Effects of Modified Air Quenches on the High-Speed Melt Spinning Process

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SYNOPSIS

A high molecular weight polyethylene terephthalate was spun into fibers in the speed range from 3,000–7,000 mpm. The effect of modifying threadline dynamics through a combination of enhanced and/or retarding air quenches on the resulting spinning performance, fiber structure, and mechanical properties was examined. Particular combinations of these threadline temperature profile modifications were shown to result in significant improvements in spinning performance and as-spun fiber structure. Extensive characterization of select fiber samples revealed higher orientation and crystallinity, larger crystal dimensions, and greater mechanical properties. These results also demonstrated the ability to provide continued improvement in fiber properties at very high take-up speeds where typically a decline is observed. It is concluded that the threadline temperature profile can be altered in such a way as to significantly enhance the resulting spinning performance and fiber structure over a wide range of take-up speeds.

INTRODUCTION

This study was performed as a continuation of the previously published study on modifying threadline dynamics in the high-speed melt spinning process.[1] It consisted of extending the previous experiments by using a higher intrinsic viscosity polyethylene terephthalate (PET) (0.95 dL/g vs. 0.57 dL/g), as well as a broader range of take-up speeds. Intent of the original experiment was to enhance the level of orientation and mechanical properties of the as-spun filaments by altering the threadline dynamics. The dynamics were modified by controlling the temperature profile of the threadline through the use of either an on-line zone cooling (OLZC) or heating (OLZH) device, as well as combinations of these devices (OLZCH). Description and illustration of the positions and temperatures over which these devices were operated are presented in the experimental section. As described in the earlier experiments, the ultimate objective of this work is to develop a one-step high-stress spinning process capable of producing highly oriented PET filaments with the mechanical properties necessary to replace, and surpass, conventionally drawn filaments. The following sections outline the procedure followed and the results obtained thus far on the progression toward this ideal one-step process (OSP).[2]

EXPERIMENTAL

Fiber Spinning

A high molecular weight PET with an intrinsic viscosity of 0.95 dL/g was used to produce all the fiber samples from which the presented data were collected. For each sample produced, the following process conditions remained constant: extrusion temperature of 305°C, 5.0 denier monofilament product, and a single-hole 0.6-mm exit diameter conventional spinneret. The term denier is defined as the weight in grams of 9,000 m filament or yarn as designated.

The best way to distinguish the fiber sample sets is the type of quench modification imposed during spinning. These will be referred to in the following manner: on-line zone cooling (OLZC), on-line zone heating (OLZH), and a combination of first on-line

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zone cooling and then heating (OLZCH). These samples were prepared to determine the effect of various combinations of threadline cooling conditions on the stability of the spinning process and the resulting properties of the as-spun filaments. The OLZC chamber was held constant at a position of 12.7–33.0 cm below the spinneret and a temperature of 23°C. As for the OLZH chamber, its position and temperature were varied over the ranges from 17.5–137.7 cm below the spinneret and 90–310°C. Figure 1 illustrates the positioning for each type of quench condition. The specifications of each of these cooling or heating devices are as follows:

Zone Cooling

Air Flow:	300 fpm, radially inward
Dimensions:	length, 20.3 cm; inside diameter, 8.3 cm

Zone Heating

Air Flow:	300 fpm, radially inward
Dimensions:	length, 12.7 cm; inside diameter, 8.1 cm

For each of these combinations of cooling and/or heating, the take-up or winding speed was varied over the range from 3,000–7,000 mpm or the highest speed possible above which the threadline became unstable.

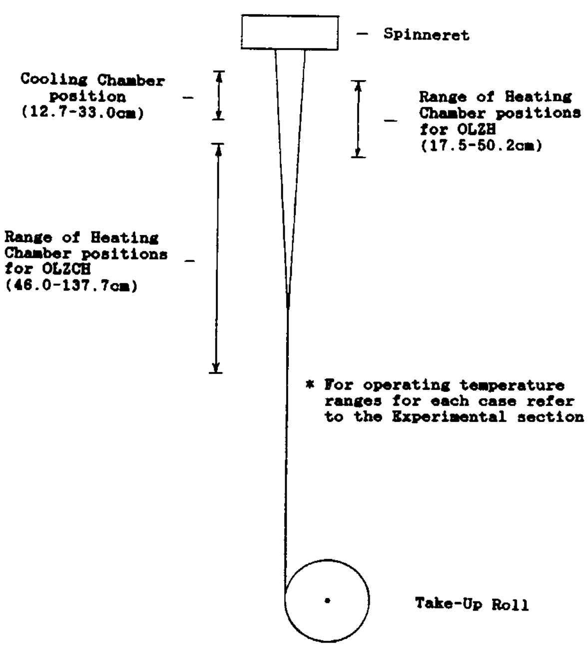


Figure 1 Illustration of the set-up used for the various types of spinline modifications attempted: OLZC, OLZH, and OLZCH.

