Deformation mechanism of amorphous poly(ethylene terephthalate) as a function of molecular weight and entanglements

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(Received 12 July 1993; revised 1 September 1993)

The deformation mechanism of amorphous poly(ethylene terephthalate) (PET) has been studied as a function of molecular weight and entanglement density in predrawn films. PET chips (intrinsic viscosity = 0.6–4.9 dl g^{-1}) were dissolved in mixed solvent of 1,1,1,3,3,3-hexafluoro-2-propanol and dichloromethane. The polymer solutions (polymer conc. = 2–40 wt%) were frozen at -30°C and then most of the solvent was removed at -30°C under vacuum, resulting in amorphous films with various entanglement densities. The films were drawn by solid-state coextrusion at 70°C. It was found that the initial polymer concentration used for film preparation had a marked effect on the maximum achievable extrusion draw ratio (EDR_{max}) of the films, especially for higher molecular weights. The optimum concentration decreased and the highest EDR_{max} increased with increasing molecular weight. The deformability was also affected by the stress-induced crystals, which might act as net points. The tensile modulus and strength of drawn films were related to draw ratio and molecular weight. The higher the draw ratio and molecular weight, the higher were the tensile properties of drawn samples. The improved efficiency of draw with higher molecular weight was explained by the suppression of disentanglement and relaxation of oriented amorphous molecules during deformation; both are important in the development of structural anisotropy and continuity along the draw direction.

(Keywords: poly(ethylene terephthalate); deformation; films)

INTRODUCTION

The drawing behaviour of poly(ethylene terephthalate) (PET) has been studied extensively for many years to produce high modulus and high strength PET fibres and films[1–5]. Ito *et al.*[6–8] have shown that the initial morphology and molecular weight of PET have a remarkable effect on the deformability and tensile properties of the resultant drawn materials. At a given draw ratio, the tensile strength of drawn films increased with increasing molecular weight, similarly to polyethylene[9], nylon 6[10] and polyacrylonitrile[11]. However, it has been reported that the attainable maximum draw ratio of melt-crystallized polyethylene decreases with increasing molecular weight[12,13]. Thus, the question is how to increase the drawability of high molecular weight PET in order to produce high modulus and high strength PET materials by drawing. The drawability of semicrystalline polymers has been related to draw condition, macromolecular entanglement[14], chain rigidity and supermolecular structure of predrawn materials[15].

The main purpose of this paper is to study the effects of molecular weight and entanglement density on the deformation behaviour of PET. It is known that the important factors affecting entanglement density in predrawn films are the molecular weight and concentration of the polymer from which as-cast film is made. Recently, we obtained high molecular weight PET (intrinsic viscosity (i.v.) = 2.2–4.9 dl g^{-1}) from a commercially available PET (i.v. = 0.6 dl g^{-1}) by solid-state polymerization. Amorphous PET films with various entanglement densities and molecular weights were obtained by a solution-casting method. These samples were suitable for studying the relation between entanglement density and deformation behaviour of PET.

EXPERIMENTAL

Samples

High molecular weight PET was obtained by solid-state polymerization of a commercially available PET (i.v. = 0.6 dl g^{-1}). The details have been reported elsewhere[8]. The intrinsic viscosities of as-polymerized samples were in the range of 2.2–4.9 dl g^{-1}.

For the preparation of amorphous films with various entanglement densities, polymer solutions with different concentrations (2–40 wt%) were prepared by dissolving the polymer in mixed solvent of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and dichloromethane (DM) (50/50, v/v) at room temperature. The polymer solutions in the cast were frozen at -30°C and then most of the solvent was removed at -30°C under vacuum to minimize structural change during drying. The maximum polymer concen-

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0032-3861/94/06/1210-06

tration available by directly dissolving high molecular weight PET in HFIP/DM was around 10 wt%. Solutions of higher polymer concentration were prepared by evaporating the solvent from lower concentration solution. Melt-quenched amorphous films were also prepared for comparison, by hot press followed by quenching in ice/water.

