

Efficient Circumferential Superdrawing

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ABSTRACT: Amorphous poly(ethylene terephthalate) (PET) can be stretched at low tension without causing any observable crystallization at temperatures above the glass-transition temperature. The resulting increased length with no measurable change in orientation is called superdrawing. Superdrawing of hollow PET fibers in the circumferential direction was demonstrated earlier. This behavior is accompanied by an increase in fiber voids caused by a combination of air expansion and water permeation. The present work describes efficient techniques for superdrawing in the cir-

cumferential direction only. The process develops large void (>65%) fibers starting from standard 15% void spun supply. It is not possible to obtain such large voids in the longitudinal direction in low denier-per-filament fibers via direct melt spinning. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 123–127, 2005

Key words: circumferential superdrawing; amorphous poly(ethylene terephthalate); glass-transition temperature

INTRODUCTION

A linear, amorphous, low-oriented polymer heated above its glass-transition temperature can be extended to its nearly molecular diameter without developing much orientation. This is the process of longitudinal superdrawing.¹ Any crystallinity, crosslinking, or molecular orientation limits this process. Because the fibers are very weak, the extension process must take place at nearly zero tension levels. A viscoelastic model of poly(ethylene terephthalate) (PET) superdrawing, relating the fiber stress as a function of extension with good agreement with experimental results,² is

$$\text{fiber stress} = \frac{E_0}{1 + \alpha\tau} \{(\tau\alpha)^2[1 - e^{-t/\tau}]^2 + (\tau\alpha)[1 - e^{-t/\tau}]\} \quad (1)$$

where E_0 is the initial modulus, α is the rate of extension, τ is the time constant, and t is the time. At any stage, the superdrawing extension can be stopped and the fiber subjected to a standard mechanical draw, below the glass-transition temperature, to achieve normal molecular orientation and fiber physical properties.

Circumferential superdrawing of hollow, amorphous PET fibers is achieved by immersing them in hot water above the glass-transition temperature (T_g)

of the polymer. The fundamentals and kinetics of the process were described earlier.³ During the process, the fiber wall thickness remains relatively constant (slightly reduced) compared to the initial state, whereas the final inside and outside diameters are enhanced.

The increase of the hollow fiber void during superdrawing is due to air expansion inside the void and water permeation. When the hollow fiber is immersed in hot water, the air inside it expands, causing a partial void increase almost instantaneously. However, this only accounts for about 20% of the void increase during the superdrawing process. The remainder is the contribution of water permeation when the fiber is immersed in a hot bath. The driving force is the partial pressure gradient of water. Initially, the bore side is dry, but as water permeates, its partial pressure inside the bore begins to increase until it reaches the water vapor pressure at the bath temperature. With increased pressure inside the bore, the hollow fiber wall deforms plastically with the resultant volume/void increase in order to maintain a total pressure of 1 atm. At a steady state, a dynamic equilibrium of water transport exists across the fiber wall. A photomicrograph of fibers both before and after circumferential superdrawing is shown in Figure 1.

The kinetics of the circumferential superdrawing of hollow PET fibers in water presents the change in hollow fiber void content as a function of time.³ The governing equation is indicated below as a function of the initial fiber geometry, temperature, and water-polymer interaction:

