Direct measurements of crystallite size distribution in ultra-high modulus polyethylene fibres

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The preparation and properties of drawn and hydrostatically extruded ultra-high modulus polyethylenes have been described in a number of previous publications[1-4]. The structure of these novel materials is clearly of considerable interest, and a number of techniques have been applied to their investigation, including wide-angle and small-angle X-ray diffraction[3,5,6], Raman spectroscopy[6] and broad line nuclear magnetic resonance[5]. A summary of the present position has been presented recently[7]. A key observation is that the average crystal length (previously termed the longitudinal crystal thickness), determined from the integral breadth of the (002) reflection increases with draw ratio from a value which is comparable to the long period of ~200 Å (determined from small-angle X-ray diffraction) to a value which is several times the long period, the latter remaining approximately constant[8]. At the highest draw ratios the average crystal length is ~500 Å, which is much less than that associated with extended chain crystals. On the basis of a statistical model it has proved possible to relate the mechanical stiffness directly to the degree of crystal continuity determined from the integral breadth data which provide a measure of the weight-average crystal thicknesses[9]. For a more complete understanding it is necessary to obtain direct information on the distribution of crystal lengths. This requirement has produced the incentive for the transmission electron microscopy studies described here.

A series of oriented linear polyethylene (LPE) fibres was prepared for these experiments using the small-scale production facilities recently established at Leeds University. Spun monofilament of a suitable grade of LPE homopolymer (Rigidex 50 manufactured by BP Chemicals International Ltd; $\bar{M}_w$ = 101 450, $\bar{M}_n$ = 6180) was drawn in a glycerol bath at 120°C between moving rollers. To produce an adequate range of structures, draw ratios of 10, 22 and 32 were chosen. The fibres were characterized by their room temperature 10 s isochronal creep moduli determined as described in previous publications[1,2] (*Table 1*).

Small lengths of fibre were embedded in Spurr resin and thin longitudinal sections were microtomed with a diamond knife at room temperature. The specimens were sectioned in a direction parallel to the *c*-axis of the fibre. The sections were examined in a JEOL 100CX transmission electron microscope operated at 100 kV. A useful lifetime in the electron beam of 25 C m^{-2} was assumed, allowing tilted beam dark field images derived from the (110) and (200) reflections to be recorded on Kodak 4463 film at an instrumental magnification of 5.1k.

Figure 1 shows a selected area electron diffraction pattern from a thin longitudinal section of the draw ratio 22 sample. The spread of the diffraction arcs is similar to that seen in X-ray diffraction patterns of the original fibre, and indicates that the cutting process has caused little disruption of the material. *Figure 2* shows a dark field image of the draw ratio 22 material derived from the (110) and (200) reflections. Similar micrographs have been obtained for the other samples. An important feature of the dark field images is that the crystallites are uniformly distributed throughout the section, with no evidence of grouping in microfibrillar entities.

Single crystallite width and length measurements have been made on micrographs equivalent to a specimen area of 9 $(\mu m)^2$ in 30 nm steps, giving 300–450 readings. The weight fraction distributions* of lengths are shown for three draw ratios in *Figure 3*, and the weight-average widths and lengths are summarized in *Table 1*. It must be emphasized that the crystallite lengths measured from an image derived from an equatorial reflection may not show the true extent of the crystals in the *c*-axis direction[10]. This may be due to either (i) changes in azimuthal orientation of the (110) and (200) lattice planes causing tilting out of the Bragg condition, or (ii) loss of lateral order while the chains maintain axial regularity. Therefore, the true lengths may be greater

Table 1

Draw ratio	Modulus (GPa)	Crystal length (A)	Crystal width (A)
10	8	200	199
22	20	246	237
32	44	324	242

