

# Effect of Low-Temperature Annealing on Dimensional Stability of Poly(ethylene 2,6-naphthalene dicarboxylate) Fibers Melt-Spun at High Speed

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**ABSTRACT:** To investigate structural factors, necessary to obtain a valuable industrial fiber possessing excellent thermomechanical properties, poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) fibers were produced by high-speed melt-spinning to a take-up speed of 8 km/min, followed by low-temperature annealing between the glass-transition temperature ( $T_g$ ) and exothermic cold crystallization temperature ( $T_{c\text{ cold}}$ ), where little transition of crystalline phase, as well as little thermal degradation, takes place. Their thermomechanical behavior, as well as structural variations, were investigated through differential scanning calorimetry, Rheovibron, thermomechanical analysis (TMA), and tensile testing. Two types of the  $\alpha$ - and  $\alpha'$ -dispersions were observed at near  $T_g$  and at a temperature 50–60°C higher than  $T_g$ , respectively. The dispersions were affected by rearranged structures, which are generated by developing an inhomogeneous taut structure with rigidity of aromatic segment and aliphatic segment. The  $\alpha$ -dispersion seemed to reflect an inhomogeneous taut structure by the less nearly arranged segments. Consequently, at intermediate take-up

speeds between 2 and 6 km/min the inhomogeneous taut structure may be partially formed, but the homogeneously ordered structure may be enlarged as the take-up speed and annealing temperature increased. Thermal shrinkage increased above the  $\alpha$ -dispersion temperature, which suggested that the onset point of dimensional change in PEN fibers was attributed to  $\alpha$ -dispersion. In the case of annealed fibers, the start of length change coincided with the respective annealing temperatures, which indicated that dimensional stability could be gained from restraining the inhomogeneous taut structure in the amorphous region without the transition of crystalline phase by annealing between  $T_g$  and  $T_{c\text{ cold}}$ . Therefore, to obtain dimensional stability in PEN fibers, it is supposed that the inhomogeneous taut structure exhibited by the  $\alpha$ -dispersion should be controlled. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 212–218, 2005

**Key words:** poly(ethylene 2,6-naphthalene dicarboxylate) (PEN); stabilization; mechanical properties; high-speed spinning; annealing

## INTRODUCTION

Poly(ethylene 2,6-naphthalene dicarboxylate) (PEN), containing a naphthalene ring in its backbone, has higher glass-transition temperature ( $T_g$ ) and higher melting temperature ( $T_m$ ) than those of poly(ethylene terephthalate) (PET). The PEN molecule, consequently, is much stiffer than that of PET, and is expected to give high-performance fibers having excellent physical properties. The PEN filament exhibits good thermal resistance and high modulus, comparable to those of rayon fiber, and tenacity similar to that of PET filament, thus underscoring the considerable potential of PEN filament in such engineering uses as industrial cord and automobile tire cord.

PEN is reported to have multiple crystal modifications,  $\alpha$ - and  $\beta$ -types. The  $\alpha$ -modification is obtained by crystallization at temperatures lower than 200°C

from a glassy or melt state,<sup>1</sup> whereas the  $\beta$ -modification can be formed when crystallized at temperatures higher than 220°C.<sup>2</sup> The  $\beta$ -modification possesses higher crystal density but shorter  $c$ -axis length than that of the  $\alpha$ -modification, which means that the molecules in the  $\beta$ -modification are more densely packed but less extended along the chain axis. The  $\beta$ -crystal can be obtained through high-speed spinning and high-temperature annealing.<sup>4–11</sup> However, such high-temperature annealing is close to the melting temperature, where thermal degradation is prone to occur.

Hence, to use PEN as an industrial fiber, enhancement of thermomechanical properties, such as dimensional stability, is necessary, and these properties are related to its residual stress and molecular orientation in amorphous regions after the processing history. In this article, we describe the effect on dimensional stability of low-temperature annealing between the glass-transition temperature ( $T_g$ ) and exothermic cold crystallization temperature ( $T_{c\text{ cold}}$ ) for PEN fibers spun at high speed. The high-speed-spun PEN fiber already has good mechanical properties but actually, for the

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industrial uses, the dimensional stability should be improved at even higher temperatures than  $T_g$ . Therefore, we considered use of low-temperature annealing without thermal degradation, and investigated the relationship between structure and mechanical properties in our additional annealing process.

