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On the plastic deformation of chain-extended polyethylene

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Deformation of the lamellar microstructure (average lamellar thickness ~ 500 nm) of a high molecular weight chain-extended polyethylene after drawing five-fold has been investigated using a variety of microscopic and other techniques. As the interlammelar regions in this material are expected to be qualitatively similar to those in chain-folded polyethylene, the former may be considered as a large scale copy of the latter. It is shown that: the great majority of lamellae survive the draw with their thickness along **c** only slightly reduced although ~ 20% appear to become disrupted; many lamellae undergo a high shear parallel to **c**, although not always a uniform one; lamellar rotation and interlammelar shear probably also occur as may the formation of voids and/or crazes; drawing does not involve melting.

1. Introduction

The plasticity of semi-crystalline polymers, shown by their ability to be drawn, is among their most useful and interesting properties. Much attention has been given to understanding the relevant mechanisms and quite detailed molecular interpretations have been made [1]. Nevertheless, the physical texture even of undrawn polymer is difficult to elucidate and the problems are still more severe for drawn material. Above all, information on the basic sub-unit, the lamella, generally comes from methods such as low-angle X-ray diffraction which measure average properties. Whenever microscopic techniques have been used, as in the case of spherulitic polymer [2] or in the simplified case of solution-grown crystals [3, 4], plastic deformation has been observed to be a most complicated process. Microscopic techniques do not, however, readily reveal lamellae in a chain-folded polymer, so that the study of the drawing of chain-extended polyethylene (CEPE) brings with it two considerable advantages. First although lamellae still contain folded molecules, they are much thicker than their chain-folded counterparts (the range of dimensions being typically 0.1 to 5 μm) with the largest easily visible in the optical microscope. The great thickness is a legacy of crystallization into (or annealing in) the high-pressure hexagonal phase [5] and cannot, according to present knowledge, be reproduced by treatments at atmospheric pressure. The second advantage is, therefore, that the crystal thickness and melting point provide unequivocal measures of whether melting did or did not occur during drawing. This is a mechanism which despite rebuttal in its simplest form [1, 6] still continues to receive support [7].

2. Materials and methods

2.1. Specimen preparation and drawing

The material used in this study was "Hifax 1900"* a high-density polyethylene of very high molecular weight. The manufacturers estimate the weight average molecular weight to be greater than 2×10^6 and state that the chains are nearly branch free.

Samples were melt-crystallized in a high pressure piston and cylinder apparatus which has been described in detail elsewhere [8]. Before high pressure crystallization, the polyethylene was compression moulded into a 1 mm thick sheet from which a dumb-bell shaped specimen was cut. The dumb-bell, which had a total length of 4.0 cm,

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* Hercules Powder Co Ltd.

a gauge length of 1.7 cm and a gauge cross-section of 0.4 cm × 0.1 cm, was located in a metal mould of the same shape which was then placed in the piston and cylinder apparatus. A small hole in the mould allowed the pressure transmitting fluid, silicone oil, to reach the specimen; the temperature within the high pressure chamber was recorded via a thermocouple attached to the mould. A pressure of 5.3_5 kbar was imposed and the temperature was raised to 260° C over a period of several hours. This temperature, which is above the melting point measured by high pressure DTA, was maintained for 5 min after which it was reduced at a controlled rate of $0.6 \pm 0.1\,\mathrm{K\,min^{-1}}$ to below 230° C, a temperature substantially lower than the expected crystallization temperature [9]. Heaters were then switched off. The pressure during the crystallization was 4.9_5 kbar, slightly lower than the initial imposed pressure because a piston-seal friction correction term changed sign when the piston changed its direction of motion as cooling began. When cool the specimen was removed and washed in cold xylene.

Specimens were drawn on an Instron Model 1112 tensile testing machine to a permanent engineering strain of 400% (i.e. a draw ratio of X5); this was measured from an ink grid stamped on the specimen prior to deformation. A temperature of 80 ± 2° C was maintained in the region around the specimen by means of an Instron Model 3111 temperature cabinet; this temperature was measured with a thermocouple placed close to the specimen. The cross-head speed was 0.05 cm min^{-1} which gave a strain-rate of 0.03 min^{-1}, referred to the initial gauge length.

