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Non-linear mechanical behaviour in a highly oriented liquid crystal copolyester

D. I. Green*, H. Zhang, G. R. Davies and I. M. Ward†
IRC in Polymer Science and Technology, University of Leeds, Leeds, LS2 9JT, UK
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Oriented liquid crystal copolyesters are mechanically non-linear at surprisingly low levels of strain when stretched in the orientation direction. As the static strain increases the axial Young's modulus also increases in an asymptotic fashion, the effect being most marked above the glass transition. Several models, each with its own distinct philosophy, have been advanced to account for this behaviour. In order to evaluate critically the various models we have studied the non-linear behaviour of a highly oriented random copolyester film over a wide temperature range. We have also measured the shear modulus of the film and similar fibres (where a wider temperature range can be covered) since this is a key parameter in the various theories. On the basis of comparisons between measured and predicted shear moduli we conclude that the models proposed by Allen and Roche, and by Zhang, Davies and Ward describe the non-linearity best, especially at high temperatures where the units of structure are free to rotate, while the model of Northolt and van der Hout is unsatisfactory. None of the models is applicable well below the glass transition. We also note that all the models are exponential in character, whereas better fits to the data are obtained with other empirical asymptotic expressions.

(Keywords: liquid crystalline polymers; mechanical behaviour; copolyester)

INTRODUCTION

The low strain non-linear mechanical behaviour of oriented liquid crystal polymers (LCPs) has been reported by a number of groups[1-7]. As the level of static (axial) stress is increased, the axial Young's modulus increases in an asymptotic fashion. Several models, each with its own distinct philosophy, have been advanced to account for this behaviour[1,4,5,8]. Most are based upon the proposition that very small elemental rotations in highly oriented systems cause a large increase in the macroscopic axial modulus by reducing the microscopic contributions due to shear, which are large, and dependent upon $\langle\sin^2\theta\rangle$, where θ is essentially the angle between the chain axis and the orientation direction.

In order to evaluate critically the various models, we have studied the non-linear behaviour of a highly oriented LCP film over a wide temperature range. The shear modulus obtained from least-squares fits to the non-linear modulus data is compared with that measured directly on the sample or on fibres (where a wider temperature range can be covered). In addition, the macroscopic axial modulus is compared with the chain modulus determined from X-ray measurements.

EXPERIMENTAL

Materials

A thermotropic main chain liquid crystal copolyester consisting of 73% *p*-hydroxybenzoic acid (HBA) and 27% 2,6-hydroxynaphthoic acid (HNA) was studied. Oriented films and strands were provided by Hoechst-Celanese (Summit, NJ, USA) under the trade name Vectra A950. In some previous publications[6,9,10] this is referred to as CO73:27.

Non-linear axial compliance, S'_{33}

The non-linear stress–strain behaviour was examined by measuring the 1 Hz dynamic compliance, S'_{33}, as a function of static stress on a non-resonance dynamic mechanical modulus apparatus. The apparatus and technique of measurement are described in previous publications[7,11-13]. It is worthwhile, however, to record the specific experimental method developed to minimize systematic effects due to stress relaxation of the sample, which might otherwise have rendered the data of limited discriminatory value.

The specimens were first held under a constant 120 MPa stress for several hours; there then followed a similar period during which they were subjected to a small dynamic stress about the 120 MPa static value (the whole procedure designed to minimize later stress relaxation effects and to seat the sample properly in the clamps). The dynamic compliance was measured, first at the average experimental stress (120 MPa) and then sequentially above and below this, with the compliance at 120 MPa being monitored constantly to ensure that the sample properties were not changing significantly. Results were an average of at least five measurements, at a frequency of 1 Hz, with runs acquired in order of descending temperature. Dynamic strains were 0.04% rms at every temperature and stress. Ten minutes was allowed after changing the static stress before measuring the dynamic data.

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*Now at Manchester Museum, The University of Manchester, Manchester M13 9PL, UK

†To whom correspondence should be addressed

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X-ray compliance

The X-ray or chain compliance was measured by recording the shift in 2θ-space of the 43° aperiodic meridional reflection (d-spacing of 0.21 nm) as a function of the stress applied in the axial direction. The technique and apparatus are fully described elsewhere[10,14]. Measurements were made from 0 to 150°C and the stress at a molecular level within the sample was assumed to be equal to the applied stress. A stress programme similar to that described above was followed.

