Chain and fibrillar slip in oriented polyethylene

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High-density polyethylene sheet was oriented by cold drawing and deformed in tension at angles of 40° and 51° to the draw direction at 22° C and at 62° to the draw direction at 105°C. The macroscopic deformation was analysed with the aid of a grid of dots printed on the surface. Rotations of the molecular chain axis and the lamella surface were measured using wide- and low-angle X-ray diffraction.

The macroscopic deformation was found to approximate closely to slip in the direction of alignment of the molecular chain axis. It is concluded that this was produced entirely by chain slip in the first stage of deformation after which fibrillar slip also took place. Fibrillar slip appeared to start after a smaller amount of chain shear at 105° C than at 22° C.

1. Introduction

The predominant mode of deformation in oriented high-density polethylene deformed at room temperature has been shown to be slip in the direction of alignment of the molecular chain axis. The evidence has come from observations made on shear bands [1, 2], and from strain measurements made on test pieces which deformed homogeneously [3-5]. It has been suggested [4-7] that this type of macroscopic deformation could be produced in two ways: (1) by the molecular chains within the individual chain-folded lamella slipping past one another, thus shearing the lamella in the process, (2) by fibrils, formed of stacks of lamellae, slipping past one another without deforming the lamellae within the fibrils. These modes of deformation will be referred to here as chain slip and fibrillar slip respectively. In each mode, slip is in the direction of the molecular chain axis, thus both modes will produce the same deformation geometry in a test piece observed macroscopically (that is, on a scale too large to resolve the fibrillar and lamellar structure) but should be distinguishable with the aid of low-angle X-ray diffraction patterns (LAXP) from which, together with wide-angle X-ray diffraction patterns (WAXP), measurements of lamella deformation can be made. Using this technique Young *et al.* [5] reported chain slip as the predominant mode of plastic deformation in oriented high-density polyethylene deformed in compression, with the suggestion that some fibrillar slip had also occurred. Shinozaki and Groves [4], on the other hand, concluded that while in their tension experiments chain slip occurred in both oriented high-density polyethylene and oriented polypropylene, fibrillar slip took place in the latter but not in the former.

The present paper describes an investigation into the deformation modes of oriented high-density polyethylene tested in tension at 22° C and at 105° C, from which we conclude, in contrast with [4], that fibrillar slip did occur.

2. Experimental

The material used was high-density polyethylene (Rigidex type 2, BP Chemicals Ltd) having a melt flow index of 0.2, a density of 0.96×10^3 kg m^{-3} and a weight average molecular weight of 115 000. Pellets of this material were compression moulded into 1 mm thick sheets at 190° C and quenched into water at 15° C. The sheets were oriented by drawing at 20 $\pm$ 2° C to their natural draw ratio of 8, resulting in a reduction of thickness to 0.2 mm. A square grid of ink dots 0.15 mm apart was then printed on the surface of the oriented sheet with one of the principal grid directions (to be denoted as the y direction) parallel to the direction in which the molecular chain axes had been aligned by drawing (to be denoted as the c direction). The principal grid direction initially at right-angles to

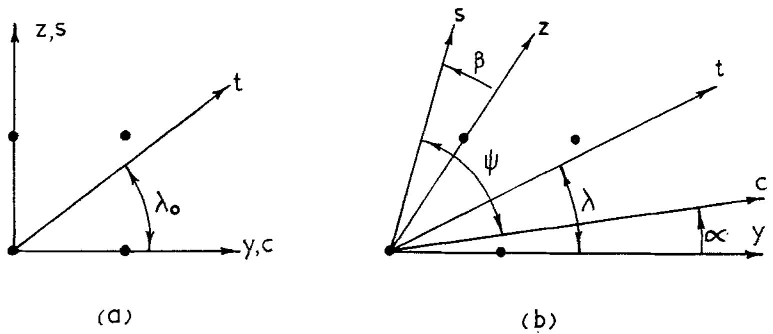


Figure 1 Diagram showing the unit square of the ink dot grid and directions and angles referred to in the text (a) before deformation (b) after deformation. y and z are principal grid directions, t is the direction of the edge of the test piece and the tensile axis, c is the molecular chain axis direction, s is the trace of the lamella surface. Angles α and β have been exaggerated.

y is denoted by z. Fig. 1a is a diagram showing these directions. (After deformation y and z were no longer at right-angles, nor were y and c parallel, as shown in Fig. 1b). The direction perpendicular to the yz plane is denoted by x.

