JOURNAL OF MATERIALS SCIENCE 8 (1973) 1177–1184

The structure of high-density polyethylene with a single-crystal texture

R. J. YOUNG, P. B. BOWDEN
Department of Metallurgy and Materials Science, University of Cambridge, Cambridge, UK

The structure of specially prepared high-density polyethylene with a single-crystal texture has been examined by wide-angle and small-angle X-ray diffraction and by electron microscopy. The bulk of the crystallites in the sample are found to be oriented within 8° of a perfect single-crystal texture. The small-angle X-ray diffraction patterns suggest that lamellar crystals are present oriented approximately perpendicular to the chain direction. Replicas taken from fracture surfaces indicate that the structure fractures cleanly parallel to (100) which, taken together with other evidence, suggests that molecules fold by adjacent re-entry in (100) planes. Etching in fuming nitric acid reveals a lamellar crystal structure which is consistent with that deduced from small-angle X-ray diffraction. Replicas which were taken of etched surfaces after deformation showed crystals which were tilted with respect to the chain direction. This is consistent with the deformation having taken place by [001] chain slip within the lamellae [1].

1. Introduction

In order to study the physical properties of polyethylene it is desirable to use material with a well-defined structure. Single crystals grown from dilute solution [2] are useful for this purpose but suffer disadvantages from being small. An approach often used for the study of bulk polyethylene is to use polycrystalline material with a single-crystal texture [1, 3-6]. Methods of preparation of this material vary in detail but the general principles are the same. The first stage is normally some form of preliminary orientation which is then followed by annealing at an elevated temperature. After deformation but before annealing the structure is generally not very well defined. On annealing, the X-ray reflections become sharper but the diffraction spots generally start to split [3], indicating that even though the crystals grow larger and become more regular, there is some loss of orientation.

In the present work, oriented polyethylene samples have been annealed at 4 kbar in closed dies that permit no change of shape during the anneal. Under these conditions the diffraction spots do not split and the initial degree of orientation appears to be retained or even improved upon. By annealing polyethylene under hydrostatic pressure it is possible to produce large increases in density [7, 8] and to obtain crystallites with the "extended-chain" structure [9]. Southern and Porter [10] have obtained very highly oriented samples of extended-chain polyethylene under the special conditions of pressure and flow that are found in a capillary viscometer.

2. Preparation of the single-crystal-textured material

The apparatus used and details of preparation of this material have been described in an earlier paper [1]. Injection-moulded bars of Rigidex 9 (supplied in the form of granules by British Petrochemicals Ltd) were compressed in such a way that their length was allowed to increase as their thickness decreased while their width was kept constant. The nominal compressive strain applied was 0.84 ($\lambda = 0.16$). This compression-oriented material was annealed in a piston-and-cylinder arrangement that allowed a pressure to be applied and which did not permit the sample to change its shape during the anneal. A standard annealing pressure of 4 kbar and a standard annealing time of 15 min were employed throughout.

It was found that the density of the sample increased as the annealing temperature was raised and the results are shown in Fig. 1. The density was measured in a density gradient col-

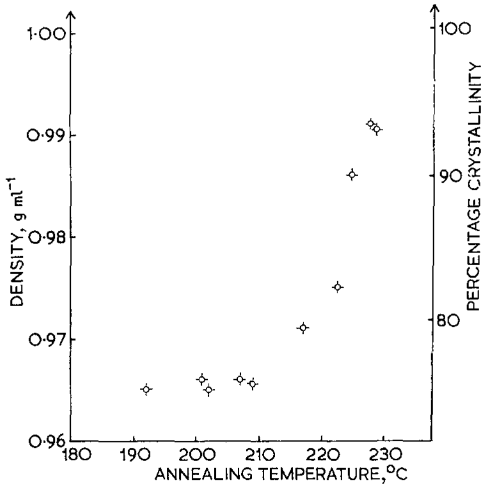

Figure 1 Specimen density as a function of annealing temperature. These results are for material annealed for 15 min at a pressure of 4 kbar. The degree of crystallinity has been calculated assuming that the crystal density is 1.00 g ml^{-1} and the density of the amorphous material is 0.86 g ml^{-1}. The specimen density increased as the melting point (230°C at 4 kbar) was approached and above this temperature the material melted and the density decreased.

umn made up with carbon tetrachloride and xylene at a temperature of 25 ± 1°C. The material whose mechanical properties were described in the earlier paper [1] had been annealed under pressure at about 200°C (density 0.966 g ml^{-1}) and was transparent and ductile. It is the structure of this material that is reported in detail in the present paper. Samples annealed at temperature above 210°C were brittle and would not undergo plastic deformation. Samples annealed at 229°C had an extended-chain structure and this material has also been examined.