Shear compliance, S'_{44}

The compliance of film samples cut at 45° to the orientation direction was measured in an attempt to obtain the shear compliance of the film. Unfortunately, as described later, this method could not be used above 60°C. Torsion pendulum measurements were therefore made on highly oriented strands of the same material. The first method, although less accurate (15% error), has the advantages that the measurements are made directly on the films, and being a non-resonance technique the frequency can be varied. The second method is considered accurate (5% random error[6,11]), but suffers from the disadvantages that the measurements are made on highly oriented strands rather than the film samples, and that the frequencies of measurement at different temperatures are not constant. The technique of measurement of the shear compliance of highly oriented LCP strands has been described previously[9,13]. Results were obtained over a wide temperature range with the sample under a small axial stress.

The 45° compliance method[12] is less familiar, has not previously been applied to LCP materials, and therefore bears more detailed discussion. The compliance of high aspect ratio samples (>40) cut at 45° to the orientation direction was measured. The samples were clamped in a non-resonance dynamic modulus apparatus and the compliance measured at 0.1, 1 and 10 Hz and at a variety of temperatures. The 45° measurements were not acquired in order of decreasing temperature as lateral stresses appeared irreversibly to affect the sample at elevated temperatures (> 60°C). Samples were subjected to a small static stress (< 30 MPa) and small dynamic strain (< 0.05%).

The relation between the compliance at 45° to the orientation direction and the shear and tensile compliances of the polymer sample is[12]:

$$S^{45} = 0.25[S_{11} + S_{33} + (2S_{13} + S_{44})] \qquad (1)$$

where S^{45} refers to the 45° compliance and the other symbols have their standard meanings. The terms in $2S_{13}$ and in S_{33} are small in comparison to the others on the right-hand side of equation (1) and of opposite sign but similar magnitude; these are therefore neglected and we write:

$$S_{44} = 4S^{45} - S_{11} \qquad (2)$$

hence S_{44} can be readily calculated from measured values of S^{45} and S_{11}. Unfortunately, however, reliable data could not be obtained above 60°C due to irreversible changes which occurred during the measurements.

Transverse compliance S'_{11}

Measurements were made on high aspect ratio specimens cut perpendicular to the orientation direction of the film. The compliance was measured at 0.1, 1 and 10 Hz at a variety of temperatures using the same apparatus as that used to measure S'_{33}. Measurements were not made in order of decreasing temperature, since there was evidence of irreversible structural changes under transverse stress at elevated temperatures. Again, specimens were subjected to low static stresses (< 30 MPa) and dynamic strains (< 0.05%) since they tore readily, especially at elevated temperatures.

ANALYSIS

Non-linear dynamic mechanical measurements

We deal here with the procedure of fitting the experimental data to a possible functional form. Rather than restrict ourselves only to an exponential form, as has been the case previously, we consider three possible simple forms in order to test the dependence of the extrapolated values on the functional form used. The functions are chosen on the basis that they are simple expressions, which are asymptotic at infinite stress, and are written:

$$J = A + B\exp(-C\sigma) \qquad \text{Exponential} \qquad (3)$$

$$J = A + \frac{B}{1 + C\sigma} \qquad \text{Inverse} \qquad (4)$$

$$J = A + \frac{B}{(1 + C\sigma/2)^2} \qquad \text{Inverse squared} \qquad (5)$$

where A, B and C are adjustable parameters, J is the experimentally measured compliance and σ is the static stress. The equations are written such that, if approximated by a power series in σ, the constant and linear terms are the same. A, B and C are therefore as comparable as is easily possible. Curve fitting is accomplished by standard least-squares techniques.

