

Preparation of High Performance PET Fiber by Solution Spinning Technique

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SYNOPSIS

High molecular weight poly(ethylene terephthalate) (PET, IV = 3.30 dL/g) was extruded in attempts to prepare high performance fiber using the solution spinning method. Solution preparation, fiber coagulation, and mechanical properties of resultant fibers were examined. An as-spun fiber exhibited high deformability when appropriate coagulation conditions were used. Tenacity and modulus of the resultant drawn fibers achieved 12.9 and 230 gpd, respectively, at draw ratio above 10. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

High strength/high modulus fibers produced from flexible polymers have been studied by many workers.¹⁻¹⁶ However, most published reports on the structure and mechanical property of such fibers have involved polyethylene that could be drawn to extremely high draw ratios by various techniques.^{1,2,12-16} This led to products with ultrahigh modulus (~ 200 GPa). Success of the solution spinning of ultrahigh molecular weight polyethylene has prompted investigations of superdrawing of other kinds of flexible polymers.¹⁷⁻²⁰

Poly(ethylene terephthalate) (PET) is one of the most important commercial polymers, particularly in the form of oriented fibers. Also, it has great potential as a candidate for high performance fibers based on its theoretically predicted properties of crystalline modulus and strength.²¹⁻²³ Usually, PET fibers are obtained industrially by melt spinning, followed by hot stretching and heat treatment. Using this route, however, it is still difficult to produce tenacity and modulus above certain well-established levels, probably because of the low molecular weight of the parent polymer and the relatively low deformability of the crystalline PET fibers.

Molecular weight has been shown to have a marked effect on the mechanical properties of oriented polymers, and as is well known, generally, the higher the molecular weight, the higher the tensile strength.^{23,24} It follows that considerable effort is being expended on the production of high molecular weight polymers and their subsequent extrusion to form, hopefully, high performance fibers.

However, when the melt spinning route is employed to produce fibers with superior properties using PET of ultrahigh molecular weight, it is very difficult to spin the polymer because the melt viscosity is very high due to the ultrahigh molecular weight of the polymer and the fluidity of a melt thereof is very low. Then, if a higher spinning temperature is used to reduce the melt viscosity, a serious molecular weight drop occurs. These problems have directed attention to the solution spinning method.²⁵⁻²⁷ In the present study, the solution spinning method has been employed in attempts to prepare high strength/high modulus PET fibers.

EXPERIMENTAL

Sample Preparation

The high molecular weight PET sample used was supplied by The Goodyear Tire and Rubber Company. The intrinsic viscosity (IV) of the chips reported by Goodyear is 3.30 dL/g, determined in tri-

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Table I Dissolution Conditions for High IV PET

IV (dL/g)	Solvent	Concn. (%)	Dissolution	
			Temp. (°C)	Time (min)
3.30	Nitrobenzene	20	200	60
3.30	<i>m</i> -Cresol	15	150	40
3.30	Phenol/tetrachloroethane (50 : 50; w : w)	15	145	30
3.30	Dichloroacetic acid	12	110	40
3.30	Trifluoroacetic acid/ dichloroethane (40 : 60; w : w)	12	20	360

fluoroacetic acid. In our laboratory, the IV of the same chips was measured in phenol/tetrachloroethane (60 : 40; w : w) and was found to be 3.16 dL/g.

