

# Two-Stage Drawing of Acetone Treated Poly(ethylene Terephthalate) Fibers

MASAYOSHI ITO, HISAKAZU MIYA, and MIHO WATANABE,  
*Department of Chemistry, and TETSUO KANAMOTO, Department of  
Applied Chemistry, Science University of Tokyo,  
Kagurazaka, shinjuku-ku, Tokyo 162, Japan*

## Synopsis

Acetone-treated fibers of poly(ethylene terephthalate) were drawn by a two-stage drawing technique: cold-drawing at 25°C followed by hot-drawing at 230°C by tensile force. The maximum achievable draw ratios (TDRs) for the treated and the untreated original fibers were 11.5 and 9.5, respectively. The highest modulus and strength of 28 and 1.2 GPa, respectively, were obtained by drawing the treated fibers with the highest TDR. These values were about 20% higher than those for the untreated drawn fibers with the highest TDR. Although annealing of the untreated drawn fibers under tensions significantly improved the tensile modulus up to the maximum modulus for the treated drawn fibers, the tensile strength of such annealed fibers decreased remarkably due to the degradation occurring during annealing. The crystallinity of the drawn sample from the treated fiber was higher than that from the untreated fiber, leading the former to a higher structural stability against heat than the latter. These results were explained by the existence of small and/or less perfect crystals in the treated fibers induced by acetone.

## INTRODUCTION

The production of high modulus and high strength poly(ethylene terephthalate) (PET) fibers has been the subject of intense research in recent years.<sup>1-7</sup> We have shown<sup>4</sup> that the predrawn morphology of PET has a marked effect on the ductility and tensile properties of drawn materials. It was found<sup>6,8</sup> that the solution-spun fibers from high molecular weight PET could be drawn to a draw ratio of 11 by two-stage tensile drawing. The tensile modulus and strength of the resultant fibers reached 29.5 and 1.4 GPa, respectively. The increased ductility of as-spun fibers and high levels of mechanical properties of the drawn fibers were related to the existence of small and/or less perfect crystals and of residual solvent in the as-spun fibers. Also, the effectiveness of two-stage draw was emphasized in the production of high modulus and high strength oriented PET.<sup>8</sup> However, the process for the preparation of drawn fibers requires the high molecular weight polymer to be dissolved in a solvent, extruded, and then drawn.

Sheldon and Blakey<sup>9</sup> studied the crystalline structure of acetone-induced PET crystals and reported that the acetone had no influence on the crystal structure, but that the wide angle X-ray diffraction patterns of the acetone-induced crystals exhibited broad reflections, suggesting a smaller crystallite size. Such crystalline morphology seems to be similar to that observed in the as-spun fibers produced by a solution-spinning method.<sup>8</sup> It is thus expected

that high modulus and high strength PET fibers can be obtained by the two-stage drawing of acetone crystallized fibers.

The purpose of this paper is to report the effects of predrawn morphology induced by acetone liquid on the drawing behavior and the properties of resultant drawn fibers.

## EXPERIMENTAL

### Samples

Initially amorphous, unoriented PET fibers with a diameter of about 65  $\mu\text{m}$  were kindly supplied by Toyobo. The intrinsic viscosity of the fibers was 0.9 dL/g. The acetone used was an analytical reagent quality. As-received fibers were dried at 50°C for 24 h under vacuum, and then they were immersed in acetone liquid at room temperature for a varying length of time. Following this liquid treatment, the fibers were blotted twice on filter paper to remove excess acetone from the sample surface. A two-stage draw technique was utilized for both treated and untreated original fibers. The fibers were drawn by tensile force at room temperature (cold drawing), followed by tensile drawing at 230°C (hot drawing).

