

Drawing Rate Effects on Morphological Parameters in Nylon-6, PET, and PBT Filaments

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Synopsis

Influence of drawing velocity on morphological parameters of nylon-6, PET, and PBT filaments has been studied. The drawing was carried out at approximately 20°C above the effective glass transition temperature of these materials. The results are explained in terms of drawing-induced changes in temperature and in rate of crystallization.

INTRODUCTION

In synthetic fiber formation processes, drawing the filaments to increase the order and thus improve the mechanical properties constitutes a routine and necessary step. It is common knowledge in this operation that increasing the extent of drawing leads always to an increase in the overall order and in the stiffness and strength, unless one carries it to the extent where the filaments are visibly damaged. The effect of drawing velocity is much more complicated. For example, the birefringence of nylon-6 has been reported to increase,¹ decrease,² or be essentially unaffected³ by rate of drawing. Although isolated studies have been carried out with several polymers,¹⁻⁹ a comprehensive understanding of rate effects has not emerged from these. The complexity arises from the combination of factors such as viscoelastic effects, the induced changes in temperature and stress which can alter the crystallization rate in either direction, and the duration of transformation. The present study, although not extensive enough to answer all the questions, is meant to be the beginning of a systematic study. The initial concentration is on the rate effects in the drawing of PET, PBT, and nylon-6 filaments drawn after reaching comparable temperatures, viz., approximately 20°C above the effective glass transition temperature of the respective materials.

EXPERIMENTAL

Materials and Conditions

The fibers used in this study were nylon-6, poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT), produced at a winding speed of 1000 m/min. The samples were then drawn at various speeds with a constant temperature of the material entering the drawing zone. The drawing setup is shown schematically in Figure 1, and the drawing conditions for all the three materials are listed in Table I. Here, the feed temperature and draw rate are

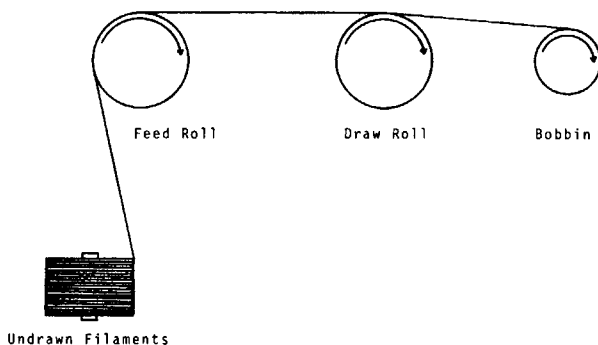


Fig. 1. Schematic diagram of drawing system.

the temperature and speed, respectively, of the feed roll. In each case the temperature of the filaments just before entering the drawing zone (feed temperature) was approximately 20°C above the effective glass transition temperature. To obtain this at different rates of drawing, the filaments were wrapped 15–20 times over the feed roll, maintained at the respective temperatures.

Morphological Parameters

Crystallinity estimates were obtained from measurements of density in the cases of nylon-6 and PET and the heat of melting in the case of PBT. The density measurements were made with a density gradient column prepared with a mixture of carbon tetrachloride and toluene. With the assumptions that the system contains only two phases (crystalline and amorphous) and that the total volume of the system is a sum of the volumes of these two phases, the crystalline volume fraction was estimated. The heat of melting of PBT filaments was obtained with a duPont 910 Differential Scanning Calorimeter coupled to a duPont 990 programmer. Indium was used as a standard sample for calibration. Since no crystallization exotherm was observed during the heating process, crystallinity was estimated by the ratio of enthalpy of melting of the specimen and the heat of fusion of perfectly crystalline PBT (34.5 cal/g¹⁰).

Hermans' crystalline orientation functions were obtained from the azimuthal scans of (002)/(200) reflection of nylon-6, ($\bar{1}05$) for PET, and ($\bar{1}06$) for PBT, using a Phillips wide angle X-ray diffractometer with a nickel-filtered slit system.

TABLE I
Drawing Conditions of Undrawn Nylon-6, PET, and PBT Fibers

Fibers	Draw ratio ^a	Feed temp (°C)	Draw rate (m/min) (speeds of feed roll)
Nylon-6	2.5	25 ^b	5, 10, 20, 40, 80, 160, 320
PBT	2.1	60	5, 10, 20, 40, 80, 160, 320
PET	3.6	90	5, 10, 40, 60, 120, 180, 240

^a Draw ratio: speed of draw roll/speed of feed roll.

