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Multiple kinks in lamellar linear polyethylene

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Injection-moulded specimens made of linear polyethylene with preferred orientation of the molecular chains (*c*-axes) in the direction of injection were deformed in a bending test. Ultra-thin sections of the deformed material were made following chlorosulfonization. Examination using transmission electron microscopy revealed that deformational and superstructural elements can be elucidated simultaneously using this method. Deformation in the observed regions with multiple kink bands is found to be inhomogeneous and concentrated in two shearing processes: one along the borders of the kink band and the other within a kink band at an acute angle to the border of the band. It must be concluded from the formation of the lamellae in the kink bands that deformation, even within a kink band, is inhomogeneous and is predominantly concentrated in the shear zones, while the lamellar stacks lying between the shear zones appear under electron microscopy, to be nearly undeformed.

1. Introduction

The observation is repeatedly made in deformation experiments on polymeric materials that the deformations are not homogeneously distributed throughout the volume, but are concentrated in certain regions of the specimen. Examples of such local deformation zones are crazes, which occur mainly in amorphous polymers during tensile loading [1, 2] but which were also observed in semicrystalline polymers, e.g. polyethylene [3] and polypropylene [4] during low-temperature deformation. Shear bands are another type of local deformation and occur primarily in amorphous materials during compressive loading [5, 6]. Recently, Friedrich [7] was able to show that such shear bands may also occur in spherulitic polypropylene under compressive stress at low temperatures.

A third type of local deformation structure, usually designated as a kink band, has to date only been observed in semi-crystalline polymers. Its occurrence does not appear to be associated with any special deformation process since, for polyethylene alone, kink bands were found in material which had been deformed under tensile stress [8, 9], bending [10, 11], shear [12] and compressive loads [10, 13, 14].

Despite the numerous studies conducted in this area of work it obviously has not yet been possible to directly observe the structure within the kink bands in polyethylene. In this paper, successful attempts to elucidate the microlocal structure in these kink bands with the aid of transmission electron microscopy will be reported.

2. Experimental procedure

The experiments were conducted on a linear polyethylene, Hostalen GD6250 (from Hoechst AG, Germany). Strips 1 mm thick, 15 mm wide and 87 mm long were made by injection moulding. To create the kink bands, the bending method was selected by the predetermined specimen geometry. The strip was bent back through 180° over a rod 6 mm in diameter and fixed in this position with a second rod placed in the transverse direction (see Fig. 1a). The bent specimen was then aged for 450 hours under normal conditions (room temperature, normal pressure, room atmosphere, etc.). Afterwards the mounting was removed, whereupon the bend of initially 180° (while in the mounting) decreased over a period of hours to a bending angle of approximately 100° (see Fig. 1b). For the purpose of staining [15, 16], the specimen was then placed in chlorosulfonic acid for 216 hours and, following this, in 1% aqueous uranyl acetate solution for approximately 1000 hours at room temperature.

