



Effect of Vibration on Drawing and Annealing of High-Speed Spun Poly(trimethylene terephthalate) Fiber

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Abstract: The physical properties of poly(trimethylene terephthalate) (PTT) fibres were improved by means of vibration in the hot-drawing and annealing, which may be caused by the developed molecular packing. For high-speed spun PTT fibers, it was not until at the take-up speed of 3~4 km/min that the orientation induced crystallization started to emerge due to extensional stress occurred in spin line; confirmed from the results of WAXD and DSC. The PTT fibers obtained at the take-up speeds of 2~3 km/min and then drawn and annealed with vibration possessed low density and weight-crystallinity, but their birefringence was especially high. Moreover, the estimation of both refractive index parallel and normal directions to fiber axis using the interference microscopy showed that the refractive index parallel to the fiber axis was very high, which enhanced the mechanical properties of PTT fiber. Accordingly, the well-oriented chains along the fiber axis allow the PTT fiber to have better physical property such as elastic recovery although the PTT fiber has low density and crystallinity compared to PET and PBT. In effect, the PTT fiber possesses lower birefringence of over 10 times than those of PET and PBT due to its chain conformational characteristics. Therefore, we do suggest that the structural assessment against the subsequent mechanical properties according to various processes in the PTT fiber is preferred to be estimated through the respective refractive indices of parallel and normal to the fiber axis rather than conventional methods such as birefringence, crystallinity, and crystalline orientation.

Keywords: PTT, hot-drawing with vibration, annealing with vibration, the orientation induced crystallization, high-speed spinning

Introduction

Although the polymerization of poly(trimethylene terephthalate) (PTT) was first reported by Whinfield and Dickson of Calico Printing Ink Co. in 1941, it was not until a great reduction in the manufacturing cost of 1,3-propanediol occurred in the mid 1990s that the commercial production of PTT became possible. The 1,3-propandiol is being produced by Shell of USA, Degussa of Germany and DuPont of USA in large quantities [1], as interests in the commercial production of PTT fibers has increased. In Korea, PTT products are being produced by the collaboration of S company and Shell Chemical Co. with research being carried out simultaneously. They are still produced with insufficient data when compared to the case of poly(ethylene terephthalate) (PET). PTT has excellent properties such as elastic recovery and dyeability due to its odd methylene units unlike PET and poly(butylene terephthalate)

(PBT) of even methylene units, and its general property lies in between PET and nylon. Thus, we expect to conduct investigations which can give manufacturing techniques for a qualified DTY fiber in the PTT fiber.

Though the high-speed melt spinning has an industrial advantage in point of increasing production, what is more important is the qualified DTY fiber attains through the orientation and orientation induced crystallization in high-speed spinning. The high-speed spinning can develop the fibrous structure under an extensional deformation, i.e. a neck-like deformation, and its morphological structure has effects on fiber properties such as mechanical and optical. However, for the PTT fiber, an excessive extensional stress occurred during high-speed spinning seems to be existent even after the end of processing, and it causes a structural change with time even at room temperature. Accordingly, the post-spinning processes such as drawing and annealing is required to increase the intermolecular packing.

The molecular mobility in drawing and annealing is increased with vibration as a function of frequency and temperature, and simultaneously the local temperature is increased due to intermolecular friction by external vibration. The necking in the usual drawing is easy to occur due to the fact that the extensional force is concentrated on a weak point [2-4], and this necking causes an excessive residual stress after process. Accordingly, the techniques of drawing and annealing with vibration could improve the chain orientation and the orientation induced crystallization.

In this paper, the PTT fibers were spun at take-up speeds up to 6 km/min, and subsequently their fiber formation mechanism and property were investigated. To improve the intermolecular packing and orientation, the vibration was included in the drawing and annealing processes of the as-spun fibers. Therefore, we could obtain information on manufacturing conditions for a qualified DTY fiber throughout by estimating the fine structure and properties of PTT fiber drawn and annealed with vibration after high-speed spinning.

Results and discussion

Wide-angle X-ray Diffraction

WAXD scans of PTT fibers spun with take-up speeds from 1 to 8 km/min are shown in Figure 1, which indicates that the diffraction arcs by (010) plane in the equatorial starts to emerge at the take-up speeds of 3~4 km/min faintly and the arcs become obvious at the take-up speed of 4 km/min and above. It may be caused by the orientation induced crystallization of PTT molecular chains due to the excessive extensional stress occurred during high-speed spinning. The diffraction intensities of the arcs increased and the appearance of the arcs e sharpen and sharpen with increasing take-up speed. It may be due to the fact that the PTT crystalline perfectness increases, i.e. the crystallization increases and the crystalline planes are more ordered.

The PTT fiber spun with the take-up speeds of 1~6 km/min were drawn and annealed with vibration at 80°C, and their X-ray diffraction photographs were shown in Figure 2. The (010) diffraction arcs are already noticeable at the take-up speed of 1 km/min and this diffraction arcs turns out to be obvious with increased take-up speed.

