

The plastic deformation of oriented polypropylene and polyethylene: deformation mechanisms

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Polypropylene and high-density polyethylene, oriented by hot drawing, have been tensile tested *in situ* in a low angle X-ray camera. Two orientations of polypropylene, $\theta_0 = 31^\circ$ and $\theta_0 = 60^\circ$, and one orientation of polyethylene, $\theta_0 = 30^\circ$, were examined. (θ_0 is the initial angle between the tensile axis and the molecular axis.) Low-angle and wide-angle X-ray patterns were taken at successive stages of increasing strain up to approximately 100%. The rotations of the molecular axis and lamellar normal for both materials oriented near $\theta_0 = 30^\circ$ were quantitatively consistent with predominantly intermolecular shear, occurring within the lamellae. In the case of polypropylene, it is proposed that small amounts of interlamellar and interfibrillar shear were also present.

At $\theta_0 = 60^\circ$, the polypropylene was shown to deform by void opening or fibril separation, followed by intermolecular shear. The behaviour of polypropylene was consistent with the yield criterion based on a fibre reinforced composite model which was presented in a previous paper [1].

1. Introduction

The role of the various morphological elements in the large-strain deformation of crystalline polymers is not well understood. It is of particular interest to study the behaviour of lamellae in oriented polymers, where the orientation allows an exact analysis of the movements of (1) the molecular axis, (2) the lamellar normal and (3) the fibrillar axis (in specimens having a fibrillar structure).

Many of the recent investigations of the mechanisms of deformation in oriented crystalline polymers have been concerned with various forms of polyethylene [2-9]. Both interlamellar slip and intermolecular slip in the chain direction have been suggested as possible modes of deformation. The latter has been shown to be a dominant mechanism in oriented high-density polyethylene [2-4], although twinning and a phase transformation can also occur under appropriate stresses [5]. Recent work on the compression of this material at an angle to the molecular axis [6] has shown that a large part of the recoverable elastic part of the compression

cannot be attributed to intermolecular slip whereas the permanent plastic part of the strain is due to intermolecular slip. In low-density polyethylene, much work has been done on drawn, rolled and annealed material in which the lamellar normal is inclined to the initial draw direction and to the molecular axis. Tensile and compressive tests on this material at elevated temperatures, slightly below the annealing temperature, have shown a rotation of the lamellae which was interpreted as an interlamellar slip process, when the load axis was parallel to the initial draw direction [7]. Under compression, intermolecular slip within the lamellae becomes dominant when the lamellae have rotated so as to be normal to the compression axis [8]. The range of these experiments was extended by Keller and Pope [9]. At room temperature, they found that deformation occurred by intermolecular slip and by lamellar separation which was thought to occur by strain of amorphous interlamellar material, whereas the effect of interlamellar slip was negligible. As the temperature of deformation

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approached the annealing-temperature intermolecular slip became less important and interlamellar slip increased, becoming dominant at high temperature, in agreement with earlier work [7]. At all but the highest temperatures of deformation, the macroscopic strain corresponded to the change in the small-angle spacing resolved along the strain axis, showing that the deformation of the stacks of lamellae giving rise to the small-angle X-ray pattern accounted for the total deformation. At the highest temperature the macroscopic strain exceeded the strain shown by the small-angle pattern and it was suggested that this could be accounted for by the deformation of amorphous interfibrillar material.

Furthermore it has been shown in doubly-oriented (lamellae) nylon-11 [10] that intermolecular slip can be induced under shear stresses applied parallel to the molecular axis. The deformation mechanism therefore depends not only upon the conditions of testing (type of stress, temperature, initial orientation), but also upon the type of polymer. The deformation mechanisms in oriented polypropylene, an important commercial material, have yet to be studied, although considerable work has been done on the plastic deformation of spherulitic polypropylene [11-14].

In an earlier paper [1], a study of the tensile yield criterion for oriented polypropylene was reported. It was shown that a criterion previously applied to fibre-reinforced composites was suitable for describing the orientation dependence of yield stress. The criterion predicted three distinct modes of deformation, one of which was shear parallel to the molecules over the orientation range from $\theta_0 = 20^\circ$ to $\theta_0 = 50^\circ$. The purpose of this paper is to compare the mechanisms of deformation of oriented polypropylene with some of the predictions of this criterion, and also with the mechanisms of deformation of oriented high-density polyethylene.

2. Experimental

Two polymers were used in these experiments. The first was polypropylene, prepared from the same initial material and drawn under the same conditions as those described earlier [1]. The final material was fibrous with the molecular axis parallel to the initial draw direction and with the lamellae perpendicular to it. Two orientations, $\theta_0 = 31^\circ$ and $\theta_0 = 60^\circ$, were

tested (θ_0 is the initial angle between the molecular axis and the tensile axis). The dimensions of the tensile specimens were the same as those used previously [1], except that the thickness perpendicular to the molecular axis-tensile axis plane was reduced to 1 mm. The reduced thickness of the specimen did not affect the deformation behaviour significantly. Furthermore, the step-straining procedure necessary for these experiments did not alter the deformation mode since low-angle X-ray patterns (LAXP) and wide-angle X-ray patterns (WAXP) taken before and after deformation in specimens pulled at a continuous elongation rate of $1.3 \times 10^{-3} \text{ sec}^{-1}$ showed exactly the same changes as the first and final patterns of a specimen strained in steps by the same total amount. These differences in conditions of testing therefore had no effect on the results.