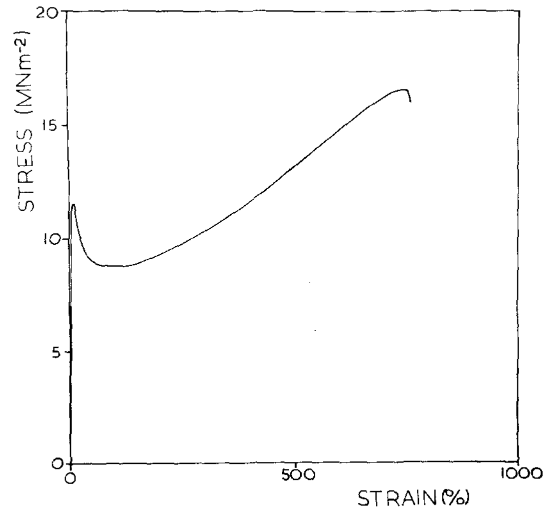

Figure 1 Stress–strain curve for chain-extended "Hifax" Polyethylene when tested at 80° C.

2.2. Techniques of examination

Several complementary techniques have been used to elucidate the morphology of chain-extended Hifax and the changes produced in it by drawing. Structure was directly observed by microscopy at three levels, polarizing optical microscopy (POM) of thin sections embedded in Canada balsam, scanning electron microscopy (SEM) of surfaces fractured under liquid nitrogen and etched with fuming nitric acid at 60° C for 36 h and transmission electron microscopy (TEM) of shadowed carbon replicas of fracture surfaces taken from specimens which had been presoaked in cold xylene for 2 h prior to fracture.

Structural changes were also detected by three other techniques. Gel permeation chromatographic analysis (GPC) of material degraded by fuming nitric acid for 3 days at 60° C provided a measure of lamellar thickness. Measurements were made with a Waters Associates 200 Model GPC operated at 130° C into which samples were injected at 0.25% concentration in o-dichlorobenzene. Differential scanning calorimetry (DSC) of 1.3 mg samples was carried out on a Perkin Elmer DSC 1B at a scan rate of 4 K min^{-1} and finally density measurements were made with a xylene/carbon tetrachloride gradient column held at 23.0 ± 0.1° C.

3. Results

3.1. Macroscopic tensile behaviour

A typical stress–strain curve for chain-extended (CE) Hifax tested under the conditions given in Section 2.1 is shown in Fig. 1. As can be seen there is a maximum at which the nominal stress is 11.7 MN m^{-2} and the stain is 8.7%, after this the stress fell to a minimum of 8.8 MN m^{-2} increasing then to 16 MN m^{-2} at fracture. The rate of stress increase after the minimum was due partly to strain-hardening and partly to the fact that the shoulders of the specimen were subject to plastic deformation. After the test the specimen showed a permanent deformation of X 6.5*. Although the

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* The sample used in this present study of structural changes was not pulled to break and accordingly had a slightly lower draw ratio of X5.

