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Letter

Anisotropy in the Shear Modulus of Glassy Polymers

Robertson and Joynson [1] have studied the stress/strain properties of some uniaxially drawn, glassy polymeric films, in simple shear, as a function of the angle (θ) between the direction perpendicular to the shear and the orientation axis of the material. The sense of the angle θ is indicated in fig. 1. The materials studied were uniaxially drawn poly(2,6-dimethylphenylene oxide) and poly(4,4′-dioxydiphenyl-2,2-propane carbonate) with draw ratios 1.65 and 1.46 respectively. For both materials, it was observed that the shear stress, at a total shear strain of 4/3, passed through a pronounced maximum at θ between 55 and 60° and a less pronounced minimum at θ between 145 and 150°.

Similar studies have now been made on uniaxially drawn amorphous poly(ethylene terephthalate) film with a draw ratio of 5. The apparatus used was similar to that described by Robertson and Joynson [1], having two clamps separated by 0.0195 cm constrained to move parallel to one another by low-friction linear bearings, and could be attached to an Instron tensile testing machine for measurements of force and displacement.

The initial shear moduli of the film in different directions could not be measured accurately because of the impossibility of clamping the film so that it was completely flat, the stress/strain curve having therefore a curved toe. There were, however, two approximately equal maxima when θ was equal to 45 or 135°. Such a result is to be expected. After drawing, the increase in the tensile modulus in the draw direction is much greater than the reduction in the tensile modulus in the perpendicular direction. Since, for small strains, shear is equivalent

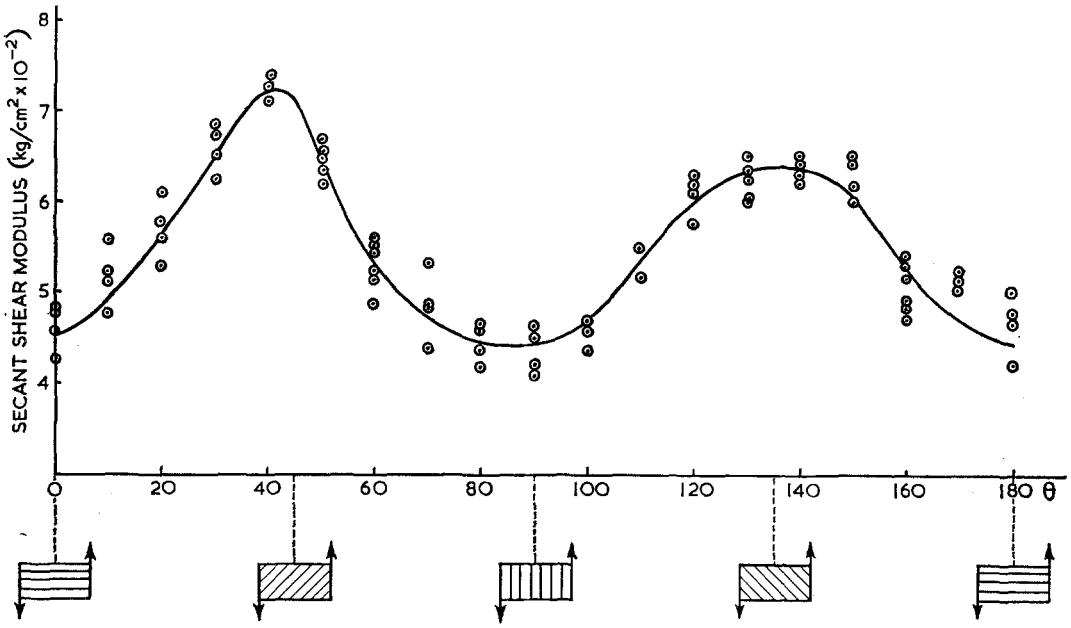

Figure 1 Secant shear modulus (at 100% total shear strain) as a function of θ, the angle between the direction perpendicular to the shear and the orientation axis of the material, for poly(ethylene terephthalate), draw ratio 5.

to simultaneous extension and compression at 45° to the shear direction [2], maxima in the shear modulus should occur when either compression or extension in the draw direction is greatest.

The results are shown in fig. 1 for the secant modulus (stress referred to initial cross-section over total strain) at 100% shear strain. (The nominal shear strain rate was 256%/min.) At such a strain, drawing has occurred in all the samples and, as the stress/strain curve thereafter is relatively flat, the secant modulus gives a measure of the shear yield stress. Again there are two maxima at θ approximately equal to 45 and 135°, but in this case the first maximum is appreciably the larger. Fig. 1 also shows the relationship between the shear and draw directions, the latter being also the direction of the maximum of the angular distribution function for the polymer chain segments in the drawn polymer. It will be seen that the maxima occur when the polymer chains are being most severely extended or compressed. The maximum corresponding to chain extension is more pronounced, as would be expected if the oriented polymer chains were in a state of metastable equilibrium and under a residual tensile stress.

The results of Robertson and Joynson [1] differ markedly from ours in showing only one maximum and one minimum in the range $0° \leqslant \theta \leqslant 180°$, but this difference could be due simply to the residual stress effect being relatively larger with their polymers. A possible explanation at a molecular level is that both the polycarbonate and poly(phenylene oxide) investigated by Robertson and Joynson would be expected to be much more sterically hindered than the poly(ethylene terephthalate) of the present investigation.

It is intended to extend this investigation to a number of polymers showing different degrees of steric hindrance and to investigate the effect of different degrees of orientation.

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