JOURNAL OF MATERIALS SCIENCE 6 (1971) 485–489

A Simple Model for Mechanical Anisotropy in Specially Oriented Sheets of Low-Density Polyethylene

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The anisotropy of the elastic modulus of specially prepared sheets of drawn, rolled and annealed low-density polyethylene has been analysed quantitatively. These materials were regarded as two-phase composites of crystalline and amorphous regions, in which the interlamellar regions of the polymer were assumed to deform under load by both pure shear and simple shear mechanisms. The anisotropy of the *a-b* and parallel lamellae structures agrees well with the predictions of this simple theory.

1. Introduction

In a recent series of publications [1, 2, 3] the mechanical anisotropy of various types of rolled and annealed low density polyethylene sheets has been analysed qualitatively in terms of two types of relaxation process. These have been termed the *c*-shear relaxation and the interlamellar shear relaxation. A further publication [4] has shown that a quantitative treatment of interlamellar shear leads to a consistent interpretation of the relationship between the observed anisotropy patterns in the losses and the orientation of the lamellae. The present paper carries the treatment one stage further by considering these materials as idealised composite materials and thus predicting the elastic moduli of a variety of structures. It will be shown that the observed experimental data are in reasonable agreement with those predicted on the basis of this simple model.

2. Theory

The morphology of rolled and annealed sheets of low density polyethylene has been extensively studied by Keller and co-workers, by Point and by Seto and Hara (see, for example [5-7]). It has been concluded that a variety of lamellar textures can be produced. The mechanical measurements have been confined to materials showing the three extreme situations illustrated schematically in fig. 1. In this figure the *YZ* plane is always the plane of the sheet.

In the *b-c* sheet, which can be prepared by annealing drawn and rolled materials at 95° C, the crystallographic *b*- and *c*-axes are in the plane of the sheet and *c* (the chain axis) is along the initial drawing direction (I.D.D.). Annealing at 104° C produces *p*-l sheet (Parallel lamellae structure) the crystal lamellae having rotated through 35 to 45° about the *b*-axis. Annealing in a narrow temperature range near 105° C produces further rotation about *b* until *a* and *b* are approximately in the plane of the sheet, and *c* is perpendicular to the plane of the sheet. This structure is termed the *a-b* sheet.

It is not possible to be dogmatic about the details of the arrangement of the lamellae in the polymer. These could exist as platelets of effectively infinite extent compared with the thickness of the interlamellar material, so that the latter could only undergo a *simple* shear deformation with the shear direction parallel to the surfaces of the lamellae. This was indeed the assumption of a previous paper [4]. It is, however, possible to be somewhat less restrictive, and to assume that the platelets are effectively only of infinite extent in one direction, say in the *Y* or *b* direction of the *YZ* plane of the diagram of fig. 1. Under these circumstances the interlamellar material could also deform when the platelets are subjected to a normal stress. The interlamellar material will then undergo *pure* shear.

These ideas lead to a very simple mathematical scheme for predicting the compliance of these

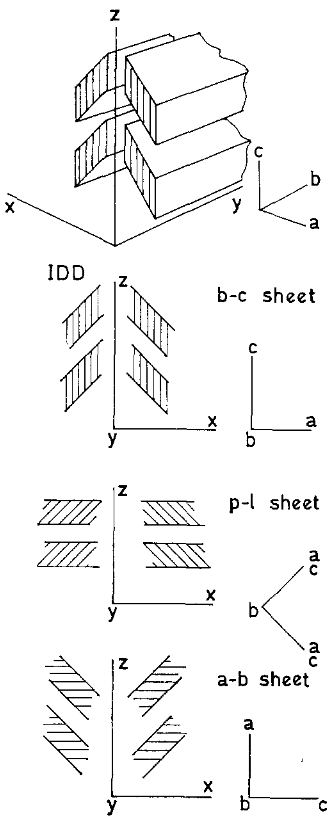

Figure 1 The three types of drawn, rolled and annealed low-density polyethylene sheet. (*YZ* is the plane of the sheet.)

structures. It will be assumed that each material can be considered to consist of parallel lamellae, which are effectively only of infinite extent in one direction. The response of the structure to stress will then be analysed as the sum of two responses, a simple shear deformation produced by the shear component of the applied stress in the planes of the lamellae and a pure shear deformation produced by the normal component of the applied stress in the direction of the lamellar plane normals.