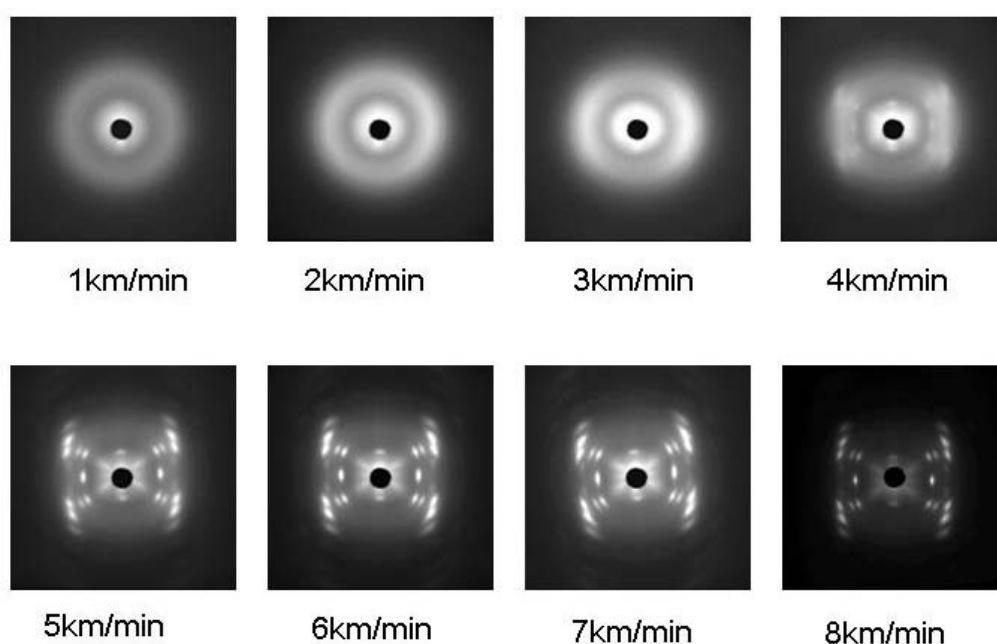


Fig. 1. WAXD patterns of PTT fibers obtained at various take-up speeds.

Furthermore, the diffraction intensity and the appearance of arcs are much higher and sharpens, which could be due to the fact that the chains already oriented through the initial high-speed spinning are drawn and annealed with vibration additionally.

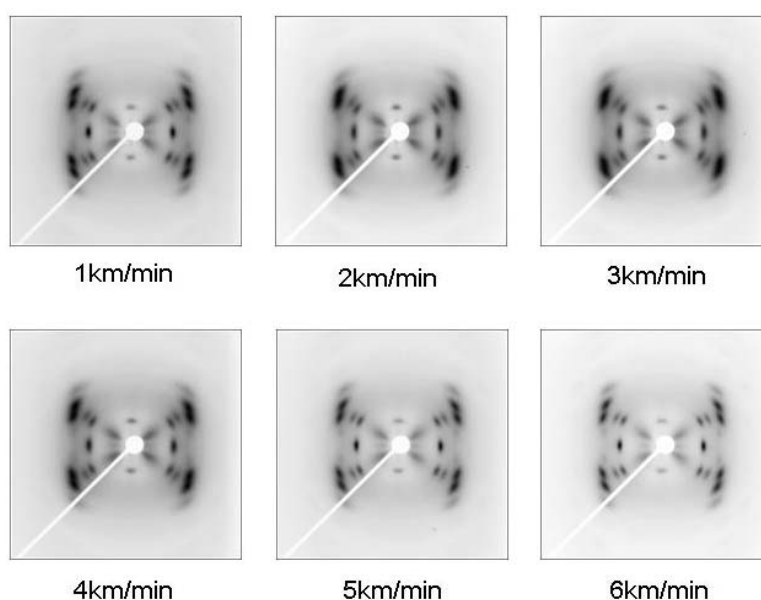


Fig. 2. WAXD patterns of PTT fibers drawn and annealed with vibration at 80 °C.

PTT fibers were also drawn and annealed without vibration at 80 °C, and their X-ray scans are shown in Figure 3, which was analogue to the WAXD scans of the fibers drawn and annealed with vibration (see the Figure 2). Accordingly, from these WAXD

results, we could attain the follows: the external vibration added during drawing and annealing hardly has any influence on improving the structural perfectness in crystalline region, but alternatively is believed to improve the intermolecular arrangement by compact packing as well as the chain orientation in amorphous region.