The solid-state coextrusion technique[16] was utilized for drawing. Predrawn films were placed between two split-billet halves of commercial polyethylene rod, and the assembly was coextruded at 70°C.

Measurements

The tensile properties along the draw axis of drawn films were measured at room temperature and at a strain rate of $1.7 \times 10^{-3}\,\mathrm{s}^{-1}$. The modulus was determined from the tangent to the stress–strain curve at a low strain (0.1%). Sample density was determined at 30°C by 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 $1.455\,\mathrm{g\,cm^{-3}}$, respectively[17]. The intrinsic viscosity of the sample was measured in a mixed solvent of trifluoroacetic acid and DM (50/50, v/v) at 30°C. Wide-angle X-ray measurements were carried out on a Rigaku RU-200B diffraction unit with Ni-filtered CuKα radiation source generated at 40 kV and 25 mA.

RESULTS AND DISCUSSION

Entanglement density

In this study, special care was taken to prepare predrawn samples suitable for studying the relation between entanglement density and deformation behaviour. Predrawn samples were obtained under conditions in which the intermolecular topology of as-cast films did not change during film preparation. In addition, thermal crystallization did not take place during the removal of solvent from the polymer solution. Wide angle X-ray diffraction patterns of dry, as-cast films confirmed that all the predrawn samples were amorphous. The temperature of coextrusion chosen was 70°C, which was low enough to suppress thermal crystallization of PET[18]. The drawability may be affected by the entanglement density and also by the stress-induced crystals formed during coextrusion.

Figure 1 shows the relation between the maximum achievable extrusion draw ratio, EDR_{max}, for various molecular weights, and the concentration of the solution from which as-cast films were prepared. For each molecular weight, with increasing the polymer concentration EDR_{max} increases first and then decreases after reaching the maximum value. In a polymer solution with a concentration (C) that is higher than the critical concentration, where EDR_{max} shows the highest value, the molecular weight between neighbouring entanglements, $(M_e)_{\mathrm{soln}}$, is given approximately by[19]:

$$(M_e)_{\mathrm{soln}} = (\rho/C)M_e = M_e/\phi \qquad (1)$$

where ρ refers to the bulk density of polymer and ϕ is the polymer volume fraction in the solution. M_e is the molecular weight between entanglements in the undiluted polymer melt. Equation (1) shows that $(M_e)_{\mathrm{soln}}$ is inversely proportional to the volume fraction of the polymer, and hence the number of entanglements per molecule for a given molecular weight is proportional to it. This means that the number of entanglements per molecule can be controlled by the concentration of the polymer solution. Above the critical polymer concentration, EDR_{max} decreases with increasing polymer concentration due to the increased entanglement density. Below the critical polymer concentration, EDR_{max} decreases with decreasing the polymer concentration. With decreasing the entanglement density, the number of net points, which act as transmitters of draw stress, decreases and thus the strength of a sample decreases, resulting in poor ductility[14]. It has been reported[20] that solution-grown crystals of polyethylene have an extremely high level of deformability despite the fact that they involve almost no entanglements. However, in that case, the adhesion and friction between crystalline lamellae act as deformable net points.