The second material examined was high-density polyethylene, oriented by hot drawing under plane strain conditions. The crystallographic axes were oriented uniquely with respect to the specimen axes. The tensile specimen ($\theta_0 = 30^\circ$) was cut from the drawn material so that the bc-plane was normal to the X-ray beam. The lamellae were perpendicular to the c-axis, but appeared to be more perfectly oriented when viewed normal to the bc-plane (along the X-ray beam).

Each of the specimens was clamped in a special tensile testing jig (Fig. 1). The jig was fixed in position on a Rigaku-Denki low-angle

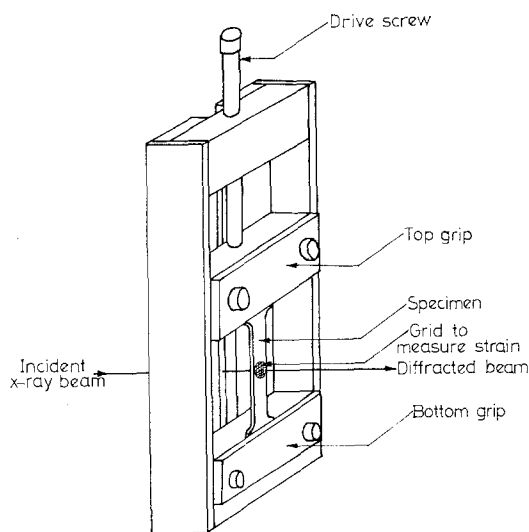


Figure 1 Tensile testing jig for X-ray examination of specimens under tension.

X-ray camera and was demountable so the specimen and jig could be handled without releasing the applied load. All tests were conducted without releasing the strain at each step of the straining. LAXP and WAXP were obtained for successively increasing strains by halting or "stepping" the strain at small increments (roughly 5%). The tests were continued to total strains of the order of 100%.

The LAXP and WAXP were obtained from identical areas of the strained specimen by simply reversing the film holder and the attached vacuum path on the X-ray bench. The specimen was not moved between the exposures for the LAXP and the WAXP so the relative orientations of the lamellar normal and molecular axis could be accurately compared.

The largest sources of experimental error were in the measurements of the strain and the orientation of the lamellar normal. The strain was checked in the following way. First the strain of one polypropylene ($\theta_0 = 31^\circ$) specimen was calculated from the overall elongation between the grips. A second identical specimen was marked with a rectangular grid of carbon evaporated in vacuum through a 200 mesh electron microscope specimen grid. The grid was aligned with one axis parallel to the tensile axis and it was centred on the incident point of the X-ray beam. In this case the strain was measured between the individual grid lines in the immediate region of the X-ray beam (optical micrographs were taken at each step). In both cases the rotation of the molecular axis as a function of the differently measured strains fell on the same curve. The overall strain as measured by the elongation between the grips was identical to the localized strain as measured by the grid line separation in the X-rayed region. At large strains (about 40%) the grid disintegrated and was not measurable.

For the polyethylene sample ($\theta_0 = 30^\circ$), the strain as calculated from the width of the grid, assuming a constant-volume plane-strain deformation, was identical to the strain as calculated from the length (parallel to the tensile axis) of the grid. This showed that the two assumptions were valid at those strains where the grid was measurable. At larger strains after the grid had disintegrated, the overall width of the specimen was used to calculate the strain.

The second source of experimental error was in the measurement of lamellar orientation. This

was minimized by measuring several sets of enlarged photographs of the LAXP and recording the data independently before using it. At larger strains, greater than about 30%, the lamellar spots on the LAXP became diffuse and the measurement error was therefore greater. Each angular measurement was made relative to the shadow of the fixed beam stop on the film. The error in measurement of the orientation of the molecular axis from the WAXP was estimated to be $\pm 1^\circ$ and of the lamellar normal from the LAXP $\pm 3^\circ$.

3. Results

The series of LAXP taken at successively higher strains are shown for polyethylene in Fig. 2. By comparison with the LAXP for polypropylene (Fig. 3), the initial structure (at 0% strain) is better ordered since the lamellar maxima are sharper. In addition the initial polypropylene LAXP shows a central streak which is elongated in a direction perpendicular to the molecular axis. This was interpreted to be fibrous scattering and is similar to the equatorial scattering observed previously [8, 11, 15]. A scanning electron micrograph of the fracture surface of such material is seen in Fig. 4. This shows a distribution of fibre sizes from diameters as large as hundreds of microns to smaller than 1000Å. From the LAXP alone, it is not possible to determine the structure of drawn polypropylene within the spectrum of possibilities: between continuous matrix with distribution of elongated voids or discrete fibres in a "matrix" of voids.

