties.

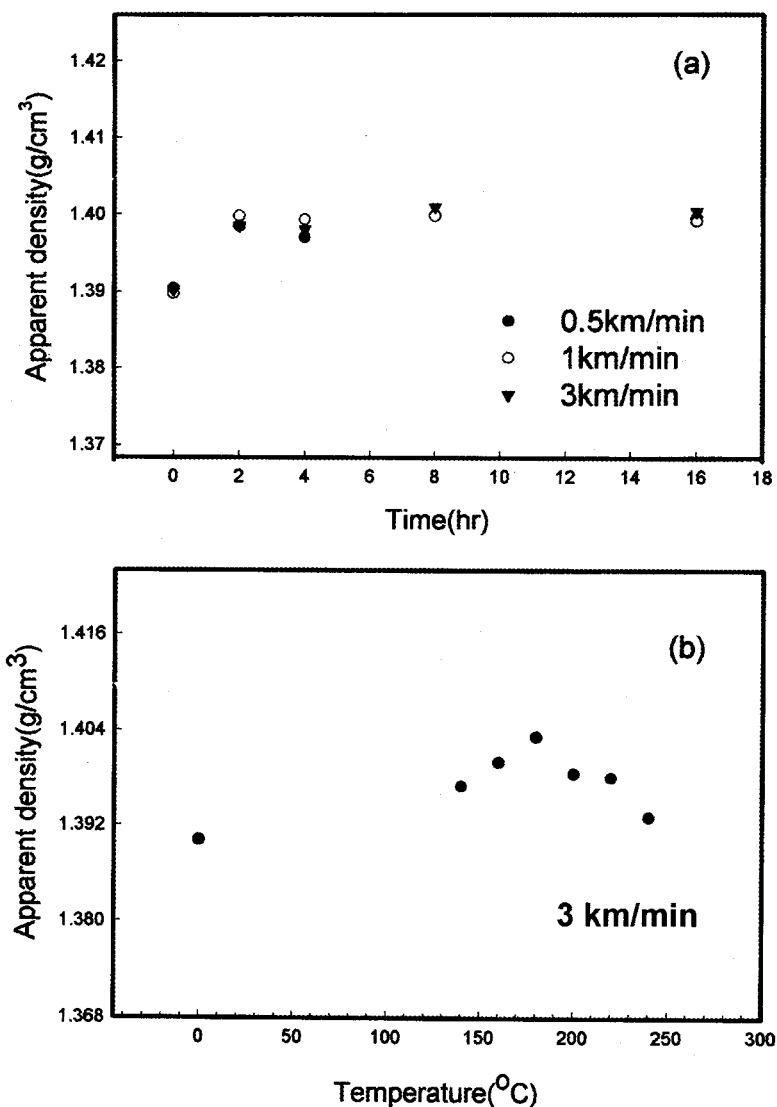


Figure 13 Effect of (a) annealing time and (b) temperature on the apparent density of fiber.

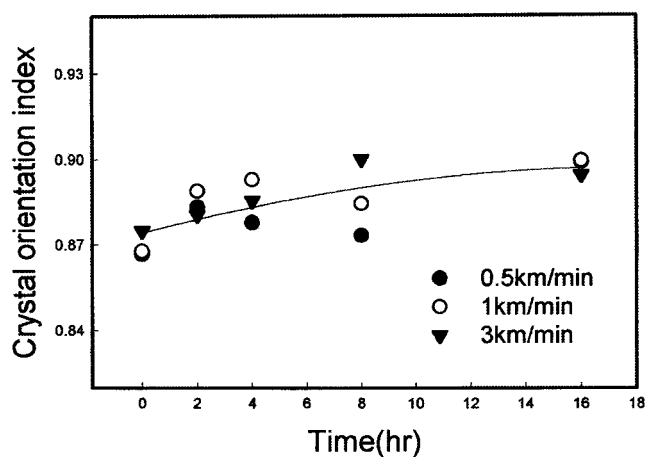


Figure 14 Effects of annealing time on the crystal orientation index of the (004) plane of fiber annealed for 8 h.

