Effects of Spinning Conditions on Morphology and Properties of Polyethylene Terephthalate Fibers Spun at High Speeds

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SYNOPSIS

Fiber spinning of polyethylene terephthalate (PET) was studied at take-up speeds ranging from 2000 m/min to 7000 m/min under various spinning conditions. Effects of changes in process variables on the molecular orientation, crystallinity, and properties of as-spun PET fibers are reported. Conventional cross-flow quench in high-speed spinning yields fibers with undesirable crimp and asymmetric structure with respect to the fiber axis. Radial-flow quench eliminates these problems. Changes in other spinning conditions, such as extrusion temperature, throughput or take-up denier, and molecular weight, may also affect the development of PET fiber structure in the high-speed threadline.

INTRODUCTION

In the past decade, extensive research was done on the high-speed spinning of synthetic fibers, and numerous articles appeared in the literature. It is well known that there are many processing parameters that may influence the development of fiber structure in the melt spinning process.[1] Effects of changing spinning speed on the structure and properties of as-spun polyethylene terephthalate (PET) fibers have been discussed in detail in the literature.[2-5] However, little attention has been directed to the investigation of effects of other spinning variables, such as extrusion temperature, cooling method, take-up denier, and molecular weight on the high-speed spinning of PET. This work is intended to fill the gap by investigating effects of the above variables on the morphology and properties of high-speed spun PET fibers.

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EXPERIMENTAL

Materials and Fiber Spinning Procedure

Two PET samples were used for melt extrusion. One sample, provided by the Celanese Corporation, has an intrinsic viscosity (IV) of 0.58 dl/g. The other, supplied by the Goodyear Company, has an IV of 0.95 dl/g. Molecular weight of PET may be related to the intrinsic viscosity (IV) by the following empirical equation:[2,6]

$$IV = 2.1 \times 10^{-4} M_v^{0.82} \quad (1)$$

where M_v is the viscosity average molecular weight. Thus, the two samples have molecular weight of *ca.* 15,700 and 28,700, respectively. The polymers were dried in a vacuum oven at 140°C for at least 16 h in preparation for all extrusion tests. A Fourne single crew extruder was used. A special spin pack, built in our college's machine shop, was used for monofilament spinning. Unless stated otherwise, a radial quench chamber was used with a flow rate of 1.3 m/s measured at the center of the bottom exit. Fibers

were wound onto a high-speed godet roll from Erdmann Electrotechnik.

Characterization Methods

Birefringence

Fiber birefringence was determined using a 20-order tilting compensator mounted in a Nikon polarizing light microscope. An average of five individual determinations was reported.

Density

Fiber density (ρ) was obtained with a density gradient column ($NaBr-H_2O$ solution) at 23 ± 0.1°C. Five specimens for each fiber were used to obtain an average reading.

Crystallinity

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

$$\chi = \frac{(\rho - \rho_a)\rho_c}{(\rho_c - \rho_a)\rho} \quad (2)$$

where ρ_c is the density of crystalline phase equal to 1.455 g/cm^3 and ρ_a is the density of amorphous phase equal to 1.335 g/cm^3 for PET.[7]

Tensile Test

Tensile tests were performed on an Instron machine model 1123. Test method ASTM D3822-82 was followed. All tests were done on single filaments 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 obtained for each fiber sample.

RESULTS AND DISCUSSION

Effects of Changes in Type of Quench Air Flow

For many years in the fiber industry, cross-flow quench has been widely employed in the melt spinning process. However, when this type of quench was used in high speed spinning, we found that severe crimps occurred in the as-spun fibers. Examination of the crimped fibers with an interference microscope revealed that the interference fringe patterns were severely asymmetric about the fiber axis. Since the cross-flow quench chamber blows air perpendicularly to the fibers from one direction, the uneven cooling was thus suspected to be responsible for the formation of the asymmetric fiber structure.

To prove this hypothesis, a radial quench chamber was designed in our laboratory. Its cross-sectional view is shown in Figure 1. A cylindrical Fujibon air filter, 20 cm long and 8.3 cm inside diameter, was used to assure uniform stable air flow around the molten filament. In spinning multiple filaments, the quench air passes through the filament ring bundle from outside to inside in the quench chamber, and then below the exit from inside to outside. It is thus similar to the "Out-In" type of commercial radial quench chambers as described recently by Fourne.[8]

Figure 2 shows the photographs of two fiber samples obtained at 7000 m/min, one spun with cross-flow quench at a flow rate of 0.28 m/s (measured and averaged along the center line of the screen), the other with radial flow quench at a flow rate of 1.3 m/s (measured at the center of the bottom exit). The crimping behavior is completely eliminated by using the radial-flow quench chamber. Interference photomicrographs of the two samples are presented

