

Two-Stage Drawing of Poly(Ethylene 2,6-Naphthalate)

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SYNOPSIS

Initially amorphous and semicrystalline films of poly(ethylene 2,6-naphthalate) with different molecular weights were drawn by two-stage drawing, that is, coextrusion at low temperatures (25–160°C) followed by tensile drawing at high temperatures (200–245°C). Both films could be drawn up to a draw ratio of 8–10 by this method under controlled conditions. The tensile modulus and strength of drawn samples were greatly affected by the draw temperature for the first stage, predrawn morphology, and molecular weight. The remarkable effects of these variables on the tensile properties are closely related to the difference in the resultant amorphous chain orientation of the samples, reflecting the disentanglements and chain slippage during drawing, and the dissipation of chain orientation after processing.

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) molecules contain naphthalene rings, which are stiffer than those of poly(ethylene terephthalate) (PET). The important aspect of PEN is the influence of an increased chain stiffness on the mechanical and thermal properties of this polymer. Detailed thermal analysis has revealed that the equilibrium melting temperature is estimated to be 337°C, and the glass transition temperature (T_g) of a completely amorphous sample is about 117°C.¹ These values are significantly higher than those of PET. The crystal modulus of PEN along the chain direction has been determined to be 142 GPa² by wide angle X-ray diffraction, which is about 40% higher than that of PET. In fact, Ouchi et al.³ report that the mechanical properties of biaxially drawn PEN are higher than those of PET. Thus, the development of highly drawn PEN in film and fiber forms may further enhance these properties and promote the application of this polymer.

PEN has been uniaxially drawn by solid-state coextrusion⁴ and tensile drawing.⁵ Although an

achievable maximum draw ratio of 5.75 has been reported, the effects of draw conditions on the resultant mechanical properties and structure of drawn PEN have not been well understood.

In our recent study on the drawing of PET, it has been found that predrawn morphology, molecular weight, draw conditions, and draw technique have a remarkable effect on the deformability and tensile properties of the resultant drawn samples.^{6–8} The fibers from high molecular weight PET could be drawn up to a draw ratio of 13 by a two-stage draw technique. The tensile modulus and strength of such highly drawn fibers reached 275 g/d and 15.5 g/d, respectively.

In this study, amorphous and semicrystalline films of PEN with various molecular weights have been drawn in a two-stage draw. The effects of predrawn morphology, molecular weight, and draw conditions on the structure and properties of the drawn PEN films have been studied by X-ray diffraction, tensile measurements, and other tests.

EXPERIMENTAL

Samples

PEN pellets, with an intrinsic viscosity (IV) of 0.56 dL/g, were kindly supplied by Teijin Co. Higher molecular weight samples were obtained by solid-

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state polymerization of porous and fibrous aggregates, which were precipitated from a polymer solution into methanol. A polymer solution (4 wt %) was prepared at room temperature by dissolving the as-received pellets in a mixture of trifluoroacetic acid (TFA) and dichloromethane (DM) (50/50, v/v). The polymerization was carried out at 255–260°C for 15–30 h under vacuum. The IV of the samples after the polymerization was in the range of 1.08 to 1.43 dL/g, depending on the polymerization time. As-received and high molecular weight PEN were compression molded at 290°C, followed by rapid quenching in ice water to obtain amorphous samples. At this stage, the IV retention was in the range of 75 to 95%, depending on the initial molecular weight: the higher the molecular weight, the lower the retention. Semicrystalline PEN films were obtained by annealing the melt quenched films at 200°C for 12 h under vacuum. No change in molecular weight was detected after the annealing. Thus, in this study, both melt quenched (amorphous) and annealed (semicrystalline) films with the IV of 0.53, 0.79, and 1.08 dL/g were utilized for drawing. A two-stage drawing technique, developed by Kanamoto et al.,⁹ was used for drawing. For the first-stage, a solid-state coextrusion technique¹⁰ was utilized. Predrawn films were placed between two-split billet halves of commercial polyethylene or poly(4-methyl-1-pentene), and the assembly was coextruded at constant temperatures ranging from 25 to 160°C. For the second stage, a conventional tensile drawing was made at constant temperatures ranging from 200 to 245°C

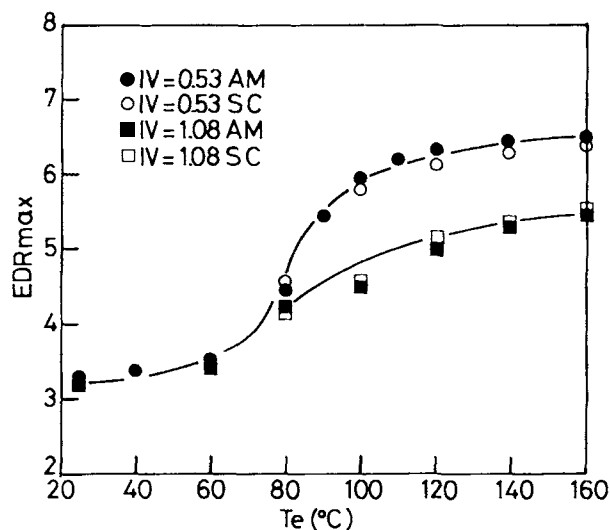


Figure 1 EDRmax vs. extrusion temperature for various samples.

