Letters

Direct observation of lamellar morphology in polyethylene

Semi-crystalline polymers, such as polyethylene, consist of crystalline sheets or lamellae, separated by disordered material of some kind. A complete description of how these lamellae are arranged within the solid would be very valuable for the proper interpretation of polymer properties, and this description is not normally available. The lamellae are of the order of 10 nm thick, so the methods used have generally been low-angle X-ray diffraction and the electron microscopy of replicas. The low-angle X-ray diffraction patterns usually contain only two or four spots so the information available is limited, and replicas can only be used on surfaces, free or fracture. Disintegration and etching methods exist but they involve drastic interference with the structure. Direct observation of the essentially unaltered structure by transmission electron microscopy would obviously be a considerable improvement. It is difficult to get sufficiently thin specimens from bulk polymers, and when this is done by low temperature ultramicrotomy, it is found that the sections are very unstable in the electron beam. Diffraction contrast disappears rapidly, and mass thickness contrast may develop in the course of radiation damage [1]. Even when these effects can be properly interpreted [2] the lamellar structure cannot be determined in detail. A technique which overcomes these problems was recently discovered by Kanig [3, 4], independently of previous similar work by Korosy and Zeigerson [5]. Polyethylene specimens are treated with chlorosulphonic acid, which diffuses into the disordered material but not into the crystalline lamellae. The acid reacts with polyethylene, substituting reactive groups for hydrogen and also forming cross-links between the chains. The reactive polar groups attract heavy metal ions, so that on treatment with a suitable salt solution, the affected regions become electron

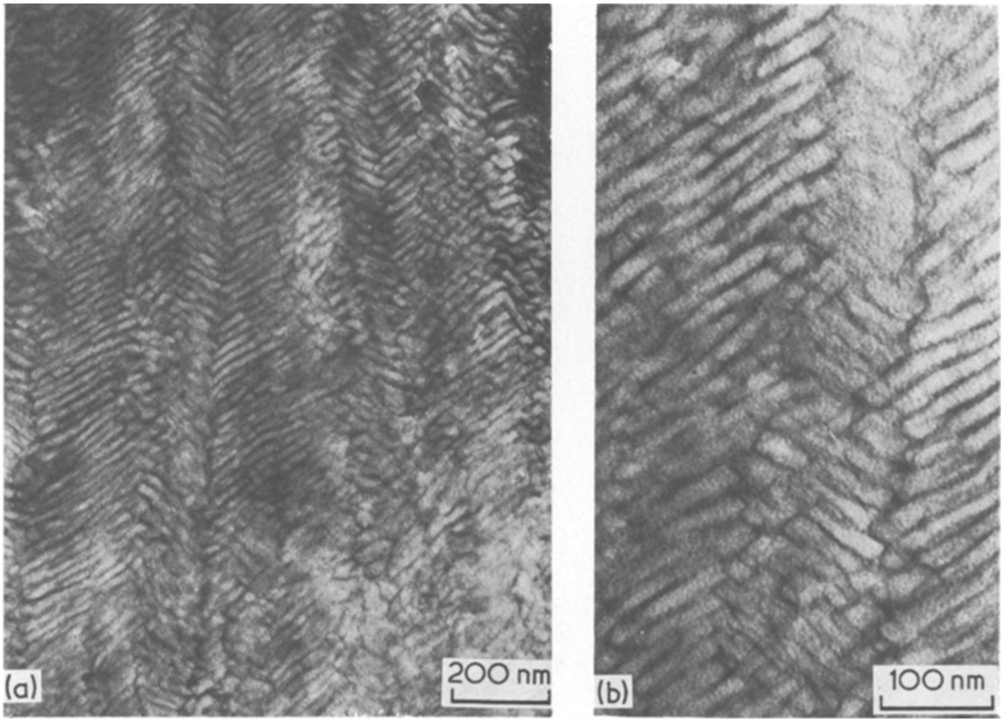

Figure 1 An ultramicrotomed section of a specimen of oriented polyethylene. The lamellar texture is made visible in the electron microscope by staining the disordered interlamellar regions. (a) A general view showing that the lamellae have two preferred orientations, and are arranged into long narrow stacks of parallel lamellae. (b) A higher magnification view showing in more detail how the lamellae pack together in herringbone pattern.

dense. The cross-links make the material rigid, so that it is less affected by sectioning, and much less susceptible to beam damage. Thus the acid treatment allows staining and also stabilizes the structure, as a fixative does in biological preparations.