## EXPERIMENTAL

### Preparation of fiber specimens

PEN pellets, supplied by Teijin Co. Ltd. (Osaka, Japan) with intrinsic viscosity of 0.62 dL/g, were extruded from a single-hole spinneret of 0.5 mm diameter at 320°C. The throughput rate was controlled to 5 g/min. Quenching air was not applied to the spinline. The polymer extruded from the spinneret was taken up by a high-speed winder placed at 330 cm below the spinning head. The highest take-up speed attained was 8 km/min.

PEN fibers, with take-up speeds of 3, 4, 5, 6, 7, and 8 km/min, were used as the annealing samples. Fiber bundles (length: 5 cm) were fixed onto a metal frame and annealed in an air oven for 30 min. The annealing temperatures, of 120, 150, 180, and 200°C, were determined by the thermal analysis result: around the  $\alpha$ -dispersion temperature ( $\sim 120^\circ\text{C}$ ), around the  $\alpha'$ -dispersion temperature ( $\sim 180^\circ\text{C}$ ), and the cold crystallization temperature ( $\sim 200^\circ\text{C}$ ), respectively.

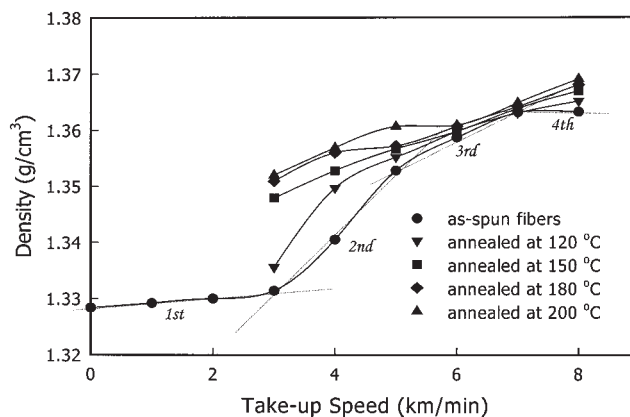
### Measurement of physical properties

Density was measured at 23°C using a density-gradient column containing *n*-heptane (specific gravity: 0.68) and carbon tetrachloride (1.59). The thermal behavior of the as-spun and the annealed PEN fibers was investigated using a differential scanning calorimeter (DSC; Shimadzu DSC-50, Shimadzu, Kyoto, Japan) at a constant heating rate of 10°C/min for a specimen of about 3 mg under dry nitrogen atmosphere. The dynamic viscoelastic behavior, for the as-spun and the annealed PEN fibers, was investigated using a DDV-II-C-type Rheovibron (Toyo Baldwin Co., Ltd. Tokyo, Japan) in the temperature range from 30 to 250°C, at a heating rate of 2°C/min and frequency of 110 Hz. Thermal shrinkage, between 30 and 250°C, was investigated using a thermomechanical analysis (TMA, Seiko Instruments, Chiba, Japan) apparatus at a constant heating rate of 10°C/min and initial load of 5 gf. Tensile properties of the filament (20 mm long) were measured using a Texttechno Fafegraph-M tensile machine (Domo, Ghent, Belgium) at a crosshead speed of 20 mm/min through 20 trials.

