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Transitions between crazing, fracture and yield under hydrostatic pressure

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A simple model is proposed to explain transitions from crazing or fracture to shear yielding and vice-versa with increasing superposed pressure. The model is based on an estimate of the local tensile component of stress in the vicinity of a flaw, distinguishing between the different physical situations which arise depending on whether or not the pressurizing medium penetrates the flaw. The model explains naturally many observations of specimens failing in a brittle manner in nominally compressive stress fields.

1. Introduction

In recent publications [1–3] it has been shown that polycarbonate (PC) and polyvinylacetate (PVAc) can craze in torsion tests under superposed hydrostatic pressures. The craze plane was found in all cases to be at approximately 45° to the specimen axis, perpendicular to the principal tensile component of the applied shear stress, as shown in Fig. 1. If the shear stress at which crazes were initiated was τ, and the hydrostatic pressure was p, then the major principal stress component in the bulk of the test piece was $(\tau - p)$. Many crazes were observed to initiate under the conditions, $\tau - p < 0$, (i.e. in completely compressive stress fields) as shown in Fig. 2. The amount of crazing seen in PC decreased with increasing pressure; only homogeneous shear deformation was observed in tests performed at pressures greater than a critical pressure.

Rabinowitz, Ward and Parry [4] also performed torsion tests, on polymethylmethacrylate (PMMA) under superposed hydrostatic pressures. They observed homogeneous shear deformation at low pressures, with a yield stress increasing strongly with increasing pressure. Above a critical pressure, samples exposed to the pressure fluid fractured in a brittle manner on 45° planes, all specimens failing in macroscopically compressive stress fields. Harris, Ward and Parry [5] observed that exclusion of the fluid from the specimen surface with a thin coating of rubber completely eliminated brittle behaviour in PMMA at all pressures, and a similar procedure also suppressed crazing in PC and PVAc [1–3]. By contrast Rabinowitz *et al.* [4] found that a heavily crystallized polyethylene terephthalate (PET) which was brittle in torsion at atmospheric pressure became ductile at all positive pressures.

Rabinowitz *et al.* [4] and Harris *et al.* [5] distinguished between these two different types of transition in terms of the differences in nature of the flaws responsible for fracture in the two materials. It was argued that the flaws in PET were internal (e.g. at spherulite boundaries) and that these were closed up by the hydrostatic pressure. PMMA was considered to fail in a brittle manner from surface flaws produced in the machining of the specimens, which were penetrated by the pressure fluid. This penetration of the fluid cancelled the crack-closing properties of the high pressure in an unspecified way, leaving the specimen to fail under the tensile component of the applied shear stress.

In this paper a more detailed analysis of the stress state around flaws in samples tested under superposed hydrostatic pressures is described. The analysis is used to describe the circumstances under which brittle–ductile (crazing–yielding) or ductile–brittle transitions may be observed under hydrostatic pressure.

2. Theory

Consider an elemental cylindrical shell in a torsion specimen with a uniform cross section, where the macroscopic shear stress is τ. Consider further an elliptical crack of semi-major axes a and b ($a \gg b$)

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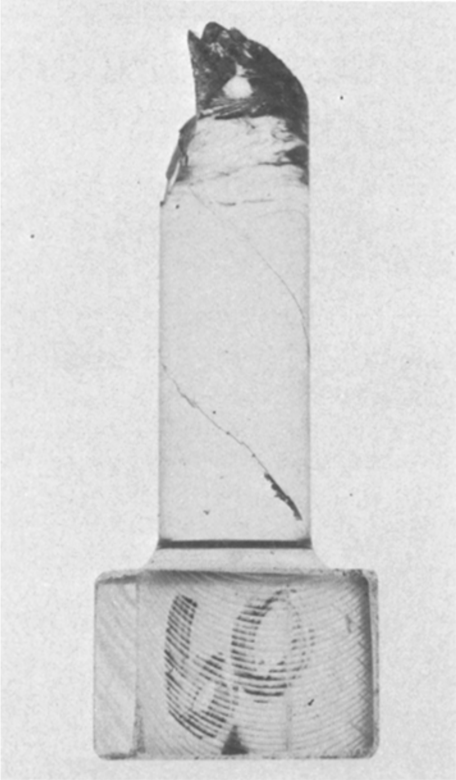

Figure 1 A torsion sample of polyvinylacetate which has crazed and fractured. The craze and crack form on a 45° spiral, growing perpendicular to the tensile component of the shear stress.