We have chosen to apply this technique to a sample of high density polyethylene prepared by drawing, rolling and annealing. This treatment produces a "double texture" specimen, where the crystallographic axes have unique directions, but there are two orientations of lamellar normals. This type of specimen has been studied by X-ray diffraction in great detail over a period of time [6–8] and it is known that one particular direction of viewing, along **b**, gives a four point pattern in low-angle X-ray diffraction, and is the most informative. This specimen was treated with chlorosulphonic acid for 6 h at 60° C, then with 0.7% aqueous uranyl acetate for 3 h, then sectioned with a diamond knife at liquid nitrogen temperatures so that the section normal is parallal to **b**. The results are a startlingly good confirmation of the texture predicted from X-ray diffraction (Figs. 1 and 2).

Firstly, the material does indeed consist of lamellae – a result generally accepted but not uniquely deducible from the X-ray pattern, and secondly the lamellae are in the predicted range of thickness and orientation. Thirdly, the lamellae of each orientation are arranged in stacks parallel to **c** (the molecular chain axis and original draw direction) as predicted from the details of the X-ray pattern.

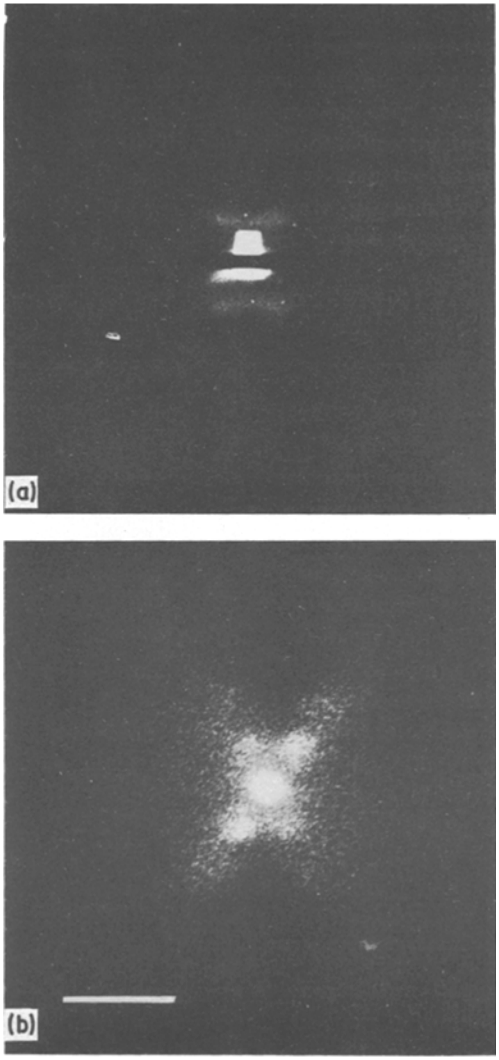

Figure 3 (a) Low-angle X-ray diffraction pattern from the specimen shown in Fig. 1. (b) Optical diffraction pattern of Fig. 1. The bar corresponds to a spacing of 12.5 nm in both patterns.

Fig. 3a is the low-angle X-ray, diffraction pattern obtained from the specimen shown in Fig. 1, viewed in the same direction, while Fig. 3b is an optical diffraction pattern taken directly from Fig. 1. Clearly they are very similar and clearly the micrographs themselves Figs. 1a and b contain much more information than the diffraction patterns. For example, one can at once see the width of the lamellae and the number of them in a stack. The thickness of the stained regions indicates the amount of disordered material present, between lamellae, between stacks (often surprisingly little) or in localized disordered regions (Fig. 1a upper right hand side).