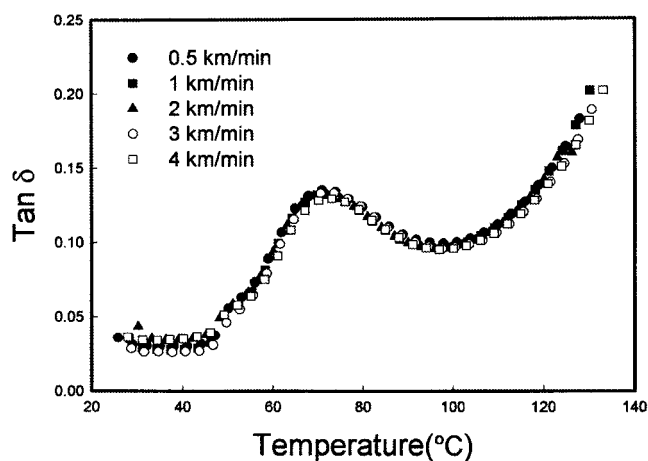


Figure 15 Temperature dependency of tan δ with take-up velocity for PET/PHB fibers.

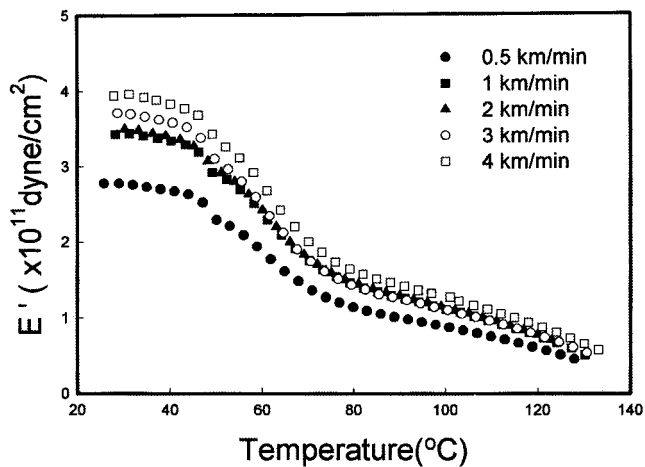


Figure 16 Temperature dependency of storage modulus (E') with take-up velocity for PET/PHB fibers.

Although high speed spun liquid crystalline fibers were thermally treated at below 240°C , the spacing of the (110) plane was increased with temperature through increasing lengths of a - and b -axes, but no change of crystal axis c . The change of crystal size after heat treatment increased with take-up velocity, which indicates that the high orientation and greater degree of crystalline perfection are advantageous for crystalline growth.

The change of density depended on the crystal size, and not on the compact packing of molecular chains in the crystalline region. The change of birefringence and initial modulus showed similar trends that depended on the other region rather than on the PHB crystal region.

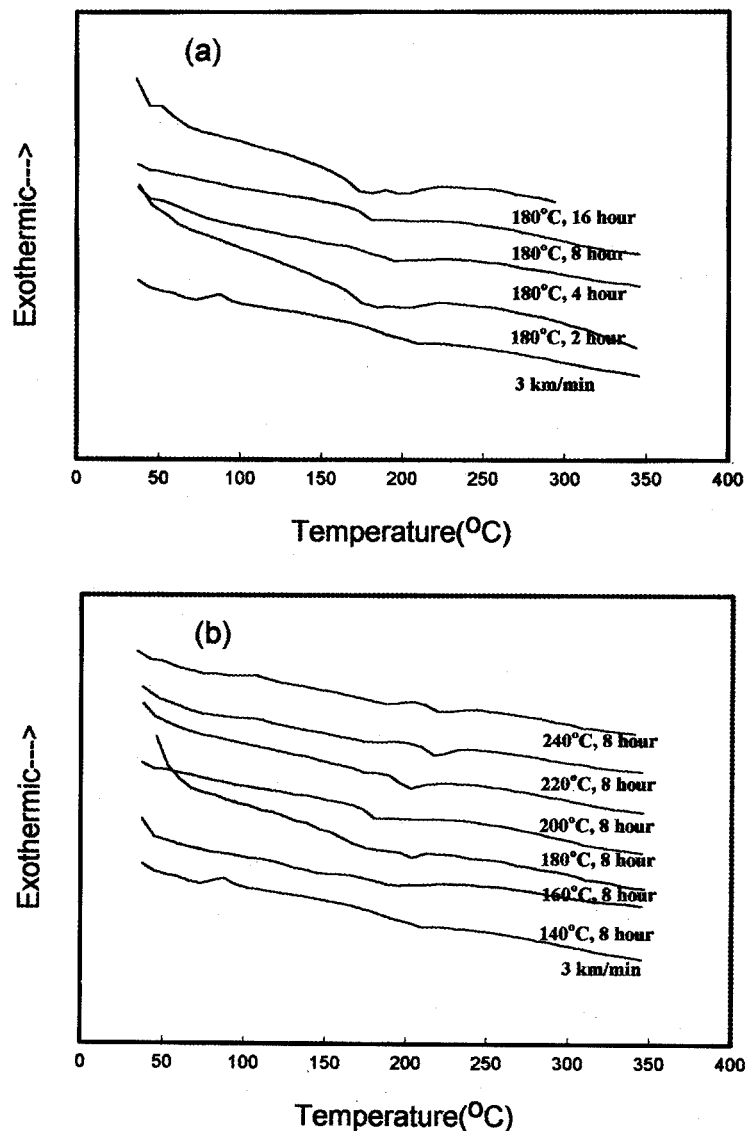


Figure 17 Effects of (a) annealing time and (b) temperature on the DSC curves of PET/PHB fibers.