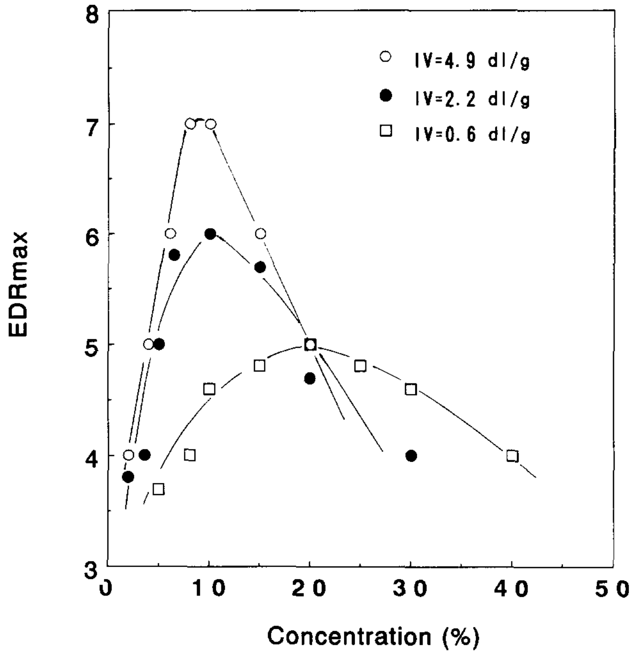

Figure 1 EDR_{max} *versus* polymer concentration at various molecular weights

Figure 1 revealed that the optimum concentration for achieving the highest EDR_{max} decreased with increasing molecular weight. Further, the highest EDR_{max} increased with increasing molecular weight. These results will be explained semiquantitatively below. *Figure 2* shows the relation between the optimum polymer concentration and molecular weight of PET (i.v.), which was derived from *Figure 1*. The decrease in the optimum concentration with increasing molecular weight was more prominent in the low molecular weight regions. We can illustrate roughly the relation between optimum polymer concentration and molecular weight by using zero shear viscosity (η_0), which can be a measure of deformation stress. The turning point of η_0 with increasing molecular weight and polymer concentration was considered as the point at which entanglement occurred, The relationship of η_0 with polymer concentration (C) and molecular weight (M_n) is given approximately by[21]:

$$\eta_0 = K(CM_n^{\alpha/\beta})^{\beta} \qquad (2)$$

where K is a universal constant and α and β are constants which are dependent on the chemical structure and

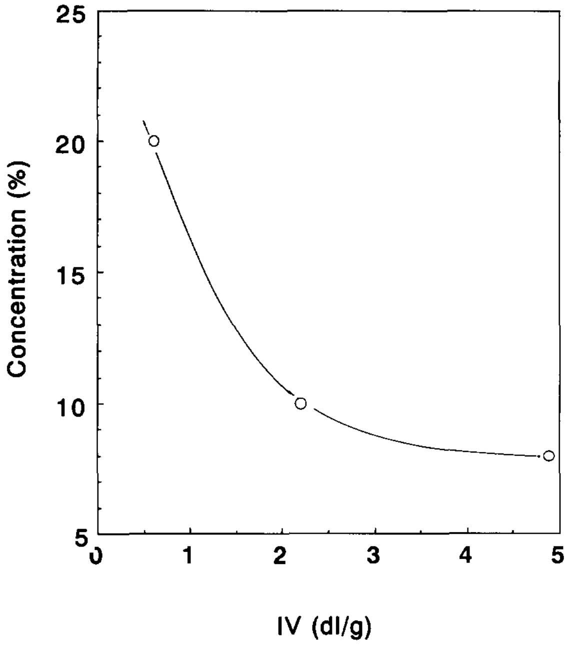

Figure 2 Optimum polymer concentration *versus* intrinsic viscosity

Table 1 Calculation of number-averaged molecular weight

I.v. (dl g^{-1})	0.6	2.2	3.5	4.3	4.9
$M_n \times 10^{-3}$	32	149	251	317	365

molecular weight of the polymer. For a concentrated polymer solution, α/β is between 0.5 and 1. For $M_n < M_e$, α is in the range of 1 to 1.6 and β is from 1 to 3. For $M_n > M_e$, α is in the range of 3 to 5 and β is from 5 to 7 (refs 22, 23). It has been reported that the M_e of PET is estimated[24] to be about 3500 (number-averaged molecular weight). From equation (1), the $(M_e)_{soln}$ of PET was estimated to be about 35000, if the initial polymer volume fraction was equated to 10%. The i.v. value was converted into number-averaged molecular weight by equation (3), and the results are shown in *Table 1*:

$$\text{i.v.} = 5.41 \times 10^{-5} M_n^{0.898} \qquad (3)$$

Equation (3) was obtained by the least-square method using the reported data[25] because, to date, no suitable relationship has been reported for high molecular weight PET. According to equation (3), the molecular weight corresponding to i.v. = 0.6 dl g^{-1} is 32000, which is smaller than $(M_e)_{soln}$ of 10% solution. In this case, the effect of polymer concentration on η_0 is small since the β value is small. Thus, a large increase in the polymer concentration is necessary to set up suitable network points formed by entanglements. At i.v. > 2.2 dl g^{-1} ($M_n > M_e$), the effect of polymer concentration on η_0 becomes prominent due to a large β value (5–7). Also $\alpha > \beta$ holds for $M_n > M_e$. In this case, η_0 is affected more by polymer concentration than by molecular weight. A small increase in polymer concentration will result in a larger increase in zero shear viscosity and hence in deformation stress for higher molecular weight, as shown by equation (2). Further, the optimum polymer concentration is sensitive to the molecular weight. This is confirmed in *Figure 1*, where the peak of EDR_{max} becomes sharper with increasing molecular weight. Evidently, the improvement of drawability through decreasing the concentration of polymer solution is more significant in high molecular weight materials than in those of lower molecular weight. For a high molecular weight PET (i.v. = 4.9 dl g^{-1}), EDR_{max} changes from 2.6 for the melt-quenched film to 7.0 for the film cast from 10 wt% polymer solution; however, for low molecular weight PET (i.v. = 0.6 dl g^{-1}) the change in EDR_{max} is only 1 (from 4 to 5) (*Figure 3*). As mentioned above, for low molecular weight PET, the number of entanglements per molecule is smaller in the polymer solution because the molecular weight is around $(M_e)_{soln}$. The lower entanglement density might result in chain slippage occurring easily during drawing and in the decrease of sample strength, which will be discussed in the next section. Thus, the effect of polymer concentration on EDR_{max} is less prominent in lower molecular weight PET.

Achievable deformation ratio

Figure 3 shows the relationship between EDR_{max} and molecular weight (i.v.) for melt-quenched films and cast films from 5 and 10 wt% solutions. For the melt-quenched films, EDR_{max} decreases with increasing molecular weight. A similar relation has been reported for melt-crystallized polyethylene[12,26]. It is known that M_e is independent of molecular weight for the melt-quenched films; however, the number of entanglements per molecule increases with increasing molecular weight. Too large a number of entanglements per molecule in melt-quenched films might suppress the deformability of high molecular weight PET. On the other hand, for the cast films, EDR_{max} increases with increasing molecular weight. The deformability of high molecular weight PET is improved by reducing the number of entanglements per molecule. However, it is also clear that EDR_{max} of film cast from 5 wt% polymer solution is lower than that of film cast from 10 wt% solution at a given molecular weight. According to equation (1), EDR_{max} should increase with decreasing polymer concentration in solution. Thus, there exists a difference between the prediction of equation (1) and experimental data. One of the probable reasons is

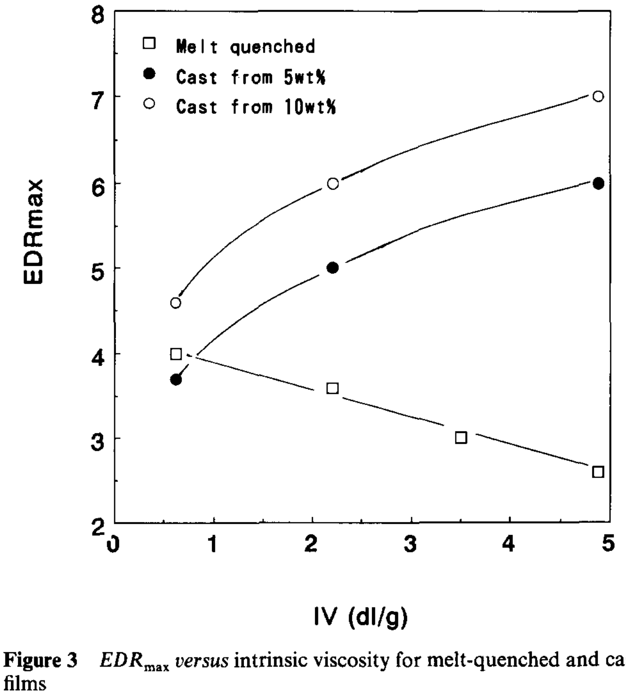

Figure 3 EDR_{max} *versus* intrinsic viscosity for melt-quenched and cast films

that the number of net points, which act as transmitters of draw stress, decreases with decreasing the polymer concentration and causes a decrease of the sample strength, resulting in poor deformability of samples. If so, the present results suggest the necessity for a suitable level of entanglement density to achieve a higher deformation ratio for initially amorphous PET films.