Aggregate modelling

We restrict ourselves to simple aggregate modelling and compare the model parameters, unit compliance and orientation, with those obtained from the non-linear modelling. The assumptions involved in aggregate modelling of highly oriented LCP structures are discussed elsewhere[14]. These result in the simplified aggregate compliance equation:

$$J_A = J_U + \frac{\langle \sin^2 \theta \rangle}{G} \qquad (6)$$

where J_A is the compliance of the aggregate, J_U is the compliance of a unit of substructure, G is the shear modulus and $\langle \sin^2 \theta \rangle$ measures the mean orientation of aggregate units. Following previous work[1], we take J_A as the compliance extrapolated to zero stress using the exponential fit since the precise extrapolation used is of little consequence so far as the model parameters are concerned. The shear modulus is that measured by a free vibrating torsion pendulum which is available over a wider temperature range than the 45° measurements. Plotting J_A against $1/G$ we obtain J_U and $\langle \sin^2 \theta \rangle$. (A small correction is made to J_A to correct it to the frequency at which the shear modulus was measured at each temperature. This is done by interpolation between the 0.1 and 1 Hz data.)

RESULTS

The non-linear data are plotted in *Figure 1* as dynamic compliance *versus* static stress. Values of the adjustable parameters, A, B and C, and of the sum of the squares of the differences between the best-fit curve and the experimental data are given in *Table 1*.

The X-ray data are plotted as apparent modulus *versus* temperature in *Figure 2*. The shear compliance measured by both experimental techniques is plotted in *Figure 3*. The aggregate model plot is shown in *Figure 4*.

DISCUSSION

Non-linear fitting

On the basis of the sum of the squares of the differences between the best-fit curves and the data, the best fit is generally provided by the inverse relationship (equation (4)), and the poorest fit by the exponential relationship (equation (3)). When the fits are examined by eye, however, all are seen to pass very close to the data points and none is dismissed at this point. At the lower temperatures the reduced stress dependence allows excellent fits to be obtained from all three expressions, of course. Only data taken at the higher temperatures show sufficient curvature to begin to discriminate between the functional forms.

Two parameters that can be examined without the need to invoke a particular physical interpretation of the equations are the compliances at zero and infinite stress. These data are plotted as compliance in *Figure 5* and modulus in *Figure 6*. It is reassuring that there is little difference in the predicted zero-stress compliance values whichever functional form is adopted, since previous aggregate modelling has relied on such values.

The predicted infinite stress parameters do depend on the functional form. The differences are best illustrated when plotted in terms of modulus, as in *Figure 6*.

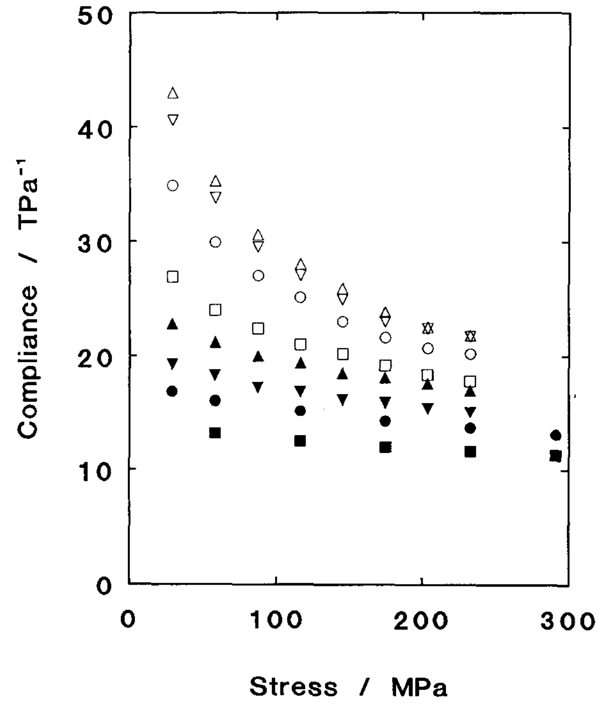

Figure 1 Compliance *versus* stress curves for Vectra film at different temperatures: △, 150°C; ▽, 140°C; ○, 120°C; □, 100°C; ▲, 80°C; ▼, 60°C; ●, 40°C; ■, 0°C

Table 1 Best-fit values for the adjustable parameters A, B and C as defined by equations (3), (4) and (5). The sum of squares column records the sums of the squares of the differences between the measured compliance and best-fit curves