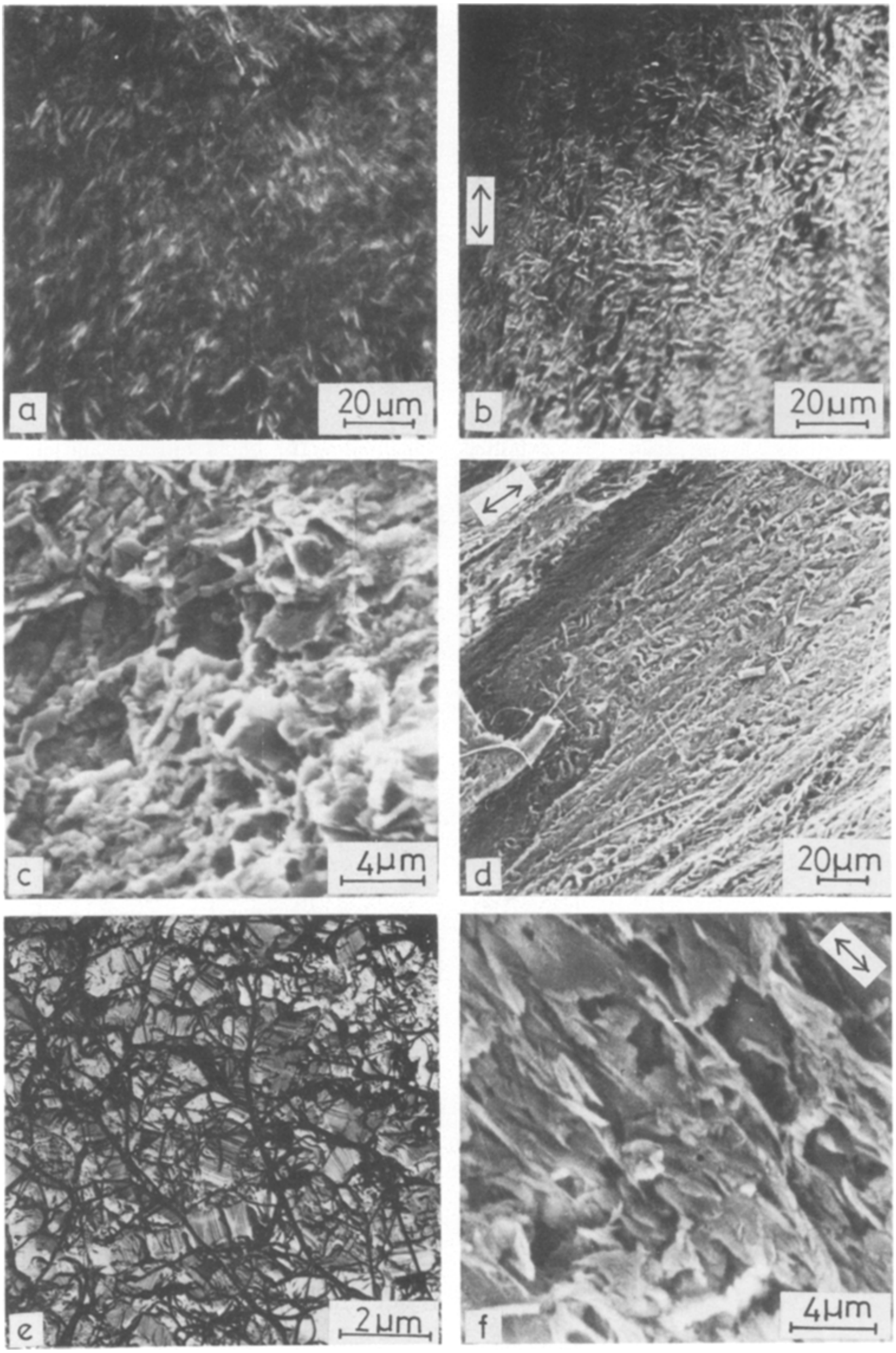

Figure 2 Morphology of CEPE before (a, c and e) and after (b, d and f) drawing × 5: (a) and (b) POM, (c), (d) and (f) SEM and (e) TEM.

draw was inhomogeneous it did not proceed via a sharp necking zone. The undrawn material had a dull white appearance and smooth surface; after draw the surface was much whiter and rougher.

3.2. Microscopy

The largest lamellae in the microstructure of CE Hifax are visible between crossed polars in the optical microscope (Fig. 2a). This is a particularly valuable technique as it is potentially non-destructive and offers the only means of observing individual lamellae continuously throughout deformation. This first paper, however, is concerned only with samples before and after drawing.

In Fig. 2a, which is the original undeformed sample, the lamellae have random orientations; those viewed approximately edge on are in bright contrast. The texture changes on drawing to that of Fig. 2b photographed with the draw direction at 45° to the crossed polars. Lamellae have evidently survived the draw, indeed many more crystals now appear in bright contrast, a consequence of molecular alignment along the draw direction. Some of these show a high uniform shear, others are noticeably crooked in ways suggesting that they also are highly sheared but non-uniformly.

More of the lamellar population is visible in the scanning electron microscope. The initial morphology is shown in Fig. 2c for comparison with the drawn specimen shown in Fig. 2d and f. At low magnification (Fig. 2d), there is close similarity with the texture of the optical image of Fig. 2b; at higher magnification (Fig. 2f), details of the constituent lamellae are quite evident. Treatment of these fracture surfaces with fuming nitric acid was necessary to uncover lamellae beneath what was otherwise a rather featureless surface.