PET solutions were prepared by dissolving the polymer in various organic solvents including phenol, tetrachloroethane, *m*-cresol, nitrobenzene,

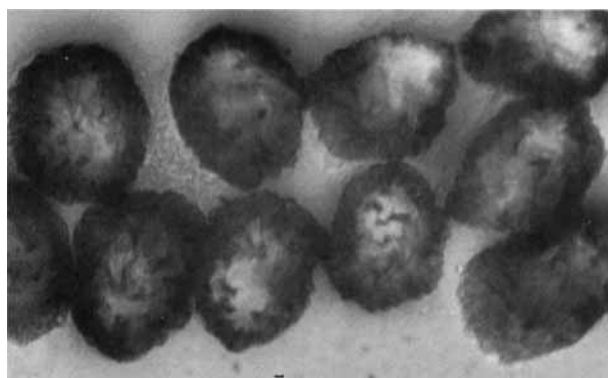
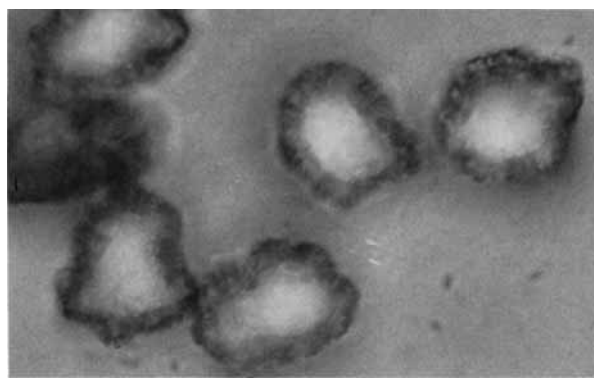
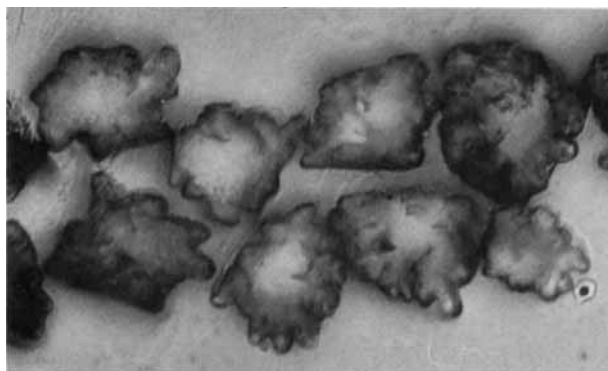
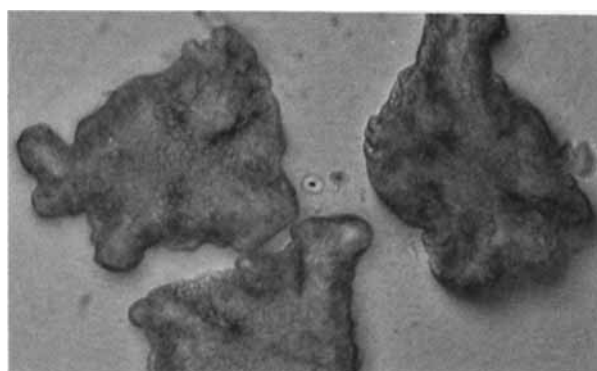
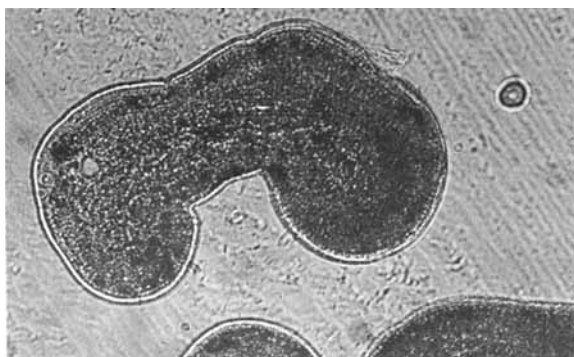
**a. Acetone****b. Methanol****c. Ethyl alcohol****d. Isobutanol****Figure 1** Effect of selected coagulants on the cross section of the as-spun fibers.