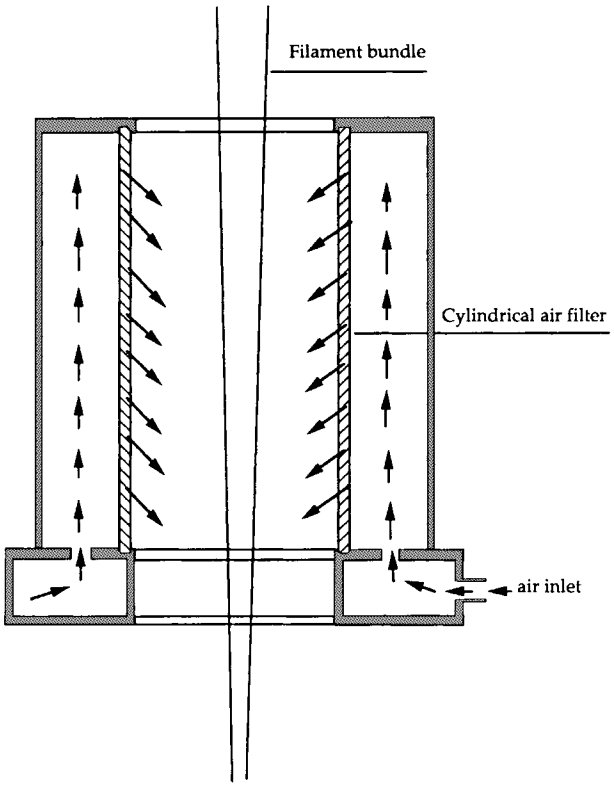


Figure 1 Cross sectional view of radial quench chamber (schematic). Arrows indicate qualitatively directions of air flow.

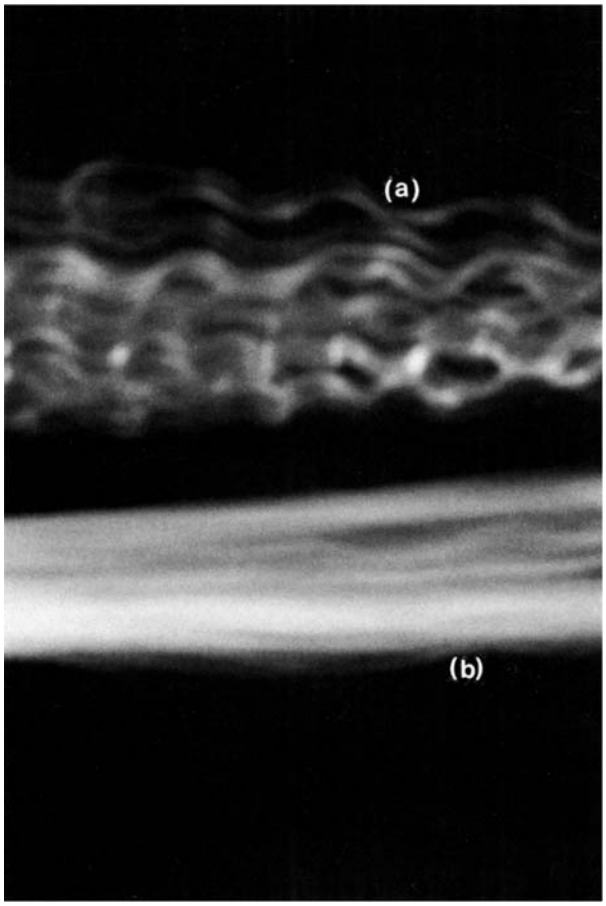


Figure 2 Photographs of PET fibers spun at 7000 m/min using two different cooling methods. (a) Cross-flow quench; (b) Radial-flow quench.

in Figure 3. The photograph in Figure 3 (a) shows the fringe pattern of the fiber spun with the cross-flow cooling air. The fringe pattern is asymmetric with respect to the fiber axis. The photograph in Figure 3 (b) shows the fringe pattern of the fiber spun with the radial cooling chamber, and it shows a symmetrical fringe pattern.

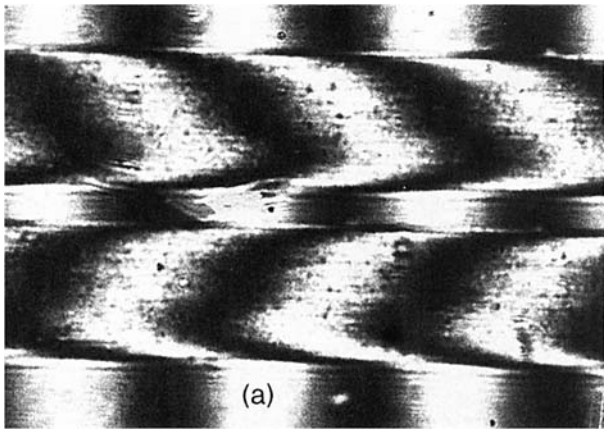
Qualitatively, the extent of the displacement of fringes by a specimen in a liquid with a given refractive index corresponds to the degree of molecular orientation. Therefore, symmetrical fringe patterns indicate that the distribution of the molecular orientation is radially symmetric about the fiber axis.

The mechanism of the formation of the asymmetric structure in the cross-flow quenched fibers is illustrated in Figure 4. The cross-flow quench chamber blows air perpendicularly to the fiber axis from one side of the molten filament, which is shown in Figure 4 (a). The side that faces the quench cabinet cools faster than the other side. As a consequence, an asymmetric distribution of temperature about the fiber axis is produced. According to Kase,[9] the elongational viscosity, η_e, is related to the temperature by the following relation:

$$\eta_e = \eta_e^* \exp\left[\frac{E}{T + 273}\right] \tag{3}$$

where E and η_e^* are material parameters of the polymer used. A decrease in temperature therefore leads to an increase in η_e. The tensile stress, σ, is given by the product of the elongational viscosity and the velocity gradient:[9]

$$\sigma = \eta_e \frac{dV}{dx} \tag{4}$$



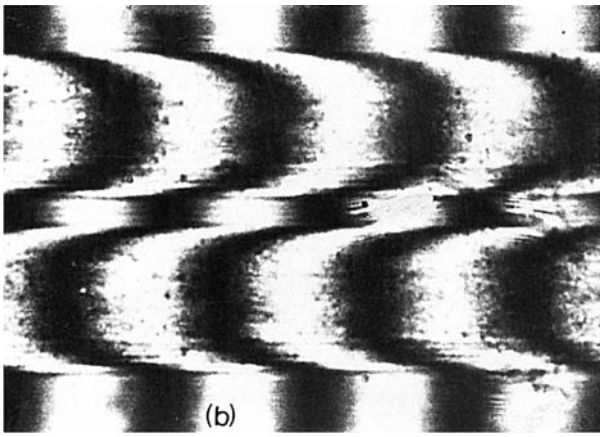


Figure 3 Interference photomicrographs of PET fibers spun at 7000 m/min using two different cooling methods. (a) Cross-flow quench; (b) Radial-flow quench.

