JOURNAL OF MATERIALS SCIENCE 6 (1971) 1397–1417

Review: The Yield Behaviour of Polymers

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Recent research on the yield behaviour of polymers is reviewed. Particular attention is given to the importance of the hydrostatic component of stress, the viscoelastic nature of the yield process, and the behaviour of oriented polymers.

1. Introduction

Although the mechanical behaviour of polymers is very sensitive to the variables of time and temperature, it is convenient to initiate the discussion with considerations of classical plasticity. We imagine that all our data refer to a given strain-rate at a fixed temperature and that time does not enter as a variable. It is similar to the approach to anisotropic mechanical behaviour in polymers, where one usually starts by assuming that all the data refer to a fixed time of response under dead loading conditions, for example, and then proceeds to an *elastic* analysis of the situation.

In the case of yield behaviour, this bypasses arguments about the observation of yield drops in polymers and whether true yield points exist. We will assume at this stage that complications due to adiabatic heating and geometric effects can be ignored and that a yield point *can* be defined.

One of the problems in adopting a simple approach of this nature is that the whole stress-strain curve is in general different for different stress fields. In tensile tests a neck is usually formed and the yield point defined as the stress at maximum observed load. In other tests such as compression tests a load drop is often not observed and the yield point is then defined as the point of intersection of two tangent lines on the load-elongation curve (fig. 1). In our discussions we will assume that these definitions of yield can be regarded as equivalent.

2. Classical Plasticity

In classical plasticity, the first aim is to find a function of all the components of stress which reaches a critical value for all tests. This is the *yield criterion*, and in its most general form it is a function of all the six independent components of stress. We can therefore write the yield criterion analytically as

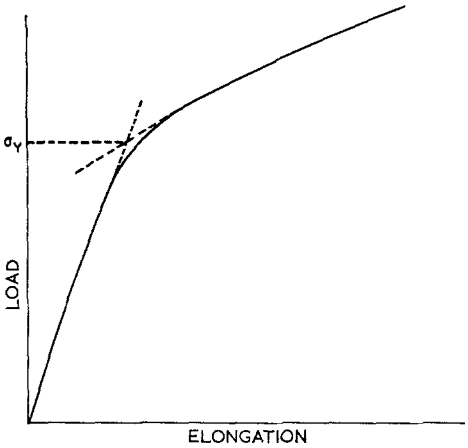

Figure 1 Definition of the yield point as the point of intersection of two tangent lines on the load-elongation curve σ_Y is the yield stress.

$$f(\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{xy}, \sigma_{yz}, \sigma_{zx}) = \text{constant}.$$

The form of this function f can be restricted on the basis of physical conditions. In the preliminary discussion we will be considering isotropic polymers. This means that f must be independent of the choice of the cartesian co-ordinate axes x, y, z. It must, therefore, be a function of the invariants of the stress tensor.

For convenience, we can now also refer the stresses to the principal axes of stress and the stress tensor becomes

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

The yield criterion can therefore be represented as a function of the three simplest stress invariants J_1, J_2, and J_3.

We have $f(J_1, J_2, J_3) = \text{constant}$,

$$\begin{aligned} \text{where } J_1 &= \sigma_2 + \sigma_2 + \sigma_3 \\ J_2 &= (\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1) \\ J_3 &= \sigma_1\sigma_2\sigma_3 \end{aligned}$$

A further simplification of the yield criterion is obtained if we also assume that the yield behaviour is independent of the hydrostatic component of stress. This has the consequence in mathematical terms that the yield criterion will be a function of the components of the *deviatoric stress tensor* σ_{ij}', obtained by subtracting the hydrostatic component of stress from the total stress tensor.

$$\sigma_{ij}' = \sigma_{ij} - p\delta_{ij}$$

where

$$\delta_{ij} = 1, i = j; \delta_{ij} = 0, i \neq j .$$

In terms of the principal components of stress the yield criterion becomes

$$f(\sigma_1', \sigma_2', \sigma_3') = \text{constant},$$

where

$$\sigma_1' = \sigma_1 - p, \sigma_2' = \sigma_2 - p, \sigma_3' = \sigma_3 - p.$$

Since $\sigma_1' + \sigma_2' + \sigma_3' = 0$, the yield criterion becomes

$$f(J_2', J_3') = 0$$

where

$$\begin{aligned} J_2' &= -(\sigma_1'\sigma_2' + \sigma_2'\sigma_3' + \sigma_3'\sigma_1') \\ &= \tfrac{1}{2}\{(\sigma_1')^2 + (\sigma_2')^2 + (\sigma_3')^2\} \\ J_3' &= \sigma_1'\sigma_2'\sigma_3' \end{aligned}$$

Another simplification of the yield criterion can be made. Let us assume that the magnitude of the yield stresses in simple tension and compression are identical. This means that the function f involves only even powers of J_3'. The simplest possible situation would be that f does not involve J_3'.

In metals, the observation in some cases of a difference between tensile and compressive yield behaviour is known as the Bauschinger effect [1] and is usually associated with the presence of anisotropy. Cold working is considered to produce internal stresses, which can be readily seen as intuitive grounds to give rise to an asymmetry in the situation with regard to tensile and compressive experiments.

This treatment of yield behaviour may appear to be excessively formal, but it is intended to emphasise the consequences of three physical assumptions:

(1) Isotropy.
(2) No dependence of behaviour on the hydrostatic component of stress.
(3) Identical yield behaviour in tension and compression.

It is worth noting that an observed difference between the tensile and compressive yield stress does not *necessarily* imply that the yield criterion involves the hydrostatic component of stress. In fact, it has been found that the Bauschinger effect in highly oriented polymers is very large compared with the effect of hydrostatic component of stress, so that the effect of the latter may be neglected to a first approximation.

On the other hand, the introduction of the effect of the hydrostatic component of stress in an appropriate manner to represent the observed results for polymers, does produce a difference between the tensile and compressive yield stresses It will be shown that the observed differences between the tensile and compressive yield stresses in isotropic polymers are consistent with direct measurements of the effect of the hydrostatic component of stress on the shear yield stress. At this point, however, even a first order phenomenological treatment of the behaviour will take us out of the realm of classical plasticity to considerations of non-linear *viscoelastic* behaviour.

2.1. Simple Yield Criteria

1. The Tresca Yield Criterion [2]

The Tresca yield criterion states that yield occurs when the maximum shear stress reaches a critical value. In mathematical terms we have

$$|\sigma_1 - \sigma_3| = \text{constant}$$

with $\sigma_1 > \sigma_2 > \sigma_3$.

This yield criterion satisfies the three simple physical assumptions discussed above i.e. material isotropy, independence of the hydrostatic component of stress and identical behaviour in tension and compression.

2. The von Mises Yield Criterion

In terms of our development, the von Mises criterion is that the yield criterion is a function of J_2' only.

i.e.

$$J_2' = \text{constant} = K^2 \text{ say} .$$

It may readily be shown that this is equivalent to

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6K^2$$

which is perhaps a more familiar form of this yield criterion.

2.2 Combined Stress States

Having prepared the ground to a certain extent, we will now consider the yield behaviour of polymers and in particular the response of a given polymer to different stress states and to combined stress states. It is then very useful to translate these analytical considerations into their geometrical consequences i.e. to consider the geometrical shape of the yield criteria in various chosen co-ordinate systems. We will consider two cases.

1. Principal stress space.
2. The Mohr circle diagrams.

1. Principal Stress Space

The consequence of the assumption of independence of hydrostatic pressure p means that σ_1, σ_2 and σ_3 in the yield criterion can be replaced by $\sigma_1 + p$, $\sigma_2 + p$ and $\sigma_3 + p$. Thus if the point σ_1, σ_2, and σ_3 lies in the yield surface so does the point $\sigma_1 + p$, $\sigma_2 + p$, $\sigma_3 + p$. The yield surface must, therefore, be parallel to the [1 1 1] direction in principal stress space and can be represented by the cross-section normal to this direction. The material isotropy implies equivalence of σ_1, σ_2 and σ_3; the assumption that the behaviour is the same in tension and compression implies equivalence of σ_1 and $-\sigma_1$. These two assumptions taken together imply that the yield surface has six fold symmetry about the [1 1 1] direction.

The cross-section of the yield criterion normal to the [1 1 1] direction therefore consists of twelve equivalent parts. The Tresca criterion gives a regular hexagon and the von Mises criterion a circle, as shown in fig. 2a.

We sometimes wish to consider a cross-section of the yield surface which lies in the plane of two of the principal stresses. This is shown in fig. 2b. The Tresca criterion looks a little odd at first sight but is easily brought to mind when we recall that σ_3 is zero. The von Mises yield criterion is an ellipse in this section.

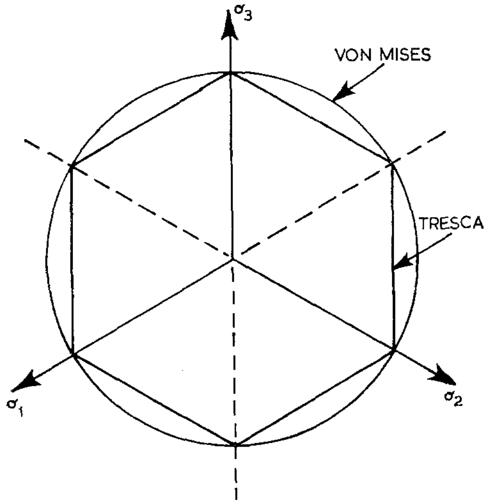

Figure 2a Cross-section of Tresca and von Mises yield surfaces normal to the [1 1 1] direction in principal stress space.

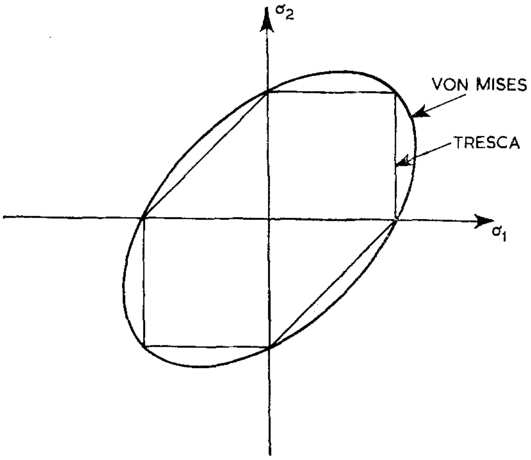

Figure 2b Cross-section of Tresca and von Mises yield surfaces in σ_1 σ_2 plane of principal stress space.

2. The Mohr Circle Diagram

A very useful way of representing data for combined stress states in the two dimensional case is the Mohr circle diagram [4]. The stresses acting on any plane in a material can be resolved into a normal stress σ acting normal to the plane and a shear stress τ acting in the plane.

