# Preparation of High-Modulus and High-Strength Fibers from High Molecular Weight Poly(ethylene Terephthalate)

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## Synopsis

High molecular weight poly(ethylene terephthalate) (PET) was obtained by solid-state polymerization of solution-grown crystals of PET that were prepared from commercially available PET. The intrinsic viscosities of the sample before and after the polymerization were 0.67 and 2.41 dL/g, respectively. As-spun fibers from the high molecular weight material were prepared by a solution spinning method using two kinds of solvents: nitrobenzene (NB) and a mixture of hexafluoro-2-propanol and dichloromethane (HD). Both as-spun fibers could be drawn up to a draw ratio of 12–13 by a two-stage drawing technique. The highest tensile modulus and strength of 275 g/d (34.4 GPa) and 15 g/d (1.9 GPa), respectively, were obtained for the drawn fibers from the HD system. These values were 15%–20% higher than those achieved for the drawn fibers from the NB system. The difference was explained on the basis of the morphological differences of as-spun fibers and the extent of molecular degradation during processing observed between the two series.

## INTRODUCTION

The drawing behavior of poly(ethylene terephthalate) (PET) has been extensively studied for many years to produce high-modulus and high-strength PET fibers and films. Although high-modulus value of 20–35 GPa has been reported for drawn PET,[1-5] it is still difficult to produce high-strength materials. We have shown[5,6] that the tensile strength of drawn PET is dependent on several factors including molecular weight, sample geometry, and draw conditions. Among these factors, the molecular weight and the cross-sectional area have been shown to have a marked effect on the tensile strength of drawn PET. The higher the molecular weight and the smaller the cross-sectional area of the samples, the higher the tensile strength could be achieved. However, the molecular weights of commercially available PET are limited to low values.

Recently, we prepared a high molecular weight PET (intrinsic viscosity = 2.41 dL/g) from a commercially available PET by solid-state polymerization. The as-spun fibers from the high molecular weight material, which were obtained by the solution spinning method, could be drawn up to a draw ratio of 13, and the tensile modulus and strength of the resultant drawn fibers reached 275 and 15.5 g/d, respectively. In this paper, the preparation and properties of high-modulus and high-strength PET fibers from high molecular weight PET will be reported.

## EXPERIMENTAL

### Material

High molecular weight PET was obtained by the solid-state polymerization of solution-grown crystal aggregates of 2–10 $\mu$m, which were prepared from a commercially available low molecular weight PET solution in nitrobenzene. Polymerization was carried out at 253°C for 24 h under vacuum. The intrinsic viscosities (IV) of the sample before and after the polymerization were 0.67 and 2.41 dL/g, respectively.

As-spun fibers from the high molecular weight material were prepared by the solution spinning method using two kinds of solvents: nitrobenzene (NB) and a mixture of hexafluoro-2-propanol and dichloromethane (50/50 v/v) (HD). The maximum polymer concentrations available by directly dissolving the PET in NB and HD were 15 and 8 wt %, respectively. However, these concentrations were too low to obtain fibers because of the low viscosity of the solutions. The concentrations were increased up to 30 and 15 wt % for NB and HD systems, respectively, by evaporating the solvents. These corresponded to the minimum solution viscosity to obtain homogeneous fibers by solution spinning. The solutions were extruded through a conical capillary die with a diameter of 0.2 mm at 170 for the former and 25°C for the latter. The wet as-spun fibers were collected on a glass bobbin tension-free. Most of the solvent in the as-spun fibers was removed at room temperature under vacuum before drawing. The last trace of the solvent was removed during hot-drawing at 230°C.

Drawn samples were obtained by a two-stage drawing technique. As-spun fibers were drawn by tensile force at room temperature (cold-drawing), followed by tensile drawing at 230°C (hot-drawing). The total draw ratio (TDR) was determined by measuring the separation between lateral ink marks on the sample before and after drawing.

### Measurements

The tensile properties of drawn samples along the fiber axis were measured at room temperature by a tensile testing machine. Sample density was determined at 30°C in the 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$^3$, respectively.[7] The intrinsic viscosity of the samples was measured in a mixed solvent of trifluoroacetic acid-dichloromethane (50/50 v/v) at 30°C.

