Matrix shear model for elastomers containing rigid platelets embedded in a soft matrix: 1. Orientation properties and stress–strain behaviour

A. J. Owen, J. Dietrich and R. Bonart
Institute of Physics III, University of Regensburg, Universitätsstrasse 31, 8400 Regensburg, FRG
(Received 5 February 1988; revised 3 May 1988; accepted 11 July 1988)

The finite deformational behaviour of materials containing rigid platelets embedded in an elastic matrix has been evaluated by assuming that the dominant microscopic deformation mechanism is shear of the matrix in a direction parallel to the plane of a platelet. The behaviour was determined for an initially isotropic sample undergoing uniaxial extension for the cases of uniform strain and uniform stress. The orientation distribution function of the platelet normals, the stress–strain diagram and orientation parameters such as Hermans' orientation factor were calculated. The predicted inclination of platelet normals for deformation at uniform stress gives an explanation for the observed 'cross-like' small angle X-ray scattering patterns found for diamine-extended polyurethane elastomers. For uniform strain, the retractive force diverges, whereas for uniform stress it is approximately proportional to the macroscopic extension ratio, with the slope showing a small minimum corresponding to a peak in the instantaneous compliance at an extension of about 10%. Hermans' orientation factor for the platelet normal distribution becomes strongly negative with increasing extension ratio for both cases.

(Keywords: shear model; elastomers; orientation; stress–strain; compliance; segmented polyurethane)

INTRODUCTION

Many polymers and composite materials contain lamellar inclusions in a relatively soft elastic matrix. For example, some diamine-extended segmented polyurethane elastomers consist of platelet-shaped hard segment domains which are embedded in a soft segment matrix[1,6].

It is of great interest to develop a model which describes the deformational behaviour of this type of material. In Owen's matrix shear model[2], rigid platelets (or lamellae) are assumed to constrain the surrounding matrix to deform by simple shear at finite strains. The purpose of this paper is to evaluate the matrix shear model further for the cases of large reversible deformations at uniform strain and uniform stress.

THEORY

Shear model

We consider an assembly of rigid platelets embedded in an incompressible, isotropic, elastic matrix. The dimensions of a platelet in the plane of the platelet are large compared with its thickness. We define a microscopic structural unit as the region of matrix material surrounding a platelet, where the platelets are imagined to be 'suspended' in the matrix. The unit is transversely isotropic about the platelet normal. If platelets are arranged in stacks we may also define a unit equivalently as the matrix material between two neighbouring parallel platelets.

The incompressibility condition requires that, in the neighbourhood of a platelet, the matrix material is constrained to deform by shear in a direction parallel to the plane of the platelet. We neglect deviations from this behaviour which occur near the edges of the platelets and away from a platelet where differently oriented structural units meet.

The geometry of the matrix shear process can be illustrated by referring to *Figure 1*. The parallelogram ABCD represents a microscopic section of the matrix material near a platelet and away from the platelet edge. The local platelet normal direction GD lies in the plane of the figure. A tensile stress is applied in the Z direction, to which AB and CD are parallel. AD and BC are parallel to the plane of the platelet. The matrix shears such that Z and GD are coplanar, i.e. the shear plane is the plane of the diagram. The shear direction is given by BC or AD, this being the direction of maximum shear stress in the plane of the platelet. ABCD is transformed to AEFD by simple shear. Simultaneously, AE (or DF) rotates back into the original direction*. The section of matrix extends by a factor $\mu = FD/CD$ and contracts laterally by $1/\mu$,

* The forces acting on the parallelogram cause a couple when the matrix shears, which rotates AE into the stretching direction. If we can neglect edge effects, e.g. when the stress field is locally homogeneous, then the behaviour of the platelet (or the unit) is determined by the shear process. This is also valid if, for the case of parallel platelets, an offset of the platelets with respect to each other occurs, or if one of the platelets is wider than the neighbouring platelet. The 'overhanging' part of a platelet can be regarded as an isolated platelet in the matrix. The same shear deformation mechanism is valid for this part as for the parallel parts. This means that the structural units are in equilibrium and will not tend to show rigid body rotation under initial loading.