Mohr circle diagrams for some simple stress states are shown in fig. 3. Pure tension with a tensile stress σ_1 is a circle of diameter σ_1, with its origin at the point $\sigma_1/2$, O. A rotation of $\theta°$ in real space corresponds to a rotation of $2\theta°$ in the Mohr circle diagram. We can therefore see that the tensile stress σ_1 gives a normal stress σ_1 and zero shear stress on a plane whose normal is parallel to the direction of σ_1 (point A), zero normal stress and zero shear stress on a plane perpendicular to this direction (point B), and a shear stress and a normal stress of magnitude $\sigma_1/2$ on a plane at 45° to this direction (point C).

A similar circle, passing through the points B, D, E represents a compressive stress σ_1, this circle being centred at the point $-\sigma_1/2$, O.

The value of the Mohr circle diagram is that it shows how the application of one set of stresses

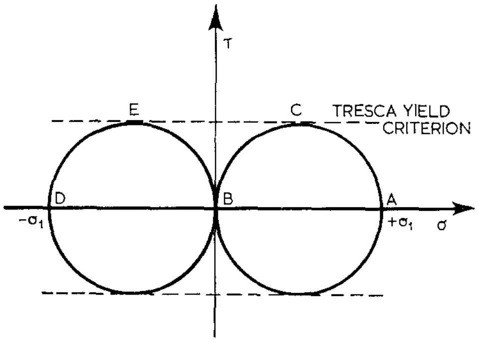

Figure 3 Mohr circle diagrams for simple stress states.

to an isotropic solid is equivalent to a number of combined stress states – all the points on the Mohr circle. It is therefore particularly valuable when we come to consider yield criteria, because the yield criterion will now be defined from experimental data as the *envelope* of the Mohr circles. For the Tresca yield criterion this envelope is simply the tangent lines to a set of circles of identical radius with their centres on the normal stress axis, i.e. the two parallel dotted lines in fig. 3.

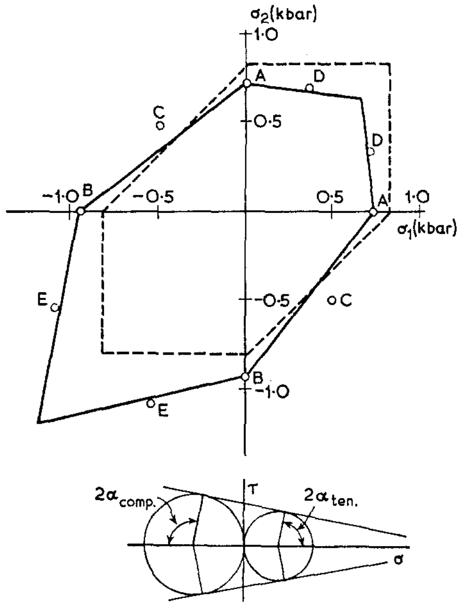

Figure 4 (a) Yield locus of polystyrene showing the pressure dependence of yielding; (b) Angle which bands make the tension and compression axes (after Argon *et al*).

2.3. Results for Isotropic Polymers

Some of the results obtained for the yield behaviour of polymers will now be considered in the light of the above discussion. The selection of these results is somewhat arbitrary but is intended to be representative.

Fig. 4 shows data for the yield of polystyrene under various stress conditions [5]: tension (A), compression (B), torsion (C), biaxial tension (D) and punch indentation (E). Although there are some reservations about the data because the specimen had been slightly preoriented it is evident that the data do not fit the Tresca or the von Mises yield criteria. This is clearly shown by the two representations of the data in principal stress space and in the Mohr circle diagrams.

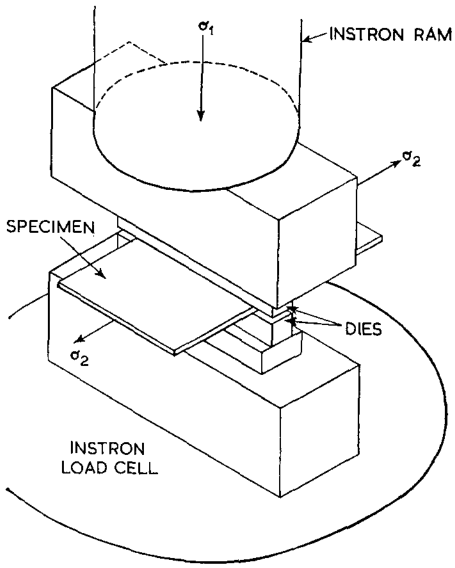

Figure 5 The experimental arrangement for plane strain compression (after Bowden and Jukes).

Somewhat similar results were obtained by Bowden and Jukes [6] using the plane strain compression technique shown in fig. 5. The polymer specimen, in the form of a sheet, is simultaneously subjected to a compressive stress σ_1 and a tensile stress σ_2. The virtue of the method is that it allows the yield behaviour to be determined for a material which is brittle in a simple tension test. Bowden and Jukes' data are shown in figs. 6 and 7. We must beware of too facile an interpretation of fig. 6. In these tests the third stress σ_3 is not measured but it is finite and is given by $\sigma_3 = \nu(\sigma_1 + \sigma_2)$ where ν is Poisson's ratio. Thus fig. 6 does not show a (001) plane in principal stress space. However, fig. 7 clearly illustrates that the data do not fit the Tresca yield criterion.

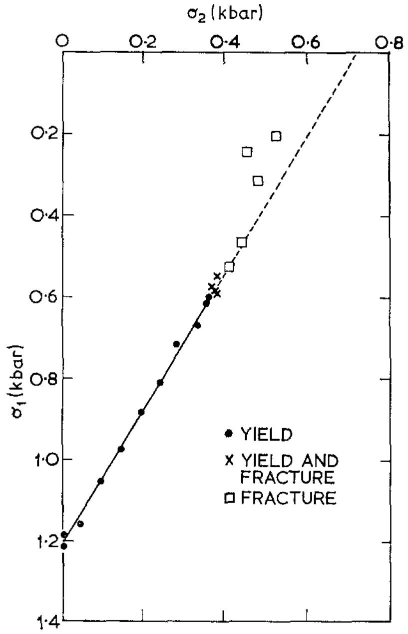

Figure 6 Measured values of the compressive yield stress, σ_1 (true stress) plotted against applied tensile stress, σ_2 (nominal stress). The full circles denote ductile yield, the crosses brittle fracture, and the combined points tests where ductile yielding occurred, followed immediately by brittle fracture. The polymer is polymethylmethacrylate (after Bowden and Jukes).

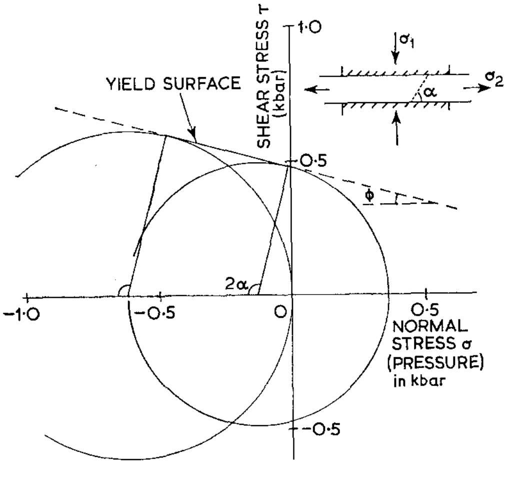

Figure 7 Mohr's circle diagram constructed from the data in fig. 3. The angle ϕ is the angle of internal friction equal to $\tan^{-1}\mu$ (after Bowden and Jukes).

Data of this type show that the yield behaviour of polymers is not consistent with either the Tresca or the von Mises yield criterion, and we have seen that in principle this can be due to three causes

(1) Lack of isotropy.
(2) Dependence on pressure.
(3) A Bauschinger effect.

There is, however, also direct evidence for the effect of the hydrostatic component of stress on the yield behaviour of polymers. The earliest research on this aspect was undertaken in Russia by Ainbinder *et al* [7] and in Britain by Holliday *et al* [8]. Recently there have been more detailed studies by three groups, at the Western Reserve Case University by Biglione *et al* [9], Rutgers University in USA by Mears *et al* [10], and at Bristol and Leeds University in Britain by Rabinowitz *et al* [11]. Fig. 8 shows results for polystyrene obtained by Biglione *et al.* Increasing the hydrostatic pressure inhibits fracture by closing up cracks, and at sufficiently high pressures the polymer yields, to be followed by an increasing tensile yield stress with increasing hydrostatic pressure. Fig. 9 shows the effect of pressure on the tensile yield stress of high-density polyethylene. These results by Maer *et al* show a three-fold increase in the yield stress for a pressure of about 5 kbar.

Finally, there are shown in fig. 10, the results of measurements by Rabinowitz, Ward and Parry, of the effect of hydrostatic pressure on the shear yield stress of polymethylmethacrylate. The shear yield stress more than doubles for a pressure of 3 kbar. These results are shown as Mohr circle diagrams in fig. 11. The data of

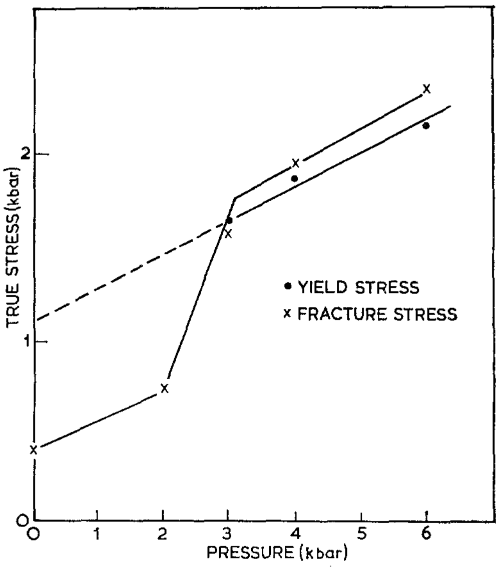

Figure 8 Polystyrene: True stress versus pressure (after Biglione *et al*).

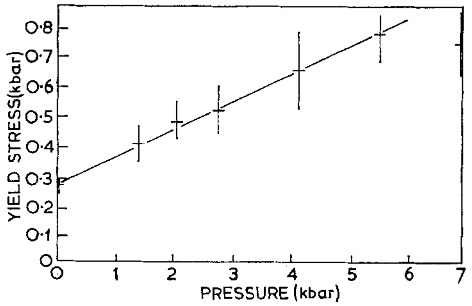

Figure 9. Polyethylene: Peak yield stress versus pressure (after Mears *et al*).

Bowden and Jukes discussed above are shown as the crossed points. They are consistent with the pressure data, but it is to be noted that they fit into a small part of the diagram. This emphasises how the use of a hydrostatic component of stress enables a much more complete exploration of yield behaviour.