## RESULTS AND DISCUSSION

### Structure and Properties of As-spun Fibers

Figure 1(a) and (b) show wide-angle X-ray diffraction photographs of as-spun fibers from the HD (a) and NB (b) systems, respectively. For the fibers from the HD system, a strong anisotropy is observed in each ring, although all the rings are broad and diffuse. On the other hand, for the fibers from the NB system, the anisotropy is less, but a clear crystalline diffraction pattern is ob-
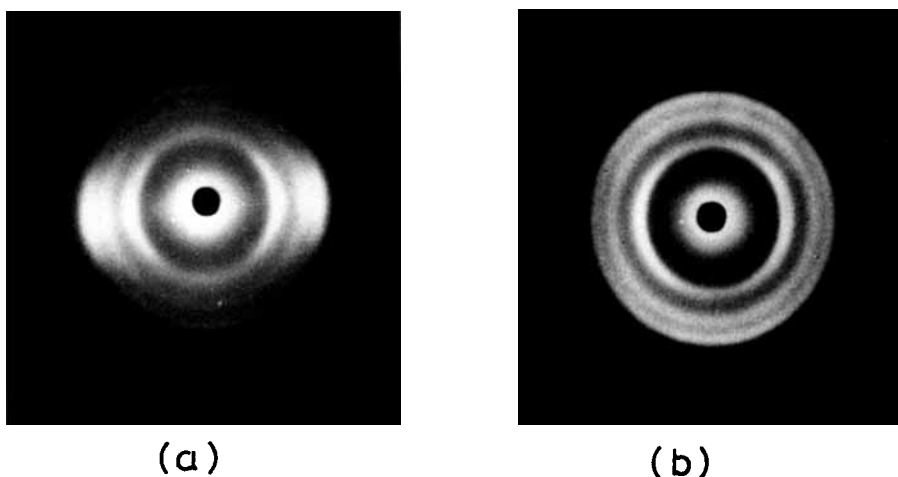
(a)                              (b)

Fig. 1.    Wide-angle X-ray diffraction photographs of as-spun fibers from HD (a) and NB (b) systems.

served. As described in the previous section, the extrusion temperature ($T_e$) for the two solvent systems was different. For the HD system, a highly viscous polymer solution and/or wet gel were extruded at 25°C with an extrusion rate $\sim 2$ m/min. The solvent was volatile enough that the polymer solution solidified immediately after coming out from the die at room temperature. A high shear stress during extrusion might induce a significant chain orientation, which would be maintained by rapid evaporation of the solvent. For the NB system, crystallization occurred below 150°C. Thus, the $T_e$ of 170°C was the lowest temperature for solution spinning of the system. The polymer solution at 170°C transformed into wet fibers after coming out from the die at room temperature. The solidification of the polymer solution was primarily due to the crystallization of PET rather than to the evaporation of NB, which has a high boiling temperature of 211°C. The molecular weight of as-spun fibers from the HD system was higher than those from the NB system, although the starting material for both fibers was the same. When NB was used as a solvent, a high dissolution temperature of 205°C was required, which resulted in a large drop of IV from 2.41 to 1.94 dL/g. On the other hand, for the HD system, the dissolution and processing for the fiber forming could be done at room temperature, which made it possible to maintain a high value of IV (93% of the starting IV).

Dry as-spun fibers from both solvent systems were drawable at room temperature. The maximum achievable draw ratio was 5–6 at room temperature, independent of the solvent systems used. The tensile modulus and strength for the cold-drawn fibers were around 30–50 and 3–4 g/d, respectively. Such low levels of mechanical properties are probably due to the low level of crystallinity (< 30%) and of chain orientation in the cold-drawn fibers. To increase the mechanical properties further, second-stage drawing was carried out at 230°C (hot-drawing) on the cold-drawn samples.

