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The cold drawing of amorphous polyethylene terephthalate

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The cold drawing of amorphous polyethylene terephthalate has been studied at constant strain rate over a wide range of temperatures for samples of different molecular weight and different initial molecular orientation (pre-orientation). The natural draw ratio was found to be dependent on pre-orientation, confirming previous studies, and for low degrees of pre-orientation it also decreased with increasing molecular weight or decreasing temperature of draw.

For all samples, there was an excellent correlation between the degree of molecular alignment achieved, as determined by optical birefringence, and the draw ratio. The birefringence of any sample could be accurately predicted from the draw ratio on the basis of previously proposed theoretical models for the development of molecular orientation.

1. Introduction

This investigation was stimulated partly by previous studies of the cold drawing of polyethylene terephthalate (PET) [1, 2] and partly by more recent work on the effect of molecular weight and morphology on the drawing of linear polyethylene [3-5]. From the spectacular effects which have been observed in the latter case, it seemed interesting to examine whether any similar phenomena are to be observed for the so-called amorphous polymers. The present paper therefore describes a study of the drawing of amorphous PET over a wide range of temperatures at a constant strain rate. It will be shown that the natural draw ratio is sensitive to the initial polymer orientation (pre-orientation), to molecular weight and to temperature, but that the effects observed are much smaller than those observed in the case of linear polyethylene.

The development of molecular orientation during drawing has been monitored by making measurements of birefringence and the results compared with theoretical expectations from previous work [2, 6].

2. Experimental

2.1. Preparation of samples

The behaviour of the polymer was studied in three forms; sheet, injection moulded dumb-bells and fibres. Sheet and injection moulded samples were used to investigate the general behaviour. Fibre samples were used to investigate the effect of pre-orientation and the development of optical anisotropy on drawing.

In all cases, the intrinsic viscosity $[\eta]$ of the polymer was determined in orthochlorphenol at 25°C. The number average molecular weight, $\bar{M}_n$, was then calculated from the Mark-Houwink relationship $[\eta] = K\bar{M}_n{}^\alpha$ with $K = 1.7 \times 10^{-4}$ and $\alpha = 0.83$ as determined previously [7].

Extruded sheet of very low molecular orientation with intrinsic viscosity 0.60 was provided by I.C.I. Plastics Division, Welwyn Garden City. The dimensions of the sheet samples are shown in Fig. 1a.

To make injection moulded samples, dried polymer was forced through the hot barrel of the extruder. This melts the polymer which was then injected into a water cooled mould. To reduce hydrolytic degradation to a minimum, the polymer was dried by holding it at 120°C for 12 h in a vacuum oven. The dimensions of the injected moulded dumb-bells are shown in Fig. 1b. All grades of polymer were supplied by I.C.I. Corporate Laboratory Runcorn. The moulding conditions were chosen such that transparent amorphous samples were obtained. To achieve this the mould had to be cold and the barrel temperature sufficiently high to completely melt

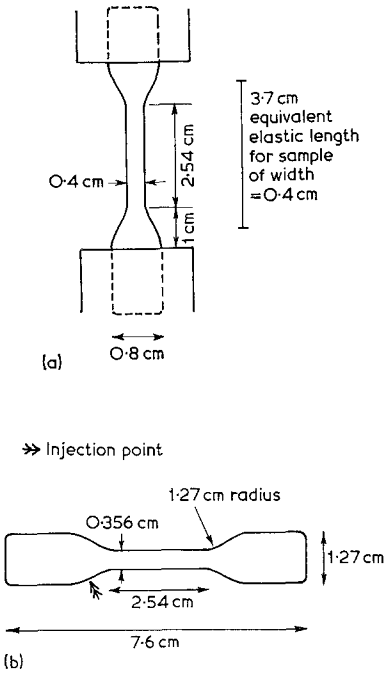

Figure 1 (a) Dimensions of sheet samples. (b) Dimensions of injection moulded dumb-bells.

all the polymer. At the same time, the time and temperature in the barrel were minimized to reduce degradation of the polymer. There was one exception to these conditions. To produce a very low molecular weight sample, the polymer of lowest initial molecular weight was injection moulded without preliminary drying. This gave an injection moulded sample of intrinsic viscosity ~ 0.33. The intrinsic viscosities, molecular weights and birefringences of the sheet and the injection moulded dumbells are summarized in Table I.

The fibres were prepared by the conventional melt-spinning process in which molten polymer is extruded through a small circular hole in a metal plate, the fibres being wound on a bobbin at a sufficient distance below the plate for the polymer to have solidified. A number of samples of different birefringence (pre-orientation birefringence), were prepared at two levels of polymer molecular weight, by changing the rate at which the fibres were wound on the bobbins, other conditions being kept constant. Table II shows the details of these fibres. It was also found desirable to obtain fibres of lower pre-orientations than those obtained directly. This was done by annealing the samples at 70° C for 12 h. In this way the birefringence was reduced to about 5×10^{-4}.