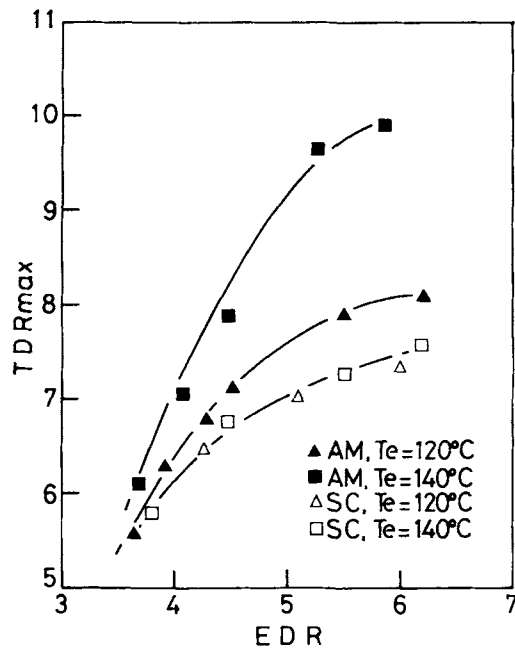


Figure 2 TDRmax vs. EDR for various samples.

on the coextrudates. The draw ratios at the first (EDR) and second (DR) stages were determined by measuring the separation between lateral ink marks on the samples before and after drawing. The total draw ratio (TDR) after the two-stage draw was defined by $TDR = EDR \times DR$.

Measurements

The tensile modulus and strength of drawn samples along the fiber axis were measured at room temperature and at strain rates of 10^{-3} and 10^{-1} 1/s, respectively, by a tensile testing machine. Sample density was determined at 30°C in a density gradient column prepared from *n*-heptane and carbon tetrachloride. Weight percent crystallinity was calculated from the observed density on the basis of a two phase model. The amorphous and crystalline densities for PEN were taken to be 1.325 and 1.407 g/cm³, respectively.¹¹ The intrinsic viscosity of the samples was measured in a mixed solvent of TFA and DM (50/50, v/v) at 30°C.

RESULTS AND DISCUSSION

Drawing Behavior

In previous papers,^{7,8} we emphasized the feasibility of two-stage draw (combination of cold drawing and

hot drawing) in obtaining high modulus and high strength PET fibers. In this study, the same technique was utilized for both amorphous (AM) and semicrystalline (SC) PEN films. The SC films were brittle due to high crystallinity (45%) and they could not be cold-drawn by conventional tensile drawing. Pereira and Porter¹² have shown that semicrystalline PET can be effectively drawn by using a solid-state coextrusion technique. They report that the technique involves deformation under pressure on a double substrate, which minimizes the stress concentration and enhances the crystal destruction. In this work, solid-state coextrusion was used for the first stage drawing. The coextrudates were further drawn at constant temperatures ranging from 200 to 245°C by conventional tensile drawing. In this study, the highest draw ratio at the second-stage was obtained at a draw temperature of 230°C. Thus, the second-stage draw was mainly carried out at 230°C.

In Figure 1, the maximum attainable extrusion draw ratio (EDR_{max}) is plotted against extrusion

temperature (T_e) for the AM and SC films with different molecular weights. A gradual increase in the EDR_{max} with T_e is observed above the T_g of 80°C, near the T_g of PEN. This increase is more prominent in the low molecular weight samples, and the EDR_{max} is higher for these samples than for the higher molecular weight ones. The highest EDR_{max} of 6, achieved here for the low molecular weight PEN, is comparable to that reported by Ghanem and Porter.⁴ It is noted that even the brittle SC films, which could not be elongated by tensile force, could be coextruded and the EDR_{max} was almost independent of predrawn morphology, similar to the coextrusion drawing of PET.^{12,13} The higher EDR_{max} for a low molecular weight PEN is likely due to the consequence of the enhanced disentanglements and chain slippage occurring during coextrusion. A detailed discussion of this will be made in the following section.

The important parameters in achieving a higher draw ratio after the second-stage drawing at 230°C were the initial EDR and T_e of the coextrudates. In