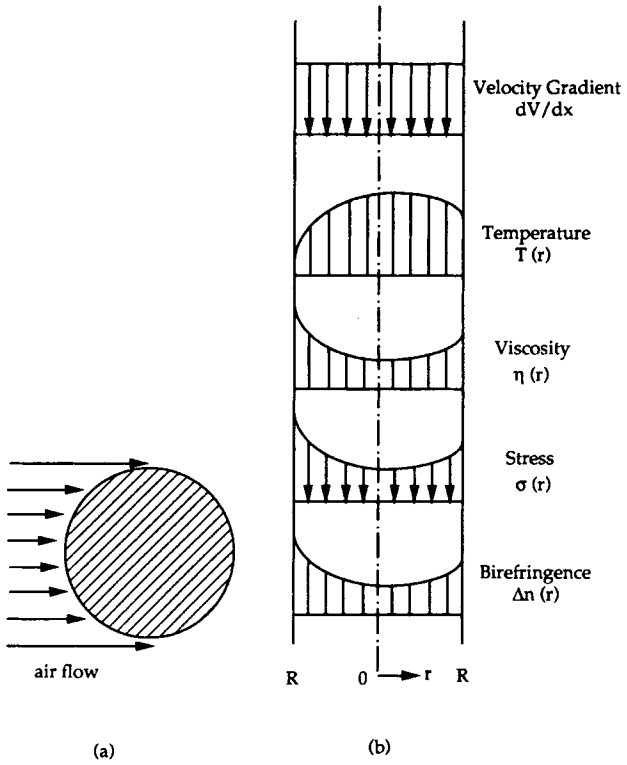


Figure 4 Mechanism of formation of asymmetric birefringence in PET fibers produced under cross-flow quench conditions. (a) Cross-sectional view of a fiber being cooled with cross-flow quench air; (b) Radial distribution of spinline parameters.

where $\frac{dV}{dx}$ is assumed constant in the cross section of the filament.[10,11] The asymmetric temperature distribution induces an asymmetric distribution of elongational viscosity and, as a consequence, of stress profile in the cross section of the filament being cooled. In the course of the structure development, the asymmetric stress distribution causes the uneven development of molecular orientation and crystallization in the filament cross section because the level of molecular orientation and crystallization rate are greatly influenced by the stress present.[12,13]

Effects of Changes in Extrusion Temperature

Figure 5 (a) shows the variation of birefringence and crystallinity with the extrusion temperature for 0.58 IV PET fibers spun at 5000 m/min. Standard deviations of the two measurements, birefringence and density, are 2–4%. Both the birefringence and crystallinity appear to decrease as extrusion temperature increases in the range of 285–310°C. Different behavior, however, was observed when the fiber was spun at 6000 m/min, which is shown in Figure 5 (b). While the crystallinity remains nearly constant, the birefringence increases slightly with increasing extrusion temperature.

The variation of fiber tenacity with extrusion temperature is shown in Figure 6 for spinning at the two different take-up speeds. The tenacity of the fibers spun at 5000 m/min decreases slightly when the extrusion temperature increases from 285°C to 295°C, and then it levels off with a further increase in the extrusion temperature. Similar to the change of birefringence, the tenacity of fibers spun at 6000 m/min slightly increases with increasing extrusion temperature.

In low-speed spinning, it is known that an increase in extrusion temperature results in a decrease of spinning stress and, as a consequence, a decrease in the birefringence and in the crystallinity of the as-spun fibers.[1,14] This explains the variation of birefringence with extrusion temperature for PET spinning at 5000 m/min. The reason for the birefringence increase with increasing extrusion temperature for spinning at 6000 m/min is unclear. The phenomenon has also been reported by Vassilatos et al.[15] It may be surmised that a neck occurs in the spinline at 6000 m/min and an increase in the extrusion temperature lowers the neck, that is, increases the necking distance from the spinneret. As a consequence, the level of the spinning stress at the neck point is increased due to the increased air drag effect. Since the birefringence in the as-spun fibers is determined by the stress level at the neck point,[16] the increase of spinning stress at the neck point may account for the birefringence increase at relatively high extrusion temperature.

As the spinning speed exceeds 6000 m/min, filament breaks are encountered frequently at extrusion temperatures below 295°C. Raising the extrusion temperature seems helpful in reducing the frequency of filament breakage, but spinning at a temperature above 310°C appears unstable at high speeds. This is probably caused, at least to some extent, by polymer degradation at the high temperature. A temperature range of 295°C to 305°C seems preferable for the high-speed spinning of PET.