In the drawn material, the lamellar maxima lie along the draw direction and are parallel to the molecular axis. In both materials ($\theta_0 = 30^\circ$ and $\theta_0 = 31^\circ$), the lamellar maxima (Figs. 2 and 3) are displaced away from the tensile axis with increasing strain. Concurrently, the molecular axes are rotating towards the tensile axis. The fibrillar axis of the polypropylene rotates in the same sense as the molecular axis.

The orientations of the three elements of interest (1) lamellae, (2) molecular axis and (3) fibrillar axis (for polypropylene) were measured relative to the tensile axis and the results plotted as a function of measured strain (Figs. 5-8).

In the case of the $\theta_0 = 60^\circ$ polypropylene specimen, the deformation progressed by necking and propagation of the neck through the

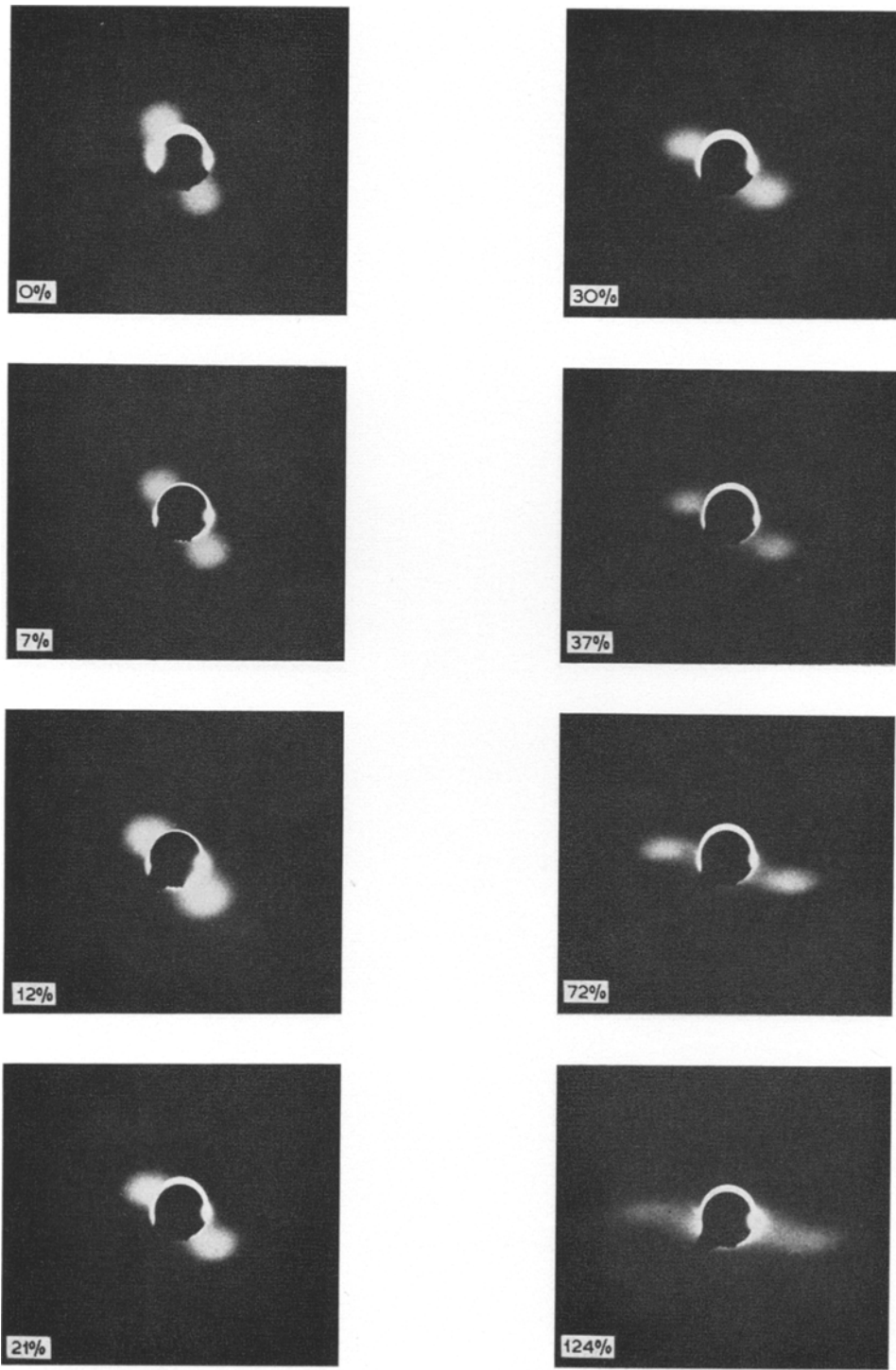


Figure 2 Changes in LAXP with increasing strain for oriented polyethylene. The tensile axis is vertical ($\theta_0 = 31^\circ$).

