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Yield criteria for amorphous glassy polymers

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Three amorphous polymers, polymethyl methacrylate, polystyrene and polycarbonate were tested in uniaxial tension, uniaxial compression, plane strain compression and simple shear, over a range of temperatures. In each test, the yield point was precisely determined via residual strain measurements after unloading. With the yield stresses determined for these four different stress states, two pressure dependent shear yield criteria, i.e, the modified Von Mises and the modified Tresca criteria, were checked and compared. It is shown that (i) in each case (material, temperature, initial ageing state), the yield locus is satisfactorily described by either one or the other of the two criteria, and (ii) each criterion can be associated with a specific deformation mode (either homogeneous or localized in shear bands). As for the temperature dependence of the yield stress sensitivity to the hydrostatic pressure, it appears to be related to the glass transition temperature (T_g) and more precisely to the α and β relaxations. Finally, the pressure dependence of the yield stress can be possibly explained as being due to two effects: (i) the influence of pressure on molecular motions leading to yielding and (ii) the influence of pressure on the microstructural state.

1. Introduction

Unlike in most metals [1], deformation in polymers is very sensitive to hydrostatic pressure. In particular, the stress level in a constant strain rate test increases with pressure [2–4]. An effect of pressure can also be seen in the difference observed between stress–strain curves in uniaxial tension and uniaxial compression which are associated with a negative and positive pressure respectively [5]. This effect also leads to a pressure dependence of the yield stress. In our study, the applied pressure never exceeds 100 MPa which is a pressure range where yield stress depends linearly on pressure [6]. Thus, we have chosen to consider only two shear yield criteria which feature a linear pressure dependence of the threshold stress: the modified Von Mises and the modified Tresca criteria. The former is an energetic criterion which postulates that yielding occurs when the distortion energy density reaches a limiting value. This limiting value depends on pressure and the dependence is assumed to be linear. Since the distortion energy density is proportional to the octahedral shear stress, the modified Von Mises criterion can be written as:

$$\tau_{oct} = \tau_{octo} + \mu_{vm} P$$

in which τ_{oct} and P are the octahedral shear stress and pressure respectively, which can be expressed, in terms of the principal stresses, as:

$$\tau_{oct} = \frac{1}{3}((\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2)^{1/2}$$

$$P = -\frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$$

Tresca's criterion assumes a limiting value for the maximum shear stress which, in the modified version of the criterion, is assumed to depend linearly on pressure, i.e.

$$\tau_t = \tau_{to} + \mu_t P$$

in which, τ_t, the maximum shear stress, can be expressed in terms of the principal stresses as:

$$\tau_t = \frac{1}{2}(\sigma_i - \sigma_j)_{max}$$

The parameters τ_{octo} and τ_{to} are the limiting octahedral shear stress and shear yield stress under zero pressure, respectively. The pressure coefficients μ_t and μ_{vm} quantify the yield stress sensitivity to pressure.

The validity of these criteria can be checked by applying different stress states and determining the corresponding yield stresses. A few studies [7–10] based on similar experimental determinations have shown that these criteria provide a rather good description of polymer behaviour. However, with regard to these previous studies we note the following:

(i) None of them uses a true yield stress; instead the yield stress used is arbitrarily assumed to be the maximum stress in the stress–strain curve;
(ii) Bowden and Jukes [9] are the only authors to have compared the validity of the two criteria quoted above;

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(iii) only two studies [11, 12] deal with the temperature dependence of the parameters of the cirteria.

In order to determine the most appropriate criterion for three polymers, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), at different temperatures from 0–90 °C and, in the case of PC at 20 °C, for different ageing states, we carried out four different deformation tests under four different stress states. For each test, the true yield point corresponding to the beginning of plastic deformation is determined via residual strain measurements after unloading [13–15]. The results as regards the most appropriate criterion and the criterion parameters values are then discussed.

2. Experimental procedure

2.1. Materials

The materials, PMMA, PS, and PC, were provided by Elf-Atochem. The glass transition, T_g, and the average number molecular weight, M_n, of these polymers have been determined from differential scanning calorimetry (DSC) experiments at a $10\,\mathrm{K\,min^{-1}}$ heating rate and gel permeation chromatography (GPC) using the universal calibration:

PMMA ($T_g = 123\,°\mathrm{C}$, $M_n = 1000\,000$), PS ($T_g = 98\,°\mathrm{C}$, $M_n = 124\,700$) and PC ($T_g = 152\,°\mathrm{C}$, $M_n = 23\,300$).

Before mechanical testing, all samples were brought to a temperature $T > T_g$ and then annealed at a temperature $T < T_g$. Such a treatment allows us to eliminate chain orientation and to create in the materials a defined microstructural state produced by a known thermal history.

In the case of PC, after the annealing treatment at $T < T_g$ (10 h at 145 °C), we applied three different cooling rates, namely 0.02° per min (slow cooling, SC), 1° per min and finally quenching in ice and water (fast cooling, FC), to bring the samples to room temperature, with a view to studying the ageing effect on criterion parameters.

2.2. Experimental techniques

For each case (material, temperature, initial microstructural state), four tests – uniaxial tension, uniaxial compression, plane strain compression and simple shear – were carried out on an Instron 1185 equipped with suitable testing rigs.