### Measurements

The amount of absorbed acetone on the fibers was determined by using a microbalance (Mettler M3). The tensile properties of drawn fibers along the fiber axis were measured at room temperature and a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$ . The gage length was 100 mm. The modulus was determined from the tangent to the stress-strain curve at a low strain (0.1%). Sample density was determined at 30°C in density gradient column prepared from *n*-heptane and carbon tetrachloride. Weight percent crystallinity was calculated from the observed density on the basis of a two-phase model. The amorphous and crystalline densities for PET were taken to be 1.333 and 1.455 g/cm<sup>3</sup>, respectively.<sup>10</sup> The intrinsic viscosity of the sample was measured in a mixed solvent of trifluoroacetic acid-dichloromethane (50/50, v/v) at 30°C. Wide- and small-angle X-ray measurements were carried out on a Rigaku RAD-III and RU-200 diffraction units with a Ni filtered Cu-K $\alpha$  radiation source at 40 kV and 25 mA. Herman's orientation factor for the crystallites,  $f_c$ , was determined from azimuthal scans of the ( $\bar{1}05$ ) reflections.<sup>11</sup> The orientation factor of the amorphous regions,  $f_a$ , was evaluated by combining the  $f_c$ , sample crystallinity, and optical birefringence data, which were measured by a polarizing microscope equipped with a Berek compensator and quartz plate as an additional compensator. The intrinsic birefringences of the crystal and the amorphous phases were taken to be 0.251 and 0.230,<sup>1</sup> respectively. Thermal analysis was carried out on a Seiko Denshi DSC-10 differential scanning calorimeter at a heating rate of 5°C/min.

## RESULTS AND DISCUSSION

### Morphology and Ductility of Acetone-Treated Fibers

It is well known that the interaction of PET with acetone lowers the glass transition temperature ( $T_g$ ). As a consequence, crystallization occurs at tem-

peratures well below those required for crystallization of dry PET. It is thus expected that the morphology of acetone treated fibers depends on the amount of acetone sorbed by the fibers. In Figure 1, the weight uptake of acetone and the achievable draw ratio ( $DR_{\max}$ ) of the treated fibers are plotted as a function of immersion time. The weight uptake was expressed in terms of the weight absorbed acetone per initial weight of dry fibers at 25°C. The  $DR_{\max}$  was determined by tensile drawing at 25°C. Up to 5 min, the uptake value increases abruptly, followed by saturation with a value of 11.5%. This value is comparable to that reported by Makarewicz and Wilkes,<sup>12</sup> although the immersion time is different from each other due to the difference of the sample thickness. The  $DR_{\max}$  increases gradually with increasing the time, followed by saturation around 8 min. The highest  $DR_{\max}$  of 7 is about 40% higher than that for the untreated fibers ( $DR_{\max} = 5$  at immersion time 0 min). It should be noted that the  $DR_{\max}$  still goes up with time even after the time when the weight uptakes are saturated (immersion time > 5 min). This means that the improved ductility by acetone is not simply related to the plasticizing effect of the fibers. Figure 2 shows the DSC thermograms of acetone-treated fibers with different immersion times. At an initial stage of immersion (immersion time 30 s), the depression of  $T_g$  and cold crystallization temperature is remarkable [Fig. 2(b)]. After a prolonged treatment (immersion time 10 min) [Fig. 2(c)], the cold crystallization peak disappears and glass transition becomes obscure, although the  $T_g$  is almost similar to that for the fibers treated for 30 s. These results suggest that the significant swelling occurs within a short immersion time, and then solvent-induced crystallization proceeds more slowly, which suppresses the cold crystallization during DSC scan. This is supported by the wide angle X-ray diffraction (WAXD) photographs shown in Figure 3. To obtain these photographs, particular attention was paid to minimize the evaporation of acetone from the samples during the X-ray exposure (about 2.5 h). The treated fibers

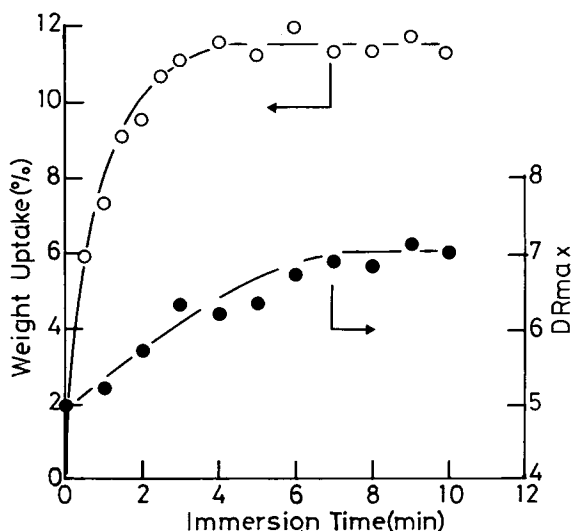


Fig. 1. Weight uptake (%) and achievable draw ratio ( $DR_{\max}$ ) at 25°C as a function of immersion time at 25°C.