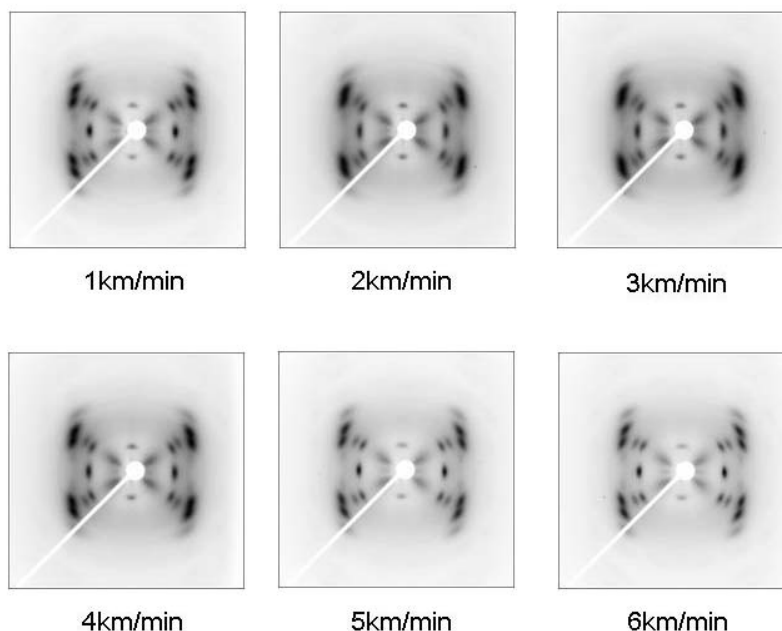


Fig. 3. WAXD patterns of PTT fibers drawn and annealed without vibration at 80 °C.

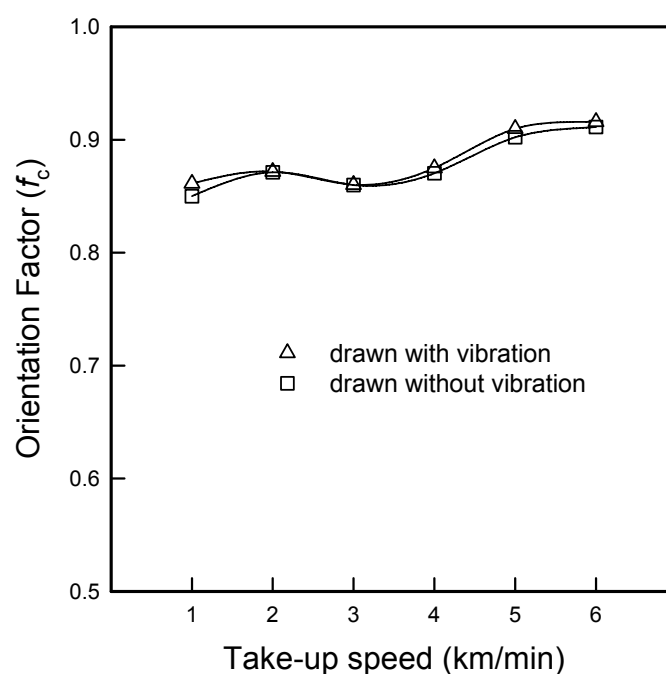


Fig. 4. Crystalline orientation factors of PTT fibers drawn and annealed with or without vibration.

The orientation factors of (010) plane calculated from the azimuthal X-ray intensity distribution are shown in Figure 4, which displays an increased tendency in the orientation factors with take-up speed. It denotes that the crystalline orientation at the take-up speeds of 1~3 km/min is generally low, but the above increases with take-up speed. This tendency could be caused by the chains already ordered by the stress in spin line during the spinning, and accordingly the crystalline orientation is hardly affected by the drawing and annealing processes with or without vibration.

Density and Crystallinity

Densities characterized using the density gradient column and weight crystallinities calculated from densities are plotted in Figure 5. The crystallinity of the as-spun fibers starts to increase outstandingly at the take-up speeds of 3~4 km/min, which corresponds with the WAXD result mentioned previously. The densities of fibers drawn and annealed with or without vibration are higher than those of the as-spun fibers for all take-up speeds, and it might be due to the increased intermolecular chain packing. The fibers obtained at the take-up speeds of 1~3 km/min possessed low densities even after drawing and annealing, and at the above take-up speed the densities increased steeply. The phenomenon might be due to the fact that the orientation-induced crystallization already attained by high-speed spinning is still retained as a well-packed structure of high crystallinity during drawing and annealing with or without vibration. There is no conspicuous difference between with and without vibration for different take-up speeds in the result of density, and hence it could be concluded that the molecular orientation of PTT is difficult to be investigated from density and crystallinity.