At 230°C the material melted under pressure. This melting point agrees very closely with that obtained by Calvert and Uhlmann for polyethylene at the same pressure [7].

3. X-ray diffraction

3.1. Wide-angle diffraction patterns

Three wide-angle X-ray diffraction patterns obtained from the material annealed at 200°C are shown in Fig. 2. The reflections corresponding to the monoclinic form of polyethylene, present in the compression-oriented material [1], have disappeared and the twinning has relaxed. The set of photographs are similar to those found by Hay and Keller [3] for low-density polyethylene which had been drawn, rolled and lightly annealed to produce a single-crystal texture. The orientation of the crystal axes is related to directions in the samples as shown in Fig. 3. The *a*, *b* and *c* crystal axes are oriented approximately parallel to the *x*, *z* and *y* specimen directions. Hay and Keller [3] found that the single-crystal texture was obtained only by very light annealing and that annealing at higher temperatures caused the crystal axes to rotate away from the specimen axes. They also found that the material underwent large anisotropic contractions associated with the rotation of the crystals.

The pressure-annealing process used by us constrains the material at a fixed shape and only allows contraction to take place in the *x* direction. Since the original compression took place in this direction this may help to improve the texture. By not allowing changes to take place in other directions, rotation of the crystals appears to be inhibited. The single-crystal texture is still retained after strong anneals to densities of at least 0.98 g ml^{-1}.

3.2. Pole figures

Pole figures of the material annealed at 200°C were obtained for us by Dr W. Gray of the Department of Engineering Science at Oxford. Such a technique allows a quantitative assessment of the degree of orientation in the sample. If the 50% contour (the locus of angles at which the diffracted intensity is 50% of the peak diffracted intensity for the reflection being examined) is taken as a reasonable indication of the spread of orientation present, then the bulk of the crystallites are oriented with [001] within 5° of *y*, [100] within 7° of *x* and [010] within 8° of *z*. This texture may be compared with that of a similar high-density polyethylene sample prepared by Buckley *et al* [6]. For that material the distribution of [001] poles was split, the two maxima being ± 5° from *y*. The bulk of the crystallites (50% contour) were oriented with [001] within 8° of *y*, [100] within 18° of *x* and [010] within 18° of *z*.

3.3. Small-angle X-ray diffraction patterns

Fig. 4 shows a set of small-angle X-ray diffraction patterns obtained for the annealed material using a Franks camera*. The first order reflections correspond to a periodicity of 290 ± 10Å in the chain direction. The photograph taken along