0032–3861/89/010092–05$03.00

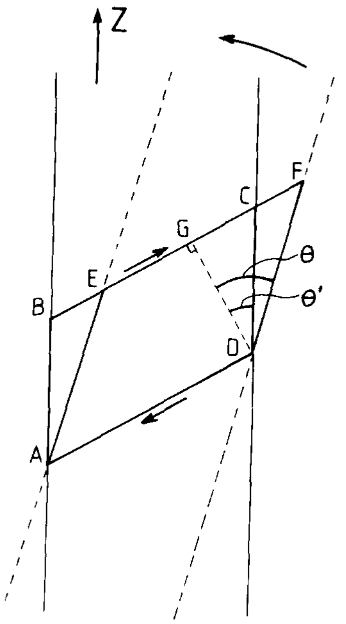

Figure 1 Rotational transformation of platelet normals due to matrix shear. DG is normal to a platelet. θ' is the angle between platelet normal and loading direction before the deformation; θ is the angle after the deformation; $FD/CD=\mu$ is the local extension ratio

whereas the dimension perpendicular to the plane of the figure is unaltered. The above deformation occurs locally in the region of each platelet, so that for each unit the angle transformation of the platelet normal can be written as

$$\cos\theta=\frac{1}{\mu}\cos\theta' \tag{1}$$

where μ is the extension ratio of the unit, θ' is the angle between Z and GD in the undeformed state and θ the corresponding angle after the deformation.

In an initially undeformed material, platelet normals are assumed to be isotropically distributed. When the material is extended by applying a tensile load, the matrix becomes sheared and the platelet orientation changes according to equation (1). However, since the mechanical properties of each unit depend on the platelet inclination (see later), we are dealing with an assembly of anisotropic units with initially different properties in the loading direction, and also with properties which change during the deformation. The relationship between the microscopic extension ratio μ of individual structural units and the macroscopic extension ratio λ cannot be generally determined, since the coupling behaviour between the differing units is not known *a priori*. This will depend on the morphology of the sample (i.e. on the juxtaposition of the various platelets) and on the resulting stress distribution. However, two special cases, uniform longitudinal strain and stress, which are analogous to the Voigt and Reuss averaging procedures in the aggregate model of Ward[3] can be readily calculated; these will now be considered and compared.

Orientation distribution of platelet normals

The orientation distribution of platelet normals $\Omega(\theta)$ is defined conventionally as the number of normals in a unit solid angle at an inclination θ to the extension direction, i.e. $\Omega(\theta)\sin\theta d\theta$ is the probability of finding a platelet at an angle between θ and $\theta+d\theta$ ($0°\leqslant\theta\leqslant 90°$). For an uniaxial extension, it follows that

$$\Omega(\theta)=\frac{\sin\theta'}{\sin\theta}\frac{d\theta'}{d\theta} \tag{2}$$

Homogeneous strain. In a situation where each structural unit has the same longitudinal strain, the microscopic extension ratio for each unit μ is equal to the macroscopic extension ratio λ, i.e.

$$\mu=\lambda \tag{3}$$

This gives, from equations (1), (2) and (3),

$$\Omega(\theta,\lambda)=\begin{cases}\lambda & \text{for } \cos\theta\leqslant 1/\lambda\\ 0 & \text{otherwise}\end{cases} \tag{4}$$

Equation (4) shows that the platelet normals are uniformly distributed in the region $\cos\theta\leqslant 1/\lambda$, and are gradually concentrated nearer the transverse direction with increasing extension ratio (*Figure 2*).

Homogeneous stress. In this case, each unit experiences the same tensile stress σ, which is equal to the applied stress. Referring firstly to a single unit, the shear stress τ resolved parallel to the platelet in the plane containing the applied stress and the platelet normal (i.e. the maximum resolved shear stress) is given by[4,5]

$$\tau=\sigma\sin\theta\cos\theta \tag{5}$$

The resulting shear strain γ in the matrix is related to the shear stress by a shear modulus G where

$$\gamma=\frac{\tau}{G} \tag{6}$$

i.e. we assume the shear modulus G of the matrix is constant even for finite strains. This corresponds to the assumption of neo-Hookean elasticity of the rubbery matrix.