## RESULTS AND DISCUSSION

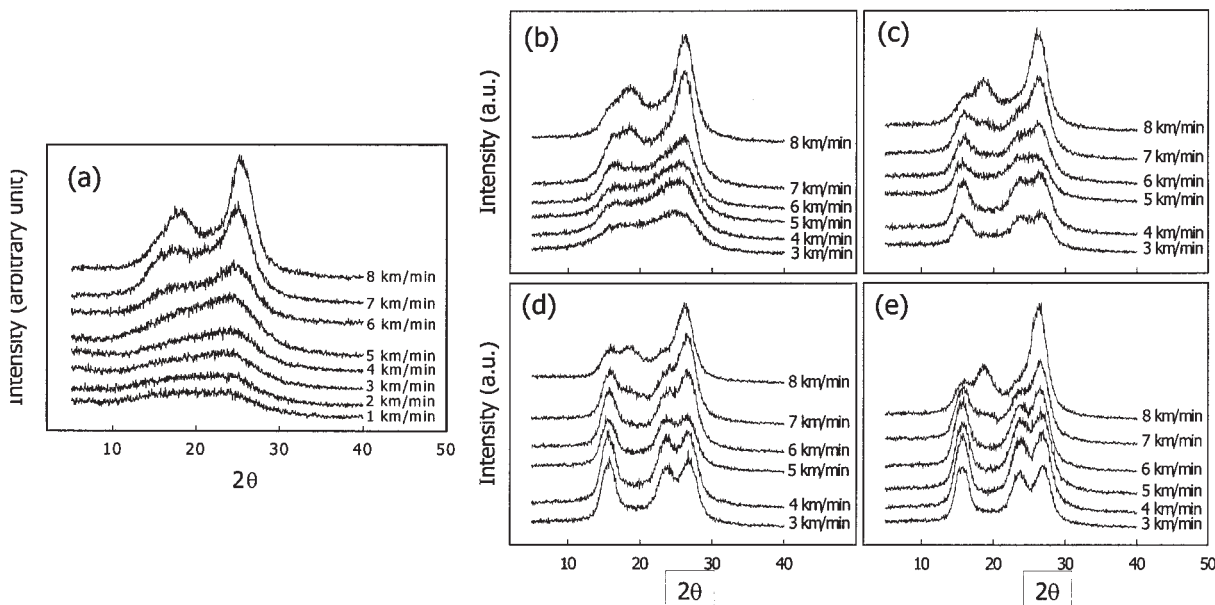
### Densities

The densities of as-spun PEN fibers, obtained at take-up speeds up to 8 km/min, followed by annealing at



**Figure 1** Densities of PEN fibers spun at various take-up speeds and annealed at selected temperatures.

120, 150, 180, and 200°C, are shown in Figure 1. The densities remained almost unchanged, at take-up speeds below 3 km/min, and started to increase sharply above 3 km/min. However, the density at the take-up speed of 8 km/min, was similar value to that at 7 km/min, which might be attributed to slow crystallization resulting from the backbone rigidity of the PEN polymer. The increasing trend with respect to take-up speed exhibited a sigmoidal curve, which is classified into four regions based on their slopes: (1) up to 3 km/min, (2) 4 and 5 km/min, (3) 6 and 7 km/min, and (4) 8 km/min. These regions might relate to the respective structural characteristics; that is, the increase of density with take-up speed could be explained as being attributed to orientation and crystallization of the molecular chains by the spinline tension during high-speed spinning. In addition, the densities of PEN fibers, annealed at 120, 150, 180, and 200°C, exhibited higher values than those of as-spun fibers throughout these take-up speeds. The variation of densities, with the annealing temperatures, also compared with the as-spun fibers, was considerable at low take-up speeds, below 5 km/min, whose preannealed fibers had exhibited less orientation and crystallization. Generally densities, at the respective annealing temperature, increased linearly with take-up speed in this range of take-up speeds. In detail, densities of fibers annealed at 120°C showed a monotonous increase above 4 km/min, except 8 km/min, and those at 150°C showed a steadily increasing tendency with take-up speed. However, densities at 180 and 200°C represent sigmoidal tendencies with the discontinuous point at the specific take-up speed, and they began a linear increase from 5 and 6 km/min, respectively. These discontinuous points are supposed to indicate a structural change on the low-temperature annealing between  $T_g$  and  $T_{c\text{ cold}}$ .



**Figure 2** X-ray diffraction profiles of PEN fibers spun at various take-up speeds (a), followed by annealing at (b) 120°C, (c) 150°C, (d) 180°C, and (e) 200°C.

