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A study of twinning in polyethylene

J. E. PREEDY
British Petroleum Co Ltd, Research Centre, Sunbury-on-Thames, Middlesex, UK

E. J. WHEELER
Department of Chemical Physics, University of Surrey, Guildford, Surrey, UK

Both $\{1\,1\,0\}$ and $\{3\,1\,0\}$ deformation twinning modes have been predicted for polyethylene. The existence of the former twinning mode has been confirmed in this work by non-photographic X-ray methods. When comparing and explaining bulk and single crystal twinning behaviour in terms of the influence of fold surface geometry, certain discrepancies arise. These may be resolved by noting that $\{1\,1\,0\}$ twins occur at relatively low stresses and that $\{3\,1\,0\}$ twins are formed under conditions of high strain during which the crystalline morphology is changed from lamellar to microfibrillar.

1. Introduction

Deformation twinning has been shown to be one of the important modes of deformation in polyethylene single crystals and in the bulk material (see review by Bowden and Young [1]). The presence of deformation twinning was first reported in samples of rolled, low density bulk polyethylene by Frank *et al.* [2]. These authors predicted twinning on both the $(3\,1\,0)$, $(3\,\bar{1}\,0)$ and the $(1\,\bar{1}\,0)$, $(1\,1\,0)$ pairs of planes of the orthorhombic unit cell, these being conjugate modes. The stresses needed to operate either of these modes are similar, being either compressive stress in a range of direction near the $[1\,0\,0]$ direction, or tensile stresses in a range of directions near the $[0\,1\,0]$ direction. In their work, the authors used photographic film to record the diffraction pattern and this particular experimental method does not give sufficient resolution to unequivocably assign the twinning to a particular mode. However, their work on low density polyethylene did show that in a heavily rolled sample, the evidence pointed to $\{3\,1\,0\}$ twinning, whereas on a rolled, annealed and drawn sample, it pointed to $\{1\,1\,0\}$ twinning. Recent work by Lewis *et al.*, using a Schulz X-ray Texture Goniometer linked with the facility of computer drawn pole figures which give a resolving power of one or two degrees, has shown that $\{3\,1\,0\}$ twinning occurs in "necked" high density polyethylene [3] and has confirmed $\{3\,1\,0\}$ twinning in rolled low density polyethylene [4].

Investigations of twinning in polycrystalline specimens with a well defined texture have been carried out by Seto *et al.* [5] and by Young and Bowden [6]. In the work by Young and Bowden, twinning was observed in two cases; after the removal of the compressive load which had been applied parallel to the *a*-axis and after compression, applied parallel to the *b*-axis. In the first case the authors state that "the diffraction pattern (from a photograph) was not sufficiently well defined to be able to identify the exact mode of orthorhombic twinning". In the second case the new orthorhombic lattice was found to be equivalent to a rotation of 73° from the parent cell. This is larger than that required for $\{3\,1\,0\}$ twinning (55°) or for $\{1\,1\,0\}$ twinning (67°). The authors again state that "this implies that if the unit cell had twinned there was an extra rotation of the cell by means of $(h\,k\,0)_0\ [k\,\bar{h}\,0]_0$ slip and makes it impossible to identify the exact twinning mode". Further work by these authors indicates the twinning mode to be $\{1\,1\,0\}$ but because of the statements quoted above, this work cannot be said to provide an unequivocable identification of the exact twinning mode.

{1 1 0} twinning has been positively identified in studies of deformed single crystals of polyethylene by Kiho *et al.* [7] and Bevis and Crellin [8]. Allan *et al.* [9] have shown evidence for {3 1 0} twinning taking place within previously deformed {1 1 0} twins. They suggest that it is necessary for the fold planes to be {1 0 0} instead of the normal single crystal {1 1 0} fold planes before {3 1 0} twinning can take place.