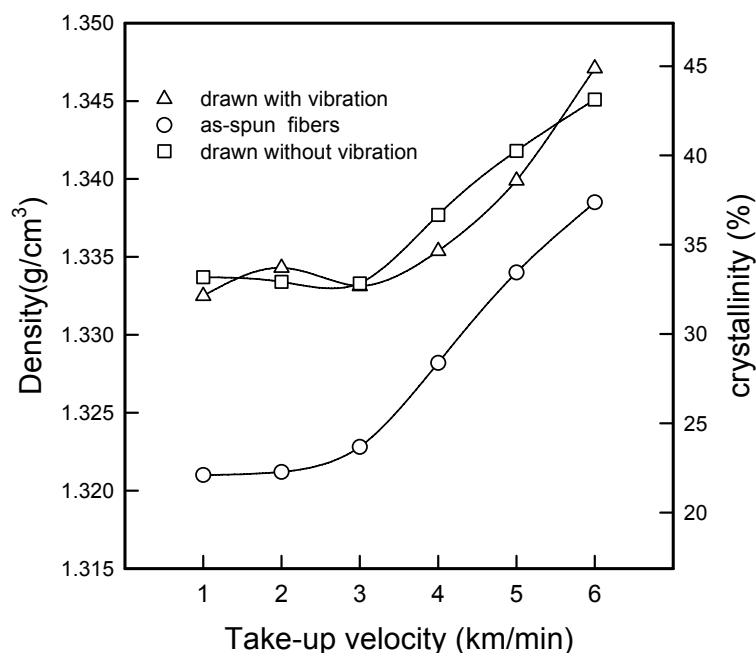


Fig. 5. Density and crystallinity of PTT fibers drawn and annealed under various processing conditions.

Thermal Analyses

The DSC thermogram of the PTT fiber spun with take-up speeds 1~8 km/min is shown in Figure 6. The cold crystallization temperature ($T_{c \text{ cold}}$) peaks decreases stupendously and shifts to lower temperatures at the take-up speeds of 3~4 km/min and above [6]. It means the orientation induced crystallization has developed with increased take-up speed, like PET. However, the melting temperatures (T_m) did not change throughout the take-up speeds, and it is regarded as a characteristic which distinguishes PTT from PET and PBT whose melting temperatures increase with take-up speeds.

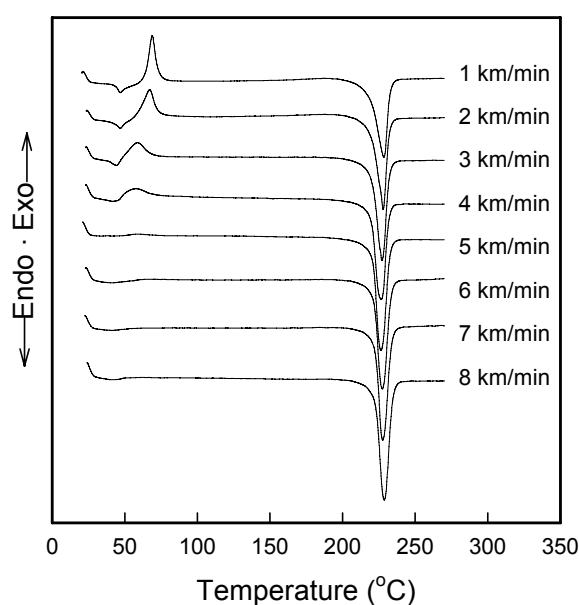


Fig. 6. DSC thermograms of PTT fibers obtained at various take-up speeds.

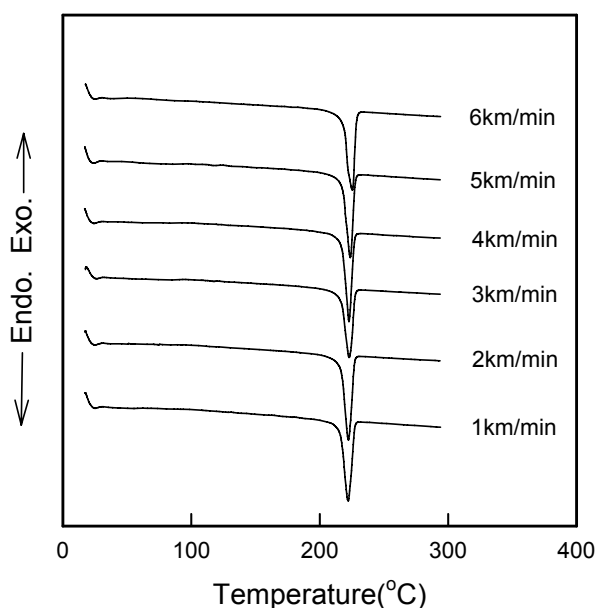


Fig. 7. DSC thermograms of PTT fibers drawn and annealed with vibration.

However, the DSC thermograms of PTT fibers drawn and annealed with or without vibration are respectively shown in Figures 7 and 8, which displays a tendency different from the above as-spun fibers. The $T_{c\text{ cold}}$ peaks disappear clearly due to the developed orientation induced crystallization by drawing and annealing. The T_m peaks increases about 3~5°C with drawing and annealing, and it means that the crystalline perfectness has improved by drawing and annealing as compared with those of the as-spun fibers. However, the vibration applied in drawing and annealing has little effect on the thermal property, especially the melting temperature, and thus it is believed that the external vibration added on drawing and annealing has contributed to improve the intermolecular packing of amorphous region.