Table II Effect of Coagulant Composition on Drawing Behavior of As-spun Fibers at Coagulation Temperature 16°C

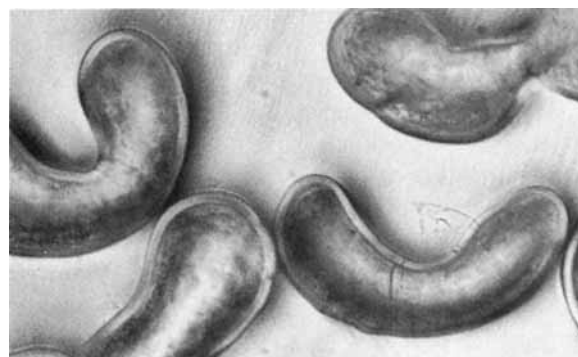
Coagulant	Draw Ratio		Notes
	Average	Maximum	
Pure methanol (meOH)	1.14	1.30	White, easy to take up
MeOH : H ₂ O = 10 : 1 (v : v)	3.08	3.65	Semitransparent, easy to take up
MeOH : H ₂ O = 5 : 1 (v : v)	4.12	4.75	Semitransparent, easy to take up
MeOH : H ₂ O = 3 : 1 (v : v)	6.81	8.80	Transparent, somewhat difficult to take up
MeOH : H ₂ O = 2 : 1 (v : v)	6.74	7.70	Transparent, difficult to take up

dichloroacetic acid, dichloroethane, and trifluoroacetic acid. The dissolving temperature required for the various solvents varies widely from room temperature to about 200°C. Polymer concentration was also varied for examining the dissolution characteristics and solution properties in the different solvents.

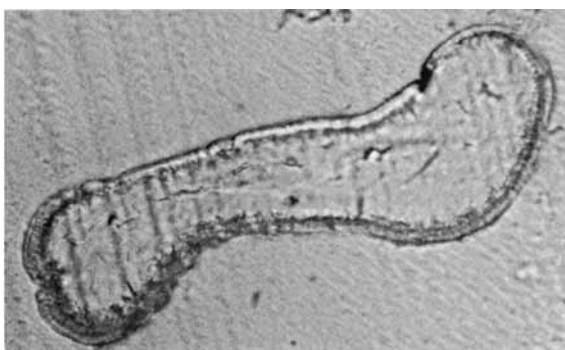
The continuous spin/draw equipment employed in this study is a typical solution spinning apparatus and a drawing device equipped with a heater plate. The polymer solutions at 20°C were extruded through a single hole spinneret, diameter 0.08 mm, into a coagulation bath. Several coagulants were tested including acetone, methanol, ethyl alcohol, isobutanol, water,



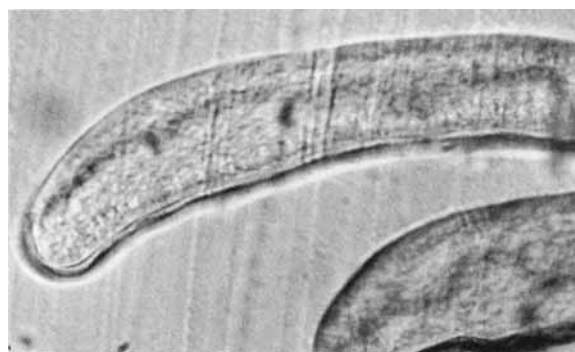
a. Temp.= 36°C



b. Temp.= 16°C



c. Temp.= 3°C



d. Temp.= -8°C

Figure 2 Effect of coagulation bath temperature on the cross section of the as-spun fibers.

