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Correlations between the transverse mechanical and shear properties in highly oriented liquid-crystal copolyesters

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Measurements of the transverse extensional compliance S_{11} of highly oriented films of two liquid-crystal copolyesters are reported over a wide range of temperature and frequency. These results are compared with measurements of the shear compliance S_{44} to show that there is a simple linear relationship between S_{11} and S_{44} over a wide temperature range. Models based on stiff fibres or on laths embedded in an isotropic incompressible matrix are advanced. These are instructive in providing some physical understanding on the basis that S_{11} is determined by shear within the structure.

(Keywords: liquid-crystal copolyesters; transverse compliance; shear compliance)

INTRODUCTION

There are few reports of the transverse mechanical properties of highly oriented liquid-crystal polymers[1,2]. This is partly because the object of orientation is usually improvement of the axial modulus, which then becomes the property of most interest, and partly because the transverse properties are usually difficult to measure. The transverse properties are, however, of importance in mechanical modelling, and are required if a complete picture of the mechanical behaviour of the material is to be obtained.

THEORY

The mechanical properties of an anisotropic elastic solid are defined by the generalized Hooke's law, which is conveniently written in the abbreviated notation:

$$e_p = S_{pq}\sigma_q$$

where e_p and σ_q are the six independent components of strain and stress, respectively, with $p, q, = 1, 2, \ldots, 6$, and for convenience we have chosen to work in terms of the compliance constants S_{pq}.

For a polymer film with orthorhombic symmetry S_{pq} form the elements of the matrix:

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{13} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix}$$

so that there are nine independent compliance constants.

For a film of fibre symmetry this matrix reduces to:

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \end{pmatrix}$$

so that there are now only five independent compliance constants. This paper presents a correlation between S_{11} and S_{44} and discusses its physical origins.

EXPERIMENTAL

Materials

Two thermotropic main-chain liquid-crystal copolyesters (LCPs) were studied. Hoechst Celanese (Summit, New Jersey, USA) provided the samples as thin films processed to a high orientation and as highly oriented strands of about 1 mm diameter. Compositions are identified by the tradename Vectra (indicating a main-chain LCP) followed by a letter and number (indicating a particular composition and annealing treatment). Vectra A950 is a two-component system made up of 73% *p*-hydroxybenzoic acid (HBA) and 27% 2,6-hydroxynaphthoic acid (HNA). It is a well characterized system which has previously been labelled CO73:27[3-5]. Vectra E950 is a four-component system made up of 60% HBA, 5% HNA, 17.5% terephthalic acid (TA) and 17.5% biphenyldiol (BP), and has previously been labelled COTBP[4,5]. The Vectra A950 film was nominally 9 μm thick and the Vectra E950 nominally 250 μm thick; both were annealed.

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Transverse mechanical properties

Experimental techniques used to characterize the transverse mechanical properties of highly oriented polymer samples are almost always inherently less accurate than those used to characterize the axial mechanical properties[6]. Drawing and spinning processes produce samples that lend themselves naturally to the measurement of the axial compliance whilst making the transverse compliances difficult to measure due to the sample shape and lack of transverse strength.

Methods used to measure the transverse compliances of highly oriented LCPs include compression of circular-section fibres between glass plates[7,8], and high-frequency modulus measurements on injection-moulded plaques of inhomogeneous orientation followed by extrapolation to the modulus of the highly oriented skin layers[1]. The fibre compression measurements rely on the specimen being circular in cross-section and of uniform high orientation, conditions that are difficult to achieve in practice. The high-frequency measurements rely on assumptions in the extrapolation and solution for all of the compliance constants.

A more direct and accurate method of finding the transverse compliance is to measure it directly on suitable samples cut perpendicular to the orientation direction. The recent availability of large uniform highly oriented LCP films has made it possible to undertake such measurements. All data are reported with respect to axes in which axis 3 is the draw direction, 2 is perpendicular to the plane of the film and 1 is in the plane of the film, perpendicular to the draw direction.

Measurements were made on high-aspect-ratio specimens cut from the Vectra films perpendicular to the orientation direction. These were clamped in a non-resonant dynamic mechanical modulus apparatus[3,4,6,9] and the compliance measured at 0.1, 1 and 10 Hz and a variety of temperatures. Measurements were not made in order of decreasing temperature, as is usually the case, since there was evidence of irreversible structural changes under transverse stress at elevated temperatures. Specimens were subjected to low static stresses (<30 MPa) and dynamic strains (<0.05%), conditions that were imposed because, when cut perpendicular to the orientation direction, the tapes tore readily.

