

Melt Spinning and Drawing of 2-Methyl-1,3-Propanediol-Substituted Poly(ethylene terephthalate)

Jaein Suh,¹ J. E. Spruiell,¹ Steven A. Schwartz²

¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996-2200

²Lyondell Chemical Company, 3801 West Chester Pike, Newtown Square, Pennsylvania 19073-2387

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ABSTRACT: The structure and properties of fibers prepared from copolymers of poly(ethylene terephthalate) (PET) in which 2-methyl-1,3-propanediol (MPDiol[®] Glycol is a registered trademark of Lyondell Chemical Company) at 4, 7, 10, and 25 mol% was substituted for ethylene glycol were studied and compared with those of PET homopolymer. Filaments were melt spun over a range of spinning conditions, and some filaments that were spun at relatively low spinning speeds were subjected to hot drawing. The filaments were characterized by measurements of birefringence, differential scanning calorimetry (DSC) crystallinity, melting point, glass transition temperature, wide-angle X-ray diffraction patterns, boiling water shrinkage, tenacity, and elongation to break. Filaments containing 25 mol% MPDiol did not crystallize in the spinline at any spinning speed investigated, whereas the other resins did crystallize in the spinline at high spinning speeds. However, compared with PET homopolymer, increasing substitution of MPDiol reduced the rate at which the crystallinity of the melt spun filaments increased with spinning speed and reduced the ultimate crystallinity that could be achieved by high-speed spinning. The rate of development of molecular orientation,

as measured by birefringence, also decreased somewhat with increasing MPDiol content. Shrinkage in boiling water decreased at high spinning speeds as the amount of crystallinity increased; however, the shrinkage decreased more slowly with increase in spinning speed as MPDiol content increased. Tenacity also decreased slightly at any given spinning speed as MPDiol content increased, but there was no significant effect on elongation to break. The addition of MPDiol in amounts up to 7 mol% increased the maximum take-up velocity that could be achieved at a given mass throughput. This result indicates that the use of higher spinning speeds could potentially increase the productivity of melt spun yarns. Copolymer filaments spun at low speeds were readily drawn to produce highly oriented fibers with slightly less birefringence, crystallinity, and tenacity than similarly processed PET homopolymer. Preliminary dyeing experiments showed that the incorporation of MPDiol improved the dyeability of the filaments. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2598–2606, 2003

Key words: polyesters; fibers; drawing; melt

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used polymers for the formation of man-made fibers. Typically, PET is melt spun at high speeds to produce partially oriented filament yarns that can be used in the as-spun condition or further processed by drawing to produce highly oriented yarns. Although PET homopolymer has many outstanding properties for textile and industrial fiber applications, it exhibits limitations in certain properties such as dyeability, pilling resistance, and handle. Many random copolymers, in which a small amount of a third component is added to PET in an effort to improve on the properties of PET resins, have been investigated for fiber applications. An extensive literature exists on the subject, though much of it is in the patent literature. Morimoto¹ gave an excellent review of the early literature,

citing numerous examples including the commercially successful substitution of isophthalic acid or *p*-hydroxybenzoic acid for terephthalic acid to produce a polyester with improved dyeability and pilling resistance.

No prior studies of 2-methyl-1,3-propanediol-substituted polyester fibers could be found in the scientific literature, although two patents were found that describe the preparation of such polymers.^{2,3} (2-methyl-1,3-propanediol will henceforth be referred to as MPDiol; MPDiol[®] Glycol is a registered trademark of Lyondell Chemical Company). The first of these patents was about polymers intended for fabricating polyester bottles with improved transparency.² The second claims that fibers produced from polymers containing up to 15 mol% MPDiol substituted for ethylene glycol have enhanced dyeability, greater strength, and reduced elongation to break.³ The present research was carried out to determine the effect of partial substitution of MPDiol for ethylene glycol in the preparation of PET-based polyester resins. From a practical perspective, the primary purpose of these studies was to determine whether such copol-

Correspondence to: J. E. Spruiell.

ymers provide specific advantages over PET homopolymer, either during the processing of the fibers or in the properties of the fibers. From a more fundamental perspective, these resins provide a model system for studying the influence of random substitution of an asymmetric monomer for part of the ethylene glycol in PET on fiber processing and final properties.

EXPERIMENTAL

Materials

A PET homopolymer (control) and four copolymers were prepared and supplied to us by Wellman, Inc. The copolymers had nominal (feed) compositions of 4, 7, 10, and 25 mol% MPDiol substituted for the ethylene glycol moiety in PET. A check on the compositions by nuclear magnetic resonance spectroscopy (NMR) gave slightly higher MPDiol content in each case (i.e., 5, 9, 12, and 33 mol%, respectively), but the correlation was good and it was decided to use the nominal compositions in describing the results of our experiments. All resins were supplied as pellets, with an intrinsic viscosity of 0.61 ± 0.01 dL/g.