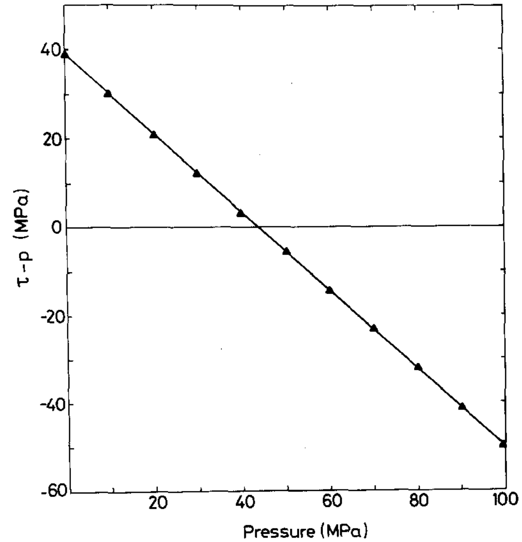

Figure 2 The net tensile stress, $\tau - p$, for craze dominated yielding in torsion under hydrostatic pressure, p. The maximum shear stress in the specimen was τ, material polycarbonate, Makrolon 2803, temperature 22° C, strain rate $10^{-4}\,\text{sec}^{-1}$.

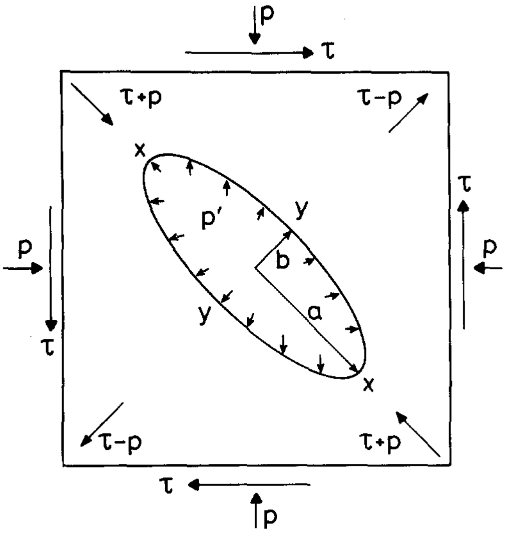

Figure 3 A schematic representation of an elliptical flaw in the most severe orientation in a region of specimen subject to a pure shear stress τ and hydrostatic pressure p. The flaw is filled with fluid under pressure p'. The maximum tensile stresses exist at the equivalent points X as described in the text.

in the most severe orientation, perpendicular to the tensile component of the applied shear stress τ, as shown in Fig. 3. Superimpose a uniform hydrostatic pressure p on the outside of the specimen and assume that the crack contains fluid at a hydrostatic pressure p'.

It can then be shown [6] that the crack acts as a stress concentrator and that the maximum tensile component of stress is the local tangential component at the ends of the major axis of the crack. This can be written [6] as

$$\sigma_{\max} = (\tau - p)\left[1 + 2\left(\frac{a}{b}\right)\right] + (\tau + p) - p'\left[1 - 2\left(\frac{a}{b}\right)\right] \qquad (1)$$

where the three contributions are readily identified with reference to Fig. 3. Consider two cases:

(i) $p' = p$ e.g. an external flaw penetrated by the high pressure fluid. In this case

$$\sigma_{\max} = 2\tau\left(1 + \frac{a}{b}\right) - p \qquad (2)$$

$$= K\tau - p \qquad (3)$$

where

$$K = 2\left(1 + \frac{a}{b}\right).$$

(ii) $p' = 0$ e.g. an internal flaw, or an external flaw in a rubber coated specimen; no fluid penetration.

