Critical Stress for Crystallization in the Threadline during High-Speed Spinning of Poly(ethylene Terephthalate)

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Synopsis

The development of structure during steady-state high-speed spinning of poly(ethylene terephthalate) has been correlated with the stress on the threadline. In particular, it is shown that a critical stress at the freeze point of 0.08–0.09 g/denier (9.5–10.6 MPa) is necessary for the occurrence of threadline crystallization independent of polymer molecular weight or process variables such as windup speed or filament character.

INTRODUCTION

A model for the steady-state melt spinning of poly(ethylene terephthalate) (PET) was recently presented by George.[1] An important variable that may be calculated from George's model is the stress at the so-called "freeze point" in the PET threadline where the "freeze point" is defined as that location on the steady-state threadline where the yarn velocity has reached 95% of its final value.[2,3] In a subsequent paper, George, Holt, and Buckley[4] applied this model to a study of the structure development during high-speed spinning of PET. A major conclusion of this work was the observation that the occurrence of threadline crystallization could be uniquely correlated to the calculated stress at the "freeze point" over a wide range of windup speeds (WUS). A calculated characteristic minimum stress of 0.08 g/denier[†] (9.5 MPa) was predicted to be necessary for the formation of a crystalline steady-state PET threadline.

In this paper, results of experimental work related to measurements of the stress at the "freeze point," σ_{fp}, during steady-state melt spinning of PET are reported. The work was conducted on PET samples with a range of intrinsic viscosities from 0.64 to 0.91 dL/g in orthochlorophenol at 25°C. In addition, steady-state spinning was conducted over a wide range of fiber diameters (denier) in an effort to define the influence of σ_{fp} on both threadline crystallization and orientation.

EXPERIMENTAL

The PET samples used in this work were obtained from Fiber Industries, Inc., Charlotte, NC.

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[†] 1 g/denier = 1.18×10^9 dyn/cm^2 = 118 MPa (density = 1.34 g/cc).

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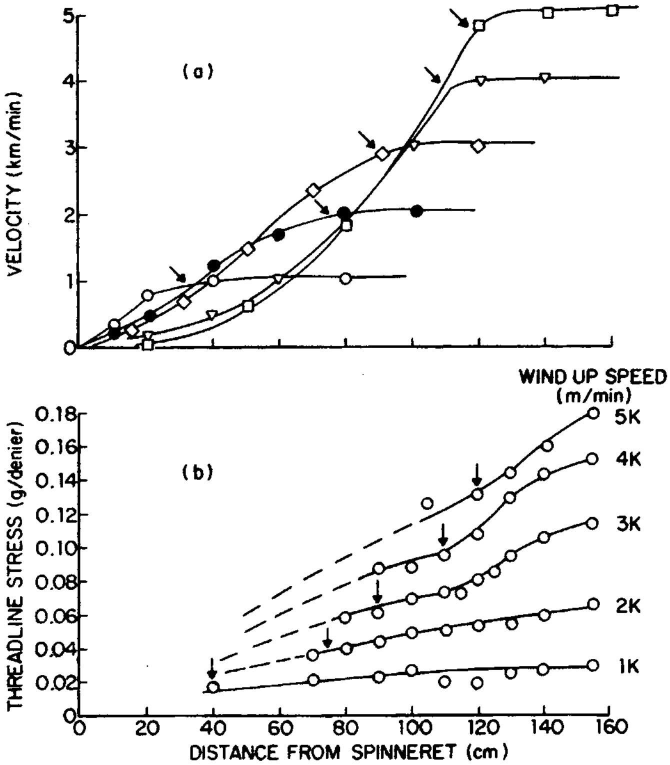

Fig. 1. (a) Velocity profiles for 0.64 IV PET spun to 6 dpf at various windup speeds as a function of the distance from the spinneret (arrows indicate the location of the freeze point). (b) Threadline stress as a function of distance from the spinneret at various windup speeds for 0.64 IV PET (arrows indicate the location of the freeze point).

Threadline velocity profiles were measured with a DISA laser doppler anemometer (LDA) at windup speeds (WUS) in the range 1.0–5.0 km/min at a number of different mass flow rates so as to obtain filaments of the appropriate denier per filament (dpf) since

$$\text{dpf (g/9 km)} = \frac{\text{flow rate (g/min} \cdot \text{hole)}}{\text{WUS (km/min)}} \times 9 \qquad (1)$$

The location of the "freeze point" [2,3] was obtained from the velocity profiles at 95% of final velocity. Density of the filaments samples was measured in a gradient column containing calcium nitrate in distilled water at 23°C. Birefringence of the samples was measured on a Leitz polarizing microscope with a Berek compensator. At least five birefringence measurements were made to ensure an accuracy to within ±0.002.