It is the purpose of this paper to re-examine the twinning arising from rolling and annealing followed by drawing, and to confirm that the twinning mode is {1 1 0} as originally suggested by Frank *et al.* [2] thereby positively identifying {1 1 0} twinning as a deformation mode in bulk polyethylene. In addition we have examined the reports of twinning with a view to rationalizing the occurrence of {3 1 0} and {1 1 0} twinning in different morphological forms and under different conditions of deformation. This has required further characterization of the lamellar textures in samples of deformed polyethylenes previously reported by the present authors and in which {3 1 0} twinning was observed [3, 4].

2. Experimental

The material studied was low density polyethylene, Alkathene WJG11, made by ICI Ltd. The polymer chips were compression moulded at 160° C into a sheet of 0.5 mm thickness. Strips 3 cm wide were cut from the sheet and given the treatment which produces a texture analogous to that in single crystals. The treatment is as follows: initially the sheet is drawn 300 to 400% and then lightly rolled (i.e. to produce a thickness reduction of 15 to 20%). This produces a (1 0 0) [0 0 1] texture. Secondly the sheet is clipped between two thin sheets of aluminium and immersed for 1 min in a silicone oil bath at 107° C. The aluminium sheets maintain the flat shape of the specimen. In this treatment the *a*- and *c*-axes are known to rotate about the *b*-axis [11]. This sample is designated X1. It was then redrawn along the original drawing direction with a permanent extension $L/L_0 = 1.5$.

The method of studying orientation in polymers, using the Schulz Texture Goniometer linked with the ability to plot the pole figures by means of a computer program has been described previously [3]. In this work only the (1 1 0) and (0 2 0) pole figures have been examined in order to define the textures present. The original drawing and rolling direction and the transverse direction are defined as the north–south and east–west directions respectively on the pole figures. The contour levels are chosen to give ten contours, at equal levels, between the minimum and maximum intensities.

Before and after extension, sample X1 was examined by small-angle X-ray diffraction. The SAXD photographs were recorded in a Rigaku-Denki point collimated goniometer. In addition to these specimens, two samples, which had previously been shown to have undergone {3 1 0} twinning were examined by SAXD to characterize their lamellar textures. These samples were heavily drawn high density polyethylene as described in [3] and designated here as X2, and the heavily

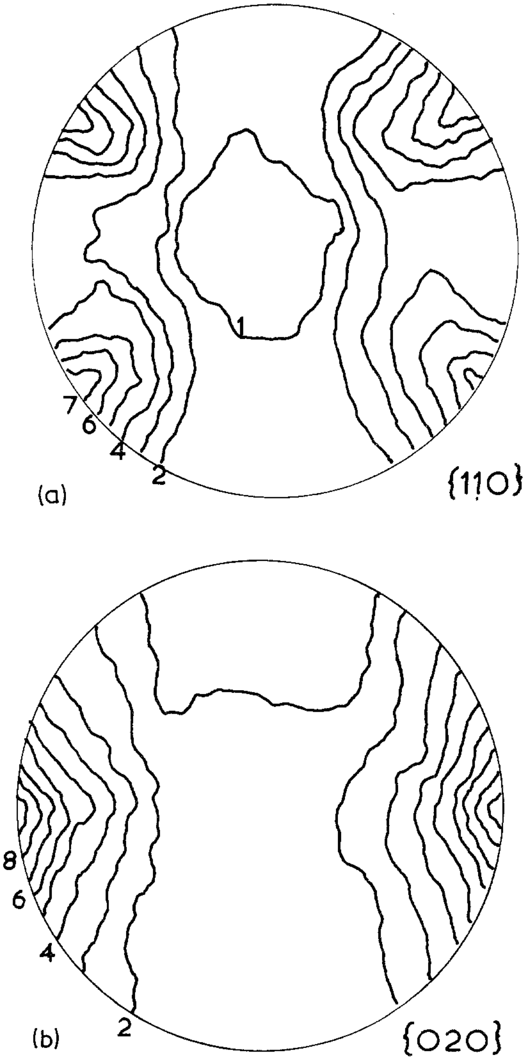


Figure 1 Low density polyethylene, drawn, rolled and annealed at 107° C.