$$\text{void (\%)} = A + B\tau(1 - e^{-t/\tau}) \quad (2)$$

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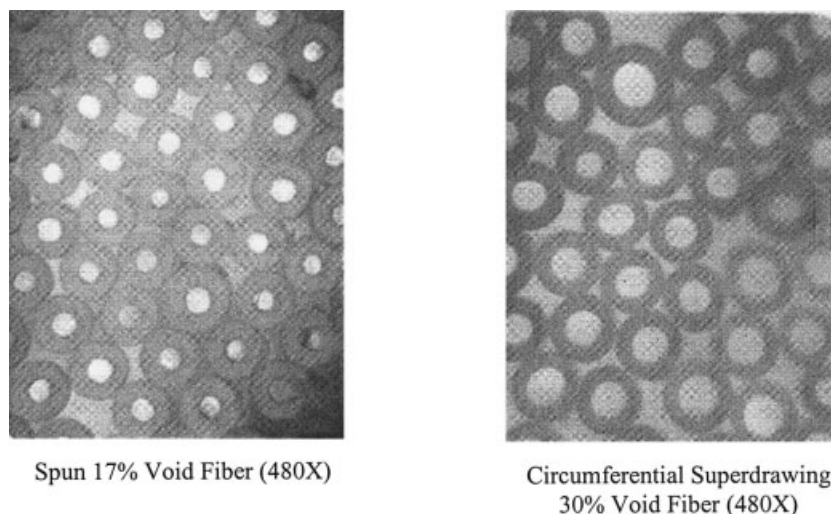


Figure 1 Photomicrographs of spun and circumferential superdrawing fibers.

Here, A is the initial state parameter, B is the transient state parameter, and τ is the steady-state parameter representing the maximum time required for completion of the process. The behavior is characterized by a rapid rise in the fiber void with a subsequent steady state.

Hollow fibers are high value-added products that are widely used in household textiles such as insulation and filling materials. The present work to obtain ultralarge void fibers will help find new applications in technical and biomedical textiles and in the chemical processing industry for liquid/gas separation.

EXPERIMENTAL

Circumferential superdrawing of hollow PET filaments is achieved in the laboratory by immersing samples of spun fibers in water above the T_g of PET. The fibers were spun at low-oriented yarn conditions of 1000–1600 m/min and they had the following properties: denier = 8.0, tenacity = 1.64 g/den, elongation = 285.6%, and spun void = 17%. The filaments are wrapped on a stainless steel F-shaped fork and the two ends tied together (Fig. 2). This ensures a constant length of fibers both before and after treatment with no shrinkage. In addition, the fibers are subjected to superdrawing in the circumferential direction only with no contribution from longitudinal superdrawing. The fiber void is measured using discreet density gradient bottles containing mixtures of $\text{CCl}_4/n\text{-C}_6\text{H}_{14}$.

The hollow portion of the fiber causes a decrease in the apparent fiber density. The fiber density is determined by placing a group of specimens in solution having different known densities and noting whether the specimens float or sink. The specimens are prepared by cutting about 100–200 fibers from a bundle with dulled scissors in 3-in. sections. The dull cut seals

the ends. The fibers are formed into a closed loop of 0.75-in. diameter by twisting one end around the other for ease of handling. When the specimen floats in one solution and sinks in the next higher density solution, the density of the specimen is calculated as the average of the densities of the two solutions. The void content is then 1 minus the ratio of the specimen density to the density of a solid fiber (1.345 g/cm^3), expressed as percent. The method provides a technique for obtaining data rapidly, which is necessary for process control and product release. In addition, the void of a large group of fibers can be measured simultaneously, thereby giving an average value. An alternate method of photomicrographic analyses, although not as efficient, may also be used but provides more accurate data. Here each fiber dimension must be evaluated independently and an average obtained over the desired range.

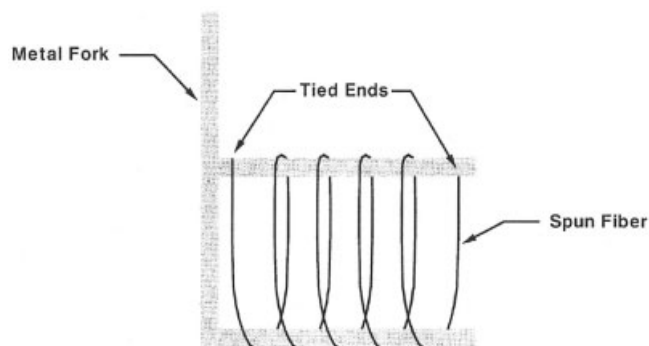


Figure 2 A schematic of the circumferential superdrawing apparatus.

Efficient circumferential superdrawing techniques

Various approaches were undertaken to increase the void level of the hollow filaments. These are discussed below.