Shear properties

The experimental technique used to characterize the shear compliance S_{44} was by free vibrating torsion pendulum. This technique of measurement has been described previously[3,4,6,9] and was adopted with negligible modification in the measurements reported here. It is considered accurate (estimated 5% random error[10]), but suffers from the disadvantages that the measurements are made on highly oriented strands, rather than on the film samples, and that the frequencies of measurement are not constant as a function of temperature.

RESULTS

Figure 1 shows the transverse compliance of Vectra A950 and of Vectra E950 at 0.1, 1 and 10 Hz as a function of temperature. In both cases, considerable irreversible deformation of the samples was observed to occur above 60°C: sample extensions of 2% at 80°C and up to 6% at 100°C were noted. Above this temperature, necking and macroscopic reorientation (with the chain axes rotating towards the axis of applied stress) were observed. The measurements at 80°C and above are therefore not considered representative of the unmodified LCP structure.

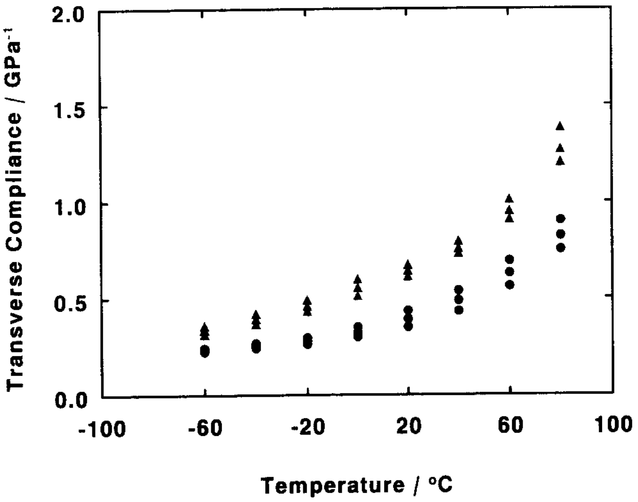

Figure 1 The transverse tensile compliance of Vectra A950 9 μm film (●) and Vectra E950 250 μm film (▲) measured as a function of temperature at 0.1, 1 and 10 Hz. Measurements were made under 20 MPa static stress, the sample being conditioned until a steady state was reached prior to measurement. Above 60°C large irreversible deformations were noted which changed the sample properties

Figure 2 shows the shear compliance of Vectra A950 and of Vectra E950 measured over a wide temperature range using a free vibrating torsion pendulum.

Errors

The measured transverse compliance values are considered relatively accurate, with a variety of small errors combining to give a total estimated error of no more than 5%[10]. Random errors in the shear measurements are similarly considered to be no more than 5%[10]. Both of these estimates are made considering both measurement reproducibility and possible small systematic errors.

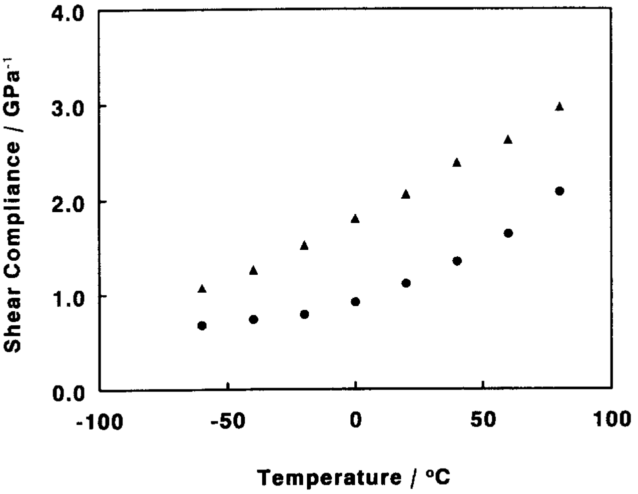

Figure 2 Shear compliance of Vectra A950 (●) and of Vectra E950 (▲) as a function of temperature at frequencies between about 0.2 and 0.5 Hz

There was concern that the shear measurements, made on strands with a different morphology to the film samples (the strands have highly oriented outer layers, but only poorly oriented cores[11]), might not be representative of the fully oriented LCP. As discussed previously[10], however, the measured shear properties of the strands are governed almost exclusively by the properties of the outer layers, and even in the extreme case where a core of inhomogeneous orientation occupied the innermost half of the strand, the measured shear compliance would only be changed by a few per cent.