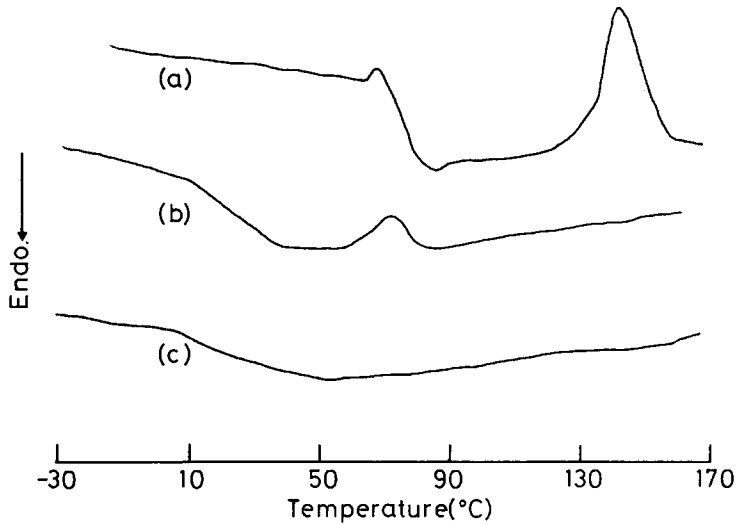


Fig. 2. DSC scans of the fibers: (a) original untreated fiber; (b) immersion time 30 s; (c) immersion time 10 min.

were packed in a capillary tube just after the treatments. After that, both ends of the tube were sealed by cement. Then the samples were exposed to the X-ray beam. The fibers treated for 30 s [photograph 3 (a)] show only an amorphous halo. However, the crystalline reflections are observed for the fibers treated for 10 min [photograph 3 (b)], although each diffraction ring is broad and diffuse. When most of the acetone was removed under vacuum from the treated fibers (immersion time 10 min), the diffraction rings became sharp (see Fig. 4), and simultaneously the fibers lost their ductility. These results indicate that, under the presence of acetone, the solvent-induced crystals are less perfect and/or their sizes are very small. With decreasing the amounts of acetone trapped in the fibers, the solvent-induced crystals increase in their perfection and sizes, leading to the brittle state.

Figure 5 shows nominal stress vs. strain curves recorded at constant temperatures ( $T_e$ ) of 25 and 80°C, and at a constant crosshead speed of 100 mm/min for the original (untreated) and the acetone-treated (immersion time 10 min) fibers. At  $T_e = 25^\circ\text{C}$ , the stress at yield for the treated fiber [Fig. 5 (b)] is about 35% for the untreated one [Fig. 5 (a)]. The results are qualitatively consistent with the data reported by Blakey and Sheldon.<sup>13</sup> As shown in Figure 2, the  $T_g$  of the treated fibers is around 15°C. Thus, the curve of the treated fibers at 25°C ( $T_g + 10^\circ\text{C}$ ) is compared with that of the untreated fiber at 80°C ( $T_g + 10^\circ\text{C}$ ) [Fig. 5 (c)]. Although both curves show a similar trend with strain, the stress at yield and stretching force for the former are about four times higher than those for the latter. The high stress at yield for the treated fibers are primarily due to the existence of solvent-induced crystals, since the molecular mobility in the noncrystalline regions for the treated fibers at 25°C may be comparable to that for the untreated fibers at 80°C. As seen in Figures 1 and 5, the  $\text{DR}_{\text{max}}$  at 25°C for the untreated fibers is around 5, and the ductility is not improved even for drawing above the  $T_g$  of the untreated fiber. It should

