Effects of draw conditions on deformability and draw efficiency of high molecular weight poly(ethylene terephthalate) fibres

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The effects of draw conditions on the deformability and efficiency of uniaxial draw were studied for solution-spun fibres from high molecular weight poly(ethylene terephthalate) (intrinsic viscosity = 2.6 dl g^{-1}). The fibres could be drawn up to a draw ratio of 16.4 by three stages of draw (tensile draw at 80°C + solid-state coextrusion at 90°C + tensile draw at 200°C). During the solid-state coextrusion, crystal destruction and orientation of non-crystalline segments in the predrawn fibres took place, leading to further deformation at the third stage of draw. The tensile modulus and strength of the resultant highly drawn fibres reached 39 and 2.3 GPa, respectively. The improved ductility and efficiency of draw developed as a result of changes in supermolecular structure and in the number of net points due to entanglements and stress-induced crystals during deformation.

(Keywords: poly(ethylene terephthalate); draw conditions; deformability)

Introduction

The deformation of thermoplastics in the solid state has provided oriented polymers with enhanced tensile properties. Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic with wide industrial applications. Although attempts have been made[1-3] to increase the modulus and strength of drawn PET, it is still difficult to produce high modulus and high strength materials, owing to the low deformability of PET[4]. In fact, the tensile modulus of commercially available drawn fibres is only 10–15% of crystal modulus along the chain direction of PET.

In our previous paper[5], the deformation mechanism of amorphous PET was studied as a function of molecular weight and entanglement density in the predrawn films. It was found that the mechanism could not be simply explained by the entanglement concept, assuming the classical theory of rubber elasticity. The difficulty arises from the change in the number of entanglements during deformation, with chain slippage and disentanglement occurring to a much greater extent in low than in high molecular weight PET. Stress-induced crystallization also takes place. The disentanglement and chain slippage lower draw efficiency. Fakirov and Evstatiev[6] reported that a very high draw ratio of 20 was achieved for PET by a two-stage cold drawing, with each stage followed by high-temperature annealing. But the tensile modulus and strength of the resultant highly drawn samples were only 18.6 and 0.6 GPa, respectively. Thus, the question is how to increase the drawability of PET with high efficiency. The utilization of high molecular weight PET reduces the disentanglement and hence chain slippage during deformation, leading to an increase in the efficiency of draw[5]. However, the number of entanglements per molecule increases with molecular weight, which suppresses the extent of deformability. We have shown that amorphous fibres spun from high molecular weight PET can be obtained by solution spinning[1]. The as-spun fibres have a controlled number of entanglements for draw evaluation.

It is well known that semicrystalline PET films are brittle and cannot be cold drawn by conventional tensile drawing. Pereira and Porter[7] have shown that semicrystalline PET can be effectively drawn by solid-state coextrusion. Their technique involves deformation under pressure on a double substrate, which minimizes the stress concentration and enhances the crystal destruction. The report implies that the stress-induced crystals probably change from permanent to deformable net points by solid-state coextrusion. Taking this into consideration, the drawing of solution-spun fibres from high molecular weight PET has been examined by a multistep draw technique (combination of tensile drawing and solid-state coextrusion). Under optimum draw conditions the fibres could be drawn up to 16 times the original length. The tensile modulus and strength of the resultant highly drawn fibres were 39 and 2.3 GPa, respectively.

Experimental

Materials. High molecular weight PET (intrinsic viscosity = 2.6 dl g^{-1}) was obtained by solid-state polymerization of a commercially available PET (intrinsic viscosity = 0.6 dl g^{-1}). The details have been reported elsewhere[8].

Fibres from the high molecular weight PET were prepared by a solution-spinning method using a mixed solvent of 1,1,1,3,3,3-hexafluoro-2-propanol and dichloromethane (50/50, v/v). The polymer concentration in solution was 9 wt%, which provides an appropriate

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entanglement density for achieving the maximum draw ratio[5]. The solutions, made by directly dissolving polymer in the mixed solvent at room temperature, were extruded through a conical capillary die with a diameter of 0.2 mm at room temperature. As-spun fibres were coagulated in water and then dried at 40°C under vacuum before drawing. Wide-angle X-ray diffraction patterns of dry as-spun fibres confirmed that all the predrawn fibres were amorphous.

