Analysis of polynomial yield criteria applied to oriented polymers

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The anisotropic and isotropic yield properties of PET are described in terms of a tensor polynomial yield criterion published by Malmeister and Tsai-Wu. It is shown in detail how the criterion can be applied to oriented polymer films under the condition of plane stress. The coefficients of the polynomial are related to yield strengths measured in simple experiments. Experimental results obtained for oriented and isotropic PET are shown, and an analysis of the data in terms of the theory is included. In the discussion a comparison is made with the Hill and Hoffman yield criteria for anisotropic materials.

(Keywords: yield; anisotropy; poly(ethylene terephthalate); poly(vinyl chloride); polypropylene; tensor polynomial; strength coefficients)

INTRODUCTION

Most commonly used polymeric materials can have a relatively high degree of mechanical anisotropy. It may be observed that the highly anisotropic capabilities of polymers can only be matched, and surpassed, by composite materials with oriented fibre reinforcements, or laminates. Since composite materials are important structural engineering materials, therefore recent theoretical developments of anisotropic failure criteria have mainly occurred in that area[1].

We wish to consider a theory published by Malmeister[2], describing the anisotropic strength behaviour of polymers and fibre reinforced plastics. The theory is formulated in terms of general variables, including time, and in principle can be applied to any of the failure phenomena such as brittle failure, yield, creep failure, etc. In one of its forms the equation involves constant stress (or strain) rates which corresponds to a typical experimental situation when measuring yield strength. Thus with appropriate boundary conditions the theory can be applied to describe the yield behaviour of anisotropic polymers at constant temperature and in simple loading experiments.

The translation of Malmeister's paper was followed by publication by Tsai and Wu[3] of a 'General Theory of Strength for Anisotropic Materials'. The Tsai–Wu theory is in essence identical with that of Malmeister and therefore will be referred to by their joint names.

In this paper we apply the above-mentioned theory to poly(ethylene terephthalate) (PET) with biaxial orientation, and also to published results for oriented poly(vinyl chloride) (PVC) and polypropylene (PP).

THEORY

Definition of stresses and yield strength

A Cartesian space is defined by a set of reference axes 1, 2 and 3. Let a body be a bulk polymer (not a single crystal) of general anisotropy with the x, y and z axes identifying directions of any material (molecular) symmetry, as shown in *Figure 1*.

Consider that the body is in mechanical equilibrium, i.e. the sum of forces and the sum of momentum of forces applied to the body are equal to zero.

Imagine that the polymeric material is cut through, and forces are applied over the new surfaces in such a way that the body does not change shape nor volume, and remains in equilibrium. Then a surface element δS, with a normal vector $\tilde{n}$ has a force vector $\tilde{f}$ acting on it.

In the frame of reference 1–2–3 the vectors $\tilde{n}$ and $\tilde{f}$ will have components n_i and f_i. The stress tensor is defined by (under the condition that $\delta S \to 0$):

$$\tilde{\sigma} = \tilde{n}\tilde{f} \qquad (1)$$

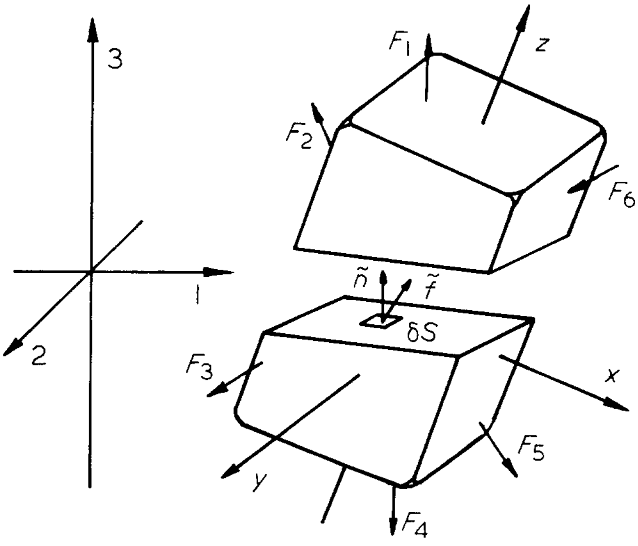

Figure 1 Cartesian space is defined by the axes 1, 2 and 3. The material has structural symmetry axes x, y, z and is loaded by forces in mechanical equilibrium

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In general the stress has nine components of which only six are independent. We use the contracted notation:

$$\sigma_k = \left|\begin{array}{ccc} \sigma_1 & \sigma_6 & \sigma_5 \\ & \sigma_2 & \sigma_4 \\ & & \sigma_3 \end{array}\right| \qquad (2)$$

If the material is rotated, and the orientation of the surface element δS becomes such that $\vec{n}$ and $\vec{f}$ are co-linear, then the stress tensor components become principal stresses, with the off-diagonal terms equal to zero.

Notice that the material symmetry axes *x*, *y*, *z* are independent of, and not related to, the stress tensor nor its components. In the remainder of the paper it will be assumed that the principal stress directions coincide with the Cartesian 1, 2, 3-axes, whereas the material can assume any arbitrary orientation.

We treat polymeric materials as pseudo-elastic, i.e. anelasticity, and creep and stress relaxation effects are not taken into account. It is assumed that all experiments are carried out at a constant stress rate (or corresponding strain rate), and that on loading the material will ultimately yield and show plastic deformation.

The yield point or yield strength is defined as the stress at the onset of plastic deformation. This definition is made with reference to an experimental stress–strain curve. For polymers the yield point may be defined as the point of intersection of two lines tangent to the 'elastic' and 'plastic' sections of the stress–strain curve[4]. We note that this may not be related to any molecular mechanism, and differs from crystalline materials for which the yield point is usually defined as the elastic limit.