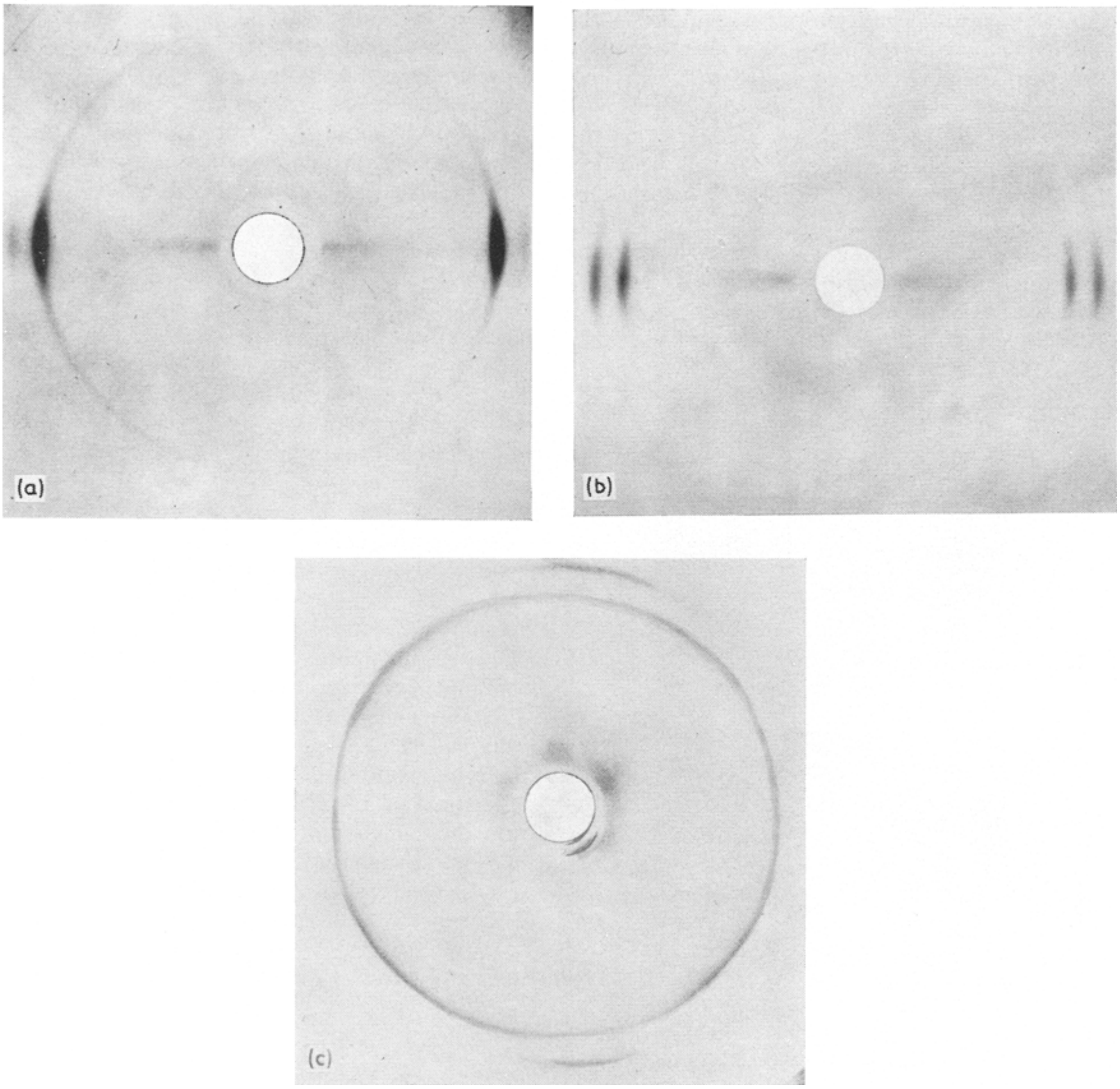

Figure 2 Wide-angle X-ray diffraction patterns for the pressure-annealed material. (a) Taken with the beam parallel to x with y vertical. The (110) reflections are strong and (200) is weak. (b) Taken along z with y vertical. Both the (110) and the (200) reflections are strong. (c) Taken along y with x vertical. (110) has four broad maxima whereas (200) has only two.

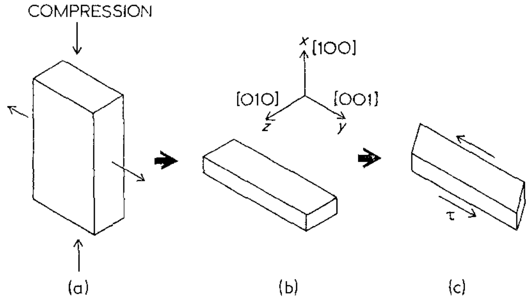

Figure 3 Notation used throughout to describe the relation between the crystal axes and the specimen axes (cf. [3]). (a) Isotropic sample. (b) Oriented and annealed specimen with a single crystal texture. (c) Specimen sheared as in Fig. 7b.

the x-direction (Fig. 4a) shows quite well-defined spots whereas in the photograph along z (Fig. 4b) the spots are elongated perpendicular to y.

For any diffracting object the width of the maxima in a diffraction pattern in any direction is inversely proportional to the dimension of the object in that direction [11]. In a diffraction pattern from small particles *all* reflections including the central spot will be broadened. This broadening will be greatest in the direction in which the crystals are smallest [11].