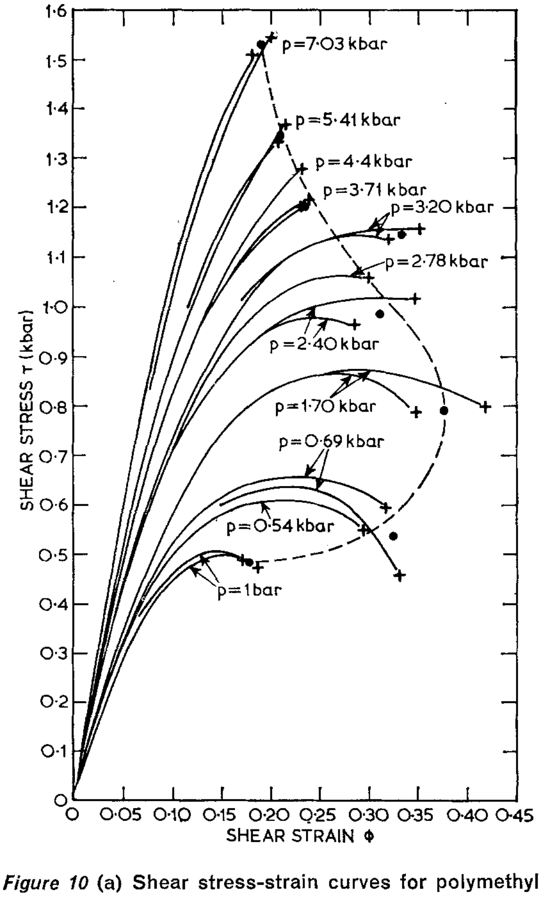

Figure 10 (a) Shear stress-strain curves for polymethylmethacrylate showing fracture envelope.

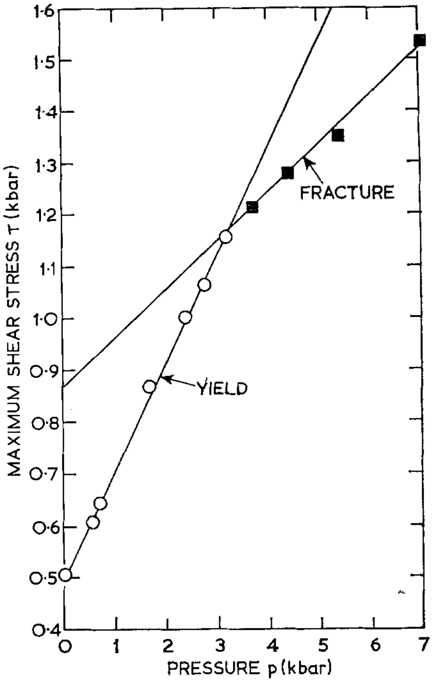

Figure 10 (b) Maximum shear stress τ as a function of pressure for polymethylmethacrylate. ○, yield; ■, fracture (after Rabinowitz *et al*).

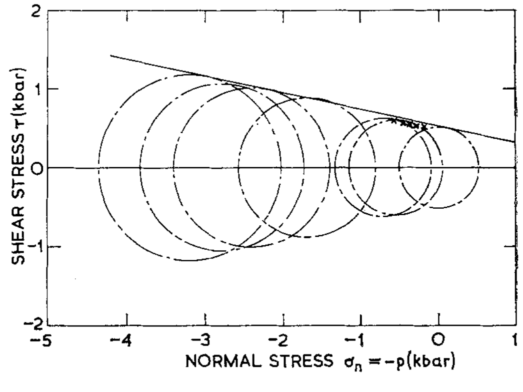

Figure 11 Mohr-circles for yield behaviour of polymethylmethacrylate. The common tangent gives the yield plane at ~30° (after Rabinowitz *et al*).

3. Modified Yield Criteria

We must now produce a modified yield criterion which describes the observed pressure dependence. Let us first proceed along the lines of classical time independent plasticity.

3.1. The Coulomb Yield Criterion

An even earlier yield criterion than the Tresca maximum shear stress criterion was due to Coulomb [12] and originally applied to soils.

The Coulomb yield criterion states that the critical stress for yielding to occur in any plane in the material increases linearly with the pressure applied normal to this plane.

Thus

$$\tau = \tau_c + \mu\sigma_n$$

where τ_c is a critical shear stress called the "cohesion" of the material. μ is a "coefficient of friction" and σ_n is the compressive stress on the shear plane; μ is often written as $\tan\phi$, for reasons which will now be made evident.

Consider uniaxial compression under a compressive stress σ_1 where yield occurs on a plane whose normal makes an angle θ with the direction of σ_1. The shear stress $\tau = \sigma_1 \sin\theta\cos\theta$, and the normal stress $\sigma_n = \cos^2\theta$.

The Coulomb yield criterion $\tau = \tau_c + \sigma_n \tan\phi$ then becomes

$$\sigma_1 \sin\theta\cos\theta = \tau_c + \sigma_1 \tan\phi\cos^2\theta$$

i.e. yield occurs when

$$\sigma_1(\cos\theta\sin\theta - \tan\phi\cos^2\theta) \geqslant \tau_c\,.$$

In practice this is achieved by yield occurring in the plane which maximises the quantity $(\cos\theta\sin\theta - \tan\phi\cos^2\theta)$ so that yield occurs for the smallest value of the applied compressive stress σ_1.

This maximisation gives $\tan\phi\tan 2\theta = -1$ or

$$\theta = \pi/4 + \phi/2$$

The direction of yielding therefore defines the angle ϕ where $\tan\phi = \mu$, and we reach the very interesting conclusion that this yield criterion not only defines the stress condition for yielding but also the direction in which the material will deform, i.e. the yield plane.

This conclusion is brought out very clearly by consideration of the Mohr circle diagrams for a typical polymer (see fig. 7). The yield surface is two lines each making an angle ϕ with the normal stress axis. We will now discuss how this relates to measurements of the directions of yielding.

3.2. Observation of Shear Zones or Deformation Bands

In the compressive measurements of Argon *et al* [5], deformation bands were observed. These are shown in fig. 12. The angle between the band packets and the direction of compression is 38°, a result which is clearly consistent in principle with the Coulomb yield criterion.

The shear zones shown in fig. 13 from the plane strain compression results of Bowden and Jukes [6] on polymethylmethacrylate showed a similar directionality. Again this result is to be expected on the basis of a Coulomb yield criterion. However, as remarked by Bowden and Jukes, there are problems in obtaining an exact fit to the data, partly due to the uncertainty of corrections for elastic strains during deformation and partly due to lack of confidence in the Coulomb yield criterion as being capable of dealing with the situation completely.

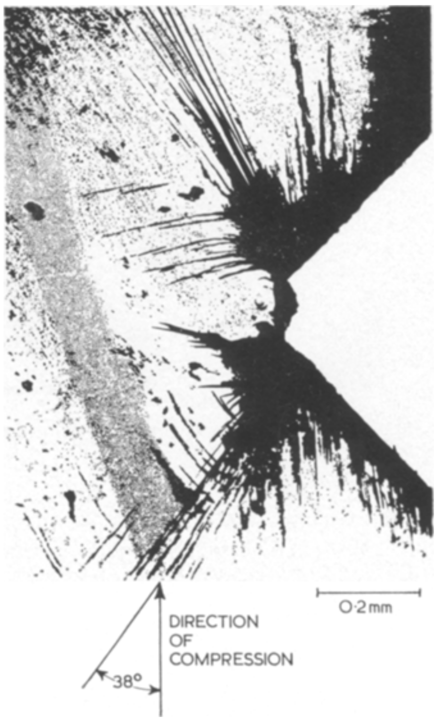

Figure 12 Two deformation band packets radiating out of a notch in a compression specimen of polystyrene (after Argon *et al*).

3.3. A Modified von Mises Yield Criterion

The Coulomb yield criterion was introduced to explain the yield behaviour of soils, and it is intuitively reasonable to imagine that the normal stress on the yield plane plays a part in the shear process of yield in such a material.

For a yielding polymer our intuitive analogy is with the flow of a viscous liquid, where again the shear stress is the critical quantity, but if the liquid is compressible we would imagine that the hydrostatic component of stress will also be important.

The results for the pressure dependence of the

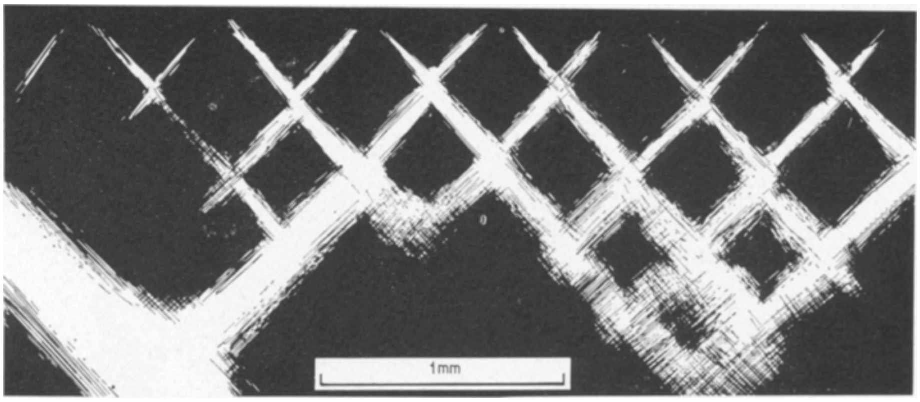

Figure 13 Shear zones obtained in plane strain compression (after Bowden and Jukes).

shear yield behaviour of polymethylmethacrylate [11] (fig. 10) show a very good linear dependence of yield stress on hydrostatic pressure. To a good approximation we have

$$\tau = \tau_0 + ap$$

where τ = shear yield stress at pressure p, τ_0 = yield stress at atmospheric pressure and a is the coefficient of increase of yield stress with hydrostatic pressure.

We will see that this simple form of a pressure dependent yield criterion is most satisfactory when we come to attempt a general rate theory for yield in polymers which includes the effect of pressure dependence.

Somewhat more sophisticated proposals have been made by Maers *et al* [10] and by Sternstein [13]. Maers *et al* [10] have considered a yield criterion originally proposed by Hu and Pae [14] to describe the effects of very high pressure on the yield of metals. The second deviatoric stress invariant J_2' is considered to be a function of the first stress invariant i.e. the hydrostatic pressure. We have

$$J_2' = \mathrm{K}^2 + \alpha J_1 + \beta J_1^2$$

where

$$J_1 = \sigma_1 + \sigma_2 + \sigma_3$$

and

$$J_2' = \tfrac{1}{2}[(\sigma_1 - p)^2 + (\sigma_2 - p)^2 + (\sigma_3 - p)^2]$$

For their experiments of simple tensile stress under a hydrostatic pressure $J_1 = \sigma - 3p$ and

$$J_2' = \tfrac{1}{3}\,\sigma^2$$

The yield criterion becomes

$$\tfrac{1}{3}\sigma^2 = \mathrm{K}^2 + \alpha(\sigma - 3p) + \beta(\sigma - 3p)^2$$

which gives

$$\sigma = \frac{3(\alpha - 6\beta p)}{2(1 - 3\beta)} \pm \left[\left(\frac{3\mathrm{k}^2}{1 - 3\beta}\right) + \frac{9(\alpha^2 - 4\alpha\beta + 12\beta p^2)}{4(1 - 3\beta)^2}\right]^{\frac{1}{2}}$$

The experimental data can be fitted to this equation by a suitable choice of K, α and β. Sternstein's criterion [13] is somewhat simpler. A three-dimensional analogue of the Coulomb criterion is proposed.

$$\tau_{\mathrm{oct}} = \tau_0 - \mu\sigma_{\mathrm{m}}$$

where τ_{oct} is the octohedral shear stress at a pressure p, $\sigma_{\mathrm{m}} = I_1/3$, where I_1 is the first stress invariant, and τ_0 is the octohedral shear stress at zero pressure. Fig. 14 shows data obtained by Sternstein and Ongchin [13] for polymethylmethacrylate. There is a good fit to the data, although the range of the pressure term is rather

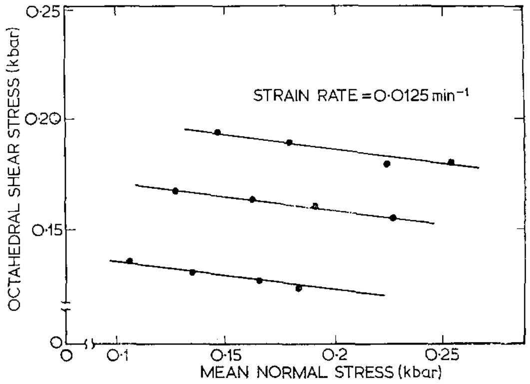

Figure 14 Octahedral shear stress as a function of mean normal stress (after Sternstein and Ongchin).

small compared with that obtained from measurements of tensile or shear yield under a hydrostatic pressure.