The Malmeister and Tsai–Wu anisotropic failure criterion

The central idea of this failure criterion is the existence of a strength tensor which is related to the tensor of the ultimate stresses attained in the polymer at the point of failure. Then the failure surface in the stress space can be described in terms of a tensor polynomial, given below in contracted notation:

$$f(\sigma_i) = F_i\sigma_i + F_{ij}\sigma_i\sigma_j + F_{ijk}\sigma_i\sigma_j\sigma_k + \cdots = 1 \qquad (3)$$

where $i, j, k = 1, 2, \ldots, 6$. F_i, F_{ij} and F_{ijk} are the components of the strength tensor, whereas σ_i, σ_j and σ_k are the components of the applied stress tensor. Equation (3) has the property of invariance under the transformation of axes by translation and rotation[3].

It has been shown by both Malmeister and Tsai–Wu that the first two terms adequately represent the yield surfaces of anisotropic materials. (For a general discussion of the meaning of the tensor polynomials the reader is referred to an article by Wu[5].) Consequently, we limit the above equation to the linear and quadratic terms only, and write

$$F_{ij}\sigma_i\sigma_j + F_i\sigma_i = 1 \quad \text{(contracted notation)} \qquad (4)$$

It may be observed that the components of the strength tensor, F_{ij} and F_i, must be symmetric, i.e. (i) $F_{ij} = F_{ji}$, and (ii) F_i is symmetric when expressed in non-contracted notation. This symmetry is derived from the reasonable expectation that yield surface should be path independent. In geometrical terms equation (4) describes the failure surface in the six-dimensional space defined by individual stress components $\sigma_1, \sigma_2, \ldots, \sigma_6$.

For a material of finite yield strength in all directions the components of the strength tensor must fulfil a stability condition[2,3].

General anisotropy under plane stress condition

We arrange the loading of the material in *Figure 1* in such a way that all stress components containing the 2-axis vanish. Consequently, there will be three independent stress components left and equation (4) will reduce the two-dimensional case:

$$F_{11}\sigma_1^2 + F_{33}\sigma_3^2 + F_{55}\sigma_5^2 + 2F_{13}\sigma_1\sigma_3 + 2F_{15}\sigma_1\sigma_5 + 2F_{35}\sigma_3\sigma_5 + F_1\sigma_1 + F_3\sigma_3 + F_5\sigma_5 = 1 \qquad (5)$$

Equation (5) represents the failure criterion in one plane for a material of general orientation and anisotropy. It is characterized by nine independent strength constants which can be determined experimentally. The equation has the following properties: it allows for different strengths in tension and compression, which are assumed to be natural properties of the polymer. Also it allows for different strengths in positive and negative shear (this is illustrated in *Figure 2*). The nine strength constants are determined by the properties of the polymer in the one plane, and the quation describes a yield surface in three-dimensional stress space defined by the stress components σ_1, σ_3 and σ_5.

Finally, it can be remarked that the elastic symmetry of the polymeric material under test need not be known and equation (5) applies to the general case where the material axes and the principal stress axes do not coincide.

Polymers with orthotropic yield strength properties

If we rotate the material in *Figure 1* so that the material axes *x* and *z* coincide with the reference axes 1 and 3, then the number of strength constants is reduced[2,3,5], i.e.

$$X_5 = \bar{X}_5, \qquad F_{15} = F_{35} = F_5 = 0 \qquad (6)$$

The strength tensor measured in the one plane of the material is now given by six independent constants:

$$F_i = \left|\begin{array}{c} F_1 \\ F_3 \\ 0 \\ 0 \\ 0 \\ 0 \end{array}\right| \qquad F_j = \left|\begin{array}{cccccc} F_{11} & 0 & F_{13} & 0 & 0 & 0 \\ & & F_{33} & 0 & 0 & 0 \\ & & & 0 & 0 & 0 \\ & & & & F_{55} & 0 \\ & & & & & 0 \\ & & & & & \end{array}\right| \qquad (7)$$

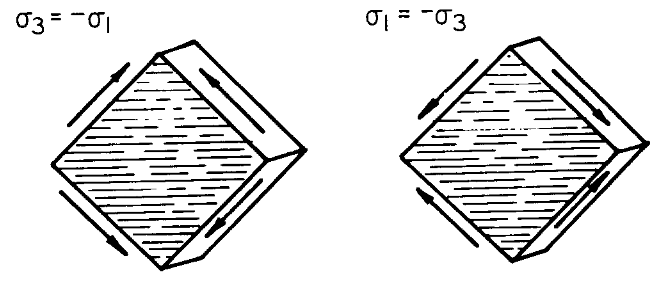

Figure 2 Illustration showing the difference between positive and negative shear strength in a material with preferred molecular orientation