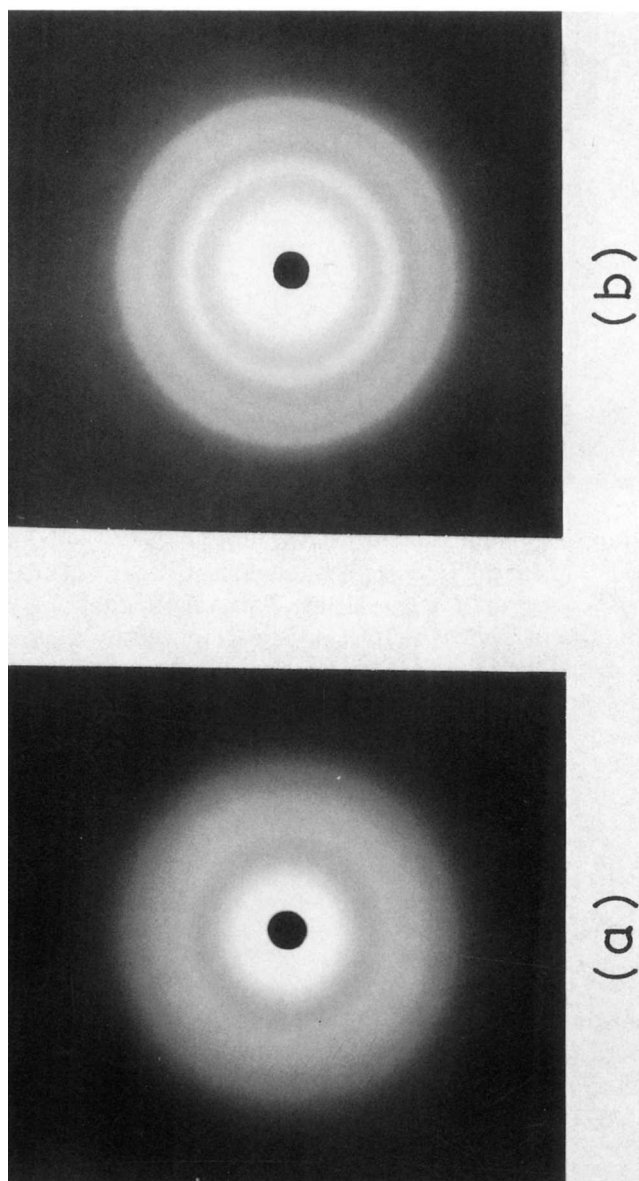


Fig. 3. Wide-angle X-ray diffraction photographs of treated fibers: (a) immersion time 30 s; (b) immersion time 10 min.

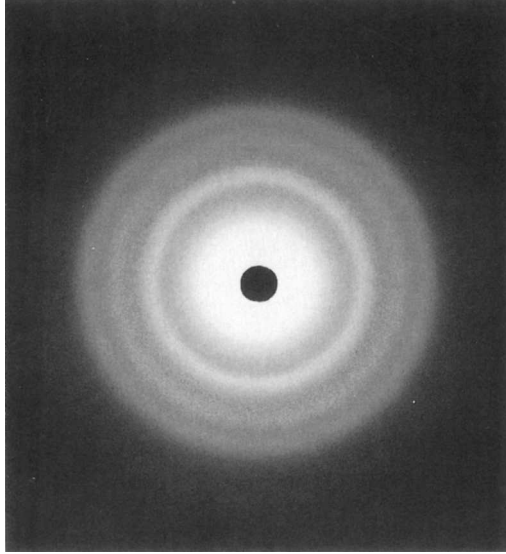


Fig. 4. Wide-angle X-ray diffraction photograph of dry sample of treated fibers (immersion time 10 min).

be noted that the deformability of the treated fibers at 25°C is higher than that of the untreated fibers at 80°C, despite the fact that the stress at yield for the former is higher than that for the latter. This means that the presence of acetone and small and/or less perfect crystals induced by acetone plays an important role in the improvement of the drawability of the treated fibers. As discussed above, the superstructure of acetone-treated fibers is extremely com-