Bauwens [15] has proposed a relationship similar to that of Sternstein and Ongchin based on tension and torsion tests on hollow cylindrical specimens of polyvinylchloride. The experimental arrangement is shown in fig. 15. The torsion apparatus was incorporated in an Instron tensometer.

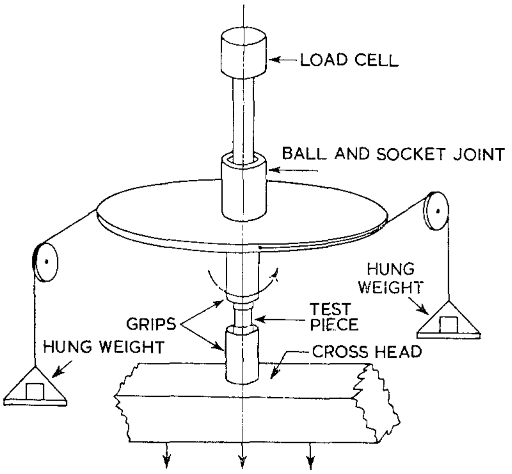

Figure 15 Apparatus for combined tension and torsion tests (after Bauwens).

The tensile elongation was applied at a constant rate parallel to the axis of the specimen, and the shear stress applied by hanging weights over the pulleys. Care was taken to reduce the final data to identical strain rates in tension and torsion.

The yield criterion was assumed to take the form

$$\tau_{\text{oct}} + \mathrm{A}p = f(\dot{e}, T) \qquad (3.1)$$

where A is a constant.

With this assumption it can be shown that the yield stresses in the tension-torsion experiment can be fitted to an ellipse, which differs from the von Mises ellipse. Fig. 16 shows a comparison of the experimental data with the fit to an ellipse on the basis of (3.1). There is a good fit, but a major weakness of this representation of yield behaviour is that it implies that the relationship between the tensile and compressive yield stresses σ_t and σ_c respectively, is given by

$$\frac{\sigma_t}{\sigma_c} = \frac{\sqrt{2} - \mathrm{A}}{\sqrt{2} + \mathrm{A}}$$

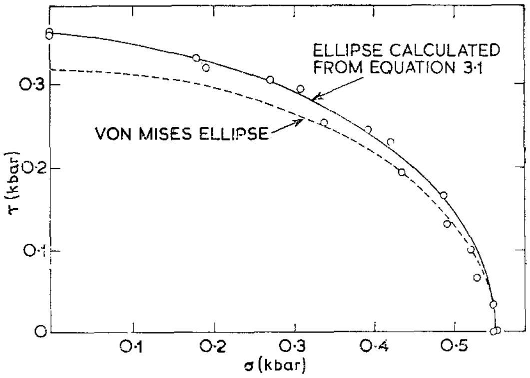

Figure 16 Plot of τ versus σ at the yield limit for tension-torsion tests. Experimental data are compared to the ellipse corresponding to equation (3.1) and to the von Mises ellipse (after Bauwens).

i.e. that it is independent of the strain rate and temperature. As will be discussed below, this is not generally true.

4. The Viscoelastic Nature of Yield Behaviour

The yield behaviour of polymers is very dependent on temperature and the rate of testing. A comprehensive treatment must therefore consider these features as well as deal with the situation of combined stresses, which we have embodied in the yield criterion. The best situation would be that a molecular theory of yield would quite naturally incorporate all these features, and we will eventually discuss present progress along these lines.

Many of the investigations into the viscoelastic nature of yield behaviour have chosen as their starting point the Eyring viscosity equation. This approach has been taken by Roetling [16], Haward and Thackray [17], Bauwens [18], Holt [19] and in his earlier work by Robertson [20].

In the high stress region where yield occurs the Eyring theory gives the relationship between strain rate $\dot{e}$ and applied stress σ

$$\text{as } \dot{e} = \mathrm{A} \exp \frac{(\Delta U - \sigma v)}{kT} \qquad (4.1)$$

where A is a constant, v is the activation volume, k is Boltzmann's constant and T is the absolute temperature. ΔU is the activation energy for the flow process.

The argument is then that at the yield point the time rate of change of stress is zero, although the strain rate is constant. It is also argued that up to the yield point the stress and strain rate are uniform over the specimen. Bypassing a slight uncertainty about the distinction between conditions at the yield point and immediately prior to it we can then regard equation (4.1) as defining the relationship between the yield stress and strain rate.

A simple rearrangement of equation (4.1) gives the yield stress σ_y in terms of the strain rate at yield $\dot{e}$ as:

$$\frac{\sigma_y}{T}=\frac{\Delta U}{\nu T}+\left(\frac{k}{\nu}\right)\frac{\ln \dot{e}}{A} \qquad (4.2)$$

This suggests that plots of σ_y/T against log (strain rate) for a series of temperatures should give a series of parallel straight lines. Fig. 17 shows a set of results for the tensile yield stress of polycarbonate by Bauwens *et al* [18] together with calculated lines based on this equation with constant values of ν and ΔU. The fit is very satisfactory, confirming that the Eyring equation gives a good start to describing the yield behaviour.

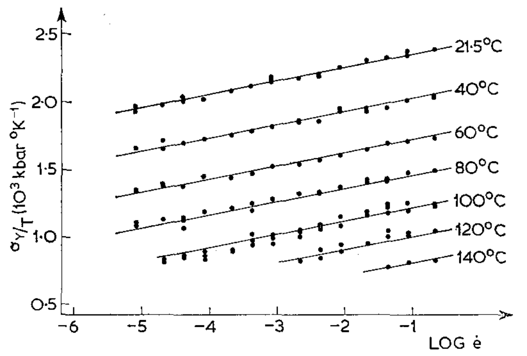

Figure 17 Measured ratio of yield stress to temperature as a function of logarithm of strain rate ($\dot{\epsilon}$ in sec^{-1}) for polycarbonate. The set of parallel straight lines is calculated from the Eyring equation (after Bauwens *et al*).

Haward and Thackray [17] have discussed the possible interpretation of the Eyring activation volume obtained by such procedures, and have considered that the most relevant comparison is with the size of the statistical random link in the polymer chain in dilute solution. We can then obtain some idea of the volume of the polymer chain which moves in the yield process.

Table I contains comparative figures for a number of polymers and is taken from Haward and Thackray's paper. It can be seen that the activation volume varies from about two to ten times that of the statistical random link. This result is very much in accordance with expectation, as it appears very reasonable to suppose that yield involves the cooperative movement of a larger number of chain segments than would be required for a molecular conformational change in dilute solution.

TABLE I A comparison of the statistical segment volume for a polymer measured in solution with the flow volumes derived from the Eyring Theory (after Haward and Thackray).

Polymer	Volume of statistical link in soln (Å^3)	Eyring flow volume V (Å^3)
polyvinylchloride	380	8600 23°C 5000 49°C 12000
polycarbonate	482	6440 25°C 6240 0°C 4300
polymethylmethacrylate	910	4660, 3900 3100 4100
polystyrene	1220	9600 2700
cellulose acetate	2060	8800 20300
cellulose trinitrate	2620	6070 23°C 6000 54°C
cellulose acetate	2060	17400 20°C 28000 33°C

So far the question of pressure dependence of yield behaviour has been ignored. We will now consider data for polyethylene terephthalate [11]. The particular specimens were crystalline and isotropic (Arnite A150, BIP Chemicals Ltd). The next two figures show the relevant data. In fig. 18 there are results obtained by Dr R. A. Duckett [21] for tensile and compressive yield stresses at 20 and 50°C over three decades of strain rate. The compressive yield stresses were measured as the intersection of two tangents on the stress strain curve. It can be seen that over this comparatively small range of strain rates, both the tensile and compressive yield stresses, although different in magnitude, are linearly related to the logarithm of the strain rate. The compressive yield stresses are approximately 1.10 ± 0.03 times the tensile yield stresses over the strain rate range, but there is a tendency for

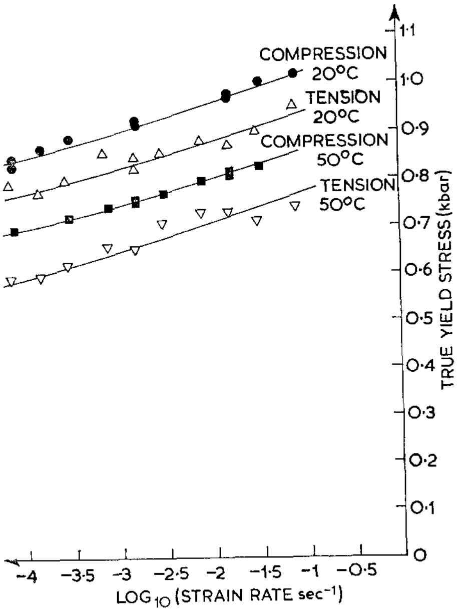

Figure 18 The tensile and compressive yield stress of isotropic polyethylene terephthalate versus $\log_{10}$ (Strain-rate) at 20 and 50° C (Data obtained by Dr R. A. Duckett).

the compressive yield stresses to be the more rate dependent.

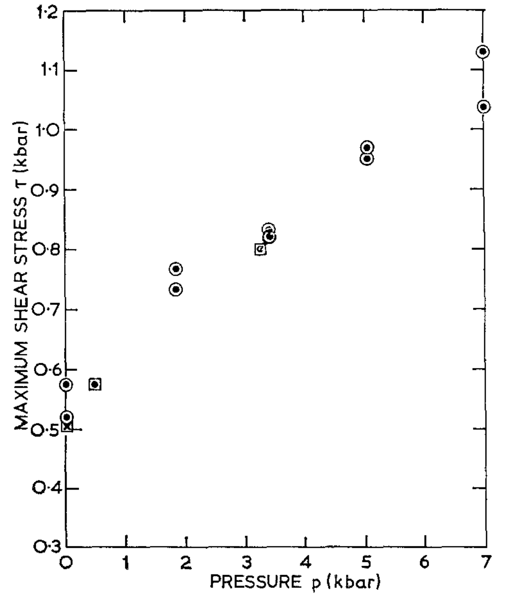

Figure 19 Maximum shear stress as a function of pressure for polyethylene terephthalate. ○, as received; □, annealed; ●, yield; ×, fracture (after Rabinowitz *et al*).