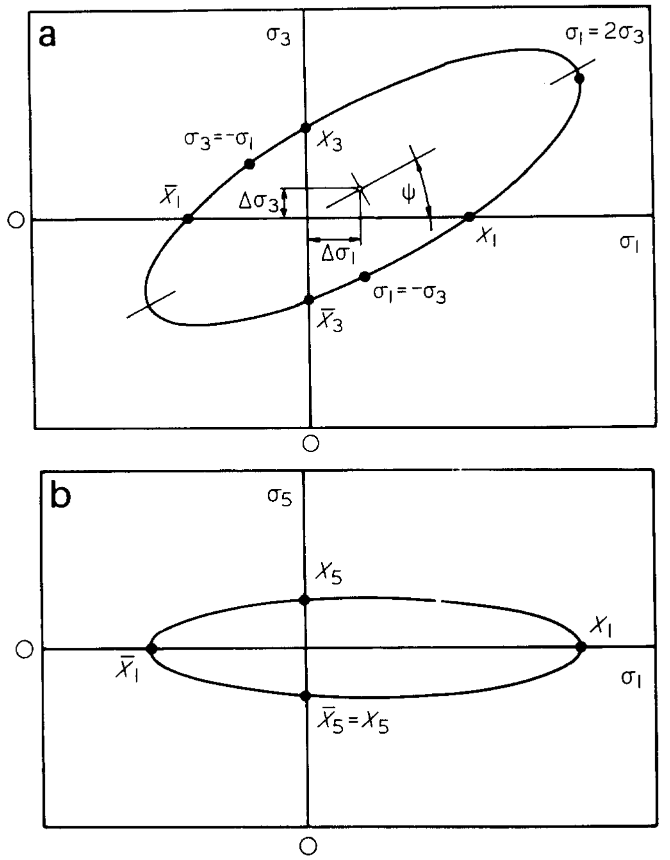

Figure 3 (a) Yield ellipse in the σ_1–σ_3 plane. $\Delta\sigma_1$ and $\Delta\sigma_3$ give the position of the centre of the ellipse. X_1 and X_3 denote the yield points in uniaxial tension, and X_1 and X_3 correspond to uniaxial compression. (b) Yield ellipse in the σ_1–σ_5 stress plane. X_5 and $\bar{X}_5$ denote pure shear yield strengths

and equation (5) reduces to:

$$F_{11}\sigma_1^2+F_{33}\sigma_3^2+F_{55}\sigma_5^2+2F_{13}\sigma_1\sigma_3 + F_1\sigma_1+F_3\sigma_3=1 \quad (8)$$

Malmeister and Tsai–Wu give the following formulae for calculating the strength constants:

$$\begin{gathered} F_{11}=\frac{1}{X_1\bar{X}_1} \qquad F_1=\frac{1}{X_1}-\frac{1}{\bar{X}_1} \\ F_{55}=\left(\frac{1}{X^5}\right)^2 \\ F_{33}=\frac{1}{X_3\bar{X}_3} \qquad F_3=\frac{1}{X_3}-\frac{1}{\bar{X}_3} \qquad (9) \\ F_{13}=\frac{2}{U^2}\left[1-\frac{U}{2}\left(\frac{1}{X_1}-\frac{1}{\bar{X}_1}+\frac{1}{X_3}-\frac{1}{\bar{X}_3}\right)\right. \\ \left.-\frac{U^2}{4}\left(\frac{1}{X_1\bar{X}_1}+\frac{1}{X_3\bar{X}_3}+\left(\frac{1}{X_5}\right)^2\right)\right], \end{gathered}$$

In equations (9) X_i denotes strengths measured in uniaxial tension and in pure shear, whereas $\bar{X}_i$ corresponds to the same measurements but under negative stress (i.e. uniaxial compression and negative pure shear), and U is the yield strength measured by applying uniaxial tensile load at 45° to the x and z axes.

If the strength constants of equation (8) satisfy the stability conditions[2,3], then the quadratic equation describes an ellipsoid in the three-dimensional stress space defined by σ_1, σ_3 and σ_5 (notice that this is not the same as the Haig–Westergaard principal stress space[6]). We can illustrate the yield surface by its two traces; (i) on the $\sigma_1-\sigma_3$ plane, and (ii) on the $\sigma_1-\sigma_5$ plane, (as shown in *Figures 3a* and *3b*). The position of the ellipse relative to the σ_1 and σ_3 axes in *Figure 3a* is given by the usual analytical geometry equations[7]:

$$\begin{gathered} \psi=\tfrac{1}{2}\arctan(2F_{13}/(F_{11}-F_{33})) \\ \Delta\sigma_1=(F_{13}F_3-F_{33}F_1)/2(F_{11}F_{33}-F_{13}^2) \qquad (10) \\ \Delta\sigma_1(F_{13}F_1-F_{11}F_3)/2(F_{11}F_{33}-F_{13}^2) \end{gathered}$$

The ellipse in *Figure 3b* is symmetrical around the σ_1 axis since $X_5=\bar{X}_5$. We note that σ_5 is an independent stress component and cannot be represented in the σ_1–σ_3 plane.

The three principal yield strengths, equivalent to the three principal axes of the ellipsoid, are orthogonal in the stress space. Tsai–Wu call such materials, whose strength is described by equation (8) as 'orthotropic'. This name has nothing to do with the elastic symmetry of the polymer. In fact oriented polymers with orthogonal or hexagonal symmetry or transversely isotropic (fibre symmetry) will have such orthotropic strength properties in planes in which the axes of molecular symmetry coincide with the axes of principal stress.

Yield behaviour of isotropic polymers

For an isotropic polymer we must have:

$$X_1=X_3=X,\ \bar{X}_1=\bar{X}_3=\bar{X},\ X_5=\sqrt{X\bar{X}/3},\ \text{and}\ U=X \qquad (11)$$

Therefore from equation (9) we find,

$$F_{11}=F_{33}=\tfrac{1}{3}F_{55}=\hat{F},\ F_1=F_2=\bar{F},\ F_{13}=\tfrac{1}{2}F_{11} \qquad (12)$$

Equation (8) now becomes

$$\hat{F}(\sigma_1^2+\sigma_3^2+3\sigma_5^2-\sigma_1\sigma_3)+\bar{F}(\sigma_1+\sigma_3)=1 \qquad (13)$$

For an isotropic polymer we may rotate the stress axes arbitrarily until the shear stresses vanish, so that we obtain:

$$f_1(\sigma_{1p}^2+\sigma_{3p}^2)+f_2(\sigma_{1p}+\sigma_{3p})=1 \qquad (14)$$

where σ_{1p} and σ_{3p} now denote principal stresses. Consequently equation (14) can now be written in a general form as

$$f_1(\mathrm{II})+f_2(\mathrm{I})=1 \qquad (15)$$

where I and II are the first and second stress invariants, and f_1 and f_2 are constants. An equation of this form has been described by Tschoegl[8] for the yield behaviour of isotropic polymers. Equation (15) allows for the natural difference between tensile and compressive strengths of the isotropic material. Also the presence of I indicates that yield behaviour is influenced by hydrostatic pressure. And finally, since all the stress states in the plane of the material can be described by the two principal stresses σ_{1p} and σ_{3p},

