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The lamellar structure of oriented high-density polyethylene

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The lamellar structure of a high-density polyethylene oriented to give a single-crystal type of texture has been studied by electron microscopy and X-ray diffraction. Structures shown by the Kanig technique [6, 7] and a replication technique of electron microscopy are consistent with one another and with the small-angle X-ray diffraction patterns of this type of material, but the electron microscope observations show local regions of highly misoriented lamellae which are not detectable by X-ray diffraction. In regions where the lamellar orientation is that expected from the X-ray patterns the lamellae are wide and irregularly wavy.

1. Introduction

High-density polyethylene can be oriented so as to produce a single-crystal type of crystallographic tecture and a single lamellar preferred orientation. This can be achieved either by biaxial hot-drawing [1, 2] or by a plane-strain compression process [3, 4]. In each case a sheet of material is produced with the *c*-axis in the plane of the sheet and parallel to the extension direction, the *b*-axis in the transverse direction in the sheet and the *a*-axis normal to the plane of the sheet. The *a*- and *b*-axes are much less sharply oriented than the *c*-axis. Small-angle X-ray patterns indicate a single preferred orientation for the crystalline lamellae, the width of the scattering maxima being typically greater when the X-ray bema is in the *b* direction than when it is in the *a* direction. This material has been used in studies of deformation processes and their orientation dependence [1, 3, 5].

Recently, a staining technique for revealing the lamellar structure of polyethylene in sections cut for transmission electron microscopy has been described [6, 7]. This technique has been successfully applied to reveal the lamellar structure of polyethylene oriented to give a four-point small-angle diffraction pattern [8]. This paper reports the results of an investigation of the details of the lamellar structure in single-crystal texture high-density polyethylene, using the Kanig technique.

2. Experimental details

Single crystal texture material was prepared by a method similar to that of Young *et al.* [3]. Samples cut from a compression moulded sheet of Rigidex 2 were compressed in plane strain at 120° C to a compression ratio of 6.7. After cooling under load the samples were annealed in an oil bath at 126° C for 1 h, lightly clamped to prevent warping.

Electron microscope specimens were cut with a cryo-ultramicrotome from oriented samples which had been treated with chlorosulphonic acid according to the Kanig technique [6, 7]. The microscope specimens were then stained in 1% uranyl acetate solution. As a check against the Kanig technique, a replication method was also used. In this, a sample was etched for 2 h in nitric acid at 60° C following which a gold–palladium shadowed replica was taken from the surface.

Pole figures and small-angle X-ray diffraction patterns were obtained from the oriented material by the usual methods.

3. Results

The pole figures showed the texture to be of the single crystal type, similar to that reported by Gray and Young [4] but with about twice the spread in orientation of the (2 0 0) and (0 2 0) poles in the *ab* plane, probably as a result of the

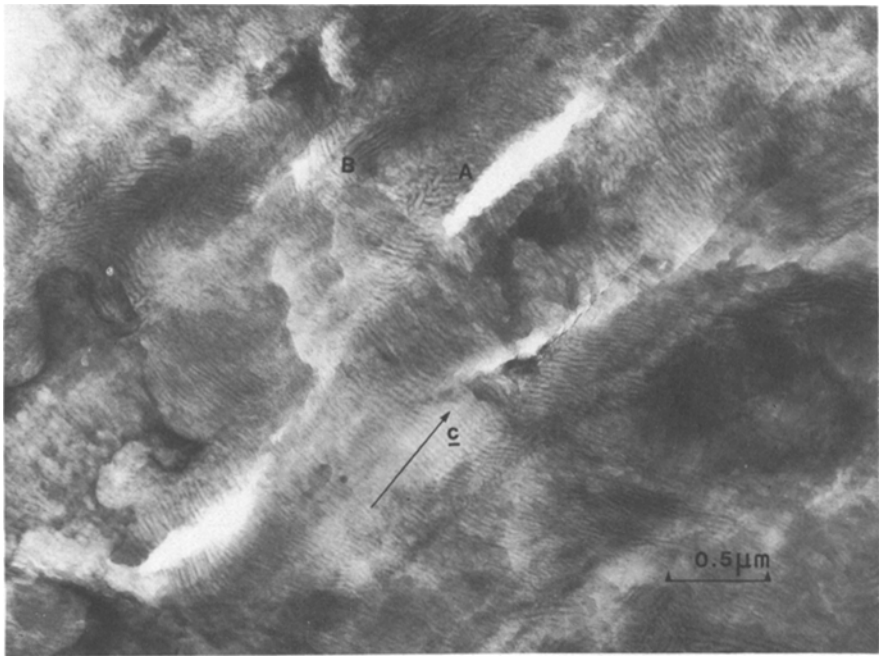

Figure 1 Lamellar texture in a stained microtome section of single-crystal texture polyethylene. In this and all subsequent figures the plane of the electron microscope specimen is parallel to the plane of the compressed sheet, i.e. the preferred (1 0 0) plane orientation.

lower compression ratio used in the present work. The material contained no monoclinic phase. Small-angle X-ray patterns showed single diffuse scattering maxima, of greater width when the beam lay along the *b* direction than when it lay along the *a* direction.