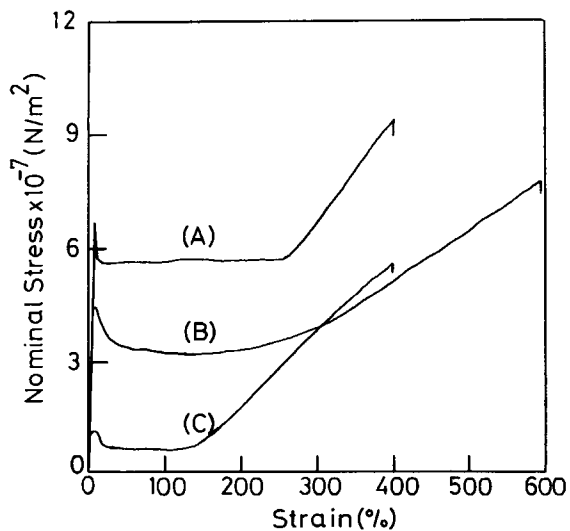


Fig. 5. Nominal stress-strain curves of untreated and treated (immersion time 10 min) fibers: (A) untreated  $T_e = 25^\circ\text{C}$ ; (B) treated  $T_e = 25^\circ\text{C}$ ; (C) untreated  $T_e = 80^\circ\text{C}$ .

plex. This makes it difficult to understand the mechanism for the improved deformability observed in the treated fibers. A possible explanation for the high drawability, however, can be made by comparing the stress-strain curves in Figure 5. In the untreated fibers at 80°C, the stress on draw begins to increase abruptly at a strain of  $\sim 150\%$ , and the stress exceeds the value for the treated fibers at a strain of  $\sim 300\%$ . The sharp increase in the stress arises from the well-known stress-induced crystallization of PET. On the other hand, for the treated fibers, a rapid increase in the stress starts at a strain of  $\sim 300\%$ . However, the slope is not so steep as in drawing of the untreated fibers. The most crucial effects of the acetone treatment on drawing PET fibers are to reduce the strain hardening without loss of the fiber strength (Fig. 5). The mobility of amorphous segments is markedly increased by the acetone which is preferentially dissolved in the amorphous regions, as was revealed by the large decrease in  $T_g$ . The plasticization increases the deformability of only amorphous regions. As the small crystallites induced by acetone treatment may act as net points fixing the ends of plasticized amorphous segments, the strength of the fiber may be maintained even in the presence of the plasticizer, as shown in Figure 5.

### Two-Stage Drawing

In a previous paper,<sup>8</sup> we emphasized the importance of two-stage draw (combination of cold drawing and hot drawing) in obtaining high modulus and high strength PET fibers. In this study, the same technique was utilized for both treated and untreated fibers. Both treated (immersion time 10 min) and untreated originally amorphous fibers were drawn by tensile force to the  $DR_{\max}$  at room temperature. Then, the samples were drawn further in a tensile tester at 230°C. The tensile properties of the resultant drawn fibers were dependent on several parameters including the total draw ratio ( $TDR = DR_{\max} \times DR$  for the hot drawing), the draw stress on hot drawing, and the load applied to the samples during cooling after the hot drawing. The higher the stress and the load, the higher mechanical properties of drawn fibers could be achieved. In this study, the hot drawing was carried out under a draw stress of  $\sim 50 \text{ kg/mm}^2$  by controlling the crosshead speed. After the hot drawing, the samples were cooled to room temperature under a constant sample length. Thus, the load applied to the samples increased during cooling from  $\sim 50 \text{ kg/mm}^2$  at the draw temperature of 230°C to  $\sim 65 \text{ kg/mm}^2$  at room temperature. In Figures 6 and 7, tensile modulus and strength of the samples are plotted against TDR. The achievable maximum TDR for the treated and untreated fibers were 11.5 and 9.5, respectively. This means that the achievable draw ratio at the second-stage (hot drawing) is 1.6–1.9, independent of acetone treatments. During the hot drawing at 230°C, the residual acetone was removed, and, simultaneously, solvent-induced crystals increased in their perfection and sizes and stress-induced crystallization proceeded, all of which might reduce the ductility of the treated fibers. Both the tensile modulus and strength increase with increasing TDR. The highest modulus and strength of 28 and 1.2 GPa, respectively, were obtained for the treated fibers with the highest TDR. These values are about 20% higher than those achieved for the untreated drawn fibers with the highest TDR.