According to the classical theories of rubber elasticity[14], the maximum draw ratio of a permanent network (λ_{max}) varies with the number of statistical chain segments between crosslinks, N_c as:

$$\lambda_{max} = (N_c)^{1/2} \tag{4}$$

The assumption that the majority of the entanglements trapped in the polymeric solid will act as permanent crosslinks gives:

$$N_c = N_e \tag{5}$$

Here, N_e is the number of statistical chain segments between entanglements, which equals M_e/m_s, m_s being the molecular weight of a statistical chain segment. Substitution of equation (5) into equation (4) and introduction of the concentration dependence of M_e, given by equation (1), finally yield:

$$\lambda_{max} = (N_e/\phi)^{1/2} = \lambda_{max1}\phi^{-1/2} \tag{6}$$

Here, λ_{max1} is λ_{max} at $\phi = 1$, and equals $(N_e)^{1/2}$. At present, a value of m_s for PET is not available. Thus we suggest that λ_{max1} might be estimated according to the dilute solution theory. The minimum draw ratio (DR_{min}) necessary for full chain extension from a random coil in the θ condition is expressed as follows[27].

$$DR_{min} = \frac{\text{molecular chain length } (L)}{\text{molecular dimension } \langle r_0^2 \rangle^{1/2}} = \frac{L}{KM^{1/2}} = \frac{L_m M^{1/2}}{KM_m} \tag{7}$$

where M is molecular weight and L_m and M_m are the length estimated using the normal bond angle and length, and the molecular weight, respectively, for a monomer repeat unit. If disentanglement does not occur during deformation, M is replaced by M_e and λ_{max1} equals DR_{min}. For PET, $L_m = 10.8$ Å, $M_m = 192\,\mathrm{g\,mol^{-1}}$ and $K = 0.97$ Å $\mathrm{g^{1/2}\,mol^{1/2}}$ (ref. 28). The molecular weight between neighbouring entanglements in a PET melt is about 3500, which leads to $\lambda_{max1} = 3.43$. Thus, λ_{max} at the optimum concentration can be calculated for each molecular weight by using equation (6), and the results are shown in *Table 2*. It is evident that EDR_{max} is only 60–70% of λ_{max}. These results suggest that the deformation mechanism of amorphous PET cannot be explained simply by the entanglement concept.

Table 2 Calculation and observed data of maximum draw ratio

I.v. (dl g^{-1})	C (wt%)^a	λ_{max}	EDR_{max}	EDR_{max}/λ_{max} (%)
4.9	8	11.5	7.0	60.9
2.2	10	10.3	6.4	62.1
0.6	20	7.3	5.0	68.5