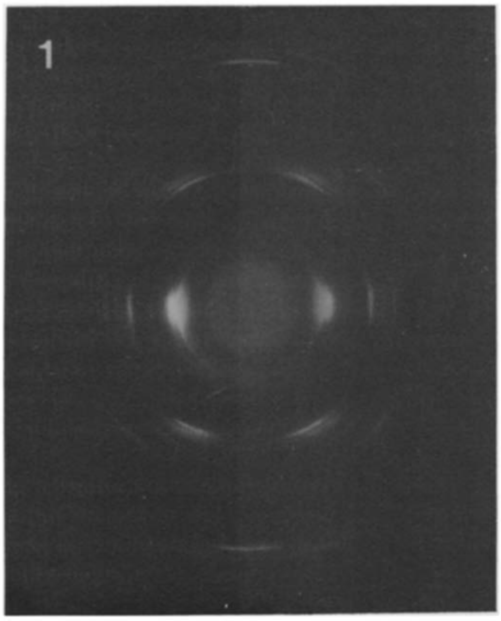

Figure 1 Electron diffraction pattern from a thin longitudinal section of draw ratio 32 material

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* The weight fraction F_l of crystallites of length l is proportional to the number with length l, multiplied by l

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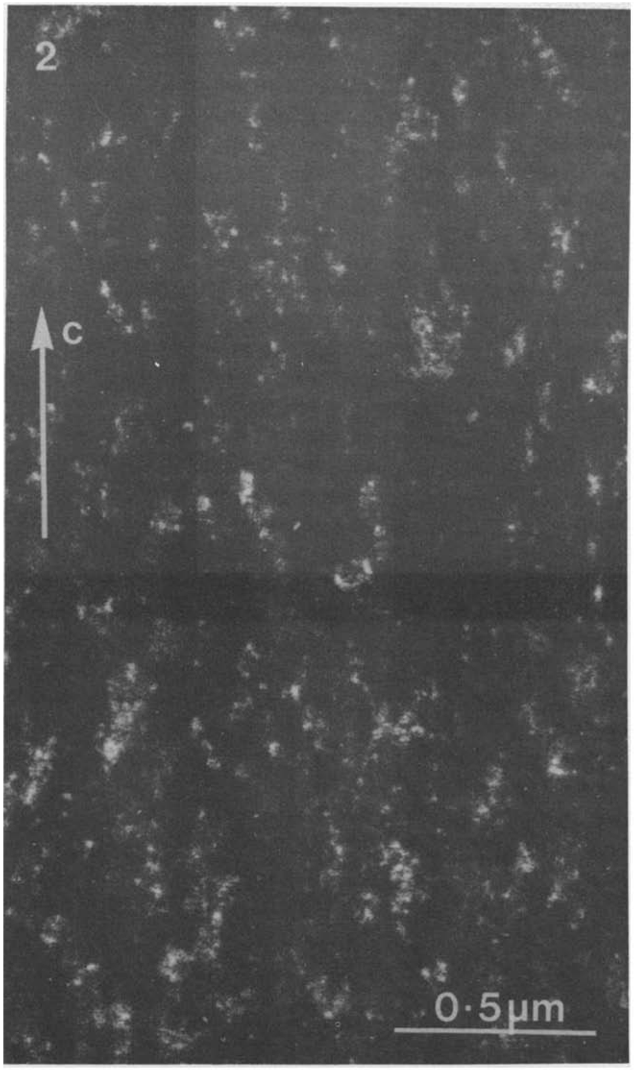

Figure 2 Dark field image of draw ratio 22 material, derived from (110) and (200) reflections

than those reported here. A proposed analysis of images derived from the relatively weak (002) reflection should clarify this point.

The crystal widths for all three specimens are in the range 200–250 Å whereas the lengths increased with draw ratio from 200 up to 324 Å at draw ratio 32. This behaviour is similar to that observed for drawn tapes by Clements, Jakeways and Ward[8], although the highest values for the lengths are somewhat lower than those obtained previously. This is consistent with the monofilament process producing rather lower levels of modulus than the tape process, as noted before[11].

