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The Strain-rate, Temperature and Pressure Dependence of yield of Isotropic Poly(methylmethacrylate) and Poly(ethylene terephthalate)*

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The yield behaviour of poly(methylmethacrylate) (PMMA) has been investigated in tension and compression over a range of testing temperatures and strain-rates. Both tensile and compressive yield stresses were found to increase monotonically with increasing strain-rate and decreasing temperatures. Compressive yield stresses were in general found to be more dependent on strain-rate.

The results of this investigation have been correlated with previous published data for the dependence of the torsional yield stress of PMMA on hydrostatic pressure. This was done by a modification of a theory proposed by Robertson which uses the internal viscosity approach to yield in glassy polymers. The modified theory clearly explains the temperature and strain-rate dependence of the yield stress and provides a quantitative explanation of the differences in behaviour between tension and compression in terms of the dependence of yield on the hydrostatic component of the applied stress.

The tensile yield behaviour of isotropic amorphous poly(ethylene terephthalate) (PET) sheets has also been investigated over a wide range of temperatures and strain-rates. No torsion or compressive yield stresses are available because of the sheet form of the PET, but the results obtained in tension are shown to be fully consistent with the above theory, and with other published work.

1. Introduction

Many workers have attempted to extract from the complex non-linear mechanical behaviour of isotropic glassy polymers simple failure criteria which can be used to predict yield behaviour under the combined stresses of constant strain-rate and temperature e.g. [1-3]. These approaches draw on experience obtained in investigations of the yield behaviour of metals and soils. The von Mises criterion, successful for describing the yield of metals [4], has been found to be inadequate for dealing with polymeric materials because of the observed difference in yield stress between tension and compression. The latter has been attributed to a dependence of yield stress on the hydrostatic component of stress, but the limited range of experimental data presently available does not allow a clear distinction to be drawn between a pressure dependent von Mises yield criterion and the Coulomb criterion used widely in soil mechanics [2, 3]. However, a modification of the von Mises criterion proposed by Hill [5] to allow for anisotropy has been used successfully to describe the tensile yield of anisotropic polymers [6-8].

Other papers have concentrated on the dependence of tensile stress on testing temperature and strain-rate. Many of the discussions centre around the problem of establishing time-temperature superposition, e.g. [9-12]. All the polymers investigated show a monotonic increase of yield stress with increasing strain-rate and some authors assert that there is an approximately linear relationship between stress and the logarithm of strain-rate. The yield stress for most glassy polymers decreases linearly with increas-

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ing temperature over a wide range of temperatures below the glass transition temperature.

In this investigation an attempt has been made to link together the two approaches to yield outlined above. The tensile and compressive yield stresses of poly(methylmethacrylate) have been measured over a range of temperatures and strain-rates. It was found that the compressive yield stress was more sensitive to strain-rate than the tensile yield stress. The theory for yielding of isotropic glassy polymers proposed by Robertson [13] has been modified to allow for the effect of hydrostatic pressure. Using this modified theory it has been possible to correlate quantitatively the tensile and compression data from this investigation with the data obtained on the same material in torsion tests under an overall hydrostatic pressure [14].

The tensile yield stress of isotropic amorphous poly(ethylene terephthalate) sheet has also been measured over a wide range of temperatures and strain-rates and fitted to the above theory using parameters deduced from the literature.

2. Experimental

The poly(methylmethacrylate) (PMMA) tensile and compression specimens were machined out of 1 in. (2.54 cm) thick sheets of ICI "Perspex". The tensile specimens were approximately 4.3 mm in diameter with a straight gauge length of 2.5 cm. Compression specimens were circular cylinders with a diameter of 6.4 mm and length of 12.8 cm.

The poly(ethylene terephthalate) (PET) was supplied by ICI Plastics Ltd with a thickness of approximately 0.64 mm. The optical birefringence of the material was measured as less than 5×10^{-5} and the yield stress in the plane of the sheet was found to be isotropic within experimental error. The tensile specimens were dumbbell shaped with a straight gauge length of 2.5 cm width 4 mm.