Hence

$$\sigma_{\max} = 2\tau\left(1+\frac{a}{b}\right)-2p\left(\frac{a}{b}\right) \tag{4}$$

For $\frac{a}{b} \gg 1$ then

$$\sigma_{\max} = K(\tau - p). \tag{5}$$

Exactly analogous equations can clearly be derived for the local tensile stresses at the tips of cracks perpendicular to the tensile axis of a specimen subjected to tension, σ, under superposed hydrostatic pressure p, depending on whether or not fluid penetrates the crack. They are

$$\sigma_{\max} = K\sigma - p \tag{6}$$

with fluid penetration

and

$$\sigma_{\max} = K(\sigma - p) \tag{7}$$

no fluid penetration.

It can be seen that in each of these situations it is possible to establish positive (tensile) stresses at crack tips even at high superposed pressures providing that sufficiently high values of τ (or σ) may be achieved without the intervention of plastic yielding. In order to proceed with this discussion of brittle behaviour under superposed pressures the following simplifying assumption is now made. It is assumed that ductile behaviour will ensue if the macroscopic shear stress in the specimen reaches the yield condition before the local tensile stress reaches a critical value, say σ_c. It is well established that the shear yield stress of most polymers is substantially pressure dependent and the possibility arises that the overall stress levels may increase with pressure to the point where the local tensile stress exceeds the critical value and either crazing or brittle behaviour will then occur. This situation is illustrated diagrammatically in Fig. 4a. The yield stress has been assumed to increase approximately linearly with pressure according to $\tau_{\text{yield}} = \tau_0 + \alpha p$ as is commonly observed. Two possible fracture lines are drawn depending on whether or not fluid penetration of the crack occurs.

$$\tau = \frac{1}{K}(\sigma_c' + p) \quad \text{where} \quad \sigma_c' = \sigma_c'(p, \dot{\epsilon}, T, \text{fluid})$$

with fluid penetration, (8)

or

$$\tau = \frac{\sigma_c}{K} + p, \quad \text{where } \sigma_c = \sigma_c(p, \epsilon, T)$$

without fluid penetration. (9)

The failure criteria defined in Equations 8 and 9 have interesting implications with respect to the nominal principal tensile stress, in the body, $\tau - p$ (or $\sigma - p$ in tension under superposed pressure). According to Equation 9

$$\tau - p = \frac{\sigma_c}{K} = \text{constant} > 0 \tag{10}$$

when fluid penetration does not occur. By contrast

$$\tau - p = K^{-1}[\sigma_c' - p(K-1)]$$

with fluid penetration. (11)

If $K \gg 1$ then it is clearly possible that $(\tau - p) < 0$ and so the nominal stress field is purely compressive. Note that with fluid penetration it would be expected that chemical effects are likely to reduce the critical stress required for craze initiation as suggested in the figure (i.e. $\sigma_c' \leqslant \sigma_c$), although plasticization at the tip may cause crack blunting for certain polymer/fluid combinations (giving $\sigma_c' > \sigma_c$). Note also the high pressure dependence for crazing or fracture from internal flaws (slope = 1) compared with that expected with fluid penetration, (slope = $1/K \ll 1$).

The figure suggests that either (a) a ductile–brittle DB transition will occur with failure at high pressures occurring from a crack containing pressurized fluid, or (b) that ductile behaviour will be observed throughout. It is extremely unlikely that brittle failure will result at high pressures from a flaw without fluid penetration since $(\mathrm{d}\tau_{\text{yield}}/\mathrm{d}p) \simeq \alpha \ll 1$, for all polymers tested.