Ultra-thin sections were made with the Reichert

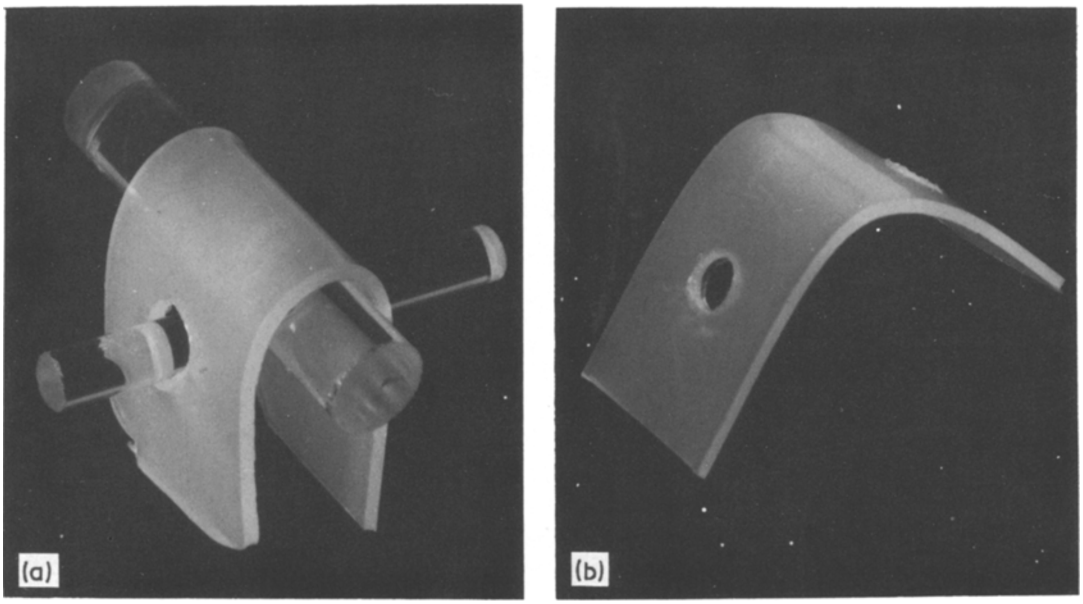

Figure 1 **Polyethylene strips (a) in the bending jig and (b) after relaxation after bending.**

Ultra-microtome OmU 2 using glass knives after oriented embedding of the material in epoxy resin. The ultra-thin sections were transferred to copper grids for electron microscopy and examined in a Siemens ELMISKOP 101 electron microscope employing 100 KeV electrons and using the conventional transmission method.

3. Results

A lamellar structure is formed in all injection-moulded specimens, with lamellar thicknesses of 10 to 15 nm and a preferred arrangement of the lamellae perpendicular to the direction of injection. It was possible to show this using both electron microscopy with orientated-cut specimens (the lamellar normal can be seen running parallel to the injection direction in all ultra-thin sections containing the injection direction) and using X-ray texture analysis. Fig. 2 [(002) pole-figure recorded in arbitrary units] shows a distinct alignment of the *c*-axis in the direction of injection. However, it is not possible to gain any clear indication of preferred directions for the *a*- and *b*-axes from the (200), (020) and (110) pole-figures also recorded.

The connection between the injection, deformation and cutting geometry can be seen in Fig. 3. The direction of injection (ID) corresponds to the preferred orientation of the molecular chains and the transverse direction (TD) corresponds to the bending axis. Specimens were taken from the concave side of the bent strip. The orientation was selected such that the cut surface contained the injection direction ID and the normal direction ND. Regions exhibiting deformation zones were observed in many of the ultra-thin sections. In Fig. 4 the boundary between the embedding material and the specimen corresponds to the direction of compression in the bending experiment. Parallel

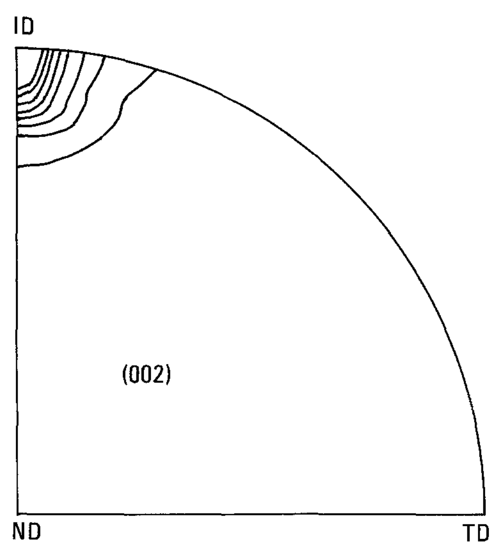

Figure 2 (002) pole-figure of an injection-moulded polyethylene specimen (arbitrary units). ID = injection direction; ND = normal direction; TD = transverse direction.