All tests were performed on an Instron tensile testing machine, inside an environmental chamber within which the temperature could be controlled to within $\pm 0.5°$ C both above and below room temperature. Tensile tests over a wide range of strain-rates were performed on PMMA at 60 and 90° C and on PET at -25, 20, 40, 50 and 60° C. A minimum of 20 min was allowed for each specimen to reach thermal equilibrium. Compression tests on PMMA were conducted at room temperature, both in direct compression between the machine crosshead and a compression type load cell, and also using a compression cage in conjunction with a tensile load cell.

True yield stresses were obtained by relating the maximum observed load to current cross-sectional area. A correction to all measurements was made to allow for deformation of the machine and compression cage.

3. Results

The results obtained are shown graphically in figs. 1 and 2. Fig. 1 represents the variation of tensile and compressive yield stresses of PMMA with $\log_{10}$ (strain-rate) at various temperatures. In order for easy comparison to be made between tension, compression and torsion data and also with the Robertson theory, the shear component of the yield stress is plotted as the ordinate and $\log_{10}$ (shear strain-rate) as the abscissa. In fig. 2 the results obtained for the tensile yield of PET at -25, 20, 40, 50 and 60° C are plotted as the tensile component of stress versus $\log_{10}$ (tensile strain-rate).

Fig. 3 is taken from Rabinowitz *et al* [14] and represents the variation of torsional yield stress of PMMA at constant (room) temperature and shear strain-rate (4×10^{-4} sec^{-1}) with superposed hydrostatic pressure. (The material used was identical to that used in the current investigation.)

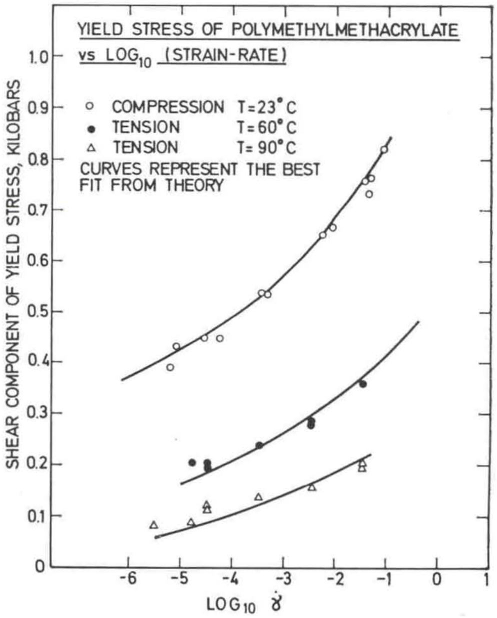

Figure 1 The variation of tensile and compressive yield stresses with strain-rate and temperature, PMMA.

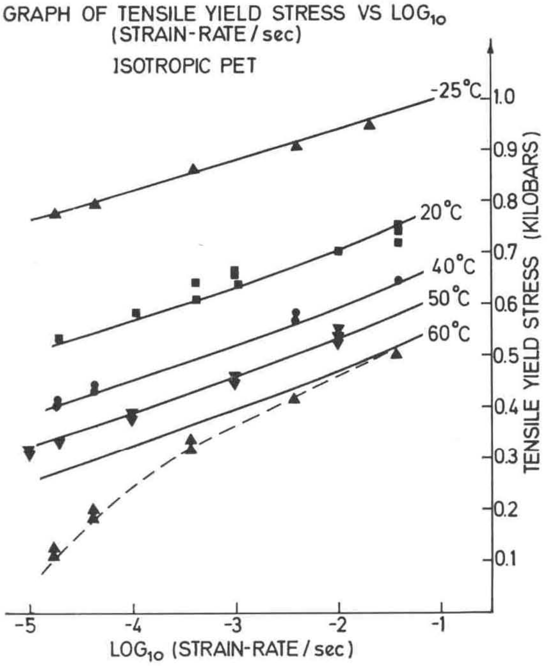

Figure 2 The variation of the tensile yield stress of isotropic PET with temperature and strain-rate.