Solubility parameter analysis: High temperature approach

The permeation of water in hollow PET fiber contributes approximately 80% of the void increase. Hence, another liquid penetrant with higher solvency and thus possibly a higher rate of permeation in PET should yield a larger void increase. The central property of the penetrant for solubility is the solubility parameter (δ_o).⁴ It is related to the three interacting forces as

$$\delta_o^2 = \delta_D^2 + \delta_p^2 + \delta_H^2 \quad (3)$$

where δ_D is the "dispersion" type (nonpolar) interaction component, δ_p is the polar interaction component, and δ_H is the hydrogen bonding interaction component.

The closer the value of δ_o is for a given liquid and PET, the more alike the two compounds are, consistent with the saying "like dissolves like." The solubility parameter for water is 23.4 whereas that of PET is 11.3 (cal/cm³)^{1/2}. The δ_o for PET was calculated using the structural formula method of Small.⁵

Table I shows the various penetrants selected and the relative location of PET with respect to various organic solvents. The solubility parameters of the penetrants were both above and below PET, although less farther apart than water. The boiling point of all liquids selected was above the T_g of PET (>70°C) because superdrawing occurs above this temperature. Spun samples of hollow fibers were immersed in each liquid at 100°C for 30 s. After exposures to hot solvent, the fibers were immediately quenched in cold water to stop the process and then left to dry under a hood. The fiber geometry and void level were determined at the exposure condition. In all cases, the void fraction de-

TABLE I
Solubility Parameter of Penetrants

| Penetrant | Solubility parameter [(cal/cm ³) ^{1/2}] | Boiling point (°C) | Void (%) |
|--------------------|---------------------------------------------------------------|--------------------|----------|
| Water | 23.5 | 100 | 30.4 |
| Ethylene glycol | 14.6 | 197 | 16.7 |
| Diethylene glycol | 12.1 | 245 | 12.6 |
| Benzyl alcohol | 12.1 | 204.7 | 9.0 |
| Triethylene glycol | 10.7 | 290 | 14.8 |
| Acetic acid | 10.1 | 118 | 3.8 |
| Toluene | 8.9 | 110.8 | 6.0 |
| Xylene | 8.8 | 144 | 7.1 |
| PET | 11.3 | | 16.6 |

TABLE II
Low Boiling Liquid Penetrants

| Solvent | Boiling point (°C) | Void (%) |
|----------------------|--------------------|----------|
| Methanol | 64.7 | 45 |
| Ethanol | 78.4 | 65 |
| 2-Propanol | 82.5 | 35 |
| <i>n</i> -Butanol | 117 | 31 |
| <i>n</i> -Pentane | 36 | 33 |
| Carbon tetrachloride | 76.8 | 24 |
| Acetone | 56.5 | 9 |
| Water | 100 | 30.4 |

creased as indicated by the discreet density liquid method. This is possibly due to rapid crystallization of PET in the presence of hot solvents, indicating an apparent void decline. Thus, the use of hot solvents by themselves does not show any promise as a means of void increase.

Microwave analysis

Samples of hollow fiber spun product were soaked in water at room temperature for a few hours. Enough time was allowed for water to saturate and completely occupy the fiber void. The water-treated samples were then transferred into a microwave oven. Subsequent exposure to microwaves boils the water, which in turn results in void enhancement. The exposure time was varied from 5 to 60 s. In all cases, no increase in fiber void was observed. This is possibly attributable to the fact that the amount of water in the void is not enough to raise the temperature of the polymer mass above its T_g ; hence, no circumferential superdrawing occurs.

Alcohol process: Low temperature technique

The contact of spun hollow fibers with hot solvents does not result in an increase of void size, which is possibly due to crystallization of PET as discussed earlier. A different approach using cold solvents was developed to enhance the void size. In the circumferential superdrawing process, the void increase is a combination of two phenomena discussed earlier. The two processes are air expansion in the fiber void and water permeation.

