Crystallite thickness measurements on ultra-high modulus linear polyethylene: effect of draw temperature

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The effect of draw temperature on the longitudinal crystal thickness $\bar{L}_{002}$ and long spacing L has been determined for a series of drawn linear polyethylene samples. It was found that both $\bar{L}_{002}$ and L increase almost exactly in proportion with increasing draw temperature. The structural significance of the results is discussed, especially with regard to the interpretation of mechanical stiffness.

Keywords Crystal thickness; long spacing; drawn polyethylene

INTRODUCTION

Recently we have established that one of the major effects of drawing of linear polyethylene is a significant increase in the value of longitudinal crystal thickness as determined from wide-angle X-ray scattering[1]. In a number of publications[2-4] it has been shown that these measurements provide the basis for an interpretation of the dynamic tensile behaviour, the thermal expansion and the thermal conductivity of highly oriented linear polyethylene.

Our purpose is to report the findings of a recent study on the variation of longitudinal crystal thickness and long spacing, determined from small-angle X-ray scattering, for specimens of highly oriented linear polyethylene prepared at different drawing temperatures. It will be seen that the results provide further corroborative evidence for the interpretation of the structure of these materials which we have advanced over the past few years.

EXPERIMENTAL

Oriented specimens of linear polyethylene were prepared by drawing isotropic sheets in air at various temperatures. Further details of the drawing process are given elsewhere[5,6]. In this study two grades of linear polyethylene were used, Rigidex 50 and H020-54P, both manufactured by BP Chemicals International Limited. Details about these grades and of the final products can be found in *Table 1*.

Small angle X-ray scattering (SAXS) patterns were obtained using a Franks small angle camera attached to a Siemens microfocus X-ray tube. The scattering was recorded photographically and the long spacing L estimated from the pattern on the film.

Longitudinal crystal thicknesses ($\bar{L}_{002}$) were estimated from the broadening observed in wide-angle scattering patterns. The procedures followed in the determination of $\bar{L}_{002}$ have been described in detail elsewhere[1].

Dynamic mechanical measurements were performed at 20 Hz on samples 5 cm long. A full description of the experimental arrangements has been given in a previous publication[7]. In all cases, the sample stress was measured by a non bonded resistance strain gauge transducer and the strain measured by a similar transducer connected by a calibrated spring to the vibrator which produced a sinusoidal sample strain. The signals from the two transducers were compared in amplitude and phase, providing a direct measure of modulus and $\tan\delta$. The measurements were performed in the temperature range $-160°$ to $+80°$C but only the $-50°$C plateau modulus is of interest here.

Sample crystalline mass fractions were estimated from the melting behaviour determined using a Perkin-Elmer DSC-2 differential scanning calorimeter. The crystalline mass fraction was calculated from the relation:

$$\alpha_m = \Delta H / \Delta H_0$$

where ΔH is the sample enthalpy of fusion and ΔH_0 is the enthalpy of fusion of a polyethylene crystal of infinite dimensions ($\Delta H_0 = 70$ cal g^{-1}).

RESULTS AND DISCUSSION

The measured values of $\bar{L}_{002}$ are plotted against draw ratio in *Figure 1* while the values of L are plotted in *Figure2*. It should be noted that, as observed before, there is a general increase in the value of $\bar{L}_{002}$ with increasing draw ratio, and yet the value of L remains more or less constant. However the long spacing does depend upon the temperature of drawing, an observation which is quite consistent with those of previous investigations. In the

Table 1 Summary of final products and preparation details

Grade	$\bar{M}_w$	$\bar{M}_n$	Draw temperature (°C)	Draw ratios
Rigidex 50 (Sample 1)	101 450	6 180	75	9,13,21,25,30
H020–54P (Sample 2)	312000	33000	75	10,17
			95	15,21
			115	10,15,20,25,30