Threadline stress profiles were obtained using a tensiometer designed at Celanese Research Company. The tensiometer employs the usual three-point bending geometry. However, to ensure minimum disturbance of the threadline a deflection angle of only 5° was employed. Further, when the threadline changes direction over the surface of a tensiometer pin, the centrifugally gen-

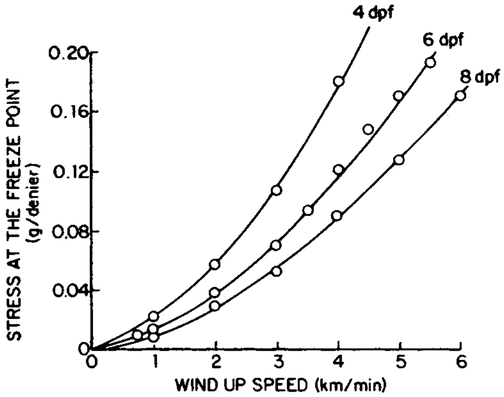

Fig. 2. Stress at the freeze point as a function of windup speed for 0.91 IV PET at different deniers per filament (dpf).

erated tension opposes the force exerted on the surface due to the tension in the threadline. A consequence of these effects—the so-called yarn forwarding effects—is that the measured tension is lower than the true tension in the threadline. The magnitude of the centrifugally generated tension, which is given by mv^2, where m is the mass per unit length of the threadline and v is its velocity, becomes particularly large at windup speeds in excess of about 3 km/min. As such, the true tension in the threadline was arrived at by adding the calculated magnitude of the centrifugally generated tension to the measured tension for each measurement. In addition, air bearings were employed in the tensiometer design to minimize the frictional effects during measurements particularly at high threadline velocities.

RESULTS AND DISCUSSION

Velocity profiles for a 0.64 IV PET spun to 6 dpf at various WUS are shown in Figure 1(a). Locations of the "freeze point" at each WUS are indicated by arrows. The stress profile data under the same conditions are shown in Figure 1(b) with the arrows representing the stress at the "freeze point," σ_{fp}, at each WUS.

A plot of σ_{fp}, obtained as indicated above, as a function of WUS for the three different fiber diameters (dpf) studies is shown in Figure 2 for the 0.91 IV PET. A strong effect of dpf on σ_{fp} is apparent particularly at high windup speeds as is expected. In Figures 3(a) and 3(b), the density ρ and birefringence $\Delta\eta$ of the filaments obtained are shown as functions of windup speed. It is quite apparent that structure development is highly dependent on windup speed and further that the windup speed for the onset of threadline crystallization is distinctly different for each fiber diameter.

In Figures 3(c) and 3(d), the density and birefringence data are plotted against σ_{fp} for this set of samples. It is clear from these plots that the controlling factor for structure development in steady-state spinning of PET is the stress at the "freeze point" since the data for the various fiber diameter all show essentially the same behavior when plotted against this variable. Moreover, a minimum

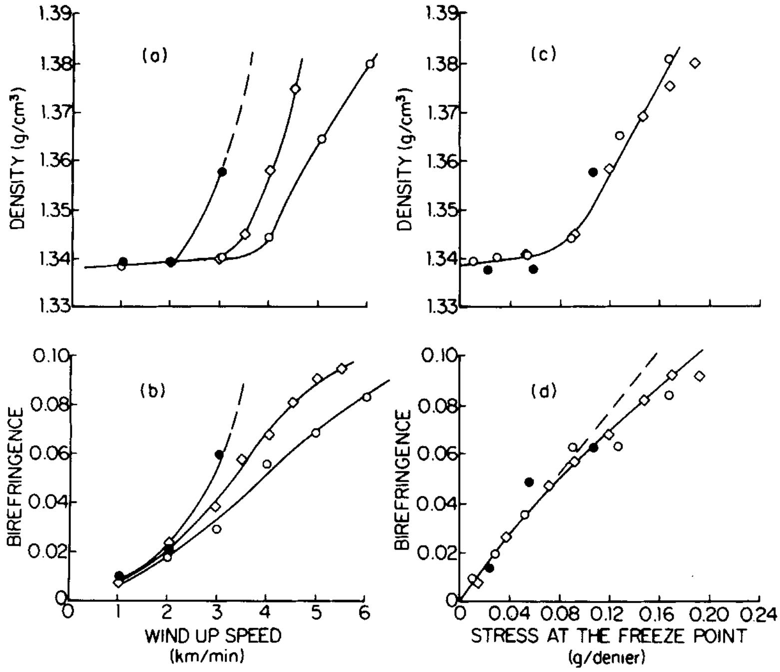

Fig. 3. (a) Density and (b) birefringence as functions of windup speed for the samples spun from 0.91 IV PET; see Figure 2. (c) Density and (d) birefringence as functions of stress at the freeze point on samples from 0.91 IV PET; see Figure 2. (●) 4 dpf; (◇) 6 dpf; (○) 8 dpf.

stress of 0.08–0.09 g/denier (9.5–10.6 MPa) would seem to be necessary for the occurrence of threadline crystallization during high-speed spinning of PET.