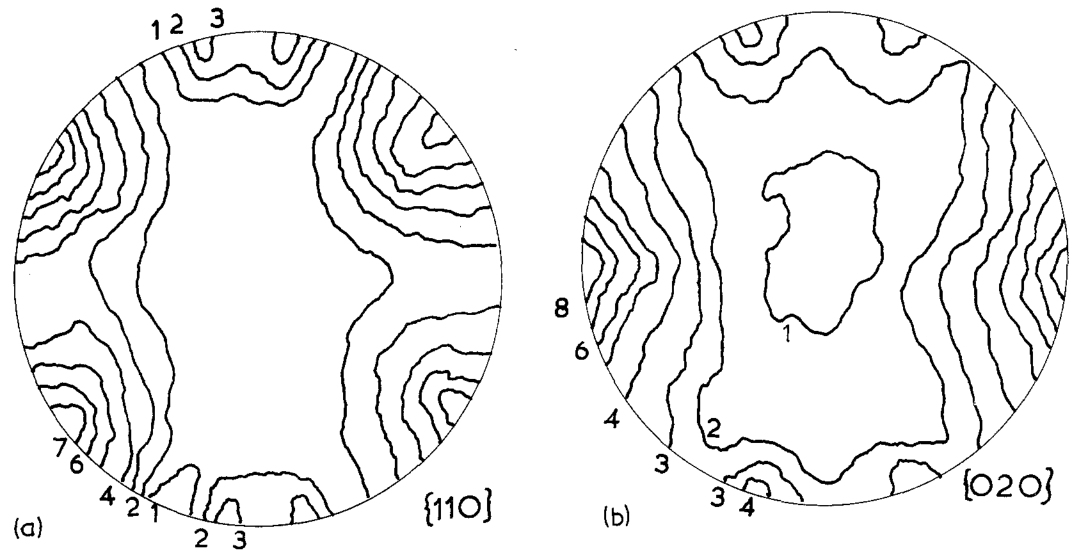


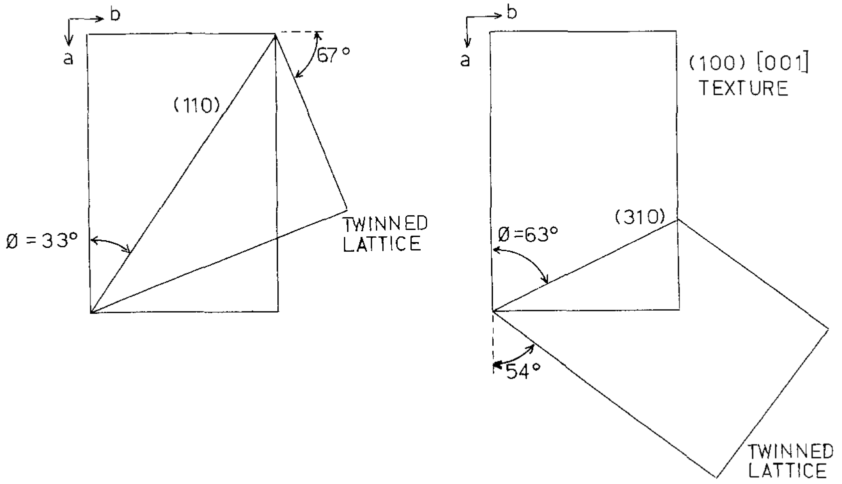
Figure 2 Low density polyethylene, drawn, rolled, annealed at 107° C and redrawn along the *a*-axis.

rolled low density polyethylene, described in [4] and described here as X3.