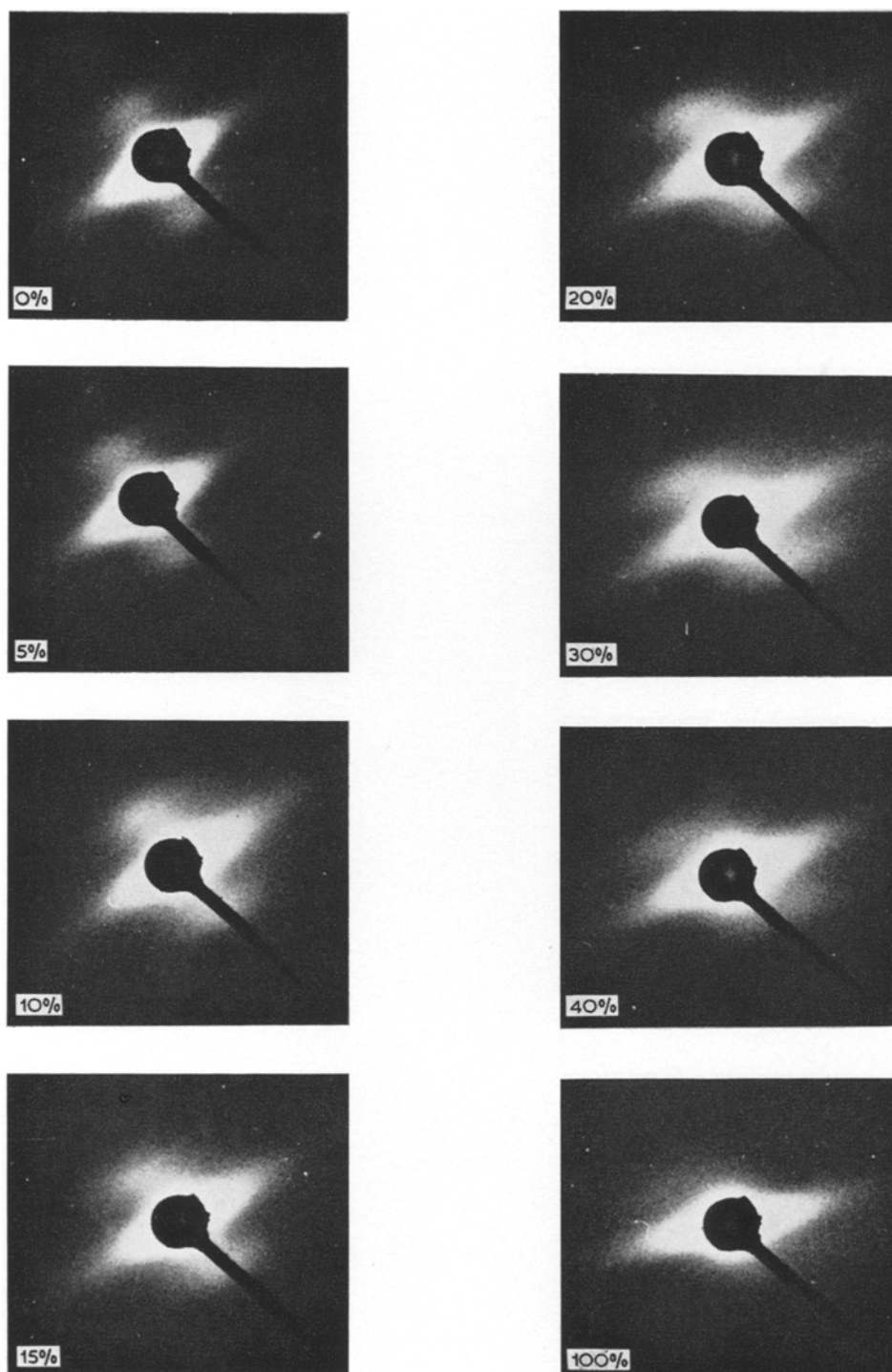


Figure 3 Changes in LAXP with increasing strain for oriented polypropylene. The tensile axis is vertical ($\theta_0 = 31^\circ$).