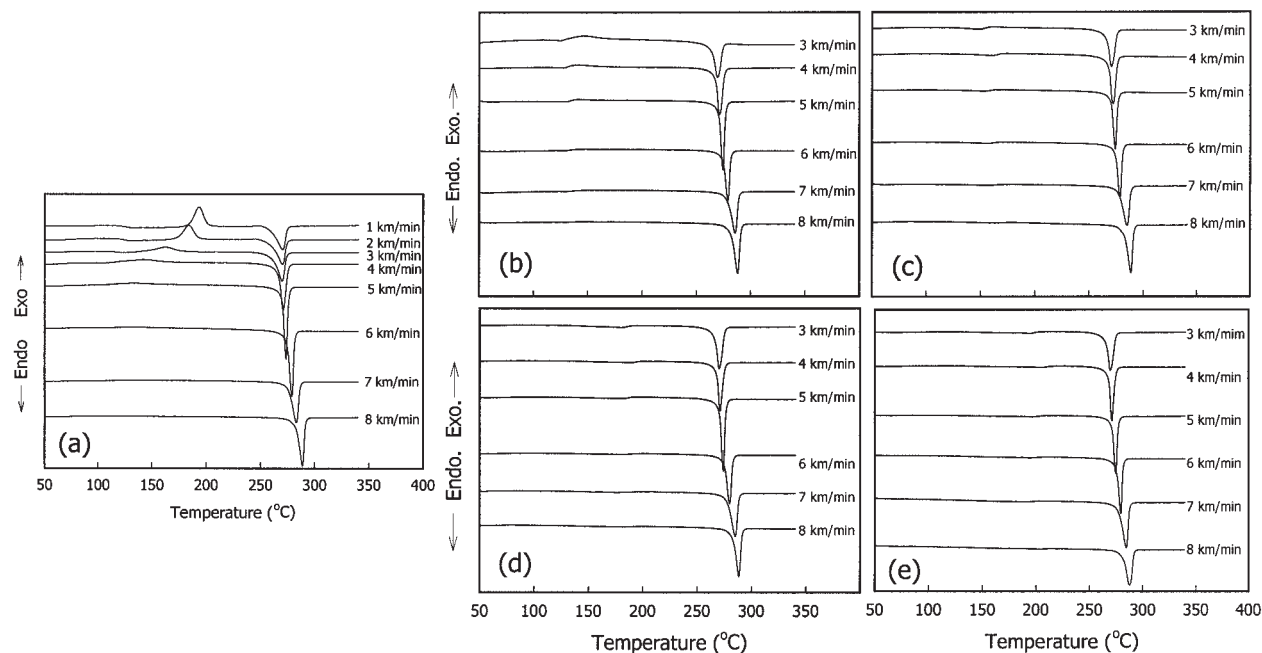
### Crystalline structure

The X-ray diffraction profiles of as-spun and annealed PEN fibers, at various take-up speeds, are shown in Figure 2. The diffraction patterns of PEN exhibit the (010), (100), and ( $-110$ ) planes of  $\alpha$ -crystal at  $2\theta = 15.6, 23.3,$  and  $27.1^\circ$  and the (020) and (200) planes of  $\beta$ -crystal at  $2\theta = 18.6$  and  $26.6^\circ$ , respectively. The as-spun fibers showed that the peak intensity increased above 3 km/min (from the 2nd region; see Fig. 1) and that separated diffraction peaks were obtained at take-up speeds  $> 5$  km/min (the 3rd and 4th regions; see Fig. 1). The fiber taken up at 8 km/min (the 4th region; see Fig. 1), having the leveled-off density, more clearly showed the diffraction by the  $\beta$ -crystals, although the diffractions of  $\alpha$ -crystals were also visible. The crystalline diffraction peaks were distinct and separated from each other, indicating that the well-developed crystalline structure was formed through the annealing process. For the fibers annealed at 120°C, all the peaks became more intense without crystalline transition, particularly the (020) plane of the  $\beta$ -crystal at  $2\theta = 18.6^\circ$ . For PEN fibers annealed at 150 and 180°C, those taken up at 3–5 km/min (the 2nd region; see Fig. 1) exhibited, comparatively distinctly, three crystalline reflections corresponding to the (010), (100), and ( $-110$ ) planes of  $\alpha$ -crystals but, in particular, the diffraction intensity at 5 km/min seemed to be much weaker than that of the others because of the coexistence of two modifications. As the take-up speed increased, the reflections, by the (020) plane of the  $\beta$ -crystals, were clearly observed. For the fibers annealed at 200°C, well-separated diffraction peaks, generated from the respective crystalline modifica-

tions, were obtained. The change of discontinuous point and slope, mentioned in Figure 1, could be explained through a connection with the transition of crystalline modification with the take-up speed at the respective annealing temperatures. Nevertheless, by the annealing process between  $T_g$  and  $T_{c,cold}$ , there seems to be no transition of crystalline modifications and the crystallinity of each modification appears to be improved.

### Thermal behavior

The DSC thermograms of PEN fibers, taken-up at various speeds and annealed at 120, 150, 180, and 200°C, are shown in Figure 3. The slopes indicating glass transition ( $T_g$ ) were clearly observed around 120°C for the fibers obtained below 5 km/min, but became obscure with increasing take-up speed. The exothermic cold crystallizations ( $T_{c,cold}$ ) were observed around 200°C, which gradually shifted to lower temperature and weakened with increasing take-up speed, and finally disappeared when the take-up speed exceeded 5 km/min. The decreasing tendency of  $T_{c,cold}$  with increasing take-up speed might be attributable to increasing stress-induced crystallization rate, being developed by spinline stress, and the disappearance of  $T_{c,cold}$  above 5 km/min might be attributable to development of orientation-induced crystallization during spinning. The  $T_{c,cold}$ , at the take-up speeds higher than 6 km/min, was not observable. At the same time the melting peaks shifted slightly to higher temperature and finally reached near 290°C at 8 km/min. The increase of  $T_m$  with take-up speed in