Effects of Changes in Take-Up Denier

Final filament diameter or take-up denier per filament is controlled by extrusion rate and take-up speed. In studying the effect of take-up speed on

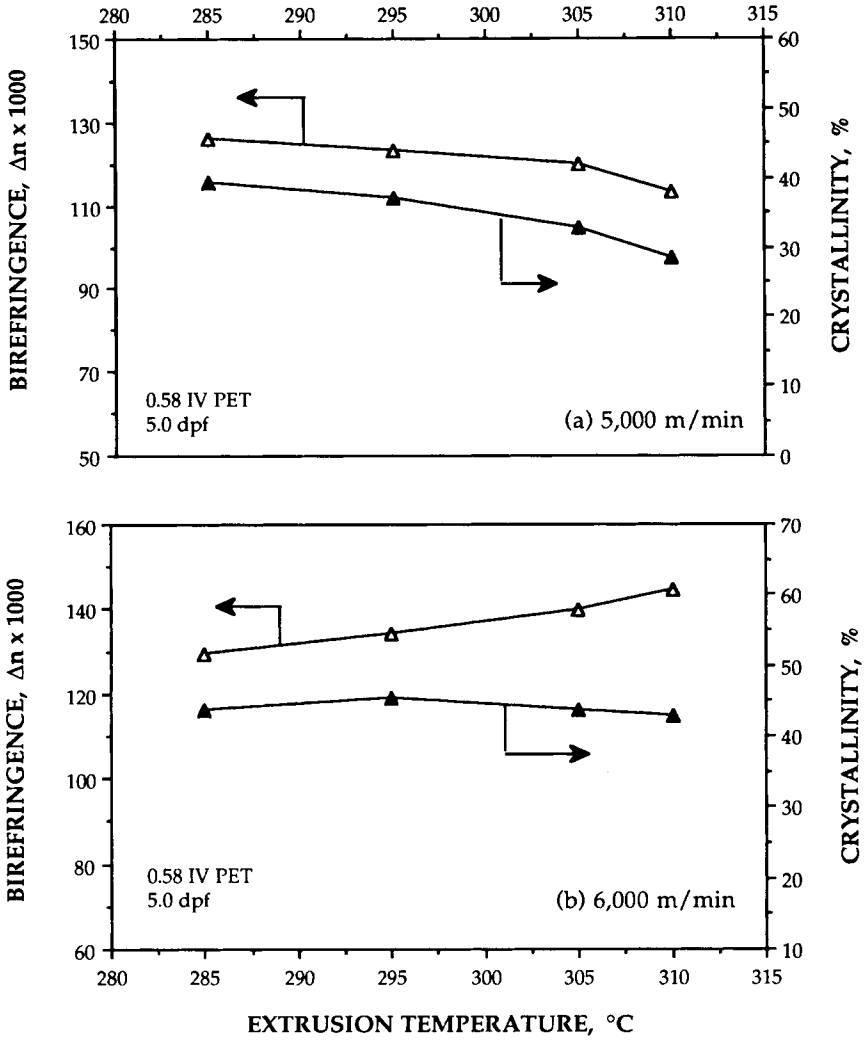


Figure 5 Effects of extrusion temperature on birefringence and crystallinity of PET fibers. (a) Spun at 5000 m/min; (b) Spun at 6000 m/min.

fiber structure and properties, one of the two variables, either the extrusion rate[2,3] or the take-up denier,[4,5] is often fixed while the spinning speed is varied. This section will discuss the effects of changing the take-up denier by varying the extrusion rate at given take-up speeds.

Figures 7 (a) and (b) show the change of birefringence and crystallinity with take-up denier for fibers spun at 5000 m/min at 6000 m/min, respectively. It is seen that both the birefringence and crystallinity at 5000 m/min decrease with increasing take-up denier. At 6000 m/min, however, the situation changes. The crystallinity first increases slightly with increasing take-up denier. It reaches a maximum at *ca.* 5.0 take-up denier and then decreases slighty with further increase in take-up denier. Birefringence changes with the take-up denier almost in the same way as does the crystallinity. These changes are, however, less significant compared with those observed at 5000 m/min.

Shimizu et al.[8] reported the changes of birefringence and density as a function of the reciprocal fiber diameter at various take-up speeds. They found that, as the reciprocal fiber diameter increases (i.e., the denier decreases), the birefringence and crystallinity increase in the fibers spun at speeds equal to or below 5000 m/min. At 6000 m/min, the corresponding changes appear reversed. At 7000 m/min, the tendency becomes even more obvious. Fiber diameter D (cm) and denier (DN) are related by the equation:

$$D = 10^{-2}\sqrt{\frac{DN}{90\pi\rho}} \qquad (5)$$

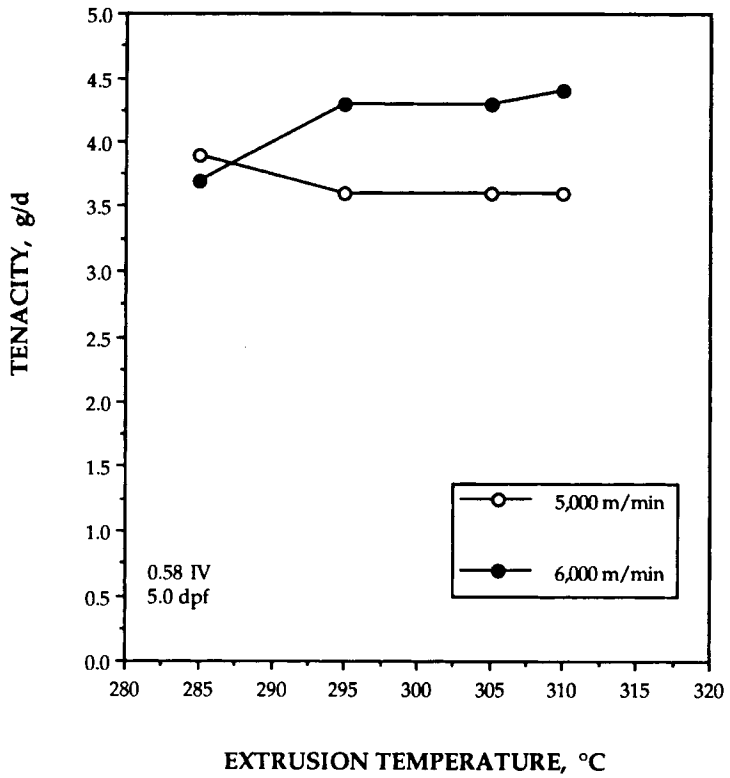


Figure 6 Effect of extrusion temperature on tenacity of PET fibers spun at indicated take-up speeds.