Drawing. The draw techniques were chosen with regard to the transition temperatures of PET: glass transition temperature, T_g, 70°C; melting temperature, $T_m > 240°C$. As-spun fibres were drawn by a tensile force at 80°C up to a draw ratio of 6.5. The drawn fibres were then utilized for each of two draw methods: (A) the drawn fibres were coextruded at 90°C, followed by tensile drawing at 200°C under a constant load; (B) the drawn fibres were drawn by tensile force at 210°C, followed by tensile drawing at 200°C under a constant load. The total draw ratio (*TDR*) was determined by measuring the separation between lateral ink marks on the sample before and after drawing.

Measurements. The tensile strength of drawn samples along the fibre axis was measured at room temperature and at a strain rate of $1.7 \times 10^{-3}\,s^{-1}$ by a tensile testing machine. The modulus was determined from the tangent to the stress–strain curve at low strain (0.1%). Sample density was determined at 30°C in a density gradient column prepared from n-heptane and carbon tetrachloride. Weight per cent crystallinity was calculated from the observed density on the basis of a two-phase model. The amorphous and crystalline densities for PET were taken to be 1.333 and 1.455 g cm^{-3}, respectively[9]. The intrinsic viscosity of the samples was measured in a mixed solvent of trifluoroacetic acid–dichloromethane (50/50, v/v) at 30°C. The birefringence was measured by a polarizing microscope equipped with a Berek compensator and quartz plate as an additional compensator.

Results and discussion

The purpose of this work is to determine the properties of highly drawn PET fibres made at high draw efficiency. Amorphous fibres with high molecular weight were prepared by the solution-spinning method[1]. Our previous work[5] revealed that the initial polymer concentration used for film preparation had a marked effect on the maximum achievable draw ratio, especially for higher molecular weights. The optimum polymer concentration found for PET, with intrinsic viscosity of 2.2 dl g^{-1}, was around 10 wt%. In this study, the molecular weight weight utilized for the solution spinning was 2.6 dl g^{-1}. Thus, a polymer concentration of 9 wt% was chosen, from which as-spun fibres were prepared at room temperature. The dried, as-spun fibres could be drawn up to a draw ratio of 6.5 at 80°C by a tensile force. The draw ratio achieved was similar to that obtained in the previous work[5].

The combination of coextrusion and tensile drawing was then examined to obtain more highly drawn fibres with high draw efficiency. The solid-state coextrusion method is expected to enhance the deformability of the crystalline region[7]. Further, tensile drawing under high tension might exert a considerable constraint on the mobility of oriented non-crystalline chain segments and thus restrict their relaxation, leading to an increase in draw efficiency[10]. In this study, two draw sequences (methods A and B) were evaluated for the effect of coextrusion draw on the subsequent deformability of PET. *Table 1* summarizes the ultimate draw conditions for achieving the highest deformation ratio by each method. As stated in the Experimental section, the samples utilized for methods A and B were drawn fibres with a draw ratio of 6.5, which were obtained by tensile drawing of as-spun fibres at 80°C. The maximum total draw ratio (TDR_{max}) obtained by method B is around 12, similar to that obtained previously by two-stage tensile draw[1]. On the other hand, the TDR_{max} obtained by method A is considerably higher than that obtained by method B.