From equations (5) and (6), the angle transformation relating θ', θ and σ is

$$\gamma=\tan\theta-\tan\theta'=\frac{\sigma}{G}\sin\theta\cos\theta \tag{7}$$

Using equation (2), the orientation distribution function for a uniform stress σ is then given by

$$\Omega(\theta,\sigma)=\frac{(1-A\cos^2\theta)(1+A\cos^2\theta(1-2\cos^2\theta))}{(\cos^2\theta+\sin^2\theta(1-A\cos^2\theta)^2)^{3/2}} \tag{8}$$

where $A=\sigma/G$ (cf. eq. (4) for uniform strain).

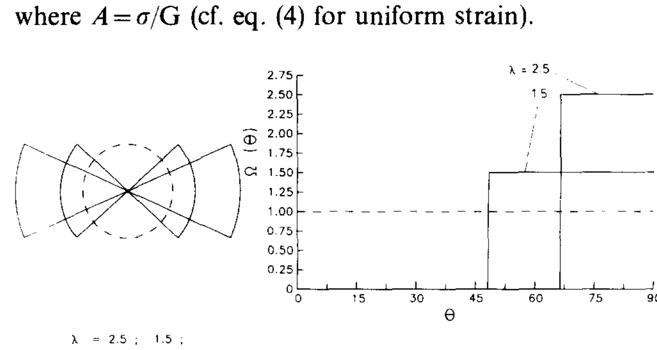

Figure 2 Homogeneous strain: orientation distribution of platelet normals

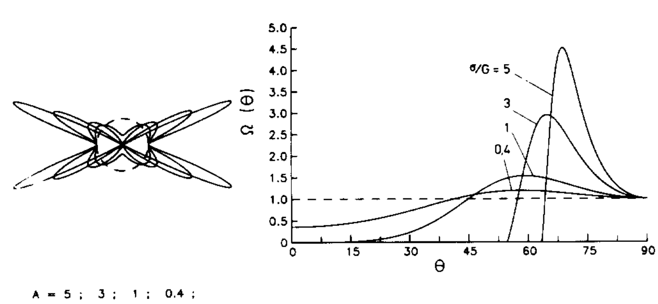

Figure 3 Homogeneous stress: orientation distribution of platelet normals for $\sigma/G=0.4$, 1, 3 and 5. These values are equivalent to extension ratios λ of 1.06, 1.15, 1.40 and 1.60 (*Figure 5*)

Ω is plotted in *Figure 3* for various values of A. With increasing stress, the fraction of platelets with normals parallel to the extension direction is reduced; for $\sigma > G$ or $A > 1$ there are only normals in the region $\cos\theta < (1/A)^{1/2}$. The most striking feature about the distribution is that the platelet normals take up a preferred inclination to the stretching direction, which becomes increasingly pronounced with increasing stress.

Stress–strain behaviour

It is straightforward to show from equations (1), (5), (6) and (7) that the stress–strain characteristic for a single unit with initial orientation θ' can be written as

$$\sigma(\mu,\theta')=\frac{G\mu^2}{\cos^2\theta'}\left\{1-\frac{\sin\theta'}{(\mu^2-\cos^2\theta')^{1/2}}\right\} \tag{9}$$

This expression is plotted in *Figure 4* for various values of the initial orientation θ'. *Figure 4a* shows curves for $\theta' \leqslant 45°$ while *Figure 4b* is for $\theta' \geqslant 45°$. (These have been plotted separately in order to avoid the confusion of overlapping curves.) At small strains, units with $\theta'=45°$ have the lowest modulus (i.e. the slope of the 45° curve is the smallest). With increasing deformation, units with $\theta<45°$ become more compliant, since they rotate into a more compliant orientation. Units with $\theta>45°$ become increasingly stiff. (The unit with $\theta'=90°$ is infinitely stiff.) At very large strains (*Figure 4c*) the units with the smallest starting orientations θ' eventually have the lowest stresses, in order of increasing θ'.