^b The T_g of dry nylon 6 is approximately 36°C. At approximately 65% RH, the effective T_g , i.e., the temperature above which evidence of major segmental mobility can be seen, is approximately 5°C. This effect can be seen, for example, in melt spinning of nylon-6, where the fiber, which is essentially fully amorphous when entering the package, crystallizes after equilibration with the moisture in the atmosphere.

Birefringence was measured using a Zeiss polarized optical microscope and a Calcite Ehringhaus compensator. From radial WAXS scans, average crystal sizes were obtained using the Scherrer equation.¹¹ The samples were spun in their plane during the measurement to eliminate orientation effects. The contributions from crystal imperfections and strain effects were ignored in the calculations. The (020) reflection for nylon-6, ($\bar{1}05$) for PET, and ($\bar{1}06$) for PBT were used.

From the meridional scans of small angle X-ray scattering using a Rigaku Denki small-angle X-ray diffractometer, average long period spacings were calculated using the Bragg equation.

Tenacity, initial modulus, and elongation at break were obtained on an Instron Tensile Tester.

RESULTS

Figure 2 shows estimates of crystallinity of PET, PBT, and nylon-6 as a function of draw rate. For all three materials, the changes in the degree of crystallinity are quite small in the range of draw rates used here. Similar results are obtained regarding average size of crystals in these systems (Fig. 3). These results show clearly that the nature of crystallization and melting/recrystallization during drawing of these polymers is independent of drawing rate under the conditions used here.

The lack of sensitivity to drawing rates is also seen in the average crystalline orientation (Fig. 4) and the birefringence (Fig. 5) of all three polymers drawn at different rates. Computations of amorphous and average orientation functions through decomposition of the measured birefringence into contributions from the crystalline and amorphous fractions in the materials show that these

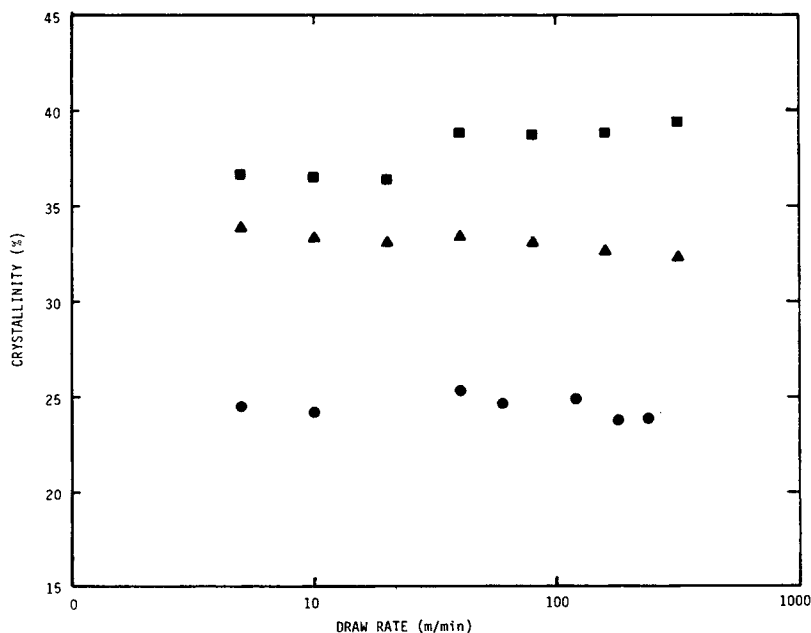


Fig. 2. Estimate of crystalline fractions of drawn fibers: (■) nylon-6; (▲) PBT; (●) PET.

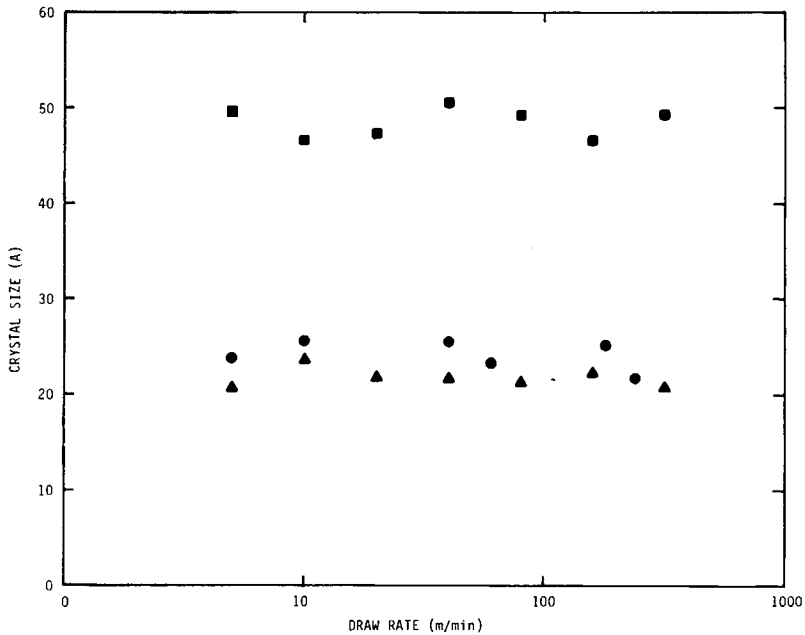


Fig. 3. Average crystal size of drawn fibers: (■) nylon-6 (020); (▲) PBT (I06) (●) PET (I05).