**Figure 3** DSC thermograms of PEN fibers spun at various take-up speeds (a), followed by annealing at (b) 120°C, (c) 150°C, (d) 180°C, and (e) 200°C.

our results might be caused by formation of more compact crystals, as a result of the orientation-induced crystallization at still higher temperature, caused by development of the discontinuous necking behavior at increasingly higher temperature, which corresponded to increasingly shorter distances from the spinneret.<sup>8</sup>

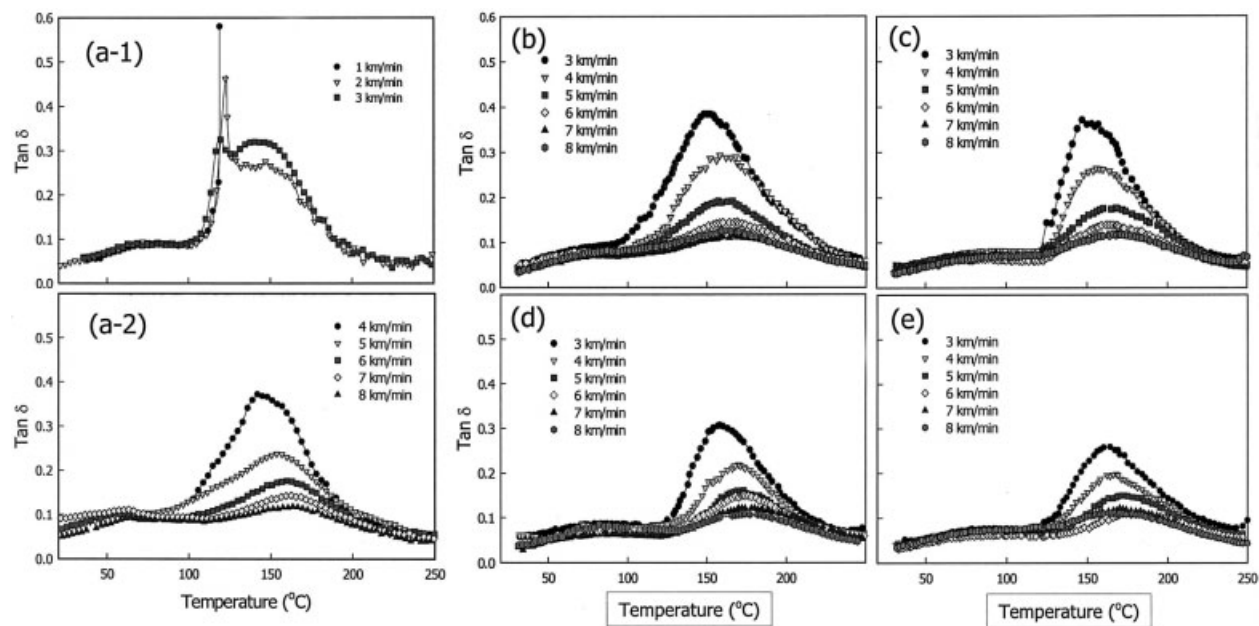
For the annealed fibers, the  $T_m$  around 270°C shifted to higher temperature throughout the annealing conditions as did those of as-spun fibers, and it is ascertained that the crystalline structure was virtually unchanged by the low-temperature annealing between  $T_g$  and  $T_{c\text{ cold}}$ . However, an exothermic slope appeared around each annealing temperature, gradually becoming indefinite as the annealing temperature and take-up speed increased: the slope was believed to be a kind of glass-transition effect caused by low-temperature annealing. Because the annealing conditions between  $T_g$  and  $T_{c\text{ cold}}$  might be insufficient to obtain a structural setting effect, the movement of amorphous molecules is considered to be partially generated at these temperatures. Consequently, as a consequence of low-temperature annealing, it is believed that the  $T_g$  of PEN fiber shifted to higher temperatures with increasing annealing temperature.