In uniaxial tension, the specimen shape was a normalized dumb-bell and in uniaxial compression a cylinder of 20 mm height and 8 mm diameter. The corresponding height : diameter ratio of 2.5 : 1 is a good compromise that prevents buckling and also minimizes barrelling [16]. During loading, the strain is measured by an Instron extensometer. After unloading, the residual strain was measured either by the extensometer or by an optical microscope which allows comparison of the distance between two marks before and after deformation. For both tests, the stress was obtained from the measured values of force and strain by the following expression:

$$\sigma = \frac{F}{S_0(1 - \nu\varepsilon)^2}$$

in which F, S_0, ν, ε are the measured force, the specimen initial cross-section, Poisson's ratio and the true strain, respectively.

We used a Poisson's ratio value of 0.5 which corresponds to an isovolume deformation. Transverse strain measurements carried out by means of a video recording apparatus during uniaxial compression of up to 15% strain showed that a ν value of 0.5 generates an error of less than 1% on the stress value. In uniaxial tension, this expression is only valid before neck formation.

For the plane strain compression test described elsewhere [17], we used specimens of 24 mm width and 2 mm thickness for a die breadth of 3.5 mm. These dimensions satisfy the conditions for having the best plane strain state [17, 18]. Friction between dies and specimen was reduced to a negligible level by applying a PTFE spray (Lubriflon). During loading, the strain is measured with an accurate strain gauge system fixed on to the jaws. The residual strain after unloading is obtained directly by measuring the difference between the deformed and the undeformed part of the specimen with a linear voltage displacement transducer (LVDT) transducer.

Of the different test rigs devised for the shear test and reviewed by Bowden [19], we used the one consisting of a U-bolt and a hook symmetrically shearing a prismatic specimen into two sections. This device was described and used previously by Sternstein *et al.* [20]. The sheared zones of the sample have a $6 \times 10\,\mathrm{mm^2}$ cross-section and a 1 mm width. These dimensions satisfy the conditions determined by Sternstein *et al.* [20] and G'Sell *et al.* [21] to minimize flexure and buckling effects. The effect of normal stresses on the shear stress could be estimated from equations proposed by G'Sell *et al.* [21]. It turns out to be less than 0.5% under our experimental conditions.

For each of the four tests studied, Table I features the expressions for the stress and strain tensors, octahedral and maximum shear stresses, hydrostatic pressure and equivalent strain in terms of principal stresses or strains.

In order to compare the yield stresses obtained from the four tests so as to be able to determine the pressure effect, all the other variables influencing the yield stress must be fixed. The main ones are temperature, initial microstructural state (ageing state) and strain rate. The strain rate considered here is an equivalent one obtained from an expression previously defined and used by other authors [17, 22, 23]. In strain increment terms, this expression is:

$$\mathrm{d}\varepsilon_{\mathrm{eq}} = \frac{(2)^{1/2}}{3}\left((\mathrm{d}\varepsilon_1 - \mathrm{d}\varepsilon_2)^2 + (\mathrm{d}\varepsilon_1 - \mathrm{d}\varepsilon_3)^2 + (\mathrm{d}\varepsilon_2 - \mathrm{d}\varepsilon_3)^2\right)^{1/2}$$

Due to some compliance of the different test rigs, a constant crosshead speed does not provide a constant strain rate during loading. Yet, we observed that the strain rate becomes nearly constant around the maximum load, as expected, and also that the strain rate variation occurring before yielding has a negligible effect on the measured yield stress value.

TABLE I Expressions of significant stresses and strains in terms of principal stresses or strains

	Uniaxial tension	Shear	Uniaxial compression	Plane strain compression
Stress tensor	$\begin{vmatrix} \sigma_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$ $(\sigma_1 > 0)$	$\begin{vmatrix} \sigma_1 & 0 & 0 \\ 0 & -\sigma_1 & 0 \\ 0 & 0 & 0 \end{vmatrix}$ $(\sigma_1 > 0)$	$\begin{vmatrix} \sigma_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$ $(\sigma_1 < 0)$	$\begin{vmatrix} \sigma_1 & 0 & 0 \\ 0 & \nu\sigma_1 & 0 \\ 0 & 0 & 0 \end{vmatrix}$ $(\sigma_1 < 0)$
Strain tensor	$\begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & -\nu\varepsilon_1 & 0 \\ 0 & 0 & -\nu\varepsilon_1 \end{vmatrix}$ $(\varepsilon_1 > 0)$	$\begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & -\varepsilon_1 & 0 \\ 0 & 0 & 0 \end{vmatrix}$ $(\varepsilon_1 > 0)$	$\begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & -\nu\varepsilon_1 & 0 \\ 0 & 0 & -\nu\varepsilon_1 \end{vmatrix}$ $(\varepsilon_1 < 0)$	$\begin{vmatrix} \varepsilon_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\frac{\nu}{1-\nu}\varepsilon_1 \end{vmatrix}$ $(\varepsilon_1 < 0)$
Maximum shear stress (τ_t)	$\frac{\sigma_1}{2}$	σ_1	$-\frac{\sigma_1}{2}$	$-\frac{\sigma_1}{2}$
Octahedral shear stress (τ_{oct})	$\frac{(2)^{1/2}}{3}\sigma_1$	$\frac{(6)^{1/2}}{3}\sigma_1$	$-\frac{(2)^{1/2}}{3}\sigma_1$	$-\frac{(2)^{1/2}}{3}\sigma_1(1+\nu^2-\nu)^{1/2}$
Hydrostatic pressure (P)	$-\frac{\sigma_1}{3}$	0	$-\frac{\sigma_1}{3}$	$-\frac{\sigma_1}{2}$
Equivalent strain (ε_{eq})	$\frac{2}{3}\varepsilon_1(1+\nu)$	$\frac{2}{3}(3)^{1/2}\varepsilon_1$	$-\frac{2}{3}\varepsilon_1(1+\nu)$	$-\frac{2}{3}\varepsilon_1\frac{(1-\nu+\nu^2)^{1/2}}{1-\nu}$