Temp. (°C)	Function^a	A (TPa^{-1})	B (TPa^{-1})	C (TPa^{-1})	Sum of squares
150	Exp	20.5	32.9	13.1	1.0
	Inv.	12.6	45.5	17.2	0.3
	Inv. Sq.	16.7	39.0	15.1	0.4
140	Exp	20.6	29.3	13.3	0.31
	Inv.	13.8	41.1	18.4	0.08
	Inv. Sq.	17.4	35.2	16.0	0.07
120	Exp	18.5	22.4	11.2	0.85
	Inv.	12.2	31.0	12.7	0.57
	Inv. Sq.	15.5	26.8	12.1	0.64
100	Exp	16.3	13.5	9.1	0.23
	Inv.	11.8	18.9	9.1	0.12
	Inv. Sq.	14.2	16.3	9.2	0.16
80	Exp	15.7	8.75	7.9	0.11
	Inv.	12.4	12.5	7.1	0.067
	Inv. Sq.	14.1	10.6	7.5	0.087
60	Exp	14.0	6.59	7.3	0.067
	Inv.	11.2	9.52	6.2	0.050
	Inv. Sq.	12.6	8.04	6.8	0.061
400	Exp	11.9	5.72	5.0	0.010
	Inv.	9.27	8.46	3.9	0.005
	Inv. Sq.	10.6	7.09	4.4	0.007
0	Exp	10.2	3.84	4.5	0.007
	Inv.	8.47	5.73	3.6	0.004
	Inv. Sq.	9.38	4.79	4.1	0.006

^{a} Exp. = exponential; Inv. = inverse; Inv. Sq. = inverse squared

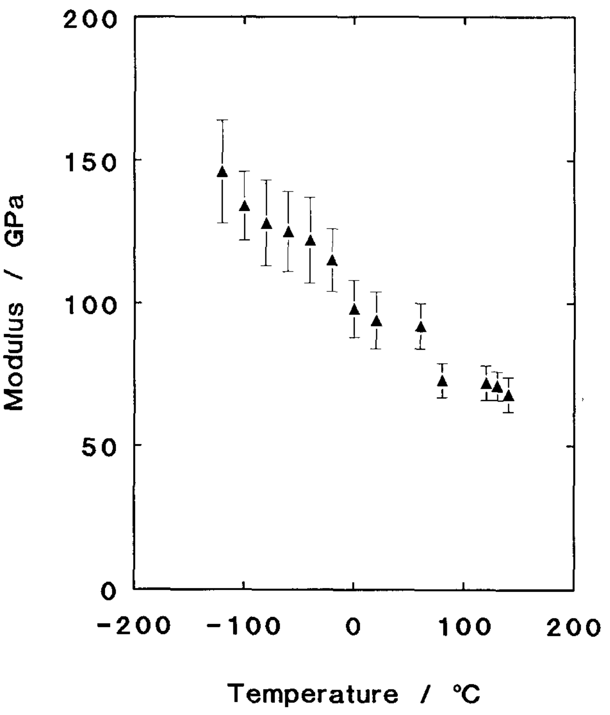

Figure 2 Measured X-ray modulus of Vectra tape as a function of temperature

The exponential form predicts a high, temperature-dependent infinite stress modulus; the inverse form predicts a higher infinite stress modulus which is less temperature dependent, especially above about 80°C; the inverse-square form predicts values intermediate between these extremes. Intuitively, one might expect that the

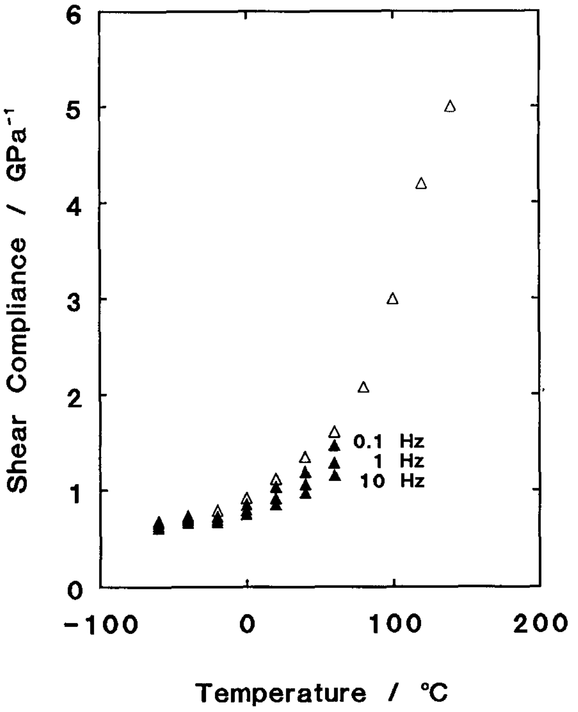

Figure 3 Shear compliances measured by torsion pendulum (△) and by 45° compliance measurements (▲)