As stated in ref. 1, these devices were used in an attempt to modify the usual monotonically decreasing temperature profile experienced in the conventional spinning process. As has been shown in much of the literature, both the level of orientation and crystallinity developed during spinning are very dependent on the temperature profile imposed on the threadline. It was, therefore, the intent of this work to examine the extent to which the orientation, crystallinity, and mechanical properties could be enhanced by modifying the threadline temperature profile with varying degrees of imposed and retarding air quenches.

Characterization Methods

Mean Birefringence

Filament birefringences were determined using a Leitz compensator mounted in a Nikon polarizing microscope. The values reported represent the average of five individual measurements. Mineral oil of refractive index 1.48 was used as the immersion liquid.

Radial Birefringence/Lorentz Density

The radial birefringence and Lorentz density characterizations were performed using a Jena interference microscope, a video camera with a controller box and splitter, and an IBM portable computer. References 3, 4, and 5 provide a detailed description of the general technique used to perform this characterization.

Tensile Properties

Tensile tests were performed on the Instron machine model 1123. Initial modulus, breaking tenacity, and elongation to break were calculated in accordance with ASTM D3379-75. All tests were performed on single filaments of standard 2.54-cm gauge length using a full-scale load of 50 g, a crosshead speed of 20 mm/min, and a chart speed of 100 mm/min. An average of 10 individual measurements was obtained for each sample lot.

Density

Filament densities were determined with a density gradient column composed of a $NaBr–H_2O$ solution maintained at 23 ± 0.1°C. Five specimens for each sample lot were used to obtain an average value.

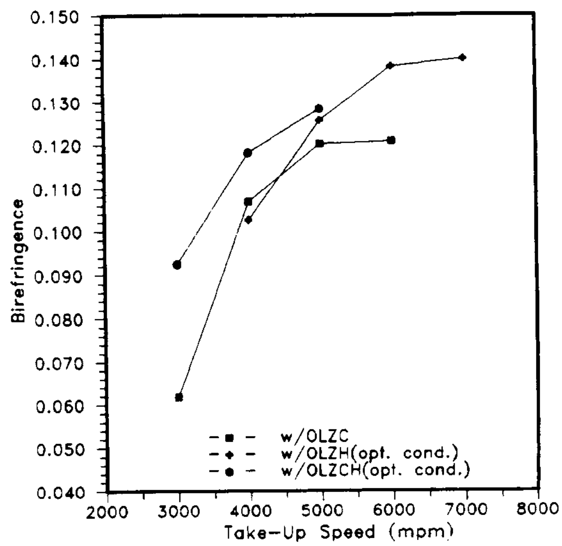


Figure 2 Birefringence vs. take-up speed for as-spun PET fibers prepared with various spinline modifications. See Table I for individual value and error listings.

Crystallinity

Weight fraction crystallinity, X_c, was calculated using the following equation:

$$X_c = ((d - d_{am})/(d_{cr} - d_{am}))\cdot(d_{cr}/d)\cdot 100\%, \quad (1)$$

where d is the average density of the filament sample lot, d_{cr} is the density of the crystalline phase (1.455 g/cc), and d_{am} is the density of the amorphous phase (1.335 g/cc).

X-ray Diffraction

Equatorial scans of each sample lot selected for this characterization were produced using a Siemens Type-F X-ray diffractometer with nickel filtered CuK_α radiation (30 kV, 20 mA). The crystal sizes (L) were determined according to the Scherrer equation with an added correction factor of 0.9 for lattice distortion being applied:

$$L_{hkl} = 0.9\lambda/\beta \cos \Theta, \quad (2)$$

where β is the half width of the reflection peak, Θ is the Bragg angle, and λ is the wavelength of the X-ray beam. The interplanar spacings (d) were calculated using the following equation:

$$n\lambda = 2d \sin \Theta, \quad (3)$$

where again λ is the wavelength of the X-ray beam and Θ is the Bragg angle. The number of repeat units was calculated as the ratio of each crystal size to the respective interplanar spacings (L/d). Note, all the equatorial scans were resolved into three reflection peaks (010, $\bar{1}10$, 100) using the Pearson VII technique.[5]