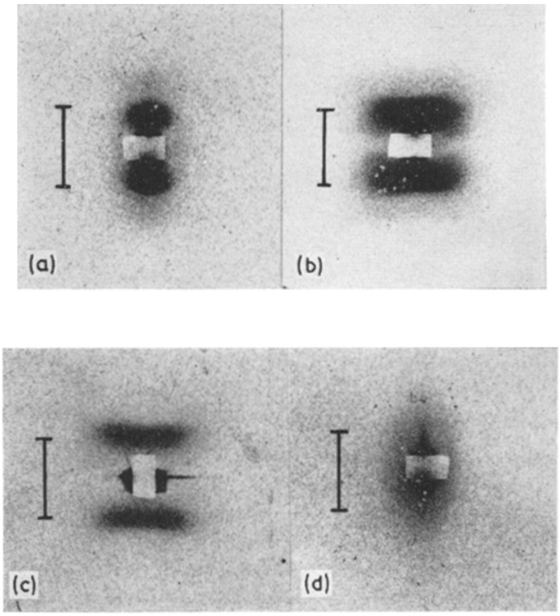

Figure 4 A set of small-angle X-ray diffraction patterns for the annealed material taken using a Franks Camera with Cu$K\alpha$ radiation. The scale bar represents 0.01 radians. (a) Taken with the beam along x with y vertical. The discrete reflections correspond to a periodicity of about 290Å in the chain direction. (b) Taken with the beam parallel to z with y vertical. The two streaked reflections correspond to a periodicity of about 290 Å in the chain direction. (c) As (b) but with the beam-stop rotated through 90°. (d) Taken with the beam parallel to y with x vertical. In this case there are no discrete reflections but there is some diffuse scatter around the main beam.

Non-zero-order reflections in small-angle patterns of oriented polymers will also be broadened if the crystal lamellae are tilted about the chain direction because of the angular spread of the diffracting entities. It is normally assumed that in small-angle patterns of polymers the lamellae are sufficiently large that they do not cause broadening of the maxima [4]. The broadening in the x-direction of the pattern in Fig. 4b implies that either the crystals are less than 100Å wide in the x-direction (i.e. they are not lamellae at all) or that there is a distribution of lamellar crystals present with their surface normals spread in the xy plane within ± 40° of y. However, if the crystals were narrow the central spot would be broadened to the same extent as the other reflections. Fig. 4c, obtained by rotating the specimen with respect to the beam stop, shows that it is not broadened at all. This pattern has been turned through 90° so that the chain-direction is still vertical. The pattern obtained with the beam along y (Fig. 4d) shows a small amount of diffuse scattered around the main beam but has no discrete maxima away from the central spot.

Fig. 5 shows the model of the lamellar structure which is proposed in order to explain the small-angle patterns in Fig. 4. It is interesting to compare this model with the structure proposed for single-crystal textured material produced by Hay and Keller [3]. With the beam along z, they obtained a four-point small-angle diffraction pattern and along x they observed no small-angle reflections at all. This would suggest that there were no lamellae present with the surface normals parallel to the chain direction of their material. The model they proposed was of two discrete sets of lamellae with surface normals at ± 30° to y in twin orientation to each other, in fact a structure similar to that in Fig. 5

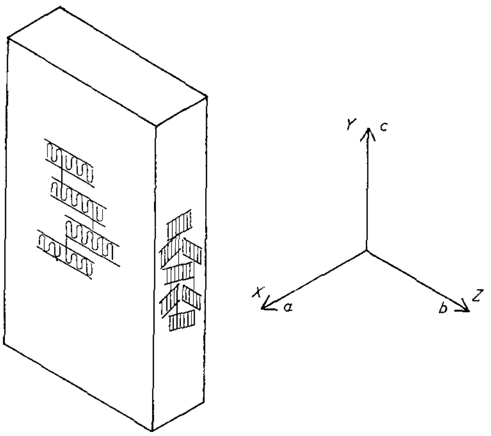

Figure 5 Model proposed for the lamellar structure of the annealed material based upon the small-angle patterns in Fig. 4.

with the lamellae in the intermediate positions absent.

4. Electron microscopy

4.1. Replicas of fracture surfaces

The material annealed at 200°C fractures very easily along the chain direction in the *yz* plane. However, it is more difficult to fracture in the *xy* plane and very difficult to cause fracture perpendicular to *y*, the orientation direction.