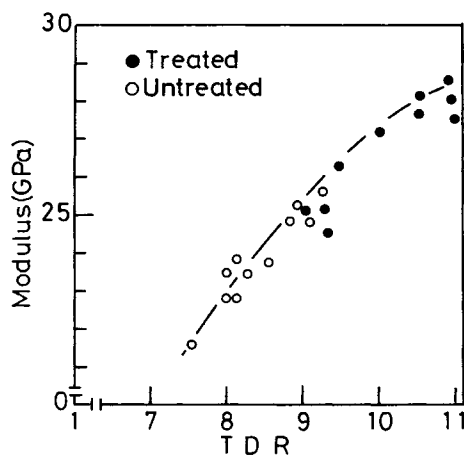


Fig. 6. TDR dependence of the tensile modulus for the untreated and treated (immersion time 10 min) drawn fibers.

### Structure of Two-Stage Drawn Fibers

Table I summarizes the structural parameters for both treated and untreated drawn fibers. It should be noted that the sample crystallinity and modulus for the treated drawn fibers are higher than those for the untreated drawn fibers, despite the fact that the chain orientation in amorphous regions ( $f_a$ ) for the former is lower than that for the latter. These results imply that the crystallinity plays an important role in the mechanical properties of drawn fibers. Itoyama<sup>5</sup> studied the effects of prolonged annealing of cold-drawn PET on the structure and properties. He reports that the prolonged annealing results in an increase in the crystalline orientation and crystallinity, which leads to the improvement of tensile modulus of drawn PET. We have also examined the effect of annealing on the structure and tensile properties.

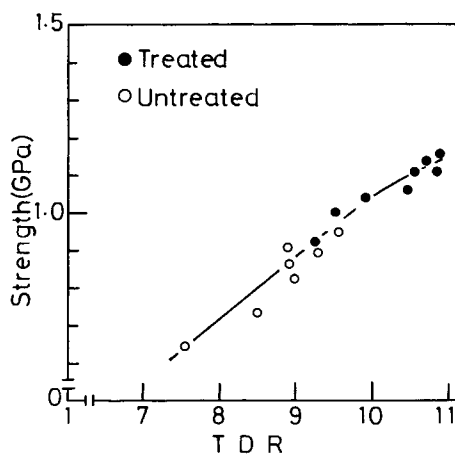


Fig. 7. TDR dependence of the strength at break for the untreated and treated (immersion time 10 min) drawn fibers.



TABLE I  
Structural Parameters and Physical Properties of the Samples

Sample	TDR	$X_c^a$ (%)	$L^b$ (Å)	$f_c$	$f_a$	Modulus (GPa)	Strength (GPa)
Treated	10.0	68	171	0.896	0.58	27.2	1.2
Untreated	8.5	50	170	0.887	0.98	24.4	1.0

<sup>a</sup>  $X_c$  = crystallinity.

<sup>b</sup>  $L$  = long period.

In this study, the drawn fibers were annealed at 230°C under a constant load of  $\sim 45 \text{ kg/mm}^2$  in an air oven. The properties and structural parameters of annealed specimens are shown in Table II. It is clearly seen that, for the untreated drawn fibers, the annealing results in an increase in the crystalline orientation ( $f_c$ ), crystallinity, and modulus. These results are consistent with the report by Itoyama,<sup>5</sup> although the conditions for annealing are different from each other. It is noted that, on annealing the untreated drawn fibers, the  $f_a$  decreases and the crystallinity increases with increasing annealing time, approaching the comparable values for those observed in the treated drawn fibers. These results suggest that the highly oriented amorphous segments are preferentially incorporated into crystalline phases during annealing. Under the present annealing conditions, the relaxation of the oriented amorphous segments is likely a minor mechanism for the decrease in the  $f_a$  value, since the modulus increases, and simultaneously the  $f_a$  decreases with increasing the annealing time. In contrast to the annealing of the untreated fibers, the treated drawn fibers show actually no changes in the crystallinity,  $f_c$ ,  $f_a$ , and tensile modulus even after the prolonged annealing for 3 h.