The finest detail was revealed in transmission electron microscopy. Fig. 2e is of the initial sample showing lamellae partly obscured by pulled threads. Replicas of drawn samples are shown in Fig. 3a, c and e. The best resolution was obtained from specimens which were soaked in cold xylene prior to fracture in liquid nitrogen; this appears to counter the crack-propagating effect of voiding and/or crazing which is likely to lead to the featurelesss fracture surfaces already mentioned. Lamellae are detected after draw, most readily by the characteristic striation along **c** of the $\{hk0\}$ (prism) faces; such areas are outlined in Fig. 3b, d and f which refer to Fig. 3a, c and e, respectively.

The extensive areas between the exposed $\{hk0\}$ faces can be seen from stereoscopic pairs to be mostly basal lamellar surfaces; they may also include disordered material. Particularly clear examples of $\{hk0\}$ faces are shown in Fig. 3c and e.

Analysis of fifty or so lamellae observed within micrographs of deformed material indicated that all the fine parallel striations were aligned within 35° of the draw direction and that 80% of them were within 15°. In contrast to the situation before draw (Fig. 2e) the striations observed within most of these lamellae were not normal to the lamellar interfaces as may be seen in Fig. 3. Values of the angle θ (Fig. 4a) between the striation direction (**c**) and lamellar interface normal (**n**) lay between 0° and as high as 75° although most were between 30° and 60°. A small proportion of lamellae appeared to have survived the draw without any deformation (i.e. $\theta = 0$). Very often the value of θ varied within one lamella and sometimes this variation was discontinuous. These last two types of deformation are illustrated schematically in Fig. 4b (discontinuous) and c (continuous); they appeared to be more common in lamellae with striations which made a small or zero angle to the draw direction. Some similar types of deformation have been observed in the case of PTFE [10, 11].

3.3. Related measurements

The lamellar thicknesses of CEPE can be assessed from the distribution of chain lengths (measured by GPC) on nitrated samples. Following work on chain-folded PE it is thought that nitric acid eats away lamellar surfaces leaving a distribution of stem lengths closely related to the original distribution of crystal thicknesses. This is a technique which has been shown to correlate well with lengths computed from fracture surfaces when both are available; in cases such as in this paper, however, it is the only one so far available. The normalized distributions before and after drawing are shown in Fig. 5 and can be seen to be similar, with the original having a weight average mean of 6400 Å and the drawn sample one of 5480 Å. This is a significant difference experi-