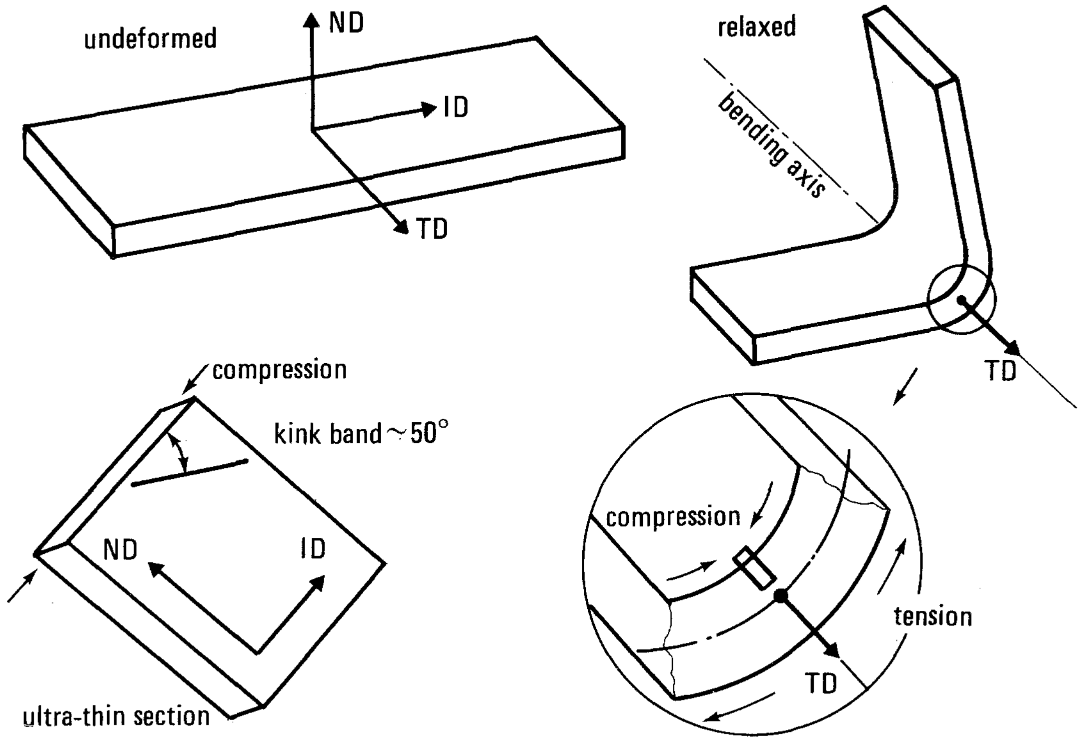

Figure 3 Illustration of the injection, bending and cutting geometry (arbitrary units). ID = injection direction; ND = normal direction; TD = transverse direction.

bands with different hatching characteristics are visible, inclined at approximately 50° to the compression direction. At higher magnification (Fig. 5) it can be seen that the hatching characteristic is caused by shear zones (light zones) consisting of highly deformed material which is hardly capable of incorporating staining substance. (To some extent the light zones are also torn up). The shear zones run at an angle to the borders of the kink bands (mean value of about 45°) and are nearly parallel within a band. In addition, the shear zones usually correspond in orientation in every other band, while at the borders of adjoining bands they meet almost at a right angle. In this fashion a herring-bone pattern is formed which is not necessarily symmetrical. At higher magnifications the crystal lamellae are also distinguishable (Figs 6 and 7). They also run at an angle (average about 20°) to the borders of the bands and are roughly parallel to each other in every second band. The

Figure 4 Micrographs of multiple kinks with inclination of approximately 50° to the compression direction (overall view). Arrow indicates injection direction (× 4000).

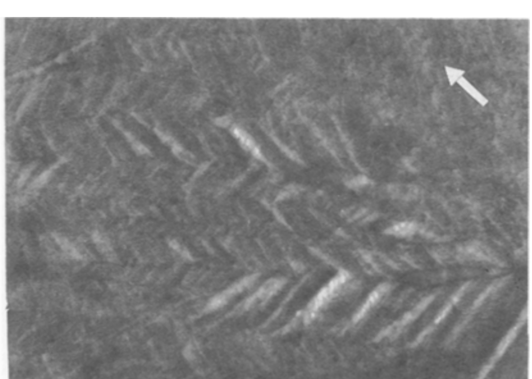

Figure 5 Micrograph of multiple kinks showing kink band borders and shear zones. Arrow indicates injection direction (× 30 000).

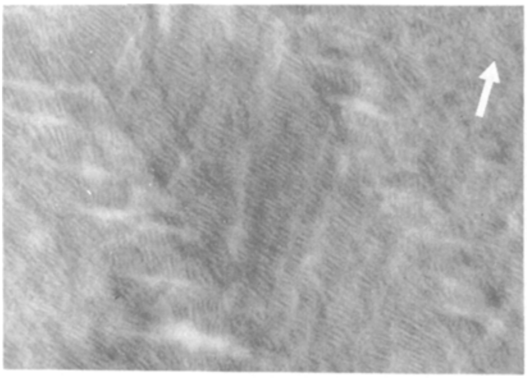

Figure 6 Micrograph of multiple kinks showing, in addition to the lamellar arrangement the kink band borders and shear zones. Arrow indicates injection direction (× 60 000).