TABLE I Sheet and injection moulded samples

Sample preparation	Intrinsic viscosity	$\bar{M}_n$	Birefringence $\times 10^3$
Injection moulding	0.44 ± 0.02	12 000	~ 1
	0.33 ± 0.02	9 000	~ 1
	0.77 ± 0.10	23 000	~ 1
	0.88 ± 0.10	29 000	~ 1
Extruded sheet	0.60	16 000	0.5

2.2. Tensile tests

The samples were extended on an Instron tensile testing machine at a constant cross-head speed of 0.02 cm sec^{-1}. An environmental cabinet was used to control the temperature.

To determine the draw ratio, the deformation of a set of ink marks on the surface of the samples was measured, using a travelling microscope. The neck was allowed to extend to about 80% of the gauge length. At this point the specimen was instantly relaxed and allowed to recover at 20° C for at least 30 min. The pattern of ink marks was then remeasured, using only those marks well inside the cold drawn region. The natural draw ratio was calculated from the ratio of the drawn length to the undrawn length in the draw direction.

2.3. Optical measurements

The birefringences of the initial samples (the pre-orientation birefringences) were measured with an Ehringhaus Compensator used in a Zeiss polarizing microscope. This method cannot be used to measure large path differences

TABLE II Fibre samples

Wind-up speed (cm sec^{-1})	Pre-orientation birefringence $\times 10^3$		Fibre diameter ($\times 10^3$ cm)
	$[\eta] = 0.50$	$[\eta] = 0.70$	
500	—	1.5 ± 0.5	5.0
600	1.1 ± 0.3	—	5.0
1500	5 ± 1	6 ± 1	3.5
2500	10 ± 1	11.5 ± 1.5	2.7

because of the difference in dispersion between the Calcite crystal in the compensator and PET. The birefringences of the drawn fibres were, therefore, measured with a Zeiss interference microscope, determining the two refractive indices parallel and perpendicular to the fibre axis, by use of immersion liquids. The refractive indices could be determined in this way to within ± 0.002, which is about the variation along the length of the drawn fibre. All measurements were carried out with a 5510 Å green filter and refer to this wavelength.

3. Results and discussion

3.1. The natural draw ratio of amorphous samples

The results obtained on the sheet and injection moulded samples are shown in Fig. 2. Each result is the average of three tests in which the draw ratios differed at most by 0.1. Although these results suffer from the limitation that there was some variation in the pre-orientation of the injection moulded samples, the pre-orientation was always small (see Table I) and does not prevent two major conclusions from being made. First, the natural draw ratio of PET decreased as the temperature was reduced. This effect had not been observed in previous work [2] over a smaller temperature range, and shows that the polymer strain hardens more rapidly at low temperatures. On the view that the natural draw ratio represents the ultimate extensibility of a network, this result suggests that thermal motions at high temperatures may reduce the number of effective entanglements.

Secondly, Fig. 2 also shows that the draw ratio is systematically reduced with increasing molecular weight. Previous birefringence/shrinkage studies of PET [8] showed that the polymer could be considered as a rubber network at temperatures above the glass transition. Moreover, the number of chains per unit volume increased markedly with increasing polymer molecular weight, the number of monomers per chain decreasing correspondingly. The effect of molecular weight observed was greater than that predicted by Flory's correction [9] which takes into account the non-contribution of the ends of the polymer molecules to the network. We therefore conclude that both decreasing temperature and increasing molecular weight act in the same direction to increase the number of effective entanglements and hence reduce the natural draw ratio.

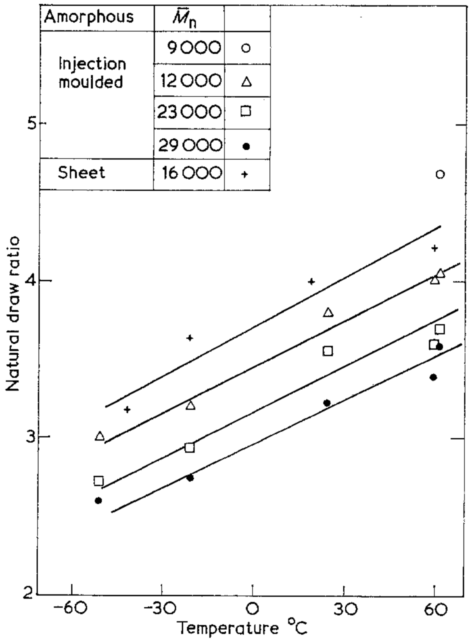

Figure 2 Variation of natural draw ratio with temperature for samples of different molecular weight.