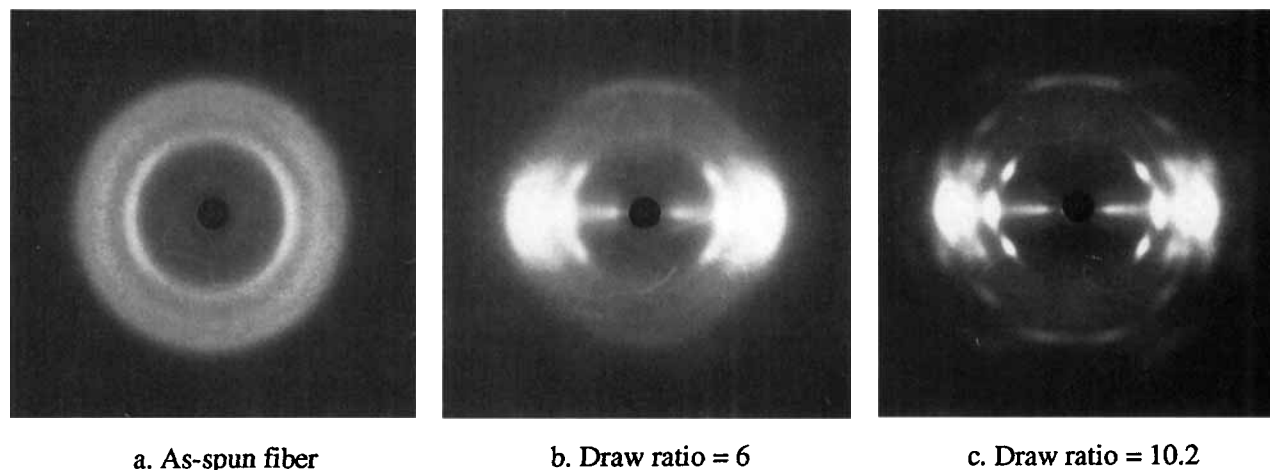


Figure 3 Wide-angle x-ray diffraction patterns of as-spun and drawn fibers.

as well as some aqueous mixtures. The length of the bath was 65 cm and it was equipped with temperature control. The average extrusion speed at the spinneret was about 80 m/min. The solidified as-spun fibers were stretched by a conventional two-stage drawing method, where the fibers were heated by passage over a heater plate and the drawing process was conducted between the feed roll and take-up roll. The draw-orientation conditions could be changed by controlling the heater plate temperature and the roll speeds. Some as-spun fibers were drawn at room temperature to draw ratios of 2–5, but most as-spun fibers were stretched at room

temperature at a rapid rate to the “natural draw ratio” of ca. 6 times and then drawn additionally at 180–200°C at a relatively slow rate (10 m/min) to draw ratios of 7–11. The actual draw ratio was determined from the linear densities of the sample measured before and after drawing.

Characterization of Fibers

Some fibers were characterized in the as-spun and drawn condition to determine the effects of processing on certain structural features. Microscopic

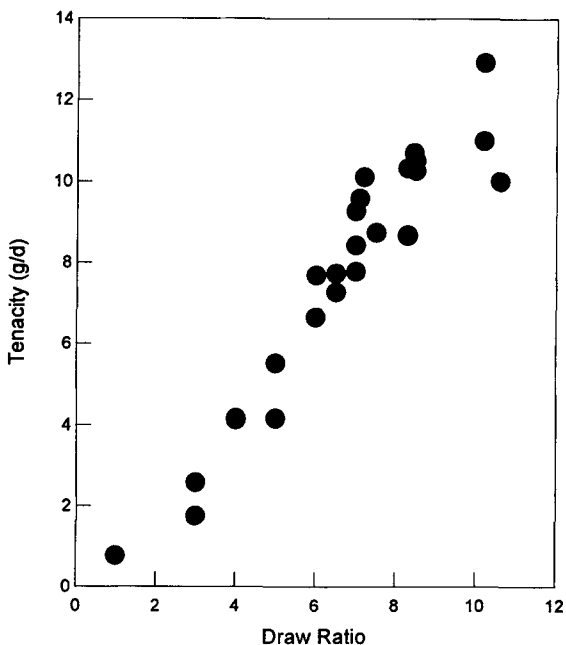


Figure 4 Tenacity of solution spun/drawn PET fibers as a function of draw ratio.