parameters are unchanged when the drawing rate is changed.¹² These drawn fibers, especially PET and PBT, did not show a clear long period spacing. The data from nylon-6, shown in Figure 6, is consistent with the response in the other morphological parameters. As one would readily infer from these data, the mechanical properties of these materials are also essentially unaffected.¹² Figure 7 shows the modulus of drawn fibers as an example. No discernable trends were observed in tenacity (3–4 g/denier for nylon-6 and PBT and ~5 g/denier for PET) and breaking elongation (50–60% for nylon-6 and 10–20% for PBT and PET).

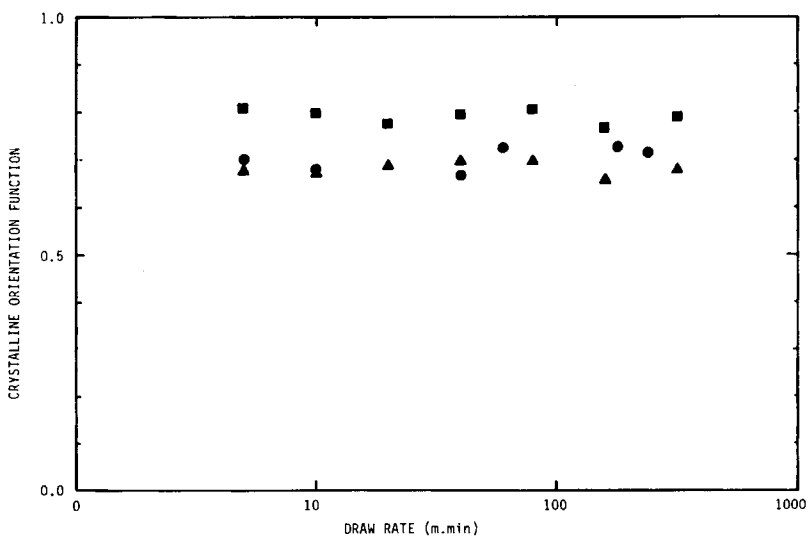


Fig. 4. Hermans' crystalline orientation of drawn fibers: (■) nylon-6; (▲) PBT; (●) PET.

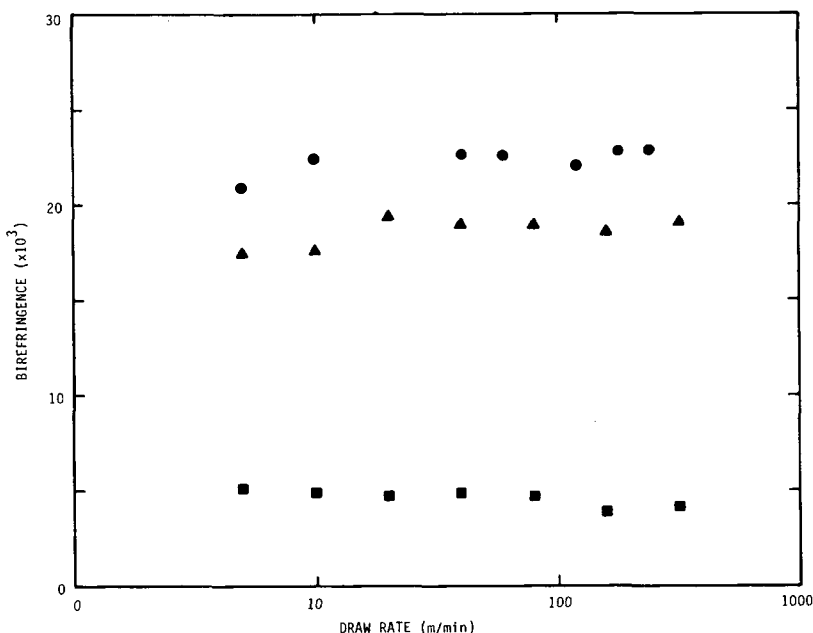


Fig. 5. Drawing rate effects on birefringence: (■) nylon-6; (▲) PBT; (●) PET.