In this study, for the four tests, the equivalent strain rate in the yield region is $2 \times 10^{-3}\,\mathrm{s}^{-1}$ which corresponds to a few minutes loading time.

2.3. Yield stress determination

In order to determine the true yield stress via the strain recovery method [13–15], it is first necessary to deform different specimens up to different strains and, after unloading and strain recovery, to measure the residual strain. Residual strain versus applied strain is then back-extrapolated to zero residual strain. We call the corresponding applied strain the yield strain, ε_y. The stress corresponding to this strain on the stress–strain curve is the yield stress (see Fig. 1).

In an earlier paper [15], strain recovery tests allowed two non elastic deformation processes to be clearly distinguished. One produces a macroscopic deformation which is mainly recovered in a short time at the test temperature (anelastic deformation). The second one produces a macroscopic deformation which recovers only after a very long time (plastic deformation). As mentioned in that paper, the residual strain after unloading corresponds to the plastic deformation only after a very long time lapse if recovery takes place at a temperature far below T_g or after about 1 h if recovery takes place at a temperature of $T_g - 20\,^\circ\mathrm{C}$. If the time allowed for recovery is less than that, the anelastic component of the strain may not be completely recovered. However, it was experimentally observed that, beyond a recovery time comparable with the loading time, even if the anelastic component of the strain is not completely recovered, the limiting strain value obtained by extrapolation is independent of recovery time (Fig. 2(a and b)). For practical convenience, in the present study the yield stress was obtained from the limiting strain determined with a one day recovery time at the loading temperature.

From Figs 1 and 2, we can see that, contrary to the usual belief, the yield point does not necessarily correspond to the maximum stress. Indeed, the onset of plastic deformation can occur substantially earlier (see Fig. 1 and similar results in references [13, 14]) or even later (see for example Fig. 2(a and b)). Nevertheless, under the experimental conditions adopted in this study, the difference between the yield stress and the maximum stress never exceeds 10%.

The experimental errors on the yield stress value, regarding test reproducibility, applied stress state

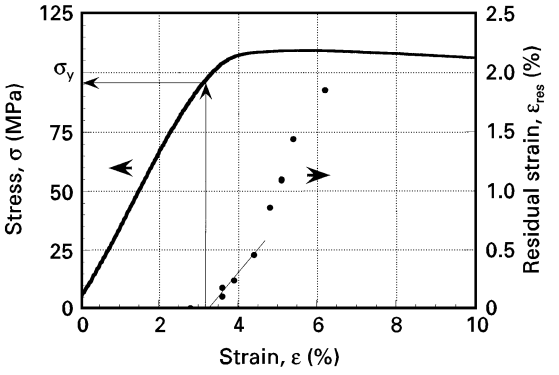

Figure 1 PS in plane strain compression at 20 °C: Yield stress determination from stress versus strain and residual strain (after one day at 20 °C) versus maximum applied strain curves.

inaccuracy and yield stress determination, are estimated to be less than 3%.

In the case of PMMA at $T < 60\,^{\circ}\mathrm{C}$ and PS at 20 °C, the yield stress in uniaxial tension could not be determined because the specimens broke before yielding.