Fracture surfaces were prepared by cooling the specimens in liquid nitrogen and forcing a crack through with a razor blade. Replicas were taken by pressing cellulose acetate soaked in acetone onto the fracture surfaces and allowing it to dry. The replicas were then peeled off and shadowed by evaporating Gold-Palladium alloy onto the surface from an oblique angle. The direction of shadowing was always parallel to the chain direction. Carbon was then evaporated on and the cellulose acetate dissolved away in acetone. Fig. 6a is an electron micrograph of a replica of a fracture surface in the *yz* plane. This surface is flat and smooth with very few fibrils coming out of it. Fig. 6b is a replica of a fracture surface in the *xy* plane. It is very rough and there is much torn material sticking out of the surface. Fractography has often been used to determine the planes on which the molecules fold in single crystals [2, 13]. It is found that cracks parallel to the edges of sectors in polyethylene single crystals do not pull out fibrils, which implies that the fold-planes are parallel to the sector edges. A possible explanation of the difference in appearance of the fracture surfaces in Fig. 6 is that the fold plane in the crystals is (1 0 0) and so fracture in the *xy* plane cuts across molecular folds whereas fracture in the orthogonal *yz* plane does not. There is other evidence to suggest that molecules fold on (1 0 0) planes in bulk polyethylene. Dreyfuss and Keller [14] have noted that single crystals of polyethylene *can* be found with (1 0 0) sectors. In addition they noted that by crystallization from concentrated solution lath-shaped streamer-like crystals are formed in which the sides are parallel to (1 0 0) planes. Bank and Krimm [12] have evidence for (1 0 0) folding from infra-red work. Their results also confirm that folding is mainly on (1 1 0) planes in single crystals. Since it is possible to have a (1 0 0) fold-plane in single crystals, (1 0 0) folding bulk polyethylene is not unreasonable and a molecule folded on (1 0 0) would lie along the growth direction of a spherulite [2]. Regular folding also

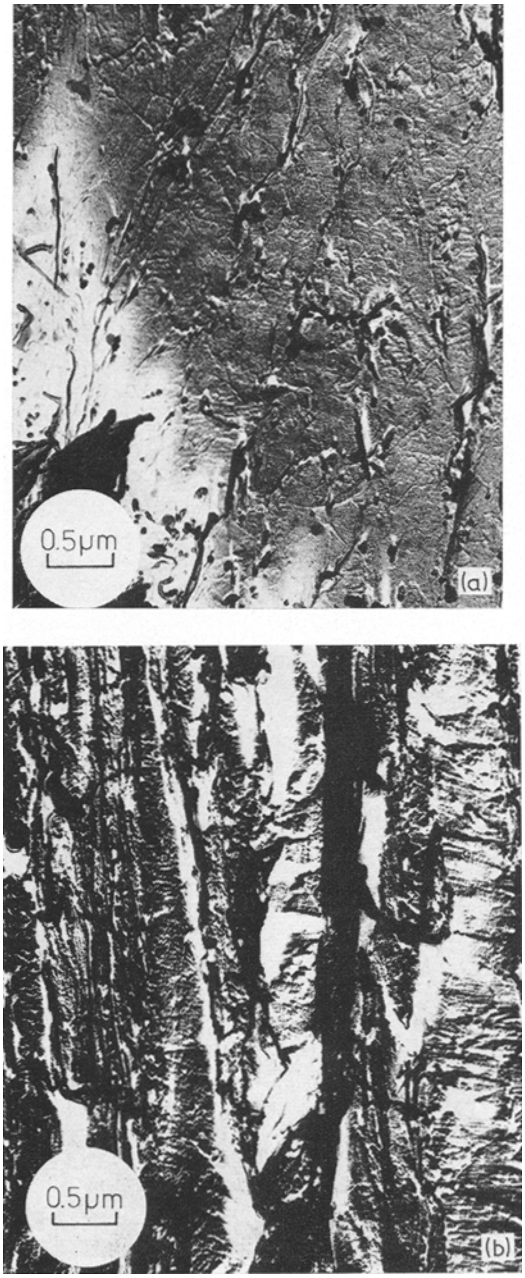

Figure 6 (a) Electron micrograph of a replica of the *yz* plane of the single-crystal textured material. The *y* direction is vertical. This surface is smooth which implies that this could be the plane in which the molecules fold. (b) The *xy* plane of the single-crystal-textured material with the *y* direction vertical. On this replica it can be seen that this section is very rough and many fibrils have been pulled out. This implies that molecular links have been severed and supports the idea of (1 0 0) folding.

implies that the molecules must leave and re-enter the crystals in directly adjacent positions. The molecules in the crystal lamellae in Fig. 5 are drawn such that they fold in the (1 0 0) planes by adjacent re-entry.