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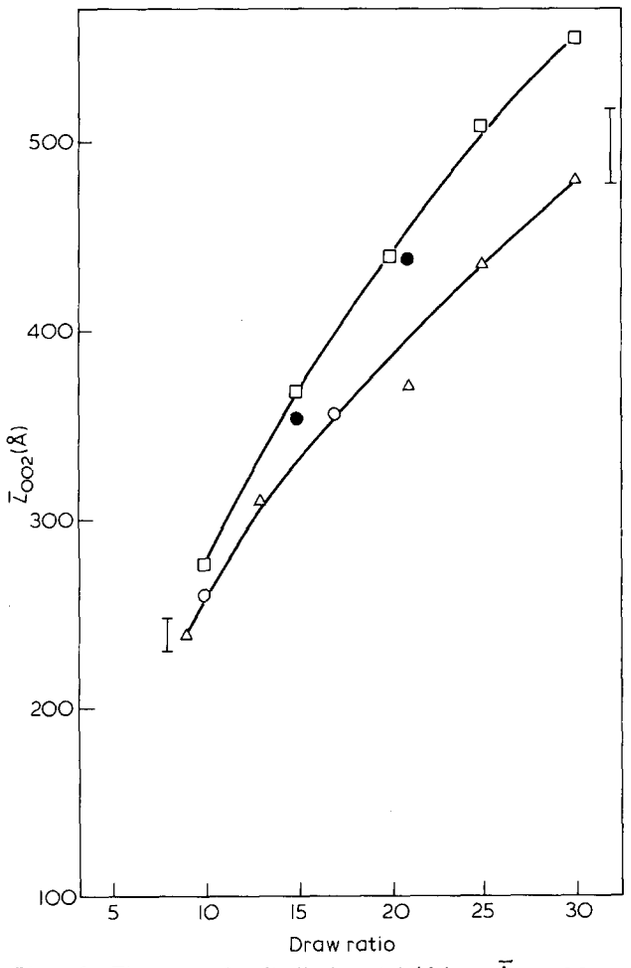

Figure 1 The average longitudinal crystal thickness $\bar{L}_{002}$, as a function of draw ratio. (△) Rigidex 50; (○) H020–54P, T_d = 75°C; (●) H020–54P, T_d = 95°C; (□) H020–54P, T_d = 115°C

present results, a novel dependence of longitudinal crystal thickness upon draw temperature is found, and the effects of molecular weight appear to be insignificant.

At a simple level these results are easily interpreted in terms of the structural model proposed by Gibson, Davies and Ward[2]. This model considered that the oriented stacks of lamellae characteristic of low draw ratio LPE become increasingly linked by crystalline bridges as the draw ratio is increased. The parameter p defines the probability of a crystalline sequence traversing the intercrystalline region to link two adjacent lamellae, and is given by:

$$p=(\bar{L}_{002}-L)/(\bar{L}_{002}+L) \quad (1)$$

where, as before, $\bar{L}_{002}$ is the longitudinal crystal thickness and L is the long spacing. Moreover, at temperatures above that of the γ relaxation, a quantitative correlation between the Young's modulus E' (the −50°C storage modulus) and p can be established:

$$E'/E_c=\chi p(2-p) \quad (2)$$

where χ is the volume fraction of crystallinity and E_c is the crystal modulus of LPE in the chain axis direction. The quantity $\chi p(2-p)$ is simply the volume fraction of crystalline bridges.

If we adopt this model of the structure of highly drawn linear polyethylene, then the effect of draw temperature is simply one of scale. Increasing the temperature of draw, increases the longitudinal scale of the structure. Moreover, since both $\bar{L}_{002}$ and L increase in proportion, or very nearly so, this model describes quite adequately the mechanical behaviour of samples produced at different temperatures. For instance, the −50°C plateau moduli of samples produced under the same conditions excepting the value of draw temperature, are more or less identical. *Figure 3* illustrates that this is indeed the case. Within the limits of experimental accuracy, the identity $E'/E_c=\chi p(2-p)$ is corroborated. The stiffness E' at −50°C is wholly determined by the volume fraction of crystalline sequences which span two or more adjacent lamellae, $\chi p(2-p)$. If we consider the effect of draw temperature in the light of this proposition, we must conclude that although increasing draw temperature increases the scale of the structure, it does not increase the axial modulus, because the volume fraction of crystalline sequences which span two or more adjacent lamellae remains unaltered.