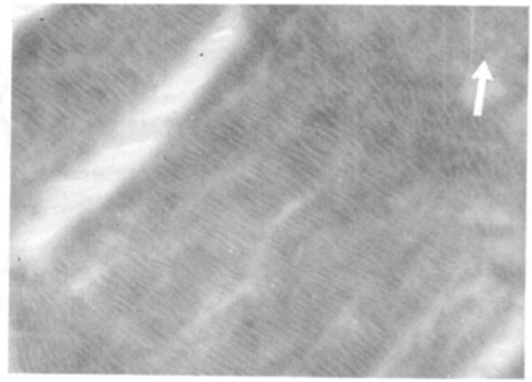

Figure 7 Micrograph showing a section from a kink band with an expanded shear zone. Arrow indicates injection direction (× 70 000).

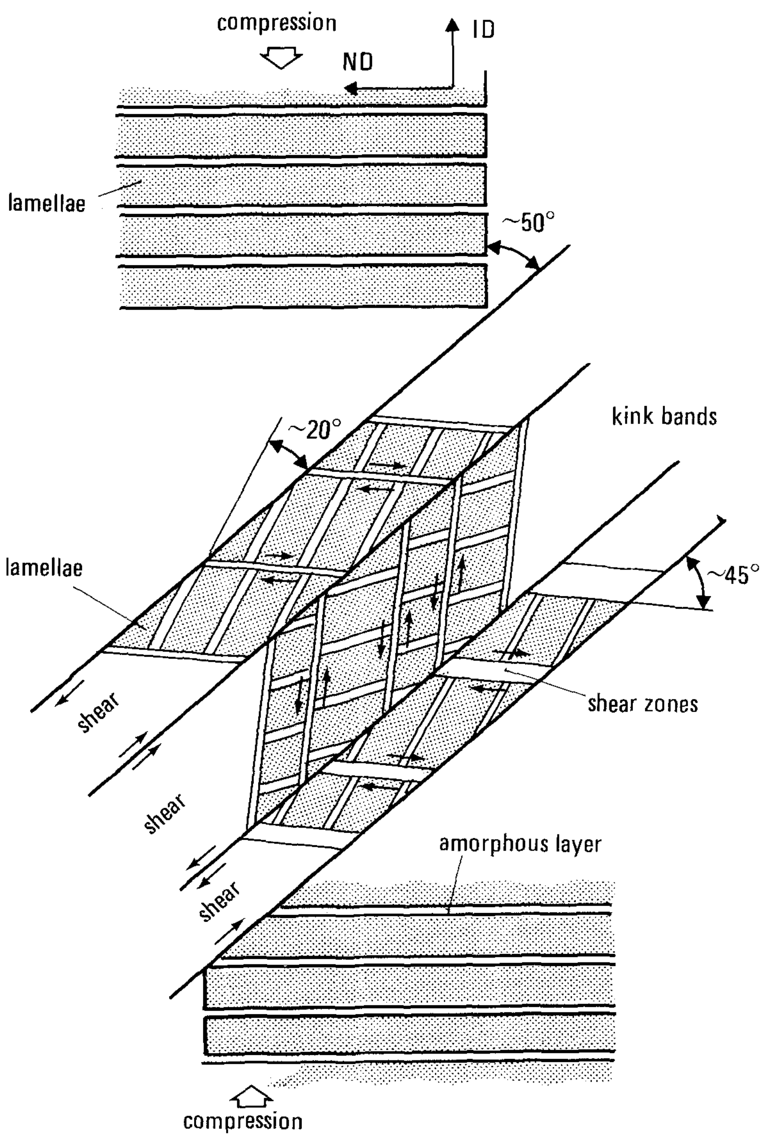

Figure 8 Schematic representation of the orientation relation between specimen geometry and observed structural features.