3. Results

The (1 1 0) and (0 2 0) pole figures for the drawn, rolled and annealed sheet are shown in Fig. 1a and b, respectively. The (1 1 0) pole figure shows two pairs of maxima, each pair at angles of 57° either side of the rolling direction and each member of the pair at angles of 33° either side of the transverse direction. The (0 2 0) pole figure has two maxima along the transverse direction, 90° either side of the sheet normal direction. These indicate that crystallographic *b*-axis is along the transverse direction, and that the *a*-axis is along the initial drawing and rolling directions, both being in the sheet. Since polyethylene has an orthorhombic unit cell, this means that the *c*-axis is perpendicular to the sheet surface and so has an orientation similar to solution-grown single crystals.

The pole figures for the sample, after the further treatment of drawing along the *a*-axis, are shown in Fig. 2a and b. In the (1 1 0) pole figure (Fig. 2a) two new pairs of maxima, around the equator, 10° either side of the sheet normal are seen. The (0 2 0) pole figure also shows four new maxima



(110) TWIN

(310) TWIN

Figure 3 (1 1 0) and (3 1 0) twinning in polyethylene.

around the equator, 22° either side of the sheet normal. These indicate that a position of the crystalline lattice has moved through an angle of about 68° with respect to the parent structure. Using the unit cell dimensions, it can be shown that for {1 1 0} twinning, the twinned lattice would be at an angle of 67° to the original lattice (Fig. 3). Since this corresponds to the observed movement it is concluded that drawing along the *a*-axis in a (0 0 1) [0 0 1] texture causes {1 1 0} twinning.

The SAXD patterns are diagrammatically represented in Fig. 4. The pictures for X1 before and after extension (Fig. 4a and b) show well defined four-point patterns. The pictures for X2 and X3 (Fig. 4c and d) show strong equatorial scattering with only weak, if any, evidence for a four-point pattern. These are discussed more fully later.

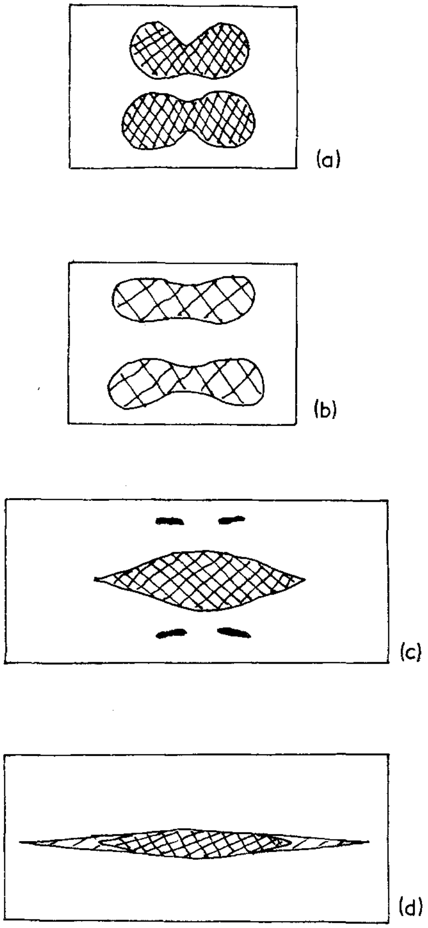


Figure 4 SAXD diagrams for deformed bulk polyethylene samples. (a) X1, low density polyethylene, drawn, rolled and annealed at 107° C. (b) after extending X1 in the y direction. Extension ratio $L/L_0 = 1.5$. (c) X3, heavily rolled low density polyethylene. (d) X2, heavily drawn high density polyethylene.

4. Discussion

A comparison of the deformation behaviour of various polyethylenes subjected to different types of deformation, has revealed a number of anomalies with regard to both twinning modes and their mechanisms. The anomalies have arisen when attempting to reconcile the respective influences of the various stress systems and conditions and crystalline lamellar fold structures upon the operative twinning modes. The consideration of further structural properties or changes has therefore become necessary. These various points are discussed below.