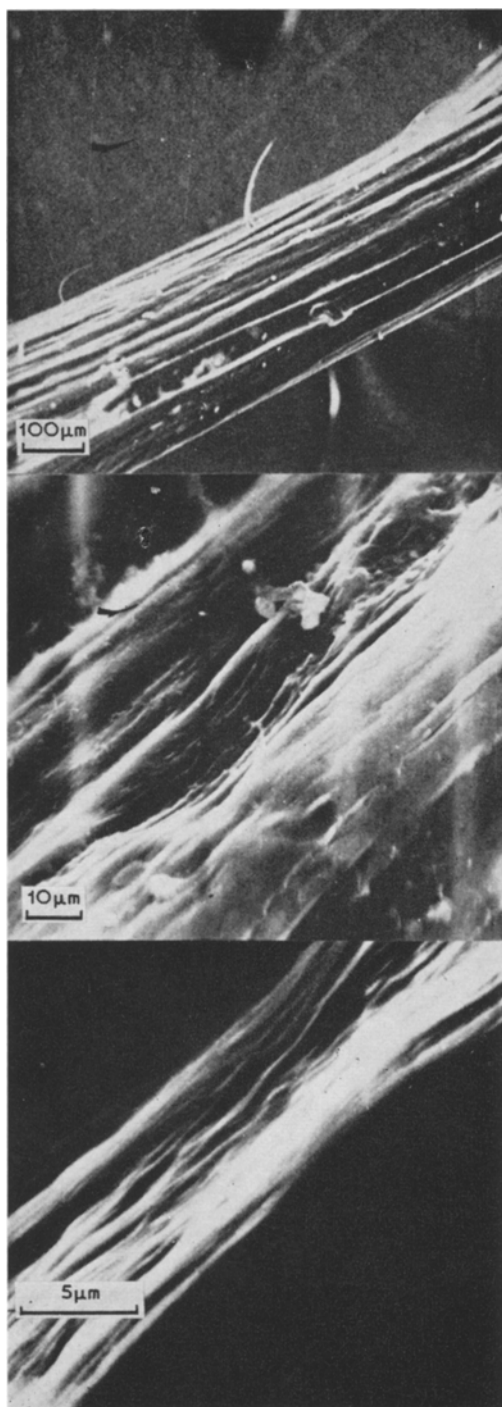


Figure 4 Scanning electron micrographs of a fibre projecting from a fracture surface of oriented polypropylene. The different magnifications show the large range of fibre sizes.

gauge length. Consequently the strain was highly localized and not accurately measurable. With increasing strain the molecular axis rotates smoothly towards the tensile axis. The LAXP series revealed a shortening and broadening of the fibrillar streak (Fig. 9) which was clearly visible only on the negative. There was a general increase in the amount of diffuse scattering about the central spot.

4. Discussion

There are three modes of shear which seem likely to occur in oriented polymers (1) interlamellar, (2) intermolecular and (3) interfibrillar. The last is possible in the fibrous oriented polypropylene. The intermolecular and interlamellar shear modes may be distinguished because their shear planes are perpendicular to each other in both materials. Since the gripped ends are constrained to be parallel to the tensile axis, shear on one or other of these planes will result in a rotation of the shear planes. This is analogous to lattice rotation accompanying slip in single crystals of metals. Interlamellar shear results in a rotation of the lamellae towards the tensile axis, so the lamellar normal rotates away from the tensile axis. In this case the molecules are carried along with the lamellae and the molecular axis rotates away from the tensile axis.

It is seen that for both polyethylene and polypropylene oriented near $\Theta_0 = 30^\circ$, the molecular axis rotates towards the tensile axis (Figs. 7 and 8). It is obvious that interlamellar shear is therefore not the predominant shear mode operative in these cases.

The sense of the rotation of the molecular axis is that expected for intermolecular shear. It is possible to calculate the expected orientation of the molecular axis (Θ_1) as a function of strain assuming intermolecular shear. Assuming that the orientation of the tensile axis is fixed, we have [17]:

$$\frac{l_1}{l_0} = \frac{\sin \Theta_0}{\sin \Theta_1} \quad (1)$$

where l_0 and l_1 are the lengths before and after extension, respectively, and Θ_0 , Θ_1 , are the angles between the tensile axis and molecular before and after extension. Whence:

$$\Theta_1 = \sin^{-1} \left(\frac{l_0}{l_1} \sin \Theta_0 \right). \quad (2)$$

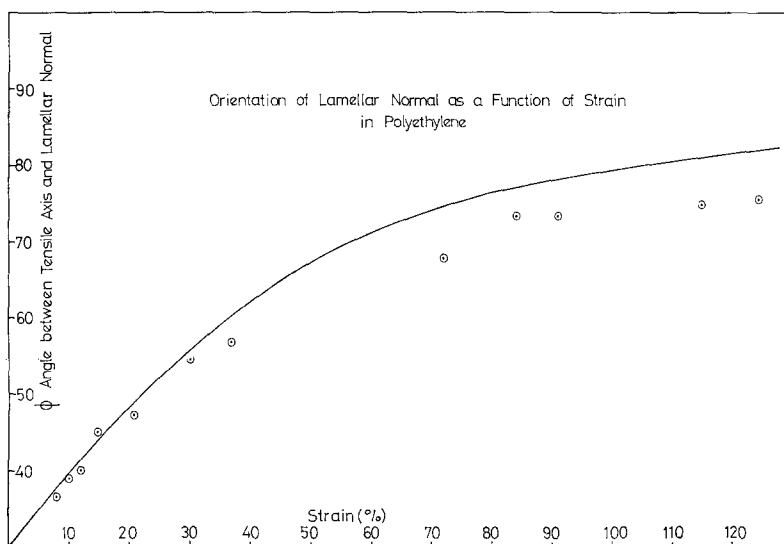


Figure 5 Orientation of lamellar normal (α) as a function of strain for polyethylene ($\theta_0 = 30^\circ$). The experimental measurements are shown relative to the curve predicted by [4].