It will be assumed that the interlamellar material is incompressible and has a shear modulus G. For the application of a normal stress to the lamellae, the response is given by the finite elasticity relationships (see, for example, [8]).

For an extension ratio λ in the direction of the lamellar plane normal, the principal extension ratios are λ, $1/\lambda$, 1 there being no extension in one direction in the lamellar plane.

The stress-strain relationship is then

$$\sigma = G\left(\lambda^2 - \frac{1}{\lambda^2}\right)$$

where σ is the applied stress.

For a small strain e, $\lambda = 1 + e$ and $\sigma = 4Ge$.

We will now consider the cases of the parallel lamellae sheet and the *a-b* and *b-c* sheets in turn.

2.1. Parallel Lamellae Sheet

The modulus in the initial draw direction E_0 is clearly identical with that for the pure shear deformation discussed above, and we can immediately conclude $E_0{}^{\mathrm{pl}} = 4G$.

E_{45}, the modulus in the plane of the sheet (the YZ plane) at an angle of 45° to the I.D.D. can be calculated as follows:

A stress σ in the 45° direction can be resolved into a shear stress $\sigma/2$ acting in the lamellar plane direction, together with a normal stress $\sigma/2$ in the lamellar plane normal direction. The resultant strain in the 45° direction e_{45} is then given by the sum of the two contributions due to simple shear and pure shear:

$$e_{45}{}^{\mathrm{pl}} = \frac{1}{2}\left(\frac{\sigma}{2}\right)\frac{1}{4G} + \frac{1}{2}\left(\frac{\sigma}{2}\right)\frac{1}{G} = \left(\frac{\sigma}{G}\right)\frac{5}{16}$$

This gives $E_{45}{}^{\mathrm{pl}} = 3.2G$.

In this analysis we will assume that the deformation of the crystalline lamellae under stress can be neglected, under conditions such as we have now calculated where interlamellar shear is the major deformation mechanism.

2.2. The *a-b* Sheet

We will assume for simplicity at present that the lamellar plane normals are oriented at an angle of 45° with the initial draw direction. For the modulus in the *a* direction the lamellae are then all inclined at 45° to the applied stress and the modulus would be identical to that for the E_{45} modulus in the parallel lamellae sheet i.e. $E_{\mathrm{a}} = E_{45}{}^{\mathrm{pl}} = 3.2G$.

Now consider the application of a stress σ at an angle of 45° to the *a* direction in the plane of the sheet. This stress can be resolved into two components as follows:

(i) A stress normal to the lamellar planes of magnitude $\sigma \cos^2 \gamma$, where γ is the angle between the applied stress and the lamellar plane normal. For this case $\gamma = 60°$.

This stress gives an extensional strain

$$\frac{\sigma \cos^2\gamma}{4G}$$

in the direction of the lamellar plane normals, which gives an extensional strain

$$\frac{\sigma \cos^4\gamma}{4G} = \frac{\sigma}{64G}$$

in the loading direction.

(ii) A shear stress parallel to the lamellar planes of magnitude $\sigma \sin\gamma \cos\gamma$. The corresponding shear strain parallel to the lamellar planes is

$$\frac{\sigma \sin\gamma \cos\gamma}{G},$$

which gives an extensional strain in the loading direction of magnitude

$$\frac{\sigma \sin^2\gamma \cos^2\gamma}{G} = \frac{3\sigma}{16G}$$

Adding the two contributions, the total extensional strain in the 45° direction due to the stress σ is given by

$$e_{45}{}^{\mathrm{ab}} = \left\{\frac{1}{64} + \frac{3}{16}\right\}\frac{\sigma}{G} = \left(\frac{13}{64}\right)\frac{\sigma}{G}$$

i.e. $E_{45}{}^{\mathrm{ab}} = 4.9G$.