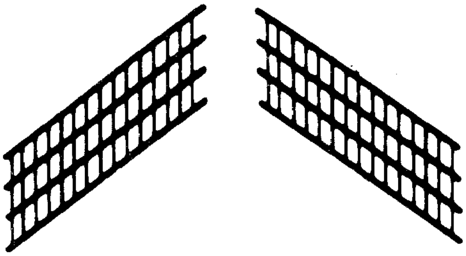

Figure 2 A schematic picture of the texture, as predicted for this type of specimen by Hay and Keller [7] from X-ray results. The thick lines denote lamellar surfaces, the thin lines denote molecular chains.

It is also clear from the micrographs in Fig. 1 that the lateral boundaries between stacks are zigzag lines. It follows that these boundaries are not parallel to the molecular chain direction, which is parallel to the long axis of the stacks. Either the chain direction changes within the lamellae, or the straight chain traverse length must decrease towards the boundary. A change of direction seems unlikely as no discontinuity is seen within the lamellae, so we believe that the crystals taper, producing a new kind of defect structure.

This extremely clear picture of the lamellar structure in a bulk oriented polyethylene is very encouraging and raises hopes that the interior of a bulk polymer will at last become accessible to direct electron microscope examination. The method is now being applied to similar samples as part of a systematic examination. It is hoped that subsequent publications will describe both methods and results in more detail.

Acknowledgements

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References

1. J. DLUGOSZ and A. KELLER, *J. Appl. Phys.* **39** (1968) 5776.
2. D. T. GRUBB and A. KELLER, *J. Mater. Sci.* **7** (1972) 822.
3. G. KANIG, *Kolloid Z. u. Z. Polymere* **251** (1973) 782.
4. *Idem, Kunststoffe* **64** (1974) 470.
5. F. DE KÖRÖSY and E. ZEIGERSON, *J. Appl. Poly. Sci.* **11** (1967) 909.
6. I. L. HAY and A. KELLER, *J. Mater. Sci.* **1** (1966) 41.
7. *Idem, ibid* **2** (1967) 538.
8. A. KELLER and D. P. POPE, *ibid* **6** (1971) 453.

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Characteristics of electron-transparent regions in unthinned, rapidly quenched foils

The extremely rapid quenching of molten material, often referred to as splat-cooling, was introduced by Duwez and co-workers in 1960 [1]. Basically, the technique involves the solidification of a small amount of melt on a massive substrate. An essential feature of this method is that the molten material is very thin, thus allowing cooling rates of $10^{6\circ}$ C sec^{-1} or greater to be attained.

One of the most common techniques used is the gun technique [1, 2] in which the melt is blast-atomized onto a substrate. It was noted by Willens [3] that regions of foils produced by this technique are suitable for electron microscopy without further thinning. However, the characteristic features of these thin areas have never been investigated. It has been assumed that during the quenching process, certain droplets spread into a layer thin enough for direct electron microscopy upon striking the substrate. A necessary condition, of course, is that further droplets do not solidify on top of these films.

The morphology of electron-transparent areas in splat-cooled foils was studied and the results are presented in this short communication. A Cu–40 at.% Zr alloy was splat-cooled using the gun technique. A JEM-200 electron microscope equipped with a scanning electron microscopy attachment was used. It was possible, with this attachment, to observe the same area in the scanning transmission electron microscopy mode (STEM) and in the normal scanning electron microscopy mode (SEM). Two separate areas were observed in detail, and two different mechanisms for thin area formation were found. Fig. 1 shows an SEM of the top surface of a splatted foil in the region surrounding a transparent area. The expected overlapping of droplets is easily recognized. Fig. 2 is an STEM of the same area. The apparent process by which this electron-transparent region was formed is as follows. While a flattened molten droplet was solidifying on the substrate, another, smaller droplet (A in Fig. 1), already partially solidified, impinged upon the molten area and then rolled to the side (the substrate was not horizontal, but inclined). Owing to this impact, a considerably thinner area was left behind. The material solidified before the thinner "valley" could be filled. The fact that the small droplet remained spheroidal (droplet A) is due to the solidification of the droplet while still in flight, as pointed out by Jones [4].

The second mechanism by which an electron-transparent area in the splatted foil was produced is illustrated in Fig. 3 and 4, micrographs taken in the SEM and STEM modes, respectively. Apparently, a molten droplet was spreading across