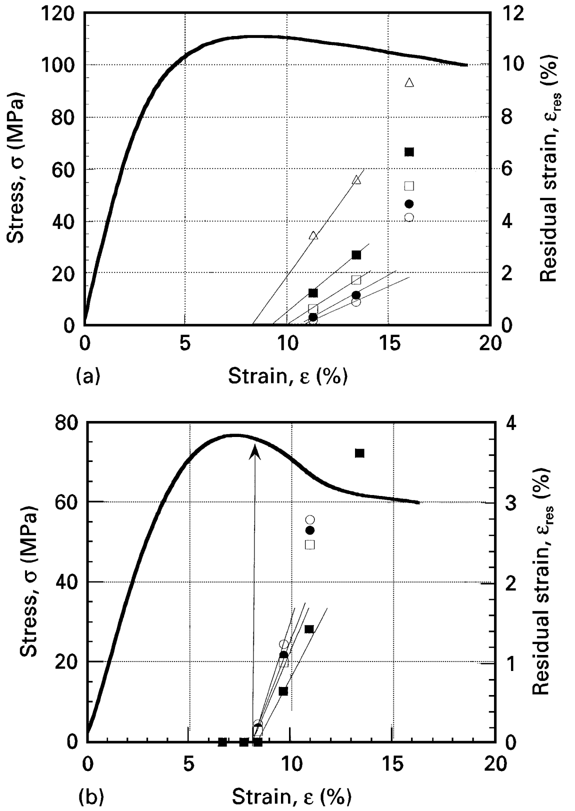

Figure 2 Stress versus strain and residual strain versus maximum applied strain curves. (a) PMMA in uniaxial compression at 20 °C: residual strain after different recovery times at 20 °C: 5 s (△), 30 s (■), 2 min (□), 10 min (●) and 60 min (○). (b) PC in uniaxial compression at 20 °C: residual strain after different recovery times at 20 °C: 1 h (○), 15 h (●) and 3000 h (□), and after 1 h at 130 °C (■) where $\varepsilon_{\mathrm{res}} = \varepsilon_{\mathrm{pl}}$ (see reference [15]).

3. Results

From the yield stress values measured under different stress states, it is possible to assess the validity of the two proposed criteria by plotting the octahedral shear stress and the maximum shear stress versus hydrostatic pressure (e.g., see Fig. 3). In the perfect case, the experimental points should fall on a straight line. Thus, a linear regression analysis is applied and from the value of the correlation coefficient ($R \leqslant 1$) the validity of the criterion can be quantitatively assessed. Results are reported in Table II. Values of the parameters obtained from the criterion that proved to be the most representative are written in bold characters. The corresponding yield envelopes on the $\sigma_3 = 0$ plane are represented in Fig. 4(a–d).

Under certain conditions, e.g., PMMA at 0 °C and 20 °C and PS at 20 °C in uniaxial tension (negative pressure), shear yielding is preceded by crazing leading to brittle fracture. Under such conditions, the corresponding portion of the shear yield envelope is not met and must be replaced by a craze yield envelope.

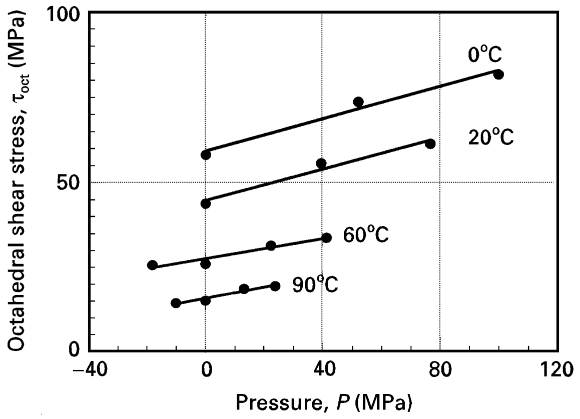

Figure 3 PMMA, τ_{oct} versus P; at each temperature, one experimental point was obtained for each type of test. The lines on the figure are linear regressions.

TABLE II Experimental values of criteria parameters

PMMA	Tresca			Von Mises		
T(°C)	μ_t	τ_{to}(MPa)	R_t	μ_{VM}	τ_{octo}(MPa)	R_{VM}
0	0.28	69	*0.95*	**0.23**	**59**	***0.99***
20	0.28	52	*0.97*	**0.23**	**45**	***0.98***
60	0.20	31	*0.96*	**0.14**	**27**	***0.96***
90	0.23	18	*0.97*	**0.17**	**16**	***0.97***
PC	Tresca			Von Mises		
T(°C)	μ_t	τ_{to}(MPa)	R_t	μ_{VM}	τ_{octo}(MPa)	R_{VM}
20	**0.10**	**37**	***0.93***	0.05	33	*0.51*
90	**0.18**	**26**	***1.00***	0.12	23	*0.84*
20 (FC)	**0.12**	**34**	***0.94***	0.03	30	*0.62*
20	**0.10**	**37**	***0.93***	0.05	33	*0.51*
20 (SC)	**0.08**	**39**	***0.93***	0.05	35	*0.37*
PS	Tresca			Von Mises		
T(°C)	μ_t	τ_{to}(MPa)	R_t	μ_{VM}	τ_{octo}(MPa)	R_{VM}
20	**0.19**	**42**	***0.95***	0.18	35	*0.69*
90	0.49	4.3	*0.98*	**0.39**	**4.8**	***0.99***