As seen in Table I, the crystallinity of the treated drawn fibers is about 20% higher than that of untreated drawn fibers. A large number of crystallites initially present in the drawn fibers may exert considerable constraint on the mobility of noncrystalline molecules and thus restrict their mobility. Figure 8 illustrates the annealing time dependence of the tensile strength and intrinsic viscosity of the samples. A remarkable decrease in the tensile strength is observed for both treated and untreated drawn fibers with increasing the annealing time. Also, the intrinsic viscosities of the samples decrease with increasing the time, in parallel to the strength. Thus, the drop in the tensile strength is likely due to the molecular degradation during the heat treatments. With increasing

TABLE II  
Structural Parameters and Physical Properties of Annealed Samples

Annealing time (h)	Treated				Untreated			
	0	1.0	2.0	3.0	0	1.0	2.0	3.0
TDR	10.0	10.0	10.0	10.0	8.5	8.5	8.5	8.5
$X_c$ (%)	68	70	71	71	50	56	68	73
$f_c$	0.896	0.900	0.895	—	0.887	0.899	0.900	—
$f_a$	0.58	0.55	0.55	—	0.98	0.76	0.52	—
Modulus (GPa)	27.2	27.3	27.5	27.5	24.4	26.5	27.0	27.2

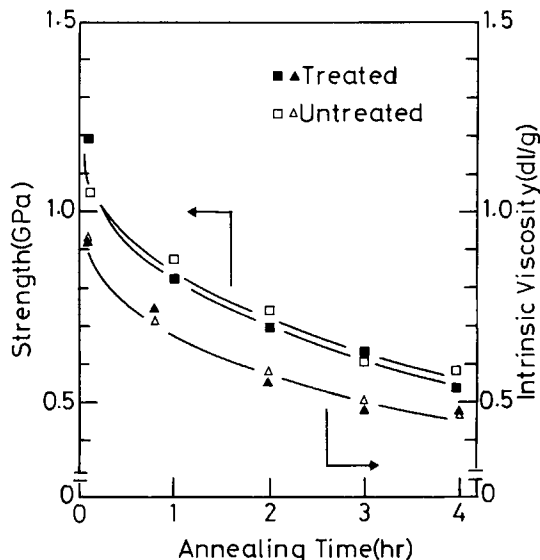


Fig. 8. Annealing time dependence of the strength at break and intrinsic viscosity for the drawn samples from untreated (TDR = 8.5) and treated (immersion time 10 min, TDR = 10) fibers.

the annealing time, the modulus for the untreated drawn fibers increases, and simultaneously tensile strength decreases. This means difficulty in the production of high modulus and high strength PET fibers by the heat treatments. The presence of less perfect and/or small crystals, induced by acetone treatments, enhances the development of the improved crystallites during drawing. Such drawn fibers exhibit a high crystallinity, without a long heat treatment, resulting in the production of high modulus and high strength fibers.

## CONCLUSION

A two-stage drawing technique was utilized for drawing both acetone-treated and untreated originally amorphous PET fibers. The achievable draw ratio by the first-stage cold drawing of the treated fibers was about 40% higher than that for the untreated fibers. The improved cold drawability of the treated fibers were explained by the existence of small and/or less perfect crystals induced by acetone and by the plasticization with the residual acetone trapped within amorphous regions. By the second-stage drawing, the treated and untreated fibers could be drawn up to draw ratios of 11.5 and 9.5, respectively. The acetone-induced morphology enhanced the development of the crystalline phase during drawing. Such drawn fibers with a higher crystallinity exhibited high modulus and high strength values with high structural stability against heat. The highest modulus and strength of 28 and 1.2 GPa, respectively, were achieved for the acetone treated fibers with the highest draw ratio. These values are about 20% higher than those for the untreated drawn fibers with the highest draw ratio. Although the tensile modulus of the untreated drawn fibers could

be increased by annealing under tensions, the strength was markedly decreased due to the extensive molecular degradation occurred during annealing.

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