It should be pointed out that the results presented here are apparently at variance with the results of etching and gel permeation chromatography experiments carried out in this laboratory[8]. These latter results suggested that no significant change in the crystal length distribution takes place upon drawing at higher temperatures. However we should remember that two such fundamentally different methods of appraising the structure of these drawn materials are unlikely to yield identical results. Moreover, the effect of draw temperature appears to be a small

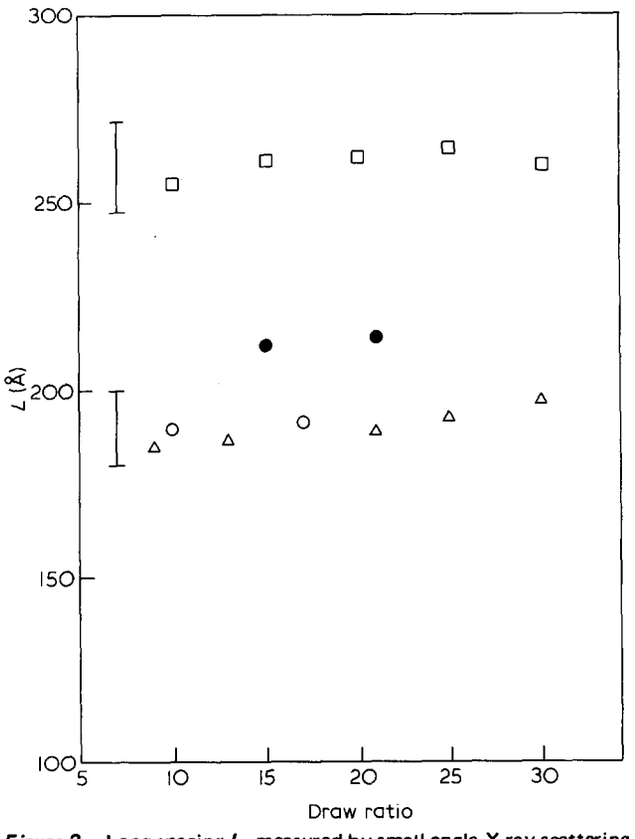

Figure 2 Long spacing L, measured by small-angle X-ray scattering, as a function of draw ratio. (△) Rigidex 50; (○) H020–54P, T_d = 75°C; (●) H020–54P, T_d = 95°C; (□) H020–54P, T_d = 115°C

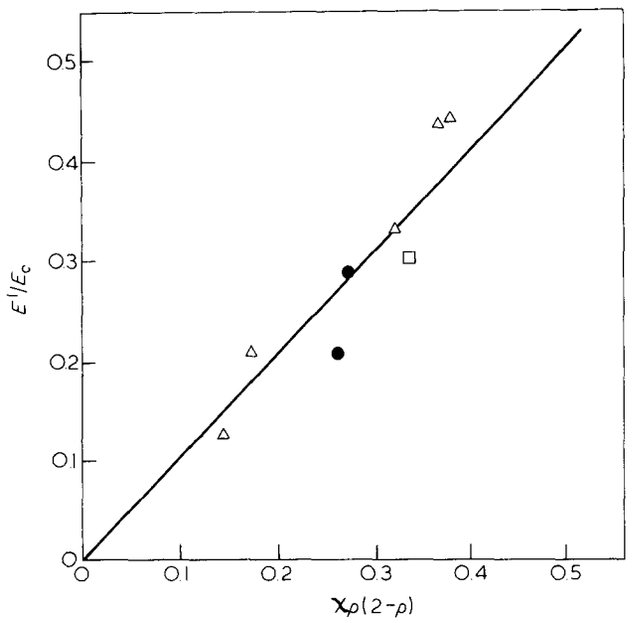

Figure 3 A comparison of axial low temperature moduli (measured at −50°C) with the predictions of the 'Random Intercrystalline Bridge Model'. (△) Rigidex 50; (●) H020–54P, T_d = 95°C; (□) H020–54P, T_d = 115°C

perturbation only, superposed upon the much larger effects of draw ratio. The effect of draw temperature is significant, and becomes more so as the draw ratio is increased. (The curves in *Figure 1* are diverging). This casts some doubt upon the rigour of the identity $E'/E_c = \chi p(2-p)$, but within the limits of experimental accuracy the correlation still holds.

CONCLUSIONS

It is known that long spacings, estimated from small angle X-ray scattering for drawn LPE, increase with increasing temperature of draw. Wide angle X-ray scattering measurements have shown that longitudinal crystal thicknesses also increase with increasing temperature of draw.

The observation that the ratio of longitudinal crystal thickness to long spacing (or more strictly the parameter p) only depends on draw ratio, to a first approximation, is consistent with previous observations on the dependence of the Young's modulus of these materials: the modulus depends primarily on the draw ratio and is largely independent of molecular weight and draw temperature.

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