^{a} C is the optimum polymer concentration, given in *Figure 1*

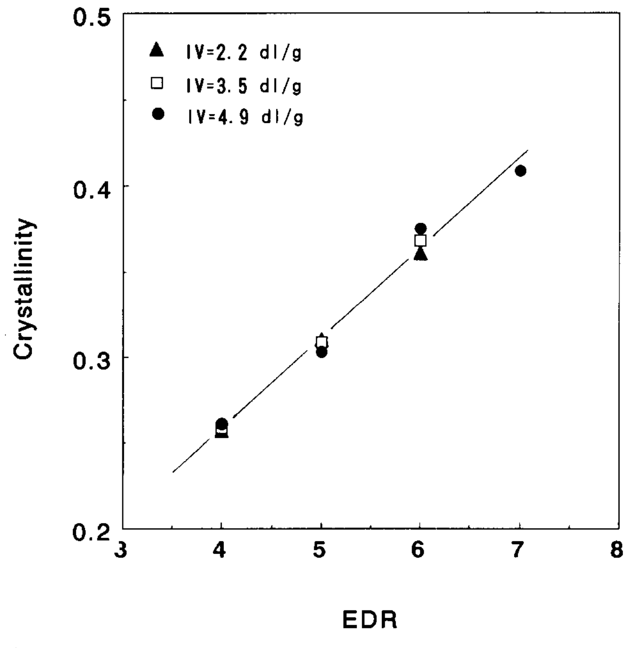

Figure 4 Crystallinity *versus EDR* at various molecular weights

Figure 4 shows the relationship between crystallinity of the coextrudates for each molecular weight, and *EDR*. It is clear that stress-induced crystallization takes place during coextrusion. The crystallinity of drawn samples was independent of molecular weight and was primarily determined by *EDR*. At a given draw stress, the rate of stress-induced crystallization might decrease with increasing molecular weight due to the increased relaxation time[29]. On the other hand, the efficiency of draw, as evaluated by the total molecular orientation (in *Figure 7*), decreases with decreasing molecular weight, which also decreases the rate of stress-induced crystallization. The efficiency of draw will be illustrated in the next section. Thus, the apparent crystallinity of the coextrudates is independent of molecular weight due to these two opposing effects. In this study, all the coextrusion work was carried out at 70°C. However, the temperature might be too low to deform the stress-induced crystals, since the relaxation temperature of PET crystals has been suggested[7] to be around 150°C. Once stress-induced crystals are formed, such crystals might act as net points, which might change the apparent number of net points.

Efficiency of draw

The efficiency of draw is one of the important parameters for evaluating the degree of chain extension and orientation. Here, the efficiency of draw was evaluated from the mechanical properties of drawn samples. It has been shown that the mechanical properties of drawn samples are greatly affected by the cross-sectional area of the sample. Thus, the drawn films, of thickness about 50 μm, were cut into narrow strips to obtain a cross-sectional area in the range 4×10^{-4}–$6 \times 10^{-4}\,\mathrm{cm^2}$. In this section, for simplicity, the structure and properties of drawn films are shown only for the samples prepared from films cast from 10 wt% polymer solution.

In *Figure 5*, the tensile modulus of drawn samples for two different molecular weights is plotted against *EDR*. At each molecular weight, the modulus increased almost linearly with increasing *EDR*. Further, at a given *EDR*, the modulus value was larger for high molecular weight than for low molecular weight samples. In *Figure 6*, the tensile strength of drawn samples for various molecular weights is plotted against *EDR*. The larger the *EDR* and the higher the molecular weight, the higher was the tensile