4.2. Etched fracture surfaces

It has been shown by Peterlin and Sakaoku [15] for polyethylene that fuming nitric acid at 80° C attacks the amorphous material between the crystals in preference to the crystalline areas revealing the lamellar crystal structure. Fracture surfaces were etched in fuming nitric acid for 6 h at about 80°C. After etching, the material split very readily in the *yz* plane into layers and so it was only possible to make replicas of the *yz* surface. This is further evidence for the lack of molecular links in the *a* direction between the (100) planes.

It proved to be impossible to make replicas of the etched surfaces using cellulose acetate since the etched material was very fragile and could not be separated from the replicas. Instead, replicas were made by depositing the Gold-Palladium and the carbon directly onto the etched suface and subsequently dissolving the polyethylene in "Decalin" (decahydronaphthalene) at 150° C. The replica was found to float off the surface of the polyethylene as soon as it was put into the liquid.

Hill and Keller [16] have observed the lamellar crystal structure directly in thin films of oriented polyethylene. They found that the lamellae were of constant thickness but were rather wavy causing the interlamellar spacings to vary. The periodicity deduced from the small-angle X-ray diffraction maxima is expected to and was found to depend upon the lamellar separation and not the lamellar thickness. The irregularity in spacing is the reason that the diffraction spots are spread and only one or two orders are ever observed.

Fig. 7a is an electron micrograph of a replica of the etched material. Since the amorphous material is preferentially etched, the shadowing material will pile up on the projecting crystals. It can be seen from Fig. 7a that there is a periodicity of 300 ± 50Å in the chain direction.