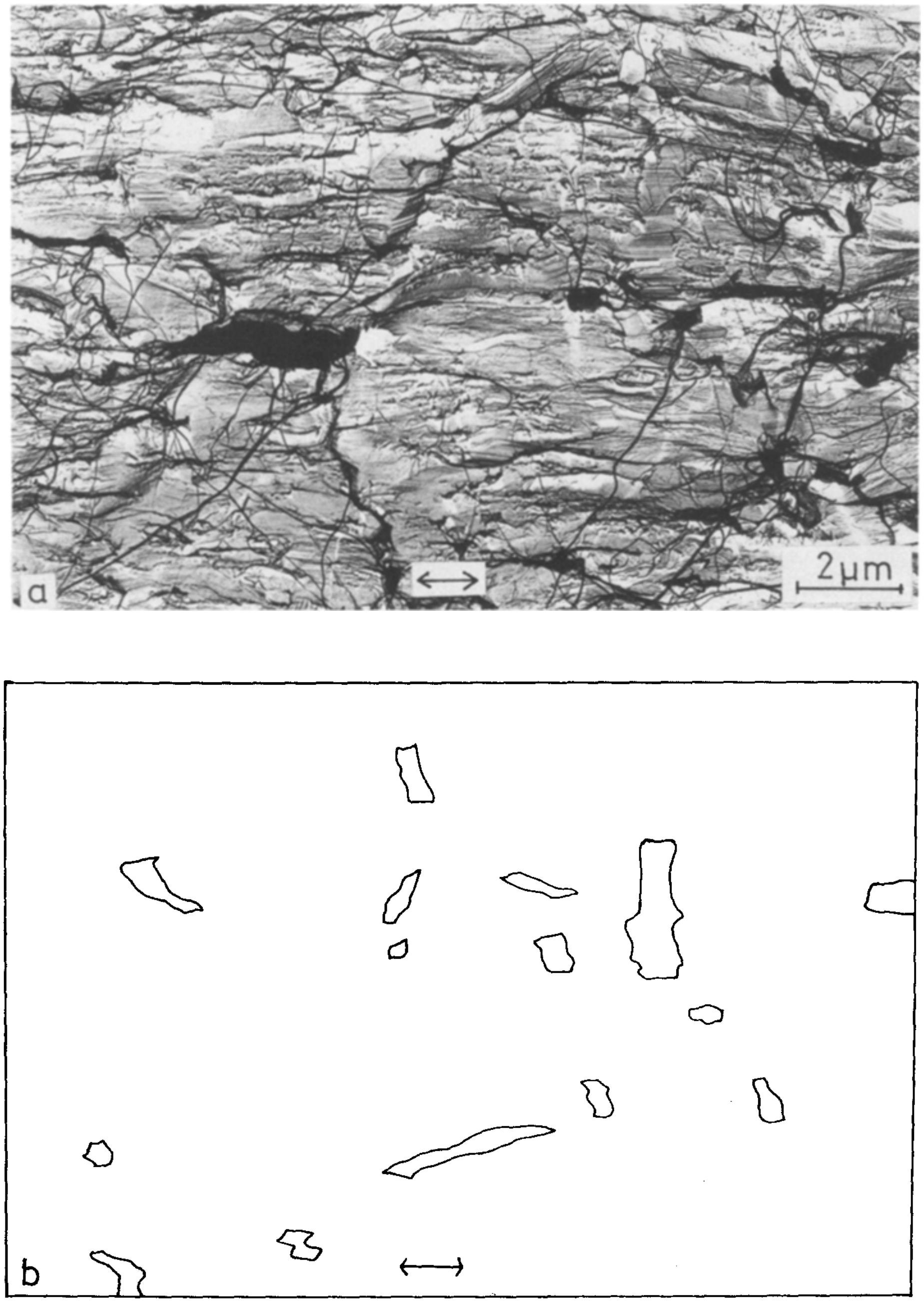

Figure 3 Fracture surface replicas of drawn CEPE as seen in TEM (a), (c) and (e). Masks (b), (d) and (f) outline striated $\{h\,k\,0\}$ faces in (a), (c) and (e) respectively.

mentally, but the crystals evidently retain a thickness characteristic of chain-extended growth rather than chain-folded.

This conclusion is reinforced by the melting behaviour. Fig. 6 shows three melt thermograms relating to undrawn, drawn and nitrated drawn specimens. The effect of drawing is to leave the melting peak at almost the same temperature but to introduce a low-melting shoulder. Material associated with this shoulder disappears after 3 days nitration. The residual peak is shifted to lower temperatures by ~ 5 K compared with the original, a phenomenon almost certainly due to superheating associated with very long molecules. Essentially similar behaviour has been reported in PTFE for which superheating effects disappear