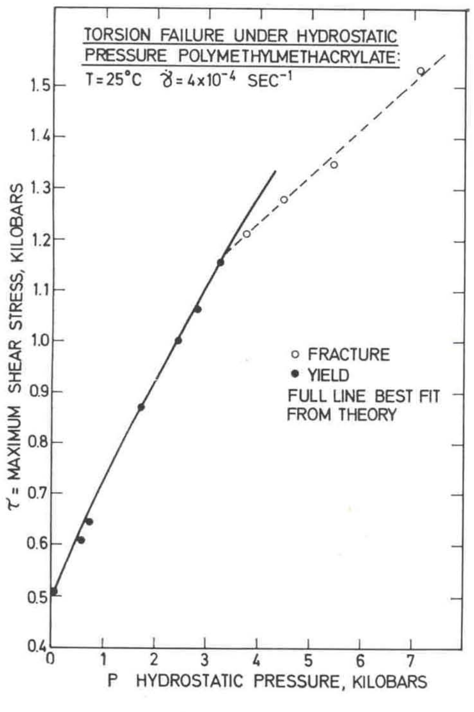

Figure 3 The variation of torsional yield and fracture stress of PMMA with hydrostatic pressure (from [14]).

4. Discussion

The present results confirm, at least for PMMA, what is already well established, namely that the yield stress of an isotropic polymer depends on (*1*) temperature, (*2*) strain-rate and (*3*) hydrostatic pressure. It is believed, however, that they represent the first set of data to link these three aspects on the same material. Let us discuss first points (*1*) and (*2*) above.

The tensile and compressive yield stresses of poly(methylmethacrylate) and poly(ethylene terephthalate) are observed to increase with increasing strain-rate and with decreasing temperature. It should be noted that in general the plots of yield stress versus log (strain-rate) have a small but definite curvature, indicating that the theory of Eyring [15] in terms of a single simply activated flow process is not applicable to the present data. Our data differ from those of Bauwens-Crowet *et al* [16] and Holt [12] in this respect, but are in general agreement with the data of Roetling [18]. The theory to be described predicts a definite curvature in this type of plot which we therefore consider to be of greater generality than the linear behaviour.

Owing to the brittle nature of PMMA, in tension at room temperature, it was not possible to obtain direct comparison between tension and compression, but data from other work [1, 2, 14] clearly indicates that compressive yield stresses would be higher than tensile yield stresses. Further, the data from this paper shows the greater sensitivity of the compressive yield to strain-rate than the tensile yield.

It will be shown that the difference in behaviour between tension and compression can be attributed quantitatively to the dependence of yield on the hydrostatic component of stress. The theory is based on that of Robertson [13].

The tensile behaviour of PET also shows a slight curvature in the plots of stress versus log strain-rate. Additionally, at the higher temperatures, the stress was found to decrease more rapidly with decreasing strain-rate than at the lower temperatures. This was accompanied by the formation of tensile crazes before yielding at the high temperatures and low strain-rates, i.e. the normal shear mode of failure was preceded by craze formation.

5. Theory

A phenomenological theory of yielding has been developed from Robertson's theory [13] which uses the measured dependence of shear yield stress on hydrostatic pressure to predict the observed difference in absolute magnitudes of tensile and compressive yield stresses, quantitatively and also their different sensitivities to temperature and strain rate.

Following Robertson, it is assumed that structural elements of the polymer can exist in either of two energy states with a difference in energy of say ΔE (*N.B.* this effectively assumes the planar zigzag model for the polymer chain). In equilibrium it is proposed that the fraction in each state is given by the Boltzmann distribution. (The glassy polymer is considered as being quenched in the state it occupied at the glass transition temperature T_g.) Thus before the application of stress the fraction of elements in the high energy state is

$$\chi_i = \frac{\exp(-\Delta E/k\theta_g)}{[1 + \exp(-\Delta E/k\theta_g)]} \tag{1}$$

where $\theta_g = T_g$ if the test temperature $T < T_g$ and $\theta_g = T$ if $T > T_g$.