DISCUSSION

The experimental results show clearly that the morphological features of the fibers, drawn at the "feed" temperatures used in this study, are relatively insensitive to the rate of drawing. The reason for this appears to be in the choice of drawing temperatures. The rate of drawing determines the time of deformation-induced transformation. Due to viscous dissipation and any additional crystallization accompanying drawing, the internal temperature of the polymer increases, and this increase is greater at higher rates of drawing. The increase in temperature can cause a change in the rate of crystallization in either direction, depending on the temperature of the material entering the drawing zone. If drawing is carried out at temperatures significantly below that at which the rate of crystallization is maximum, the increase in temperature would cause an increase in the rate of crystallization. Under these conditions, one would expect

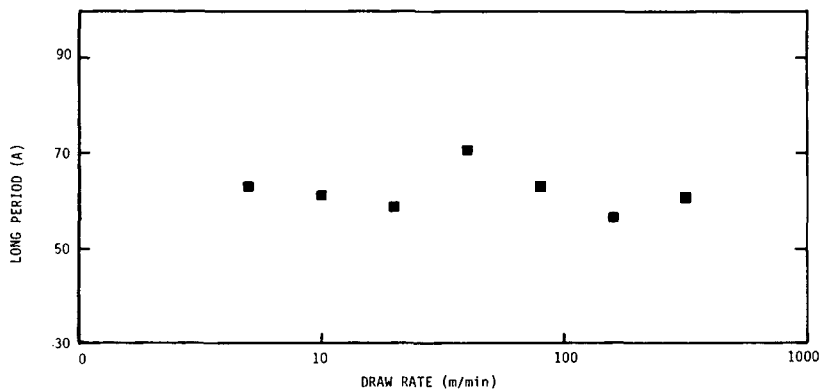


Fig. 6. Long period of nylon-6.

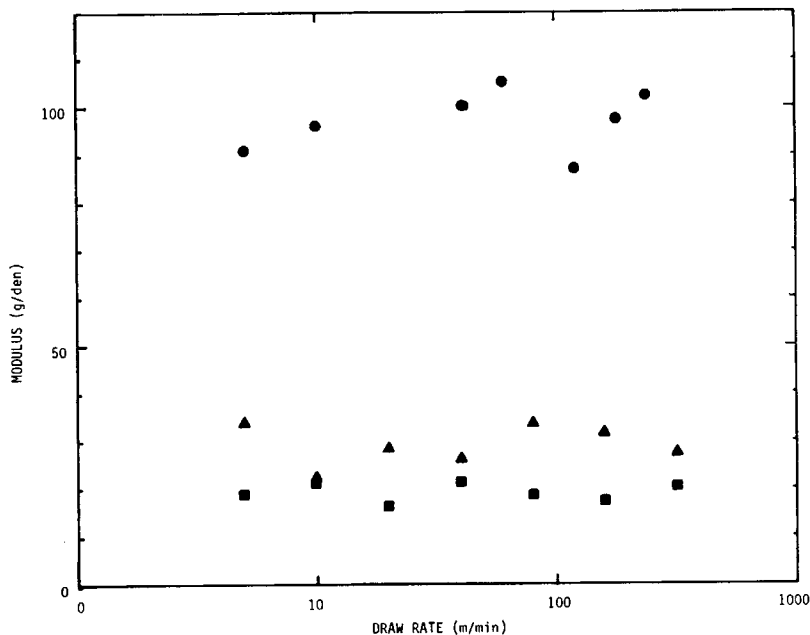


Fig. 7. Initial modulus of drawn fibers (nominal strain rate: 100%/min): (■) Nylon-6; (▲) PBT; (●) PET.

the crystallization rate to increase with increasing rate of drawing. This, however, also reduces the time of deformation-induced transformation in the process. The net effect of these two factors determines the morphological parameters in the drawn filaments. Under the conditions used in the present study, these two effects are seen to essentially compensate each other. The results show clearly that drawing at temperatures not far from the glass transition temperature offers a relatively stable situation as far as rate-induced fluctuations in morphology are concerned. It is interesting to note that the "feed" temperatures used here for nylon-6 and PET are those used routinely in the manufacture of continuous filament textile yarns. The influence of feed temperature in the range of T_g and T_m is being studied currently in our laboratories.

There is need for a comprehensive, systematic study of the influence of the precursor temperature in the range between T_g and T_m of these materials. An important aspect that has not been considered in the present work is the tension developed during drawing and its possible effects on the quality of the process. The increase in temperature during drawing, especially due to viscous dissipation, is likely to change with the feed temperature. Quantitative information regarding these changes is currently unavailable.

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