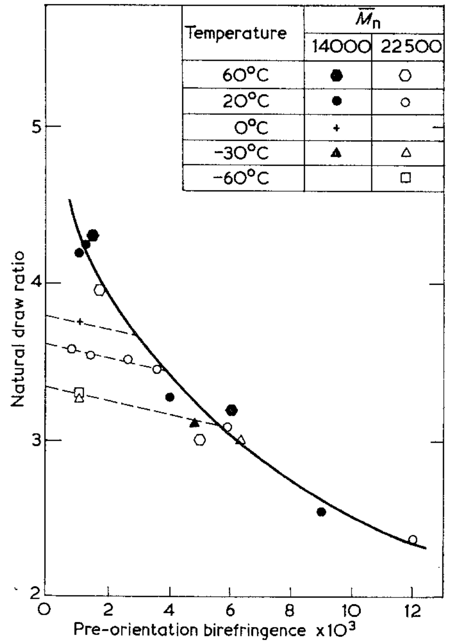

Figure 3 Effect of pre-orientation on natural draw ratio for fibre samples.

These conclusions are confirmed by the results obtained for the fibre samples, which are summarized in Fig. 3, where the natural draw ratio is plotted as a function of the pre-orientation birefringence for two molecular weights over a range of temperatures. The results now show the additional effect of pre-orientation birefringence, which was previously established [1,2] by studies on polymers of normal molecular weight of about 1.8×10^4. The influence of pre-orientation has been interpreted on the basis that the natural draw ratio represents the stretching of a network to a total limiting extension, which is independent of the division of extension between the extrusion and drawing processes [2, 10]. Comparing Figs. 2 and 3, it can be concluded that the effect of molecular weight on the natural draw ratio was of the same order of magnitude for both injection moulded and fibre samples. For example, extrapolating a natural draw ratio for isotropic material from Fig. 3, at 20°C, for $\bar{M}_n = 14\,000$, the natural draw ratio was 4.2, while for $\bar{M}_n = 22\,500$ the natural draw ratio was 3.6. This is very similar to the effect shown in Fig. 2. The results in Fig. 3 also confirm the effect of temperature on natural draw ratio, although it is important to note that this effect is reduced by increasing degrees of pre-orientation and that the 20 and 60°C samples have very similar natural draw ratios even at the lowest pre-orientation. It also appears that the molecular weight effects are reduced to negligible proportions at high pre-orientation. These results, taken together, suggest that the mechanism of network deformation may be different at very low degrees of pre-orientation, as had indeed been suspected in the previous studies [10]. The conclusion is that a limiting network extensibility of about 4.0 exists for moderate and high degrees of pre-orientation, and for these samples the natural draw ratio is independent of molecular weight and temperature. At very low degrees of pre-orientation, higher natural draw ratios can be achieved, these now being dependent on temperature and polymer molecular weight.

3.2. Optical anisotropy

The birefringences of the drawn fibres were examined in the light of previous studies [2] and a theoretical model for molecular reorientation [11]. In this model it is assumed that the optical anisotropy results from the orientation of anisotropic structural units, whose optical properties are identical to those of the fully oriented fibre. The units are assumed to possess transverse isotropy and are defined by P_1, the principal polarizability of the unit parallel to its symmetry axis and P_2, the polarizability in the plane perpendicular to this axis. In the cold drawing of an isotropic fibre, it is assumed that the symmetry axes of the units undergo the same changes in direction as lines connecting pairs of points in a body undergoing uniaxial deformation at constant volume. This type of deformation has been called pseudo-affine [12] to distinguish it from the affine deformation scheme of rubber elasticity [13]. The aggregate model gives the birefringence Δn of the partially oriented fibre as

$$\Delta n = \tfrac{1}{2}\Delta n_{\max}(3\,\overline{\cos^2\theta} - 1) \qquad (1)$$

where $\Delta n_{\max}$ is the maximum birefringence observed in the partially oriented fibre and $\overline{\cos^2\theta}$ is the average value of $\cos^2\theta$ for the aggregate, where θ is the angle between the axis of a unit and the draw direction. In a previous paper [11] values of $\overline{\cos^2\theta}$ have been tabulated in terms of the draw ratio.

A later paper [6] extended this approach to the drawing of pre-oriented fibres, assuming that the pre-orientation at extrusion induces affine deformation comparable to the stretching of a cross-linked rubber network. There is, therefore, a complicated two-stage development of orientation, and this was discussed analytically. It was shown that Equation 1 becomes

$$\Delta n - \beta\Delta n_i = \tfrac{1}{2}\Delta n_{\max}(3\,\overline{\cos^2\theta} - 1) \qquad (2)$$

where Δn_i is the pre-orientation birefringence and β is another orientation function which was tabulated in the previous paper, and is approximately unity.