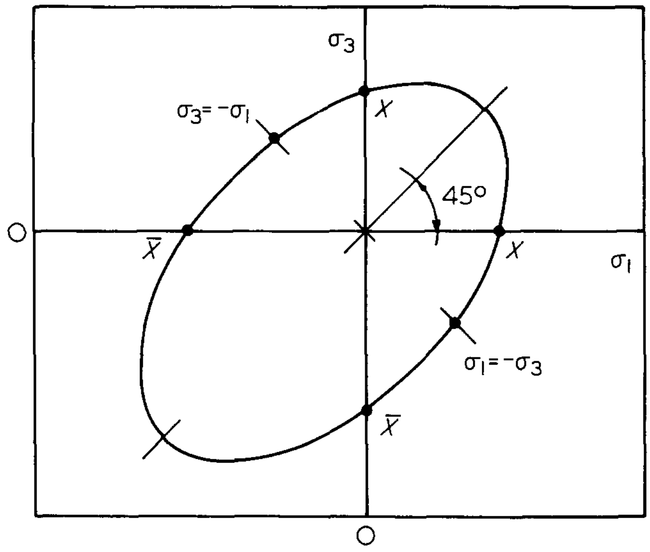

Figure 4 Yield ellipse for an isotropic material in plane stress showing dependence on hydrostatic pressure. σ_1 and σ_3 can be taken as tensor stress components or as principal stresses. Notice the difference between tensile, X, and compressive, X, yield strengths

the yield surface degenerates from three-dimensional ellipsoid to two-dimensional ellipse as shown in *Figure 4.*

Off-axis yield strength for oriented polymers

Now let us consider the measurement of strength in an anisotropic polymer along a direction inclined by an angle θ to the material x-axis, as shown in *Figure 5.*

Since equation (4) (or equation (8)) holds true for any set of reference axes, therefore we may write

$$F_{ij}\sigma_i\sigma_j+F_i\sigma_i=F'_{ij}\sigma'_i\sigma'_j+F'_i\sigma'_i=1 \qquad (16)$$

Assume that in the reference state, the coefficients F_{ij} and F_i are known. The coefficients F'_{ij} and F'_i in the rotated state must be determined.

The strength tensor coefficients are related to each other through the usual tensor transformation rules. For the case of uniaxial tension (or compression) we have all $\sigma'_{i,j}=0$ except $\sigma'_1=X_{1\theta}$ (or $-\sigma'_1=\bar{X}_{1\theta}$). Equation (4) becomes:

$$F'_{11}(\sigma'_1)^2+F'_1\sigma'_1=1 \qquad (17)$$

After transformation of the strength tensor[9,10], equation (17) can be written in terms of the reference coefficients as:

$$\begin{aligned}&[\tfrac{1}{8}(3F_{11}+3F_{33}+2F_{13}+F_{55})+\tfrac{1}{2}(F_{11}-F_{33})\cos^2\theta\\&\quad+\tfrac{1}{8}(F_{11}+F_{33}-2F_{13}-F_{55})\cos 4\theta]X_{1\theta}^2\\&\quad+[\tfrac{1}{2}(F_1+F_3)+\tfrac{1}{2}(F_1-F_3)\cos 2\theta]X_{1\theta}-1=0 \qquad (18)\end{aligned}$$

The roots of equation (18) give the tensile strength ($X_{1\theta}$) and the compressive strength ($\bar{X}_{1\theta}$) along the off-axis direction.

For the case of pure shear all $\sigma_{i'j}=0$ except $\sigma'_5=X_{5\theta}$ (or $-\sigma'_5=X_{5\theta}$). Again using equations (4) and (16) and the tensor transformation rules we obtain:

$$\begin{aligned}&[\tfrac{1}{2}(F_{11}+F_{33}-2F_{13}+F_{55})\\&\quad-\tfrac{1}{2}(F_{11}+F_{33}-2F_{13}-F_{55})\cos 4\theta]X_{5\theta}^2\\&\quad+[(F_3-F_1)\sin 2\theta]X_{5\theta}-1=0 \qquad (19)\end{aligned}$$

Thus equation (19) can be used to calculate the off-axis shear strength in a material of general anisotropy in terms of its orthotropic strength properties.

EXPERIMENTAL MATERIALS

The material investigated was poly(ethylene terephthalate) which is used to make thin walled bottles for carbonated soft drinks. The polymer was made by solid state polymerization. The inherent viscosity of the studied material was 0.72, corresponding to a weight average molecular weight of about 60 000. The material was used in its natural state without pigmentation. In our investigations we have used; (i) samples of ready-made bottles representing the anisotropic material, and (ii) samples of the injection moulded parisons representing the isotropic state of the polymer. The amorphous and isotropic state of the parisons was ascertained by WAXD and by measurement of the Young's modulus in different directions. It was evident from the diffraction pattern that no noticeable preferred molecular orientation was present, and the measurements of Young's modulus gave a constant value of 2.3 $\mathrm{GNm^{-2}}$, within an experimental error of $\pm 5\%$.

The film obtained from the walls of the bottles showed marked anisotropy. (The bottle is made in a two-stage process with biaxial hot stretching approximately ×2 in the longitudinal direction of the bottle, and ×4 in the hoop direction.) The birefringence of the film was measured using the Carl–Zeiss Ultraphot II microscope fitted with rotary compensator and a quartz plate. The average value was 0.08 ± 0.002. From the WAXD recordings the crystallinity of the material was estimated to be around 20–30%. The Young's modulus in the hoop direction was measured to be 5.6 $\mathrm{GNm^{-2}}$ and in the longitudinal direction to be 3.1 $\mathrm{GNm^{-2}}$.