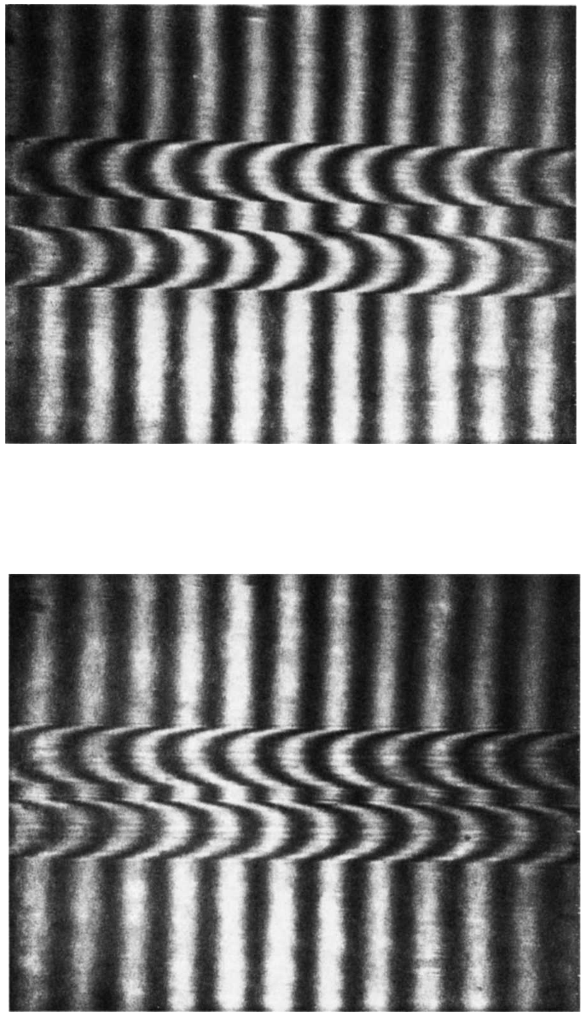
RESULTS

To discuss the mean birefringence values shown in Figure 2, it will first be necessary to define the term "optimum condition" (opt. cond.) and how it applies to both OLZH and OLZCH. As stated earlier, the

Table I Mean Birefringence and Tensile Property Values of As-Spun Fiber Samples

Take-Up Speed (mpm)	OLZC Temp., Pos.[a] (°C)/(cm)	OLZH Temp., Pos.[a] (°C)/(cm)	Mean Birefringence	SD (n = 5)	T/E/M (gf/d)/(%)/gf/d)	SD (n = 10)	Observed Spinning Performance
OLZC							
3,000	23/12.7–33.0	—	0.062	0.0005	3.2/257/21.5	0.13/21.1/1.71	Good
4,000	23/12.7–33.0	—	0.107	0.0014	3.5/153/38.1	0.26/26.9/2.66	Good
5,000	23/12.7–33.0	—	0.120	0.0011	3.9/122/47.7	0.22/15.0/7.32	Fair
6,000	23/12.7–33.0	—	0.121	0.0006	3.6/80/57.7	0.31/12.5/4.89	Poor
OLZH (opt. cond.)							
5,000	—	160/17.5–30.2	0.126	0.0017	4.4/133/45.4	0.32/13.8/4.63	Good
6,000	—	240/17.5–30.2	0.138	0.0023	5.0/108/60.3	0.41/10.0/8.43	Fair
7,000	—	310/17.5–30.2	0.140	0.0031	4.6/72/70.0	0.63/11.9/4.62	Poor
OLZCH (opt. cond.)							
3,000	23/12.7–33.0	160/102.0–114.7	0.093	0.0012	3.2/201/28.7	0.17/23.3/2.96	Good
4,000	23/12.7–33.0	130/79.0–91.7	0.118	0.0004	3.5/146/44.3	0.23/13.6/4.23	Good
5,000	23/12.7–33.0	150/125.0–137.7	0.128	0.0010	4.0/115/49.9	0.08/9.5/3.86	Fair

[a] Temp., Pos. refers to the temperature of the air circulating within the chamber and the distance of the chamber away from the face of the spinneret.



(a)

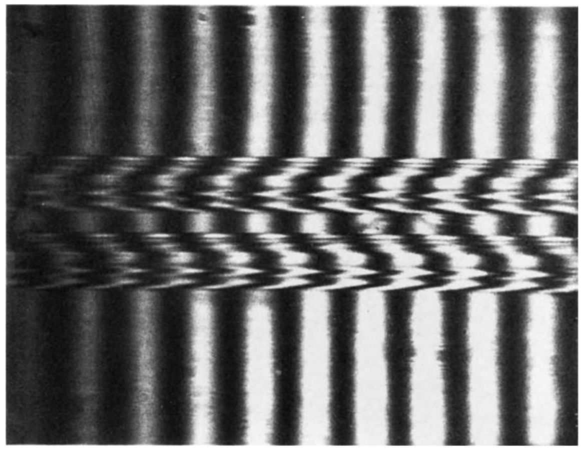
(b)

Figure 3 Interference fringe patterns of as-spun PET fibers. (a), 3,000 mpm w/OLZC; (b), 3,000 mpm w/OLZCH (opt. cond.).

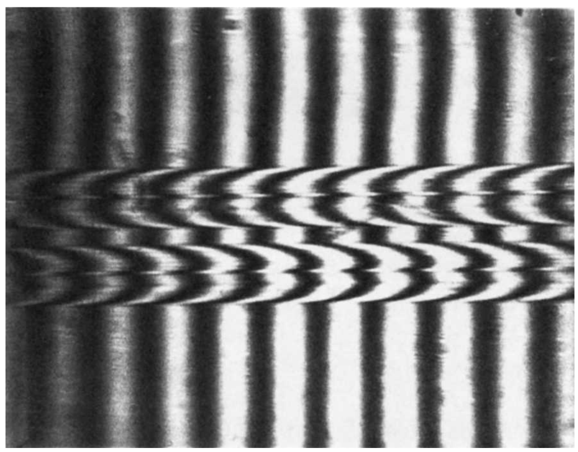
variables associated with the use of either OLZH or OLZCH are the position of the heating chamber and the temperature of the air circulating within the chamber. Therefore, in each case, the optimum condition refers to that particular position and temperature of the zone heating chamber that resulted in the production of as-spun filaments with the highest mean birefringence. *This definition is irrespective of the distribution of orientation across the filament and is not intended to necessarily imply the presence of an optimum structure.* The identification of these so-called optimum processing conditions was found at each of the take-up speeds for which the collection of a satisfactory sample was possible.