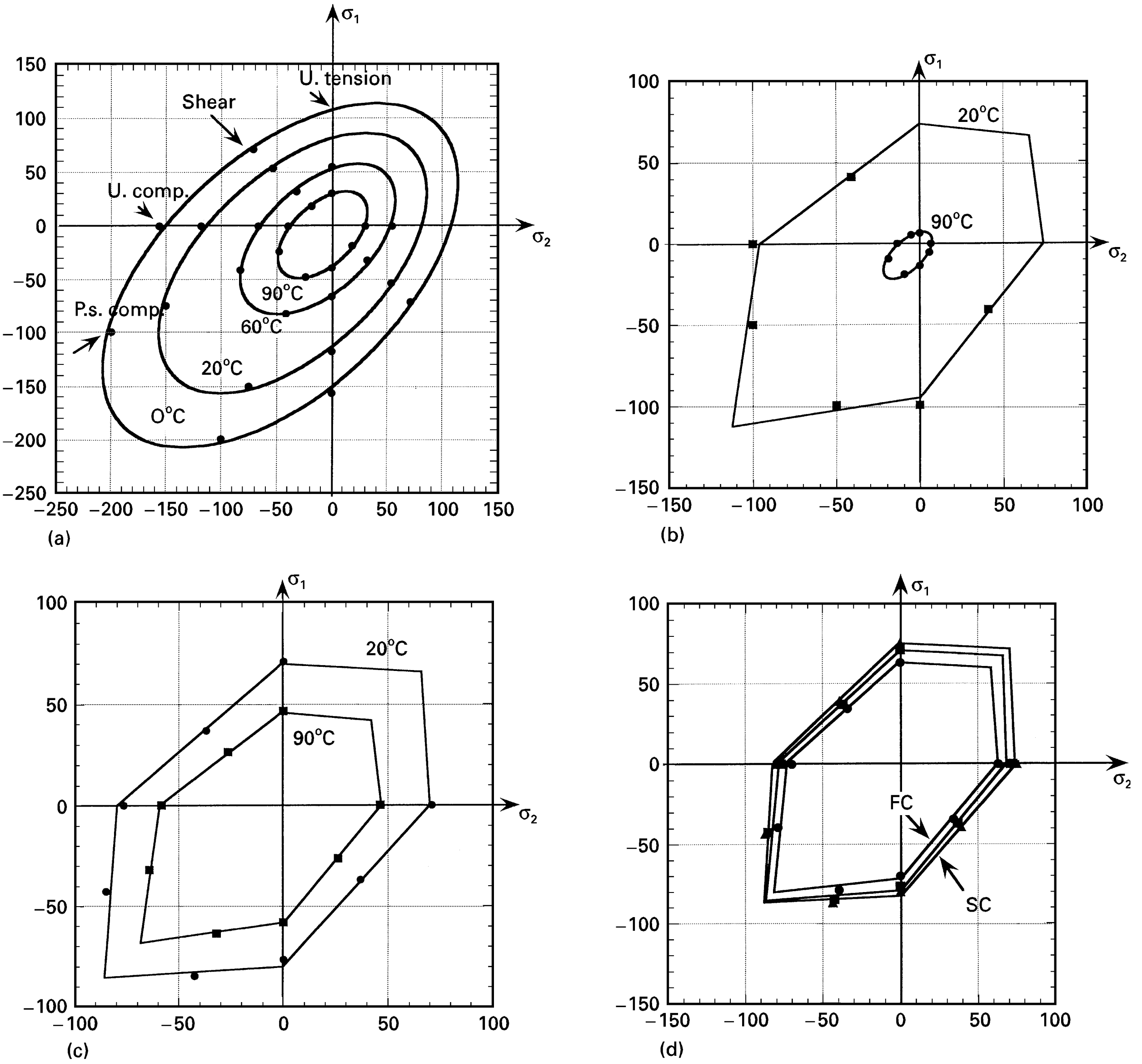

Figure 4 Experimental points and best criterion envelopes in the $\sigma_3 = 0$ plane: (a) PMMA at four temperatures, (b) PS at two temperatures, (c) PC at two temperatures and (d) PC at 20 °C for three initial ageing states (see text).

4. Discussion

4.1. Yield criterion and deformation mode

Our results show that under the adopted experimental conditions, the modified Tresca criterion always provides a satisfactory description of the shear yield threshold since $R_t > 0.93$. The modified Von Mises criterion is equally satisfactory or even better for PMMA over the examined range of temperatures and for PS at 90 °C.

At 20 °C, our results confirm those of Bowden and Jukes [9] who concluded that the modified Von Mises criterion more closely represents the behaviour of PMMA and the modified Tresca criterion more closely represents the behaviour of PS.

In metallurgy, some mild steels, unlike most metals, show a plastic deformation with shear bands and follow the Tresca criterion [6, 24]. Taylor and Yarrow [24] justified this experimental finding by calculations on granular structure. It appears sensible to use a yield criterion based on the maximum shear stress in the bands (Tresca) when the plastic deformation is actually localized in shear bands and conversely, a yield criterion based on a non directional parameter such as the octahedral shear stress (Von Mises) when plastic deformation is diffused throughout the whole material. Bowden and Jukes [9] agree with Taylor and Yarrow [24] in the interpretation of their results on PMMA and PS. The PS samples featured fine bands and the yield data were better described by the modified Tresca criterion. On the other hand the PMMA samples featured large diffuse yield zones and the best criterion was a modified Von Mises criterion.