Description of testing samples

The parisons were in a shape of a tube closed at one end, approximately 15 cm long, 3 cm diameter and 4 mm wall thickness. From these we have carefully machined cylindrical specimens of 26.2 mm outer diameter, 24.4 mm inner diameter and 104 mm in overall length. The specimens had threaded ends for gripping, and the gauge was carefully polished to remove lathe machining marks. These specimens were suitable for measuring yield strengths in uniaxial and biaxial tension.

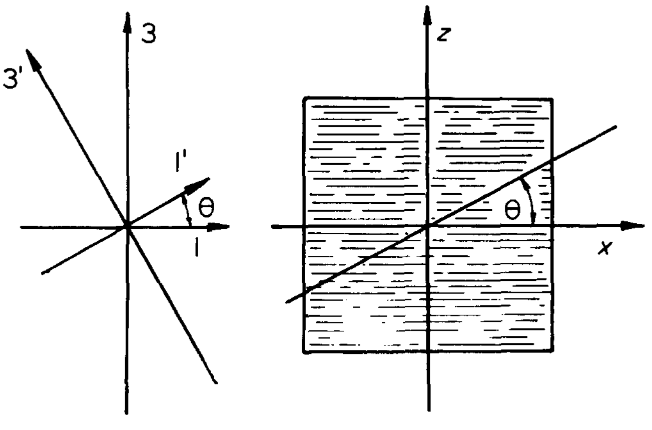

Figure 5 Relationship between the new 1′ and 3′, and the old 1 and 3 reference axes, and the off-axis θ-direction in an anisotropic material

Table 1 Off-axis tensile yield properties of PET

Angle between tension and hoop direct [deg.]	0	10	20	45	65	80	90
Yield strength [MPa]	145	115	103	75	70.5	61	62

Table 2 Off-axis shear yield properties of PET

Angle between shear and hoop direct [deg.]	0	30	45	60	90	120	135	165
Yield strength [MPa]	42.6	63.1	62.0	49.1	41.8	41.0	41.0	39.9

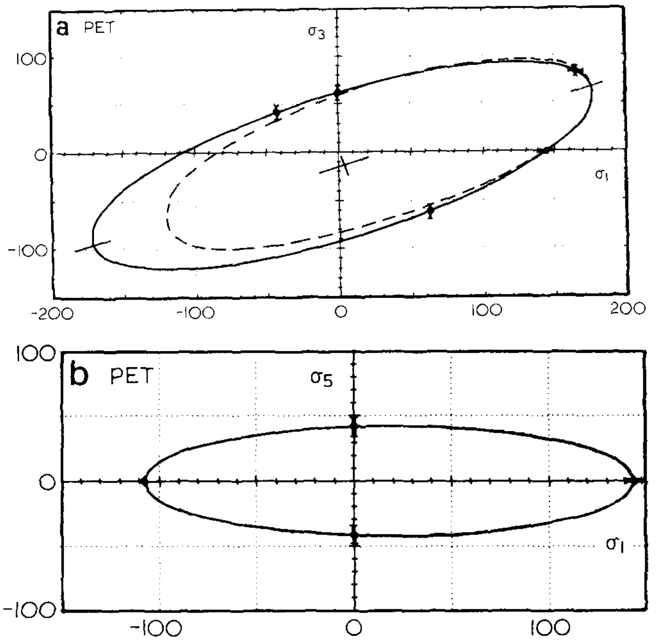

Figure 6 (a) Yield ellipse in the σ_1–σ_3 plane for biaxially oriented PET. The solid line drawn according to equation (8) and coefficients (20). The points correspond to measured yield strengths. Broken line shows change in shape of ellipse when shear strengths are reduced by 5% only. (b) Yield ellipse in the σ_1–σ_5 plane. The points correspond to measured yield strengths

To carry out measurements in compression the cylinders were cut short to between 10 to 20 mm to avoid buckling and to minimize end effects.

The bottles, which had approximate dimensions of 30 cm in length and 11 cm in diameter, were cut open, and by removing the top and bottom parts, resulted in a sheet of PET film about 20×30 cm. Dumb-bell shaped specimens 115 mm long, 6 mm wide at the gauge, were cut out from the film at various orientations with respect to the hoop direction. The thickness of the specimens varied between 0.33 and 0.36 mm. These specimens were used to measure the yield strengths in uniaxial tension. Due to the small thickness dimension of the film, compressive yield strengths in the plane of the film could not be measured.

METHOD OF TESTING

All mechanical tests were carried out on an Instron Universal Testing Machine in a temperature controlled room. The temperature of testing was 20°±1°C. The specimens were loaded under constant cross-head speed condition, which was chosen for the various types of specimen to approximate equal material strain rate of 0.1 min^{-1}.

The extension of the thin film specimens was measured using an Instron extensometer. The deformation of the cylindrical specimens was measured by means of the cross-head movement. No attempt was made to measure the deformation of specimens for the shear yield, and the off-axis tensile yield type.

The load was measured by appropriate load cells, and the relevant dimensions of each specimen were recorded prior to testing.

To measure the yield strengths in shear in the plane of the film the method of Sternstein *et al.*[11] was followed.

RESULTS

In the bottle bursting tests plastic deformation was observed in the cylindrical portion. The pressure at the onset of yield was measured to be equal to 0.98 MPa. Assuming that the stresses in the walls of the bottle approximate the case of a pressurized long cylinder[12], we calculated the stresses at yield; $\sigma_1 = 2\sigma_3 = 165 \pm 6$ MPa.