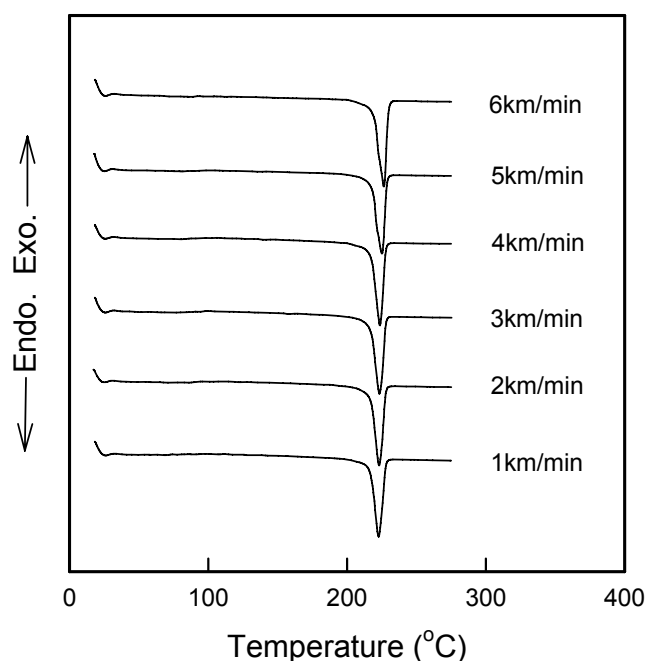


Fig. 8. DSC thermograms of PTT fibers drawn and annealed without vibration.

Birefringence

The birefringence of the fibers drawn and annealed with vibration as well as the as-spun fibers obtained at the take-up speeds of 1~6 km/min characterized by an interference microscope are plotted in Figure 9. The birefringence for the as-spun fibers increases steeply up to 4 km/min, at which the orientation induced crystallization, may have started. At 5 km/min the birefringence decreases slightly and then increase gently with increase in the crystallinity by the orientation induced crystallization. Unlike the results of WAXD and density, for the PTT fibers drawn and annealed with or without vibration, the birefringence at the take-up speed of 1~3 km/min where the crystallinity and the crystalline order are very low, is much higher than those of the as-spun fibers. The molecular conformation of PTT is *gttg* and adopts the helix structure where the benzene ring keeps the tilting angle of 58° against the fiber axis [7]. Accordingly, the refractive index of normal to the fiber axis is also increased with that of parallel to the fiber axis and subsequently the total birefringence becomes low. Thus, at the take-up speeds of 4~6 km/min where the crystallinity increases, the birefringence hardly increases. Although it was not

crystallized yet at the take-up speeds of 1~3 km/min, the molecular chains might be oriented along the fiber axis and accordingly the birefringence might be increased as compared with the as-spun fibers. It is regarded as the result caused by increased orientation and crystallinity because of the effect of vibration and drawing.

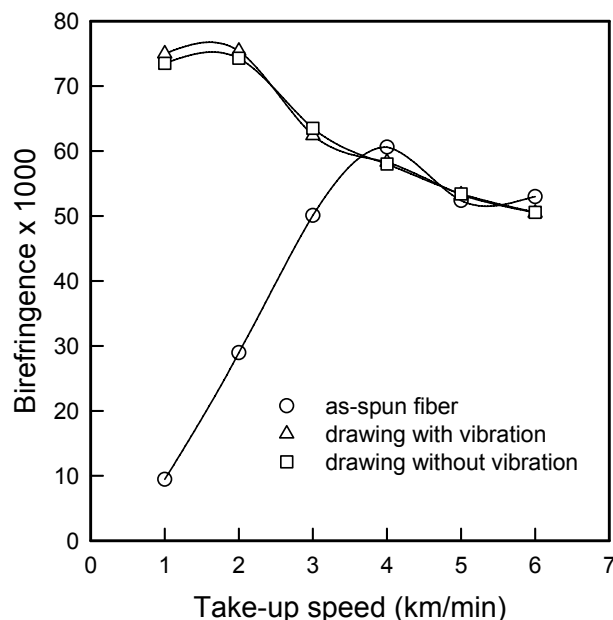


Fig. 9. Birefringence of PTT fibers drawn and annealed with or without vibration.

Generally, while analyzing the birefringence, we are actually prone to make an error in the analysis of separate orientation of crystalline and amorphous orientation in explaining the molecular orientation due to the calculation from the birefringence characterized by a polarized microscope without consideration of two refractive indices parallel and normal to the fiber axis. Hence, in this study, the birefringence of PTT fiber is estimated from both refractive indices normal and parallel to the fiber axis using the interference microscopy. Figure 10 plots both refractive indices normal and parallel to fiber axis as well as the birefringence, and their tendencies are investigated concurrently. The birefringence increases up to 4 km/min steeply, slightly decreases around 5 km/min, and then increases gently. It might be a special tendency unlike other polyesters, due to the fact that the refractive index normal to the fiber axis has increased remarkably. This phenomenon might be attributed to the chain conformation of PTT being the helix structure like a spiral staircase. We have already reported that the molecular packing normal to the fiber axis has increased, confirmed from the increase of the refractive index normal to fiber axis [6]. This phenomenon is attributed to the very low intrinsic birefringence of the PTT fiber because of the benzene ring tilted to 58° against fiber axis in crystalline region [7].