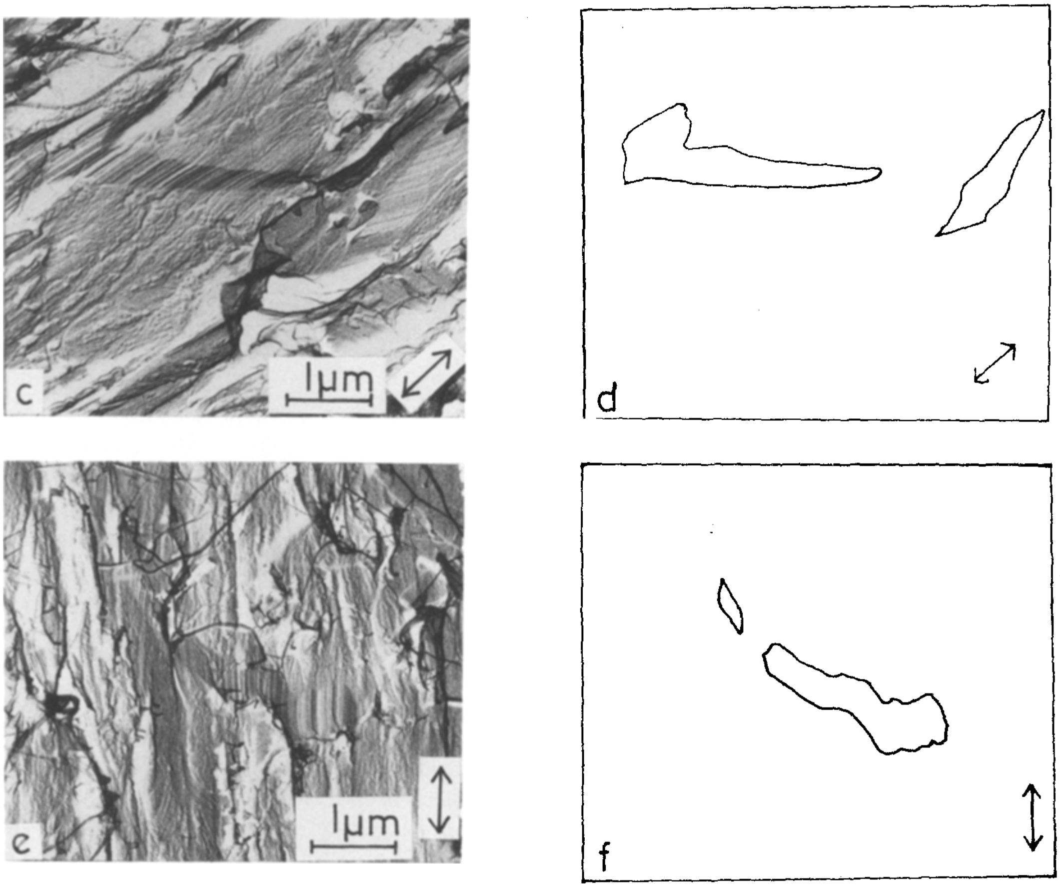

Figure 3 continued.

with increasing molecular scission [12]. The density before draw was measured to be 0.986 Mg m^{-3}, but after draw, specimens at first floated on top of the column. After 24 h soaking in the column liquid, however, they sank to the 0.980 Mg m^{-3} level. This shows that while the gross density is lowered by drawing, the microscopic value remains appropriate to thick chain-extended lamellae.

4. Discussion

4.1. Plasticity in chain-extended polyethylene

CEPE is unique among synethetic polymers in generally having crystalline lamellae thick enough to be visible in the optical microscope and offering the possibility of direct observation of individual lamellae throughout plastic deformation. When first prepared, however, CEPE was notorious for its brittleness and indeed this seemed a very reasonable property for a structure then presumed to be of fully extended chains and well-defined interfaces. Nowadays the picture is different [13]. The structure produced by crystallization of molten PE at high pressures is not one of fully-extended chains but of thick lamellae within which molecules are generally folded. Following recent practice [9, 13] such lamellae are termed chain-extended because crystallization has proceeded via the hexagonal high pressure phase into the usual orthorhombic phase. So far as is known they are essentially large-scale copies of their chain-folded counterparts crystallized directly into the orthorhombic phase.

When isotropic CEPE is fractured it reveals $\{hk0\}$ (prism) faces almost exclusively, showing that these provide the preferred mode of failure. In the case of uniaxially oriented CEPE, systematic brittle fracture between lamellar basal surfaces has also been observed in tensile tests along the common **c** axis [14]. This behaviour is a consequence of the segregation of low molecular weight and other slowly crystallizing polymer. When this component is removed prior to high

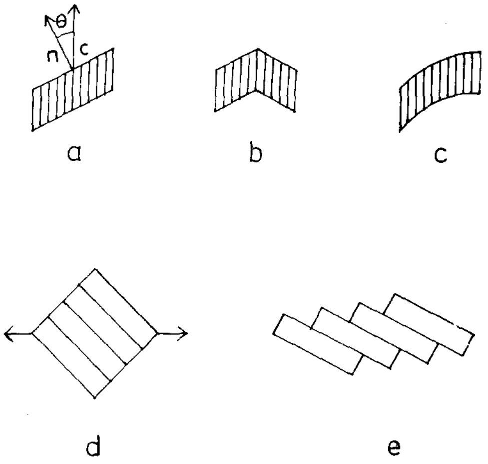

Figure 4 Schematic illustration of types of lamellar shear observed in drawn CEPE (a), (b) and (c), and of interlamellar shear (d) and (e).

pressure treatment, provided the remainder of the material is of sufficiently high molecular weight, samples show some ductility in tension along **c** at room temperature. Our unpublished experiments show, not unexpectedly, that for tensile stresses in other directions, brittle fracture in $\{hk0\}$ planes still occurs unless the molecular weight is high.