Melt spinning and drawing procedure

Prior to melt spinning, the resins were dried by heating under modest vacuum for 8 h at 110°C (10 h for the 25 mol% copolymer). Filaments were spun using the same equipment used in earlier studies from our laboratory.⁴⁻⁸ The melt spinning experiments were performed using a screw extruder (Fourné Associates of West Germany) equipped with a constant-displacement melt pump that provided a constant extrusion rate. The PET homopolymer and all MPDiol-substituted copolymers, except the 25 mol% MPDiol resin, were spun with the same temperature settings; the temperatures of zones 1, 2, 3, and 4 (spinneret) in the extruder were 273, 295, 280, and 265°C, respectively. The settings for the 25 mol% MPDiol copolymer were 210, 280, 280, and 265°C, respectively. Molten polymer, supplied by the melt pump, was forced through a filter mesh and then through either a four-hole or single-hole spinneret with capillary diameters of 0.762 mm and $L/D = 5.0$. Using the four-hole spinneret, filaments were spun with total mass throughputs for all four holes ranging from ~ 2.5 to 12 g/min (0.625–3.0 g/min/hole). The mass throughput for filaments spun with the single-hole spinneret ranged from ~ 2.15 to 8.25 g/min/hole.

Filaments spun at speeds below ~ 1200 m/min were wound onto a 6-in. diameter bobbin with a Lessona winder. For higher take-up speeds, up to 6000 m/min, the filaments were wound directly on a high-speed godet. The spinline length was kept constant at 3.5 m (350 cm).

TABLE I
Temperatures Used for the Drawing Experiments

T_1 (°C) First Stage	T_2 (°C) Second Stage
80	90
80	110
85	95
85	110
90	100
90	110

The take-up velocities, V , were determined using the continuity equation, assuming a steady-state spinning process:

$$W = \rho AV = \rho \pi \left(\frac{D^2}{4} \right) V \quad (1)$$

where W is the measured mass throughput, ρ is the filament density, and D is the filament diameter. It is important to note that this method of determining the take-up velocity underestimates the actual take-up velocity due to change of filament diameter when the filament is allowed to relax. However, it is believed that this effect is similar for all the resins and should not have an appreciable effect on the comparisons made.

The PET homopolymer and the MPDiol-containing resins were subjected to post-spinning drawing experiments using a two-stage continuous drawing technique. Drawing was carried out on samples that were melt spun with take-up velocities of 600 and 1200 m/min. The temperature of the second stage (draw roll) was always chosen to be a bit higher than that of the first stage (hot-plate). The resins were drawn under a range of drawing temperatures, as indicated in Table I.

The draw ratios (DR) were determined from the following equation:

$$\text{Draw Ratio (DR)} = \frac{l_f}{l_o} \cong \frac{W_o}{W_f} \quad (2)$$

where W_o is the weight in grams of one meter of fiber before drawing and W_f is the weight in grams of one meter of fiber after drawing.

Filament characterization

Filament birefringence was measured with an Olympus polarizing microscope, with a 10- or 30-order Berek compensator.

The degree of crystallinity was determined by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 with an intercooler and nitrogen gas purge. Equipment calibration was performed periodically with an indium standard [$\Delta H = 28.45$ J/g; T_m

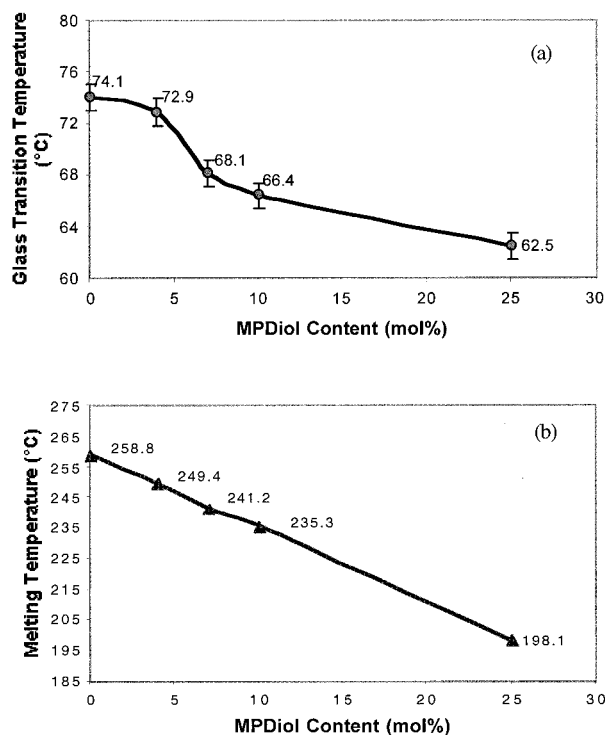


Figure 1 (a) Glass transition temperature and (b) peak melting temperature as a function of MPDiol content.

(onset) = 156.61°C]. Test runs involved heating from 50 to 290°C at a scanning rate of 20°C/min. Although each test run was normalized to the sample mass, care was taken to ensure that the mass of each sample remained fairly consistent (5–7 mg) for data precision. The degree of crystallinity for each fiber sample was found by subtracting the enthalpy of crystallization from the enthalpy of melting and dividing the difference by the specific heat of melting for PET ($\Delta H_{c, \text{PET}} = 140 \text{ J/g}$).