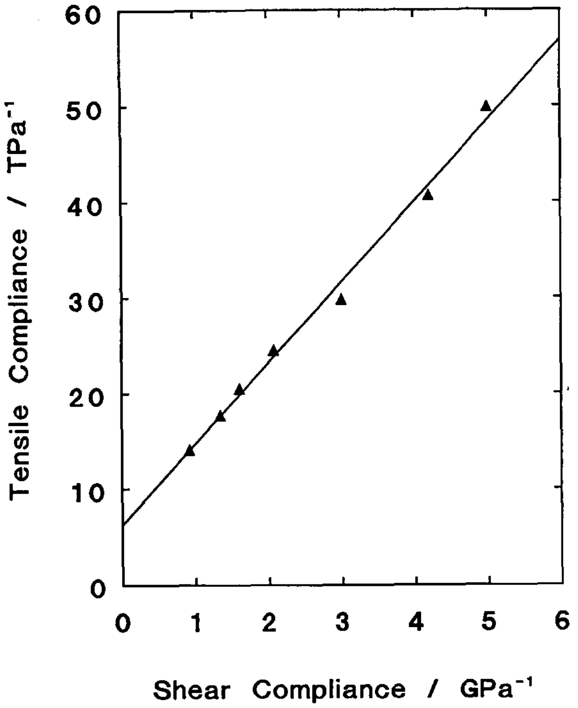

Figure 4 The simplified aggregate model for Vectra A950

modulus of the fully aligned chain would not be particularly temperature dependent and therefore prefer the inverse form. The exponential form is, however, generally predicted by theories.

Measured X-ray chain moduli are compared with predicted infinite stress moduli in *Figure 7*. The measured chain modulus and predicted infinite stress moduli are expected to be similar, although there is a frequency difference to be taken into account since the chain modulus is measured at an extremely low equivalent frequency whereas the infinite stress moduli are based on 1 Hz data. We see that the X-ray chain modulus is generally in good agreement with the infinite stress moduli but that the exponential model predicts an infinite stress modulus which is significantly less than the chain modulus above the glass transition. This is a further suggestion that the inverse forms should be considered.

Exponential models

We consider exponential forms, despite the comments above, since the readily accessible theoretical treatments

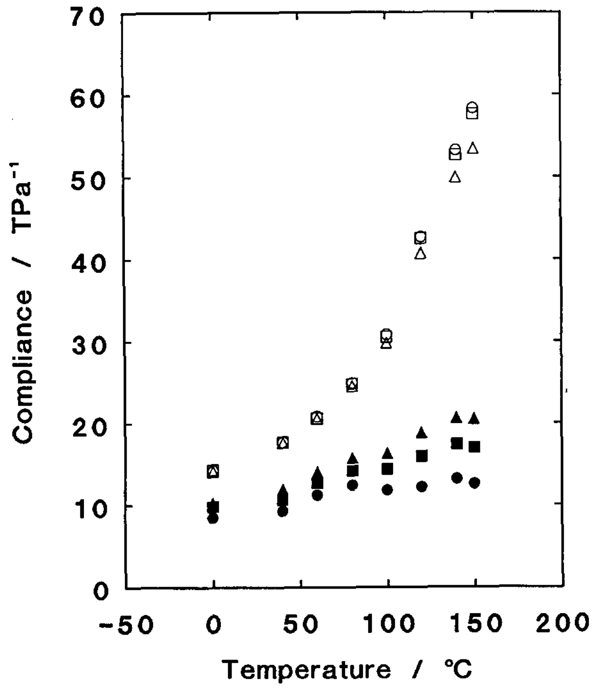

Figure 5 Predicted zero (open symbols) and infinite stress (solid symbols) compliances. △, Exponential function; ○, inverse function; □, inverse squared function