If this is plotted as a function of strain $(l_1 - l_0)/l_0 \%$, it is seen that for both polypropylene ($\theta_0 = 31^\circ$) and polyethylene ($\theta_0 = 30^\circ$), the measured values are close to the expected curve (Figs. 7 and 8). The agreement between the predicted and observed molecular orientations confirms that the mode of deformation is shear parallel to the molecules, but does not distinguish between shear occurring homogeneously within crystalline lamellae and shear occurring heterogeneously between stacks of lamellae.

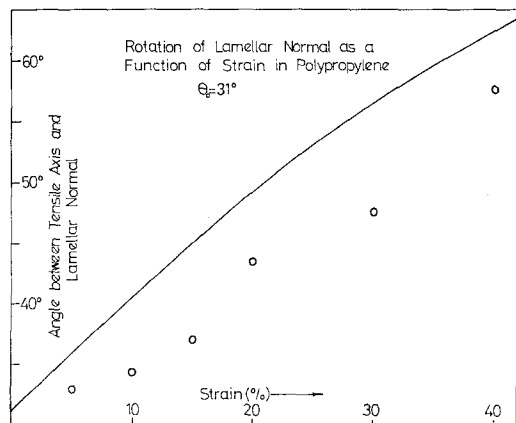


Figure 6 Orientation of lamellar normal (α) as a function of strain for polypropylene ($\theta_0 = 31^\circ$). The experimental measurements are shown relative to the curve predicted by [4].

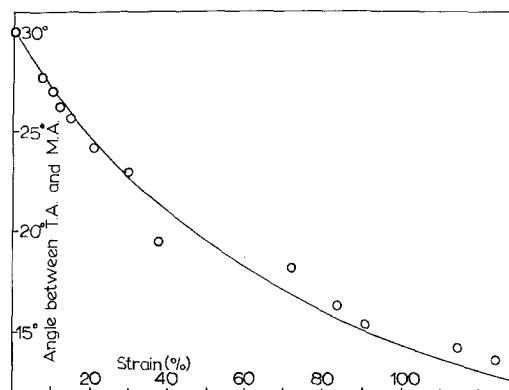


Figure 7 Orientation of the molecular axis (θ_1) as a function of strain for polyethylene ($\theta_0 = 30^\circ$). The experimental measurements are shown relative to the curve predicted by [2].

Evidence on this point may be obtained by examining the re-orientation of lamellae with strain. The LAXP is interpreted as arising from stacks of lamellae, one of which is shown in Fig. 10 [16]. In this model the linear lattice of real space (the lamellae as repeating units) transforms to layer lines in the diffraction pattern. The normal to the layer lines lies parallel to the repeat direction of the lamellae. The transform of the individual lamella is a "sausage-shaped" unit passing through the origin and elongated normal to the plate-like

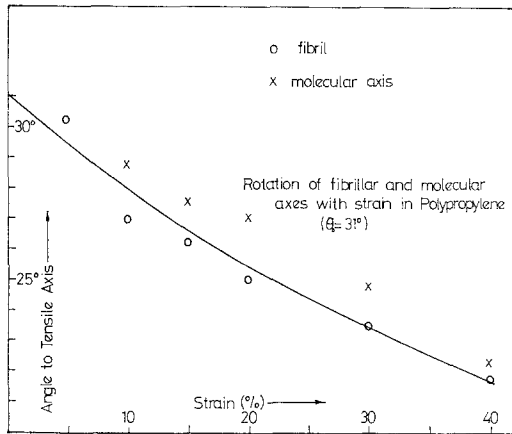


Figure 8 Orientation of the molecular axis (θ_1) as a function of strain for polypropylene ($\theta_0 = 31^\circ$). The experimental measurements are shown relative to the curve predicted by [2].

lamella. The product of the two transforms, results in the diffraction-pattern maxima.

If intermolecular shear occurs, the lamellae are deformed as shown in Fig. 11. The linear lattice remains in the same orientation after deformation so the layer lines do not rotate. However the plane of the lamella rotates, so the "sausage" rotates away from the tensile axis. The resultant maxima are elongated spots translated along layer lines in a direction away from the tensile axis. Superimposed on this motion is the overall rotation of the molecular axis, and hence the whole LAXP, towards the tensile axis (θ_1). This is the qualitative behaviour observed for both materials oriented near $\theta_0 = 30^\circ$ in their LAXP's (Figs. 2 and 3).