It should be mentioned that, to take into account the volume fraction of platelets, G may be regarded as equal to G_m/V_m where G_m is the actual shear modulus of the matrix and V_m is the volume fraction of the matrix. (The platelets, having a volume fraction $1-V_m$, have been assumed to be infinitely stiff.)

Homogeneous strain. For this condition we can take a vertical line through the curves of *Figure 4* to obtain the stress in each unit at a particular strain $\lambda=\mu$. This situation is problematical for units with θ' near 90°, since the stress then becomes infinitely large. Thus, for homogeneous strain, the model does not allow us to calculate a stress–strain curve for an initially isotropic sample. This unrealistic situation suggests that in reality an inhomogeneous strain will occur, in order to reduce stress concentrations.

Homogeneous stress. A horizontal line through the curves of *Figure 4* shows that, when the stress is uniform, the strain is inhomogeneous. The stress–strain curve of the 'aggregate' of units and the instantaneous compliance along the stress–strain curve can be calculated, as follows: for a single structural unit, the increase in free energy (or elastic energy density) due to shearing (see eq. (7)) can be written

$$F(\theta,\sigma)=\frac{1}{2}G\gamma^2=\frac{\sigma^2}{2G}\sin^2\theta\cos^2\theta \tag{10}$$

We restrict ourselves to the case of a reversible deformation at constant volume. The free energy of the aggregate is found by averaging over all the structural units

$$F(\sigma)=\langle F(\theta,\sigma)\rangle=\frac{\sigma^2}{2G}\langle\sin^2\theta\cos^2\theta\rangle$$
$$=\frac{\sigma^2}{2G}\int_0^{\pi/2}\sin^2\theta\cos^2\theta\,\Omega(\theta,\sigma)\sin\theta\,d\theta \tag{11}$$