DISCUSSION

The axial and shear moduli ($1/S_{33}$ and $1/S_{44}$) of many LCP materials have been reported[3,4]. In contrast, very few data relating to the transverse mechanical properties, particularly as a function of temperature or frequency, are available.

Changes in the axial modulus with temperature have been explained on the basis of an aggregate model in which changes in shear modulus coupled with the slight misorientation of units within the aggregate cause the fall in tensile modulus with temperature due to the increasing importance of inter-unit shear[12,13]. The variation in shear modulus with temperature is, however, attributed to changes at a molecular level within the LCP.

We first show that an aggregate-type model does not explain the temperature variation of the transverse compliance of the LCPs. The equation predicted for the transverse tensile compliance of an aggregate of units of structure with transverse isotropy is[6]:

$$\begin{aligned} S_{11} &= 0.125\langle 3\cos^4\theta + 2\cos^2\theta + 3\rangle S^{\mathrm{U}}_{11} \\ &\quad + 0.25\langle 3\cos^2\theta\sin^2\theta + \sin^2\theta\rangle S^{\mathrm{U}}_{13} \\ &\quad + 0.375\langle \sin^4\theta\rangle S^{\mathrm{U}}_{33} \\ &\quad + 0.125\langle 3\cos^2\theta\sin^2\theta + \sin^2\theta\rangle S^{\mathrm{U}}_{44} \qquad (1) \end{aligned}$$

where the unsuperscripted coefficient refers to the compliance in the macroscopic frame and coefficients with the superscript U refer to compliances of units of structure; θ is the misorientation angle between the symmetry axes of the unit and the aggregate; and the angle brackets indicate averages of the orientation parameters. This relation can be radically simplified for the highly oriented systems under consideration. We have good evidence that $\langle\cos^4\theta\rangle \cong \langle\cos^2\theta\rangle \cong 1$ and that $\langle\sin^4\theta\rangle$ and $\langle\sin^2\theta\rangle$ are small. Since $S^{\mathrm{U}}_{33} \ll S^{\mathrm{U}}_{11}$, the third term in equation (1) is immediately eliminated. Also, using the best available estimates[9,10], $S^{\mathrm{U}}_{13}\langle\sin^2\theta\rangle \ll S^{\mathrm{U}}_{11}$, eliminating the second term, and $S^{\mathrm{U}}_{44}\langle\sin^2\theta\rangle \ll S^{\mathrm{U}}_{11}$, eliminating the fourth. This leaves the very simple relationship:

$$S_{11} \cong S^{\mathrm{U}}_{11} \qquad (2)$$

Simply put, the transverse compliance of the aggregate is equal to the transverse compliance of the unit in highly oriented systems. This mirrors the situation for the shear modulus, where $S_{44} \cong S^{\mathrm{U}}_{44}$ as has been shown previously[14].

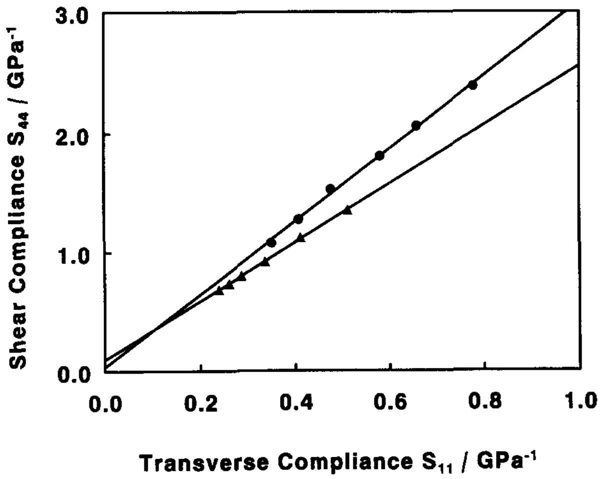

Figure 3 Shear compliance *versus* transverse tensile compliance at 0.3 Hz, for Vectra A950 (●) and Vectra E950 (▲)

In common with the shear modulus, therefore, the temperature variation of the transverse modulus is the result of processes at the microscopic level affecting the weak interchain van der Waals interactions. With this in mind, it seems possible that there may be some correlation between the shear and transverse mechanical properties.

Figure 3 shows the shear compliance plotted against the transverse compliance over a wide temperature range for Vectra A950 and Vectra E950. Since the transverse static stress induced structural changes in the samples at temperatures of 60°C and above, these results are excluded.