Other possible classifications of behaviour are possible if the material is brittle at atmospheric pressure, depending on whether or not the specimen is protected from fluid penetration. For example in Fig. 4b it is envisaged that in a sealed specimen the behaviour would be ductile throughout. Chemical interactions between fluid and an uncoated specimen would reduce the critical stress for craze initiation to give rise to brittle behaviour at low pressures. The possibility of the uncoated polymer becoming ductile at higher pressures would depend on whether or not the pressure dependence of the yield stress was less than or greater than that of the fracture stress calculated from Equation 8. Fig. 4c indicates the possibility of a BD transition occurring at two

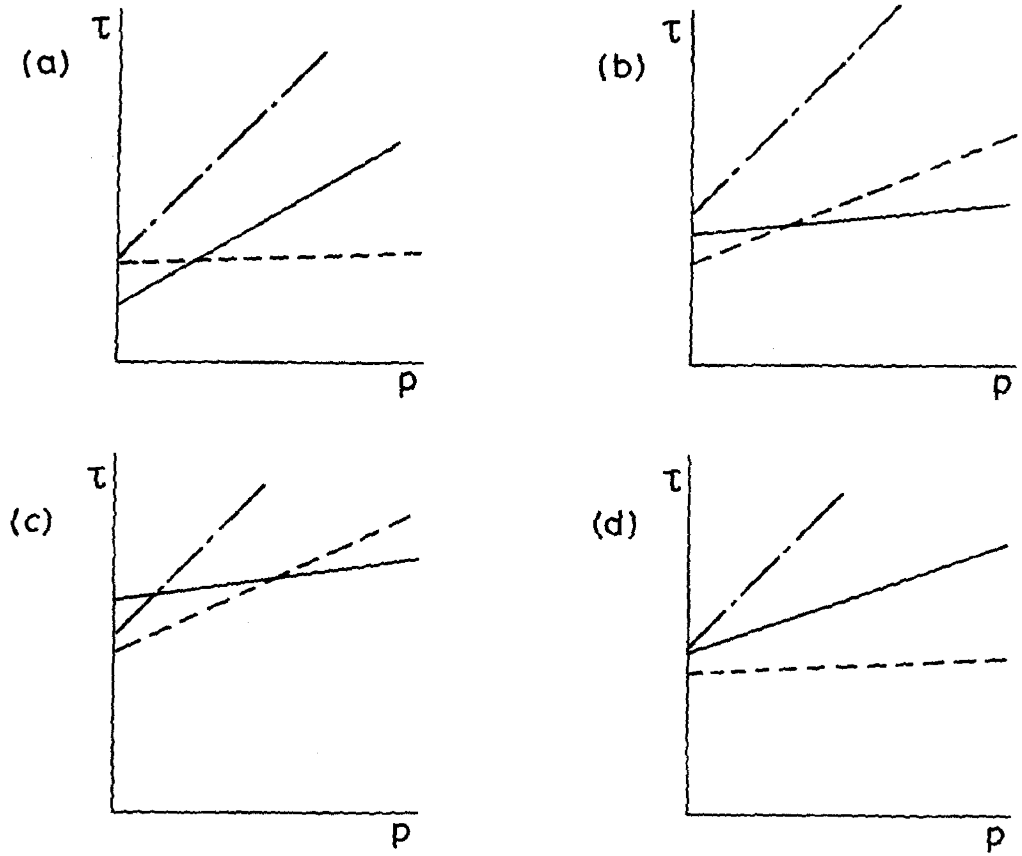

Figure 4 Possible failure models under hydrostatic pressure: —— shear yield $\tau = \tau_0 + \alpha p$; —·—·— fracture with no fluid penetration, Equation 9; – – – fracture with fluid penetration, Equation 8. (a) $\tau_0 < \sigma_c'/K < \sigma_c/K$, $1 > \alpha > K^{-1}$; fully ductile (sealed) or ductile–brittle (unsealed) (b) $\sigma_c'/K < \tau_0 < \sigma_c/K$, $1 > K^{-1} > \alpha$; ductile (sealed), brittle–ductile (unsealed) (c) $\sigma_c'/K < \sigma_c/K < \tau_0$, $1 > K^{-1} > \alpha$; brittle–ductile, transition pressure higher when unsealed (d) $\sigma_c'/K < \tau_0 < \sigma_c/K$, $1 > \alpha > K^{-1}$; fully ductile (sealed), brittle (unsealed).

different pressures depending on whether or not fluid penetration of cracks occurs, whereas brittle behaviour at all pressures is illustrated in Fig. 4d for the case of fluid penetration. The high pressure dependence expected for crazing with no fluid penetration clearly precludes the possibility of brittle behaviour in "sealed" specimens.