2.3. The *b-c* Sheet

If all the plane normals are considered to be oriented at 45° to the initial drawing direction and no other deformation mechanism is operative, then one would expect the anisotropy to be the same as for the *a-b* sheet i.e. $E_c{}^{\mathrm{bc}} = 3.2G$ and $E_{45}{}^{\mathrm{bc}} = 4.9G$.

2.4. General Results for a Distribution of Orientations of Lamellar Planes

The true situation in the material is probably one where there is some distribution of orientation of lamellar planes. Consider a distribution of lamellar plane normals in a plane normal to the sheet containing the initial drawing direction (I.D.D.).

If β is the angle between a lamellar plane normal and the I.D.D. and α the angle in the plane of the sheet which the applied stress makes with the drawing direction, then the angle γ between the applied stress and a lamellar plane normal is given by

$$\cos\gamma = \cos\alpha \cos\beta\,. \tag{1}$$

The general result for the modulus at an angle α to the I.D.D. in the plane of the sheet can be written as

$$E_\alpha = \left\{\frac{\overline{\cos^4\gamma}}{4G} + \frac{\overline{\sin^2\gamma \cos^2\gamma}}{G}\right\}^{-1} \tag{2}$$

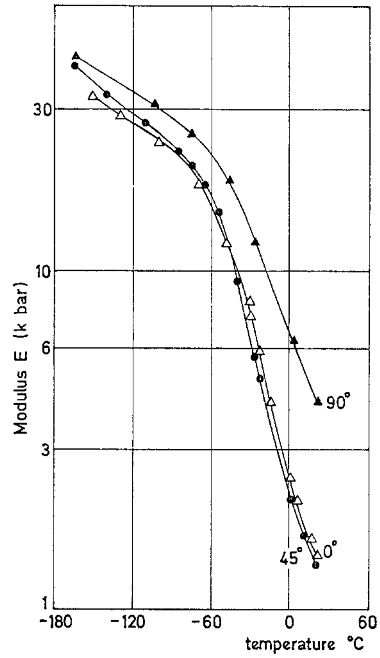

Figure 2 Variation of modulus with temperature for the parallel lamellae sheet in the 0°, 45° and 90° directions.

where the bar over the expressions denotes an average over the distribution of lamellar planes.

Substituting (1) into (2) we have

$$E_0 = \left\{\frac{\overline{\cos^4\beta}}{4G} + \frac{\overline{\sin^2\beta \cos^2\beta}}{G}\right\}^{-1}$$

and

$$E_{45} = \left\{\frac{\overline{\tfrac{1}{4}\cos^4\beta}}{4G} + \frac{(\overline{\tfrac{1}{2}\cos^2\beta} - \overline{\tfrac{1}{4}\cos^4\beta})}{G}\right\}^{-1}$$

3. Comparison of Theory with Experimental Results

The modulus measurements were made using a dead-loading technique on the apparatus described in [1]. The results for the parallel lamellae sheet are presented for the first time (see fig. 2.), the modulus being measured ten seconds after application of the load, and at a strain of ½%. The results for the *a-b* and *b-c* sheets are taken from [1].

Table I shows the predicted and experimental modulus results at room temperature for these three types of anisotropic sheet.

3.1. Parallel Lamellae Sheet

It is seen from Table I that the ratio of E_0/E_{45} is predicted to be

TABLE I Predicted and experimental modulus results.

Parallel Lamellae			*a-b* Sheet			*b-c* Sheet		
	Predicted	experimental (kbs)*		Predicted	experimental (kbs)		Predicted	experimental (kbs)
E_0	4G	1.50	E_a	3.2G	1.24	E_c	3.2G	2.4
E_{45}	3.2G	1.33	E_{45}	4.9G	1.71	E_{45}	4.9G	0.69
E_b	.	4.2	E_b	.	2.48	E_b	.	2.5

*1 kb = 10^8 Nm^{-2}.

$$\left(\frac{4}{3.2}\right) = 1.25\ ;$$

and the measured values at room temperature give

$$\frac{E_0}{E_{45}} = \left(\frac{1.50}{1.33}\right) = 1.12_5\ .$$

The measured anisotropy is slightly less than that predicted, and is probably a consequence of there being some distribution of lamellar planes, i.e. not perfect orientation of planes.