where ρ is fiber density in g/cm^3. The observation of the current study, therefore, is essentially consistent with that made by Shimizu et al.

A decrease in fiber take-up denier leads to an increase in the spin draw ratio and an increase in the cooling rate, which should help to increase the level of molecular orientation and crystallization rate.[1] This may explain the phenomena observed at the relatively low take-up speed, that is, 5000 m/min or below. At higher take-up speeds, however, neck-like deformation occurs.[3] Little effect was observed by varying the overall spin draw ratio.[18] As discussed earlier, the stress at the neck becomes a critical factor determining the level of molecular orientation. Thus, increasing the take-up denier or fiber diameter at high speeds above 5000 m/min has the same effect as increasing the extrusion temperature, that is, the necking position is lowered and the stress at the neck is increased. However, the birefringence and crystallinity appear to decrease slightly when the take-up denier exceeds 7.5 dpf at 6000 m/min. This may imply that the dominating factor controlling the fiber structure development may vary with the variation of overall spinning conditions.

Effects of Changes in Molecular Weight

Figure 8 shows the change of birefringence with take-up velocity for PET with two different molecular weights, 15,700 (IV = 0.58 dl/g) and 28,700 (IV = 0.95 dl/g). The birefringence of the low IV PET increases rapidly as the take-up velocity increases from 3000 m/min to 6000 m/min and then levels off as the take-up velocity further increases. The birefringence of the high IV PET increases very rapidly from 2000 m/min to 4000 m/min take-up speed and levels off at *ca.* 5000 m/min. It is seen that the birefringence of the high IV PET is higher than that of the low IV at any given speed below 5000 m/min and that the relation is reversed at speeds above that. It is difficult to collect fiber samples from the high IV PET at speeds above 6000 m/min because of the high frequency of filament breakage. Crystallinity of the fibers is plotted as a function of take-up velocity in Figure 9. The crystallinity of the fibers spun from the low molecular weight PET remains low in the speed range of 3000 m/min to 4000 m/min. It increases rapidly when the take-up velocity is increased from 4000 m/min

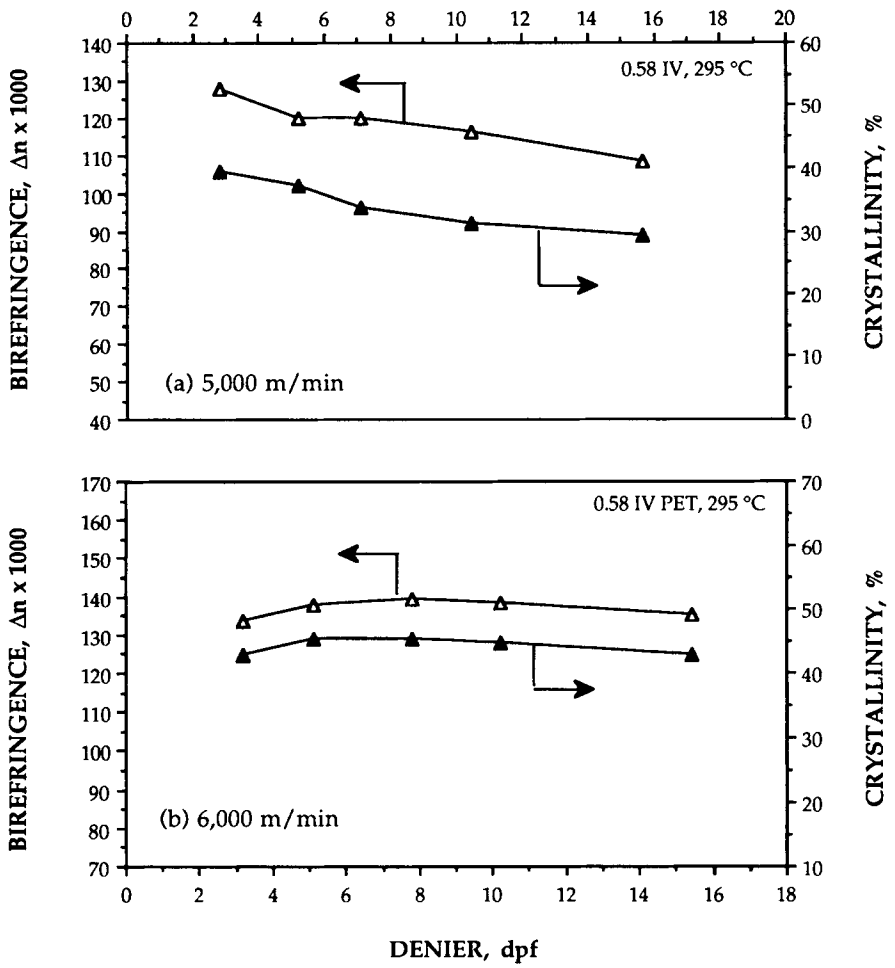


Figure 7 Effects of take-up denier on birefringence and crystallinity of PET fibers. (a) Spun at 5000 m/min; (b) Spun at 6000 m/min.