Fig. 19 shows results obtained by Rabinowitz *et al* [11] for the effect of hydrostatic pressure on the shear yield stress of the same material. These results are similar to these obtained for polymethylmethacrylate discussed in Section 2.3 above.

As we have seen one of the simplest ways of representing this shear yield stress data is to write

$$\tau = \tau_0 + ap$$

The data for crystalline isotropic PET give

$$a = 0.075\,.$$

This suggests that the Eyring equation may be very simply modified to include the effect of the hydrostatic component of stress.

$$\dot{e} = \mathrm{A} \exp - \left\{ \frac{\Delta U - \tau\nu + p\Omega}{KT} \right\} \quad (4.3)$$

where τ is the shear yield stress, p is the hydrostatic component of stress and Ω is the "pressure activation volume".

In this very simple modification we see that

$$\left(\frac{\partial\tau}{\partial p}\right)_{\dot{e}.\mathrm{T}} = \frac{\Omega}{\nu}$$

gives the quantity measured in the shear yield stress experiments by Rabinowitz *et al.*

For the tension and compression experiments, the shear and hydrostatic components of stress are given in terms of the observed yield stress σ by

$$\tau = \frac{\sigma}{2}\,, \quad p = -\frac{\sigma}{3}$$

and

$$\tau = \frac{\sigma}{2}\,, \quad p = +\frac{\sigma}{3}\,, \text{ respectively.}$$

We can therefore write an apparent activation volume for the tensile and compressive yield behaviour as

$$(\nu_{\mathrm{app}}) \text{ tension} = \frac{\nu}{2} + \frac{\Omega}{3}$$

$$(\nu_{\mathrm{app}}) \text{ compression} = \frac{\nu}{2} - \frac{\Omega}{3}$$

The tensile and compressive yield data shown in fig. 19 give a value for Ω/ν of 0.13 ± 0.035. From such simple starting considerations, this value is sufficiently close to the directly measured value of 0.075 to suggest that the approach is a sensible one, although a more sophisticated representation may be required.

Having introduced the subject of the viscoelastic nature of the yield behaviour by discussing the use of the Eyring equation it is now desirable to redress the balance somewhat by [illegible] its shortcomings. The Eyring equation implies [illegible]

$$\left(\frac{\partial\sigma_{\mathrm{y}}/T}{\partial \ln \ddot{e}}\right)_T$$

should be independent of temperature. This is not generally true, although it was shown by Bauwens to hold for polycarbonate as we saw above. In many cases $(\partial\sigma_{\mathrm{y}}/\partial \ln \dot{e})_T$ is approximately independent of temperature, and in fig. 20 we see some data for the compressional yield behaviour of polymethylmethacrylate [19] in which $(\partial\sigma_{\mathrm{y}}/\partial \ln \dot{e})_T$ *decreases* with increasing temperature which implies that the activation volume should increase with increasing temperature.

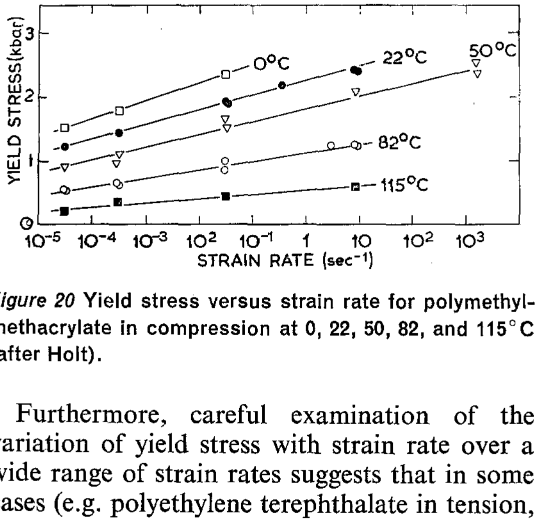

Figure 20 Yield stress versus strain rate for polymethylmethacrylate in compression at 0, 22, 50, 82, and 115°C (after Holt).

Furthermore, careful examination of the variation of yield stress with strain rate over a wide range of strain rates suggests that in some cases (e.g. polyethylene terephthalate in tension, polymethylmethacrylate in compression) there is distinct curvature on the plots of yield stress against the logarithm of the strain rate.

For these reasons, together with the desirability of obtaining a more satisfactory molecular theory of yield than is offered by the Eyring equation, we will consider in detail more involved theories of yield behaviour.

4.1. The Robertson Theory of Yield

Robertson [22] has developed a molecular theory of yield behaviour which can be regarded as a slightly more elaborate version of the Eyring viscosity theory. It has the merit of attempting to incorporate structural ideas, rather than leaving the discussion at a purely phenomenological level.

For simplicity it is assumed that the polymer chain contains only two local stable conformational states. These are the extended chain trans low energy state, and the cis high energy state, which Robertson terms the flexed state. It is proposed that in equilibrium the fraction in each state is given by the Boltzmann distribution, governed by the free energy difference ΔU_1 between the two equilibrium states.

The glassy polymer is considered as being quenched in the state it occupied at the glass transition temperature T_{g}. Thus prior to the application of stress the fraction of elements in the high energy state is

$$\chi_{\mathrm{i}} = \exp\left\{-\frac{\Delta U_1}{k\theta_{\mathrm{g}}}\right\} \tag{4.4}$$

where $\theta_{\mathrm{g}} = T_{\mathrm{g}}$ if the test temperature $T < T_{\mathrm{g}}$ and $\theta_{\mathrm{g}} = T$ if $T > T_{\mathrm{g}}$.

In the isotropic polymer there is no preferred orientation of the structural elements which take part in the yield process whether these are segments of the polymer chain or small aggregates of segments of chains.

Consider a structural element whose relevant direction makes an angle θ with the direction of the applied shear stress. A shear stress τ is considered to change the energy difference between the two conformational states from ΔU_1 to $(\Delta U_1 - \tau v \cos\theta)$. v is again the activation volume, and $\tau v \cos\theta$ represents the work done by the shear stress in the transition between the two states. The application of the shear stress tends to increase the fraction of elements in the upper energy state for elements in some orientations, and decrease it for other orientations, the fraction of elements in the upper state, with orientation θ being

$$\chi_f(\theta) = \frac{\exp\{-(\Delta U_1 - \tau v \cos\theta)/kT\}}{[1 + \exp\{-(\Delta U_1 - \tau v \cos\theta)/kT\}]} \tag{4.5}$$

Clearly the fraction of flexed elements increases on application of a shear stress τ for orientations such that

$$\frac{\Delta U_1 - \tau v \cos\theta}{kT} \leqslant \frac{\Delta U_1}{k\theta_{\mathrm{g}}} \tag{4.6}$$

For one part of the distribution of structural elements, applying the stress tends to make for an equilibrium situation where there are more flexed bonds and this can be regarded as corresponding to a rise in temperature. For the other part of the distribution, the effect of stress can be regarded as tending to lower the temperature. Robertson now argues that the *rate* at which conformational changes occur is very dependent on temperature (similar to the viscoelastic behaviour at low strains described by the WLF equation). It is assumed that the rate of approach to equilibrium is so much faster for those elements which flex under the applied stress and hence tend to a higher equilibrium temperature, that changes in the others can be ignored in calculating the maximum bond fraction which can occur under a given applied stress.

The maximum fraction of elements in the upper flexed state averaged over all orientations can be shown to be

$$\chi_{\max} = \frac{kT}{2\nu\tau}\left\{ ln\left(\frac{1 + \exp\{-(\Delta U_1 - \tau\nu)/kT\}}{1 + \exp(-\Delta U_1/k\theta_g}\right) + \left(\frac{\nu\tau}{kT} + \frac{\Delta U_1}{kT} - \frac{\Delta U_1}{k\theta_g}\right) \frac{\exp(-\Delta U_1/k\theta_g)}{1 + \exp(-\Delta U_1/k\theta_g)}\right\} \quad (4.7)$$

With this fraction of elements in the upper state the polymer is structurally equivalent to that of the melt at a temperature θ_1 where

$$\chi_{\max} = \frac{\exp(-\Delta U_1/k\theta_1)}{(1 + \exp - \Delta U_1/k\theta_1)} \quad (4.8)$$

The strain rate $\dot{e}$ corresponding to the temperature θ_1 is then calculated from the WLF equation, and can be shown to be

$$\dot{e} = \frac{\tau}{\eta_g} \exp - \left\{2.303\left[\left(\frac{C_1 C_2}{\theta_1 - T_g + C_2}\right)\frac{\theta_1}{T} - C_1\right]\right\} \quad (4.9)$$

where C_1, C_2 are the "universal" WLF parameters and η_g is the universal viscosity of a glass at T_g.

TABLE II Table of coefficients for yield in polymethylmethacrylate (after Robertson).

c_1	17.44° C
c_2	51.6° C
ΔU_1	1.44 kcals/mole
T_g	105° C
η_g	10^{13} - $10^{14 \cdot 6}$ poise
ν	140 Å^3

Table II shows the results obtained by Robertson for a best fit to data for the yield behaviour of polymethylmethacrylate. It is extremely encouraging to find that physically reasonable values can be given to the quantities η_g, ν and ΔU_1.

Duckett, Rabinowitz and Ward [23] have modified the Robertson model to include the effect of the hydrostatic component of stress p. It was proposed that p also does work during the activation event and that the energy difference between the two states should therefore be modified to

$$\Delta U_1 - \tau\nu\cos\theta + p\Omega$$

where Ω is a constant with the dimensions of volume.

Thus when p is positive (as in a compression test) the effective barrier height is increased and when p is negative (as in a tension test) the effective barrier height is reduced.