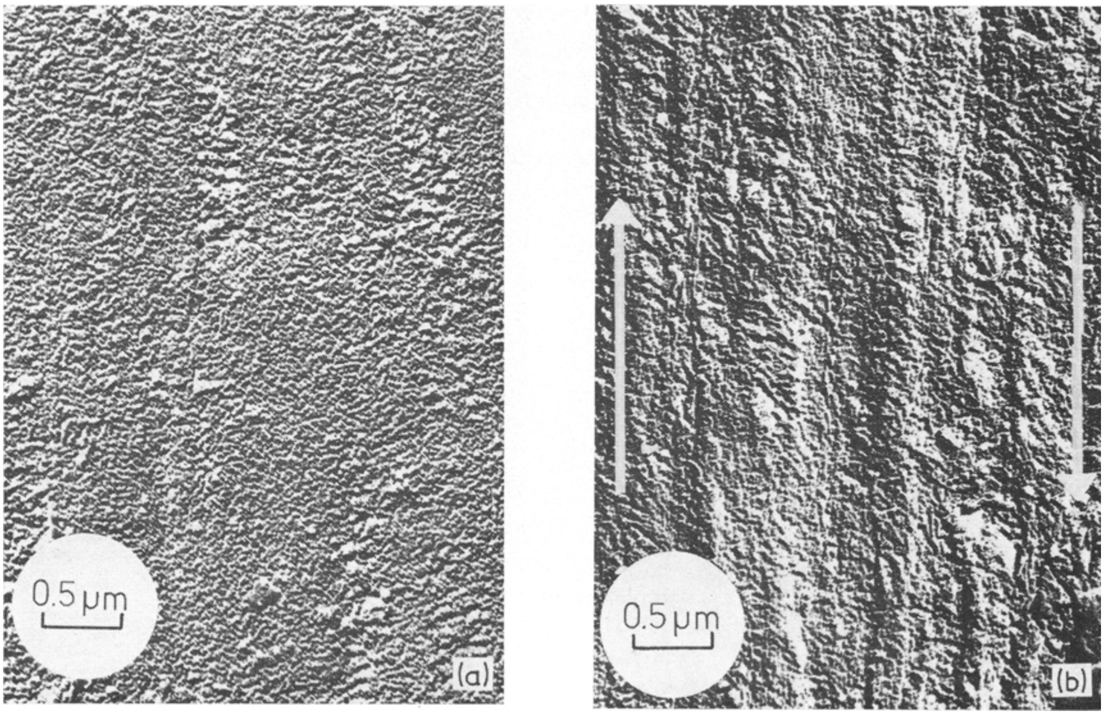

Figure 7 (a) Direct observation of the lamella crystal structure. The *y*-direction is vertical and the surface has been shadowed parallel to this direction. This section is similar to that in Fig. 6a but it has been etched in fuming nitric acid to reveal the lamella structure. (b) Replica of the same samples as in Fig. 7a but from an area that has been sheared plastically to a shear strain of 0.3 as indicated by the arrows.

This is consistent with that deduced from small-angle X-ray diffraction patterns in Fig. 4. Assuming that the shadowing reveals the lamellar crystal structure, the lamellae appear to be rather wavy but oriented approximately perpendicular to the chain direction.

4.3. The lamellar structure after deformation

Fig. 7b is a replica of an etched surface of a specimen that was deformed by a simple shear parallel to the chain direction as described in an earlier paper [1]. The deformation geometry was such that the maximum shear deformation could be observed as a shear in the perpendicular (1 0 0) plane. Wide- and small-angle X-ray diffraction showed that deformation had taken place by [0 0 1] slip within the lamella crystals and that after deformation the lamellae were tilted with respect to the chain direction [1]. From Fig. 7b it can be seen that after deformation the lamellae are no longer approximately perpendicular to the chain direction but are all tilted in the same direction, as expected from the small-angle X-ray data.

5. "Extended-chain" polyethylene

Samples annealed in the region of the melting-point with densities of above 0.99 g ml^{-1} were found to be opaque and very brittle. They crumbled into small fragments and there was no preferred cleavage plane. They would even fracture quite easily across the direction of molecular alignment. Fig. 8 shows an electron micrograph of a replica of a fracture surface of this material and a wide-angle X-ray diffraction pattern of the same material in the same orientation. From the diffraction pattern it can be seen that the material still has a degree of molecular orientation but the reflections are more spread than in the lightly annealed material. It can be seen from the electron micrograph that the material appears to be made up of large crystals up to 5000 Å thick in the chain direction and even larger in the transverse direction. These large crystals are typical of an "extended-chain" structure. Andrews and Ward [17] have quoted values of the molecular weight of Rigidex 9. They find M_n to be equal to 18000 and M_w to be 155000. This means that molecules both longer and shorter than 5000 Å will be present. In this structure, according to Rees and Bassett [8] molecules below 5000 Å in length are in a fully extended configuration whereas the longer ones are still folded. Since the extended-chain crystals