Isotropic CEPE is ductile, therefore, if it consists of high molecular weight polymer with no low molecular weight tail. Hifax 1900 satisfies these criteria and displays ductile fracture at room temperature, although, as yet, it has only exhibited draw at elevated temperatures. It seems likely that the reason why ductility is obtained with a high molecular weight is that the strength and toughness of the interlamellar material will be greater due to an increased number of interlamellar connections; as a consequence it will be able to support the critical stress required to operate slip systems and also act to blunt cracks. Moreover, the degree of crystallinity in chain-extended high molecular weight material is slightly less than that found in the case of medium molecular weight, possibly due to an increased number of intractable entanglements in the former. If, as a result, a slightly thicker intercrystalline amorphous layer resulted, it has been suggested that this would more easily accommodate the deformation of lamellae which are not expected to be able to undergo a general shape change [15]. Since the ratio of basal surface area to lamellar volume is less in CEPE it may be expected that chain topology in these surfaces plays a less significant role in determining slip systems.

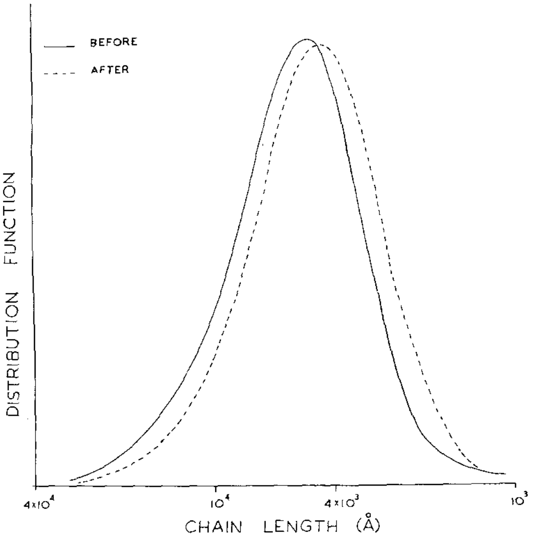

Figure 5 The effect of draw on lamellar thickness as revealed by GPC of nitrated material.

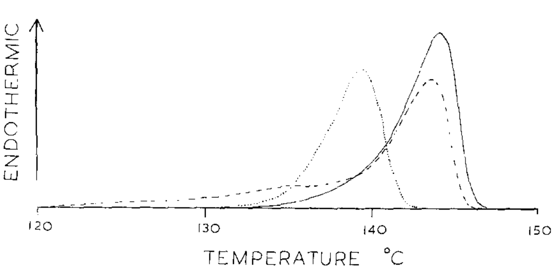

Figure 6 Melt endotherms of CEPE —— before and ---- after drawing; . . . drawn and nitrated.

It is noteworthy that in the sample used in this study, the ratio of the average molecular length ($\sim 2 \times 10^5$ Å) to average crystal thickness ($\sim 5 \times 10^3$ Å), which gives an average upper limit for the number of folds, is ~ 40, a value within the range of typical chain-folded polyethylenes. As this figure is approximately the number of folds per average molecule and is likely also to be a measure of the number of interlamellar links, it would seem quite probable that interlamellar regions in chain-extended Hifax are similar to those in typical chain-folded PE samples, so that the two may reasonably be regarded as differing only in lamellar thickness.

At higher levels of textural organization there can be marked differences between CEPE and chain-folded material in that recrystallized CEPE has its own characteristic texture whereas the latter is generally spherulitic. However, CEPE can be prepared in spherulitic form by annealing chain-folded PE in the hexagonal phase. Preliminary studies of lamellar deformation in such samples indicate that it is qualitatively the same as that described in this paper.