The argument then follows that of Robertson exactly and the maximum fraction of elements in the upper state averaged over all orientations is modified to

$$\chi_{\max} = \frac{kT}{2\nu\tau} \left\{ ln\left(\frac{1 + \exp\{-(\Delta U_1 - \tau\nu + p\Omega)/kT\}}{1 + \exp(-\Delta U_1/k\theta_g)}\right) + \left(\frac{\nu\tau}{kT} + \frac{p\Omega}{kT} + \frac{\Delta U_1}{k\,T} - \frac{\Delta U_1}{k\theta_g}\right) \frac{\exp(-\Delta U_1/k\theta_g)}{1 + \exp(-\Delta U_1/k\theta_g)}\right\} \quad (4.10)$$

In addition to the parameters C_1, C_2, ΔU_1, T_g, η_g and ν required by the original Robertson treatment, this modified theory includes the parameter Ω. An approximate relationship between Ω and ν can be obtained from the data of Rabinowitz, Ward and Parry on the effect of hydrostatic pressure on the shear yield behaviour of polymethylmethacrylate. These data show that the shear yield stress at constant strain rate is an approximately linear increasing function of hydrostatic pressure. Reference to equation (4.9) shows that over the range of shear stresses observed by Rabinowitz *et al* [11] at constant strain rate, θ_1 must be approximately independent of pressure. Examination of equation (4.10) indicates that if $\tau\nu - p\Omega =$ constant then θ_1 is approximately independent of pressure. It was therefore concluded that to a good approximation

$$\frac{\Omega}{\nu} = \left(\frac{\partial\tau}{\partial p}\right)_{\dot{e}} = 0.204\,,$$

as observed by Rabinowitz *et al.*

Data for tensile and compressive yield stresses of polymethylmethacrylate at various strain rates and temperatures were analysed according to this modified Robertson treatment. For the tensile and compressive tests τ and p were taken to be $\sigma/2$ and $\pm\,\sigma/3$ respectively, where σ is the observed axial yield stress. $\dot{e}$ was assumed to be equal to one half the applied axial strain rate. The maximum shear stress on the specimen and the applied hydrostatic pressure were used for τ and p in the torsion tests. The best fits to the data are shown in figs. 21, 22, and the final values for the parameters used to generate these fits are shown in Table III.

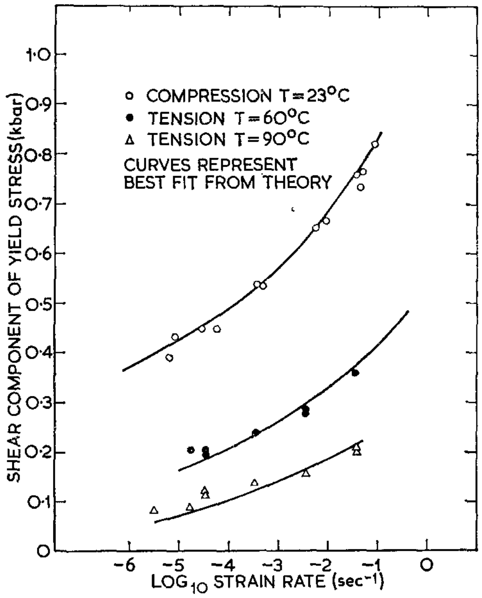

Figure 21 Yield stress of polymethylmethacrylate versus $\log_{10}$(strain rate) (after Duckett *et al*).

TABLE III Table of coefficients for yield in polymethylmethacrylate including effect of hydrostatic pressure (after Duckett, Rabinowitz, and Ward).

C_1	11.1°C
C_2	55.9°C
ΔU_1	0.88 kcal/mole
T_g	105°C
η_g	10^{12} poise
v	109Å^3
Ω/v	0.175

Although the curve fitting is not perfect, it is sufficiently good to permit three tentative conclusions

(1) The difference between the tensile and compressive yield stresses can be attributed to the effect of the hydrostatic component of stress.

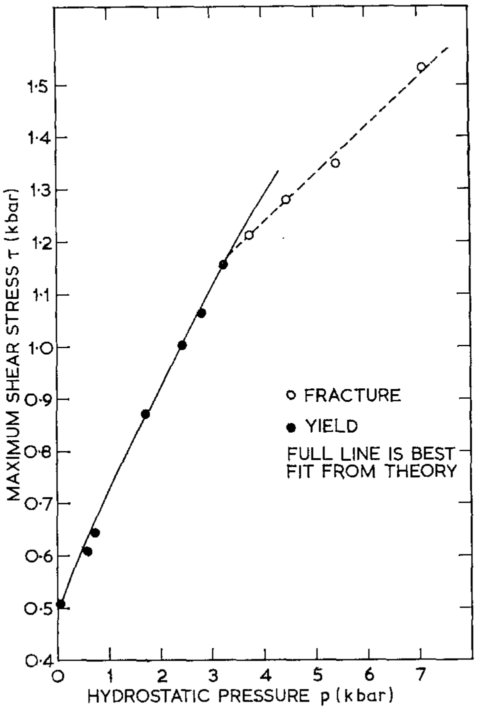

Figure 22 Torsion failure under hydrostatic pressure for polymethylmethacrylate Temperature = 25°C Strain rate = 4×10^{-4} sec^{-1} (after Duckett *et al*).

(2) The general features of the rate dependence of yield stress may be represented in terms of an effective viscosity which is pressure, temperature and shear stress dependent.

(3) The yield behaviour relates to the low strain viscoelastic relaxation behaviour, through the WLF equation or perhaps more exactly by some modification of the WLF equation.

It is at this stage that we see the continuity between yield behaviour and low strain viscoelastic behaviour. A general conclusion is that further advances in our understanding may well be achieved by a reappraisal of non-linear viscoelastic behaviour from the view point of yield phenomena.

5. The Yield Behaviour of Oriented Polymers

5.1. Simple Yield Criteria for Anisotropic Materials

(1) The critical resolved shear stress law of Schmid

The simplest yield criterion for anisotropic materials is the critical resolved shear stress law of Schmid [24], which has had wide application to the yield behaviour of simple crystals of metals and ceramics. This law states that yield occurs when the resolved shear stress in the slip direction in the slip plane reaches a critical value. For a tensile stress σ making angles α and β with the slip direction and the normal to the slip plane respectively this gives the critical resolved shear stress τ_c as

$$\tau_c = \sigma \cos \alpha \cos \beta$$

(2) *Hill's extension of the von Mises yield criterion* Hill [25] has proposed that the von Mises yield criterion can be extended to anisotropic materials which possess three mutually orthogonal planes of symmetry at every point, i.e. materials whose intrinsic symmetry is at least orthorhombic.

The intersections of the three orthogonal planes define the principal axes of symmetry, and these directions are chosen as Cartesian axes of reference. The yield criterion then takes the form

$$F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx})^2 + H(\sigma_{xx} - \sigma_{yy})^2 + 2L\sigma_{yz}^2 + 2M\sigma_{zx}^2 + 2N\sigma_{xy}^2 = 1$$

where F, G, H, L, M and N are parameters which characterise the anisotropy of the yield behaviour.

This yield criterion satisfies two of the basic requirements of the known yield behaviour of isotropic metals.

(1) The yield criterion is independent of the hydrostatic component of stress, i.e. the normal stress terms appear as differences.

(2) There is no Bauschinger effect, i.e. it contains only even power terms in the stress components.

In addition this yield criterion reduces to the von Mises yield criterion for vanishingly small anisotropy.

5.2. The Stress-Strain Relations for Anisotropic Materials

The Schmid critical resolved shear stress law implicitly defines the direction of the strain increments, because it supposes that only a shear process is occurring. In metals a slip band is observed and the deformation consists of a simple shear in the band direction.

For his extension of the von Mises yield criterion Hill proposed plastic strain increment relations which are analogous to the Lévy–Mises equations [26, 3] for an isotropic plastic material. Referring the strain increments to the principal axes of anisotropy.

$$\begin{aligned}
de_{xx} &= d\lambda[H(\sigma_{xx} - \sigma_{yy}) + G(\sigma_{xx} - \sigma_{zz})] & de_{yz} &= d\lambda L\sigma_{yz}\\
de_{yy} &= d\lambda[F(\sigma_{yy} - \sigma_{zz}) + H(\sigma_{yy} - \sigma_{xx})] & de_{zx} &= d\lambda M\sigma_{zx}\\
de_{zz} &= d\lambda[G(\sigma_{zz} - \sigma_{xx}) + F(\sigma_{zz} - \sigma_{yy})] & de_{xy} &= d\lambda N\sigma_{xy}
\end{aligned} \quad (5.1)$$

It is particularly important to note that in this case (unlike the case for isotropic materials) the principal axes of the plastic strain increments only coincide with the axes of anisotropy when the principal axes of stress coincide with the latter.

5.3. Experimental Studies of the Yield Behaviour of Oriented Polymers

In isotropic polymers the onset of yield is often accompanied in tensile tests by the formation of shear zones or deformation bands. If an oriented polymer is subjected to a tensile test in which the axis of the applied tension is not parallel to the initial draw direction (IDD), the deformation is sometimes concentrated in a very striking manner into a narrow deformation band. The deformation bands which form are of two types. One type is nearly parallel to the initial draw direction and has the appearance of a slip band in metals; the other is more diffuse, makes a larger angle with the draw direction and has the general appearance of a kink band in metals. In the last few years, there has been considerable investigation of these deformation bands in polymers, both with a view to understanding yield behaviour and with regard to the molecular reorientation processes which take place.

(1) Kink Bands in Nylon

One of the earliest studies of deformation bands in oriented polymers was made by Zaukelies [27], who investigated the formation of kink bands in oriented bristles of nylon 6:6 and nylon 6:10 when the bristles were compressed along their axis in a tensometer.

Electron micrographs of the cleavage surface of bristles containing the kink bands suggested that there was gross reorientation of the material in the kink bands in a similar manner to that occurring in crystalline materials. Zaukelies therefore sought to explain his results in terms of Orowan's equation [28] which relates the direction of a kink band in a single crystal to the parameters of the crystal lattice. It was proposed that the slip plane was the (010) plane, and that a number of planes acted in unison as a single lamella.

The direction of the kink bands changed with temperature and controlled experiments at 25 and 100° C suggested that at the lower temperature two (010) planes form a lamella for slip, whereas at the higher temperature three planes act together. Zaukelies also proposed various dislocation motions as explanations for the slip processes. These early results are of considerable interest and suggest that a more extensive investigation would prove rewarding, particularly as recent studies of deformation bands in other polymers have cast some doubts on the validity of interpreting these phenomena in terms of the plasticity of crystalline materials.

(2) Deformation Bands in Polyethylene

In oriented high density polyethylene sheets, a very clear deformation band can be observed when the sheet is subsequently extended in a direction which is oblique to the initial draw direction. A striking example of this is shown in fig. 23 from the investigation of Keller and Rider [29]. The deformation band shows a remarkable resemblance to slip bands in metals.

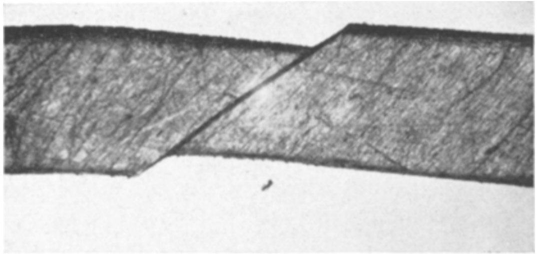

Figure 23 A deformation band in a drawn and annealed sheet of high density polyethylene (after Rider and Keller).

From their studies in polyethylene, Kurakawa and Ban [30] concluded that in some cases, when there was only a small angle between the initial draw direction and the tensile axis in the redrawing, the band direction was in the c-axis direction (i.e. the (001) direction in the crystalline regions of the polymer) and coincided with the c-axis direction in the band. In other cases, the deformation band was noted to be a little inclined to the (001) direction. They therefore suggested, but without definitive proof, that the basic deformation was not simple slip in the (001) direction, but a combination of (001) slip and mechanical twinning.