The filament shrinkage was measured in boiling water. Filament sections a few centimeters long were immersed in the boiling water for 180 s. The %shrinkage was calculated from the following equation:

$$\% \text{Shrinkage} = \left(\frac{L_i - L_f}{L_i} \right) 100 \quad (3)$$

where L_i is the initial sample length (before shrinkage) and L_f is the final sample length (after shrinkage).

Tensile properties of filament samples were measured at room temperature on a Table Model 1122 Instron tensile tester using a gauge length of 25 mm and a constant crosshead speed of 50 mm/min. Six filament specimens from each sample were tested to break and the properties averaged.

Wide-angle X-ray diffraction (WAXD) flat plate patterns were used to compare the relative crystallinity and orientation of the crystalline phase in the fila-

ments. The flat plate patterns were obtained with nickel filtered $\text{CuK}\alpha$ radiation and a wavelength of 1.542 Å.

RESULTS AND DISCUSSION

Melt spun filaments

Basic thermal properties

The values of the glass transition temperature and melting temperature of fibers spun at low speed ($\sim 1400 \text{ m/min}$) and that have a very low amount of molecular orientation are shown in Figure 1. The incorporation of MPDiol into the PET chain lowers both the glass transition temperature and the melting temperature, as expected based on earlier studies of copolyesters containing primarily ethylene terephthalate units.^{1,9,10} The melt temperature decreases approximately linearly with MPDiol content, whereas the glass transition temperature decreases in a more complex way. The physical chemistry of these changes will be discussed in a subsequent paper. We are concerned here merely with the effect of MPDiol content on fiber properties. Certainly, glass transition temperature and melting point are important fiber properties because they control the temperature range for processing and use of the fibers.

DSC crystallinity

Our DSC crystallinity measurements indicate that increasing the percentage of the MPDiol comonomer lowers the crystallinity of the melt spun filaments. This result is illustrated in Figure 2 for filaments spun with a mass throughput of $\sim 2.1 \text{ g/min/hole}$. The actual mass throughput for each resin is shown in the legend of Figure 2.

The PET homopolymer filaments exhibit the well-known increase of crystallinity with take-up velocity caused by stress-induced crystallization.^{11,12} Except for the 25 mol% MPDiol filaments, the crystallinity of

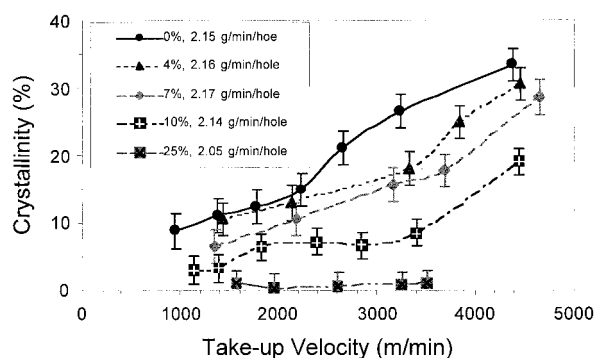


Figure 2 Crystallinity as a function of take-up velocity for filaments prepared with a nominal mass throughput of 2.1 g/min/hole.

the other resins also increased as take-up velocity increased. Within our ability to make the measurements, the 25 mol% MPDiol samples showed virtually no crystallinity at any take-up velocity. At the same take-up velocity, the crystallinity decreases with the increase of MPDiol content. This result suggests that the MPDiol is unable to be incorporated into the PET crystal structure. The process of sorting through the polymer segments and rejecting the MPDiol units would be expected to reduce the rate of crystallization and lower the ultimate crystallinity that is obtained. Because the development of crystallinity, at some level, is an important attribute, we concentrate our attention henceforth on the resins with MPDiol content of <25 mol%.

Studies of the effect of mass throughput showed that increasing the mass throughput resulted in slightly lower crystallinity at any given take-up velocity. This result can be explained on the basis that cooling rate in the spinline is faster for the lower mass throughput, which leads to an increase of spinline stress and molecular orientation in the filaments spun with the lower mass throughput at any given spinning speed. In turn, the latter results in greater stress-induced (molecular orientation enhanced) crystallization. It is noteworthy that higher cooling rate in the absence of molecular-orientation-enhanced crystallization would be expected to lower crystallinity rather than increase it because of the shorter time available for crystallization in the appropriate temperature range. However, it is well known that crystallization in as-spun PET fibers is virtually all stress induced.^{11,12}

Birefringence

The birefringence as a function of take-up velocity is shown in Figure 3(a) for filaments spun with a mass throughput of ~ 2.15 g/min/hole. The error bars shown for PET are also representative of the errors in the other data. Note that the birefringence of all the resins is the same, within experimental error, up to a take-up velocity of ~ 2000 m/min. At higher spinning speeds, the PET homopolymer develops birefringence slightly faster than the copolymers because of the greater stress-induced crystallization in the PET homopolymer. In the case of stress-induced crystallization, the crystals nucleate and grow with high levels of orientation; thus, higher crystallinity also leads to higher overall molecular orientation and birefringence. Below ~ 2000 m/min oriented crystals do not contribute significantly to the birefringence. However, above this take-up velocity, oriented crystal nucleation and growth contribute to the overall orientation measured by the filament birefringence. This interpretation is consistent with the PET literature^{11,12}