Microscopic observations on plane strain deformed samples under polarized light reveal the deformation mode as is shown in Fig. 5 (a–e). PMMA deforms with large diffuse zones over the examined range of temperatures. PS shows very thin bands at 20 °C whereas the deformation is homogeneous with large diffuse zones at 90 °C. PC shows shear bands under all conditions studied. Yet, these are wider than in PS. In PC at 20 °C, shear bands become more definite after the sample has been aged. These observations are in accordance with previous ones. Indeed, Bowden and Raha [25] observed that the temperature below which

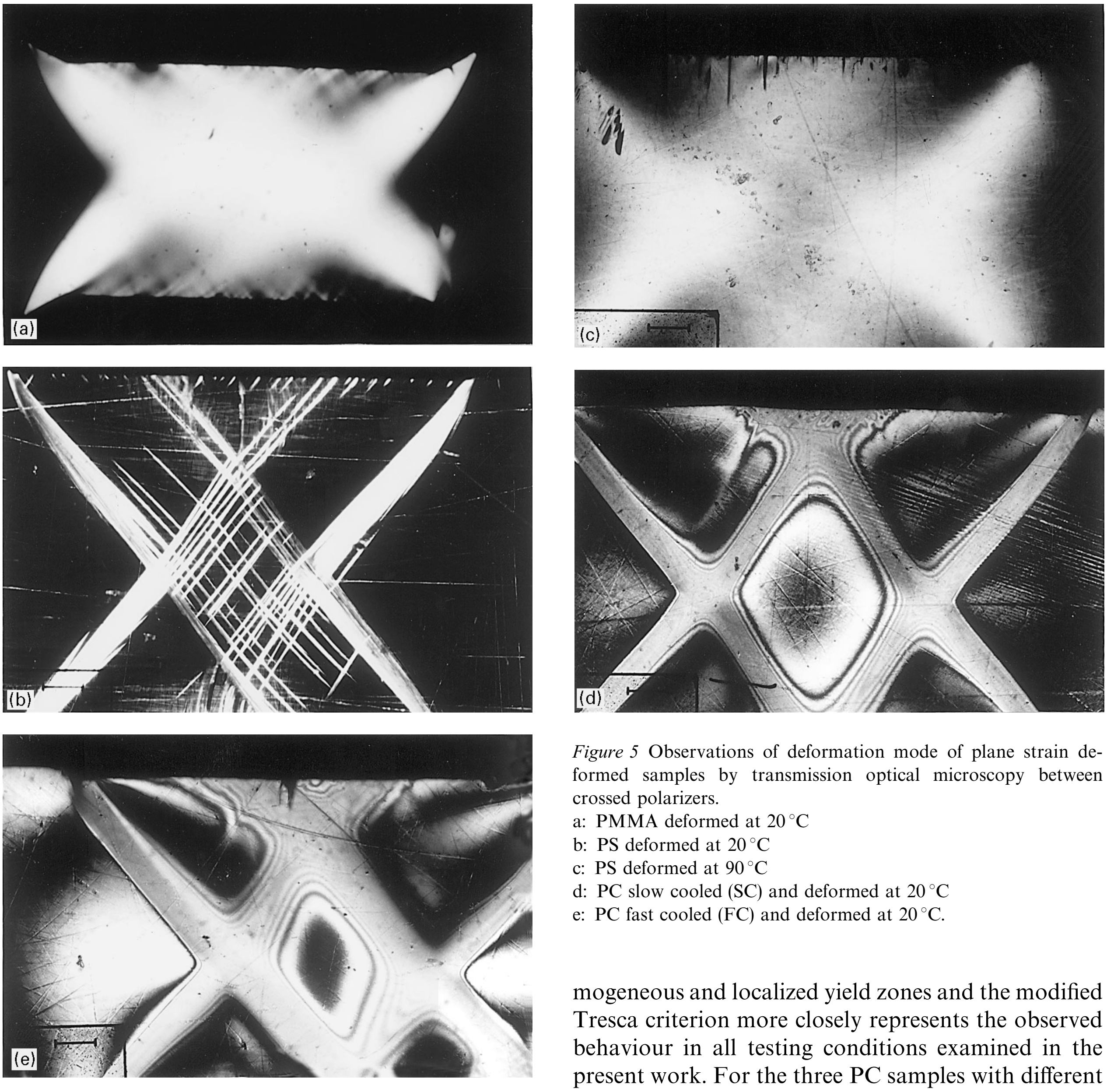

Figure 5 Observations of deformation mode of plane strain deformed samples by transmission optical microscopy between crossed polarizers.
a: PMMA deformed at 20 °C
b: PS deformed at 20 °C
c: PS deformed at 90 °C
d: PC slow cooled (SC) and deformed at 20 °C
e: PC fast cooled (FC) and deformed at 20 °C.

the sample deforms with shear bands and above which it deforms with large diffuse zones is about 60 °C and it is lower than – 100 °C for PMMA. As for PC, Withney and Andrews [7] observed at 20 °C an intermediate behaviour between PS and PMMA and Ishikawa and Narisawa [26] clearly showed that the more aged the sample is, the more definite the shear bands are.

From the observations made on PS, it appears that which criterion is best depends on the deformation mode: at 20 °C where the deformed sample features neat shear bands, the modified Tresca criterion is the best one whereas at 90 °C where the deformed sample features diffuse yield zones the modified Von Mises criterion is the best one.

The results obtained with PMMA agree with the preceeding ones. The deformed samples always display diffuse yield zones and the Von Mises criterion turns out to fit the data slightly better than does the Tresca criterion.