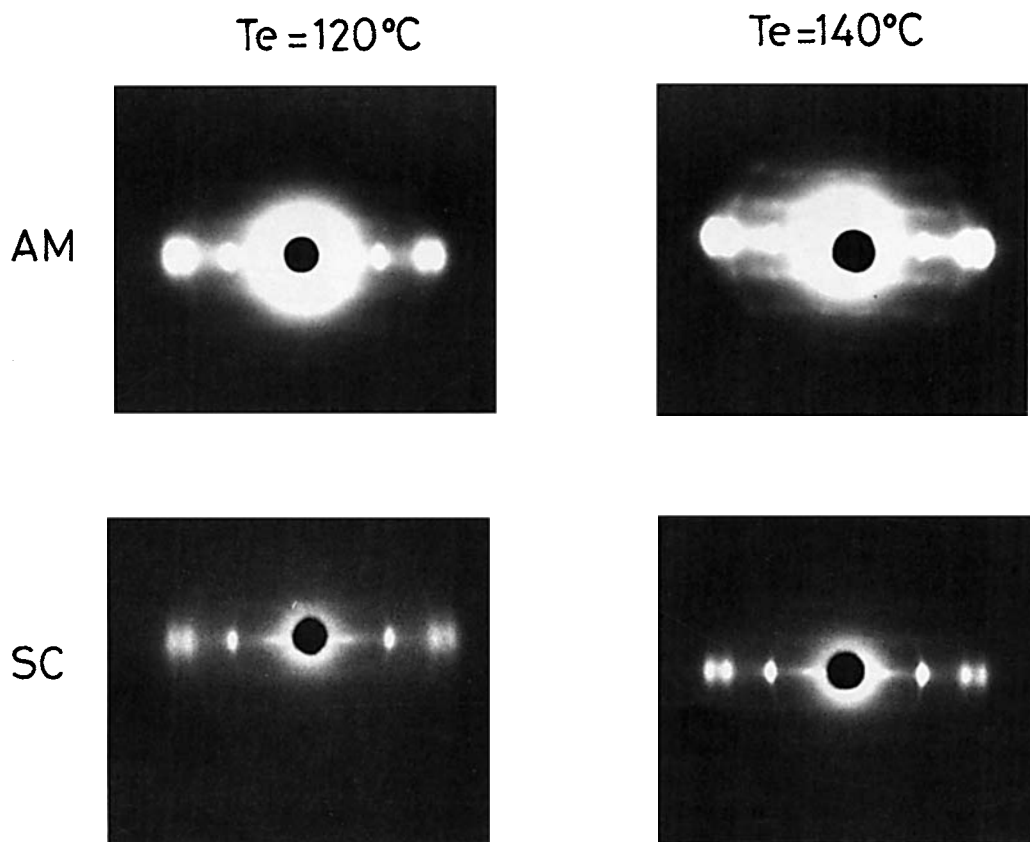


Figure 3 WAXD photographs of coextrudates with EDR 6 from AM and SC films with IV of 0.53 dL/g.

Figure 2, the maximum attainable total draw ratio (TDRmax) is plotted against the initial EDR at $T_e = 120$ and 140°C for the post-drawing of the coextrudates prepared from PEN with IV of 0.53 dL/g . The TDRmax for all the coextrudates increases with increasing initial EDR. It was found that the attainable draw ratio at the second stage was almost independent of the initial EDR and was less than 2 for all the coextrudates. The coextrudates from AM films show a marked T_e dependence of the TDRmax: the higher the T_e , the higher the TDRmax. Thus, the highest TDRmax of 10 was achieved by second-stage drawing of a coextrudate with EDR 6 prepared from AM film at $T_e = 140^\circ\text{C}$. However, at any given TDR, the tensile modulus and strength for the two-

stage drawn samples from coextrudates prepared at 140°C were lower than 70% of values for those from coextrudates prepared at $T_e \leq 120^\circ\text{C}$. Therefore, the high TDRmax with a poor efficiency of draw, observed for the coextrudates prepared from AM films at 140°C , might be responsible for the presence of fewer and/or less effective network points in the coextrudate with a low molecular weight. The ductility of the coextrudates from SC films was not affected by T_e , and TDRmax was lower than that for the coextrudates from AM films. Such important effects of predrawn morphology on the structure and ductility of coextrudates and final products have been studied by wide angle X-ray diffraction.