### Mechanical Properties of Two-stage Drawn Fibers

Figures 2 and 3 show the tensile modulus and strength of two-stage drawn fibers. The tensile properties were dependent on several parameters, including
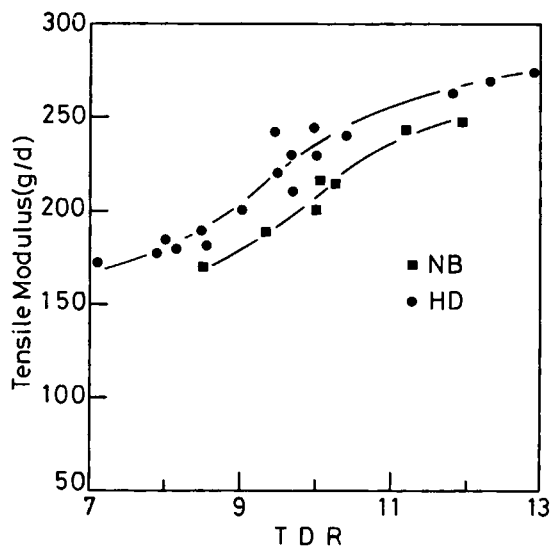
Fig. 2.   Tensile modulus vs. TDR for NB and HD systems.

the total draw ratio (TDR), molecular weight, and the load applied to the samples during cooling after the hot-drawing, as described in the previous work.[5] The higher the load, the higher were the resultant mechanical properties of drawn fibers that could be achieved. Thus, the plots in Figures 2 and 3 depict samples that were prepared under the highest load applicable to the samples at each TDR. The achievable maximum TDRs for both solvent systems were 12–13. Both the tensile modulus and strength increase with increasing TDR. The highest modulus and strength of 275 g/d (34.4 GPa) and 15.5 g/d (1.9 GPa), respectively, were obtained for the fibers from the HD system at the
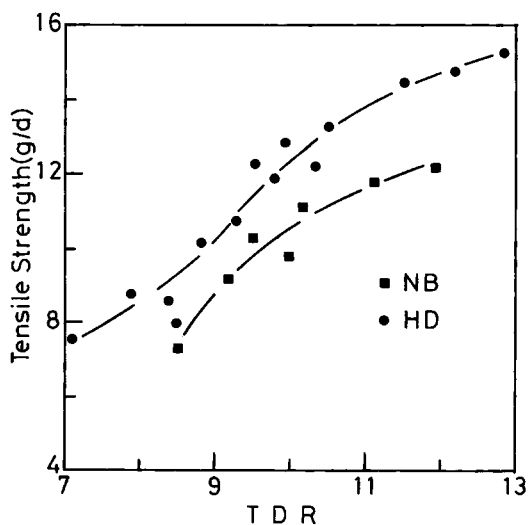


Fig. 3.   Tensile strength vs. TDR for NB and HD systems.

highest TDR. These values are 15%–20% higher than those achieved for fibers from the NB system.

As seen in Figures 2 and 3, the efficiency of draw is apparently higher for fibers from the HD system than for fibers from the NB system. This is more prominent in the tensile strength vs. TDR plot. The difference can be explained by three factors. The first is the difference in the morphology of as-spun fibers. In the as-spun fibers from the HD system, a significant degree of chain orientation is evident [Fig. 1(a)]. This means that the actual deformation ratio is higher than the calculated TDR since the draw ratio of as-spun fibers has been taken to be 1. On the other hand, the preorientation is less in the as-spun fibers from the NB system. The second is the difference in the molecular weight of two-stage drawn fibers. During hot-drawing, further molecular degradation occurred that induced the IV drop from 2.20 to 2.05 dL/g for the HD system and 1.94 to 1.70 dL/g for the NB system. However, the drawn fibers from the HD system still keep a high IV value compared with fibers from the NB system. We have reported[6] that the tensile strength of drawn PET increases with increasing molecular weight, as in other polymers.[8] The third is the difference in the load applied to the samples during cooling. For example, the load applied to the drawn fibers (TDR = 10) from the NB and the HD systems were about 60 and 75 kg/mm$^2$, respectively. The load applicable to the samples increases with increasing amorphous chain orientation ($F_a$) in the first-stage drawn samples.[5] The $F_a$ values at a given draw ratio for the drawn fibers from the HD system were higher than those from the NB system. This arises from the difference in the actual deformation ratio, as mentioned above.