It is possible to calculate the expected re-orientation of the lamellar normal in the following way. The shearing of the molecules causes a rotation of the lamella surface of magnitude $\tan^{-1} \alpha$ where α is the glide strain. Added to this is the overall rotation due to the change in θ_1 given by Equation 2. The new orientation of the lamella normal is given by:

$$\phi = \tan^{-1} \alpha + \theta_1 .$$

The expression for the glide strain is [17]:

$$\alpha = \frac{1}{\sin \theta_0} \left\{ \sqrt{\left[\left(\frac{l_1}{l_0} \right)^2 - \sin^2 \theta_0 \right]} - \cos \theta_0 \right\} . \tag{4}$$

In Figs. 5 and 6, the measured lamellar normal orientation is shown in comparison

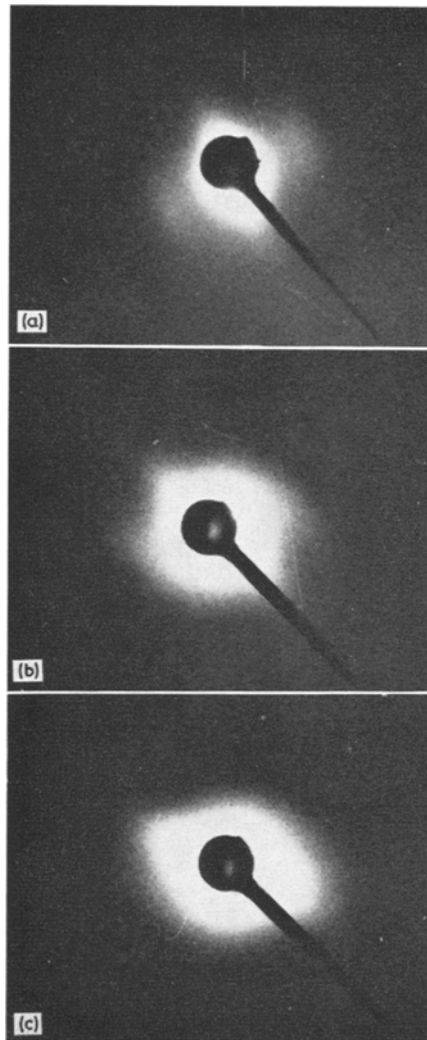


Figure 9 Changes in LAXP with increasing strain for polypropylene ($\theta_0 = 60^\circ$). The tensile axis is vertical.

with the expected curve. In polyethylene the experimental points fall closely on the calculated curve (Fig. 5), supporting the original postulate of intermolecular shear occurring homogeneously within the lamellae.

However for polypropylene ($\theta_0 = 31^\circ$), there appears to be a significant discrepancy. In the plot of the lamellar normal (Fig. 6) the experimental points deviate from the predicted curve by an amount approximately equal to the measurement error ($\pm 3^\circ$). However, the deviation is systematic and not random as might be expected for measurement error.

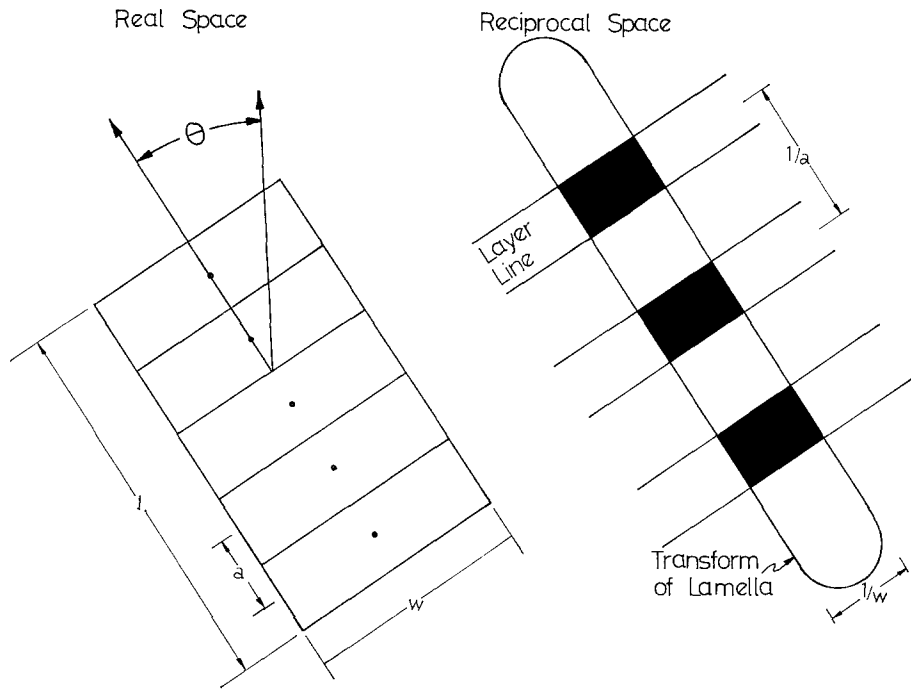
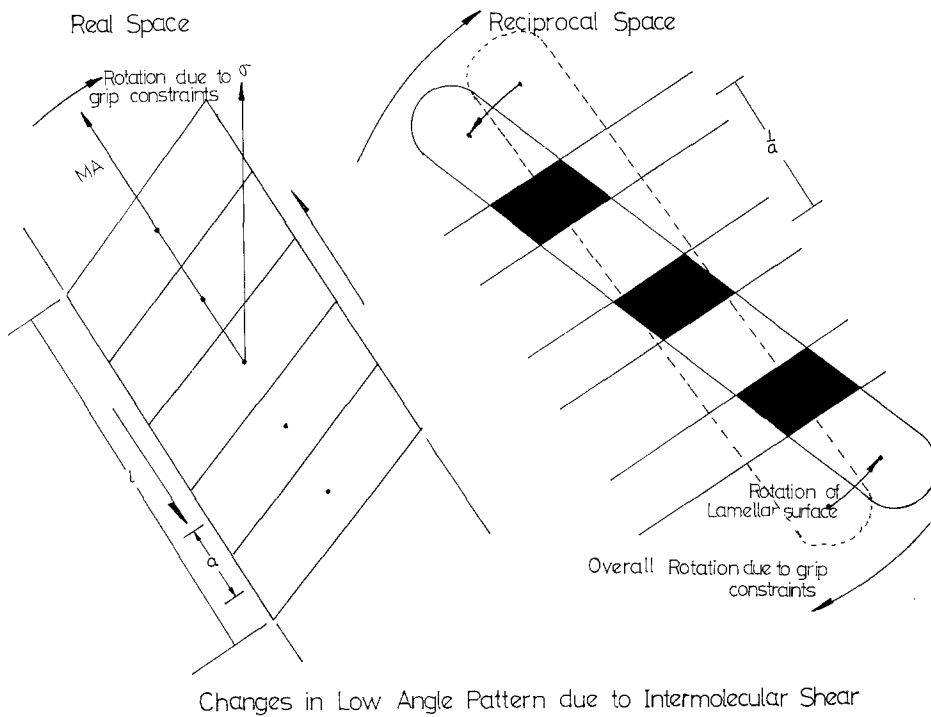