The present work positively confirms the existence of {1 1 0} twinning in deformed bulk polyethylene. This is obtained following permanent extension parallel to the *a*-axis in a (0 0 1) [1 0 0] texture. It has been shown by Young and Bowden [6] that the orientation and deformation mechanisms may change as the elastic extension vanishes with the removal of the load. However, these authors observed that the removal of the load caused orthorhombic twinning. There is no evidence to suggest that the mode of the orthorhombic twinning changes as a result of releasing the elastic extension.

The occurrence of {3 1 0} twinning in bulk polyethylene appears to be associated with compressive stresses parallel to the *b*-axis. When high density polyethylene is drawn so that it "necks" there is a thickness reduction of about 80% and a width reduction of about 20%. The resulting texture has been shown to be a (1 0 0) [0 0 1] texture with twinning on the {3 1 0} plane [3]. It has been shown that, if the polyethylene is drawn in such a manner that no width reduction occurs, then the result is a pure (1 0 0) [0 0 1] texture [10]. This suggests that the contraction along the transverse direction (which is the *b*-direction in the (1 0 0) [0 0 1] texture) may be a factor in causing the {3 1 0} twinning.

Similarly, heavily rolled low density polyethylene subjected to a thickness reduction of about 80% also acquires a (1 0 0) [0 0 1] texture together with {3 1 0} twinning [4]. The explanation for this, as proposed by Hay and Keller [11], is that the (1 0 0) [0 0 1] texture is the primary consequence of the rolling. However, as the roller pressure is acting, the amorphous chains in the polymer are

TABLE I Twinning modes in deformed polyethylene

Deformation	Magnitude and direction of stress	Twinning mode observed	Authors
Bulk polymer			
Drawn	High stress, compressive parallel to *b*-axis	{3 1 0}	Lewis *et al.* [3]
Heavy rolling	High stress, compressive parallel to *b*-axis	{3 1 0}	Lewis *et al.* [4]
Sample drawn/rolled annealed and redrawn	Final redrawing – low stress, tensile parallel to *a*-axis	{1 1 0}	Present work
Single crystal type texture compressed perpendicular to the chain direction	Low stress, compressive parallel to *b*-axis	{1 1 0}	Young and Bowden [6]
Single crystal	Low stress, tensile parallel to *a*-axis	{1 1 0}	Kiho *et al.* [7] Bevis *et al.* [8]
	Low stress, tensile parallel to *a*-axis in portions which have undergone (1 1 0) twinning	{3 1 0}	Allan *et al.* [9]

extended, and this elastic energy is released as the roller passes. This results in compressive forces in the transverse direction (*b*-direction) which provide the driving force for the twinning.

This *prima facie* evidence, that the twinning mode depends upon the direction of the applied stress, is not in agreement with the theories of twinning in which a tensile stress parallel to the *a*-axis has an effect equivalent to that of a compressive stress parallel to the *b*-axis [2]. Also the observations of {3 1 0} twinning [3, 4] do not agree with the observation of {1 1 0} twinning in the compressed single crystal type material of Young and Bowden [6]. Lastly, the theoretical and practical work on deformations in single crystals of polyethylene confirm {1 1 0} twinning as the preferred twinning mode for crystals which experience tensile stresses parallel to the *a*-axis.

The major observations of twinning in deformed polyethylene are summarized in Table I.

An explanation for these discrepancies may be found in the observation that the operative twinning mode in deformed single crystals is dependent on the geometry of the fold surface [9]. The diamond shaped crystals have separate sectors, having either a (1 1 0) or $(1\,\bar{1}\,0)$ fold surface. In one sector only (1 1 0) twinning occurs. In the other $(1\,\bar{1}\,0)$ twinning occurs and the twinned portion then retwins on the (3 1 0) plane. As a result of the twinning process the fold planes within the (1 1 0) twin in the $(1\,\bar{1}\,0)$ and (1 1 0) twin sectors become $(1\,\bar{1}\,0)$ and (1 0 0) respectively. The (3 1 0) twinning occurs only in the portion where some of the fold structure is of the (1 0 0) type. The (1 1 0) fold structure gives rise to (1 1 0) twinning. Bank and Krimm [12] have shown that in bulk polyethylene the fold surface is predominantly of the (1 0 0) type. Some authors have suggested that the {3 1 0} twinning in deformed bulk polymer is a consequence of the (1 0 0) fold planes [1]. However, this argument does not adequately explain the presence of both {1 1 0} and {3 1 0} twinning in bulk polyethylene. The observations of Allan *et al.* [9] are important in that they demonstrate the importance of the fold surface in influencing the twinning mode.