Fig. 4 shows the results for the cold drawn pre-oriented fibres, plotting the quantity $\Delta n - \beta\Delta n_i$ as a function of draw ratio. Three samples extended past their natural drawn ratio are also indicated. The three curves are calculated from the tabulated values of the previous paper for different values of $\Delta n_{\max}$. The results for 20°C gave a best fit to Equation 2 with $\Delta n_{\max} = 0.235 \pm 0.005$, consistent with the results of other recent work [14, 15].

The following conclusions can be drawn from consideration of all the data.

(1) There is no difference in the optical behaviour of the low and high molecular weight samples. It can be concluded that the reorientation mechanism is independent of molecular weight, and that the degree of alignment relates only to the draw ratio.

(2) There is no observed difference in the

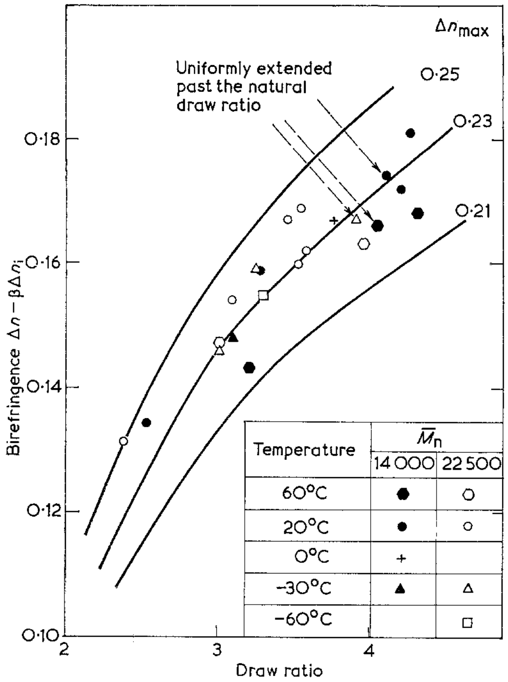

Figure 4 Modified birefringence ($\Delta n - \beta\Delta n_i$) as a function of draw ratio.

pattern of development of optical anisotropy with draw ratio over the temperature range 20 to − 60°C. Again the degree of alignment relates only to the draw ratio.

(3) The results at + 60°C do appear to be significantly lower than those at other temperatures. It is suggested that the deformation at this high temperature begins to deviate from pseudo-affine deformation and begins to change to affine deformation. This suggestion receives confirmation from other recent work on drawing PET where the development of optical anisotropy has been compared with changes in the infra-red spectrum [16].

(4) Those samples extended past the natural draw ratio still developed orientation in an identical manner to those extended to the natural draw ratio only. This indicated that the mechanism of alignment still relates to the draw ratio and is not altered by the change from the inhomogeneous deformation during necking and cold drawing to homogeneous plastic deformation beyond this extension.

(5) The theoretical model proposed previously [6] is adequate to describe the results, i.e. the orientation during cold drawing fits the pseudo-affine deformation scheme. It should perhaps be pointed out that the results are not a very sensitive test for the additional term $\beta\Delta n_i$ which takes into account pre-orientation because this term is small in the region of interest in this work. The previous studies [2] were a better test for this part of the theory. It is very satisfactory that the results at 20°C and lower temperatures suggest a value for $\Delta n_{max} = 0.235 \pm 0.005$ which is consistent with other recent studies of molecular orientation in PET using broad line nuclear magnetic resonance [14] and laser Raman spectroscopy [15].

4. Conclusions

(1) The results of the present study are consistent with previous conclusions regarding the influence of pre-orientation on the natural draw ratio of amorphous PET. With the exception of the very lowest pre-orientation samples, the drawing behaviour is consistent with a constant network extensibility, irrespective of the division of extension between the extrusion and drawing processes.

(2) In samples of very low pre-orientation, the natural draw ratio is dependent on the drawing temperature. The natural draw ratio of such samples is also dependent on molecular weight. The effects are significant, in that the draw ratio may vary by a factor of about two, but do not suggest any remarkable changes of kind in the mechanism of deformation, only changes in the nature of the molecular network and its degree of extensibility.

(3) The development of molecular alignment is consistent with a simple continuum view of the mechanism of deformation and the pseudo-affine deformation scheme appears to hold for the drawing process even if the natural draw ratio is changed by molecular weight or temperature.

In these experiments on amorphous PET, in distinction to those on crystalline linear polyethylene, the draw ratios are comparatively small. In the polyethylene case, the mechanism of draw at high draw ratios is clearly quite different from that observed at low draw ratios in both polyethylene and PET. At high draw ratios in polyethylene, it can be concluded that there is substantial pulling out of chain folds [17] rather than the reorientation of the initial material on a simple continuum basis, and indeed the degree of molecular alignment as revealed by birefringence can remain substantially constant [18].

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