3.2. The *a-b* Sheet

E_{45}/E_a is predicted to be 4.9/3.2 = 1.53, and the measured ratio is 1.38. Again there is less measured anisotropy than predicted on the simple model, and this is also probably a consequence of there not being perfect lamellar orientation. It is worth noting that if $\beta = 39°$ (instead of 45°) the predicted anisotropy agrees exactly with that measured. From the low-angle X-ray pattern of *a-b* sheet [1], this is seen to be a very reasonable estimate of the angle β.

Finally, the theory predicts that $E_a^{ab} = E_{45}^{pl}$ and this is borne out quite well by the experimental results. ($E_a^{ab} = 1.24$, $E_{45}^{pl} = 1.33$ kb at 20°C).

3.3. The *b-c* Sheet

Here there is very little agreement with the theoretical model. Firstly, the value of E_{45} is very much lower than the predicted value. This can be attributed to the *c*-shear relaxation [1-3] which lowers the E_{45} modulus very greatly, and swamps the interlamellar shear at room temperature. In the *a-b* sheet, the *c*-axis is out of the plane of the sheet. Consequently *c*-shear does not take place when a stress is applied in the plane of the sheet, and the anisotropy is then due mainly to the orientation of the lamellae.

Secondly, the value of E_c^{bc} is 2.4 kbars compared with a value of 1.24 kbars for E_a^{ab} in the *a-b* sheet and 1.33 kbars for E_{45} in the *p*-sheet. We would not expect the *c*-shear relaxation to make any contribution to the compliance in this case. If, as we believe from the viscoelastic studies [2, 3] the interlamellar shear relaxation predominates in determining the value of E_c^{bc} and if the proposed model is appropriate, the results suggest that the interlamellar material is less compliant in the *b-c* sheets than in the parallel lamellae or *a-b* sheets. A possible explanation may lie in the different annealing treatments for the preparation of these sheets. The parallel lamellae and *a-b* sheets are prepared by annealing at temperatures of 104 and 105°C respectively, which is extremely close. The *b-c* sheet on the other hand was prepared by annealing at a lower temperature, 95°C. It is possible that at the lower annealing temperature the interlamellar material does not relax to the same extent, and therefore that the modulus in the initial draw direction (the *c* direction) retains a contribution due to the constraints of extended tie molecules.

In the proposed model it is assumed that the compliance in the direction of the *b*-axis is very small. The results in table I show that this is only an approximation, and moreover that the value of E_b is different for the different sheets. A more sophisticated treatment would require that these considerations be taken into account. In physical terms there are at least two possible origins for a significant value of compliance in the *b*-direction. Firstly, there is a lack of complete crystal continuity in the *b*-direction. This factor is incorporated in the Takayanagi models [9] by including a certain amount of "series" connection of the disordered interlamellar material. Secondly, there is the lack of perfect lamellar orientation which allows some shear deformation in the *b*-axis direction. There is not sufficient structural evidence at the moment to support a quantitative treatment of these possibilities. On the other hand, the divergence of the experimental data from the prediction of this simple model may prove useful in attempts to diagnose the physical reasons for departure from the idealised structures.

4. Conclusion

The analysis of these polyethylene sheets in terms of simple composite materials gives a satisfactory understanding of the elastic anisotropy of the *p-l* and *a-b* sheets. It is remarkable that the sheets of different structure are so closely complementary from the viewpoint of their mechanical behaviour.

It should be pointed out again that it has been assumed in calculating the mechanical anisotropy that there is no deformation in the direction of the *b*-axis. This assumption allows a simple theoretical treatment to be adopted, but a more sophisticated treatment would require it also to be taken into account.

Acknowledgement

A. J. Owen is indebted to the Science Research Council for a research studentship.

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Received 14 January and accepted 17 April 1971.