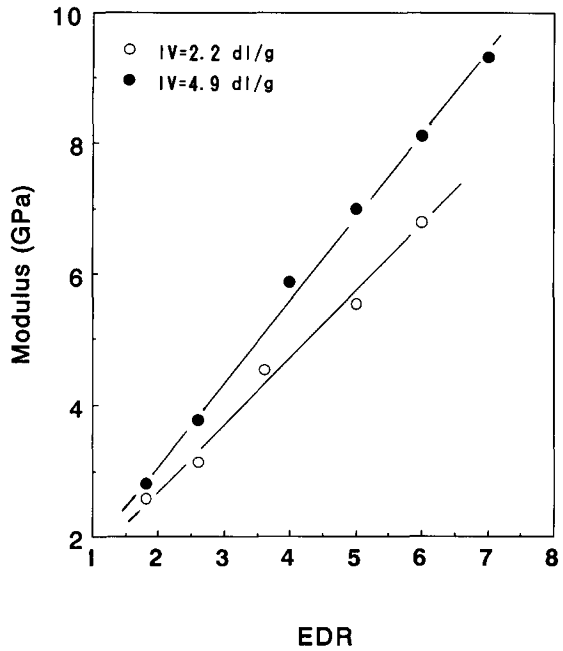

Figure 5 Tensile modulus *versus* *EDR* at various molecular weights

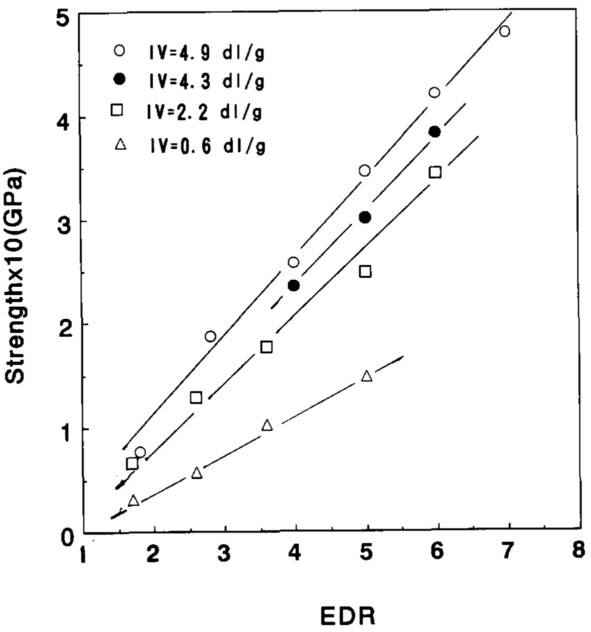

Figure 6 Tensile strength *versus* *EDR* at various molecular weights

strength that could be achieved. As seen in *Figure 1*, the higher the molecular weight, the higher the EDR_{max} that could be obtained at the optimum polymer concentration. Thus, higher modulus and higher strength could be achieved for the higher molecular weight PET.

Figure 7 shows the birefringence (Δn) dependence on the molecular weight at *EDR* values of 5 and 6. At each *EDR*, the Δn increased with increasing molecular weight. This means that the average chain orientation at a given deformation ratio increases with increasing molecular weight. Thus, the increased efficiency of draw shown in *Figures 5* and *6* arises from the increased chain orientation. As seen in *Table 2*, EDR_{max}/λ_{max} increases with decreasing molecular weight, which means that the degree of chain extension at a given deformation ratio decreases with increasing molecular weight if disentanglement does not occur during deformation. However, the efficiency of draw decreases with decreasing molecular weight. These results suggest that disentanglement occurs during deformation, which results in a lowering of the number of entanglements, and hence the extent of chain slippage might be enhanced. Smith *et al.*[14] found that chain slippage occurred to a much greater extent in low molecular weight than in high molecular weight polyethylene. Therefore, the poor mechanical properties for lower molecular weight films arise from the low degree of chain extension and orientation due to the lack of essential network in predrawn films. On the other hand, as mentioned above, stress-induced crystals, which might also act as net points, are formed during deformation.