The refractive indices of both directions and the birefringence of PTT fibers drawn and annealed with vibration are plotted in Figure 11. The birefringence of PTT fibers obtained above for the take-up speed of 3 km/min decreases steadily with increase in take-up speed. It indicates that the refractive index parallel to fiber axis reach a saturation level while the refractive index normal to fiber axis increases with crystallinity. From a phenomenological standpoint, the birefringence of PTT fibers decreases gradually with increase in take-up speed, but from the position of the

crystallinity and the crystalline orientation, the fibers obtained at high-speed take-up speeds and then drawn and annealed with vibration possesses an improved chain packing and high crystallinity.

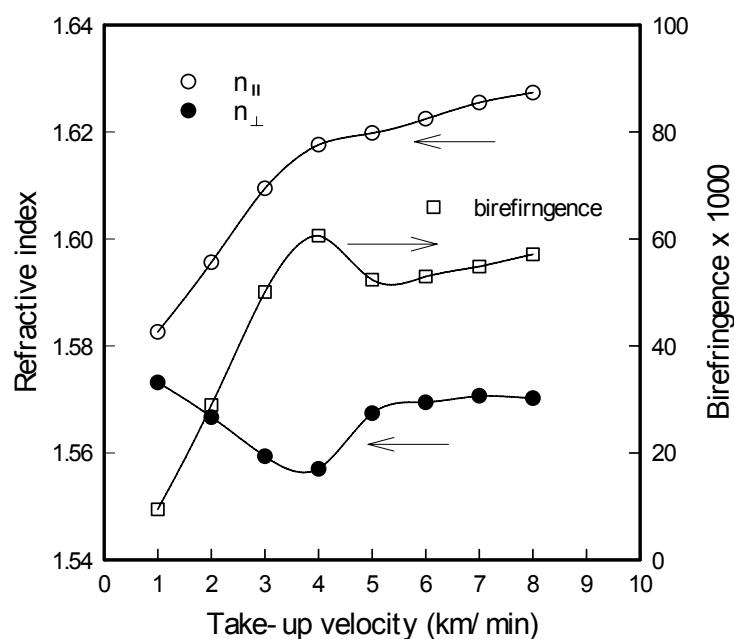


Fig. 10. Refractive index and birefringence of PTT fibers obtained at various take-up speeds.

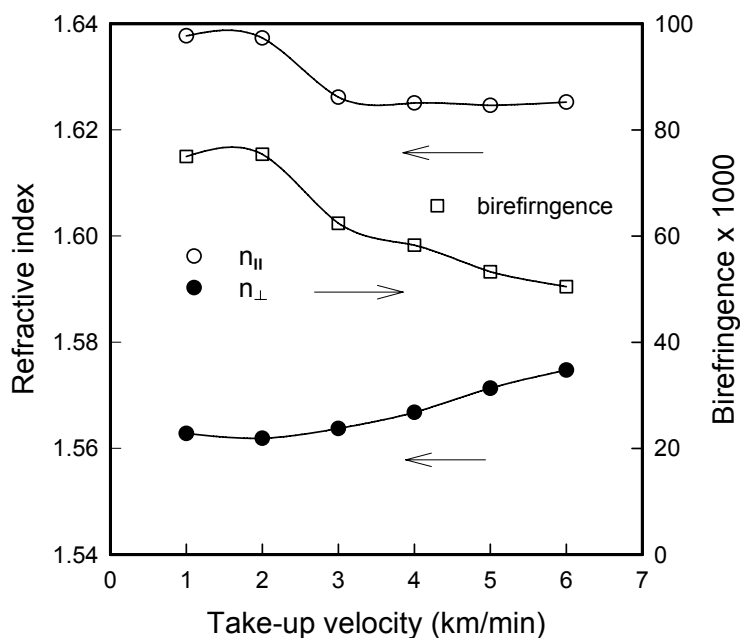


Fig. 11. Refractive index and birefringence of PTT fibers drawn and annealed with vibration.

With increase in the crystallinity, the refractive index normal to the fiber axis increases gently by 1~3 km/min and then steeply at 4~6 km/min. This tendency

corresponds with the results of WAXD and density. Analyzed from both directions normal and parallel to the fiber axis, the refractive index along the fiber axis is of higher orientation at the take-up speeds of 1~3 km/min than others. This result is believed to be different from the typical analysis of fine structure. Characteristically, it is known that the crystalline orientation increases and the molecular orientation also increase when the density has increased. However, in the PTT, we could understand that the one of low crystallinity possesses high molecular orientation along the fiber axis regardless of the orientation and density.

Mechanical Properties

To make a comparison of mechanical properties among drawn and annealed with or without vibration as well as as-spun PTT fibers, the elongation, tenacity, modulus, and work of rupture of them are shown in Table 1. For the as-spun fibers, with increased take-up speed, the tenacity, modulus, and work of rupture is increased but the elongation decreases gradually.