Figure 2 presents a comparison of the highest mean birefringence values obtained for each type of quench modification attempted. The OLZC case represents a baseline for which the effects of the retarding quench or on-line zone heating may be compared. In the lower take-up speed range, 3,000–5,000 mpm, the use of the zone heating was most effective when operating in the lower portion of the threadline, distances relatively further away from the spinneret face, at temperatures ranging from 130–160°C; see Table I for more details. In the higher take-up speed range, 6,000–7,000 mpm, the use of the zone heating was most effective when operating at a relatively higher position along the threadline at temperatures ranging from 240–310°C; again, Table I shows more details. Also, note the ability of the retarding quench to allow for moderately stable spinning at speeds of up to 7,000 mpm without the usual decline in birefringence being observed.

Further radial birefringence/Lorentz density characterization of a number of select samples was



(a)



(b)

Figure 4 Interference fringe patterns of as-spun PET fibers. (a), 6,000 mpm w/OLZC; (b), 6,000 mpm w/OLZH (opt. cond.).

performed on those samples produced under the optimized conditions at both extremes of the take-up speeds employed. These characterizations require that quantitative measurements be performed on each sample's typical interference fringe pattern for both the parallel and perpendicular polarization directions. However, even in the highest-speed spun fibers, little variation is observed in the cross-sectional refractive index profile in the direction perpendicular to the fiber axis. Therefore, the most informative qualitative information regarding radial variations in refractive index that can be extracted from a single photograph comes from observation of the fringe patterns with the polarization set-up in the parallel direction. Photographs of these parallel polarization fringe patterns are shown in Figures 3 and 4 for take-up speeds of 3,000 and 6,000 mpm, respectively.

Figure 5 shows the radial profiles of birefringence and Lorentz density for the samples spun at 3,000 mpm with OLZC and OLZCH (opt. cond.). In comparison, the fibers prepared using OLZCH show both the birefringence and Lorentz density curves having consistently higher values across the entire radius. This indicates that the system of OLZCH has the ability to both raise and level off the distribution of birefringence, and to raise Lorentz density, across the radius of the as-spun fiber. Figure 6 shows only the radial profile of birefringence and Lorentz density for the sample spun at 6,000 mpm with OLZH. An inflexible requirement of the characterization technique is that the fiber has a symmetrical interference fringe pattern. As shown in Figure 4(a) for the case of OLZC at 6,000 mpm, this fiber sample did not meet the symmetrical fringe pattern requirement and therefore radial birefringence mea-

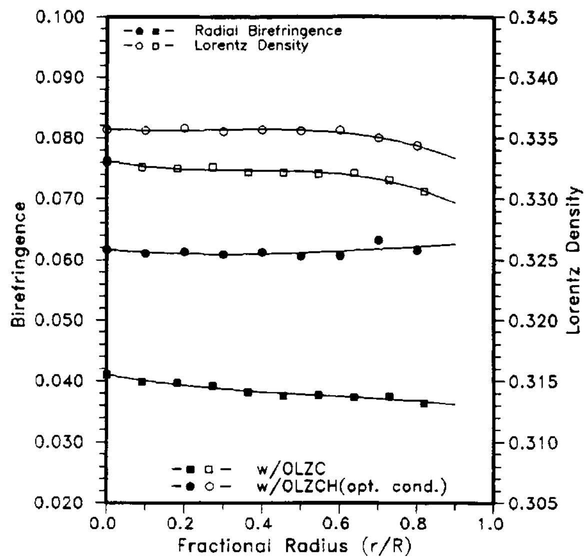


Figure 5 Radial profiles of birefringence and Lorentz density for as-spun PET fibers prepared under various spinline modifications at a take-up speed of 3,000 mpm.