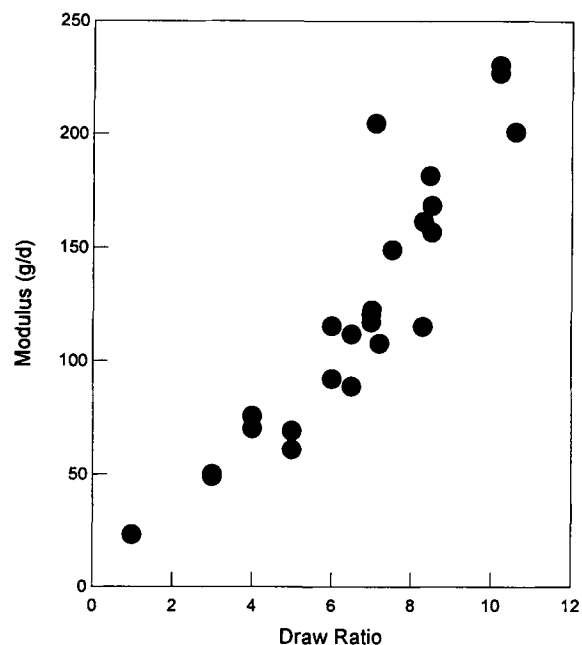


Figure 5 Initial modulus of solution spun/drawn PET fibers as a function of draw ratio.

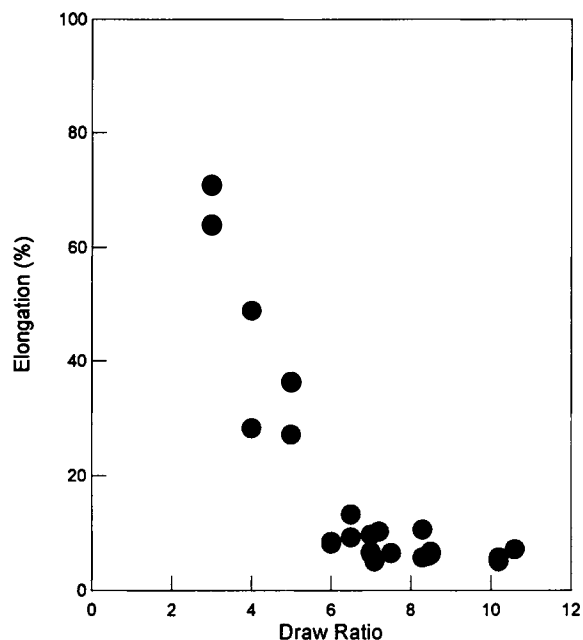


Figure 6 Elongation to break of solution spun/drawn PET fibers as a function of draw ratio.

studies followed standardized methods for the preparation of cross sections, with routine use of embedding and microtome techniques.²⁸

Fiber denier was determined by the vibroscope method in accordance with ASTM D1577. The linear density of the sample expressed by grams per centimeter, g/cm, was calculated using the following relation:

$$g/cm = t/(4L^2f^2)$$

here t is the fiber tension, L is effective fiber length, and f is the fundamental resonant frequency.

Wide-angle x-ray diffraction (WAXD) measurements were performed on a Siemens type-F diffractometer system with $CuK\alpha$ radiation. WAXD patterns were recorded by a vacuum flat camera.

Mechanical properties of as-spun, drawn, and drawn/annealed fibers were measured on an Instron machine model 1122 at room temperature. All tests were performed using a gage length of 25.4 mm and a constant crosshead speed of 20 mm/min. An average of five individual tensile determinations was reported for each sample.