In the isotropic polymer there will be a uniform distribution of orientation of the structural elements whether they be segments of the polymer chain or small aggregates of chains. The application of shear stress τ will tend to increase the fraction of elements in the upper energy state for elements in some orientations, and decrease it for other orientations. According to Robertson the shear component of stress τ changes the energy difference between the two states to $\Delta E - \tau v \cos\theta$. Here $\tau v \cos\theta$ represents the work done by the shear stress τ in the transition, and θ is some angle defining the orientation of the element with respect to the shear stress.

Therefore the fraction of elements in the upper state, with orientation θ is

$$\chi_f(\theta) = \frac{\exp[-(\Delta E - \tau v \cos\theta)/kT]}{\{1 + \exp[-(\Delta E - \tau v \cos\theta)/kT]\}} \tag{2}$$

Clearly the fraction increases for orientations such that

$$\frac{\Delta E - \tau v \cos\theta}{kT} \leqslant \frac{\Delta E}{kT_g}\,. \tag{3}$$

If the two energy states are associated with the trans and gauche chain conformations, trans being the lower energy, then an increase in gauche conformations implies a reduction in density due to less efficient packing. Hence there will be an interaction with the hydrostatic component of the applied stress. We propose, therefore, that the hydrostatic component of stress p also does work during the activation event and that the energy difference should be

$$\Delta E - \tau v \cos\theta + p\Omega\,.$$

Thus when p is positive (as in a compression test) the effective barrier height between the two states is increased and when p is negative (as in a tension test) the effective barrier height is reduced. $p\Omega$ represents the work done by the hydrostatic component of the applied stress, v and Ω having the dimensions of volume.

From this point onward we follow the argument of Robertson exactly. Because an increase in the fraction of elements in the upper state implies a tendency towards a structure characteristic of a higher temperature, and therefore more mobile, transitions from high to low energy will occur infinitely more slowly than transitions in the opposite direction. (This point is discussed at length by Robertson.) It is therefore possible to calculate the maximum fraction of elements in the upper state averaged over all orientations and this can be shown to be:

$$\begin{aligned}\chi_{\max} = {} & \frac{kT}{2v\tau} \\ & \left\{ ln \left(\frac{1 + \exp[-(\Delta E - \tau v + p\Omega)/kT]}{1 + \exp(-\Delta E/k\theta g)} \right) \right. \\ & \quad + \left(\frac{v\,\tau}{kT} + \frac{p\Omega}{kT} + \frac{\Delta E}{kT} - \frac{\Delta E}{k\theta_g} \right) \\ & \quad \left. \frac{\exp(-\Delta E/k\theta_g)}{1 + \exp(-\Delta E/k\theta_g)} \right\}.\end{aligned} \tag{4}$$

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

$$\chi_{\max} = \frac{\exp(-\Delta E/k\theta_1)}{[1 + \exp(-\Delta E/k\theta_1)]}\,. \tag{5}$$

Hence a characteristic temperature θ_1 can be calculated for the polymer under the influence of a shear stress τ and hydrostatic pressure p. We then compute the effective viscosity of the polymer at the temperature θ_1 using the WLF equation, and so the resulting strain rate can be shown to be

$$\begin{aligned}\dot{\gamma} = {} & \frac{\tau}{\eta_g} \\ & \exp - \left\{ 2{\cdot}303 \left[\left(\frac{C_1\,C_2}{\theta_1 - T_g + C_2} \right) \frac{\theta_1}{T} - C_1 \right] \right\}\end{aligned} \tag{6}$$

where C_1, C_2 are the "universal" WLF parameters and η_g is the universal viscosity of a glass at T_g. Yield is defined as the load when the displacement rate arising from the viscous strain rate $\dot{\gamma}$ just matches the crosshead speed in a conventional tensile or compression test (i.e. the elastic strain-rate is zero and the load to produce this viscous strain-rate corresponds to the observed value of maximum load).