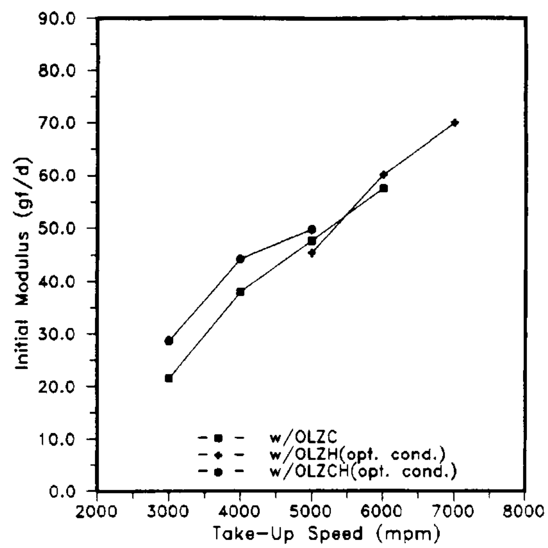


Figure 7 Initial modulus vs. take-up speed for 5.0 denier as-spun PET fibers prepared with various spinline modifications. See Table I for individual value and error listings.

surements are not valid. For the case of OLZH at 6,000 mpm, this fringe pattern does meet the symmetrical requirement from edge to edge. However, this fringe pattern exhibits a high degree of undesirable nonuniformity from center to edge, which, as shown in Figure 6, translates into a high degree of skin-core variation. A final note regarding the interference fringe patterns is how well their symmetry or lack thereof corresponds with the observed

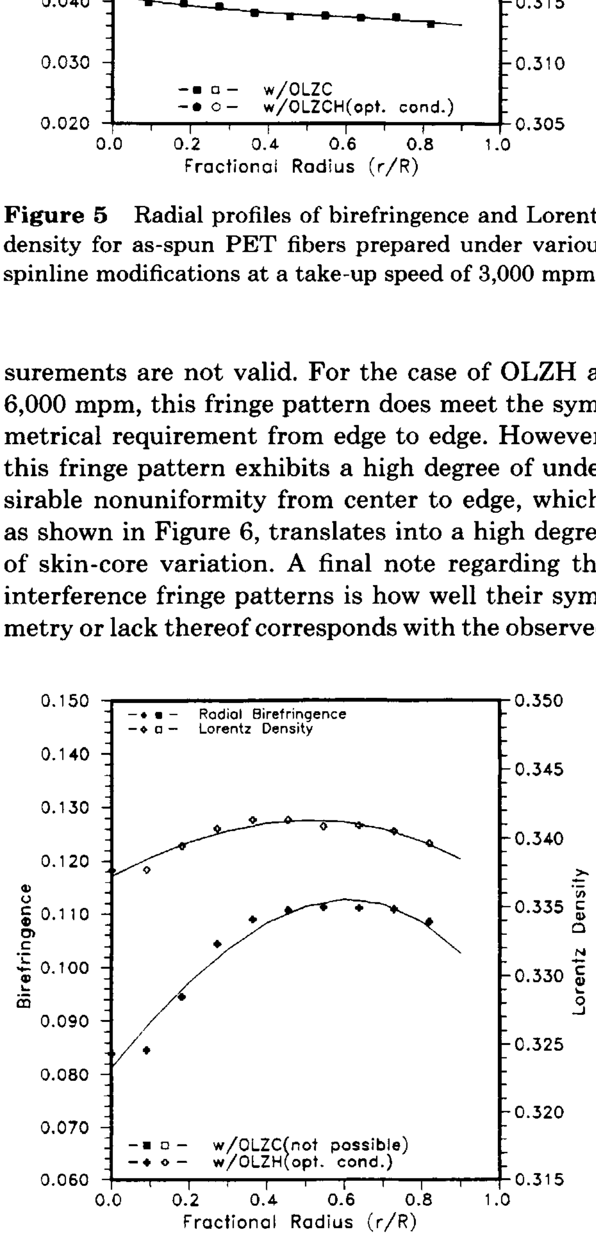


Figure 6 Radial profiles of birefringence and Lorentz density for as-spun PET fibers prepared under various spinline modifications at a take-up speed of 6,000 mpm.

stability of the spinning process during their production.

Figure 7 shows the initial modulus as a function of take-up speed for each of the attempted modified quench conditions. It is believed that the measure of initial modulus would be least skewed by nonuniformities or defects that are known to often occur in high-speed spun fibers. Therefore, as would be expected, the modulus values show a fairly good correlation with the corresponding mean birefringence values shown in Figure 2. Figures 8 and 9 show breaking tenacity and elongation to break values, respectively, for each of the attempted modified quench conditions. Tenacity values show little or no change when spinning at 3,000–5,000 mpm with OLZCH, but do show a significant increase with OLZH at 5,000–6,000 mpm. In the lower take-up speed range, 3,000–5,000 mpm, elongation values also show a good inverse correlation with mean birefringence values. A final interesting feature is that in contrast to the increasing birefringence and continued increasing modulus values at 6,000–7,000 mpm, both the tenacity and elongation values decrease and increase, respectively. This decline in the continued improvement of tenacity and elongation values above 6,000 mpm is attributed to the radial variations in orientation as well as the possible existence of crazes and/or microvoids at or near the fiber surface.[7,8]

To obtain quantitative information regarding the crystalline structure and content of the same select