Fig. 1 shows the lamellar texture revealed by the Kanig technique. The dark regions are believed to be stained non-crystalline material, largely existing between crystalline lamellae. The general appearance is of fairly wide wavy lamellae but, in addition to the small variations in orientation in a typical area, there are regions where the lamellar structure is grossly different. These are of two main types. As at A in Fig. 1, there are regions of relatively narrow, highly disoriented lamellae forming interlocking blocks somewhat reminiscent of the "parquet floor" structure observed by Grubb *et al.* in polyethylene having a four-point small-angle X-ray pattern [8]. Fig. 2 shows in more detail a region of this type. In the other type of region showing a discrepancy from the average structure, there are wider but even more highly misoriented lamellae, often lying at an angle of approximately 90° to the general orientation. An example is seen at B in Fig. 1.

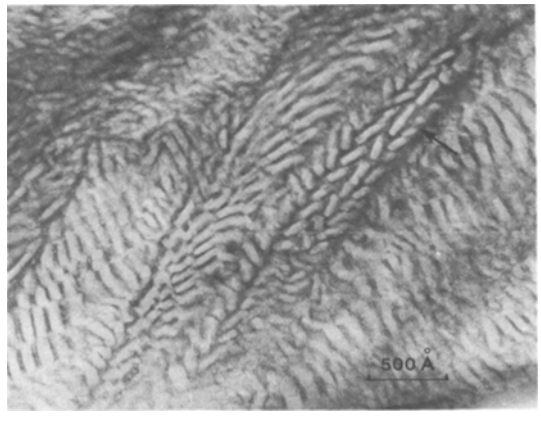

Figure 2 Misoriented lamellae in single-crystal texture polyethylene, showing "parquet-floor" structure (arrowed).

The detailed structure in a block of misoriented lamellae is shown in Fig. 3. The indication of a band of non-crystalline material crossing a straight lamellae as arrowed in Fig. 3 is uncommon.

The structure shown by the replication technique was consistent with that shown by the Kanig technique. Fig. 4 shows the decoration which is presumed to follow steps on the replica corresponding to etched interlamellar regions.

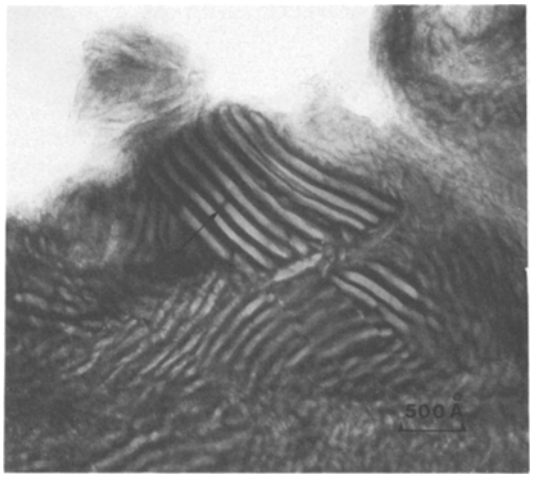

Figure 3 Detailed structure of a block of misoriented lamellae.

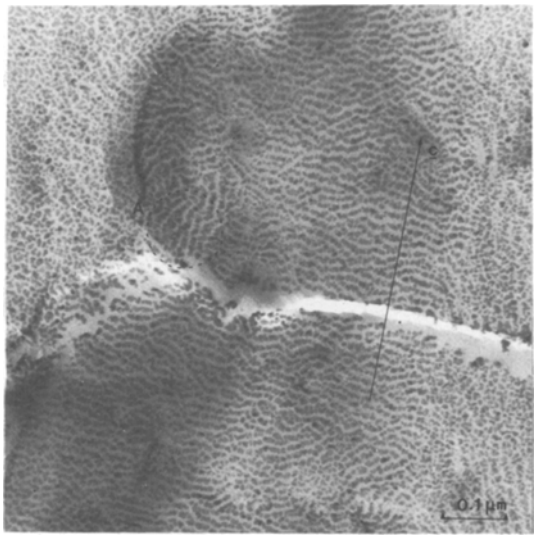

Figure 4 Etched surface of a single-crystal texture polyethylene, gold/palladium shadowed replica.