As we have already observed, these materials have been considered in terms of a statistical model[9]. This model assumes that the original lamellar stacks present after the initial stage of the drawing process (draw ratio ~10) become increasingly linked by crystalline bridges as the draw ratio is increased. The crystalline bridges are considered to be randomly placed, so that the chance of adjacent lamellae being linked by an intercrystalline bridge sequence is a problem comparable to that of relating the molecular weight distribution in a stepwise condensation reaction to the degree of polymerization. The model therefore enables the weight fraction of crystalline chains spanning a given number of lamellae to be expressed in terms of a single parameter p, the probability that a chain traverses the interlamellar region to enter an adjacent lamella. A histogram of this weight fraction distribution for a value of $p = 0.4$ is shown in *Figure* 7 of ref 9. The histograms obtained here (*Figure 3*) are very similar to those predicted by the statistical model. Indeed, the amount of crystalline material longer than the small-angle X-ray repeat distance increases progressively with draw ratio. It is of particular interest that in neither case do we observe a substantial proportion of long crystals. This is important, because it has been observed[7,9] that for high modulus it is only necessary to provide crystal continuity between adjacent lamellae, and that the situation can be described to a first approximation by the well-known Takayanagi model with the crystalline bridge sequences providing a continuous crystalline phase. The absence of very long crystals in these materials had already been suspected from melting point studies, as in many cases the melting temperature is much less than that shown by extended polyethylenes[1,12]. On the other hand, arguments for very long crystals have come from mechanical models of the ultra high modulus LPE, by Arridge, Barham and Keller[13,14], where the highly drawn polymer is regarded as a fibre reinforced composite material in which long needle-shaped crystals act as the fibre phase and are embedded in a matrix of remaining interlamellar material. This hypothesis is an attractive one but does not appear to be supported by the present results. As remarked elsewhere[7,9], although it is possible to use the advantages of a fibre composite model for relaxation behaviour,

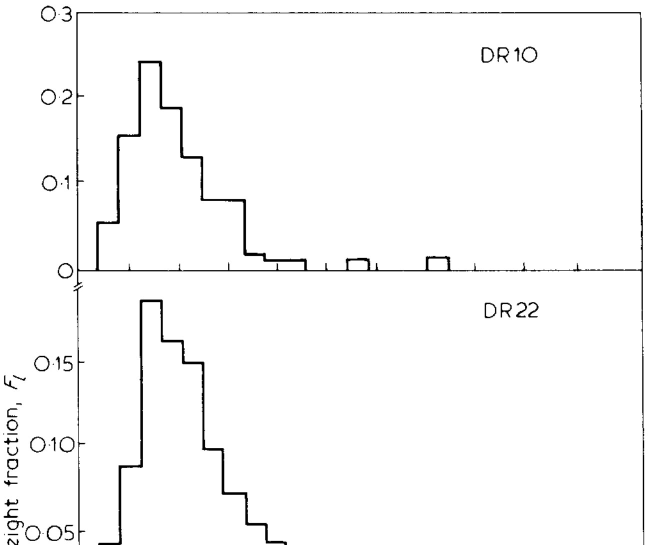

Figure 3 Histograms showing the weight fraction, F_l, of crystalline regions of length l as a function of l. Draw ratio: (a) 10; (b) 22; (c) 32

it is more consistent with the structural observations to assume that the proportions of the reinforcing fibre phase (the intercrystalline bridge sequences) are increased with increasing draw.

It is most encouraging that the results of these electron microscope studies are qualitatively consistent with previous structural studies of these materials undertaken at Leeds University, and moreover that the histograms support the model approach which has been adopted to explain the high stiffnesses. However, it is appreciated that there will be merit in more comprehensive studies. These are at present being undertaken, primarily with the intention of carrying out both electron microscopy, and more conventional wide-angle X-ray diffraction measurements on identical samples, with a view to advancing the quantitative relationships between structure and properties.