Figure 3 shows wide angle X-ray diffraction pat-

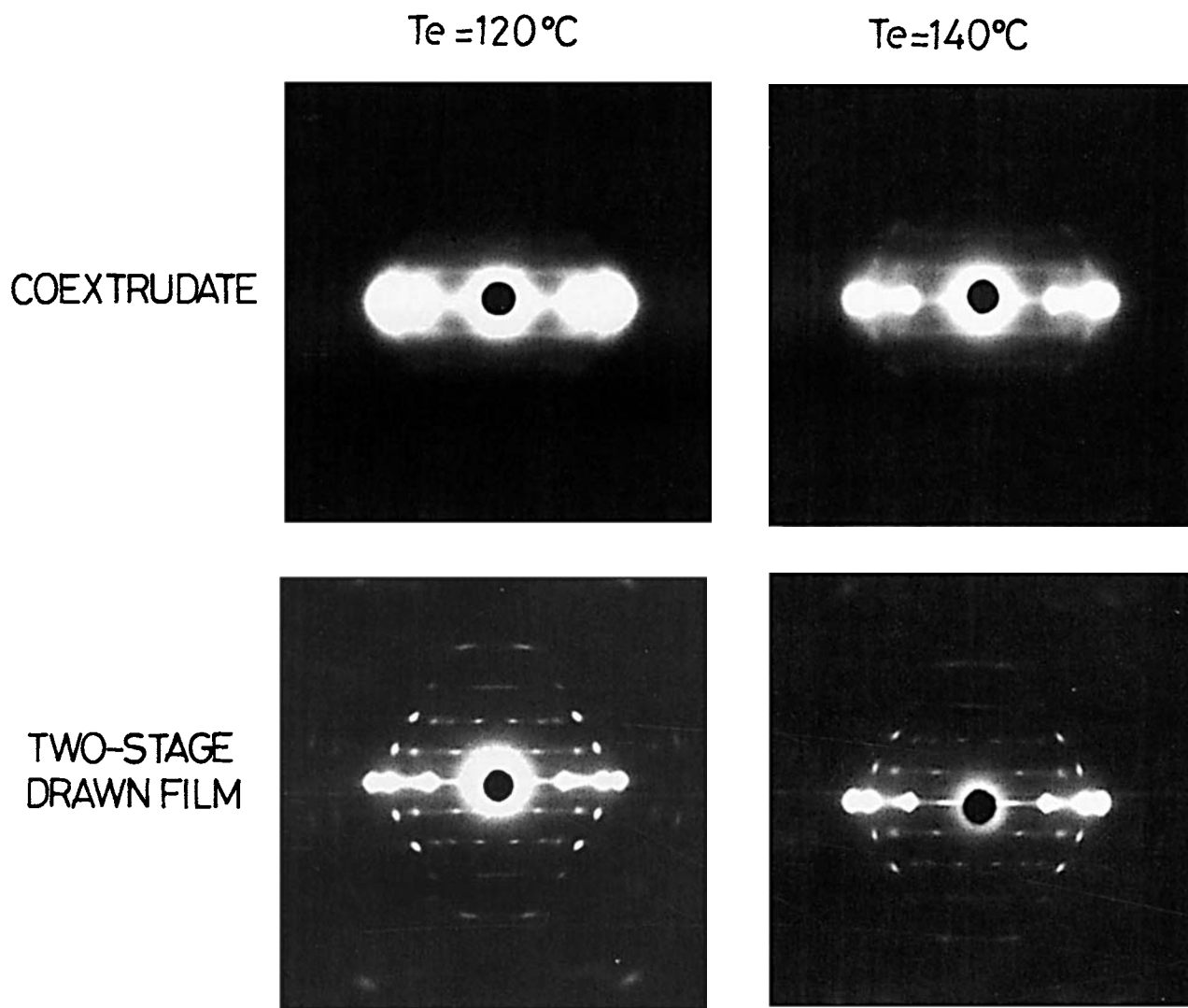


Figure 4 WAXD photographs of coextrudates with EDR 5 from AM films with IV of 1.08 dL/g and their two stage drawn films with TDR 7.2.

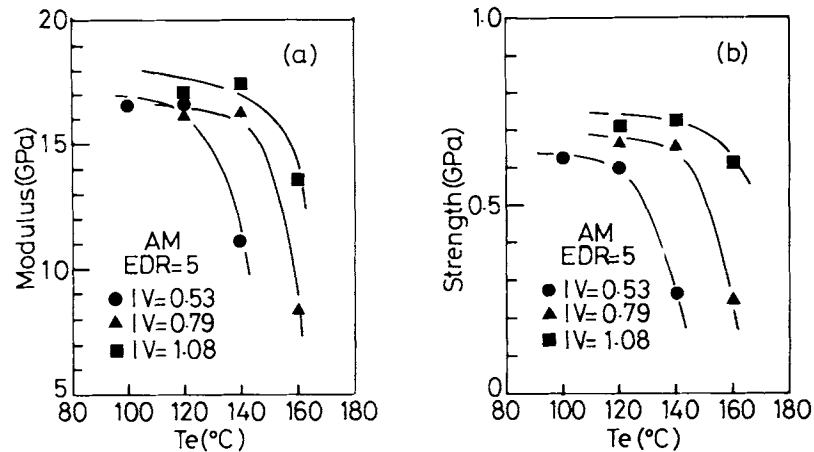


Figure 5 (a) Modulus vs. extrusion temperature and (b) strength vs. extrusion temperature for the coextrudates with various molecular weights.

terms of coextrudates with EDR 5 from AM and SC films prepared at 120 and 140°C. The diffraction patterns for the coextrudates from AM films are extremely broad and diffuse compared with those from SC films. This means that crystal perfection and/or its size for the stress induced crystals is lower than that for the crystals which are produced by the deformation of thermally induced crystals. As described above, the ductility of the coextrudates from SC film was lower than that for the coextrudates from AM film. Large crystals with high perfection might reduce the ductility of the coextrudates as they act as stable network points.

Figure 4 shows wide angle X-ray diffraction patterns of coextrudates with EDR 5 from AM films and their two-stage drawn films with TDR 7.2. Less perfect crystals, initially existing in the coextrudates,

changed into more perfect crystals after the second-stage draw. During the hot drawing at the second-stage, thermal annealing took place, which increased the crystallinity and crystal perfection. Such structural changes might reduce the ductility of the samples. More detailed discussion on the structure will be made in the next section.

Structure and Properties of Coextrudates

For all the coextrudates, both tensile modulus and strength at break increased with increasing EDR. At a given EDR, they were a function of T_e , mol wt, and predrawn morphology. Figure 5 illustrates the effects of T_e and mol wt on the tensile modulus and strength of the coextrudates with EDR 5 prepared from AM films. A marked decrease in the tensile

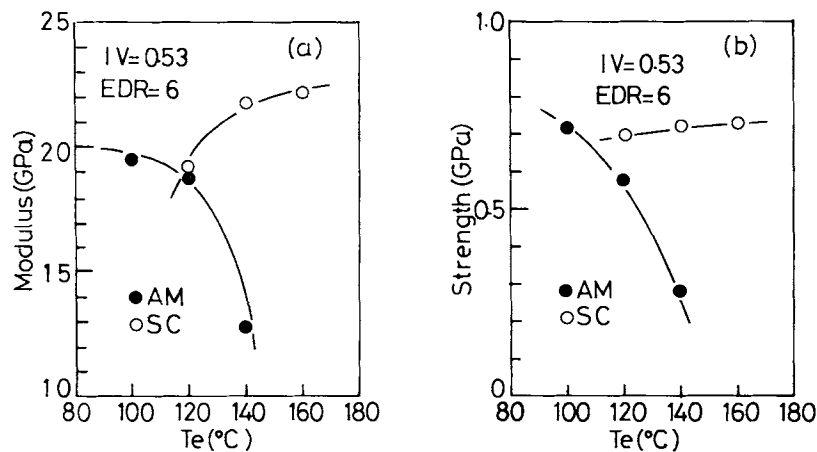


Figure 6 (a) Modulus vs. extrusion temperature and (b) strength vs. extrusion temperature for the coextrudates from both AM and SC films with IV of 0.53 dL/g.