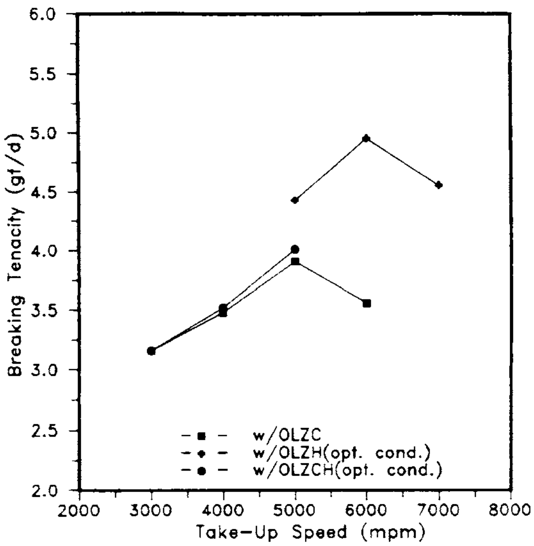


Figure 8 Breaking tenacity vs. take-up speed for 5.0 denier as-spun PET fibers prepared with various spinline modifications. See Table I for individual value and error listings.

samples for which the radial variation in orientation was examined, X-ray equatorial scans were produced and are shown in Figures 10 and 11. Figure 10 shows the resulting scans for the case of a 3,000 mpm take-up speed both with OLZC and OLZCH (opt. cond.). The 3,000 mpm OLZC scan shows a broad diffuse pattern typical of amorphous materials, whereas the 3,000 mpm OLZCH scan yielded a more well-resolved pattern typical of semicrystalline materials. Figure 11 shows the resulting scans for the case of a 6,000 mpm take-up speed both with OLZC and OLZH (opt. cond.). These scans show nearly identical, well-resolved peaks, characteristic of a high degree of crystallinity as well as large crystal sizes, but allow for no discernable differences to be claimed regarding the crystalline structure resulting from the two quench variations. As indicated in both figures, the resolved peaks correspond to the (010), ($\bar{1}$10), and (100) reflection planes.

The crystal size, interplanar spacings, and number of repeat units for each of the four samples stated above were calculated, respectively, using the equations given in the experimental section along with the data obtained from the resolved peaks shown in Figures 10 and 11. The values obtained are presented in Table II. Note, for the case of OLZCH (opt. cond.), at a take-up speed of 3,000 mpm, both the crystal size and number of repeat units showed a significant increase in comparison to the values obtained for the case of OLZC. In contrast, for the case of OLZH (opt. cond.), at a take-up speed of 6,000 mpm, both the crystal size and number of repeat units show relatively little change in comparison with the case of OLZC, with only small fluctuations being observed along each respective reflection plane. Also included in this characterization was a reference yarn produced through the conventional two-step spin-draw process, values for which are also shown in Table II.

Density measurements were also performed on these select samples to calculate the corresponding weight percent crystallinity values shown in Table II. As would be expected from the crystal size values also shown, the use of OLZCH (opt. cond.) at 3,000 mpm resulted in a significant increase in the weight percent crystallinity. As for the 6,000 mpm case, even though the variation in crystal size was minor, there was a measurable increase in the percent crystallinity value obtained through the use of OLZH (opt. cond.). The most interesting feature regarding the reference yarn is the rather intermediate crystal size and number of repeat units associated with its large percent crystallinity value.

INTERPRETATION

A number of problem areas have been identified in the literature that lead to difficulties encountered when making the transition from low- to high-speed spinning. Most relevant to the work presented here

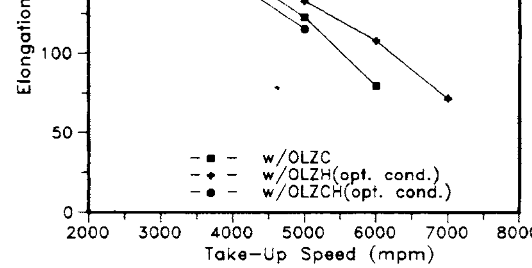
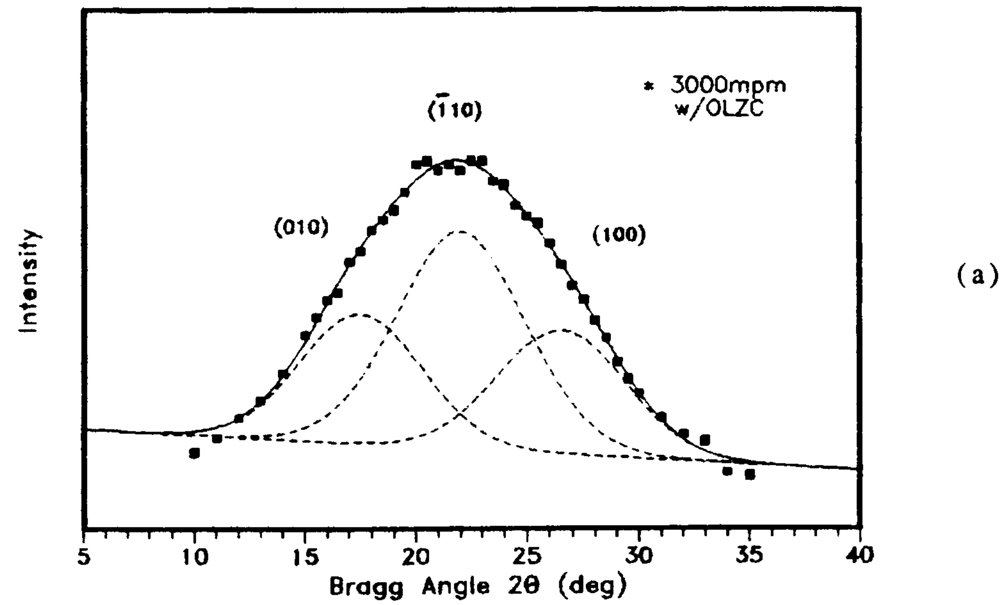