4.2. Deformation of lamellar microstructure during draw

The main conclusion of this paper is that the majority of lamellae survive the drawing process with maintained integrity. This is true for draw ratios as high as 6.5 (the maximum so far obtained) whereas in chain-folded PE it has been concluded that most crystals are disrupted by a three-fold draw [16]. Although the point has not yet been directly confirmed, there can be very little doubt that it is the same crystals which are present before and after draw. Their maintained high thickness is then highly significant and bears on the old hypothesis that drawing is effected by local melting. Were melting occurring in CEPE, recrystallization at atmospheric pressure must, according to present knowledge, be directly into the orthorhombic structure. Lamellar thicknesses and related properties such as melting point and density would then be those appropriate to chain-folded PE, i.e. significantly lower than those measured. We can be confident, therefore, that melting has not occurred during drawing. Preliminary results indicate that this conclusion also holds in the case of CEPE with spherulitic texture when drawing takes place at a neck.

It is quite clear from Figs. 2 and 3 that although many lamellae survive the draw they become highly sheared by (*hk*0) [001] slip, commonly known as chain slip. Some lamellae appear to have a uniform shear; others do not and must be non-planar. Slip in perpendicular directions (transverse slip) may also be present but the results cited do not bear on this point. Furthermore, it is a reasonable inference from the molecular rotation necessary to align molecules along **c** and from the gross extensions achieved that lamellar rotation and interlamellar shear (Fig. 4d and e), respectively, are also occurring. This should be confirmed directly when experiments to observe lamellae during draw are completed.

The diminution of lamellar thickness measured after deformation is probably real. The difference in lengths measured by the nitric acid/GPC technique (Fig. 5) is certainly significant, but it could conceivably be objected that in an oblique structure, such as that produced by deformation, greater fold surface area might lead to greater attack and lower recorded lengths. However, the nitric acid/GPC technique is not alone in showing the reduction; melting point also does. Similarly, in **c** oriented PTFE, Davitt [11] has examined fracture surfaces and found a reduction from 1700 to 1400 Å on stretching by 50% along the **c** axis and from 1700 to 1150 Å for a similar strain at 45° to **c**. A reduction is also intuitively reasonable in that if molecular ends are pulled (as they would be if they were outside lamellae and interlamellar regions suffered a greater extension than lamellae themselves) this would be likely to lead to tightening of the structure, i.e. a reduction in fold-stem length. Moreover, although the reduction observed is modest (15%) for CEPE, the same absolute amount could not occur for chain-folded lamellae without their disruption.

Although the majority of chain-extended lamellae survive the draw intact, a small proportion suffer sufficient disruption to produce a low melting tail on the melt thermogram. The precise nature of this material in drawn specimens is the subject of further experiments. The present evidence does, however, give a fair insight into its character. First, the melting tail itself suggests that it belongs to a continuous spectrum of highly defective lamellae. The concept is supported by the fact that the low melting tail has disappeared after 3 days in nitric acid (Fig. 6). Such behaviour is not found with more perfect crystals produced directly by crystallization. The proportion of sample in the low-melting tail of Fig. 6 is 20%; weight loss figures after nitric acid treatment are of similar order.

It seems quite likely that this continuous spectrum of highly disrupted lamellae could have been created by extreme deformation of the types already established for the integral lamellae, i.e. alignment of molecules and high chain slip coupled with a decrease in crystal thickness. One might in this way be able to establish parallels with the drawing of chain-folded lamellae because one can envisage circumstances where the much thinner layers could be extremely disrupted and perhaps destroyed by the processes mentioned. Moreover, because of the sensitivity of yield criteria to temperature one might also expect a dependence of final lamellar thickness on the draw temperature. Firm information on these and other important questions such as the respective roles of the various inter- and intralamellar modes of deformation should be forthcoming when experiments to observe lamellar deformation directly during draw are completed.

As is often the case with chain-folded PE it is apparent that voiding and/or crazing has occurred during the draw. This is indicated by the lower gross density and stress whitening and is consistent with the fact that xylene impregnation of the drawn material prior to immersion in liquid nitrogen reveals much more structure on fracture surfaces.

5. Conclusion

Deformation of the lamellar microstructure of chain-extended polyethylene on drawing five-fold has been investigated by a variety of microscopic and other techniques. It is concluded that most of the lamellae survive with maintained integrity (lamellar thickness along **c** only slightly reduced) although a small proportion (~ 20%) do appear to have become disrupted. Many lamellae are subject to high shear due to $(hk0)$ [001] slip. It is very probable that interlamellar shear and some form of voiding also occur. Finally, it is clear that drawing does not involve melting.

Acknowledgements

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