The indication is again of quite wide wavy lamellae, with a block of misoriented lamellae shown at A. This gives some confidence that the waviness of the lamellae and the blocks of highly misoriented lamellae shown by the Kanig technique are not artefacts of deformation introduced by the cutting of the microscope specimen.

Optical diffraction patterns taken from regions of micrographs obtained by the Kanig technique showing the predominant orientation of lamellae were in good agreement with small-angle X-ray patterns of bulk material. An example is shown in Fig. 5. When only single, diffuse maxima are observed in the diffraction pattern there is some doubt as to how accurate is the average lamellar spacing d obtained by the application of "Braggs law"

$$\lambda = 2d\theta \qquad (1)$$

where 2θ is the angle between the direct beam and the position of the peak of the diffuse maximum. It is therefore of some interest to compare

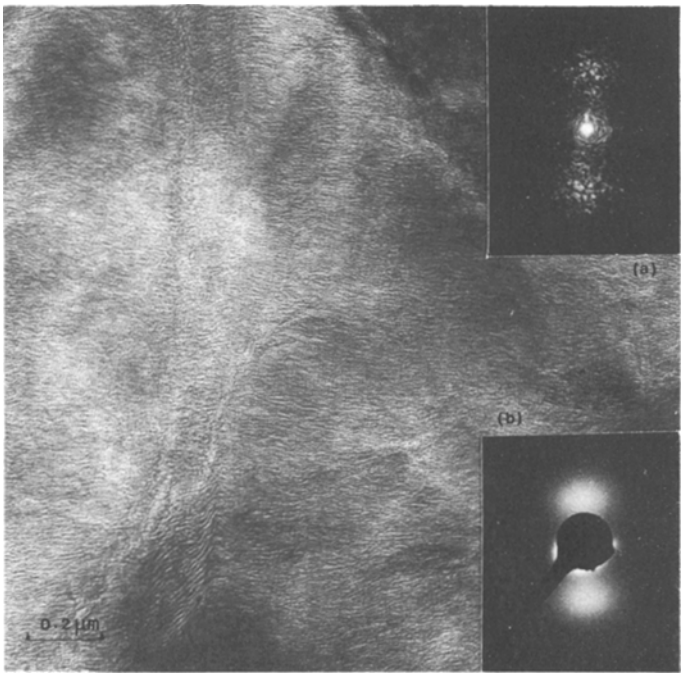

Figure 5 The predominant lamellar structure in stained single-crystal texture polyethylene. Inset (a) optical diffraction pattern, (b) small-angle X-ray diffraction pattern from bulk sample.

the spacing of the lamellae on the micrograph measured directly with that deduced by applying Equation 1 to the optical diffraction pattern. This was done in two regions and the two measurements agreed to within 2% and 4% respectively, a rather better agreement than might have been expected from the estimated error in the measurement of 2θ, of about 5%. This suggests that any systematic error inherent in Equation 1 is unlikely to exceed about 5%.

It is also of interest to compare the lamellar spacing measured from electron micrographs with the spacing obtained from small-angle X-ray diffraction patterns from the bulk material. The mean spacing from electron micrographs was 300 Å with an estimated error of ±10% arising from magnification errors. The mean spacing from small-angle X-ray patterns was 370 ± 60 Å; however, any individual small-angle pattern could be measured to an accuracy of ±15 Å. It would appear, therefore, that small-angle X-ray diffraction can give a more accurate value for the mean lamellar spacing than can electron microscopy.

4. Discussion

Electron microscopy reveals a feature of the structure of the material studied here which is not revealed by X-ray studies, namely the existence of regions of highly misoriented lamellae. In some cases these are blocky lamellae reminiscent of those observed in four-point pattern material [8]. Regions where extended lamellae are oriented at approximately 90° to the prevailing direction may be relics of the original spherulitic structure comprising regions of spherulites where the lamellae are oriented such that no interlamellar or intermolecular shear stress is acting. These regions must be few enough not to affect the X-ray patterns, but they appear to be surprisingly prominent in electron micrographs. This may be because they often appear in better contrast than the lamellae in the prevailing orientation. These latter can best be described as irregularly wavy lamellae. Terminations and branchings occur, nevertheless the width of a lamella is typically large in comparison with its thickness. The waviness of one lamella in the stack appears not to be identical to that of its neighbours, so that there are apparent thickness variations in the crystalline or amorphous regions. There is no evidence of a fibrillar structure but this does not preclude the possibility of fibrillar crystals of small lateral dimensions connecting the lamellae in a stack.

While small-angle X-ray studies give the more reliable indication of the dominant lamellar structure and the more accurate measurement of the average lamellar spacing, the electron microscope gives details of the lamellar structure, and in particular of the existence of highly defective regions in the lamellar pattern, which could not be obtained by X-rays.

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