Dumb-bell shaped tensile test pieces with a 10 mm parallel-sided gauge length of width 2.5 mm were cut from the oriented sheet at various angles to the y direction and were deformed in tension at a constant crosshead speed of 1.1×10^{-2} mm sec^{-1} (initial tensile strain rate 1.1×10^{-3} sec^{-1}) in a miniature tensile machine mounted on the stage of an optical polarizing photomicroscope. Initially and after each strain increment a photomicrograph of the ink-dot grid was taken from which the macroscopic strain in the test piece was determined. Without relaxing the strain WAXP and LAXP were obtained simultaneously using pin-hole collimation and an incident beam parallel to x. From these patterns the c direction and the lamella normal direction relative to the grid were determined with estimated errors of $\pm$ 1° and $\pm$ 2° respectively.

Some test pieces were deformed at 22°C. Others were deformed at 105°C using a heated chamber, but the WAXP and LAXP were obtained at 22°C after cooling from 105°C at constant length. Measurement showed no detectable change in strain, in birefringence nor in extinction direction during cooling and further experiments at room temperature showed that the extinction direction and the c direction were parallel at all stages of deformation. For the tests at 105°C several test pieces were used each with the same initial angle between tensile axis and y direction but each strained a different amount.

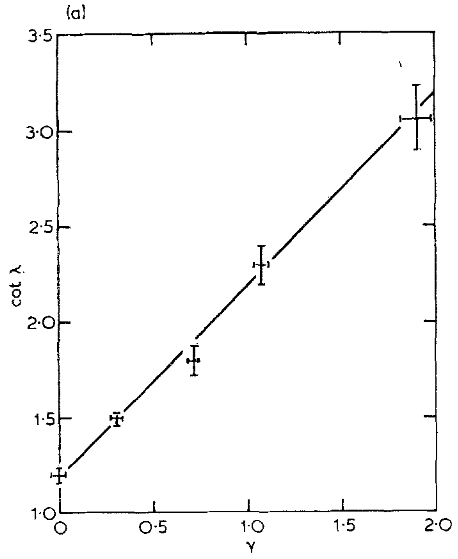
Additional WAXP and LAXP with the beam parallel to y and z were obtained from the oriented material before deformation, both before and after heating to 105°C. In the as-drawn condition before heating, WAXP showed a fibre texture with the molecular chain axes well aligned in the draw direction. LAXP obtained with beams along x and z were two-point, showing a predominance of lamellae with surfaces perpendicular to the draw direction. The LAXP also exhibited a central void streak, indicating the presence of circular-section voids elongated in the draw direction. The texture was to some extent affected by heating to 105°C. The WAXP showed no change in molecular alignment, and the LAXP obtained with beam parallel to x was still two-point, with enhanced intensity, but the void streak was no longer apparent. The LAXP obtained with the beam parallel to z was now a four-point pattern, the points connected by less intense layer lines at right-angles to the draw direction; the void streak was still visible in this pattern. To the eye the material lost the white opacity of the as-drawn condition and became transparent.

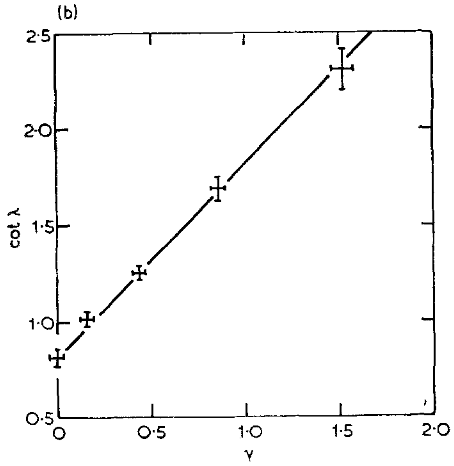
3. Results

3.1. Macroscopic deformation

The test pieces reported on here deformed uniformly over most of the gauge length and measurements were made only in the uniformly deformed regions. There was some fibrillation along the edges of the test pieces extended at 105°C to the largest strains. The maximum tensile strain was 120%.

No change in thickness in the x direction as a result of deformation could be detected; any such change must have been less than 2%, the limit set by the accuracy of the measurements. To





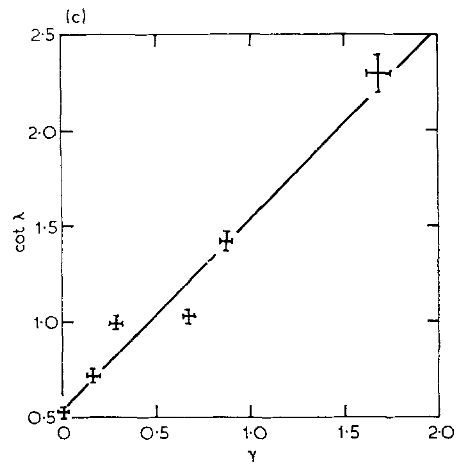


Figure 2 Cot λ plotted against γ (a) for $\lambda_0 = 40°$ tested at 22°C, (b) for $\lambda_0 = 51°$ tested at 22°C, (c) for $\lambda_0 = 62°$ tested at 105°C. The full lines are plots of Equation 2.

this accuracy the deformation was plane strain in the yz plane, as it would be if the mode was slip in the c direction.