Inspection of *Figure 3* reveals the remarkable result that the shear and transverse tensile compliances of both Vectra A950 and Vectra E950 are very simply related over a wide temperature range. To within errors, a straight line passing through the origin is obtained and we can write:

$$S_{44}(T) = kS_{11}(T) \qquad (3)$$

where k is a constant with a value of 2.5 ± 0.3 for Vectra A950 and 3.1 ± 0.3 for Vectra E950.

In an isotropic incompressible solid it is well known that the shear compliance is three times the tensile compliance[6] and k for an isotropic solid is therefore 3.0. In general, no relationship between S_{11} and S_{44} is required in an anisotropic body (although the shear compliance is often between 1 and 2 times the transverse compliance in highly oriented polymer systems at room temperature[6]). Since both S_{44} and S_{11} are almost exclusively concerned with processes affecting the interchain potentials in highly oriented LCPs, and since the nematic structure is relatively simple, some relationship between the two is perhaps not unexpected. The question is, can we understand values of k less than 3 in terms of a simple physical model of these systems?

In these highly oriented systems S_{44} and S_{11} are about two orders of magnitude greater than the axial compliance S_{33}, indicating that they are both dominated by interchain forces. In terms of developing models for the mechanical behaviour it is therefore reasonable to consider that the predominant process will be shear deformation, but with constraints produced by the long extended chains which have such a high axial stiffness that the structure can be considered to be inextensible locally in the chain-axis direction. We are therefore led to consider models that are analogous to the reinforcement of a soft matrix by inextensible rods or, perhaps as we shall see, laths. For simplicity it will be assumed that the soft matrix is incompressible. This is a justifiable assumption since it is equivalent to assuming that the shear modulus is much less than the bulk modulus.

First then, we develop a model in which an isotropic incompressible solid is reinforced by a small volume fraction of parallel high-modulus fibres. This system is not unlike a block of rubber reinforced by stiff parallel needles, and one could make the physical analogy that the rubber represents the interchain potentials and the needles the covalent forces along the LCP chains. It is convenient to develop the model in terms of rubber elasticity theory in which the strain energy function for the system is written[6]:

$$U = 0.5G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{4}$$

where G is the shear modulus and the λ_i are the extension ratios.

The lateral modulus is obtained by considering a deformation λ in the direction transverse to the direction of the reinforcing fibres. For the incompressible solid we then have $\lambda_1 = \lambda$, $\lambda_2 = 1/\lambda$ and $\lambda_3 = 1$, and the lateral stress σ is thus given by:

$$\sigma = \left(\frac{\partial U}{\partial \lambda}\right) = G\left(\lambda - \frac{1}{\lambda^3}\right) \tag{5}$$

Since, for small strains, λ can be written as $1 + \epsilon$, where ϵ is the lateral strain, we write:

$$\sigma \cong G[1 + \epsilon - (1 - 3\epsilon)] = 4G\epsilon \tag{6}$$

from which it can be seen that the value of k is predicted to be 4 since $S_{11} = \epsilon/\sigma$ and $S_{44} = S_{55} = S_{66} = 1/G$ in the limit of negligible volume fraction of fibres.

For the oriented LCPs measured here the experimental values of k are 3.1 and 2.5. Clearly, this model is taking us in the wrong direction. The constraint introduced does not affect S_{44} but it reduces S_{11} (and S_{22} similarly).

If we wish to retain physically important features of the model, we have limited scope for further development. To summarize, we believe that the following constraints are physically realistic:

1. The samples are axially very stiff such that all S_{3i} approximate to zero.
2. The samples deform easily in shear, thus leading to 'incompressible' behaviour. Taken with constraint 1 above, this predicts $S_{11} = -S_{12}$.
3. The samples are cylindrically symmetric; hence $S_{11} = S_{22}, S_{44} = S_{55}$ and $S_{66} = 2(S_{11} - S_{12})$.

The consequence of these assumptions, combining constraints 2 and 3 above, is that we must have $S_{66} = 4S_{11}$. Room-temperature ultrasonic measurements on compacted fibres (to be reported elsewhere) yield $S_{66} = 1.2\,\mathrm{GPa}^{-1}$ and $S_{11} = 0.31\,\mathrm{GPa}^{-1}$, in very close agreement with this prediction.

It must be noted, however, that we have measured S_{44}, and the simple model presented above leads to the equality of S_{44} with S_{66}, thus predicting $S_{44} = 4S_{11}$ in contradiction with the observations.