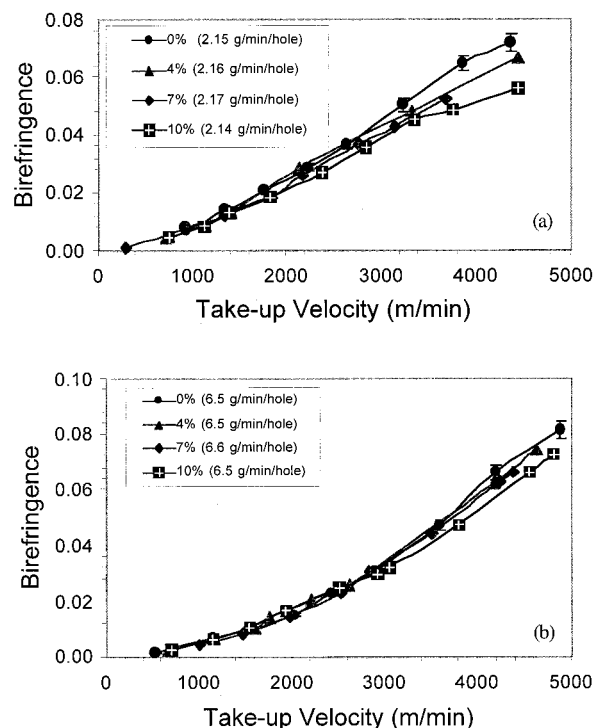


Figure 3 Birefringence versus take-up velocity: (a) nominally 2.15 g/min/hole, and (b) nominally 6.5 g/min/hole.

The birefringence of filaments spun at a higher mass throughput of ~ 6.5 g/min/hole is shown in Figure 3(b). The birefringence values rise a bit more slowly with take-up velocity at the higher mass throughput, and there is not as much separation among the different resins at high take-up velocities. These effects are attributed to the decrease of spinline stress due to the higher mass throughput.

X-ray diffraction patterns

Flat-plate X-ray diffraction patterns were made of filaments prepared from the PET homopolymer, 4 mol% MPDiol-substituted PET, and 10 mol% MPDiol-substituted PET. These patterns provide a qualitative measure of orientation and crystallinity for comparison with the values of birefringence and DSC crystallinity. The patterns of selected filaments are shown in Figure 4. Crystallinity is barely detectable in the PET homopolymer at a take-up velocity of 2230 m/min and a mass throughput of 2.15 g/min/hole. At the same mass throughput, the crystallinity and crystalline orientation of the PET homopolymer are well developed at a take-up velocity of 4370 m/min. Likewise, at the higher mass throughput of 6.5 g/min/hole, the PET homopolymer developed high crystallinity and crystalline orientation. Note, however, that at similar take-up velocities and mass throughputs, the 10 mol% MPDiol filaments exhibit substantially lower crystallinity. These results are in general agreement with the results

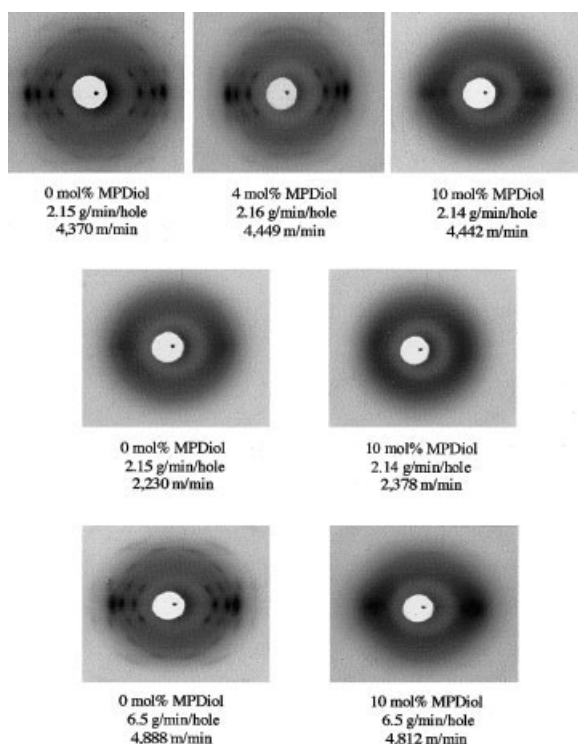


Figure 4 X-ray diffraction patterns of selected filaments at the indicated take-up velocities and mass throughputs.

of the birefringence and DSC crystallinity measurements (Figures 2 and 3). At the lower take-up velocities, only amorphous halos could be seen, which are attributed to the low degree of orientation and negligible crystallization. With increase of take-up velocities, the amorphous halos first become more concentrated on the equator, indicating improved orientation of the molecules and possible development of a mesophase. For PET and 4 mol% MPDIol filaments, sharp crystalline reflections appear at ~ 2500 m/min and increase in intensity as take-up velocity is further increased. In the case of 10 mol% MPDIol-substituted PET, the crystalline reflections were not as well developed as those of 0 and 4 mol% MPDIol-substituted PET. This result correlates well with the DSC results of Figure 2 that show a substantially lower level of crystallinity developed in the 10 mol% MPDIol-containing filaments.