to 5000 m/min. At 6500 m/min, the crystallinity of the low IV PET becomes maximized. The crystallinity of the high molecular weight PET is low at 2000 m/min. It increases rather rapidly in the speed range of 3000 m/min to 4000 m/min and levels off in the range of 5000–6000 m/min. At any given speed between 3000–5000 m/min, the crystallinity of the high IV PET fibers is significantly higher than that of the low IV PET. These phenomena may be explained by the fact that higher molecular weight PET exhibits a higher elongational viscosity at a given temperature, thus a higher spinning stress.[18] The higher spinning stress encountered in the high molecular weight PET induces a higher level of molecular orientation and crystallinity in the relatively low speed range. The phenomenon that the crystallinity of the as-spun PET fibers levels off or decreases after a certain critical speed has been reported elsewhere in the literature.[2,19] Ziabicki[20] explained the phenomenon as a result of two competitive processes, that is, rapid cooling and crystallization. The degree of crystallinity in the as-spun fibers is determined by the product of crystallization time, $\Delta\tau$, and some effective crystallization rate, K. Increasing the spinning speed tends to increase the crystallization rate, but the crystallization time, that is, the time spent by the filament in the temperature range suitable for crystallization, decreases with increasing take-up speed. At a certain critical speed, the product of $\Delta\tau$ and K reaches a maximum.[20] The reduction in crystallinity at very high speeds is therefore a necessary physical consequence of nonisothermally oriented crystallization.

Tenacity and elongation at break of the fibers are plotted, respectively, in Figures 10 and 11. In the

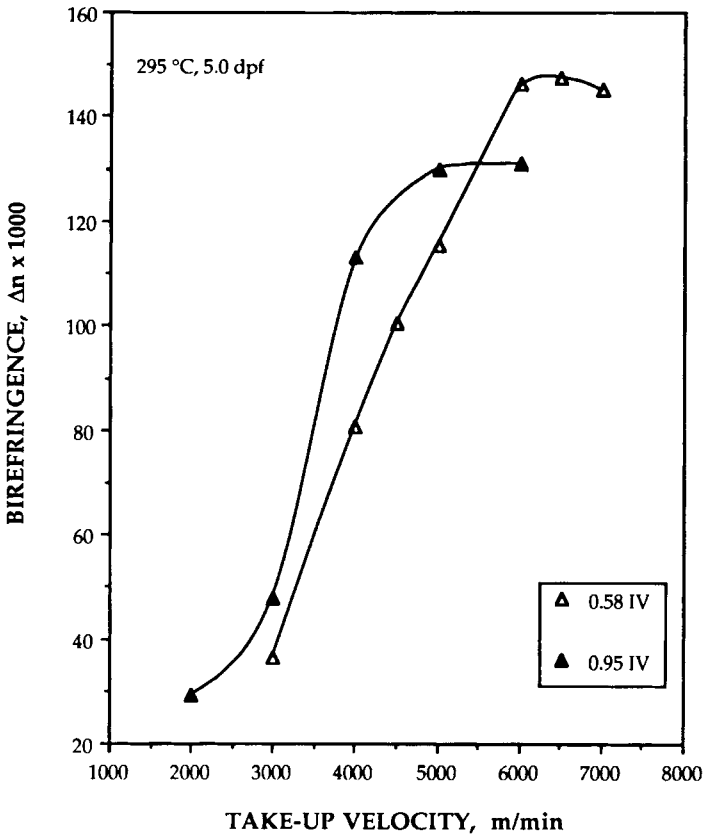


Figure 8 Birefringence vs. take-up velocity for fibers spun from PET with two different IVs.

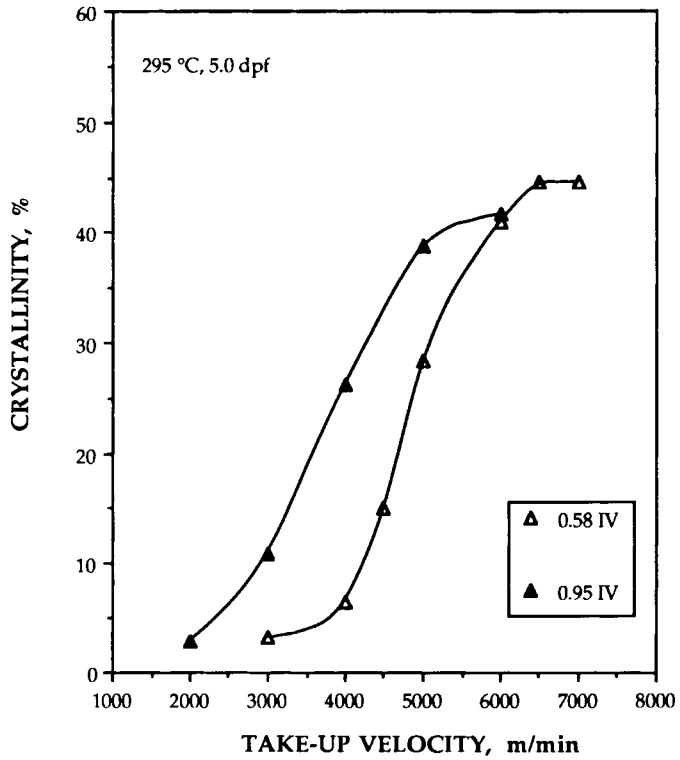


Figure 9 Crystallinity vs. take-up velocity for fibers spun from PET with two different IVs.