In the case of PC, the microscopic observations show a deformation mode intermediate between homogeneous and localized yield zones and the modified Tresca criterion more closely represents the observed behaviour in all testing conditions examined in the present work. For the three PC samples with different microstructural states examined at 20 °C, although the modified Tresca criterion is always the best one, the less aged the sample is the more the deformation tends to be homogeneous and the higher the Von Mises correlation coefficient is. It should be noted, however, that the results obtained by Rink *et al.* [14], following the same experimental procedure at 20 °C, on a different PC having a lower molecular weight fitted the Von Mises criterion.

To conclude, these results point to a relationship between the deformation mode and the yield criterion, although there can be intermediate cases for which the relationship is not so clear cut.

4.2. Criterion parameters

4.2.1. τ_o (τ_{octo} *and* τ_{to})

As expected, the temperature and annealing effects on τ_o are the same as those directly observed on any yield stress in that τ_o increases as the temperature decreases and/or as the sample ageing increases. The influence of temperature depends on the material and, more specifically, on the temperature of its main (α) and secondary (β) relaxations. At 20 °C, unlike PS and

PMMA, PC is far above the temperature of its β relaxation which implies a greater molecular mobility and, accordingly, it shows a smaller τ_o (at 1 Hz, $T_\beta = -100$, 20 and 50 °C for PC, PMMA and PS, respectively). At 90 °C, the three polymers are above their T_β and T_α becomes the key parameter: the closer the test temperature is to the T_α of the polymer, the lower τ_o is (at 1 Hz, $T_\alpha = 100$, 120 and 150 °C for PS, PMMA and PC, respectively). In Fig. 6(a and b) yield envelopes of these three polymers at 20 °C and 90 °C closely illustrate these observations.

4.2.2. Pressure parameter: $\mu(\mu_{vm}$ *and* $\mu_t)$

At 20 °C, it is worthwhile noting the level of agreement between our μ values and the mean ones which are calculated from values obtained by other authors, obtained by using different methods and, mostly, by taking the maximum stress as the yield stress. These mean values are $\mu_{vm} = 0.17$ for PMMA [2, 9, 22], $\mu_t = 0.19$ for PS [7, 9, 27, 28] and $\mu_{vm} = 0.08$ for PC [10, 12, 14, 27], whilst we find $\mu_{vm} = 0.23$, $\mu_t = 0.19$ and $\mu_t = 0.10$ for these three polymers, respectively.

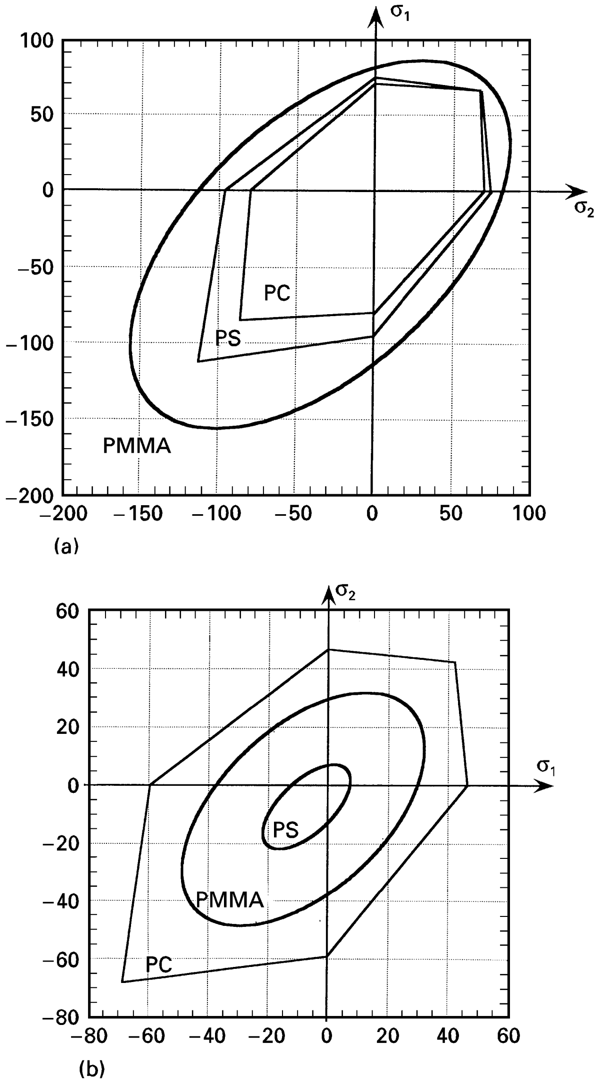

Figure 6 Best criterion envelopes in the $\sigma_3 = 0$ plane for the three polymers at (a) 20 °C and (b) 90 °C.

In previous studies on the temperature influence on μ for PMMA, Sternstein and Ongchin [11] measured a constant value of 0.15 for μ_{vm} over a narrow range of temperatures from 70–90 °C and Souahi [29] found a high value of about 0.5 for μ_{vm} around T_α. For PC, a constant value of 0.075 for μ_{vm} over a large temperature range between − 50–120 °C and a sensible increase above this value around the β relaxation temperature ($T < -50$ °C) were found by Bauwens-Crowet *et al.* [12].