Figure 10 Schematic representation of the stacks of lamellae and the resulting LAXP for untested oriented polymers.



Changes in Low Angle Pattern due to Intermolecular Shear

Figure 11 Schematic representation of the stacks of lamellae and the resulting LAXP for initially oriented polymers which have undergone intermolecular shear.

This deviation may arise from a proportion of interfibrillar shear, producing the same effect macroscopically as homogeneous intermolecular shear, but not resulting in a deformation of the lamella surface. The lamella normal would not then rotate as much as would be predicted for homogeneous intermolecular shear, although the molecular axis would follow the same rotation. An interfibrillar shear component giving a tensile strain of about 4% would account for the observed discrepancy, the majority of the deformation being carried by intermolecular shear within the lamellae. Since the discrepancy between the observed points and the predicted curve remains constant, the interfibrillar shear must occur only at low strains.

In the polypropylene case, there is additional information available from the fibrillar axis orientation derived from the equatorial streak in the LAXP. This is plotted in Fig. 8 with the molecular axis. Under any combination of intermolecular and interfibrillar shear, the fibrillar axis should follow the molecular axis exactly. However, there is a small but systematic discrepancy, with the fibrillar axis rotating approximately 1° faster than the molecular axis. The procedure for changing from LAXP to WAXP was checked and it was found that this did not introduce the observed discrepancy.

Such a discrepancy can be explained by the presence of a small amount of interlamellar shear which would lead to a slightly smaller amount of molecular rotation than fibrillar rotation. Only about 2% tensile strain due to interlamellar shear would be needed to account for the observed discrepancy.

The total deformation of the polypropylene ($\theta_0 = 31^\circ$) therefore is a combination of three different shear modes but with the intermolecular one contributing by far the largest part of the strain at large strains.

In the sample of polypropylene tested at $\theta_0 = 60^\circ$, it was clear that the sense of the rotation of the molecular axis was consistent with an intermolecular shear process. However, because of the inhomogeneous necking behaviour of this specimen, the strain was not measurable and hence quantitative observations were not possible.

The changes in low-angle equatorial scattering (Fig. 9) show that the average shape of the voids or fibres is changing with strain. It is thought that an opening out of the voids in the transverse direction would result in such

changes. Subsequent intermolecular shear would account for the rotation of the molecular axis observed. The initial fibril separation mechanism would be consistent with the mechanism of deformation postulated for large θ from the orientation dependence of yield stress [1]. In [1] it was suggested that as θ_0 approached 90° , the mechanism of yield would change from an intermolecular shear to an interfibrillar or intermolecular separation across the fibrils. The X-ray diffraction patterns bear out this hypothesis.

5. Conclusions

The observation that intermolecular shear predominates in the deformation of oriented high-density polyethylene is not new [2 to 4]. However, this investigation shows clearly that the intermolecular shear occurs homogeneously within the crystalline lamellae and not as a local shear between stacks of lamellae. This is made clear in the changes in orientation of the lamellae, which must be undergoing an internal shear process to produce the changes observed in the LAXP.

For polypropylene, the deformation for the $\theta_0 = 31^\circ$ specimen showed that intermolecular shear was again predominant, although in this case small amounts of interlamellar and interfibrillar shear were inferred. At larger angles $\theta_0 = 60^\circ$, the polypropylene showed a qualitatively different behaviour under tension, and an inhomogeneous "void opening" appeared to precede intermolecular shearing.

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