An important characteristic of method A is the utilization of coextrusion drawing at a low temperature of 90°C. As seen in *Table 1*, the draw ratio achieved by coextrusion is around 1.8, similar to that achieved by tensile drawing at a high temperature of 210°C. However, the coextrudates could be further drawn at a high temperature under a high load. The achievable draw ratio at this stage (DR_{2max}) was primarily dependent on the load. For the highest load of 58 kg mm^{-2} applied to the sample at 200°C, the DR_{2max} reached 1.4. Thus, the TDR_{max} by method A was $6.5 \times 1.8 \times 1.4 = 16.4$. The same second-stage tensile draw was also applied to fibres obtained by method B, but the increase in DR_2 was less because the tensile load applicable to the samples was limited to a low value (<25 kg mm^{-2}) owing to lower fibre strength. With coextrusion draw (method A), the draw ratio of the samples was increased from 6.5 to 11.7, and simultaneously birefringence (Δn) also increased from 0.175 to 0.208. However, the sample crystallinity decreased from 42.8 to 33.2%. During these changes, the orientation function of the crystalline regions (F_c), obtained by X-ray diffraction, remained almost constant at 0.91. Thus, the orientation function in the non-crystalline regions, F_a (which was computed by combining Δn with F_c and sample crystallinity), increased from 0.56 to 0.76. The structural changes during deformation by method B were different from those of the coextrudates, although the deformation ratio achieved was similar for the two methods ($DR_1 = 1.8$). By tensile drawing at a high temperature of 210°C (method B), the sample crystallinity increased from 42.8 to 58.5%, and simultaneously Δn increased, but the increase was small (0.18 to 0.20) compared with that observed in the coextrudates. Thus, the increase in F_a was

Table 1 Draw conditions for PET amorphous fibres

	Method A	Method B
First stage		
Draw technique	Coextrusion	Tensile draw
Draw temp. (°C)	90	210
DR_{1max}	1.8	1.8
Second stage		
Draw technique	Tensile draw	Tensile draw
Draw temp. (°C)	200	200
Load (kg mm^{-2})	58	25
Time on draw (min)	20	20
DR_{2max}	1.4	1.05
TDR_{max}[a]	16.4	12.2

[a] $TDR_{max} = 6.5 \times DR_{1max} \times DR_{2max}$

small (0.56 to 0.67). These results suggest that the enhanced deformability of the coextrudates is attributable to the low crystallinity and a high degree of chain orientation in the non-crystalline regions. Coextrusion also eliminates void formation. Such a supermolecular structure might make it possible to apply a higher tension during subsequent deformation, leading to the increase in draw ratio.

As described, the achievable draw ratio of the coextrudates (DR_2) depends on the load applied to the samples during tensile drawing at 200°C: it increased from 1.1 to 1.4 with increasing load from 10 to 58.5 kg mm^{-2}. In *Figure 1*, the F_a and sample crystallinity are plotted against the load for the final stage of draw. Although the crystallinity is almost independent of load, the F_a increases with load. Further, the measured F_c was independent of load (data not shown). These results suggest that the increase in DR_2 arises primarily from chain extension in the non-crystalline regions. In *Figure 2*, tensile modulus and strength are plotted against the load for the final draw step. Both modulus and strength increase with load. At the highest load of 58.5 kg mm^{-2}, the TDR reached 16.4. Such highly drawn fibres exhibited a tensile modulus and strength of 39 and 2.3 GPa, respectively. Although the TDR of 16.4 is slightly lower than that obtained by Fakirov and Evastatiev ($DR = 20$)[6], the tensile properties of our drawn fibres are more than double the values they reported, indicating the achievement of draw efficiency. From *Figures 1* and *2*, it is suggested that the increase in tensile properties is closely related to the increase in F_a. As the T_g of isotropic PET is around 70°C, large-scale motions are restricted at room temperature in the oriented non-crystalline segments of PET. In this case, the tensile properties of predrawn PET at room temperature are markedly enhanced by the increased chain orientation in the non-crystalline regions.

The highest deformation ratio of 16.4 exceeds the estimated highest deformation ratio (λ_{max}), which was calculated for this PET molecular weight from the classical theory of rubber elasticity[5]. However, the tensile modulus of such highly drawn samples is only 36% of the crystalline modulus of PET along the chain direction[11]. Further, the sample crystallinity and F_a at a load of 58.5 kg mm^{-2} are 67% and 0.924, respectively. These values indicate that a part of the chains is not yet fully extended and oriented, even in the drawn fibres with the highest draw ratio of 16.4. There must be uncertainty with regard to the absolute comparison of TDR_{max} with λ_{max}, since the calculation of λ_{max} was based on assumptions. During solid-state deformation, disentanglement and partial degradation of macromolecules might occur, resulting in a decrease in the draw efficiency. Some chain slippage must also have occurred. The utilization of yet higher molecular weight PET for the drawing might suppress the disentanglement and relaxation of oriented amorphous chain segments during deformation, leading to a further increase in draw efficiency[5]. These matters are under study.