Shrinkage

Shrinkage in boiling water for the filaments spun at a mass throughput of ~ 2.15 g/min/hole is shown in Figure 5(a). At low spinning speeds, the shrinkage increases due to the increase in the molecular orientation with increased spinning speed. The orientation is frozen-in below the glass transition temperature, but relaxes out, producing the shrinkage, when the filaments are heated in boiling water. At higher spinning

speeds, the development of crystallinity tends to stabilize the filaments and reduce the shrinkage for all filaments except the 25% MPDIol composition, which does not develop measurable crystallinity. As the level of crystallinity developed in the filaments increases, the shrinkage decreases. Note that the trend is consistent with the change in crystallinity due to composition change as well as with change in spinning speed. The filaments with higher MPDIol content require higher spinning speeds to achieve a given reduction in shrinkage. The shrinkage of the PET homopolymer drops off to a value of $\sim 3\%$ at the highest take-up velocities. The 4 and 7 mol% MPDIol resins also exhibit low shrinkage at high take-up velocities. Note that the 10 mol% MPDIol filaments never reach as low a value in Figure 5(a), presumably due to the development of lower ultimate crystallinity, as shown in Figure 2 and by the X-ray diffraction patterns of Figure 4.

Shrinkage data for filaments spun with a mass throughput of ~ 6.5 g/min/hole are shown in Figure 5(b). In general, higher spinning speeds are required to achieve the reduction in shrinkage because the crystallinity develops more slowly with spinning speed at this higher mass throughput.

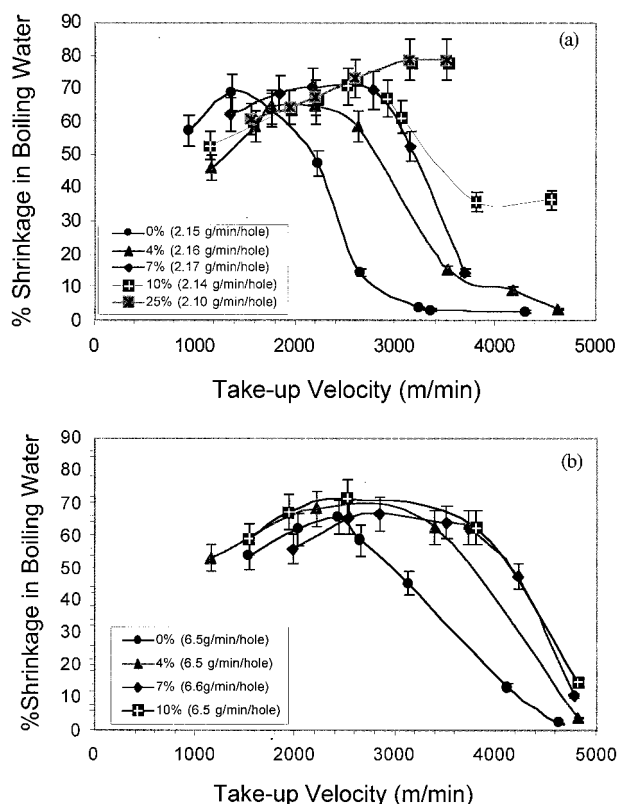


Figure 5 Shrinkage in boiling water: (a) nominally 2.15 g/min/hole, and (b) nominally 6.5 g/min/hole.

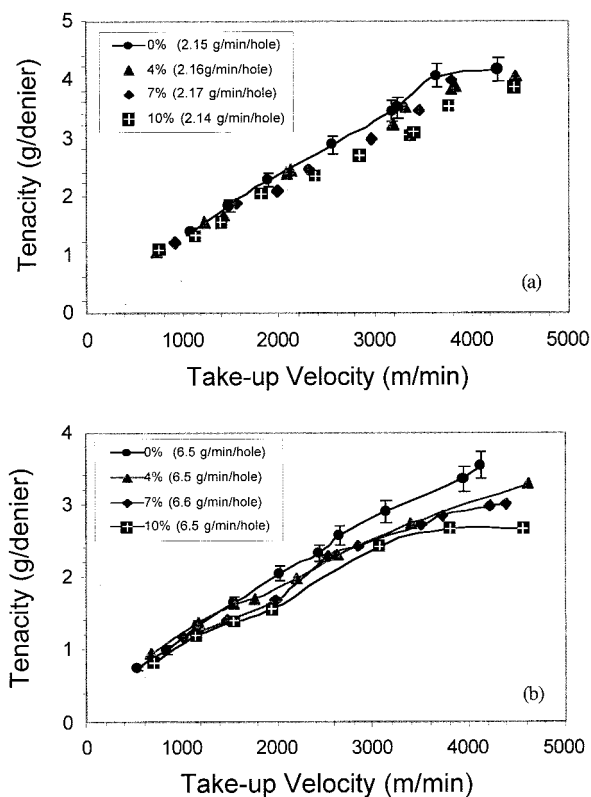


Figure 6 Tenacity of the melt spun filaments: (a) nominally 2.15 g/min/hole, and (b) nominally 6.5 g/min/hole.