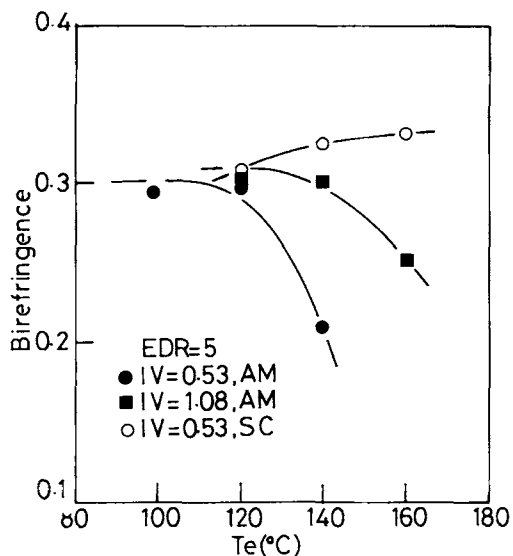


Figure 7 Birefringence vs. extrusion temperature for the coextrudates from both AM and SC films.

properties with increasing T_e is observed in the coextrudates prepared at $T_e = 120$ – 160°C , depending on the sample molecular weights. Figure 6 shows the tensile modulus and strength as a function of T_e for the coextrudates ($IV = 0.53$ dL/g) with EDR 6 prepared from both AM and SC films. In contrast to the coextrudates from AM films, the ones from SC films show an increase in the mechanical properties with T_e . In this study, the highest tensile modulus of 22 GPa was obtained for the coextrudates with EDR 6 prepared from SC films ($IV = 0.53$ dL/g) at 160°C . These tensile data, consistent with the X-ray diffraction patterns shown in Figures 3 and 4, indicate that the structures of the coextrudates, at a given EDR, are greatly affected by the predrawn morphology, molecular weight, and extrusion temperature.

Figure 7 shows the effect of T_e on the birefringence (Δn) for the coextrudates with different molecular weights. For the coextrudates from AM films, Δn decreases with increasing T_e , with this tendency more prominent in the lower molecular weight PEN. On the other hand, Δn of the coextrudates from SC films tends to increase with T_e . Figure 8 shows the crystal orientation function (f_c) of the coextrudates with EDR 5 as a function of T_e . The f_c was evaluated by the well known X-ray method. All the coextrudates show similar values of f_c and they are almost independent of T_e , initial morphology, and molecular weight. In this study, we could not determine the orientation factor of amorphous component (f_a) due to the lack of inherent birefringence values of

crystalline and amorphous phases (Δn_c and Δn_a). However, it is possible to estimate qualitatively the relation between degree of amorphous chain orientation and T_e , based on a well known equation:

$$\Delta n = X_v f_c \Delta n_c + (1 - X_v) f_a \Delta n_a + \Delta n_{fi}$$

where, X_v is the volume percent crystallinity and Δn_{fi} is the form birefringence, which is usually set to be zero. In Figure 9, the density or crystallinity (X_c) of the coextrudates is plotted against T_e . The density and hence X_c (or X_v) at a given EDR is insensitive to molecular weight and predrawn morphology. It is primarily determined by T_e , and increases gradually with increasing T_e . For the coextrudates from AM films, f_c is independent of T_e and almost constant within the T_e range studied (Fig. 8). On the other hand, the X_c increases and Δn decreases with increasing T_e (Figs. 7 and 9). These data, with the equation described above, indicate that the amorphous orientation factor (f_a) should decrease with increasing T_e . For the coextrudates from SC films, both X_c and Δn increase with T_e , and f_c stays almost constant within the T_e range. In this case, the f_a value is not necessarily decreasing with increasing T_e . For the coextrudates with EDR 6 from SC films, the dynamic loss peak temperature corresponding to the T_g of PEN increased by 5°C with increasing T_e from 120 – 140°C (data not shown). The result suggests that the amorphous orientation in the coextrudates from SC films tends to increase with T_e . From these data on the structure, it is evident that the mechanical properties of the coextrudates at a given EDR are greatly affected by the amorphous chain orientation, which is significantly affected by mol wt, predrawn morphology,

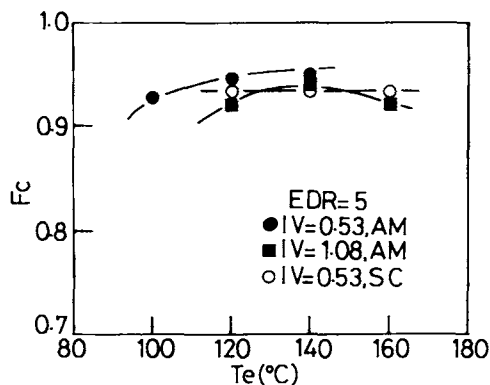


Figure 8 Crystal orientation function vs. extrusion temperature for the coextrudates with EDR 5.