The results for the off-axis measurements are summarized in the *Tables 1* and *2*.

Substitution in equation (8) for stresses using the data from (i) bursting; (ii) tension: *Table 1* for angles 0° and 90°; (iii) shear: *Table 2* for angles 0°, 45° and 135°, results in a set of six simultaneous equations with six unknowns. Calculations result in the values of the strength coefficients as follows:

$$\begin{aligned}
F_{11} &= 6.40 \times 10^{-5} \quad [\mathrm{MPa}]^{-2} \\
F_{33} &= 1.74 \times 10^{-4} \quad \text{"} \\
F_{55} &= 5.67 \times 10^{-4} \quad \text{"} \\
F_{13} &= -7.25 \times 10^{-5} \quad \text{"} \\
F_1 &= -2.39 \times 10^{-3} \quad [\mathrm{MPA}]^{-1} \\
F_3 &= 5.28 \times 10^{-3} \quad \text{"}
\end{aligned} \tag{20}$$

The yield ellipses for oriented PET are shown in *Figures 6(a)* and *(b)*.

The measurement of the tensile and compressive yield strengths on the isotropic PET gave the following results:

Tensile strength = 57.9 MPa

Compressive strength = 66.7 MPa

The corresponding yield ellipse is shown in *Figure 7*.

The use of equations (18) and (19) and the constants in (20) results in *Figure 8*, in which the solid lines correspond to the equations and the points to the data in *Tables 1* and *2*.

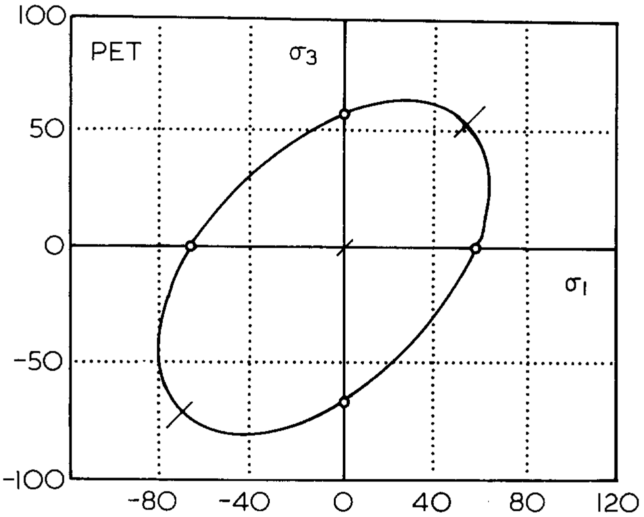

Figure 7 Yield ellipse for the isotropic PET according to the equation (15). The points correspond to measured yield strengths

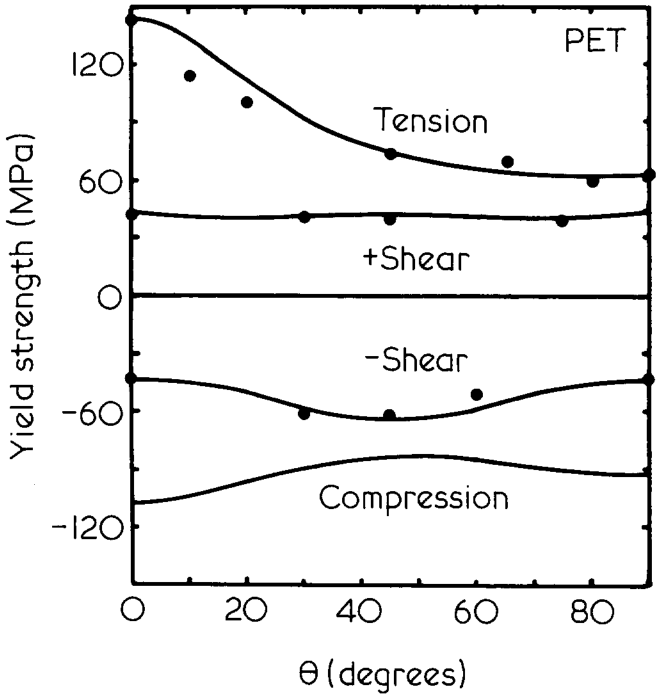

Figure 8 Variation of the off-axis yield strengths with angle θ for the oriented PET. The curves drawn according to equations (18), (19) and (20). The points drawn according to data in *Tables 1* and *2*

DISCUSSION

Relationship between yield behaviour and molecular structure

The results for the oriented and isotropic PET presented in *Figures 6* and *8* are consistent with the above described theory. The yield ellipse for the istropic PET has its major axis inclined at 45° to the σ_1 axis, and its centre is displaced towards the third quadrant indicating dependence of yield on hydrostatic pressure. According to equation (15) only two experimental measurements are required to determine the yield ellipse. It was shown in other publications[13,14] that this equation describes adequately the yield behaviour of homogeneous isotropic polymers. We may assume that the two points in *Figure 7* are sufficient, and that the ellipse represents the loci of yield strengths of this material.

For the oriented PET (*Figure 6a*) the yield ellipse is rotated towards the σ_1 axis (parallel with the hoop direction). Also the centre of the ellipse is displaced from the $\sigma_1 = \sigma_3$ line. Such a 'distortion' of the yield ellipse from its 'isotropic state' corresponds to the changes in the yield behaviour of the material resulting from the introduced molecular orientation. The elongation of the ellipse towards the hoop direction reflects the increased yield strength of the material in the direction of maximum drawing.