Tensile properties

The tensile properties of filaments prepared from the PET homopolymer and its MPDIol-substituted copolymers are shown in Figures 6 and 7. The tenacity values increase, whereas the values of strain at break decrease with take-up velocity, because the tenacity is determined by (a) the degree of chain extension and (b) the degree of molecular orientation relative to the fiber axis, the results of tenacity measurements correspond closely to expectation based on the birefringence measurements. As would be expected from examination of the birefringence data, the tenacity decreases slightly with increase of MPDIol content, at the same take-up velocity. The strain at break (Figure 7) does not appear to depend significantly on the MPDIol content.

Filament spinnability

All the resins exhibited excellent spinnability. The maximum take-up velocity for stable spinning (no breaks observed within 15 min) as a function of MPDIol content at two different mass throughputs is shown in Figure 8. The extruder temperature profile and other conditions were kept the same for all runs to exclude effects other than the MPDIol content. As shown in Figure 8, the maximum take-up velocities

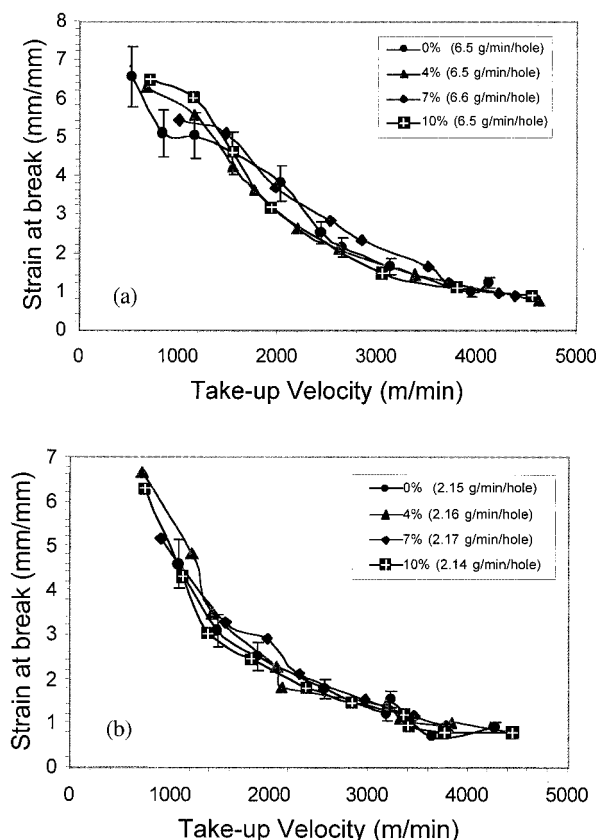


Figure 7 Strain at break: (a) nominally 2.15 g/min/hole, and (b) nominally 6.5 g/min/hole.

increase until the MPDIol composition reaches ~ 7 mol% and then decreases slightly with further increase of MPDIol content. The precise reason for this behavior is not known. However, we may hypothesize that the slower development of crystallinity initially allows a greater draw-down and higher take-up velocity before reaching the critical stress for spinline fracture to occur. At some concentration of MPDIol, the rate of development of crystallinity is insufficient to provide the deformation strengthening needed to

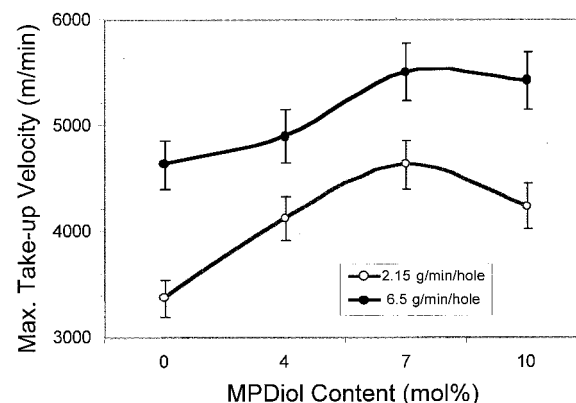


Figure 8 Maximum spinning speed as a function of mass throughput and MPDIol content.

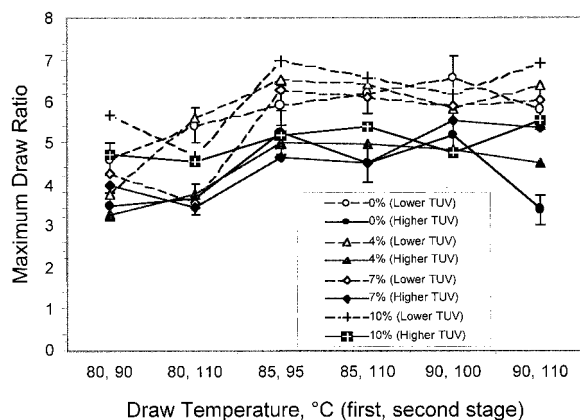


Figure 9 Maximum draw ratio as a function of drawing conditions and MPDiol content.

further increase the draw-down without fracture. At this point, a maximum is reached, and further increases in MPDiol content reduce the maximum spinning speed. In the present case, the maximum is reached at ~ 7 mol% MPDiol at both mass throughputs.