The data for the variation in σ_{fp} as a function of polymer molecular weight (or intrinsic viscosity) at a fixed fiber diameter (or dpf) are shown in Figure 4. The stress at the "freeze point" is seen to be dependent on polymer molecular weight particularly at high windup speeds. This is to be expected since the rheological component of the total stress at the "freeze point" is likely to be different due to differences in molecular weight of the samples.

However, the windup speeds required to achieve the critical stress for threadline crystallization are seen to be only marginally different. The density and birefringence data for these samples are shown in Figures 5(a) and 5(b) as a function of σ_{fp}, and the behavior is essentially identical with the data shown in Figures 3(c) and 3(d). A reason for the somewhat lower densities of the 0.91 IV filaments is not immediately apparent but may be related to differences in the rates of crystallization due to its significantly higher molecular weight.

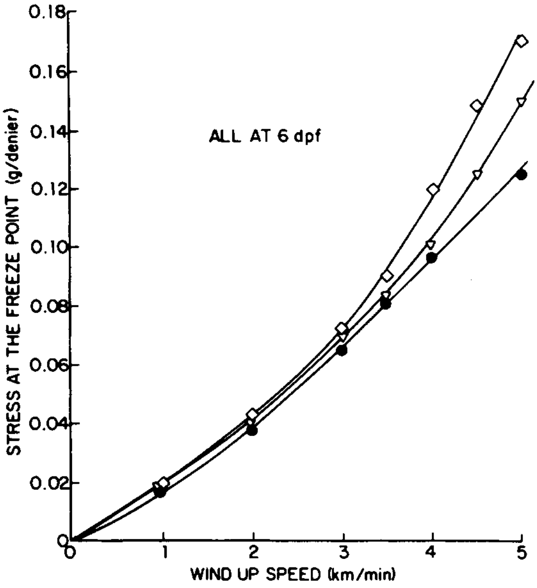

Fig. 4. Stress at the freeze point as a function of windup speed for steady state spinning of PET with three different molecular weights: (◇) 0.91 IV; (▷) 0.70 IV; (●) 0.64 IV.

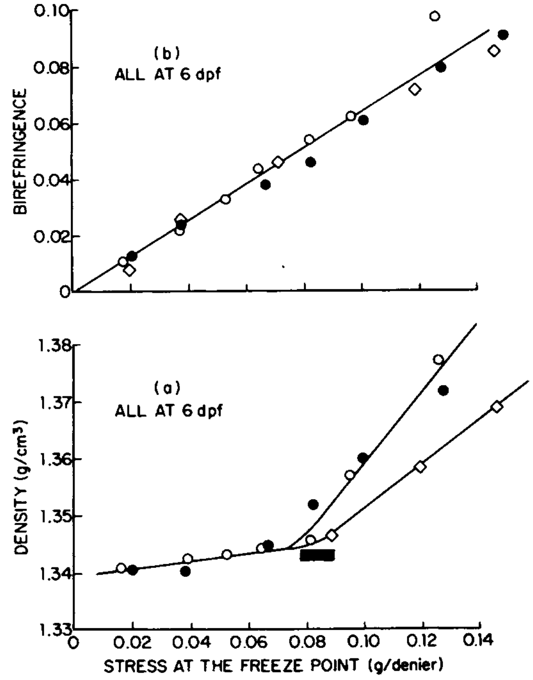

Fig. 5. Density (a) and birefringence (b) as a function of stress at the freeze point for samples in Figure 4: (●) 0.64 IV; (○) 0.70 IV; (◇) 0.91 IV; (—) stress range over which threadline crystallization is evident.

CONCLUSIONS

The data presented in this note experimentally confirm the conclusion reached by George[1] with regard to a critical stress for threadline crystallization based on his model of steady-state spinning of PET. A minimum stress of 0.08–0.09 g/denier (9.5–10.6 MPa) seems to be required for crystallization to occur. Furthermore, the data indicate that the essential parameter for the correlation of structure development and melt spinning variables is the stress at the "freeze point."

It is also noted that the orientation (or birefringence) of melt spun PET filaments varies monotonically with stress at the "freeze point." No evidence of a discontinuity in the orientation is apparent at or about the critical stress for threadline crystallization. This observation implies that the intrinsic birefringences of the crystalline and amorphous regions in PET are quite similar in keeping with independent data previously reported.[5]

Finally, the stress optical coefficient (SOC) calculated from the data in Figure 5(b) is 0.63 denier/g or about 5.8×10^{-10} cm^2/dyn, which compares favorably with the values of 6.4×10^{-10} cm^2/dyn[5] and 5.5×10^{-10} cm^2/dyn [6] previously reported in the literature and obtained on the basis of shrinkage force measurements on melt-spun PET filaments.

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