The strain in the test piece as revealed by the grid of ink dots was analysed in the following way. The y-axis of the grid was printed parallel to the c direction. Assuming that the test piece deformed by slip in the y direction, the amount of this shear γ is given by

$$\gamma = \cot \omega \tag{1}$$

where ω is the angle between the y and z grid lines, being 90° initially. If λ denotes the angle between the test piece edge (tensile axis) t and the y grid direction after a shear γ in the y direction, and λ_0 the initial value of this angle at $\gamma = 0$ (see Fig. 1), then by the geometry of simple shear in the y direction [8],

$$\cot \lambda - \cot \lambda_0 = \gamma \,. \tag{2}$$

The angles ω, λ_0 and λ were measured and γ was calculated from Equation 1. The data were then checked for their fit to Equation 2 by plotting cot λ against γ. Such graphs are shown in Fig. 2 for $\lambda_0 = 40°$ and 51° tested at 22°C and $\lambda_0 = 62°$ tested at 105°C. In each graph the full line has been drawn through the point (0, cot λ_0) to have a gradient of unity, and from the closeness of the fit it is concluded that the macroscopic deformation mode was slip in the y direction.

3.2. WAXP and LAXP

The y grid line was parallel to the c direction initially, but as deformation proceeded a small deviation developed between the two directions denoted by α in Fig. 1b. Values of α are given in Table I. The accuracy of each value is estimated to be $\pm$ 1°. In all cases the deviation was in the same sense, namely, that the acute angle between c and the tensile axis, t, was smaller than that between y and the tensile axis. Such deviations have been reported [3, 9] and attributed to the fact that there is not a perfect alignment of molecular chain axes in the oriented material. It may be noted that the deviation was in the wrong sense to be accounted for by slip between lamellae. It is assumed in what follows that the

TABLE I Measurements of the angles α and β and of the corresponding shear γ in the y grid direction

γ	α	β
$\lambda_0 = 40°$; tested at 22°C		
0	0°	0°
0.29	1°	−5°
0.61	1°	0
1.07	2°	3°
1.90	$3\frac{1}{2}$°	15°
$\lambda_0 = 51°$; tested at 22°C		
0	0°	0°
0.16	1°	−1°
0.45	1°	3°
0.87	2°	−1°
1.52	$2\frac{1}{2}$°	8°
$\lambda_0 = 62°$; tested at 105°C		
0	0°	0°
0.17	1°	3°
0.28	$2\frac{1}{2}$°	3°
0.66	$4\frac{1}{2}$°	10°
0.86	$2\frac{1}{2}$°	12°
1.67	$1\frac{1}{2}$°	20°

macroscopic deformation mode was slip in the c direction, and it is considered that, because of the small values of α, no serious error will result.

The trace of the lamella surface in the yz plane, denoted by s, (Fig. 1) was initially parallel to the z grid direction, but z and s did not remain parallel throughout the deformation. Values of β, the angle between z and s, are tabulated in Table I, β being measured from z to s with positive values of β indicating that the acute angle between s and c was larger than that between z and c, as illustrated in Fig. 1b. (Negative values of β put s between z and c.) Each β value is accurate to within $\pm$ 2°. There are significant, positive, values of β at shears of 1.52 and 1.90 for deformation at 22°C and at shears of 0.66, 0.86 and 1.67 for deformation at 105°C. That the other values of β at 22°C are significantly different from zero seems doubtful judged by their size and apparently random fluctuations.