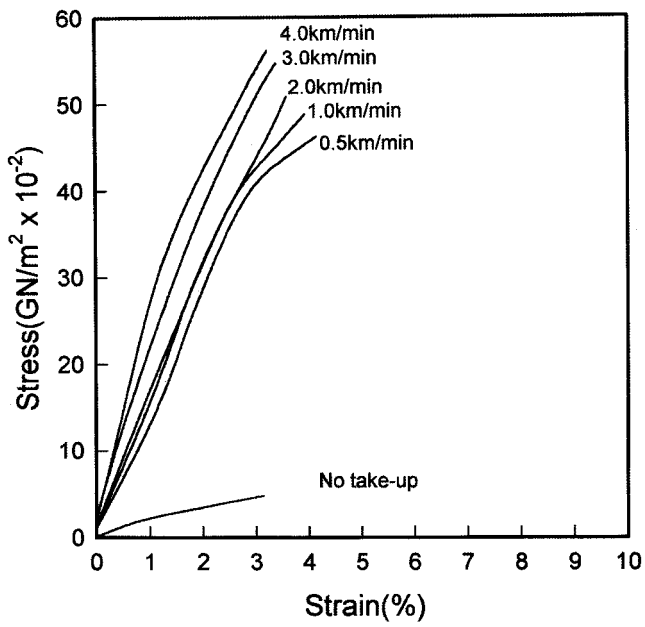


Figure 18 Stress-strain curves of PET/PHB fibers with take-up velocity.

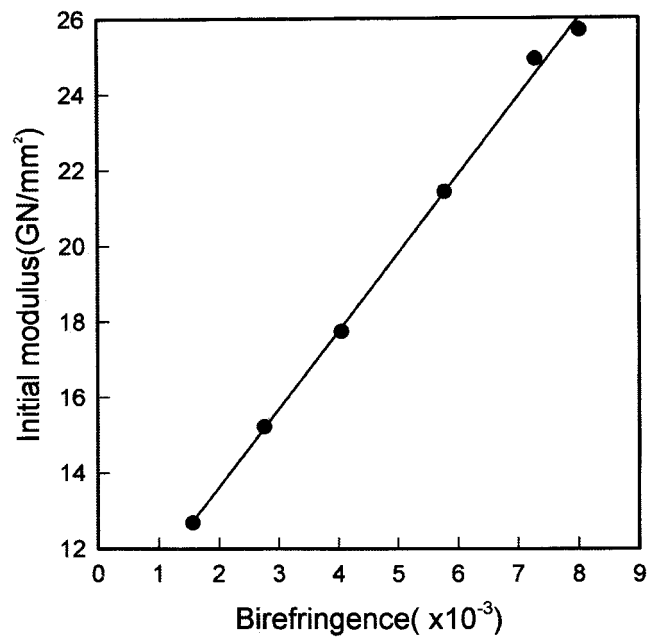
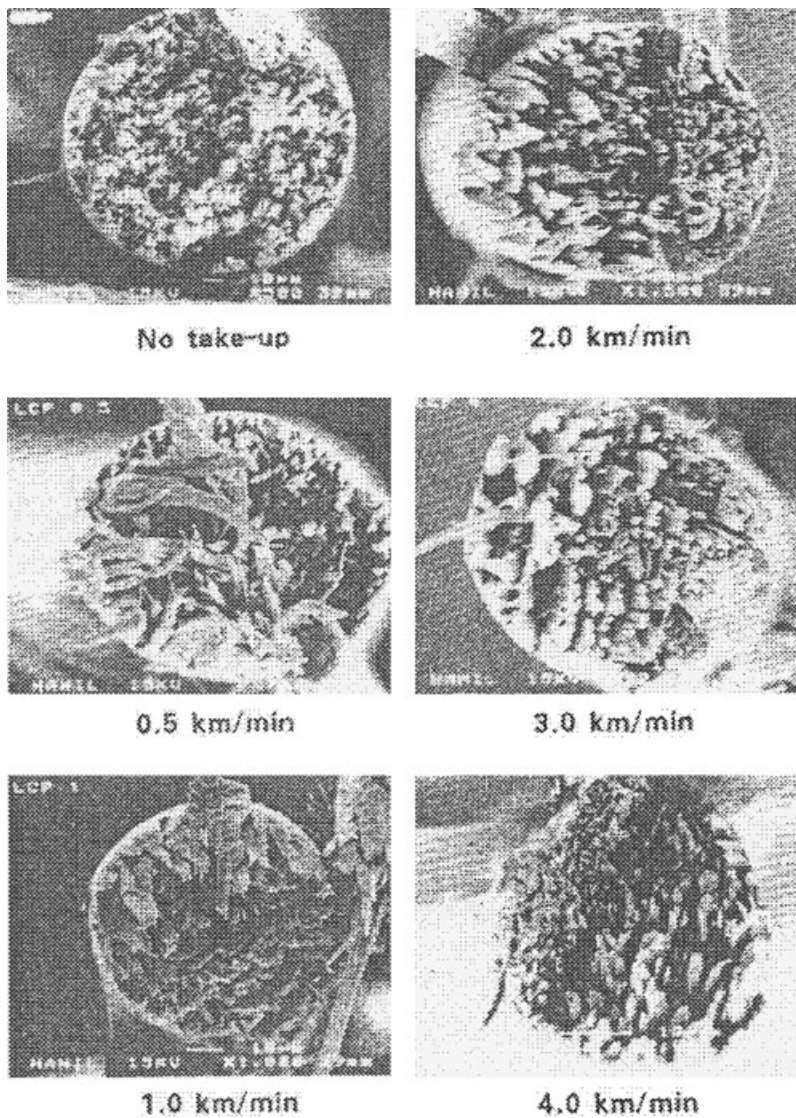