We see, therefore, that S_{44} is not constrained by the above assumptions and that k values less than 4 must come about by a reduction of S_{44}. We therefore develop the model in the light of the following morphological considerations. It has been concluded from a range of morphological studies, primarily some remarkable electron microscopy results[15], that in the Vectra A950 polymer there is a tendency for aromatic rings to stack parallel to one another locally. This is similar to the well known situation in biaxially oriented poly(ethylene terephthalate) (PET) films where the benzene rings lie in the plane of the film. It has been shown that this gives rise to a characteristic anisotropy in the shear compliances[16]. In particular, the shear compliances for shear between the plane of the benzene rings are more than an order of magnitude greater than the shear compliance for shear in the plane of the rings. Using axes in which 2 is perpendicular to the plane of the ring and 3 is the chain axis, it is found that $S_{55} \ll S_{44} \cong S_{66}$.

If we assume that similar considerations apply to the structural units in oriented Vectra A950 samples, this can give an explanation as to why the macroscopic shear compliance S_{44} is reduced. To fix our ideas with an analogy, we can consider that the matrix is now reinforced by laths rather than rods and, in addition to the tensile constraint considered above, that shear in the plane of the laths is restricted. More precisely, we have to consider that the oriented Vectra A950 samples can be considered as a transversely isotropic aggregate of structural units with orthorhombic rather than cylindrical symmetry. These orthorhombic units are envisaged to have a similar anisotropy to PET film such that $S^{\mathrm{U}}_{55} \ll S^{\mathrm{U}}_{44} \cong S^{\mathrm{U}}_{66}$. We therefore assume $S^{\mathrm{U}}_{55} = 0$ and $S^{\mathrm{U}}_{44} = S^{\mathrm{U}}_{66} = S^{\mathrm{U}}_{\mathrm{R}}$, where, for simplicity, the two 'easy-shear' coefficients are set equal to $S^{\mathrm{U}}_{\mathrm{R}}$.

The transverse compliance of such an aggregate of fully aligned orthorhombic units is given by:

$$S_{11} = 0.375S^{\mathrm{U}}_{11} + 0.25S^{\mathrm{U}}_{12} + 0.375S^{\mathrm{U}}_{22} + 0.125S^{\mathrm{U}}_{66} \tag{7}$$

and the shear compliance S_{44} is given by:

$$S_{44} = 0.5(S^{\mathrm{U}}_{44} + S^{\mathrm{U}}_{55}) \tag{8}$$

The axial constraint of the chains yields $S_{11} = S_{22} = 0.25S^{\mathrm{U}}_{\mathrm{R}}$, as before, and incompressibility requires $S^{\mathrm{U}}_{11} + S^{\mathrm{U}}_{12} = 0$. Equations (7) and (8) therefore become:

$$S_{11} = 0.25S^{\mathrm{U}}_{\mathrm{R}} \tag{9}$$

$$S_{44} = 0.5S^{\mathrm{U}}_{\mathrm{R}} \tag{10}$$

We therefore see that $S_{44} = 2S_{11}$ and that k has reduced from 4 to 2 by restricting shear in one plane of the units of structure (laths).

We can draw some correlations between the lath model and structures in the LCP materials investigated. At a molecular scale, and a local level, the polymer chains are quite lath-like, being composed of the planar aromatic monomers with a transverse aspect ratio of about 3. On a larger, but still microscopic, scale, the hierarchical structure of oriented LCPs is well known with structural models envisaging the bulk materials being assembled from fibrils on several characteristic scales, typically, 50, 500 and 5000 nm in our copolyesters[17]. Recent research shows that these fibrils are anisotropic in section, being tape- or lath-like in appearance when observed by a wide variety of microscopic techniques[15]. Lath-like structures are observed in LCP materials, and although detailed assessments of their mechanical properties have yet to be made, it seems at least possible that they might tend towards those outlined above.

CONCLUSION

We have measured the transverse tensile compliances of two highly oriented liquid-crystal copolyesters over a wide temperature range. The experimental technique is considered reliable and accurate, although our high-temperature results are not representative of the unmodified LCP structure.

Comparing the transverse tensile compliance with the shear compliance, measured on highly oriented strands, a simple relationship is noted. This can be expressed:

$$S_{44}(T) = kS_{11}(T)$$

i.e. the shear and tensile compliances maintain a constant ratio over a wide temperature range.

Models are proposed in which an isotropic incompressible solid is reinforced by stiff rod-like or lath-like structures. These predict values of 4 and 2 respectively for k. Our experimental results fall within this range, suggesting that these may well provide a useful interpretation of the mechanical properties of the systems.

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