When the tensile axis made a large angle with the IDD, kink bands were observed, and wide angle X-ray diffraction measurements were used to show that gross molecular reorientation occurred in the kink bands, as in the case of nylon.

Keller and Rider [29] have made a detailed examination of deformation bands in a variety of drawn; drawn and rolled; and drawn, rolled and annealed sheets of high density polyethylene. It was found that the band boundary was generally not parallel to the c-axis direction, and that the boundary of the kink bands did not bisect the angle between the c-axis direction on either side of the boundary. Nevertheless, the principal factor in determining the deformation behaviour appeared to be alignment of the c-axis and it was concluded that the yield behaviour approximated to slip in the direction of the c-axis.

Keller and Rider measured the yield stress as a function of the angle θ between the tensile testing direction and the IDD. They proposed that the data can be fitted by the Coulomb yield criterion and a typical set of results, shown in fig. 24, confirm that a reasonable fit can be obtained. As we have seen, the Coulomb yield criterion also defines the plane in which yield will occur. In this respect it did not satisfactorily describe the data, as the deformation band did not form in the required direction.

(3) Deformation Bands in Polyethylene Terephthalate

In oriented polyethylene terephthalate sheets,

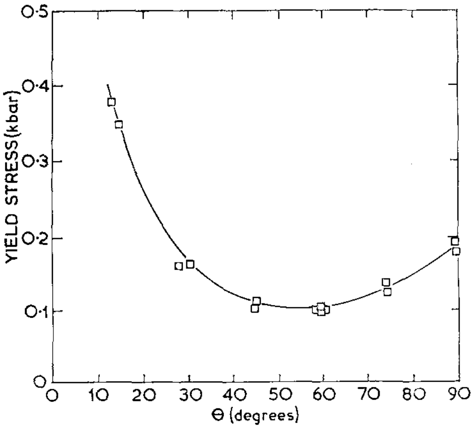

Figure 24 Tensile yield stress plotted against θ, the angle between the tensile axis and the initial draw direction for drawn high density polyethylene sheets, measured at room temperature. Full lines show fit to the Coulomb yield criterion (after Keller and Rider).

very distinct deformation bands are observed [31–33] and it is very evident that their directions do not in general coincide with the initial draw direction. It has also been shown that the variation in yield stress with the direction of the applied tensile stress, cannot be fitted either to the critical resolved shear stress criterion or to the Coulomb yield criterion. However, as shown in fig. 25, a good fit was obtained to the Hill anisotropic yield criterion.

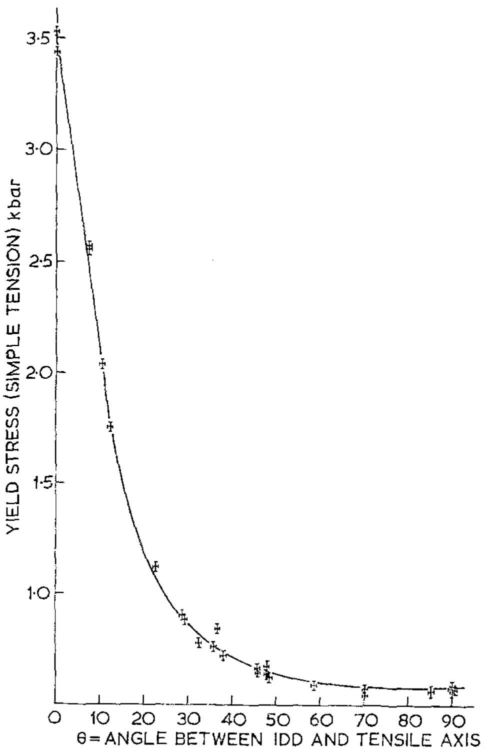

Figure 25 Graph of tensile yield stress versus direction of applied tensile stress for oriented polyethylene terephthalate sheet, showing best fit obtained to the Hill anisotropic yield criterion (after Brown *et al*).

For the plane stress tensile tests on thin sheets, the Hill yield criterion (assuming sheets of orthorhombic symmetry) reduces to

$$\sigma^2\{(G + H)\cos^4\theta + (H + F)\sin^4\theta + 2(N - H)\sin^2\theta\cos^2\theta\} = 1$$

where θ is the angle between the IDD and the applied tensile stress σ.

In fig. 25, the excellent fit was obtained by choosing the constants to give an exact fit to the data at 0, 45 and 90°. It was also found that Hill's equations for the plastic strain increments (Equations 5.1 above) gave a reasonably accurate prediction of the observed band directions.

We will choose a rectangular set of axes 0x, 0y, 0z with 0x parallel to the IDD, and 0y in the plane of the sheet. For the tensile tests on thin sheets the stress in a direction normal to the sheet is zero i.e. $\sigma_{zz} = 0$ and the Hill equations reduce to

$$\begin{aligned} de_{xx} &= d\lambda[(G + H)\sigma_{xx} - H\sigma_{yy}] \\ de_{yy} &= d\lambda[(H + F)\sigma_{yy} - H\sigma_{xx}] \\ de_{zz} &= -\,d\lambda[G\sigma_{xx} + F\sigma_{yy}] \end{aligned}$$

and

$$de_{xy} = d\lambda\, N\sigma_{xy}\,.$$

The deformation band direction is the direction of material which is common to both the deformed and the undeformed material. It therefore defines a direction which is neither rotated nor distorted by the plastic deformation. This means that the plastic strain increment must be zero in the band direction. There are two such directions in the material, one of which defines the direction of the slip deformation bands and the other the kink bands.

To find the directions where the plastic strain increment is zero, it is convenient to define a new system of co-ordinate axes in which one of the plastic strain increments is zero.

We therefore consider a set of co-ordinate axes 0x′, 0y′, 0z′ rotated about 0z from 0x, 0y, 0z through an angle β i.e. $x0x' = y0y' = \beta$.

In the new frame of reference the plastic strain increments are

$$\begin{aligned} de_{xx}' &= de_{xx}\cos^2\beta + de_{yy}\sin^2\beta \\ &\qquad + 2de_{xy}\sin\beta\cos\beta \\ de_{yy}' &= de_{xx}\sin^2\beta + de_{yy}\cos^2\beta \\ &\qquad + 2de_{xy}\sin\beta\cos\beta \\ de_{zz}' &= de_{zz} \\ de_{xy}' &= -\,(de_{xx} - de_{yy})\sin\beta\cos\beta \\ &\qquad + de_{xy}(\cos^2\beta - \sin^2\beta) \end{aligned}$$

The condition for the deformation band occurring at an angle β to the IDD is chosen to be $de_{xx}' = 0$ which gives after dividing by $\sin^2\beta$

$$de_{yy}\tan^2\beta + 2de_{xy}\tan\beta + de_{xx} = 0$$

substituting for de_{yy}, de_{xy}, de_{xx} from the Hill plastic strain increment equations, and putting $\sigma_{xx} = \sigma\cos^2\theta$, $\sigma_{yy} = \sin^2\theta$, $\sigma_{xy} = \sigma\sin\theta\cos\theta$, we obtain a quadratic equation in $\tan\beta$. Thus for each value of θ there are two predicted deformation band directions.

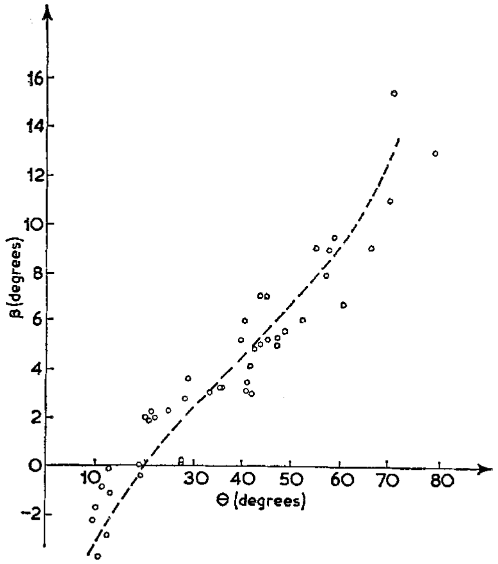

Figure 26 Graph showing deviation of deformation band direction from the initial draw direction β as a function of the angle θ between the applied tensile stress and the initial draw direction (after Brown *et al.*).

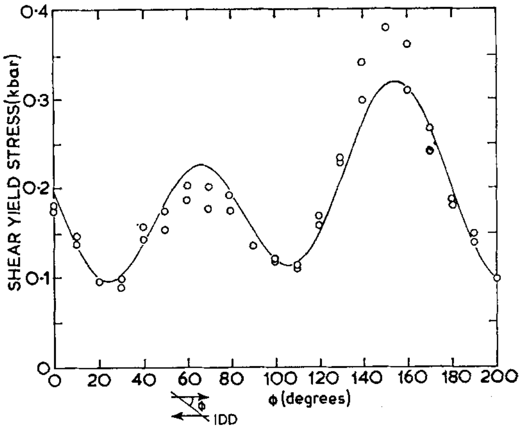

Figure 27 Graph of yield stress in simple shear against ϕ, angle between the direction of the applied shear stress and the initial draw direction, for drawn high-density polyethylene (after Robertson and Joynson).

Fig. 26 shows the good fit obtained for the slip deformation band angle in polyethylene terephthalate using the values for *F*, *G*, *H* and *N* obtained from the yield stress data. It is evident that the Hill analysis provides a good description of the plastic deformation behaviour.

(4) Simple Shear-stress Yield Tests

A valuable extension to the tensile tests on oriented sheets is provided by a series of simple shear tests undertaken under rather different experimental conditions by Robertson and Joynson [34, 35], Bridle, Buckley, and Scanlan [33] and by Brown, Duckett, and Ward [32]. It should perhaps be emphasised at the outset that it is very difficult to achieve the experimental conditions of simple shear and that in all these experiments the numerical values of the yield stresses obtained should probably be treated with caution.

In Robertson and Joynson's experiments [34] the specimen is 2.5 to 5 mm in length and the shear displacement takes place over a distance of only 0.075 mm. The shear stress was measured at an arbitrary total extension so that the results are merely akin to an engineering proof stress. Results were obtained in the first series of experiments for polycarbonate and polyphenylene oxide [34], and later for high density polyethylene and polypropylene [35]. The results for polyethylene shown in fig. 27 are the clearest, although those for the other polymers are similar in form. The shear yield stress varies in an approximately sinusoidal fashion with the angle between the direction of the applied shear stress and the IDD. The two shear stress maxima are however very different in magnitude, which Robertson and Joynson attributed to the following reason: In one case, the shear stress acts to stretch the oriented fibrils of the specimen still further. The high shear stress observed is then believed to be due to the inhibition of slip by tie molecules. In the other case the shear stress acts to compress the fibrils, which are then believed to deform by kinking, which would very likely be an easier mode of deformation.