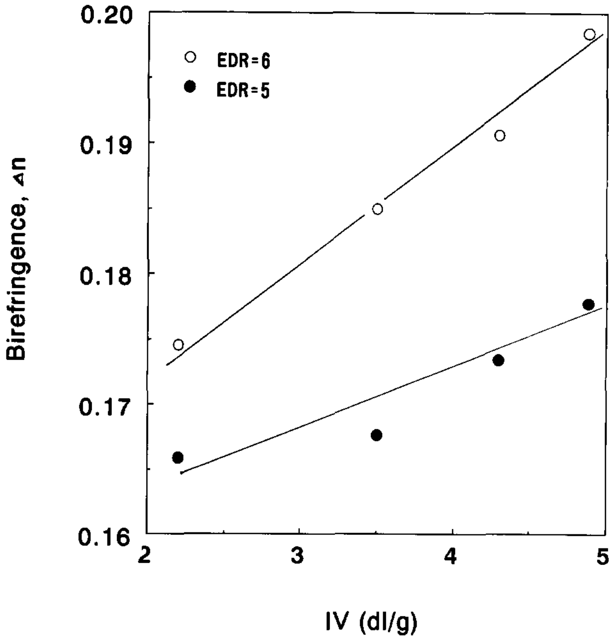

Figure 7 Birefringence *versus* intrinsic viscosity at *EDR* values of 5 and 6

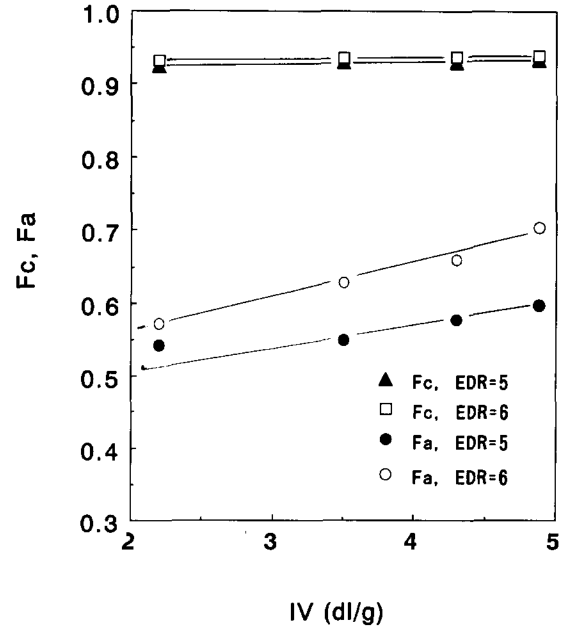

Figure 8 Orientation factors in the crystalline (F_c) and amorphous (F_a) phases *versus* intrinsic viscosity at *EDR* values of 5 and 6

Thus, the apparent density of net points changes with deformation. This might be one of the reasons why the entanglement concept does not fully explain the observed results, since the concept is valid under a constant number of entanglements.

In *Figure 8*, the chain orientation factors of crystalline (F_c) and amorphous (F_a) phases at *EDR* values of 5 and 6 are plotted against molecular weight (i.v.). F_c was evaluated by the well known X-ray diffraction method. F_a was calculated by using the equation:

$$\Delta n = \Delta n_c^0 F_c(X_c) + \Delta n_a^0 F_a(1 - X_c) \qquad (8)$$

where X_c is the crystallinity, and Δn_c^0 and Δn_a^0 are the intrinsic birefringences of the crystalline and amorphous phases, which were taken to be 0.275 and 0.22, respectively[30]. It is clear that F_c is almost independent of molecular weight. The crystallinity of drawn films at a given *EDR* was also independent of molecular weight (*Figure 4*). Therefore, the molecular weight dependence of Δn arises from the fact that the orientation of amorphous segments increases with increasing molecular weight, as shown in *Figure 8*. The results indicate that the tensile strength is determined by the degree of orientation in the amorphous phase, because F_c and crystallinity are independent of molecular weight. It is well known that the relaxation time of the molecular chain increases with increasing molecular weight, which promises a low level of disorientation in the drawn samples from high molecular weight materials. By the suppression of disorientation, we can expect an increase in the structural continuity along the draw direction in the drawn samples. Such structures might increase the mechanical properties, especially the tensile strength[31].

CONCLUSION

Amorphous PET films with various entanglement densities and molecular weights were prepared by solution casting. It has been found that the polymer concentration has a marked effect on the drawability of amorphous films, especially for higher molecular weight PET. Thus, it is necessary to control the entanglement density in order to improve the drawability of amorphous PET, especially for high molecular weight PET. Suitable amounts of entanglements are necessary for the effective drawing of amorphous PET. There exists an optimum polymer concentration for achieving the maximum $EDR_{\max}$ at a given molecular weight. The optimum concentration decreases with increasing molecular weight, but the decrease was small at higher molecular weight (i.v. $> 2.2\,\mathrm{dl\,g^{-1}}$). The highest $EDR_{\max}$ increases with increasing molecular weight at an optimum polymer concentration. The deformability is affected not only by the entanglement density, but also by the stress-induced crystals, which act as permanent net points. The tensile modulus and strength of drawn films were related to draw ratio and molecular weight. The higher the draw ratio, the higher were the tensile properties of drawn samples. At a given draw ratio, the tensile strength increases with increasing molecular weight due to the increased draw efficiency and increase in the structural continuity along the draw direction.

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