### Dynamic viscoelastic behavior

The temperature dependency of mechanical  $\tan \delta$  values, for as-spun and annealed PEN fibers, is shown in Figure 4. We observed three amorphous dispersions around 60, 120, and 175°C in the figures, and these are labeled in increasing temperature order,  $\beta$ ,  $\alpha$ , and  $\alpha'$ ,

respectively. The  $\beta$ -dispersion, at temperatures lower than  $T_g$  according to the report of Blundell and Buckingham,<sup>12</sup> reflects the rotational mode of the carbonyl group connecting with the naphthalene ring. The  $\beta$ -dispersions were nearly uniform throughout the range of take-up speeds. In particular, the amorphous dispersions, corresponding to the micro-Brownian motion of the main chains in amorphous regions, exhibited the character of two phases: the  $\alpha$ - and  $\alpha'$ -dispersions. The former might be associated with the glass transition, detected by the DSC thermogram [see Fig. 3(a)], and the latter emerged at a temperature 50–60°C higher than the  $\alpha$ -dispersion. These curves, over the entire range of take-up speeds, could be classified into three patterns with respect to their shapes. The first pattern corresponded to the take-up speed up to 3 km/min, whose  $\alpha$ -dispersions sharply increased to an unlimited value at 1 km/min and appeared as a shoulder of the  $\alpha'$ -dispersion, after increasing sharply at 2 and 3 km/min. The second patterns were those for take-up speeds up to 6 km/min, whose  $\tan \delta$  values decreased but the maximum temperatures increased gradually as the take-up speeds increased and, conversely, the  $\alpha$ -dispersion looked like a shoulder of the  $\alpha'$ -dispersion. At the third pattern, over 7 km/min, the  $\alpha$ -dispersion disappeared, whereas the  $\alpha'$ -dispersions shifted to a higher temperature and their areas decreased with increasing take-up speed. The decrease of the  $\alpha'$ -dispersion's fraction might correspond with the disappearance of the  $T_{c\text{ cold}}$  in the DSC thermogram (see Fig. 5), and is accordingly ascribed to the increase of crystalline fraction resulting



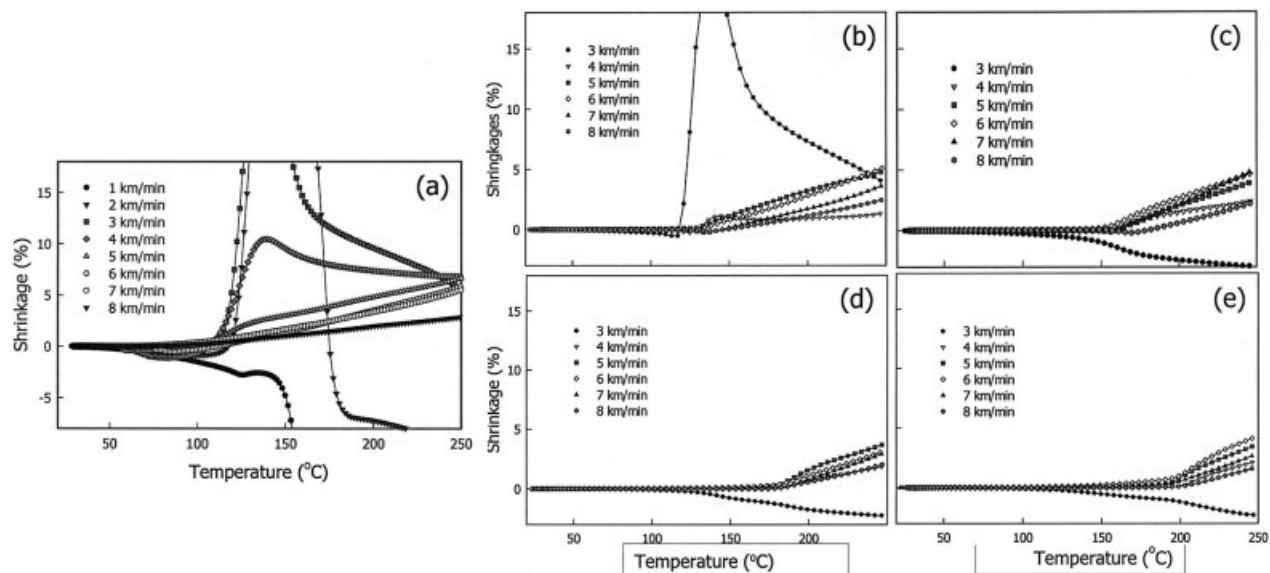


**Figure 4** Tan  $\delta$  values of PEN fibers spun at various take-up speeds (a-1) and (a-2), followed by annealing at (b) 120°C, (c) 150°C, (d) 180°C, and (e) 200°C.

from orientation-induced crystallization in the spinline. Consequently, the  $\alpha$ - and  $\alpha'$ -dispersions are believed to reflect multiple amorphous structures in the main chain, which might be developed from more-arranged and less-arranged structures. Moreover, these multiple amorphous structures might be generated by developing an inhomogeneous taut structure, with rigidity between a comparably flexible aliphatic segment and a stiff aromatic segment. For the intermediate take-up speeds, between 2 and 6 km/min, an

inhomogeneous taut structure might be partially formed but the homogeneously ordered structure might be enlarged as the take-up speed increased.