In addition to the parameters ΔE, v, T_g, C_1, C_2 and η_g required by the conventional Robertson treatment, the model includes the additional parameter Ω. An approximate relationship between Ω and v may be obtained from the results of Rabinowitz *et al*, [14]. As we have seen their results show that for PMMA the shear yield stress, at constant shear strain rate, is an approximately linear increasing function of hydrostatic pressure. Reference to equation 6 indicates that over the range of shear stresses observed by Rabinowitz *et al* at constant $\dot{\gamma}$ (0.5 kilobar $< \tau <$ 1.1 kilobar) θ_1 must be approximately independent of pressure. Examination of equation 4 indicates that if $\tau v - p\Omega =$ constant then this condition is satisfied. We therefore suggest that $\Omega/v \div (d\tau/dp)\dot{\gamma}$ and from fig. 3 take $(d\tau/dp)\dot{\gamma} = 0.2$.

The data obtained from tension and compression at various strain-rates and temperatures and the data of Rabinowitz *et al* were analysed according to this modified Robertson treatment.

For the tensile and compression tests τ and ρ were taken to be $\sigma/2$ and $\pm\,\sigma/3$ respectively, where σ is the axial yield stress $\dot{\gamma}$ is assumed to be equal to half the applied axial strain-rate. The maximum shear stress on the specimen and applied hydrostatic pressure were used for τ and ρ in the torsion tests. The values for ΔE, v, C_1, C_2, η_g, T_g suggested by Robertson, together with $\Omega = 0.2v$ do not give an acceptable fit to the data. Therefore these values were used as starting points and all the coefficients were adjusted independently by computer to give a "least squares fit" using a procedure developed by Murgatroyd [17]. In the spirit of the Robertson treatment the shear and hydrostatic components of stress and temperature were treated as independent variables, which minimised the deviations between the predicted and actual shear strain-rates for the tension, compression and torsion tests, by adjusting the constants in the equation independently. The following table (table I) shows the final values obtained for the coefficients and those predicted by Robertson for PMMA. These calculated coefficients were used to generate the full curves in figs. 1 and 3.

TABLE I Table of coefficients for PMMA

	Optimised values	Values suggested by Robertson
C_1	11.1° C	17.44° C
C_2	55.9° C	51.6° C
ΔE	0.88 kcal/mole	1.44 kcal/mole
T_g	105° C	105° C
η_g	10^{12} poise	$10^{13} - 10^{14-6}$ poise
v	109 $Å^3$	140 $Å^3$
Ω/v	0.175	0

TABLE II Table of coefficients for PET

	Optimised values	Values suggested by Robertson
C_1	15.1° C	17.44° C
C_2	75.7° C	51.6° C
ΔE	1.91 kcals/mole	1.38 kcals/mole
T_g	90° C	70° C
v	234 $Å^3$	215 $Å^3$
Ω/v	0.10	0
η_g	$10^{14.1}$ poise	$10^{13} - 10^{14.6}$ poise

No such direct data to determine a value for $\mathrm{d}\tau/\mathrm{d}p$ exists for amorphous PET owing to the difficulty of making tubular specimens from thin sheet material, and so we are forced to estimate a value from several sources. Rabinowitz *et al* [14] and Bowden and Jukes [2] observed that the yield stress of PMMA can be described by