References

1 Capaccio, G. and Ward, I. M. *Nature (Phys. Sci.)* 1973, **243**, (130) 143; *Polymer* 1974, **15**, 233

2 Capaccio, G., Crompton, T. A. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1641

3 Gibson, A. G., Ward, I. M., Cole, B. N. and Parsons, B. *J. Mater. Sci.* 1974, **9**, 1193

4 Barham, P. J. and Keller, A. *J. Mater. Sci.* 1976, **11**, 27

5 Smith, J. B., Manuel, A. J. and Ward, I. M. *Polymer* 1975, **16**, 57

6 Capaccio, G., Ward, I. M. and Wilding, M. A. Faraday Discussion 68, 1979

7 Capaccio, G., Gibson, A. G. and Ward, I. M. 'Ultra-high Modulus Polymers', (Ed. A. Ciferri and I. M. Ward) Applied Science Publishers, London, 1979, Ch 1

8 Clements, J., Jakeways, R. and Ward, I. M. *Polymer* 1978, **19**, 639

9 Gibson, A. G., Davies, G. R. and Ward, I. M. *Polymer* 1978, **19**, 683

10 Keller, A. 'Ultra High Modulus Polymers' (Ed. A. Ciferri and I. M. Ward) Applied Science Publishers, London, 1979, Ch. 11

11 Wilding, M. A. and Ward, I. M. *Polymer* 1978, **19**, 969

12 Clements, J., Capaccio, G. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* in press

13 Arridge, R. G. C., Barham, P. J. and Keller, A. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 389

14 Barham, P. J. and Arridge, R. G. C. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 1177

Direct optical and *STEM* observations of the drawing of pressure-crystallized polyethylene

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Studies of structure–property relationships for synthetic polymers are rendered particularly difficult, in comparison with other technological materials, by problems of adequate textural characterization and, especially for mechanical behaviour, the inability to examine the morphology of the same specimen before and after deformation. Whereas recent advances in electron microscopic techniques have at last made it possible to reveal representative lamellar textures in polyethylene and other polyolefins, these techniques, and, indeed, electron microscopy, with its attendant radiation damage, are not suited to the study of progressive deformation. The purpose of this Communication is to report how, in one system, that of pressure-crystallized (or anabaric) polyethylene, it has been possible to follow the progress of individual lamellae during drawing by direct optical observations allied to *STEM* (Scanning Transmission Electron Microscopy) of the same samples.

Materials and Techniques

The polyethylene used was Hifax 1900 (Hercules Powder Corporation) with a reported molecular mass (mass-average) above 2×10^6. It was crystallized using established methods[1] from the melt at 4.9_5 kbar and cooling through the crystallization region at ~0.5 K min^{-1}. This results, firstly in the formation of thick, so-called chain-extended, but actually fold-containing lamellae of the high pressure disordered hexagonal phase, which subsequently transform, at essentially constant lamellar thickness into the familiar orthorhombic modification[2]. The mass-average lamellar thickness of the samples used, determined by gel permeation chromatography following 3 days digestion in nitric acid at 60°C[3] was ~600 nm with a good proportion of lamellae being thick enough to be resolvable in the optical microscope. The specimen itself was crystallized in the form of a dumb-bell 3 mm long and 1 mm wide. From this 2.5 μm thick sections were microtomed at ~–40°C for deformation in a microstrain gauge mounted on a Zeiss Universal optical microscope. It has previously been reported[1] that Hifax 1900, and other very high molecular mass polyethylenes, are not prone to the brittleness usually associated with anabaric polyethylenes and can be extended to draw ratios of about 6 under tensile deformation at 80°C. In the present circumstances, however, it was desirable to avoid, at least initially, the provision of heating the microstrain gauge and its environment above ambient temperature so that room-temperature ductility was induced in the specimens by immersion in xylene for 24 h at 23°C.

Prior to immersion in the xylene, the section had a

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