RESULTS AND DISCUSSION

Selection of Solvent for PET Solution Spinning

The most commonly used solvents for preparing PET solutions are nitrobenzene, phenol, tetrachlo-

roethane, *m*-cresol, dichloroacetic acid, dichloroethane, trifluoroacetic acid, etc.²⁹⁻³¹ PET chip can be dissolved in these solvents over a wide temperature range from room temperature to 200°C. Examples of the dissolution conditions tested are listed in Table I. The highest polymer concentrations available by dissolving the PET in *m*-cresol and nitrobenzene are about 15 and 20 wt %, respectively. But high dissolution temperature of 150°C for the former and 200°C for the latter are required and the hot solutions solidified when cooled down. These solvents would require solution spinning to be conducted at high temperature with a certain molecular weight drop. For example, when *m*-cresol was used as solvent, the high dissolution temperature resulted in a large IV drop from 3.16 to 2.02 dL/g. The other three solutions prepared using a mixture of phenol/tetrachloroethane, dichloroacetic acid, and a mixture of trifluoroacetic acid/dichloroethane, are stable at room temperature. In particular, for the trifluoroacetic acid/dichloroethane mixture, the dissolution and processing of the fiber forming could be carried out at room temperature. This made it possible to retain a high IV (89% of the starting value). In our experiments, therefore, all spinning solutions were prepared using a solvent mixture of trifluoroacetic acid and dichloroethane (40 : 60; w : w). Polymer concentration of 8 wt % was selected for spinning, a value widely adopted by other researchers.^{27,29}

Effects of Coagulation Bath Composition

Several articles and patents have reported that acetone and methanol could be used as coagulants in the PET solution spinning process.²⁹⁻³¹ In this study, the coagulation effect of both these materials and other coagulants, including ethyl alcohol, isobutanol, and water, were examined. Figure 1 shows the photographs of the cross sections of the as-spun fibers prepared with four coagulants. In the two cases where acetone and methanol were used as the coagulant, coagulation occurred obviously first at the skin. The as-spun fibers are white, which may be attributed to the existence of many microvoids. The presence of the skin delays further coagulation of the fiber core, resulting in the formation of "skin-core" structure and a low deformability in as-spun fibers. These as-spun fibers were very fragile and essentially could not be drawn at room temperature. Such low deformability of the as-spun fibers could have been caused by an unusually fast coagulation rate. In other words, the coagulation rates of methanol and acetone are too high for the PET coagu-

lation. When ethyl alcohol was used, the photograph indicates that no obvious skin-core structure was formed, and the extrudate appears relatively transparent. Furthermore, when the PET solution was extruded into isobutanol or water, no obvious solidification was observed. The polymer extrudate looked like a transparent fluid and was so weak that wind up was nearly impossible. Following these experiments, a series of two component coagulants was prepared in which water was used as the retardant in the methanol bath and added over a wide range of concentrations. The deformability of as-spun fibers was determined in these mixtures. The results are shown in Table II. It appears that the proportion of water in the bath is a very important factor in the subsequent drawing step. It controls the kinetics of mass transfer. As the amount of retardant content increases in the spinning bath, the driving force for diffusion decreases, and the as-spun fiber becomes transparent and appears gel-like, so both the average draw ratio and maximum draw ratio are increased. For example, when the water content was 25 vol % (methanol 3 L : water 1 L), the draw ratio of as-spun fiber reached ca. 7–8.

Effects of Coagulation Bath Temperature

Examination of the effect of coagulation bath temperatures on deformability of the as-spun fiber was made after choosing the appropriate solvent system as coagulant. In the case of gel spinning of poly(vinyl alcohol), Cha et al. observed that the total draw ratio is significantly influenced by the coagulation temperature, where the highest draw ratio increases are attained at the lower coagulation temperatures.²⁰ A similar tendency has been observed in this work. With coagulation bath concentration constant at 75 vol % methanol and 25 vol % water, a progressive improvement in as-spun fiber deformability with decreasing bath temperature was clearly apparent. Achievable elongation to break of the as-spun fibers was low when a higher coagulation temperature ($\sim 40^\circ\text{C}$) was used. As the bath temperature is lowered, elongation to break increases, and reaches a maximum at around 10°C . Further lowering of the temperature occasioned the appearance of gel-like as-spun fibers, with attendant difficulty in the take-up operation. The operative mechanism associated with reduced bath temperature providing improved fiber deformability was also examined by examination of the initial structure of the as-spun fibers.