In the experiments of Brown, Duckett, and Ward [32], sheet specimens of oriented polyethylene terephthalate were subjected to simple shear in a simple jig coupled to a tensometer by universal joints [36]. In this case the stress-strain curves were determined, subject to the reservations mentioned above concerning the test method, and a typical set of these are shown in fig. 28. These stress-strain curves vary markedly in form as the angle ϕ between the shear displacement direction and the IDD changes. It is particularly noticeable that there is a clear yield drop for $\phi = 45°$ but no yield drop for $\phi = 135°$.

The qualitative explanation of these results

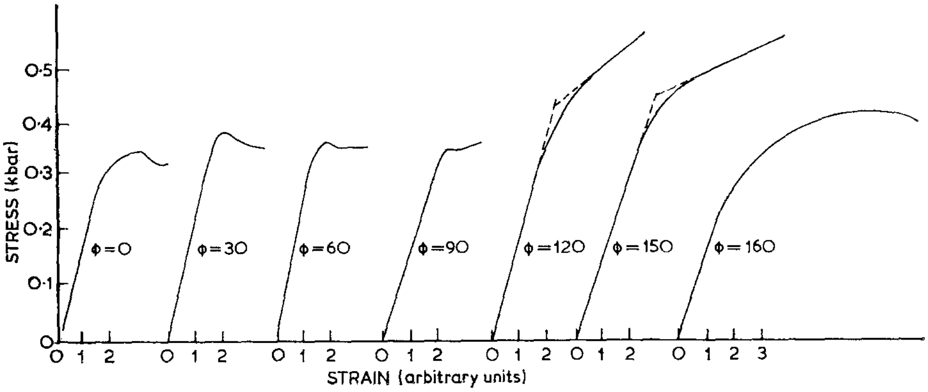

Figure 28 Typical stress-strain curves in simple shear for oriented polyethylene terephthalate. ϕ is angle between direction of shear yield stress and the initial draw direction (after Brown *et al*).

given by Brown, Duckett, and Ward is somewhat similar to that suggested above by Robertson and Joynson, although it does not depend on morphological features to the same extent. The applied shear stress can be resolved into a compressive stress and a tensile stress at right angles. When $\phi = 45°$, the IDD is parallel to the compressive component of stress, whereas when $\phi = 135°$ the IDD is parallel to the tensile component of stress. We would intuitively expect that it is easier to compress an already extended structure than to extend it further. For this reason, it is reasonable to find that the shear yield stress for $\phi = 45°$ is less than that for $\phi = 135°$. The result does imply that the compressive yield stress of oriented polyethylene terephthalate is less than the tensile yield stress. Brown, Duckett, and Ward tested this hypothesis by comparing in a subsidiary experiment the tensile and compressive yield stresses of oriented PET rods. Although this material was not so highly oriented as the sheet it was indeed found that the tensile yield stress was markedly greater than the compressive yield stress. This is in contradiction to the results for isotropic PET, where the influence of the hydrostatic component of stress makes the tensile yield *less* than the compressive yield stress. Brown, Duckett, and Ward attributed this anisotropy in the yield behaviour of the oriented sheet to a Bauschinger effect, analogous to that observed in cold worked metals.

(5) Formal Introduction of the Bauschinger Effect into the Yield Criterion

A simple method of representing the observed behaviour is to modify the Hill anisotropic yield criterion by the introduction of a term σ_i, which represents the difference between the tensile and compressive yield stresses in a direction parallel to the IDD. Choosing the x direction as the IDD as before, the yield criterion becomes

$$F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx} - \sigma_i)^2 + H(\sigma_{xx} - \sigma_i - \sigma_{yy})^2 + 2L\sigma_{yz}{}^2 + 2M\sigma_{zx}{}^2 + 2N\sigma_{xy}{}^2 = 1$$

In the simple shear tests

$$-\sigma_{xx} = \sigma_{yy} = \sigma \sin 2\phi$$
$$\sigma_{xy} = \sigma \cos 2\phi$$

and we have

$$\sigma^2\{(G + F + 4H)\sin^2 2\phi + 2N\cos^2 2\phi\} + 2\sigma\,\sigma_i(G + 2H)\sin 2\phi = 1 - (G + H)\,\sigma_i{}^2 .$$

In the unmodified Hill theory $\sigma_i = 0$ and the yield criterion predicts that the simple shear stress tests will show two maxima and two minima, each of equal magnitude. The modification due to the Bauschinger term σ_i accounts for the observed differences in the shear stress maxima, providing a much better fit to the experimental data, as is illustrated in fig. 29.

The introduction of this Bauschinger term also leads to a modification of the strain increment relations which allow prediction of the band angle in the tensile test. Brown, Duckett, and Ward found that there was some latitude in obtaining a fit for the band angle in polyethylene terephthalate, when there is such a large number of disposable constants. They showed that an equally good fit could be obtained when the Bauschinger term is included, but that the latter does not improve the fit significantly. In a recent

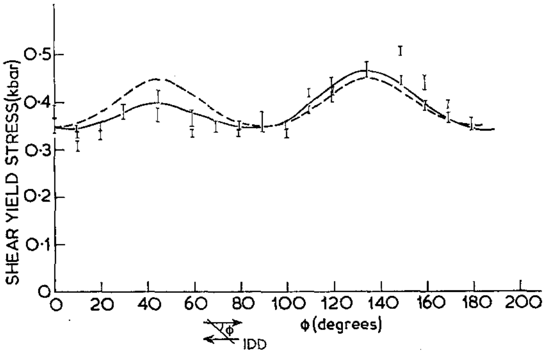

Figure 29 Graph of yield stress in simple shear versus ϕ. Dashed line is the best fit obtained from the simple Hill theory. Full line is the best fit obtained from the modified Hill theory (after Brown *et al*).

investigation of tensile deformation of polyvinylchloride, Rider and Hargreaves [37] found that the introduction of a Bauschinger term improved the fit to the band angle data to a very marked extent. As no direct measurements of the Bauschinger term had been undertaken, in this case the band angle data were used in conjunction with the yield stress data to obtain a best fit.

6. Conclusion

This review has considered in some detail two aspects of the yield behaviour of polymers, attempts to obtain yield criteria and the question of the viscoelastic nature of the yield behaviour. Recent experimental studies in isotropic polymers have highlighted the importance of the hydrostatic component of stress, and it has been shown that this also plays an important part in any theory which attempts to deal comprehensively with the viscoelastic nature of yield behaviour. In oriented polymers the difference between the yield behaviour in tension and compression can be represented formally by introducing an internal compressive stress term acting in the orientation direction. The effect of orientation is much larger than that due to the hydrostatic component of stress, so that the latter may usually be neglected in highly oriented polymers.

Acknowledgements

I wish to thank Dr R. A. Duckett for valuable discussion on many of the topics covered in this review. Figures 16, 17, 20 and 27 are reproduced by permission of John Wiley & Sons. Inc.

References

1. A. NADAI, "Theory of Flow and Fracture of Solids" (McGraw Hill, New York, 1950) p. 20.
2. H. TRESCA, *Compt. Rend. Acad. Sci. Paris* **59** (1864) 754; **64** (1867) 809.
3. R. VON MISES, *Göttinger Nachrichten, math-phys. Klasse* (1913) 582.
4. S. TIMOSHENKO and J. N. GOODIER, "Theory of Elasticity" (McGraw Hill, New York, 1951) p. 14.
5. A. S. ARGON, R. D. ANDREWS, J. A. GODRICK, and W. WHITNEY, *J. Appl. Phys.*, **39** (1968) 1899.
6. P. B. BOWDEN and J. A. JUKES, *J. Mater. Sci.* **3** (1968) 183.
7. S. B. AINBINDER, M. G. LAKA, and I. YU MAIORS, *Mekhanika Polimerov* **1** (1965) 65.
8. L. HOLLIDAY, J. MANN, G. POGANY, H. D. PUGH, and D. A. GREEN, *Nature* **202** (1964) 381.
9. G. BIGLIONE, E. BAER, and S. V. RADCLIFFE, paper presented at Brighton Conference on Fracture (April 1969).
10. D. R. MAERS, K. D. PAE, and J. A. SAUER, *J. Appl. Phys.* **40** (1969) 4229.
11. S. RABINOWITZ, I. M. WARD, and J. S. C. PARRY, *J. Mater. Sci.* **5** (1970) 29.
12. C. A. COULOMB, *Mém. Math. et Phys.* **7** (1773) 343.
13. S. STERNSTEIN and L. ONGCHIN, *Amer. Chem. Soc. Polymer Preprints* **10** No. 2, Sept. 1969, p. 1117.
14. L. W. HU and K. D. PAE, *J. Franklin Inst.* **275** (1963) 491.
15. J. C. BAUWENS, *J. Polymer Sci.* **A-2 8** (1970) 893.
16. J. A. ROETLING, *Polymer* **6** (1965) 311.
17. R. N. HAWARD and G. THACKRAY, *Proc. Roy. Soc.* **A302** (1968) 453.
18. C. BAUWENS-CROWET, J. C. BAUWENS, and G. HOMÈS, *J. Polymer Sci.* **A2 7** (1969) 735.
19. D. L. HOLT, *J. Appl. Polymer Sci.* **12** (1968) 1653.
20. R. E. ROBERTSON, *ibid* **7** (1963) 443.
21. R. A. DUCKETT, private communication.
22. R. E. ROBERTSON, *J. Chem. Phys.* **44** (1966) 3950.
23. R. A. DUCKETT, S. RABINOWITZ, and I. M. WARD, *J. Mater. Sci.* **5** (1970) 909.
24. A. H. COTTRELL, "Dislocations and Plastic Flow in Crystals" (Clarendon Press, Oxford, 1953) p. 4.
25. R. HILL, "The Mathematical Theory of Plasticity" (Clarendon Press, Oxford, 1950) p. 318.
26. M. LÉVY, *Compt. Rend. Acad. Sci. Paris* **70** (1870) 1323.
27. D. A. ZAUKELIES, *J. Appl. Phys.* **33** (1961) 2797.
28. E. OROWAN, *Nature*, **149** (1942) 643.
29. A. KELLER and J. G. RIDER, *J. Mater. Sci.* **1** (1966) 389.
30. M. KURAKAWA and T. BAN, *J. Appl. Polymer Sci.* **8** (1964) 971.
31. N. BROWN and I. M. WARD, *Phil. Mag.* **17** (1968) 961.
32. N. BROWN, R. A. DUCKETT, and I. M. WARD, *ibid* **18** (1968) 483.
33. C. BRIDLE, A. BUCKLEY, and J. SCANLAN, *J. Mater. Sci.* **3** (1968) 622.

34. R. E. ROBERTSON and C. W. JOYNSON, *J. Appl. Phys.* **37** (1966) 3969.
35. *Idem, J. Polymer Sci.* **A2 6** (1968) 1673.
36. N. BROWN and I. M. WARD, *ibid* **6** (1968) 607.
37. J. G. RIDER and E. HARGREAVES, *ibid* **A-2 7** (1969) 829.

Received 6 July and accepted 14 July 1971