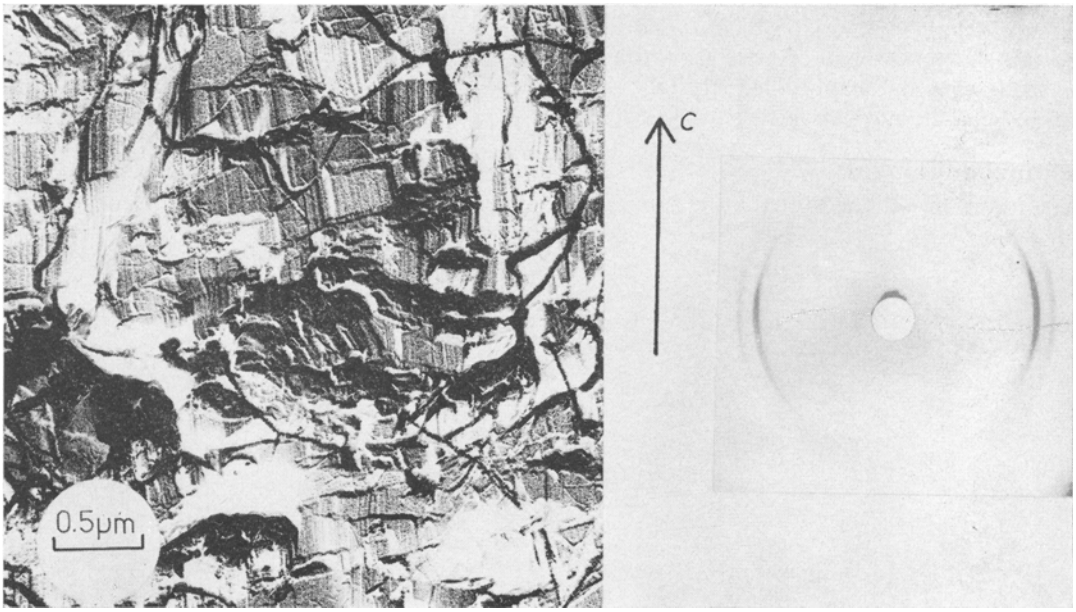

Figure 8 "Extended-chain" material. Compression-oriented material annealed at a temperature very close to its melting-point. The electron micrograph shows the presence of crystals up to 5000 Å thick in the chain-direction. The wide-angle X-ray diffraction pattern indicates that these "extended-chain" crystals retain some of the molecular orientation.

are fairly well oriented in the chain direction this implies that they have been formed by the thickening of existing chain-folded crystals rather than by separate nucleation. This is consistent with ideas put forward by Rees and Bassett deduced from their own observations on pressure-annealed material [8, 9].

6. Conclusions

It has been shown that constrained pressure-annealing of biaxially oriented polyethylene produces material with an excellent single-crystal texture and a well-defined lamellar crystal structure. Molecular folding on (100) has been put forward as a possible explanation of the appearance of fracture surfaces.

By etching fracture surfaces in fuming nitric acid it has been possible to reveal the lamellar crystal structure. The structure seen in the electron microscope is found to be consistent with that deduced from small-angle X-ray scattering. After deformation by simple shear parallel to the chain-direction it is found that the lamellar crystals which are originally perpendicular to the chain-direction become tilted with respect to it. This suggests that the deformation has taken place by chain slip. By annealing oriented polyethylene under pressure close to the melting-point it is possible to prepare oriented "extended-chain" material which supports the idea that extended-chain crystals are formed by the thickening of chain-folded crystals rather than by separate nucleation.

Acknowledgements

The authors would like to thank the Ministry of Defence (Procurement Executive) for support and the SRC for equipment grants.

References

1. R. J. YOUNG, P. B. BOWDEN, J. M. RITCHIE, and J. G. RIDER, *J. Mater. Sci.* **8** (1973) 23.
2. A. KELLER, *Rep. Prog. Physics* **31** (1968) 623.
3. (a) I. L. HAY and A. KELLER, *J. Mater. Sci.* **1** (1966) 41. (b) *Idem, ibid* **2** (1967) 538.
4. A. COWKING, J. G. RIDER, I. L. HAY, and A. KELLER, *ibid* **3** (1968) 646.
5. T. SETO and Y. TAJIMA, *Jap. J. Appl. Phys.* **5** (1966) 354.
6. C. P. BUCKLEY, R. W. GRAY, and N. G. MCCRUM, *J. Polymer Sci.* **B8** (1970) 341.
7. P. D. CALVERT and D. R. UHLMANN, *ibid* **B8** (1970) 165.
8. D. V. REES and D. C. BASSETT, *ibid* **A-2, 9** (1971) 385.
9. *Idem, J. Mater. Sci.* **6** (1971) 1021.
10. J. H. SOUTHERN and R. S. PORTER, *J. Appl. Polymer Sci.* **14** (1970) 2305.
11. (a) B. D. CULLITY, "Elements of X-ray Diffraction" (Addison-Wesley, Reading, Mass., 1956). (b) A. GUINIER, "X-ray Diffraction in Crystals, Imperfect Crystals an Amorphous Solids" (Freeman, London, 1963).
12. M. I. BANK and S. KRIMM, *J. Polymer Sci. A-2*, **7** (1969) 1785.
13. P. H. LINDENMEYER, *ibid* **C1** (1963) 5.
14. P. DREYFUSS and A. KELLER, *J. Macromol. Sci.* **B4** (1970) 811.
15. A. PETERLIN and K. SAKAOKU, "Clean Surfaces" (Ed. G. Goldfinger) (Marcel Decker, New York, 1970).
16. M. J. HILL and A. KELLER, *J. Macromol. Sci.* **B5** (1971) 591.
17. J. M. ANDREWS and I. M. WARD, *J. Mater. Sci.* **5** (1970) 411.

Received 11 January and accepted 23 March 1973.