For the annealed fiber, the  $\beta$ - and  $\alpha'$  dispersions emerged around 60 and 175°C, but the  $\alpha$ -dispersions shifted to higher temperatures between 120 and 150°C. The  $\beta$ -dispersions remained nearly unchanged throughout the range of annealing temperatures and, likewise, the as-spun fibers. The elevated  $\alpha$ -dispersion almost disappeared, except below 5 km/min, for an-



**Figure 5** Variation of thermal shrinkage with temperature for the PEN fibers spun at various take-up speeds (a), followed by annealing at (b) 120°C, (c) 150°C, (d) 180°C, and (e) 200°C.

**TABLE I**  
**Tensile Properties for the PEN Fibers Spun at Various Take-Up Speeds**

Take-up speed (km/min)	Initial modulus (g/den)	Tenacity (g/den)	Breaking strain (%)	Work of rupture (g · cm)
1	19.91	1.57	366.04	283.46
2	25.99	2.34	186.51	106.38
3	45.30	3.71	101.53	68.36
4	75.76	4.75	49.56	33.52
5	118.58	6.75	31.64	25.60
6	160.14	8.40	19.32	15.79
7	178.41	8.44	11.43	7.20
8	193.07	9.19	10.81	6.65

nealing at 120°C and only 3 km/min for annealing at 150 and 180°C, and the absence of  $\alpha$ -dispersion could contribute to decreasing the inhomogeneous taut structure by the annealing process. With increasing annealing temperature the  $\alpha'$ -dispersion's intensity gradually decreased, whereas peak temperature shifted to a higher temperature with increasing take-up speed. Consequently, the fraction of oriented crystals could be increased with take-up speed, and a homogeneous stable structure could be acquired by annealing.

### Thermal shrinkage behavior

Variations of thermal shrinkage with temperature, for PEN fibers spun at various take-up speeds and annealed at 120, 150, 180 and 200°C, are shown in Figure 5, providing evidence of temperature dependency of percentage shrinkage on length reduction. Throughout the range of these take-up speeds, the fiber length began to decrease around 120°C, where the  $\alpha$ -dispersion of PEN fibers was observed in the previous viscoelastic behavior (see Fig. 4). At the take-up speed of 1 km/min, a reverse shrinkage abruptly occurred as the temperature increased: the fiber length started to increase from 120°C, and it might not only be associated with a thermal expansion effect when exposed normally in the isotropic state, but also correspond with the loss tangent that increased unlimitedly with increasing temperature (see Fig. 4). At take-up speeds from 2 to 4 km/min, the percentage shrinkage substantially increased and then decreased because these samples probably had been oriented during the spinning for a less-crystallized anisotropy state, and the tendency became indefinite with increasing take-up speed. At a take-up speed of 5 km/min, finally, the shrinkage behaviors showed a slight discontinuity around 120°C, corresponding with the  $\alpha$ -dispersion. Above this temperature, however, there was no discontinuous point and the extent of shrinkage, at 7 and 8 km/min, remained at low values. In particular, at the take-up speed of 8 km/min, the slightly increasing tendency of shrinkage was confirmed to provide ther-

momechanical stability. The thermal shrinkage, in other words, significantly increased around the  $\alpha$ -dispersion by the inhomogeneous taut structure and, accordingly, the beginning of dimensional deformation in PEN fibers was considered to be the  $\alpha$ -dispersion temperature. Therefore, to obtain dimensional stability in PEN fiber, it was confirmed that the  $\alpha$ -dispersion should be controlled.

For PEN fibers annealed at 120°C, the as-spun fiber at 3 km/min had an abrupt decrease of fiber length at 120°C and then a broad increase above 120°C. The trend in percentage of shrinkage decreased for the fibers annealed at 120°C as the take-up speed increased. However, for annealing at 150, 180, and 200°C, the length of fibers taken up at 3 km/min increased with annealing temperatures. Above 3, up to 6 km/min, the percentage shrinkages increased at the respective annealing temperatures, but above 6 km/min, the shrinkage decreased. First of all, for every annealed fiber, the onset points of length change coincided with the respective annealing temperatures, and it is considered that dimensional stability could be gained from restraining the inhomogeneous taut structure in the amorphous region without crystalline transition by annealing between  $T_g$  and  $T_{c\text{ cold}}$ .