The angle ψ between s and c (Fig. 1) was initially 90° but decreased during the deformation of the test piece, indicating that deformation was occurring within individual lamellae. Assuming that this intra-lamella deformation was chain slip, the amount of chain shear, γ_c, was calculated from

$$\gamma_c = \cot \psi \,. \tag{3}$$

The results are shown in Fig. 3 in which γ_c has been plotted against γ, the macroscopic shear in the y direction. The full lines represent the relationship $\gamma_c = \gamma$. At low shears the chain shear was equal to the macroscopic shear but at high shears there were departures from this equality, all in the sense that the chain shear was less than the macroscopic shear. The graphs in Fig. 3 show that departure from the $\gamma_c = \gamma$ equality occurred at a lower value of γ_c in the deformation at 105°C than in the deformation at 22°C and

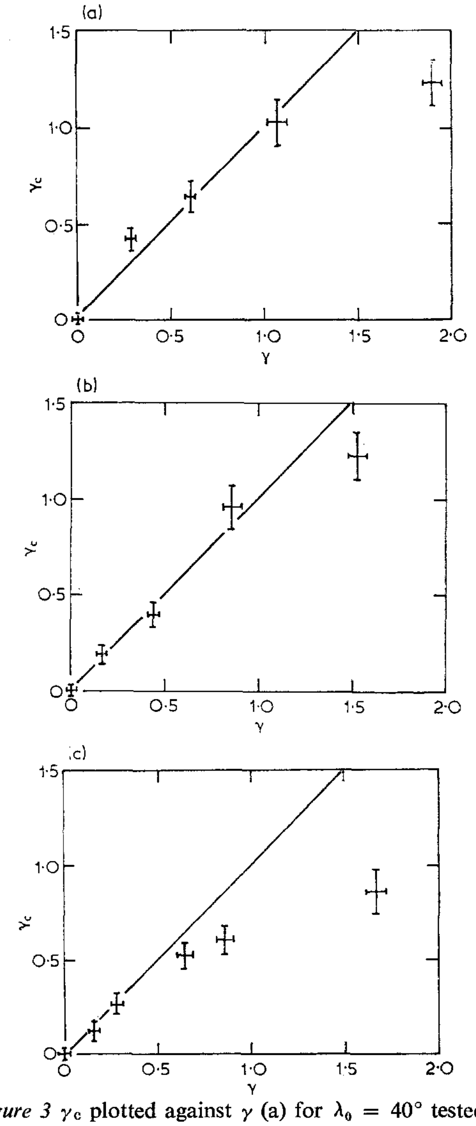


Figure 3 γ_c plotted against γ (a) for λ_0 = 40° tested at 22°C, (b) for λ_0 = 51° tested at 22°C (c) for λ_0 = 62° tested at 105°C. The full lines are plots of $\gamma_c = \gamma$.

suggest that this was due to the difference in test temperature rather than the difference in λ_0.

3.3. Chain slip and fibrillar slip

If the macroscopic deformation had been entirely due to chain slip the lamella surface trace would have remained parallel to the z grid line and angle β would have been zero, furthermore γ_c would have been equal to γ throughout. On the other hand, if fibrillar slip had been the only mode, β would have increased from zero with increasing deformation while γ_c would have been zero throughout. On this basis the results in Table I and Fig. 3 show that deformation started by chain slip alone and at a later stage a significant amount of fibrillar slip occurred. The amount of fibrillar shear, γ_f, is shown plotted against chain shear, γ_c, in Fig. 4. Here γ_f has been calculated from

$$\gamma_f = \gamma - \gamma_c \,. \tag{4}$$

The apparently negative values of γ_f are probably due to experimental error, which is thought to be about $\pm$ 0.1 for γ_f. It appears that fibrillar slip started at a lower value of chain shear at 105°C than at 22°C.

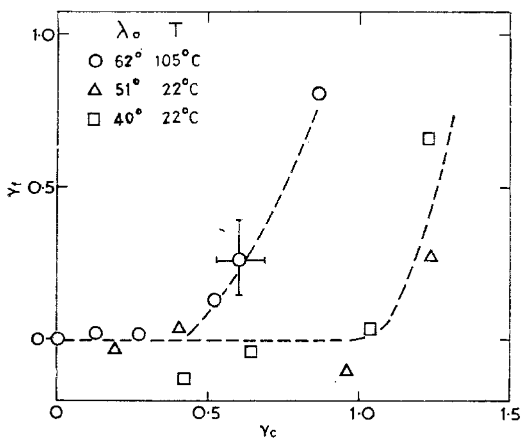


Figure 4 γ_f plotted against γ_c. For the sake of clarity the error bars are drawn for one point only. The broken lines illustrate the suggestion that the temperature of testing had a significant effect on the relationship between γ_f and γ_c.