In the cold temperature process, liquid penetrants with boiling points of <100°C were selected (Table II). A spun supply sample of hollow fibers was immersed in the liquid at room temperature for a period of 12 h (overnight). This is adequate time for the liquid to permeate inside the bore. The liquid-soaked fiber samples were then plunged in boiling water. The considerably higher vapor pressure of the liquid penetrant inside the bore over water (water is the only medium

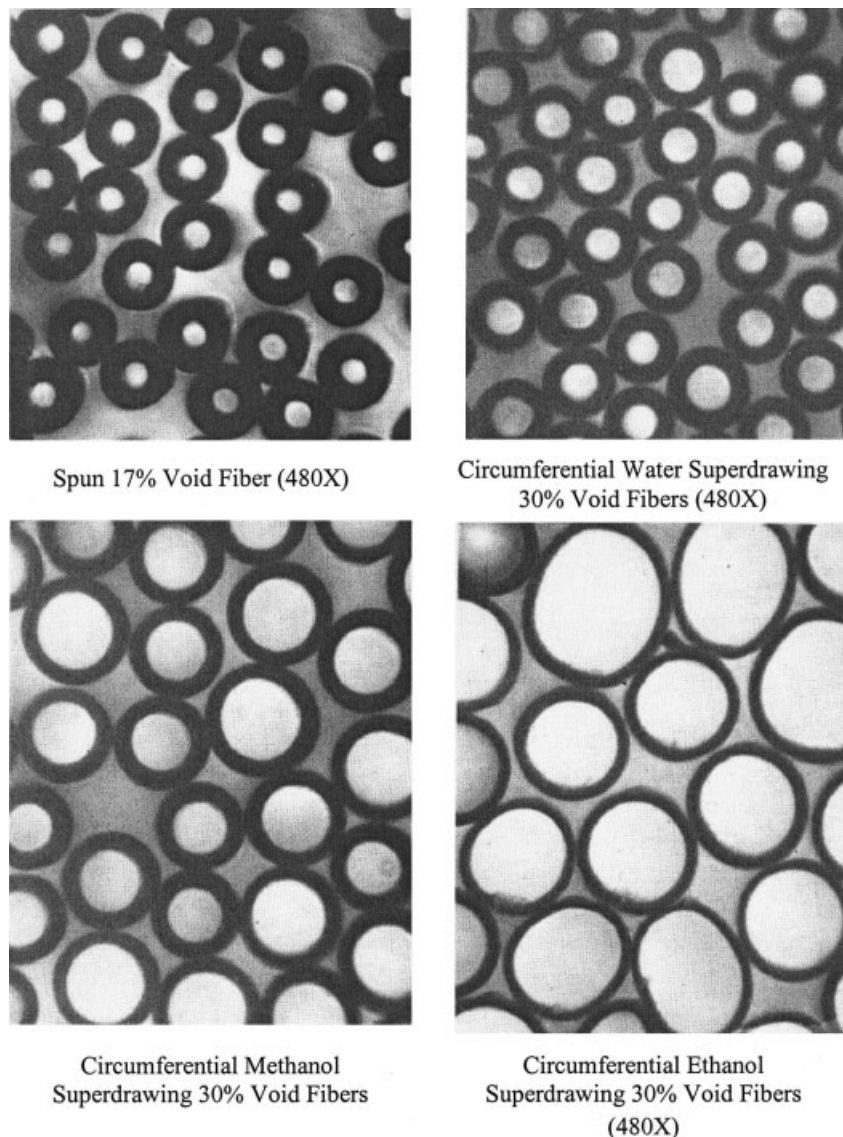


Figure 3 Ultralarge void circumferential superdrawing fibers.

used in the standard circumferential superdrawing process) at 100°C results in larger final voids.

From Table II we observe that for methanol the void obtained was 45% whereas for ethanol it was 65%. Both these solvents yield a considerably higher value than water, which results in a 30% void. Acetone showed no void increase, possibly due to the crystallization of PET. The photomicrographs in Figure 3 show changes in voids with different penetrants. In addition to the void increase, we also observe that this process maintains fiber symmetry along the axial direction (Fig. 4), and the fiber remains circular.