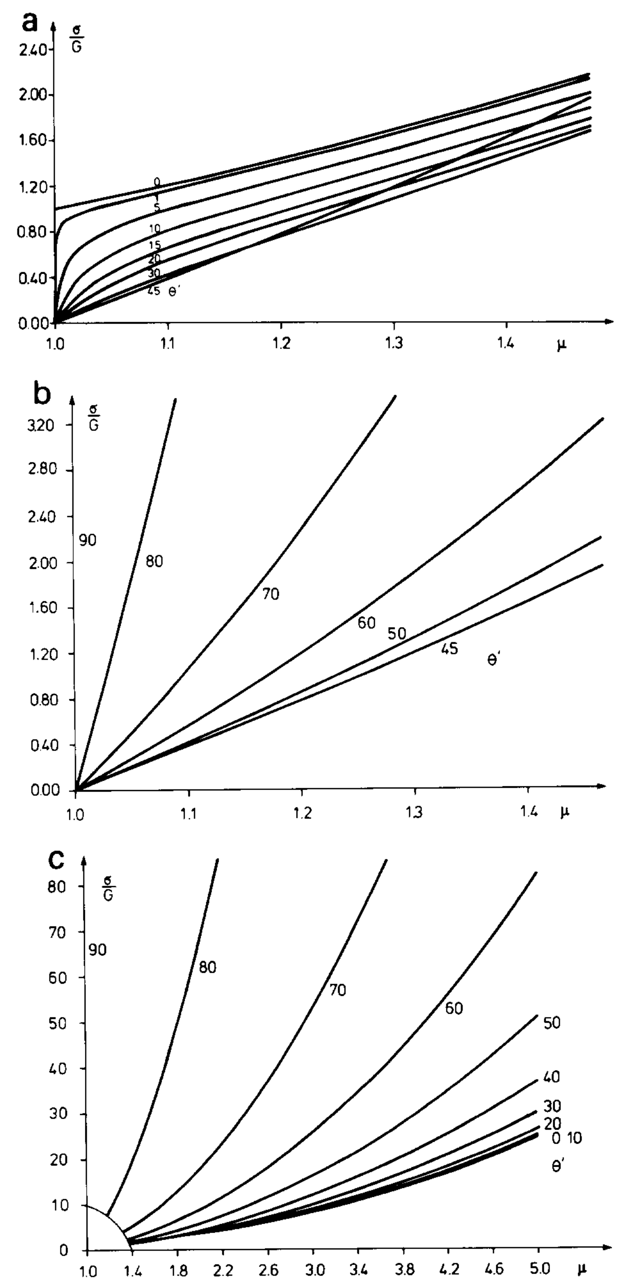

Figure 4 Stress–strain characteristic for a deformed unit defined by initial inclination θ': small deformations for (a) $\theta' \leqslant 45°$; (b) $\theta' \geqslant 45°$; and (c) large deformations

For the aggregate as a whole, the following relation is also valid

$$\mathrm{d}F=\sigma\,\mathrm{d}\varepsilon=\sigma\frac{\mathrm{d}\lambda}{\lambda} \tag{12}$$

where $\mathrm{d}\varepsilon$ is a longitudinal strain increment, and is related to a change in extension ratio $\mathrm{d}\lambda$ by $\mathrm{d}\varepsilon=\mathrm{d}\lambda/\lambda$. Furthermore, the compliance D is defined by

$$D=\frac{\mathrm{d}\varepsilon}{\mathrm{d}\sigma}=\frac{1}{\lambda}\frac{\mathrm{d}\lambda}{\mathrm{d}\sigma} \tag{13}$$

From (12) and (13) it follows that

$$D(\sigma)=\frac{1}{\sigma}\frac{\mathrm{d}F}{\mathrm{d}\sigma} \tag{14}$$

$D(\sigma)$ was then found from the slope of $F(\sigma)$ (eq. (11)). By rearranging equation (13), the stress–strain diagram was then found using the following relation

$$\lambda(\sigma)=\exp\left(\int_0^{\sigma} D(\sigma')\mathrm{d}\sigma'\right) \tag{15}$$

Equations (11), (14) and (15) were used to obtain the true stress–strain curve for the overall material by numerical integration (*Figure 5*). The compliance as a function of extension ratio λ was then found by combining the results of equation (15) with $D(\sigma)$ from equation (14). This is shown in *Figure 6*. Of note is the peak in the compliance at an extension of approximately 10%. This is also noticeable as a slight minimum in the slope of the stress–strain curve (*Figure 5*).

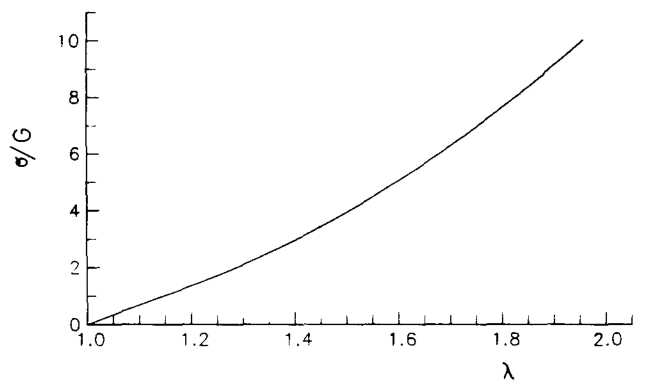

Figure 5 True stress–strain curve (uniform stress)

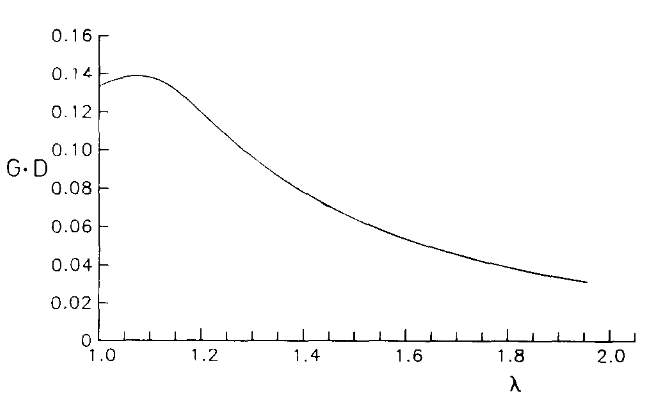

Figure 6 Instantaneous elastic compliance along the stress–strain curve (uniform stress)