A more rational explanation for the presence of {3 1 0} twinning is given by the morphology of the necked and heavily rolled samples in which this type of twinning is observed. In these two cases the deformations leading to the {3 1 0} twinning represent strains of 500 to 1000%, whereas in the other studies of bulk and single crystal material strains of 50% or less result in {1 1 0} twinning.

It is known that high deformation in drawing gives rise to the formation of microfibrils which therefore have no regular fold surfaces [13]. Recent Laser Raman studies by Marsden show that microfibrils are formed under conditions of heavy rolling [14]. The SAXD pictures for the highly deformed polyethylenes, X2 and X3, shown in Fig. 4c and d, clearly show a lack of a regular fold surface. It therefore appears likely that {3 1 0} twinning can occur when there is no, or only an ill-defined, fold surface. Thus an alternative explanation of the observation of {3 1 0} twinning in one of the single crystal sectors as described by Allan *et al.* is not that it occurs in the formed {1 0 0} fold regions, but that it occurs at the irregular folded regions which are produced at the boundaries between the {1 1 0} and {1 0 0} folded sectors.

{1 1 0} twinning is the normal mode produced under a low stress deformation and where there is a well defined regular folded lamellar surface. Such conditions prevail in the present observation of {1 1 0} twinning, the presence of regular folded lamellar being demonstrated by the SAXD photographs in Fig. 4a and b, in the work of Young and Bowden, and of course in the single crystal studies.

5. Conclusions

{1 1 0} twinning has been confirmed in deformed bulk polyethylene when tensile stresses are applied parallel to the crystallographic *a*-axes in samples possessing (0 0 1) [1 0 0] textures. This type of twinning is the normal mode at low stresses and depends upon the existence of well defined regular lamellar (1 1 0) fold surfaces. On the other hand, {3 1 0} twinning is observable in more heavily deformed bulk polyethylenes and can be explained by the destruction of the well defined fold surfaces upon the morphological changes in the crystalline regions, the disruption of the lamellar structures resulting in the formation of microfibrils.

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References

1. P. B. BOWDEN and R. J. YOUNG, *J. Mater. Sci.* **9** (1974) 2034.
2. F. C. FRANK, A. KELLER and A. O'CONNOR, *Phil. Mag.* **3** (1958) 64.
3. D. LEWIS, E. J. WHEELER, W. F. MADDAMS and J. E. PREEDY, *J. Appl. Cryst.* **4** (1971) 55.
4. *Idem, J. Polymer Sci. A–2* **10** (1972) 369.
5. T. SETO, T. HARA and T. TANAKA, *Jap. J. Appl. Phys.* **7** (1968) 31.
6. R. J. YOUNG and P. B. BOWDEN, *Phil. Mag.* **29** (1974) 1061.
7. H. KIHO, A. PETERLIN and P. H. GEIL, *J. Appl. Phys.* **35** (1964) 1599.
8. M. BEVIS and E. B. CRELLIN, *Polymer* **12** (1971) 666.
9. P. ALLAN, E. B. CRELLIN and M. BEVIS, *Phil. Mag.* **27** (1973) 127.
10. J. E. PREEDY, Ph.D. Thesis, University of Surrey (1973).
11. I. L. HAY and A. KELLER, *J. Mater. Sci.* **1** (1966) 41.
12. M. I. BANK and S. KRIMM, *J. Polymer Sci. A–2* **7** (1969) 1783.
13. A. PETERLIN, *J. Mater. Sci.* **6** (1971) 490.
14. E. MARSDEN, private communication.

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