Temperature inversion process

The expansion of air inside the void (“puff-up”) during the circumferential superdrawing process contrib-

utes partially toward the void increase as discussed previously.³ The magnitude of the void increase due to air expansion is approximately 20%, as indicated by the equation below, whereas the water permeation accounts for the remaining 80%.

$$V_2 = \left(V_1 \frac{373 \text{ K}}{298 \text{ K}} \right) \quad (4)$$

Here, V_1 is the initial fiber void and V_2 is the final fiber void. Starting with a spun supply of 17% voids, this process results in a final void level of about 20% if air expansion were the only contributing factor. The singular contribution of air expansion was obtained by dipping hollow fibers in boiling water for a small amount of time (≤ 1 s) to minimize or eliminate the

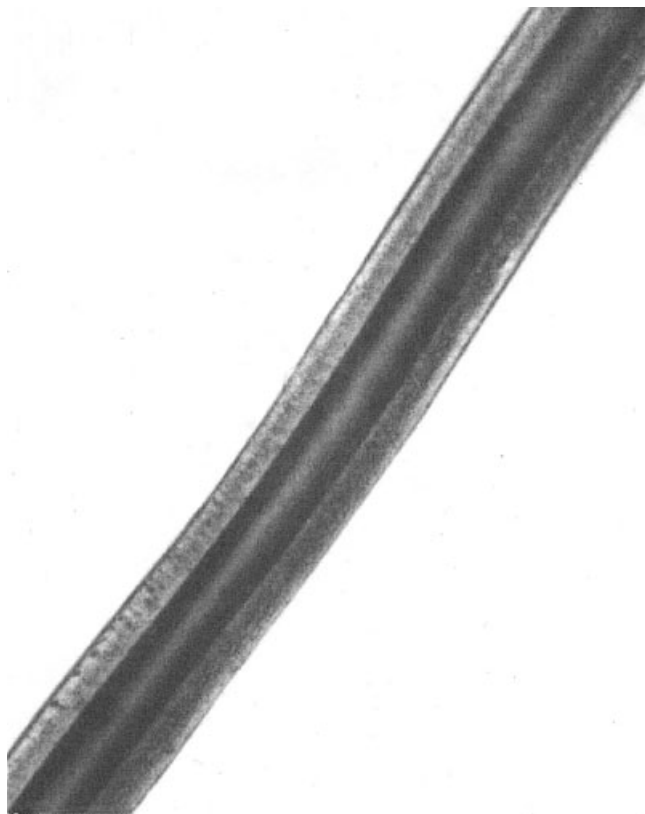


Figure 4 A photomicrograph of a longitudinal cross section of an alcohol-treated fiber.

contribution of permeation. The results indicate that this is indeed true. In addition, this suggests that the expansion of air is instantaneous.

To take advantage of the puff-up phenomena for void expansion, the initial air temperature inside the void is critical. The lower the initial temperature of air at atmospheric pressure, the greater the contribution by expansion. Hence, the final volume occupied by air

at 100°C is larger if the air was initially at 0 versus 25°C, assuming a constant pressure process.

The fibers were left in dry ice (sublimation point = -78.5°C) overnight. They were then plunged in boiling water to achieve circumferential superdrawing. The final void value obtained was 41.5%. This is considerably higher than the final void of 30% when the fibers are initially at a room temperature of 25°C. Hence, the process of first cooling the fibers and then subsequently heating them during the circumferential superdrawing process results in higher void fibers.

CONCLUSIONS

Circumferential superdrawing of hollow PET fibers conducted in water results in increased fiber voids caused by a combination of air expansion and water permeation. The fiber voids increase from about 15–17% in the initial state (spun fiber) to about 30–33% in the final product. To obtain ultralarge void fibers, two techniques are developed. One uses solvents such as methanol or ethanol to obtain final fiber voids in excess of 65%. The other method uses a temperature inversion process using dry ice to give a final void of 41.5%. It is not possible to obtain such large voids in the longitudinal direction in low denier-per-filament fibers via direct melt spinning. There is no change in fiber chemical characteristics. The physical properties are impacted primarily in the circumferential direction and will be the focus of investigation in future work.

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