### Structure of Two-stage Drawn Fibers

In Figure 4, the crystallinity of two-stage drawn fibers are plotted against TDR. For both series, the crystallinity increases slightly with increasing TDR.
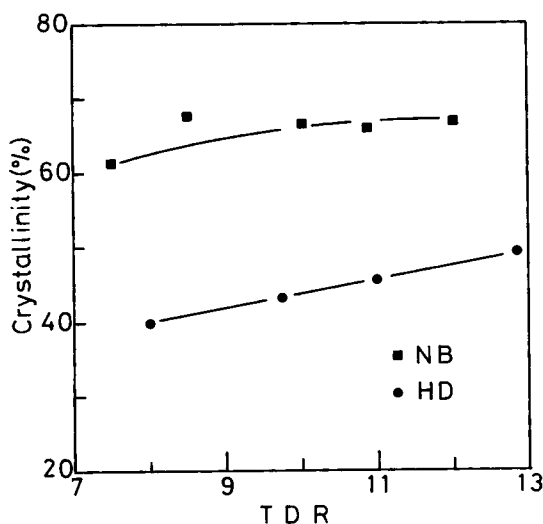


Fig. 4.   Crystallinity vs. TDR for NB and HD systems.

During the hot-drawing at 230°C, thermally and stress-induced crystallization proceeded, resulting in the increase in crystallinity. At any given TDR, the drawn fibers from the NB system show a markedly high crystallinity compared with drawn fibers from the HD system. It is to be noted that the mechanical properties of drawn fibers from the HD system are higher than those from the NB system despite the fact that the crystallinity of the former is lower than the latter.

Figure 5 shows the TDR dependence on the chain orientation factors of crystalline ($F_c$) and amorphous ($F_a$) regions of the two-stage drawn fibers. The $F_c$ was measured by the well-known X-ray diffraction method.[9] The $F_a$ was computed by combining the optical birefringence data with the $F_c$ and sample crystallinity. The intrinsic birefringences of the crystal and amorphous phases were taken to be 0.251 and 0.230, respectively.[10] The results demonstrate that the $F_c$ values for all the samples are close to each other and stay at an almost constant value of 0.95. However, the $F_a$ depends on the sample history and TDR. The $F_a$ for both series increases rapidly with TDR. Further, at any given TDR, the fibers from the HD system show a significantly high value compared with fibers from the NB system. As discussed above, the actual deformation ratio at a given TDR might be higher for the fiber from the HD system than for the fibers from the NB system, which is probably related to the difference in $F_a$ between the two series. The glass-transition temperature of isotropic PET is around 70°C. Thus, large-scale motion is almost frozen at room temperature in the oriented noncrystalline segments of PET. In this case, the mechanical properties of drawn PET at room temperature are markedly enhanced by the increased chain orientation in the noncrystalline regions.

## CONCLUSION

As-spun fibers from high molecular weight PET (IV = 2.41 dL/g) were prepared by the solution spinning method using two kinds of solvents: NB and
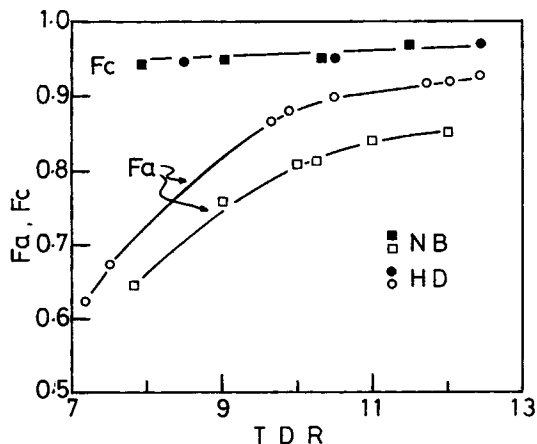


Fig. 5. Chain orientation factors in crystalline (Fc) and amorphous (Fa) regions vs. TDR for NB and HD systems.

HD. The morphology of as-spun fibers and the mechanical properties of two-stage drawn fibers were greatly affected by the solvents used. In the as-spun fibers from the HD system, a marked degree of chain orientation was evident. On the other hand, the preorientation was less in the as-spun fibers from the NB system. Both as-spun fibers could be drawn up to draw ratios of 12–13 by a two-stage drawing technique. The highest tensile modulus and strength of 275 g/d (34.4 GPa) and 15.5 g/d (1.9 GPa), respectively, were obtained for the drawn fibers from the HD system. These values were 15%–20% higher than for those achieved for drawn fibers from the NB system. The high efficiency of draw observed in drawn fibers from the HD system was explained by the high chain orientation in the noncrystalline regions, which was closely related to the preorientation existing in the as-spun fibers.

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