From our results on PMMA, it appears that μ values are largest around the β relaxation temperature. For PC, μ increases between 20–90 °C. For PS, a large increase is observed between 20–90 °C i.e., between a temperature below T_β and a temperature close to T_α.

Our results and previously reported ones, reveal a tendency of μ to increase around the β relaxation temperature and, above all, around the α relaxation one.

Concerning the ageing effect on μ, it appears that the more the sample is aged the lower is the μ value. This tendency is opposite to that found by Bubeck *et al.* [10], from data obtained in the second and fourth quadrants only of the $\sigma_3 = 0$ plane and by using a yield stress taken as the maximum stress.

Obviously, it would be necessary to perform further experiments at several other temperatures and for other annealing states to confirm the trends observed in the present study.

4.3. Origin of the pressure dependence

It has been experimentally observed by several authors that the molecular mobility is reduced by the hydrostatic pressure. Indeed, an increase in pressure results in a shift of all molecular relaxations towards higher temperatures [30–33]. In addition, previous studies [15, 34] showed, firstly that co-operative molecular motions leading to yielding are of the same nature of motions that produce the α relaxation and, secondly that they are closely linked to anelastic motions associated with the low temperatures side of the α relaxation. The pressure effect on the yield stress can then be viewed as a direct consequence of its effect on the kinetics of α motions.

4.3.1. Pressure influence on molecular motions in yield models

In order to introduce pressure into yield models via molecular motion kinetics, several authors have proposed a linear pressure modification of the activation energy associated with yield motions. Hasan *et al.* [35], modified the activation energy expression proposed in the model of Argon [36] whilst others [3, 9, 12] modified the model proposed by Eyring [37]. The μ values deduced from this equation by Ward [3] and Bowden and Jukes [9] have the same order of magnitude as the measured ones.

It is now well known that α motions corresponding to yield motions are co-operative which implies several correlated space limited motions. Thus, the energy barrier of the α motions has no real physical meaning. Accordingly, the correlation between yield stress and α relaxation dependence on pressure has to be specified.

4.3.2. *Possible molecular origin of yield stress pressure dependence*

Recently, a physical model proposed by Mangion *et al.* [38] which assumes that the α motions result from hierarchically correlated elementary β motions, has permitted a good description of dynamic mechanical spectra and stress–strain curves for PMMA [39]. This model can be slightly modified to take into account the pressure influence. Since the key parameter of this model is the β motions, the modification consists of adding a pressure parameter to the β activation energy. Thus, the previous β activation energy expression: $U_\beta \cdot f(\sigma)$, where $f(\sigma)$ is function of the applied stress, becomes $(U_\beta + \Omega P) \cdot f(\sigma)$. Using an Ω value of $10^{-4}\,\mathrm{m^3\,mol^{-1}}$ which is intermediate between the value $2 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$ determined from dielectric measurements at 112 °C by Sasabe and Saito [32] and the value $5 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}$ obtained from stress relaxation tests at a T close to T_β by Goldman *et al.* [40], calculations from this model give $\mu_t = 0.25$ at 0 °C, 0.25 at 20 °C, 0.24 at 60 °C and 0.17 at 90 °C. These values are in good agreement with the measured ones. However, this model does not describe the experimental increase of μ values in the T_α region. Thus, it appears that for temperatures near T_α, the pressure effect on α motions is not only due to its effect on β motion kinetics. Indeed, around the glass transition, pressure leads to some structural modification. As the pressure increases, density fluctuations or the concentration of defect sites decrease [41]; this leads to slower α motions [38]. To sum up, in the glassy region the polymer structure is independent of pressure and the proposed modification of β motion kinetics suffices to describe the pressure influence on α motions and then on yield stress. When the temperature approaches T_α, the structural state (defect site concentration) is pressure dependent thus also contributing to the pressure effect on yield stress.

5. Conclusion

An accurate determination of the yield point for different stress states has permitted comparison of the validity of two shear yield criteria: the pressure modified Tresca and the pressure modified Von Mises criteria. It has been observed that:

(i) For each experimental case (material, temperature, ageing state), the most appropriate criterion provides a good description of the yield behaviour.
(ii) Which criterion is more appropriate depends on the deformation mode.
– The modified Tresca criterion which uses the maximum shear stress seems more appropriate for heterogeneous deformation by shear banding.
– The modified Von Mises criterion which uses the "non directional" octahedral shear stress more appropriate for homogeneous deformation.

With regard to the parameter μ which represents the yield stress sensitivity to pressure, we can observe that:
(i) The μ values are in fair accordance with those found by other authors using other methods.
(ii) In general, the μ value increases at temperatures close to T_β or T_α. In particular, it reaches a very high value in the vicinity of T_α. For PC at 20 °C, the μ value appears to decrease when the sample is annealed.

It has also been shown that the pressure dependence of the yield stress is correlated with its dependence on α motion kinetics.

Finally, it is suggested that, in the glassy state, the influence of pressure on the α motions is mainly due to its influence on β motions. A physical model using such an assumption leads to μ values for PMMA which are in close agreement with the measured ones. Moreover, around the glass transition temperature, a second pressure effect on the α motions due to structural changes with pressure can explain the high μ values observed experimentally.

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