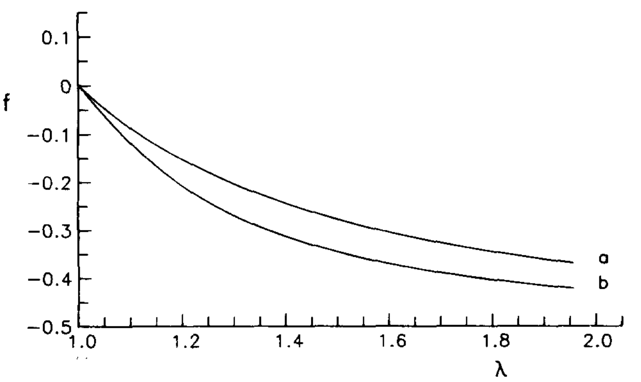

Figure 7 Hermans' orientation factor for the platelet normals. (a) Homogeneous strain, (b) homogeneous stress

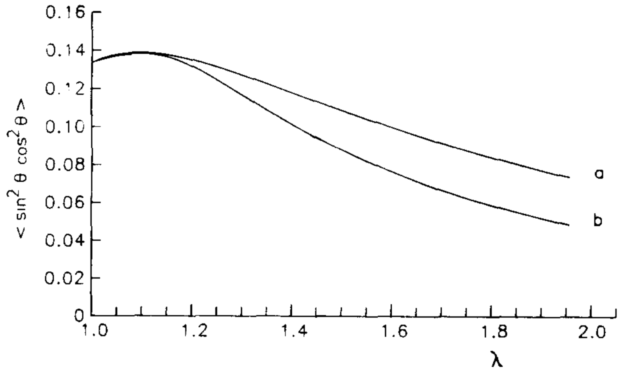

Figure 8 Orientation parameter $\langle\sin^2\theta\cos^2\theta\rangle$. (a) Homogeneous strain, (b) homogeneous stress

Orientation parameters for the distribution of platelet normals

For homogeneous strain, the Hermans' orientation factor for the distribution of lamellar normals f is given from reference 2 by

$$f=\frac{1}{2}(3\langle\cos^2\theta\rangle-1)=\frac{1}{2}(1/\lambda^2-1) \tag{16}$$

For uniform stress, $\langle\cos^2\Theta\rangle$ was calculated here numerically using equations (8) and (17), where

$$\langle\cos^2\theta\rangle=\int_0^{\pi/2}\cos^2\theta\,\Omega(\theta,\sigma)\sin\theta\,\mathrm{d}\theta \tag{17}$$

This gives $\langle\cos^2\theta\rangle$ as a function of stress σ. We then used the stress–strain behaviour of *Figure 5* to calculate f as a function of λ.

Figure 7 shows f for both homogeneous strain and stress. Similar behaviour is obtained in both cases, f becoming sharply negative initially and then levelling off gradually to approach asymptotically the value of $-1/2$, which describes the situation with all normals lying transversely.

The orientation parameter $\langle\sin^2\Theta\cos^2\Theta\rangle$ is shown for both cases in *Figure 8*. For the uniform strain case, it is given analytically by

$$\begin{aligned}\langle\sin^2\theta\cos^2\theta\rangle&=\langle\cos^2\theta\rangle-\langle\cos^4\theta\rangle\\&=1/(3\lambda^2)-1/(5\lambda^4)\end{aligned} \tag{18}$$

For homogeneous stress we performed a numerical calculation using equations (8) and (15). Both cases show similar behaviour, with a small peak occurring at about $\lambda = 1.1$, after which a monotonic decrease takes place.