$$\tau = \tau_0 + kP$$

where $k = 0.204$ from Rabinowitz (data from torsion under hydrostatic pressure) and $k = 0.175$ from Bowden and Jukes (data from plane strain compression). The latter technique produced a value of 0.172 for isotropic amorphous PET (private communication), whereas the former yielded $k = 0.075$ for isotropic crystalline PET. We therefore choose rather arbitrarily $\Omega/v = 0.1$ for this amorphous PET sheet.Treating the other six coefficients as independent variables the curves shown in fig. 2 were obtained. A list of coefficients for PET is shown in table II. No attempt was made to fit the data in the region of rapidly changing stress at 60° C where crazes were observed to precede yield. With regard to the values of the coefficients obtained the following observations seem relevant; C_1 and C_2 lie well within the range of values obtained from dynamic-mechanical experiments for both PMMA & and PET (see for example [19, 20]). The values for v, T_g and η_g also compare favourably with published data. However the values of ΔE for both PMMA and PET are in some disagreement with independent measurements. The only comparison for PMMA is with the value predicted from T_g using the Gibbs-DiMarzio relationship $\Delta E = 3.81\ T_g$ cals/mole. It can be seen that the value obtained from this investigation is only about 60% of this prediction. Our value of ΔE for PMMA should be compared with the value of 0.9 kcals/mole for polystyrene, obtained from ultrasonic measurements [21]. For PET we calculate $\Delta E = 1.91$ kcals/mole. This should be compared with the Gibbs-DiMarzio value of 1.38 kcals/mole. However, the work of Riveros and Bright Wilson [22] using microwave spectroscopy yields a value of 0.186 ± 0.060 kcals/mole for the difference in energy between the rotational isomeric states of ethyl formate, separated by a barrier height of 1.1 ± 0.25 kcals/mole for upward transitions.

The value of 0.186 kcals/mole was used by Walker and Semlyen [23] for the methyl group rotation, in a calculation which accurately predicted the measured cyclic trimer concentration in the melt of poly(ethylene terephthalate). The results would imply that the barriers to conformational changes at yield are higher than those measured in the melt. This might be because the stiffness of the terephthaloyl units is more effective in the denser material.

6. Conclusion

A modification of Robertson's molecular theory of yielding has been presented which allows the hydrostatic pressure, temperature and rate-dependence of yield to be discussed within a common formalism. Although the details of the theory are complex the theory is attractive for several reasons. Firstly because it emphasizes that yield is not a unique point on the stress-strain curve, but merely the point at which the plastic strain-rate produced by the stress just matches the machine displacement rate and secondly, it does not require that a horizontal log strain-rate shift will produce a yield master curve. Thirdly, it predicts that yield is governed by a temperature dependent activation energy (formally introduced via the WLF equation). It also suggests a possible molecular mechanism of yield in polymers.

The accuracy of the fit obtained is very promising, but clearly it is desirable to find a material with which it is possible to do tensile and compression tests over a wider temperature range and also torsion tests under hydrostatic pressure. The slight disagreement between the data for PMMA and the theory may arise in part because of the use of a crude planar zig-zag model of the polymer chain and from the approximation used for calculating χ maximum. However, we believe that the fit is sufficiently good to warrant three tentative conclusions.

(*1*) The difference between tensile and compressive yield stresses for PMMA may be attributed to interaction with the hydrostatic component of stress. *N.B.* In principle this technique should be capable of distinguishing between a modified von Mises and a Coulomb criterion, i.e. between the expressions $\Delta E - \tau v + P\Omega$ and $\Delta E - \tau v - \sigma_N \Omega'$ respectively, for the stress-modified energy difference between the two states. For the torsion tests $p = -\sigma_N$ and so $\Omega = \Omega'$ to explain the pressure dependence in torsion correctly. However, for the axial tests $\sigma_N = \pm \sigma/2$ and $p = \pm \sigma/3$, so $\Delta E - \tau v + p\Omega \neq \Delta E - \tau v - \sigma_N \Omega$. It is not felt, however, that from the present results we can choose unequivocally between these criteria.

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

(*3*) The effective viscosity relates directly to the low strain relaxation behaviour through the constants which appear in the WLF equation. This is at first sight surprising, in view of the fact that yield occurs at much higher levels of stress and strain than is usual in linear visco-elasticity.

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