3. Discussion

The data on PMMA by Harris, Ward and Parry [5] are well described by this simple analysis as shown in Fig. 5. Specimens protected from the hydrostatic fluid, yield at all pressures because the fracture stress without penetration increases directly as the pressure increases whereas the pressure dependence of the yield stress is much less than 1. Unprotected samples fail in a brittle manner at high pressures because of fluid penetration of surface flaws. Note that the necessary conditions for this type of behaviour are

(1) The material is ductile in shear at atmospheric pressure.

(2) The pressure dependence of the yield stress is rather high.

(3) There is a sufficient number of sharp surface flaws.

These conditions are easily satisfied with PMMA which has a large pressure dependence of yield stress due to the proximity of the β transition to room temperature; although it is brittle in unnotched tensile tests it is only just below its brittle ductile transition temperature of 40° C and therefore just ductile in shear. Furthermore the specimens used by Harris *et al.* [5] were machined from cast rod and were not polished and therefore satisfied Condition 3 above.

Harris *et al.* [5] observed contrasting behaviour with heavily crystallized PET. This material was brittle in torsion at atmospheric pressure (uncoated) but became ductile at the lowest opera-

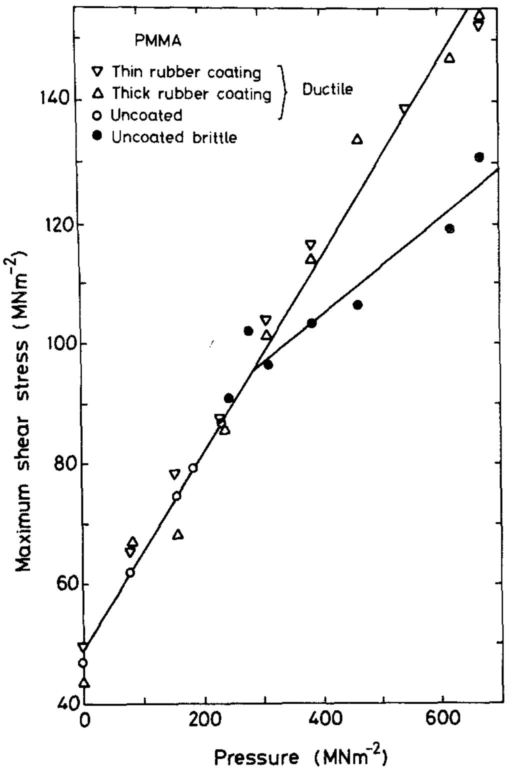

Figure 5 Maximum shear stress data versus pressure. Torsion tests on PMMA (after Harris, Ward and Parry [4, 5]).

tional pressure. This behaviour is suggestive of Fig. 4c. Optical microscopy confirmed that fracture originated at internal flaws and so there was no fluid penetration. (Internal flaws were also established as fracture nuclei in heavily crystallized PET in an independent investigation by Foot and Ward [7].) The fracture stress in this failure mode would be expected to have a high pressure dependence $(\mathrm{d}\tau_\mathrm{f}/\mathrm{d}p \approx 1)$, and therefore to exceed the yield stress at very low pressures. The yield stress has only a low pressure dependence because of the high crystallinity and the absence of any significant secondary mechanical relaxations around room temperature.