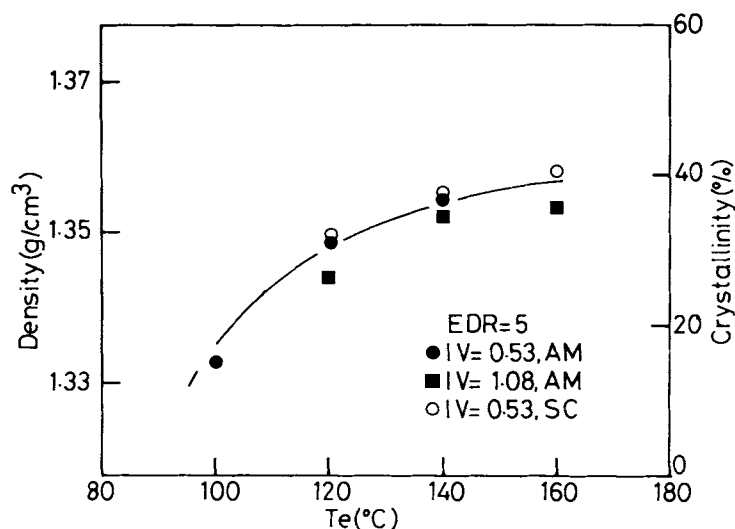


Figure 9 Sample crystallinity and density vs. extrusion temperature for the coextrudates with EDR 5.

and T_e . In AM films, the number of chain entanglements, which may act as a force transmitter to achieve an effective chain orientation, increase in proportion to the mol wt above a critical value. During coextrusion at higher temperatures, dissipation of chain orientation in the noncrystalline regions probably occurred, since no load was applied to the end of the coextrudates during coextrusion, allowing them to shrink after drawing. These tendencies are more prominent in the low molecular weight PEN, probably due to the small number of entanglements. A number of crystallites, initially present in the SC films, probably act as effective network points, which exert considerable constraint on the mobility and suppress the relaxation of amorphous segments

during coextrusion, even for a low mol wt PEN, as is also suggested by Figure 7.

Structure and Properties of Two-Stage Drawn Films

The structure and tensile properties of two-stage drawn films were dependent on several parameters, such as T_e and morphology of the coextrudates, and the total draw ratio (TDR). In Figure 10, tensile modulus and strength of the two-stage drawn films with TDR 7.2 are plotted against T_e at the first-stage coextrusion draw. The coextrudates (EDR 5), used for the second-stage draw, were prepared from AM and SC films with IV of 1.08 dL/g. The tensile

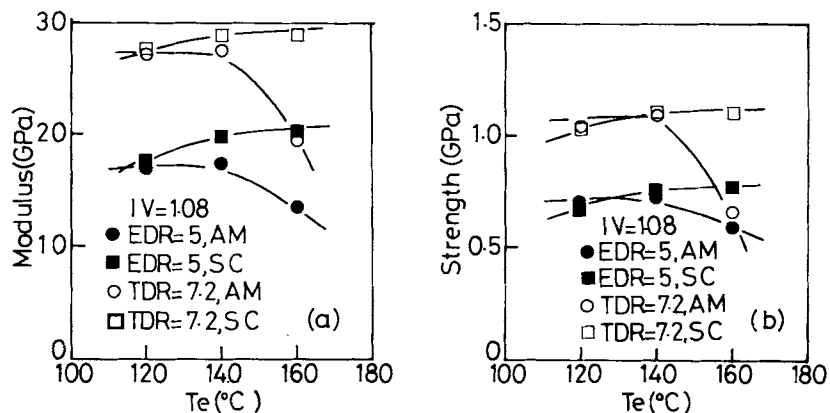


Figure 10 (a) Tensile modulus vs. extrusion temperature and (b) tensile strength vs. extrusion temperature for the two stage drawn films with TDR 7.2, and the coextrudates with EDR 5.

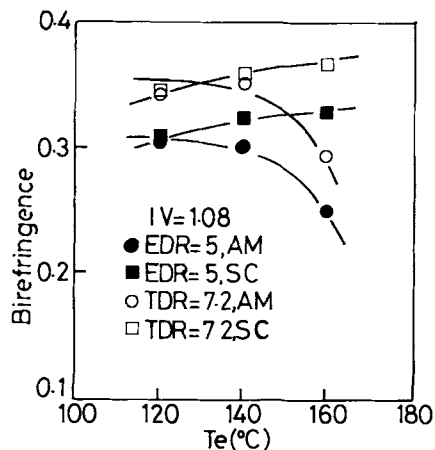


Figure 11 Birefringence vs. extrusion temperature for the coextrudates and their two-stage drawn films.

properties of the coextrudates are also shown in the same figure (Fig. 10) for comparison. The tensile properties are markedly improved by the second-stage draw. This is primarily due to the increase of

draw ratio from 5 to 7.2. An important feature of Figure 10 is the similarity of the T_e dependence of tensile properties for two stage drawn films and that for the coextrudates. The birefringence of the coextrudates and their two-stage drawn films are plotted as a function of T_e in Figure 11. Again, the T_e dependence of Δn for the two-stage drawn samples is similar to that for the coextrudates. These facts indicate that the structure of two-stage drawn samples is greatly affected by the structure developed during the first-stage coextrusion drawing.

Figure 12 shows wide and small angle X-ray diffraction photographs of a coextrudate with EDR 5, prepared from AM film at a lower T_e of 100°C, and its two-stage drawn sample with TDR 7.2. The WAXD patterns show that the crystals initially existing in the coextrudate increase in their perfection and sizes on the second-stage draw. Although no clear structural periodicity is observed on the SAXS patterns of the coextrudate, the periodicity of 174 Å becomes apparent after the second-stage draw. These results suggest that significant structural