Tab. 1. Physical property of as-spun PTT fibers drawn at various drawing conditions.

Sample		Elongation (%)	Tenacity (g/den)	Modulus (g/den)	Work of Rupture
As-spun PTT Fibers	1 km/min	482.76	1.17	16.30	241.65
	2 km/min	267.71	1.69	17.98	100.20
	3 km/min	160.25	1.85	13.85	63.69
	4 km/min	92.31	2.05	13.76	32.30
	5 km/min	66.69	1.88	13.70	18.40
	6 km/min	65.04	2.93	19.52	17.37
Drawn <i>with</i> Vibration	1 km/min	70.13	2.25	18.79	46.10
	2 km/min	76.99	3.52	21.49	37.80
	3 km/min	86.86	3.33	23.04	38.43
	4 km/min	77.34	3.09	21.08	29.75
	5 km/min	66.36	2.71	20.94	19.12
	6 km/min	62.12	2.69	20.65	15.86
Drawn <i>without</i> Vibration	1 km/min	76.72	3.28	19.73	44.45
	2 km/min	74.23	3.44	21.88	35.53
	3 km/min	91.34	3.17	21.31	36.43
	4 km/min	77.09	3.06	21.06	29.43
	5 km/min	65.03	2.54	20.34	18.12
	6 km/min	60.59	2.54	19.75	14.89

This is caused by the increased molecular orientation and the orientation induced crystallization because of the extensional stress that had occurred in high-speed spinning, like PET and PBT fibers. By comparison of drawing and annealing between with and without vibration, the PTT fibers drawn and annealed with vibration after taken-up at low speed shows much higher tenacity and modulus than others, and the work of rupture showing toughness is also higher. Therefore, the vibration on drawing and annealing had an outstanding effect on the PTT fibers drawn with vibration after taken-up at 1~3 km/min. Especially, the fiber obtained at the take-up speeds of 2~3 km/min possesses most improved mechanical property. The mechanical property in fiber is actually influenced by the molecular orientation along the fiber axis and the tie molecules in amorphous region rather than the crystalline orientation. This means that, in particular, the PTT fibers has better mechanical properties when the refractive index parallel to fiber axis is higher and normal to fiber axis is lower, as mentioned in the above birefringence result characterized using the interference microscopy. This phenomenon might be caused by the intermolecular arrangement by compact packing as well as the chain orientation in amorphous region, which is difficult to find out from the results of birefringence. Accordingly, it should be accompanied by the investigation on the entire orientation along the fiber axis rather than the crystallinity and the crystalline orientation using WAXD and density. Hereafter, to obtain PTT fibers possessing more stable structure and better mechanical properties, the intermolecular arrangement by compact packing as well as the molecular orientation in amorphous chains caused by vibration should be examined.

Experimental part

Melt Spinning Process

PTT pellets with the intrinsic viscosity of 0.92 dl/g were used for this study. Prior to the melt spinning, the pellets were dried and crystallized at 100 °C for 6 hours and at 160 °C for 8 hours, successively, and then were preserved at 110 °C under vacuum. The extrusion system consisted of an extruder with a single-hole spinneret of 0.5 mm diameter and a gear pump for the precise control of the throughput rate of 4.96 g/min. The polymer was extruded at 270°C and taken up by a high speed winder placed at 330 cm below the spinneret.

Drawing and Annealing with Vibration

The apparatus for drawing and annealing with vibration are presented in Figure 12. The experiment was performed at the frequency of 110Hz, temperature of 80 °C, and the tension of 0.2 g/den. A weight was put on the one side of the sample to attain the maximum draw ratio. For a comparative study, drawing and annealing without vibration were also completed with the same method.

The PTT fiber spun at the take-up speed 4 km/min and above possessed crimp unlike PET fiber, and the crimp rate was increased with take-up speed. Thus, in this study, the fibers obtained by high-speed spinning could be classified into two groups of the partially oriented yarn (POY) at take-up speeds 1~3 km/min and the high-speed spun yarn at 4 km/min and above. The former, POY, was drawn up to the same draw ratio with fibers obtained by high-speed spinning, and then annealed with and without vibration, respectively. In the latter, the annealing with and without vibration were done under a proper weight.

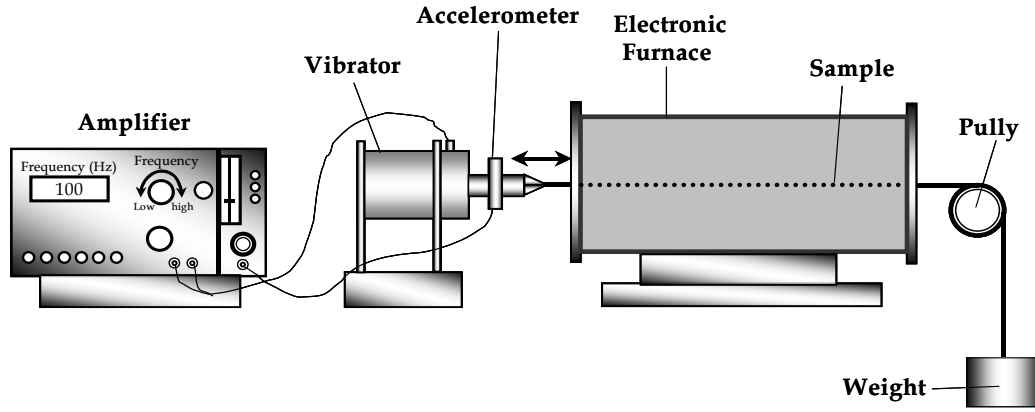


Fig. 12. Scheme of apparatus used for the drawing and annealing with vibration.