A more detailed examination of the pressure dependence of fracture and crazing from flaws with no fluid penetration was made by Matsushige, Radcliffe and Baer [8–11] on the tensile properties on PMMA, and more extensively, on polystyrene (PS). These authors [11] measured values of the pressure dependence of the craze initiation stress to be 0.75 and 0.88 for PS and PMMA respectively. Both polymers when protected from the fluid showed craze initiation and fracture before yield at low pressures, with both craze initiation and fracture having the very high pressure dependence suggested by the model.

The authors noted that the fracture data from these samples could be described by $\sigma - p \approx$ constant, for both fracture and craze initiation stresses. This is consistent with Equation 10 and implies that the maximum tensile stress at the root of any flaw was approximately independent of pressure. Their observation that, $\sigma - p$, decreased sharply with pressure and became negative at the higher pressures for specimens exposed to the fluid is in general terms consistent with Equation 11. It has little to do with the stress-cracking ability of the silicon oil used as high pressure fluid, which is relatively inert, but is related directly to the stress distribution about surface flaws penetrated by the fluid.

Above a critical pressure (~ 80MPa for PS, ~ 30MPa for PMMA) sealed samples of both materials were ductile as suggested in Fig. 4c.

The simple model described above has several limitations which it is important to recognize. The model is for the initiation of "brittle" failure. Much of the data [3, 4, 8–11] from materials which are "brittle" under hydrostatic pressure are from glassy polymers which craze before fracture. In some instances the maximum nominal stress in the material relates to a "craze dominated yield point" (CDYP) as discussed by Brown [12] and Kitagawa and Kawagoe [13]. Craze initiation and growth with increasing stress result in a rapidly increasing specimen compliance. A CDYP arises when the "plastic" strain-rate generated by craze growth just matches the applied strain-rate causing a maximum in load or torque.

The study of crazing or PC in torsion by Duckett *et al.* [2, 3] was restricted to measurements of CDYP's. The results shown in Fig. 6 [3, 14] confirm that crazing is only observed in specimens exposed to the fluid at low pressures. The pressure dependence of the CDYP is approximately independent of material, but the lower molecular weight polymer "fails" at lower stresses and over a wider pressure range than the higher molecular weight polymer. It is clear that the craze initiation stress must have a higher pressure dependence than the CDYP and independent measurements of the craze initiation stress in tension [15] are consistent with these torsion data.

Matsushige *et al.* [8–11] attempt to define an actual craze *initiation* stress from observations of

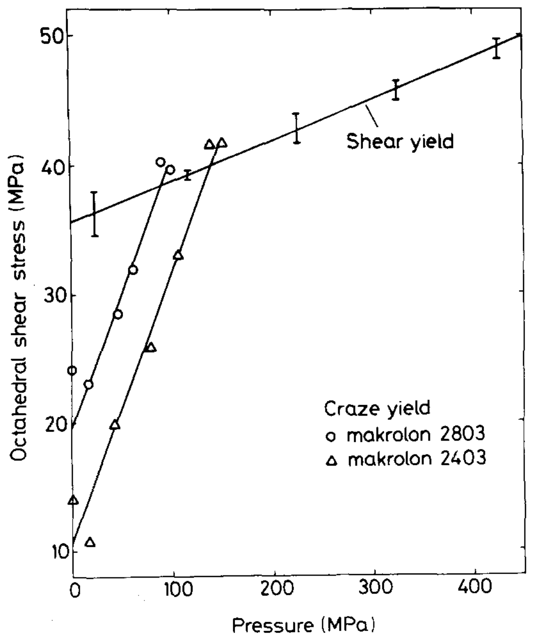

Figure 6 Octahedral shear stress data versus pressure for polycarbonate. Experimental points represent CDYPs for specimens tested exposed to the pressure fluid (dioctyl sebacate). The "shear yield" line was established for both materials with "protected" specimens (no penetration) at low pressures and with "unprotected" specimens (above the transition pressure). ○ Makrolon 2803, ($M_w \sim 20\,000$) △ Makrolon 2403, ($M_w \sim 15\,000$). $T = 22°$ C, $\dot{\gamma} \simeq 10^{-4}\,\text{sec}^{-1}$ [3].

the onset on non-linearity of the stress–strain curves, but it is unlikely that this method is of sufficient sensitivity or generality to be widely applicable.