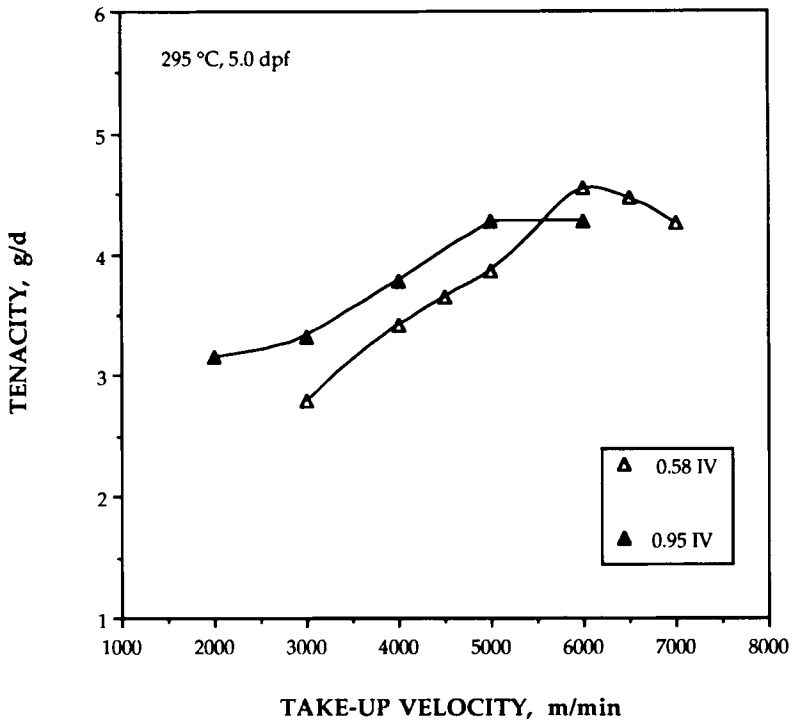


Figure 10 Tenacity vs. take-up velocity for fibers spun from PET with two different IVs.

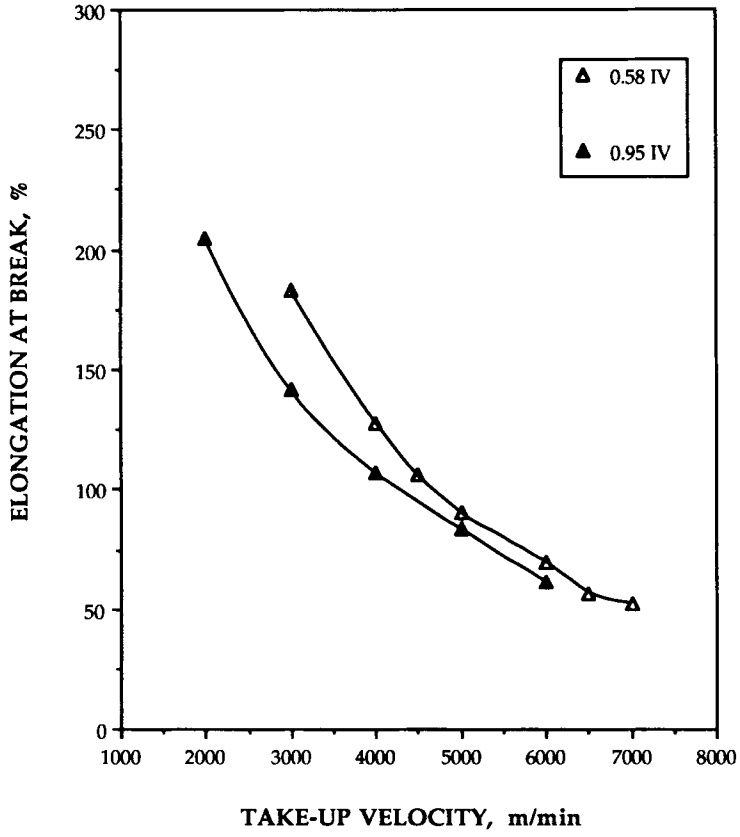


Figure 11 Elongation at break vs. take-up velocity for fibers spun from PET with two different IVs.

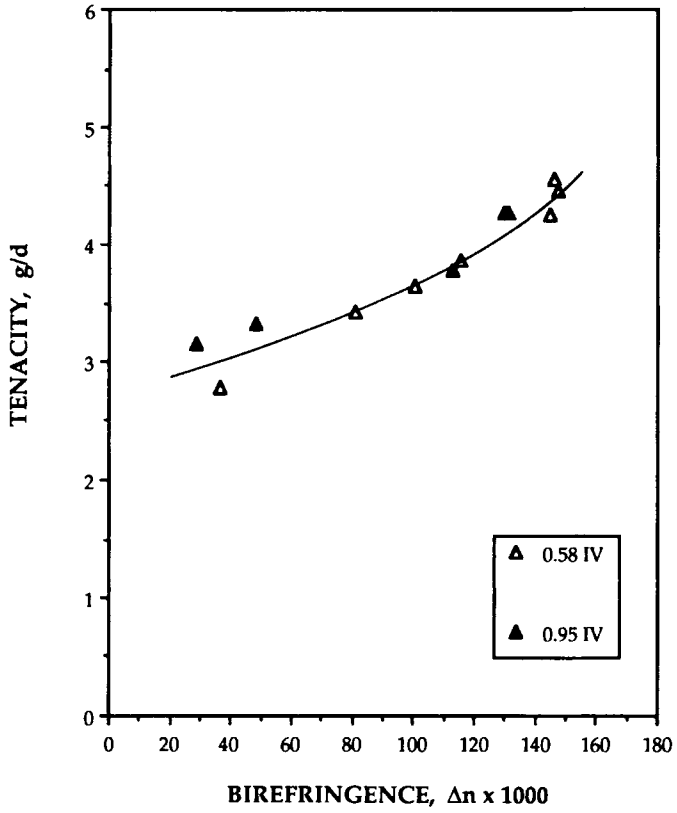


Figure 12 Plot of tenacity as a function of birefringence for fibers spun from PET with two different IVs.