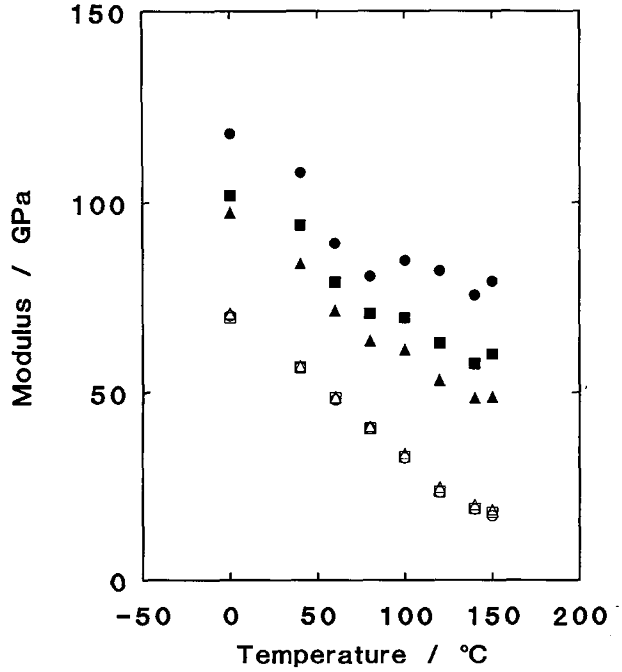

Figure 6 Predicted zero and infinite stress moduli. Symbols as in *Figure 5*

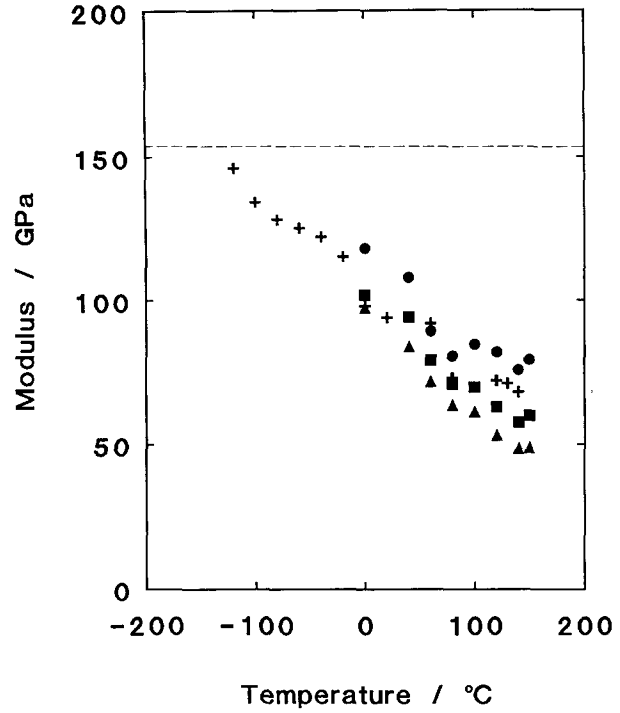

Figure 7 Comparison of the infinite stress moduli predicted by extrapolation of the various functions (symbols as in *Figure 5*) and the chain modulus measured by X-ray diffraction (+). The dotted line shows the unit modulus deduced from the aggregate modelling

predict an exponential functional form for compliance *versus* stress[1,4,5]. Two groups in particular have dealt with this problem. Allen and Roche[4] obtain the equation:

$$J_{\mathrm{A}} = J_{\mathrm{U}} + \frac{\langle \tan^2 \theta \rangle_0}{G} \exp(-2\sigma/G) \qquad (7)$$

using powerful but conceptually simple tensor transformation arguments, while Northolt and van der Hout[5] obtain:

$$J_{\mathrm{A}} = J_{\mathrm{U}} + \frac{\langle \sin^2 \theta \rangle_0}{2G} \exp(-\sigma/G) \qquad (8)$$

from a more specific structural model. Zhang *et al.*[1] have shown how an equation similar to that due to Allen and Roche can be obtained on a simple physical basis. They obtain:

$$J_{\mathrm{A}} = J_{\mathrm{U}} + \frac{\langle \sin^2 \theta \rangle_0}{G_{\mathrm{dyn}}} \exp(-2\sigma/G_{\mathrm{stat}}) \qquad (9)$$