Five points are required to determine uniquely the ellipse for the anisotropic materials. The accuracy in determining the ellipse depends on the position of the points, and the amount of error allowed. In *Figure 6a* five experimental points are shown. Each point is an average of at least six measurements, and we estimate the errors to be approximately ±5%. The shape of the ellipse in the first quadrant would not be altered noticeably by variation of ±5% of the experimental values for tensile strengths (uniaxial and biaxial). However, diminishing the value of the shear yield strengths by 5% has a pronounced effect on the shape of the ellipse in the third quadrant. This is illustrated in *Figure 6a* by the broken line. Consequently, one must note that the predictive ability of equation (8) for the yield behaviour in the third quadrant is very uncertain, unless the accuracy of measurements is increased, or the range of measurements is extended to the third quadrant.

In isotropic polymers it is usually observed that the yield strength in compression is about 10% to 30% higher than that in tension. Surprisingly, in oriented polymers the reverse is true for the directions of maximum molecular orientation. The yield strength in tension is much higher than that in compression along the hoop direction. In this respect oriented polymers resemble fibre reinforced composite materials. It is possible that the highly oriented polymers (particularly crystalline) may be considered as two phase materials; bundles of highly drawn molecules resembling the fibres, and the less oriented regions acting as the matrix. This interpretation has been used to account for the very high elastic anisotropy of polymers[15]. If this analogy is valid then the molecular mechanisms of yield in highly anisotropic polymers may be studied in terms of the behaviour of composite materials.

The yield properties of PET have been measured and studied previously[16,17]. However, we do not wish to make any comparisons between the various grades of PET. Instead, it is more instructive to discuss the yield behaviour of PET in relation to other materials. Sufficiently complete yield data are available for uniaxially oriented PVC[18] and PP[19]. From these, the strength coefficients can be calculated and the yield ellipses drawn. They are shown in *Figures 9* and *10*.

It is immediately obvious from *Figure 9* that the yield anisotropy of PVC is not very pronounced. This is consistent with the view that in noncrystalline polymers the network deformation process produces only small effects on mechanical properties[20]. The elastic anisotropy of oriented PVC is also not very pronounced[21].

The mechanical anisotropy of yield in PP (*Figure 10*) is highly developed. This is indicated by the elongation of the ellipse, its inclination towards the σ_1 axis and

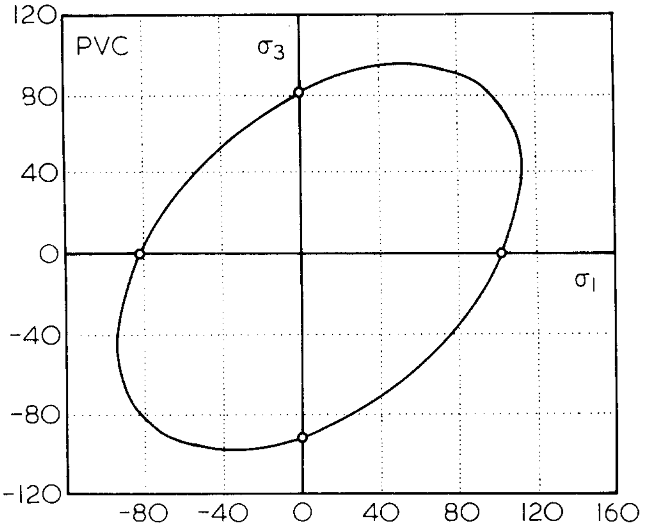

Figure 9 Yield ellipse in the σ_1–σ_3 plane for uniaxially oriented PVC constructed on the basis of data published by Rawson and Rider[18]

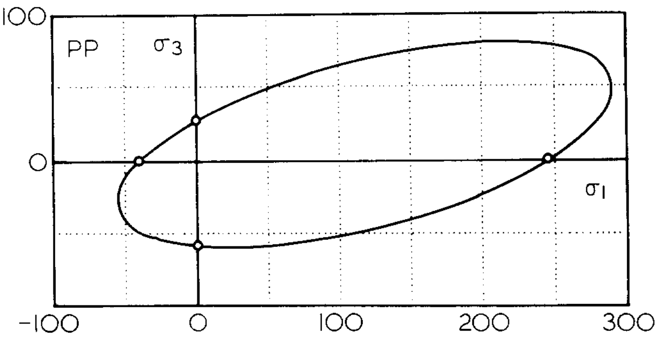

Figure 10 Yield ellipse in the σ_1–σ_3 plane for uniaxially oriented PP constructed on the basis of data published by Shinozaki and Groves[19]

displacement of its centre from the point of $\sigma_1 = \sigma_3 = 0$. This material has high crystallinity and drawing produces a large degree of molecular orientation. The crystalline entities, in the form of fibrils, can be thought of as short fibres embedded in less oriented amorphous matrix. In tension along the draw direction yielding can occur by shear on the fibre–matrix interface. This requires high stresses as compared to yielding in compression which can involve buckling or reverse shear of the crystallites, aided by the rubber-like internal stresses existing in the amorphous matrix. A further discussion of molecular mechanisms of yielding in polymers will follow in a future publication.

Hill–von Mises theory

The Hill–von Mises theory for orthotropic materials[22] was generally used in the past to describe the yield behaviour of oriented polymers. The equation is of the following form:

$$F(\sigma_2-\sigma_3)^2+G(\sigma_1-\sigma_2)^2+H(\sigma_3-\sigma_1)^2 \\ +L\sigma_{23}+M\sigma_{31}+N\sigma_{12}=1 \quad (21)$$

where σ's represent the stress components and $F, G, \ldots, N$ are the strength constants. Whereas the theory is successful in describing the yield behaviour of anisotropic metals, an early paper by Brown *et al.*[16] showed that application of equation (21) to oriented PET gave poor correlation with experimental data. Also the significance of the natural difference between tensile and compressive yield strengths was not well understood at that time.