Samples failing by craze and crack growth with fluid penetration present extreme problems of interpretation. The results of Matsushige *et al.* [8–11] on unsealed specimens show that craze breakdown and crack growth are very sensitively dependent on fluid viscosity. Brown [12], Kramer [16] and Marshall, Culver and Williams [17] describe simple models for the transport of fluid through crazed material to the growing tip. The application of these models to crazes in high pressure fluid faces many problems due to the possibilities of large (normally unknown) increases in fluid viscosity with pressure, rupture of the crazed material due to forcing fluid through it under enormous pressure gradients, uncertainties of the geometry of the craze-structure itself, etc.

Hydrostatic pressure is known to produce large changes in bulk material properties such as the elastic moduli and yield stress and it is therefore natural to expect that pressure will therefore also affect the critical stress for craze initiation. Some of the effects of pressure on mechanical or dielectric properties can be understood in terms of changes in relaxation times with pressure [18, 19] and can therefore, to a first approximation, be treated by an extension of time–temperature equivalence [20]. It is not possible to predict the way in which these effects and others will affect the craze initiation stress.

The simple model uses a craze initiation criterion which is a function only of the maximum principle stress. The crazing data of Sternstein and Myers [21] and Argon and Hannoosh [22] clearly indicate an important role for the intermediate principal stress and so the present model can only be considered as a zero order approximation. The data of Sternstein [21] and Argon [22] on PMMA and PS respectively suggested that crazing was not possible in pure torsion. This led to several theories of crazing [21–24] which required a dilatational component of the stress field for craze initiation. The observation of crazes in torsion [1, 2, 25], especially with a superposed hydrostatic pressure [3] and therefore no macroscopic dilatation, suggests the need for more extensive crazing data on many polymer systems and critical review of these theories. (Note that crazes have been observed to initiate under the action of residual pure shear stresses, after twisting into the plastic state and then storage at zero torque for times varying between a few minutes at elevated temperatures to a few months at room temperature [14].) No craze initiation has yet been seen in torsion in the absence of a liquid suggesting the role of environmental factors in reducing craze resistance (i.e. $\sigma_c' < \sigma_c$). The role of flaws in modifying local stress conditions and so promoting craze initiation has been emphasized by Argon [22]. This idea has been confirmed and strengthened by the ideas presented here. In the absence of a suitable theory the simple critical tensile stress criterion was therefore adopted.

The use of differing criteria for crazing and general yielding must be justified, especially in view of the fact that a convincing model of craze structure is based mainly on "cold-drawn" fibrils (i.e. yielded polymer) spanning the two craze/matrix interfaces. There is now a considerable body of evidence which shows that crazing depends in a different way to yielding on temperature

[26], molecular weight [15], strain-rate [2, 12, 13, 15] and environment [24, 27]. Some of these differences may perhaps be due to differences in the strain-rate due to the localization of the craze; others, for example, to the fact that craze growth may be controlled by the transport of fluid through the craze or to the need to produce free surface within a craze.

Hydrostatic pressure is also well known to affect the ductility of non-polymers, particularly when sheaths are used to exclude fluid from flaws. Typical data is described by Crossland and Dearden [28] and Chandler [29] and more have been reviewed by Bridgeman [30] and by Pugh [31]. In many instances specimens tested unsheathed show frequent premature failure, whereas specimens sheathed with rubber show increased ductility. All of these data can also be well described by the simple model presented here.

4. Conclusions

A simple model has been proposed to describe the competition between yield and fracture processes in specimens tested under pressure. The model takes explicit account of the role of stress concentration sites in generating high local tensile stresses and distinguishes clearly between the different stress distributions obtained, depending on whether or not fluid penetration can occur. It described in general terms the pressure dependence of the fracture stresses observed in both sheathed and unsheathed specimens, and provides an explanation in simple physical terms of the observation that several polymers appear to craze or fracture in totally compressive stress fields.

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