Optical photomicrographs on the cross section of PET solution spun fibers prepared at various coagulating temperatures are shown in Figure 2. Again,

bath temperature appears to influence very strongly the initial structure of the as-spun fiber. When the fiber was coagulated at 16°C or above, when coagulation rates are very likely to be extremely high, and the surface of the flowing polymer solution was solidified very rapidly, a skin-core structure was formed. The as-spun fibers are opaque and contain many voids. As the bath temperature was dropped, coagulation is retarded, and more time is available for diffusion of solvent and nonsolvent, in approximately equal volumes, across the fiber surface. As a result, the skin-core structure no longer appears, and gradually a relatively uniform structure and a higher deformability were obtained.

Structure and Mechanical Properties of Fiber Samples

Figure 3 shows WAXD patterns of: (a) undrawn fibers that were prepared using a methanol/water mixture coagulation bath (3 : 1; v : v) at 10°C ; (b) fibers uniaxially drawn 6 times at room temperature; and (c) fibers drawn 10.2 times at ca. 200°C . Figure 3(a) exhibits three uniform diffraction rings, identified as the (010), (110), and (100) reflections of the PET crystallite unit cell, and a diffuse halo that is due to the scattering of the random amorphous phase. In the cases of the two drawn fibers, the uniform diffraction rings observed in Figure 3(a) are concentrated near the equator, the pattern changed obviously from poorly resolved [Fig. 3(b)] to fairly well resolved [Fig. 3(c)], indicating that the two drawn samples are characterized by relatively high molecular chain orientation and well-developed crystal growth. However, it is worth noting the relatively wide diffraction arcs observed in the WAXD pattern of the hot drawn sample with draw ratio of 10.2 [Fig. 3(c)]. The pattern indicates that the crystalline orientation did not attain a very high level. This may reflect the difficulty in deforming the PET molecular chains using the normal hot drawing process. Other special techniques, such as zone annealing and solid-state coextrusion, might make this possible.^{24,26,32}

Figures 4, 5, and 6 show the respective relationships between tenacity, initial modulus, elongation to break, and draw ratio. These figures indicate that fiber with a high draw ratio exhibits significantly improved mechanical properties. The tenacity and modulus of PET fibers, respectively, increase rapidly with increasing draw ratio, and the elongation to break was greatly limited. The highest tenacity of 12.9 g/d and the highest modulus of 230 g/d were achieved at the high draw ratio of 10–11.

CONCLUSIONS

PET solutions were made in nitrobenzene, phenol, tetrachloroethane, *m*-cresol, and dichloroacetic acid. With all these solvents, however, high dissolution temperatures were required, and usually, a large molecular weight drop occurred. We found that the solution preparation and the fiber formation could only be carried out at room temperature using the solvent mixture trifluoroacetic acid/dichloroethane (40 : 60; w : w). This made it possible to maintain a high IV in the as-spun fibers.

A study was done to compare the effect of a variety of coagulants on the coagulation rate. As-spun fibers obtained from acetone or methanol baths showed low deformability, because the coagulation rate was too fast and then the fibers contained many voids. A series of two component coagulant baths was prepared in which water was used as the retardant. In combination with methanol, when the water content was 25 vol % (methanol 3 L : water 1 L), the as-spun fiber appears gel-like and the average draw ratio at room temperature reached ca. 7–8.

With the deformability of the as-spun fiber increasing, high tenacity/high modulus PET fibers have been obtained. The tenacity, elongation to break, and initial modulus (T/E/M) are, respectively, 12.9 gpd/5.7%/230 gpd. These values were obtained for draw ratios 10–11.

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Received August 8, 1994

Accepted November 22, 1994