### Tensile properties

The tensile properties of the as-spun PEN fibers, with various take-up speeds, and the annealed fibers, at the selected temperatures, including the initial modulus, tenacity, breaking strain, and work of rupture are described in Tables I and II. The strain decreased and the tenacity and initial modulus increased as the take-up speed increased, which might be caused by the increase of molecular orientation. On the other hand, for the annealed PEN fibers, the initial modulus and stress increased, except for take-up speeds of 6–8 km/min for annealing at 150 and 180°C compared with those of as-spun fibers. The breaking strains decreased at take-up speeds up to 6 km/min, but increased at 7 and 8 km/min. The general tendencies at low take-up speeds could be explained from a struc-

TABLE II  
Tensile Properties for the PEN Fibers Annealed at Selected Temperatures<sup>a</sup>

TS	AT	Initial modulus (g/den)				Tenacity (g/den)				Breaking strain (%)				Work of rupture (g · cm)			
		120	150	180	200	120	150	180	200	120	150	180	200	120	150	180	200
	3	48.28	60.89	65.72	68.03	3.50	3.86	3.77	3.58	90.23	86.28	76.88	68.75	54.83	59.61	54.60	47.21
	4	81.47	89.25	89.75	95.00	4.99	4.92	4.88	4.88	57.59	48.40	48.86	47.65	42.57	36.92	36.19	37.53
	5	121.02	124.41	117.37	127.22	6.03	6.28	6.22	6.42	24.75	26.23	33.11	23.52	18.75	20.90	24.77	19.05
	6	162.08	147.89	149.88	161.87	8.04	7.35	7.23	7.93	16.32	15.85	25.50	15.04	12.61	11.41	9.21	11.70
	7	179.33	169.62	169.85	177.96	8.98	8.62	8.46	7.65	12.84	12.55	22.77	11.71	8.80	8.42	7.60	7.65
	8	187.96	174.73	175.43	187.00	9.10	8.47	9.21	8.19	11.07	10.52	13.04	9.67	6.54	5.68	7.47	5.50

<sup>a</sup> AT, annealing temperature (°C); TS, take-up speed (km/min).

tural setting effect, but the converse effects at high take-up speeds might be caused by a structural relaxing effect at low-temperature annealing.

### CONCLUSION

From the investigation of thermomechanical properties, as well as structural variation of PEN fibers by high-speed spinning and low-temperature annealing, specifically measured using density, X-ray diffraction, DSC, Rheovibron, TMA, and tensile testing, the following results were obtained:

- For the crystalline structure, revealed by densities and X-ray diffractions, the  $\beta$ -modification was observed in high-speed spinning over 8 km/min, and furthermore the formation of more compact crystals, attributed to the orientation-induced crystallization at still higher temperature, could be ascertained from an increase of  $T_m$  in DSC thermograms. On the other hand, the annealing process at a relatively low temperature, between  $T_g$  and  $T_{c\text{ cold}}$ , generated no transition of crystalline modifications and improved the respective crystalline fraction in each modification.
- The amorphous dispersions, confirmed by the viscoelastic behavior, were  $\beta$ -,  $\alpha$ -, and  $\alpha'$ -dispersions, that is, in addition to the  $\alpha$ -dispersion around  $T_g$ , the  $\alpha'$ -dispersion emerged at a temperature 50–60°C higher than the  $\alpha$ -dispersion. The  $\alpha$ - and  $\alpha'$ -dispersions are supposed to reflect multiple amorphous structures in the main chain, which might be developed from a more ordered segment and a less ordered segment and also generated by developing an inhomogeneous taut structure with rigidity between a comparably flexible aliphatic segment and a stiff aromatic segment.

- The thermal shrinkage behavior notably increased around the  $\alpha$ -dispersion, probably caused by the inhomogeneous taut structure, and the phenomenon became indefinite with increasing take-up speed. Furthermore, the fiber at 8 km/min take-up speed showed very low shrinkage. Accordingly, the onset point of dimensional deformation in PEN fibers was supposed to be the  $\alpha$ -dispersion temperature.
- The tensile property improved as the take-up speed increased, probably caused by the increase of molecular orientation. For the annealed PEN fibers, compared with those of as-spun fibers, the enhanced tensile property, attributed to a structural setting effect, was observed at low take-up speeds below 5 km/min but the converse effect, attributed to a relaxed structure by low-temperature annealing at the high take-up speeds between 6 and 8 km/min, was evident.

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