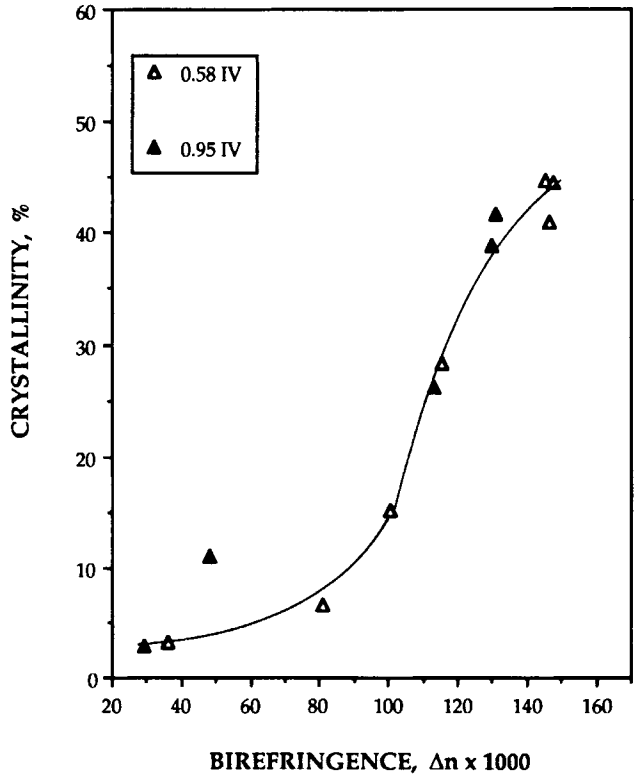


Figure 13 Plot of crystallinity as a function of birefringence for fibers spun from PET with two different IVs.

case of the low molecular weight PET, the fiber tenacity increases and the elongation at break decreases when the take-up speed is increased from 4000 m/min to 6000 m/min; the elongation at break appears to start leveling off, whereas the tenacity decreases slightly at higher spinning speed. The tenacity of the fibers spun from the high IV PET increases with spinning speed in the range below 5000 m/min; it is maximized at *ca.* 5000 m/min and decreases slightly at 6000 m/min. The fiber tenacity of the high molecular weight PET is higher than that of the low molecular weight in the speed range below 5500 m/min. But the tenacity of the high IV PET fiber spun at 6000 m/min becomes lower than that of the fiber spun from the low IV PET. The elongation at break of the high IV PET is lower than that of the fibers spun from the low IV PET in the low speed range. The changes are consistent with the birefringence changes.

Tenacities of PET fibers are plotted as a function of birefringence in Figure 12. The tenacity and birefringence of the fibers spun from PET with different molecular weights appear to follow nearly the same relationship, that is, the fiber tenacity increases with increasing birefringence in the as-spun PET fibers.

Figure 13 plots the weight fraction crystallinity vs. the birefringence of the as-spun PET fibers. For birefringence values below 0.04, the fibers are essentially amorphous (less than 4% crystallinity). Significant crystallinity does not develop until the birefringence exceeds *ca.* 0.07. This phenomenon has also been observed by Shimizu et al.[18] George and his coworkers[16] reported that the birefringence of the as-spun fibers is a function of the stress at the freeze point. They found that signficant crystallization starts to develop in the spinline when the stress at the freeze point exceeds *ca.* 0.08 g/d. Since higher spinning stress is encountered in the high molecular weight polymer, significant crystallization starts to occur at lower spinning speed. The "speed lag" is *ca.* 1000 m/min between the two polymers with 0.58 and 0.95 IV.

SUMMARY AND CONCLUSIONS

Fiber spinning of PET was conducted at take-up speeds ranging from 2000 m/min to 7000 m/min. Several spinning variables, including method of quench, extrusion temperature, and take-up denier, were varied, as well as was the polymer molecular weight. Effects of changes in these variables on the molecular orientation, crystallinity, and properties of as-spun PET fibers were investigated. Conventional cross-flow quench in high-speed spinning yields fibers with undesirable crimp and asymmetric structure about the fiber axis. Radial-flow quench has eliminated these problems. Changes in spinning conditions, such as extrusion temperature, throughput or take-up denier, molecular weight, and take-up speed, affect the development of fiber structure in the way that a tendency of increasing spinning stress will lead to an increase in molecular orientation and crystallinity in the resulting fibers. The tenacity of as-spun PET fibers increases with increasing average birefringence.

Although the birefringence, crystallinity, and properties of as-spun PET fibers are affected to some extent by changing the spinning variables discussed above, the structure and properties of high-speed spun PET fibers cannot be significantly improved solely by manipulation of the overall spinning variables. Because of the fact that the fiber structure during high-speed spinning is developed mainly in the vicinity of the neck-like deformation region,[3] it is felt that the threadline dynamics in the structure developing zone, that is, the vicinity of the neck should be judiciously modified. This subject will be discussed in the following report.[21]

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