4. Discussion

Our conclusion that the macroscopic deformation was slip in the c direction is in agreement with earlier work [1-5]. Our finding that fibrillar slip occurred after some initial chain slip is in contrast with the conclusion of Shinozaki and Groves [4] that the deformation in their polyethylene test piece was by chain slip throughout, without fibrillar slip. An examination of the graph in Fig. 5 of Reference [4] shows a discrepancy at large strains between the measured orientation of the lamellae and the orientation calculated on the assumption that all the shear is due to chain slip. This discrepancy, equal to β in our notation, is consistently of the sense which would be caused by fibrillar slip. We have measured β values from this graph and calculated γ_c and γ_f with the results shown in Table II. It does seem possible that the polyethylene of Shinozaki and Groves behaved in the same way as ours, with chain slip occurring alone in the first stages of deformation and fibrillar slip setting in at a later stage.

TABLE II Values of angle β, chain shear γ_c and fibrillar shear γ_f calculated by us from the results of Shinozaki and Groves [4] for polyethylene

Tensile strain	β	γ_c	γ_f
0→30%	0°	0→0.6	0.0
72%	$6\frac{1}{2}$°	1.2	0.4
90%	5°	1.6	0.4
124%	$6\frac{1}{2}$°	1.8	0.8

Young *et al.* [5] suggested that fibrillar slip had occurred in some of their samples. They prepared oriented polyethylene in three different ways, by compression, by compression followed by annealing, and by cold drawing. We have calculated values for γ_c and γ_f from their results and show these, together with values of β, in Table III. Only for the compression-oriented and annealed material are data available for two amounts of chain shear and here, in agreement with our results, fibrillar shear occured at the larger chain shear but not at the smaller.

Otherwise it is difficult to draw firm conclusions from the results discussed here about the circumstances in which fibrillar slip occurs, partly because of uncertainty in γ_f values and partly because of the number of possibly significant variables which were different in the different authors' experiments: for example, the formulation of the polyethylene; the method of preparation, cold drawing (present work), hot

TABLE III Values of angle β, chain shear γ_c and fibrillar shear γ_f calculated by us from the results of Young *et al.* [5]

Method of preparation	β	γ_c	γ_f
Compression-oriented	11°	0.2	0.2
Compression-oriented and	$1\frac{1}{2}$°	0.2	0.0
annealed	$9\frac{1}{2}$°	0.5	0.3
Cold-drawn*	—	0.2	0.0_5

*Lamella slip also occurred in this sample.

drawing [4], compression [5]; testing in tension (present work and [4]), testing in compression [5], measuring with strain applied (present work and [4]), measuring with strain relaxed [5].

Peterlin [6] has described a molecular model for the structure of a drawn crystalline polymer. In terms of this model we suppose that the chain shear would occur within the microfibrils and the fibrillar shear between the fibrils, and that the LAXP void streaks would emanate from voids between the fibrils. One would then look for a correlation between the presence of the void streak and the occurrence of fibrillar slip. In the present work we had void streak and fibrillar slip. In [4] there was void streak and fibrillar slip in polypropylene; there was no void streak in polyethylene and the authors thought no fibrillar slip but we think there may have been. In [5] there was fibrillar slip and no void streak in compression-oriented polyethylene and there was void streak and no fibrillar slip in cold-drawn polyethylene; perhaps the chain shear was insufficient to cause fibrillar slip in the cold-drawn material but the same amount was sufficient to cause it in the draw-oriented unannealed. From these results no clear correlation emerges.

5. Conclusions

We conclude from our work that fibrillar slip has been shown to occur in cold-drawn polyethylene tested in tension, but only after some chain slip has first taken place; the amount of prior chain slip was smaller at 105°C than at 22°C.

Comparison with [4] and [5] show that otherwise the circumstances in which fibrillar slip occur are not clear and there is no simple correlation with the presence or absence of a void streak in the LAXP.

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References

1. M. KUROKAWA and T. BAN, *J. Appl. Polymer Sci.* **8** (1964) 971.
2. A. KELLER and J. G. RIDER, *J. Mater. Sci.* **1** (1966) 389.
3. T. HINTON and J. G. RIDER, *J. Appl. Phys.* **39** (1968) 4932.
4. D. M. SHINOZAKI and G. W. GROVES, *J. Mater. Sci.* **8** (1973) 1012.
5. R. J. YOUNG, P. B. BOWDEN, J. M. RITCHIE and J. G. RIDER, *ibid* **8** (1973) 23.
6. A. PETERLIN, *ibid* **6** (1971) 490.
7. A. KELLER and D. P. POPE, *ibid* **6** (1971) 453.
8. E. SCHMID and W. BOAS, "Plasticity of Crystals" (Chapman and Hall, London, 1968).
9. L. A. SIMPSON, Ph.D. Thesis, University of Surrey, 1972.

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