Figure 9 Elongation to break vs. take-up speed for 5.0 denier as-spun PET fibers prepared with various spinline modifications. See Table I for individual value and error listings.



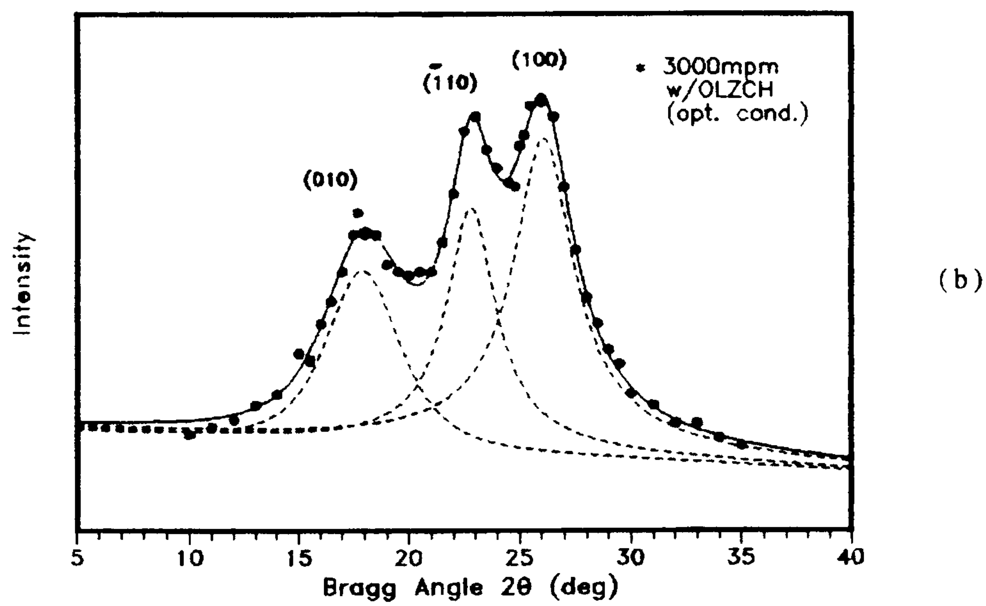
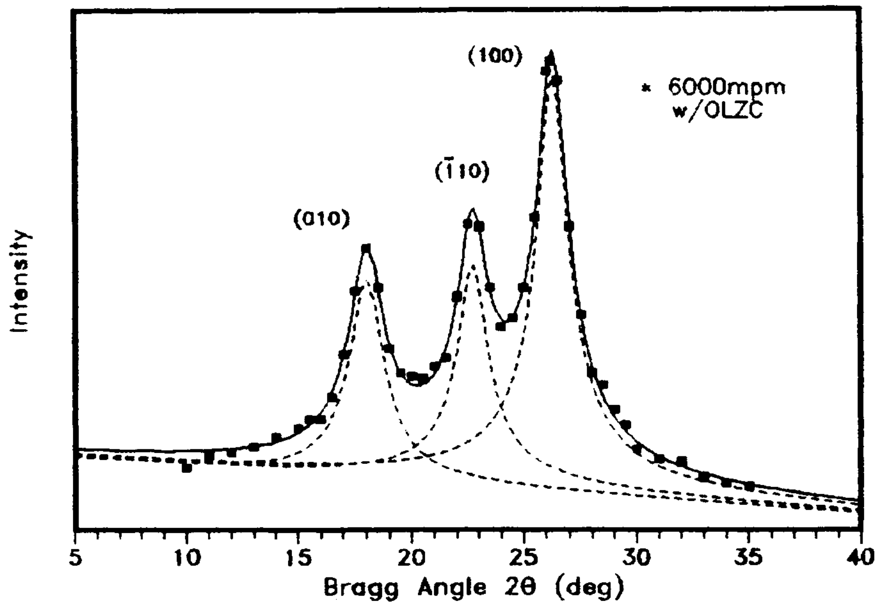
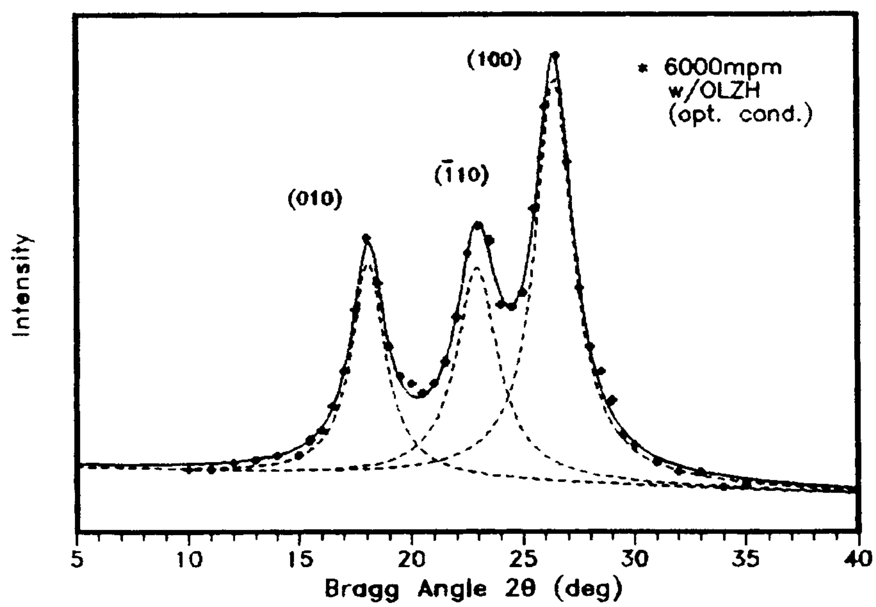