Comparison of the instantaneous compliance curve (*Figure 6*) with the orientation parameter $\langle \sin^2\theta . \cos^2\theta \rangle$ (*Figure 8*) shows considerable similarity. The reason for this is as follows: combining equations (11) and (14), we obtain

$$D(\sigma) = \frac{1}{G}\langle \sin^2\theta \cos^2\theta \rangle + \frac{\sigma}{2G}\frac{\mathrm{d}}{\mathrm{d}\sigma}\langle \sin^2\theta \cos^2\theta \rangle \quad (19)$$

For infinitesimal stresses and/or a situation where the orientation distribution is unchanged by stress, the second term is zero. This then reduces to the following result, which was obtained previously by Davies *et al.*[4] and applied to the interlamellar shear behaviour of polyethylene showing a lamellar morphology, i.e.

$$D = \frac{1}{G}\langle \sin^2\theta \cos^2\theta \rangle \quad (20)$$

In this work, we have taken lamellar rotation into account for large deformations, with the consequent change in the instantaneous compliance of the elements as they are deformed (*Figure 4*). This means that the compliance along the stress–strain curve (eq. (13)) is not given by equation (20) for large stresses. However, for small stresses there is little difference, with $\langle \sin^2\theta . \cos^2\theta \rangle$ (*Figure 8*) and D (*Figure 6*) showing a similar maximum at approximately the same extension ratio. The model presented here is constructed analogously to the single-phase aggregate model of Ward[3]. The orientation distribution of structural units changes due to the deformation, with the result that the second term in equation (19) arises. If this term is neglected, our model reduces to Ward's aggregate model with the special orientation mechanism of equation (1), in which the mechanical properties of the structural units are $S_{44} = 1/G$ and $S_{ij} = 0$ otherwise.

CONCLUSIONS

The matrix shear model presented here is an attempt to predict the reversible, finite deformational behaviour of materials containing rigid platelets embedded in an elastic matrix. We have treated the effect which we believe to be the dominant mechanism of deformation, i.e. shear of the matrix when constrained parallel to each platelet. Certain cases can be satisfactorily calculated. We have done this for both uniform longitudinal strain and stress. Deformation caused by normal stresses, and plastic and viscoelastic effects have not been considered.

With regard to applications of the model, the orientation distribution function for homogeneous stress (*Figure 3*) shows a remarkable similarity with the 'cross-like' small-angle X-ray scattering patterns found for some diamine-extended segmented polyurethane (PU) elastomers[6]. In addition, the Hermans' orientation factor (*Figure 7*) for the platelet normal distribution corresponds qualitatively with the negative orientation of hard segment C=O dipoles deduced by infra-red dichroism[7]. The instantaneous compliance curve calculated for uniform stress (*Figure 6*) also resembles the experimental curve found for a PU elastomer[2]. We are consequently encouraged to believe that the proposed matrix shear mechanism plays an important part in the deformation behaviour of these materials. The model is now being used to find the shear modulus of the soft segment matrix for various PU elastomers and to compare the results with molecular calculations.

ACKNOWLEDGEMENT

The authors thank the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1 Bonart, R. and Hoffman, K. *Colloid Polym. Sci.* 1982, **260**, 268
2 Owen, A. J. *Colloid Polym. Sci.* 1985, **263**, 991
3 Ward, I. M. *Proc. Phys. Soc.* 1962, **80**, 1176
4 Davies, G. R., Owen, A. J., Ward, I. M. and Gupta, V. B. *J. Macromol. Sci.–Phys.* 1972, **B6(1)**, 215
5 Schmid, E. and Boas, W. 'Kristallplastizitaet', Springer, Berlin, 1935
6 Boetzl, F., Schmid, J. and Bonart, R. *Makromol. Chem.* 1987, **188**, 907; Bonart, R. *J. Macromol. Sci. Phys.* 1968, **B2(1)**, 115; Ishihara, H., Kimura, I. and Yoshihara, N. *J. Macromol. Sci. Phys.* 1983–84, **B22**, 713 and 763; Desper, C. R., Schneider, N. S., Jasinski, J. P. and Lin J. S. *Macromolecules* 1985, **18**, 2755; Shibyama, M., Ohki, Y., Kotani, T. and Nomura, S. *Polym. J.* 1987, **19** (9), 1067
7 Hoffmann, K. and Bonart, R. *Makromol. Chem.* 1983, **184**, 1529