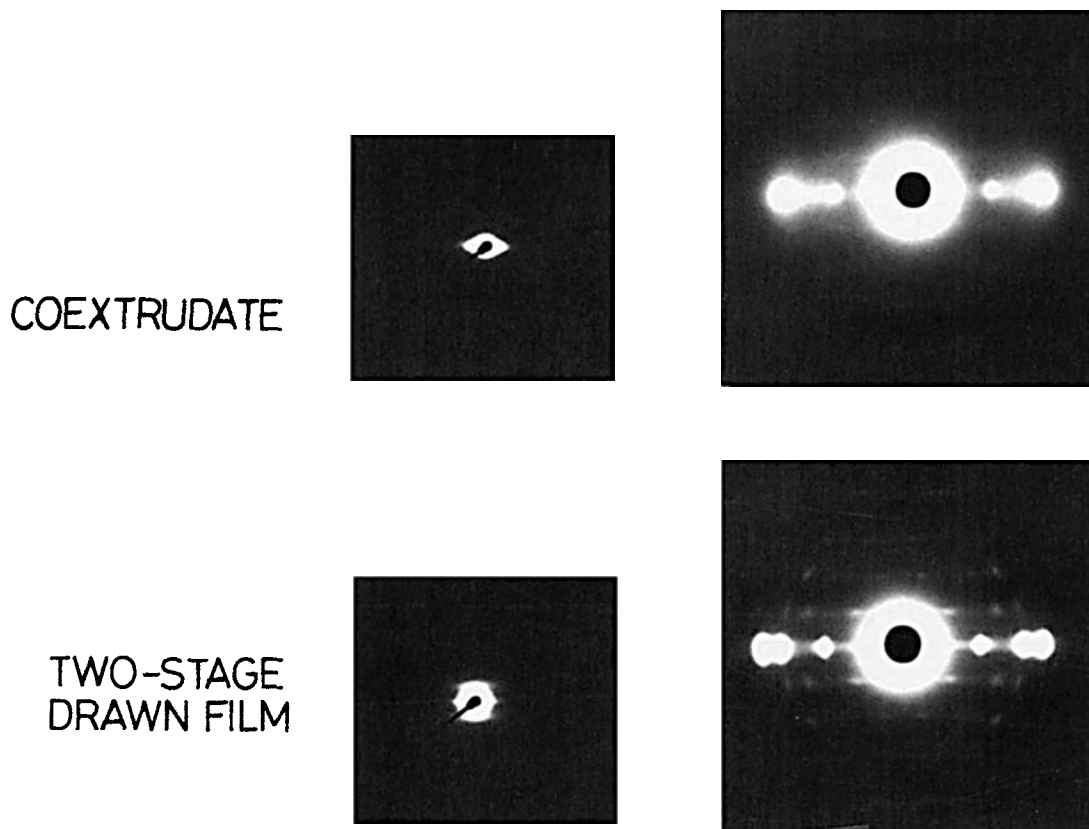


Figure 12 Wide and small angle x-ray diffraction photographs of coextrudate and its two stage drawn film.

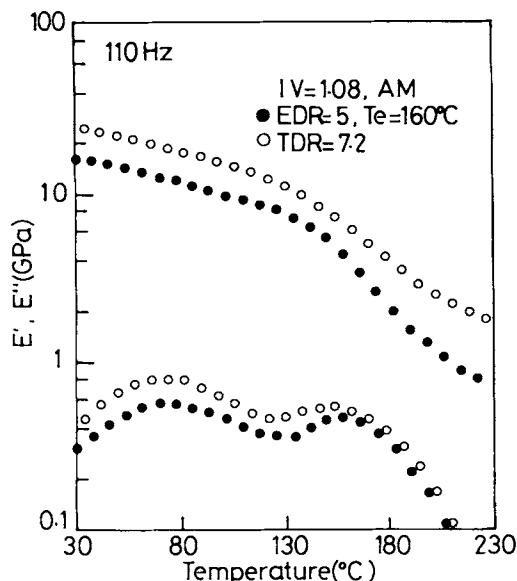


Figure 13 Temperature dependence of dynamic storage and loss moduli of the coextrudate and its two stage drawn film.

changes occurred in both the crystalline and non-crystalline phases.

Figure 13 shows the temperature dependence of the dynamic storage and loss moduli of the coextrudate with EDR 5 prepared from AM film at a higher T_e of 160°C and its two-stage drawn sample. It should be noted that the loss peak temperature, which is around 160°C, corresponding to T_g for the two-stage drawn sample, is slightly lower than that for the coextrudate, despite the fact that the draw ratio of the former is higher than the latter. The result can be explained by combining the following two data. Figure 14 shows temperature dependence of thermal shrinkage for the samples shown in Figure 13. For the two stage drawn sample, the temperature where shrinkage starts is lower than that for the coextrudate. However, the shrinkage value at the higher temperature regions is lower for the former than for the latter. Figure 15 shows the relation between sample crystallinity and extrusion temperature for the coextrudates and their two-stage drawn samples. After the second stage draw, the crystallinity increases up to around 50%, indicating a significant thermal and stress-induced crystallization occurred during the second-stage drawing at 230°C. Thus, highly oriented amorphous segments are preferentially incorporated into crystalline phases. As a result, an averaged chain orientation in the residual amorphous regions decreased. This, coupled with a relaxation of amorphous segments

at a high temperature of 230°C, might lower the loss peak temperature after the second-stage draw.

The effects of TDR and molecular weight of the two stage drawn samples on the tensile modulus and strength are shown in Figure 16. In this figure, the second-stage drawing was made on coextrudates having a tensile modulus of 17 GPa, which were prepared from both AM and SC films at appropriate T_e in the range of 100–140°C. As was shown in the previous section, the highest TDR of 10 was obtained by second-stage drawing of a coextrudate with EDR 6 prepared from AM film ($IV = 0.53$ dL/g) at $T_e = 140^\circ\text{C}$. However, the coextrudate showed an extremely low tensile modulus of 13 GPa (see Fig. 6), probably due to the disentanglements and chain slippage during coextrusion at higher T_e of 140°C. Thus, the tensile data for the two-stage drawn samples from the coextrudates prepared at $T_e = 140^\circ\text{C}$ from AM films ($IV = 0.53$ dL/g) were removed from Figure 16.