Figure 19 Relation between initial modulus and birefringence of PET/PHB fibers.



References

1. Jackson, W. J., Jr. *Br Polym J* 1980, 12, 154.
2. Jin, J. I.; Antoun, S.; Ober, C.; Lenz, R. *Polym J* 1980, 12, 131.
3. Bickel, A.; Shaw, M. T.; Samulski, E. T. *J Rheol* 1984, 28, 647.
4. Jackson, W. J., Jr.; Kuhfuss, H. F. *J Polym Sci Polym Chem Ed* 1988, 14, 2043.
5. Joseph, E.; Wilkes, G. L.; Baird, D. G. *Polymer* 1985, 26, 689.
6. Cuculo, V. A.; Chen, G. Y. *J Polym Sci Part B: Polym Phys* 1988, 26, 179.
7. Muramatsu, H.; Krigbaum, W. R. *J Polym Sci Part B* 1986, 24, 1695.
8. Muramatsu, H.; Krigbaum, W. R. *J Polym Sci Part B* 1987, 25, 2303.
9. Wu, P. P.; Hsu, S. L. *J Polym Sci Part B* 1986, 24, 827.
10. Lin, Q.; Jho, J.; Yee, A. F. *Polym Eng Sci* 1993, 33, 789.
11. Aiji, A.; Gignac, P. A. *Polym Eng Sci* 1992, 32, 903.
12. Berry, D.; Kenig, S.; Siegmann, A. *Polym Eng Sci* 1993, 33, 1548.
13. Amendola, E.; Carfagna, C.; Netti, P.; Nicolais, L.; Saiello, S. *J Appl Polym Sci* 1993, 50, 83.
14. Lee, S.; Hong, S. M.; Seo, Y.; Park, S.; Hwang, S. S.; Kim, K. U. *Polymer* 1994, 35, 519.
15. Zimmer, J. *J Appl Polym Sci* 1990, 39, 2067.
16. Blackwell, J.; Lieser, G.; Gutierrez, G. A. *Macromolecules* 1983, 16, 1418.
17. Geiss, G.; Volksen, W.; Tsay, J.; Economy, J. *J Polym Sci Polym Lett Ed* 1984, 22, 433.
18. Leiser, G. *J Polym Sci Polym Phys Ed* 1983, 21, 1611.
19. Hanna, S.; Windle, A. H. *Polym Commun* 1988, 29, 236.
20. Kaito, A.; Kyotani, M.; Nakayama, K. *Macromolecules* 1990, 23, 1035.
21. Joseph, E.; Wilkes, G. L.; Baird, D. G. *Polym Eng Sci* 1985, 25, 7.
22. Wissbrun, K. F. *Br Polym J* 1980, 12, 163.
23. Menczel, J.; Wunderlich, B. *J Polym Sci Polym Phys Ed* 1980, 18, 1433.
24. Brostow, W.; Hess, M.; Lopez, B. L. *Macromolecules* 1994, 27, 2262.