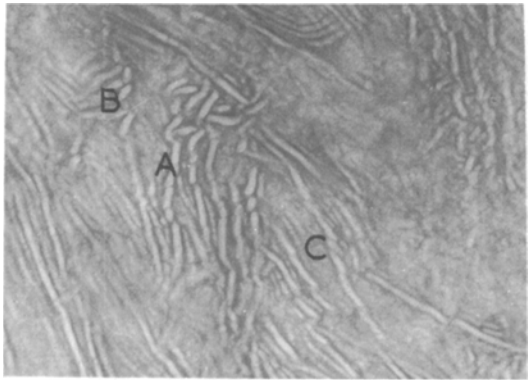

Figure 9 Micrograph of lamellar formations in non-orientated lamellar polyethylene following shear deformation (× 80 000).

lamellae are cut by the shear zones at an angle smaller than a right angle. Fig. 8 shows schematically the orientation relation between the specimen geometry and the observed structural features.

The shear zones themselves consist of "thinned-out" material. In expanded shear zones, just as in crazes, bridges and cavities can be seen. Conclusions can be drawn about the local shear field from their lateral displacement.

4. Conclusion

Upon comparing the results of this work with those of other authors it must be taken into account that, in this study, for the first time, an attempt was made to examine the local deformation zones by the application of transmission electron microscopy. This investigative method permits a number of modifications to the previously successful experimental procedures. Thus, for example, it is not necessary to make the deformation zones so large that the kink bands become macroscopically visible. Therefore it is possible to eliminate the need to bend the strip back into its original shape [11]. Instead, after the restoring forces had subsided to the extent that there was no further noticeable re-deformation, the primary deformation subsequently remaining was "fixed" [15]. The transmission electron micrographs thus show the state of deformation, following relaxation, as caused by the primary bending action and not the state created by the secondary action of bending the strip back.

The deformation bands occuring, however, still exhibit the features of kink bands which can be observed after bending back the strip:

(a) The inclination of the band borders to the direction of compression of approximately 50° (Fig. 4) coincides with the observations of other authors [14].

(b) The borders of the bands run essentially straight both in the plane defined by the injection direction (ID) and the normal direction (ND) and in the plane defined by the injection direction (ID) and the transverse direction (TD).

(c) In this manner the bands separate planar regions from each other which were forced into different orientations by the action of shearing. (It can be seen in Figs 6 and 7 that, with reference to a common band border, the lamellae in one band tilt in the clockwise direction and in the other band in the counter-clockwise direction).

Furthermore, shear zones can be distinctly detected in the kink bands. The fact that it was not possible to observe them in previous studies can be attributed to the fact that, until now, only electron microscopic examination of surfaces was conducted (scanning and transmission electron microscopy). These microscopic methods are only capable of differentiating between "normal" and "thinned-out" materials if there are genuine cavities in the thinned-out zones of the specimen. However, true cavities can only exist in expanded shear zones and would close again upon bending back the material, in a similar way to that in which cavities close in crazes which have been relaxed. Thus, the cavities visible in Figs 4, 5 and 7 also confirm that the preparatory technique used here was actually successful in fixing and elucidating a state of deformation.

The lamellae simultaneously revealed, along with the shear zones, provide further information It can be deduced from their distinct formation between the shear zones (Figs 6 and 7) that these areas were not exposed to any electron microscopically visible deformation.* By comparison, Fig. 9 shows the behaviour of lamellae in a specimen with a non-orientated lamellar structure which was also subjected to shearing deformation. During deformation the lamellae break up into small blocks (A) which tilt away from each other (B) and/or are displaced (C). Phenomena of this type have not been observed anywhere in the kink

*The possibility of an additional uniform deformation in the form of shearing of the lamellae which cannot be detected electron microscopically, cannot be excluded. Such a possibility is supported by the fact that the angle between the lamellae and the shear zones within the kink bands deviates markedly from the expected angle of 90°.

bands. Thus deformation *in* the kink bands is also discontinuous and is predominantly concentrated in the shear zones. Hence, two discontinuous deformations can be detected in the local deformation zones studied here: a shear deformation along the kink band borders, and a shear deformation being within a kink band at an acute angle to the band borders. It cannot be discerned from the results of the electron microscopic examination in what sequence the two shearing processes occur. We assume, however, that there are co-operative processes involved, since the kink band borders are maintained in the form of plane surfaces.

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