Initially the difference was thought to result from internal stresses in the material caused by the drawing process. On this basis Brown *et al.*[16] and Rawson and Ryder[18] modified equation (21) by adding a term corresponding to internal stress. The latter authors obtained value for the internal stress of the order of 20 MNm^{-2}, which they compared to rubber elasticity forces. However, a later work by Shinozaki and Groves[19] showed that the internal stress concept is not satisfactory as it turns out to be much higher than either rubber elasticity forces or the drawing forces at elevated temperature. Their general conclusion was that the Hill–von Mises theory is not suitable for anisotropic polymers.

Hoffman anisotropic failure criterion

Hoffman[23] has proposed an empirical equation to describe failure of orthotropic materials, allowing for unequal tensile and compressive strengths, in the following form:

$$C_1(\sigma_2-\sigma_3)^2+C_2(\sigma_3-\sigma_1)^2+C_3(\sigma_1-\sigma_2)^2+C_4\sigma_1 \\ +C_5\sigma_2+C_6\sigma_3+C_7\sigma_4^2+C_8\sigma_5^2+C_9\sigma_6^2=1 \quad (22)$$

In this equation the constants $C_1, C_2, \ldots, C_9$ are defined as follows:

$$C_1=\frac{1}{2}\left[\frac{1}{X_2\bar{X}_2}+\frac{1}{X_3\bar{X}_3}-\frac{1}{X_1\bar{X}_1}\right],$$

C_2 and C_3 by permutation of the subscripts 1, 2 and 3

$$\left.\begin{array}{l} C_4=\dfrac{1}{X_1}-\dfrac{1}{\bar{X}_1}, \quad C_5 \text{ and } C_6 \text{ by permutation of 2 and 3} \\ C_7=\left(\dfrac{1}{X_4}\right)^2, \quad C_8 \text{ and } C_9 \text{ by permutation of 5 and 6.} \end{array}\right\} \quad (23)$$

In equations (23) X, X_2, X_3 and $\bar{X}, \bar{X}_2$ and $\bar{X}_3$ have exactly the same meaning as defined earlier on in equation (9). However, the definition of the constants C_1, C_2 and C_3 is fundamentally different from those defined by Malmeister and Tsai–Wu, in that each of the constants depends on the strength properties in the three orthogonal directions.

Although Hoffman proposed this equation for the brittle failure of fibre reinforced composities, it has been used to describe the yield behaviour of anisotropic polymers. Indeed the same equation was proposed elsewhere[24] as a yield criterion for oriented polymers. The authors have elucidated on the advantages of this equation, and evaluated their own, and published, data in terms of the equation.

The theory of Hoffman has a major deficiency in that it cannot be simply reduced to a two-dimensional case (e.g. plane stress) for materials of orthogonal molecular symmetry. Thus, if the material in *Figure 1* is loaded in such a way that all stresses containing the 2-direction vanish then equation (22) must reduce to:

$$(C_2+C_3)\sigma_1^2+(C_1+C_2)\sigma_3^2+C_8\sigma_5^2 \\ -2C_2\sigma_1\sigma_3+C_4\sigma_1+C_6\sigma_3=1 \quad (24)$$

Using relations (23) we find that (C_2+C_3) and (C_1+C_2) can be expressed in terms of strengths in the 1 and 3 directions only. However, C_2 depends on the strengths in the three orthogonal directions. Therefore, equation (24) is indeterminate unless the strength properties in the 2-direction are measured separately. Conversely, the erroneous conclusion could be reached that application of equation (24) to biaxially oriented polymer films allows one to predict the out-of-plane strength by measuring the strength properties in the 1–3 plane only.

In his paper Hoffman gives an example of a fibre reinforced composite which has transverse isotropy. Indeed, if the axis of transverse isotropy is assumed to lie along the 3-axis then $X_1 = X_2$ and $\bar{X}_1 = \bar{X}_2$. Under these conditions equation (22) reduces to:

$$(C_2+C_3)\sigma_1^2+(C_1+C_2)(\sigma_3^2-\sigma_1\sigma_3)+C_8\sigma_5^2+C_4\sigma_1+C_6\sigma_3=1 \qquad (25)$$

In this case the equation has five independent strength constants which can be determined by five independent measurements, and therefore it is self-consistent from the analytical point of view. The limitation of Hoffman's equation in two dimensions to transversely isotropic materials has been mistakenly reported by Franklin[1] as applicable to orthotropic materials.

In summary, Hoffman's equation is limited in three dimensions to materials of orthogonal symmetry and in two dimensions for materials of transverse isotropy. Therefore, it is of limited scope and is unlikely to become useful in our understanding of yield behaviour in oriented polymers.

SUMMARY

It has been clearly demonstrated that polymers show dependence of yield behaviour on hydrostatic pressure[25]. Consequently any mathematical model for a yield criterion must include the first stress invariant. A simplification by replacement of stress invariants with deviatoric invariants is inadmissible. This means that a physical interpretation in terms of distortional energy or octahedral stress is not possible.

Irrespective of the molecular mechanisms involved, preference should be given to mathematical models which satisfy the condition of material frame indifference. The use of strength tensors in the Malmeister and Tsai–Wu theory gives transformation invariance and hence satisfies the above condition. By contrast, the Hill and Hoffman yield criteria (in which the strength constants do not form a tensor) are applicable only when the axes of molecular (material) symmetry coincide with the reference axes.

Advantages of the tensor polynomial include: (i) flexibility without redundancy; (ii) independency of F_{13} (in the Hill–Hoffman theories $-F_{13}=F_{11}+F_{12}$), and (iii) ease of application of three-, two- and one-dimensional cases by the appropriate use of the indices.

In applying the yield criterion to anisotropic (oriented) polymers one must be careful to ensure that it corresponds to a particular molecular mechanism. In reality, several molecular mechanisms may be operative in different regions of the stress state. Therefore, a thorough understanding of the underlying molecular processes is required, before any physical interpretation of the strength constants can be attempted.

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