where J_{A} is the measured compliance, J_{U} is the compliance at infinite stress, $\langle \sin^2 \theta \rangle_0$ is the zero-stress orientation parameter, G_{dyn} is the shear modulus at the dynamic frequency (in this case 1 Hz), σ is the static stress, and G_{stat} is the static shear modulus. Equation (9) is identical to equation (7) with the exception that $\langle \tan^2 \theta \rangle_0$ is replaced by $\langle \sin^2 \theta \rangle_0$ and that the frequency or time dependence of the shear modulus is explicitly included. In view of the similarity of this expression to the Allen expression, which predates it, we will generally refer to it as the Allen model since there is no significant difference between $\langle \tan^2 \theta \rangle_0$ and $\langle \sin^2 \theta \rangle_0$ in the highly oriented systems studied here.

Using these models, the parameters, A, B and C of the exponential fitting are accorded a physical meaning. We test them by investigating whether predicted parameters are in agreement with values determined directly by experiment. The parameter that can be most fairly tested is the exponent, C, which according to the Allen model ought to be $2/G_{\mathrm{stat}}$ and according to the Northolt model ought to be $1/G_{\mathrm{stat}}$. It is important to note that the shear moduli in the exponent C are static shear moduli since they are associated with the application of a static stress. More correctly, they are moduli relevant to times some tens of minutes after the application of a static stress since this is a typical time for which the stress was applied prior to obtaining dynamic data. This would correspond to dynamic moduli at about 10^{-4} Hz.

The shear modulus at 10^{-4} Hz can be estimated between 0 and 60°C by linear extrapolation on a logarithmic plot of the shear modulus measured by the 45° compliance method at 0.1, 1 and 10 Hz. The shear modulus data measured by the free vibrating torsion pendulum are available over a wider range of temperatures, and here it is possible to make an estimate of G_{stat} using the Alfrey approximation[1,15]:

$$\frac{\partial G'(\omega)}{\partial \ln(\omega)} = \frac{2}{\pi} G''(\omega) \qquad (10)$$

where $G''(\omega)$ is the imaginary part of the shear modulus[11]. *Figure 8* compares modelled and experimentally measured shear moduli over a wide temperature range.

Values of G_{stat} estimated using the Northolt model are significantly lower than those measured experimentally and we conclude that this model is not applicable to the highly oriented liquid crystal copolyesters. The Allen model estimates of G_{stat} are in much better accord with measured data. At low temperatures, however, (less than the glass transition temperature, T_{g}), there is increasing disagreement between the Allen model and experiment.

The Allen model relies on the assumption that units of structure undergo rotations rather than changing their physical properties as stress is applied. Below T_{g}, however,

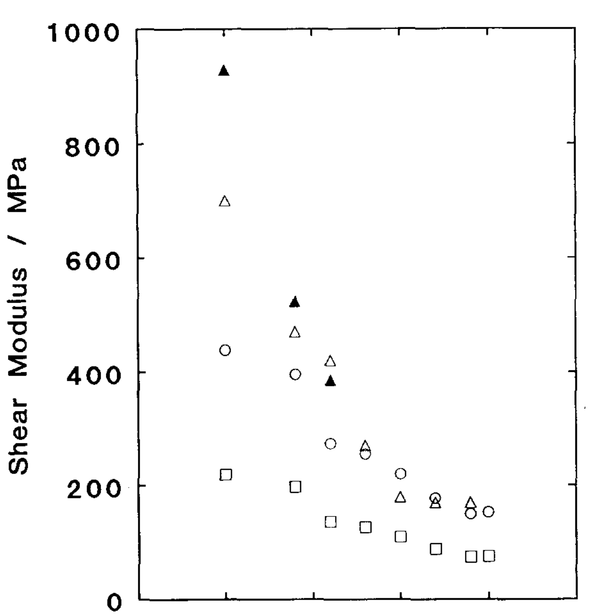

Figure 8 Comparison of the shear moduli predicted by the Allen model (○) and the Northolt model (□) with the shear modulus measured by torsion (△) or by the 45° method (▲)