Characterization of Fiber Properties

-Wide angle X-ray diffraction

For wide angle X-ray diffraction (WAXD) analysis, a Rigaku X-ray diffractometer of D/max-III-A type with Cu- α radiation through Ni filter at 40 kV-20 mA was used. Wide angle X-ray photographs were obtained at 7 cm distance from X-ray source using an imaging plate. The crystalline orientation were estimated through azimuthal scan at the (010) plane ($2\theta=15.6^\circ$, $e=g=0$, and $f=1$) [5], using the equations (1) and (2), where, ψ is angle between the c axis and draw direction and f_c is crystalline orientation factor.

$$\langle \cos^2 \psi_{010,Z} \rangle = \frac{\int_0^\pi I(\psi) \cos^2 \psi' \sin \psi' d\psi'}{\int_0^\pi I(\psi) \sin \psi' d\psi'} \quad (1)$$

$$f_c = (3 \langle \cos^2 \psi_{010,Z} \rangle - 1) / 2 \quad (2)$$

-Density and Crystallinity

Density was measured at 23 °C using a density gradient column with mixture of carbon tetrachloride (specific gravity: 1.59) and *n*-heptane (0.68). The crystallinity (x_c) was calculated from the densities using the equation (3). Here, ρ means an observed density, ρ_c is the density of PTT crystalline region (1.43 g/cm³), and ρ_a is the density of PTT amorphous region (1.31 g/cm³).

$$x_c (\%) = \frac{\rho_c (\rho - \rho_a)}{\rho (\rho_c - \rho_a)} \times 100 \quad (3)$$

-Thermal Analysis

To measure glass transition temperature, crystallization temperature, melting temperature, and crystalline perfectness with processing conditions, a differential scanning calorimetry of TA DSC 2910 was used at a constant heating rate of 10°C/min under a dry nitrogen atmosphere.

-Birefringence

The birefringence of PTT fibers annealed and drawn with vibration was measured using an interference microscope equipped with a polarizing filter placed on parallel and normal to fiber axis. The standard refractive liquid of Cargille was used as immersion liquid, and the refractive indices of the immersion liquids were measured by an Abbe refractive apparatus. The schematic of the refractive fringe obtained by an interference microscope is shown in Figure 13. Shift of the fringe d obtained from the interference microscope is proportional to the product of the thickness $2y$ and the refractive index difference between the immersion liquid N and the sample n , as shown in equation (4). The length (275 nm) between fringes is D in the equation (4) and λ is the wavelength (550 nm) of the incident light. Birefringence Δn was calculated from two refractive indices which are parallel n_{\parallel} and normal n_{\perp} to the fiber axis using the equation (5), respectively:

$$\frac{d}{D} \cdot \lambda = (n - N) \cdot 2y \quad (4)$$

$$\Delta n = n_{\parallel} - n_{\perp} \quad (5)$$

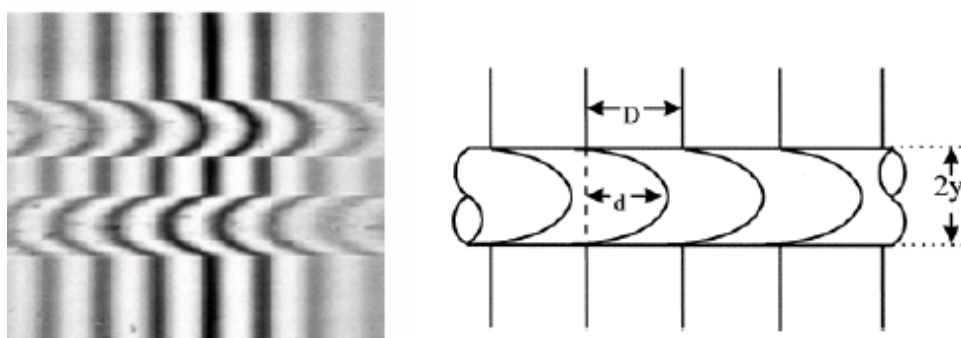


Fig. 2. Schematic of fringe pattern observed on interference microscope.

-Mechanical Properties

Stress-strain curves of 20 mm long PTT filaments were achieved using a Tinius Olsen Series 1000 tensile machine at cross-head speed of 20 mm/min, and averages of over 10 trials were used.

Acknowledgements

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