Drawing of spun filaments

The PET homopolymer and all MPDiol-substituted copolymers except the 25 mol% MPDiol resin were melt spun with mass throughputs of ~ 8.25 g/min/hole and taken-up at two different take-up velocities (600 and 1200 m/min) to produce eight filament samples for post-spinning drawing experiments. These eight as-spun filament samples were drawn (see Experimental) with six different combinations of first-stage hot plate and second-stage draw roll temperatures. The overall purpose of these experiments was to find the drawing condition(s) for the optimum mechanical properties of the drawn filaments.

The maximum draw ratio achieved at each combination of draw temperatures, as-spun take-up velocity, and MPDiol content are shown in Figure 9. The results show that the maximum draw ratios were greater for the filaments spun at the lower take-up velocity, as expected. Note, however, that the higher take-up velocity is still below the range where significant crystallinity is developed in the spinning process, even for the PET homopolymer. Consequently, the effect is largely due to higher molecular orientation developed in the filaments spun at the higher spinning speed. From the standpoint of maximum achievable draw ratio, there is a fairly wide window of draw temperature combinations that give nearly equivalent maximum draw ratios. Further, the maximum draw ratios are weakly dependent on the MPDiol content, with the 10% MPDiol resin tending to give slightly higher draw ratios, on the average.

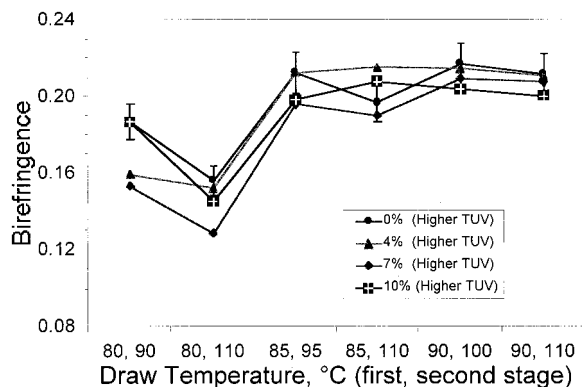


Figure 10 Filament birefringence as a function of drawing conditions and MPDiol content.

The birefringences of the drawn filaments, corresponding to the maximum draw ratios of Figure 9, are presented in Figure 10 for the filaments spun at the higher take-up velocity. The results for the lower take-up velocity filaments were quite similar. The final birefringences of all the drawn fibers are significantly greater than the birefringences of any of the as-spun filaments shown in Figure 3. Further, it is clear that drawing at the 80, 110°C (first-stage, second-stage) combination is not as effective at producing molecular orientation in the final fibers as several of the other combinations. Apparently, the low first-stage hot plate temperature combined with the high second-stage draw roll temperature allows significant relaxation of the molecular orientation compared with the cases with a higher first-stage hot plate temperature. This result is likely due to a lower level of crystallinity developed during the first-stage draw when the drawing occurs at the lower temperature. Based on the birefringence data of Figure 10, the best drawing conditions examined appear to be with a first-stage hot plate temperature of $\sim 90^\circ\text{C}$ and a second-stage draw roll temperature of $\sim 100^\circ\text{C}$.

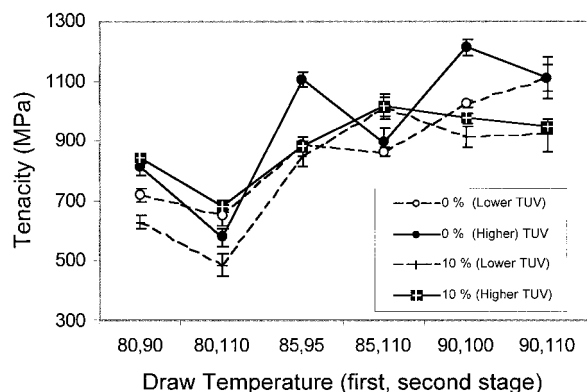


Figure 11 Tenacity as a function of drawing conditions for the PET homopolymer and 10 mol% MPDiol copolymer.

The tensile properties of the drawn filaments containing 0 and 10 mol% MPDiol are shown in Figure 11. These data correlate fairly well with the birefringence data in that the highest tenacity is obtained for a first-stage hot plate temperature of 90°C for the PET homopolymer.

X-ray diffraction patterns of selected drawn filaments indicate that the crystalline orientation in the copolymers is similar to that in the homopolymer after equivalent drawing operations. However, the DSC results show that the crystallinity of the drawn filaments decrease with MPDiol content. For example, the crystallinity of the homopolymer drawn to the maximum draw ratio at the 90,100 condition (first-stage, second stage draw temperature) is $\sim 38.8 \pm 2.0\%$, whereas the crystallinity of a similarly drawn 10 mol% MPDiol filament is $\sim 32.0 \pm 2.0\%$.

Preliminary dyeing tests were run on filaments containing 0 and 10 mol% MPDiol drawn at the 90,100°C condition to a draw ratio of 3.5 \times . Samples for dyeability evaluations were provided in a cut yarn form. The 10-g test samples were tied into loops to form puffs and then submerged into sealed jars containing 2 wt% (on weight of fiber) disperse dye solutions [Dianix Blue AD-R from Dystar (CAS E M00980), pH = 4.5]. The jars were mounted into an infrared (IR) color oven that was set to continuously rotate at 15 rpm and programmed with the following temperature cycle: heat from 25 to 100°C at 2°C/min; hold at 100°C for 45 min; and cool from 100 to 50°C at 2°C/min. Following the dyeing cycle, the samples were rinsed with cool water and hung to dry.