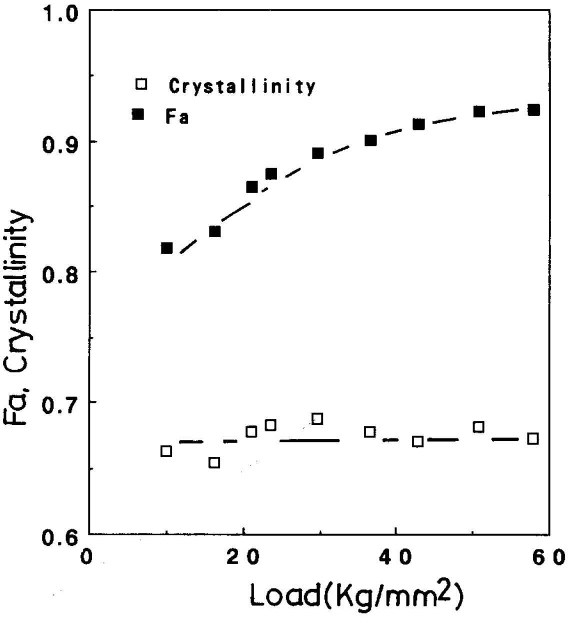

Figure 1 The crystallinity and orientation function (F_a) in the non-crystalline regions *versus* load applied to samples

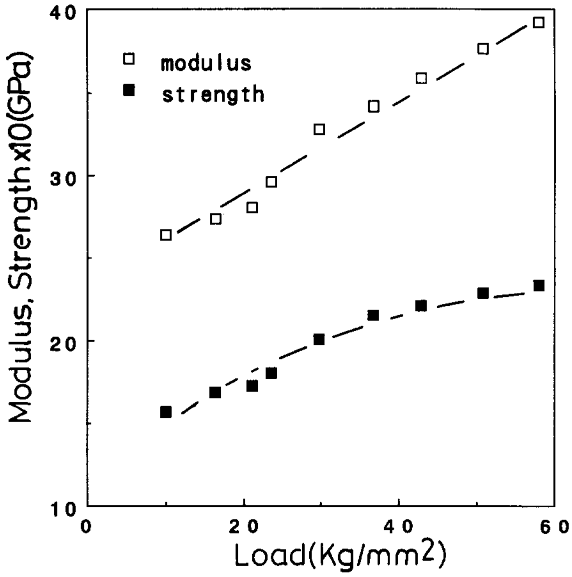

Figure 2 The tensile strength and modulus *versus* load applied to samples

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References

1 Ito, M., Takahashi, K. and Kanamoto, T. *J. Appl. Polym. Sci.* 1990, **40**, 1257
2 Kunugi, T., Ichinose, C. and Suzuki, A. *J. Appl. Polym. Sci.* 1986, **31**, 429
3 Kunugi, T., Suzuki, A. and Hashimoto, M. *J. Appl. Polym. Sci.* 1981, **26**, 1951
4 Ito, M., Tanaka, K. and Kanamoto, T. *J. Polym. Sci., Polym. Phys.* 1987, **25**, 2127
5 Huang, B., Ito, M. and Kanamoto, T. *Polymer* in press
6 Fakirov, S. and Evstatiev, M. *Polymer* 1990, **31**, 431
7 Pereira, J. R. C. and Porter, R. S. *J. Polym. Sci., Polym. Phys.* 1983, **21**, 1147
8 Ito, M., Wakayama, Y. and Kanamoto, T. *Sen-i Gakkaishi* 1992, **48** (10), 569
9 De, R., Duibeny, P., Bunn, C. W. and Brown, C. J. *Proc. R. Soc., Lond. Ser. A* 1955, **226**, 531
10 Ito, M., Takahashi, K. and Kanamoto, T. *Polymer* 1990, **31**, 58
11 Sakurada, I. and Kaji, K. *Kobunshi Kagaku* 1969, **26**, 817