The modulus increases with increasing TDR and is almost independent of the molecular weight. The results indicate that coextrudates, having a tensile modulus of 17 GPa, can be effectively drawn by the second-stage hot drawing, and the disentanglements or chain slippages are less even for a low molecular weight PEN. The highest modulus of 29 GPa was obtained at a TDR of 8. This value is 20% of the theoretical crystal modulus of PEN. It has been reported that the mechanical properties at small strain are simply related to the draw ratio, irrespective of the sample molecular weight and initial morphology if drawing was made under optimum conditions in accordance with the present results. The tensile strength also increases with increasing TDR. Further, the tensile strength at a given TDR remarkably

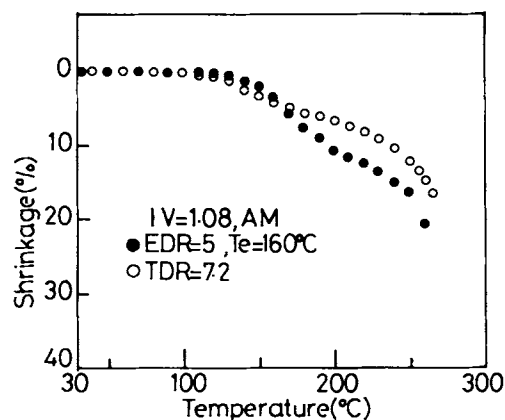


Figure 14 Thermal shrinkage vs. measurement temperature for the coextrudate and its two stage drawn film.

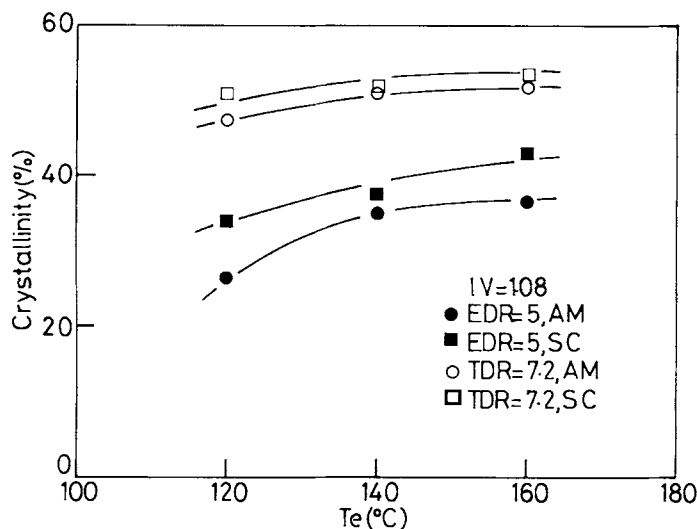


Figure 15 Sample crystallinity vs. extrusion temperature for the coextrudates and their two stage drawn films.

increases with increasing molecular weight, as in other polymers. This indicates that at a given TDR, the better the structural continuity along the draw direction that is achieved with higher molecular weight (and hence longer chains), the higher the tensile strength.

CONCLUSIONS

PEN films could be drawn up to a draw ratio of 10 by a two-stage drawing; that is, solid-state coextrusion at lower temperatures of 100–160°C followed by tensile drawing at a higher temperature of 230°C.

The efficiency of draw at the first stage coextrusion, evaluated by the tensile properties and amorphous chain orientation, were greatly affected by molecular weight, predrawn morphology, and extrusion temperature. It was found that at the second-stage hot drawing, the drawability of coextrudates was limited to below 2, independent of the initial EDR. However, at this stage, highly oriented noncrystalline segments were incorporated into crystalline phases, and also crystal perfection increased, all of which lead to a marked increase in the tensile properties and thermal stability of the two-stage drawn samples. Such structural changes for the second-stage draw were significantly affected by the structure developed

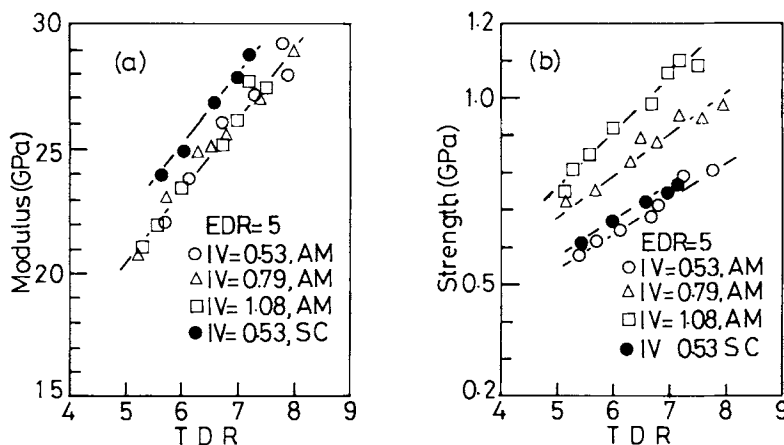


Figure 16 (a) Tensile modulus vs. total draw ratio and (b) tensile strength vs. total draw ratio for the two stage drawn films.

in the coextrudates. Thus, the higher the efficiency of draw at the first stage coextrusion, the higher the efficiency of draw for the two-stage drawn samples.

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