Visible absorption spectra run on the dye baths indicated a substantial increase in the dye exhaustion for MPDiol-substituted PET filaments. The MPDiol-containing filaments also exhibited increased color development; that is, they dye darker under equivalent dyeing conditions. Stated another way, these data suggest that MPDiol-modified PET can produce equivalent shades at lower temperatures and in an open beck exhaust dyeing process.

Further discussion of results

One of the ways that the productivity of PET filament yarns can be increased is by increasing the spinning speed,¹¹⁻¹⁴ which allows greater throughput with the same size plant and equipment. It is recognized that a reduction in the molecular orientation developed during the fiber formation process may allow higher spinning speeds to be realized. Of course, it is important to maintain the properties of the spun filaments. So, the basic idea is to develop a modified PET that can be spun at higher spinning speeds to achieve the same molecular orientation and properties in the spun filaments, thus improving productivity while maintaining properties. Stated another way, one needs to re-

duce the level of orientation developed at a given spinning speed while not changing quantities such as molecular weight that would affect the achievable properties. One previously described^{13, 14} method to achieve such a reduction in molecular orientation at a given spinning speed involves adding a proprietary material to the PET melt via a twin screw extruder. It appears that the substitution of MPDiol for a fraction of the ethylene glycol in PET is another method to achieve this result. Another advantage of the ability to spin at higher spinning speeds with the same mass throughput (Figure 8) is that this allows spinning of finer denier filaments, which produces better comfort in the textile end-use.

The available data for the present drawn fibers show that the 10% MPDiol resin can be processed to achieve similar tenacity and elongation to break as that of the PET homopolymer in drawn yarns. From the point of view of mechanical properties, one possible advantage of MPDiol-containing fibers is that it is possible to prepare filaments with similar or higher tenacity, but lower Young's modulus, from the copolymer. It is well known that reduction in crystallinity of fiber also reduces its modulus,⁷ which might produce a better fabric hand for some applications.

For draw-textured yarns, the dyeability of the MPDiol-substituted yarns may be better because of the lower crystallinity in the processed filaments. The patent of Chen et al.² claims that the substitution of a few mol% MPDiol for ethylene glycol will result in substantial improvement in the dyeability of spun and drawn yarns. The inventors found that 3-5 mol% MPDiol resulted in a 20-27% improvement in dye uptake. The preliminary measurements of dye uptake for the present drawn fibers indicated that the MPDiol-containing fibers exhibited greater dye uptake than similarly processed PET homopolymer, which is in qualitative agreement with the aforementioned patent. However, this patent also claimed improvement in the tenacity and reduction in the strain at break. However, the present data do not appear to confirm such a claim, though it is possible to prepare copolymer filaments with higher tenacity than homopolymer filaments that were prepared in some specified way.

CONCLUSIONS

Based on our results we can conclude the following:

- (1) Within the range of spinning speeds so far achieved, the 25 mol% MPDiol-substituted resin does not crystallize in the spinline to any appreciable extent. As a result, it exhibits high shrinkage at all take-up velocities. This result probably precludes the use of resins with this much MPDiol for most fiber applications.

- (2) Resins containing 10 mol% MPDiol or less do exhibit appreciable crystallization in the spinline, though the presence of MPDiol reduces the crystallinity compared with that of filaments prepared from PET homopolymer.
- (3) Up to spinning speeds of ~ 2500 m/min, all resins exhibited similar birefringence. Above this spinning speed, the rate of increase of birefringence with take-up velocity differed for the different resins, with the PET homopolymer having the highest rate of increase. It was suggested that this result is due to a greater amount of oriented nucleation and growth of crystals at high spinning speeds in the PET homopolymer than in the copolymer filaments.
- (4) Shrinkage in boiling water first increased, then reached a maximum, and finally decreased to much lower values at high spinning speeds (>3000 m/min). The minimum shrinkage achieved does increase as the content of MPDiol increases. It was suggested that the decrease of shrinkage at high spinning speeds is due to the stabilizing effect of crystallization. Higher crystallinity gives greater stability (i.e., lower shrinkage). Thus, the lower crystallinity of the MPDiol-containing filaments results in higher shrinkage values.
- (5) At the same take-up velocity, a decrease of the mass throughput increases the birefringence and crystallinity and reduces shrinkage.
- (6) At the same take-up velocity, increasing MPDiol content decreases crystallinity, birefringence, and tenacity, though the latter effects were small.
- (7) Higher maximum spinning speeds could be obtained with the addition of MPDiol. The optimum MPDiol content for this purpose appears to be substitution of MPDiol for ~ 7 mol% of the ethylene glycol that would be present in the PET homopolymer. However, the determination of the precise MPDiol content that would produce

the best combination of spinning speed and properties should be further evaluated using commercial scale equipment.

- (8) Filaments containing MPDiol can be drawn to give mechanical properties similar to those of PET homopolymer.
- (9) The chemical modification of PET studied here can potentially lead to higher productivity in textile yarn spinning due to increased spinning speeds. It may also have the potential to produce yarns with finer denier per filament.

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