Figure 10 X-ray equatorial scans of as-spun PET fibers at a take-up speed of 3,000 mpm with (a), OLZC; (b), OLZCH (opt. cond.).

are those difficulties associated with both the large temperature difference or gradient between the surface and the filament axis, as well as the different behavior of the crystallization process. Obviously, both these critical areas should be alterable to a certain extent by modifying the cooling or quench conditions imposed on the threadline. One of the major factors contributing to the present limitations associated with further increases in spinning speed is the reaching of a critical threadline tension beyond which rupture of the threadline occurs. However, this critical tension is a strong and sensitive function of both the viscosity and relaxation time spectrum for any given polymer. Since the critical tension would undoubtedly be first reached at the cooler filament surface, it seems plausible that the application of a cooling or heating zone at the appropriate position along the threadline should help to mini-



(a)



(b)

Figure 11 X-ray equatorial scans of as-spun PET fibers at a take-up speed of 6,000 mpm with (a), OLZC; (b), OLZCH (opt. cond.).

mize this difficulty and raise the spinning speed limits beyond those experienced under normal cooling conditions. This may also help to reduce the undesirable effects on the mechanical properties in the as-spun filaments associated with the radially differentiated structure. Lastly, a relatively high degree of crystallinity is required to impart the level of dimensional stability desired for high-performance end uses. The rate of crystallization is a strong function of both the amorphous orientation and temperature, and should therefore be capable, as has been shown, of being manipulated to yield a higher level of crystallinity by altering the temperature profile of the threadline.

CONCLUSIONS

Through the use of enhanced and/or retarding air quenches, modifications were made to the usually

Table II Crystal Structure Data of Select As-Spun Fiber Samples

Take-Up Speed (mpm)	Density (g/cc)	Crystallinity (wt %)	Crystal Size			Interplanar Spacing			Repeat Units (per crystal)		
			010	$\bar{1}10$	100	010	$\bar{1}10$	100	010	$\bar{1}10$	100
OLZC											
3,000	1.340	4.9	12.8	12.6	13.1	5.06	4.04	3.36	2.5	3.1	3.9
6,000	1.376	36.1	43.8	47.0	47.9	4.92	3.91	3.39	8.9	12.0	14.1
OLZH (opt. cond.)[a]											
6,000	1.380	39.8	46.1	37.9	43.0	4.90	3.87	3.37	9.4	9.8	12.8
OLZCH (opt. cond.)[a]											
3,000	1.357	19.8	21.2	31.2	26.0	4.94	3.90	3.41	4.3	8.0	7.6
Reference yarn	1.388	46.5	41.3	34.0	31.2	4.98	3.94	3.44	8.3	8.6	9.1

[a] For details regarding opt. cond., refer to Table I.

monotonically decreasing temperature profile experienced in a typical melt spinning process. The goal of these quench modifications was to examine the extent to which the as-spun fiber's orientation, mechanical properties, and crystallinity could be enhanced. The results obtained indicate significant improvements in each of the properties examined. These improvements are best illustrated by a comparison of the properties obtained through the use of either the combined zone cooling and heating (OLZCH) or the zone heating only (OLZH) with the properties achieved through the use of the standard, or baseline, zone cooling only (OLZC). However, the relative improvements in each of the properties declined as the speed was raised. A particular quench modification, the use of the zone heating chamber at a high temperature and relatively close distance to the spinneret face, allowed for significant improvements in the stability of the spinning process at the very high take-up speeds. This particular quench modification also resulted in a continued improvement in mean birefringence and initial modulus beyond the take-up speed range where a usual decline is observed. It is, therefore, concluded that the threadline temperature profile, of which all spinning variables and dynamics are a strong function, can be altered in such a way as to significantly enhance the resulting spinning performance and fiber structure.

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