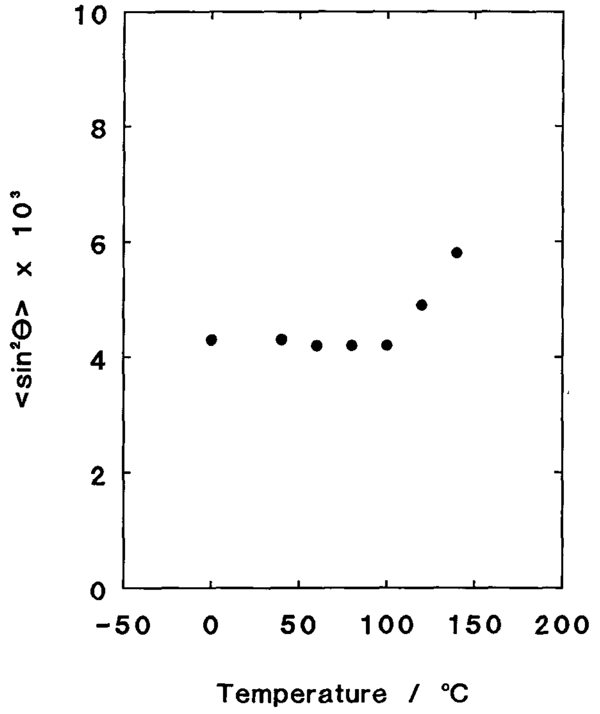

Figure 9 $\langle \sin^2 \theta \rangle$ as a function of temperature deduced from fitting the Allen model

the polymer chains have reduced mobility and changes in unit properties and structure under an axial stress may become more probable. For example, there may be significant changes in molecular packing, dihedral angles, bond angles or even bond lengths. This is not considered by the Allen model and may account for the increasing discrepancy between measured and predicted parameters at low temperatures.

The parameter B is equated with $\langle \sin^2 \theta \rangle_0 / G_{\mathrm{dyn}}$ in the Allen model. *Figure 9* shows predicted values of $\langle \sin^2 \theta \rangle_0$ as a function of temperature. The values are constant up to about 100°C and then show a slight increase, consistent with increasing disorientation above T_g.

Aggregate modelling

Following our earlier research we calculate an orientation parameter and unit compliance from the plot suggested by equation (6), the simplified aggregate compliance equation (see *Figure 4*). The model parameters deduced from this plot are:

$$J_u = 6.25 \pm 0.6\,\mathrm{TPa}^{-1} \qquad (E_u = 160 \pm 16\,\mathrm{GPa})$$

$$\langle \sin^2 \theta \rangle = 0.009 \pm 0.001$$

The aggregate model provides a sound basis for modelling the mechanical properties since there is a linear fit in *Figure 4* with a realistic intercept. Further, the aggregate unit modulus, E_u, of 160 GPa compares favourably with low temperature X-ray modulus measurements.

Making a comparison between $\langle \sin^2 \theta \rangle$ determined by the Allen model and the aggregate model we see that, although these are the same order of magnitude, the aggregate model value is significantly larger. Further, the aggregate model presupposes a temperature-independent orientation parameter whereas the Allen model suggests that the orientation parameter increases slightly above 100°C. These discrepancies are not considered serious since in neither model is the unit under consideration defined. We suppose that since the orientation parameter evaluated using the Allen model is smaller, this model deals with larger units than the aggregate model.

CONCLUSION

We have examined the low strain non-linear mechanical behaviour of highly oriented Vectra A950 film over a wide temperature range. If quality of fitting is used to distinguish possible functional forms (for compliance *versus* static stress) we find that the data are best described by simple empirical inverse or inverse square relations, with exponential relations being less satisfactory, although still good. Chain moduli measured by X-ray techniques agree well with infinite stress moduli predicted by the inverse relations over a wide temperature range. The chain modulus measured at low temperature is in good agreement with the unit modulus predicted by aggregate modelling.

The simple models considered predict exponential functional forms and provide satisfactory fits to the data. On the basis of comparisons between measured and predicted model parameters we conclude that the models proposed by Allen and Roche[4] and Zhang *et al.*[1] describe the non-linearity best, especially at high temperatures where the units of structure are free to rotate, whilst the model of Northolt and van der Hout[5] is unsatisfactory. None of the models is applicable well below T_g.

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