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Hypothetical Mechanism of Crazing in Glassy Plastics

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Crazing in glassy plastics is attributed to a stress-activated devitrification of a small amount of material at the tip of a chance nick or flaw, to a softer rubbery state. Subsequent cavitation of the softened material is then assumed to take place under the action of the same dilatant stress responsible for its formation. A transition to ductile yielding is proposed to occur when the material in the tip region undergoes large deformations before softening.

The proposed mechanism of crazing is shown to provide quantitative predictions for the magnitude of tensile stress at which crazing occurs, the increase in crazing stress with hydrostatic pressure, the transition at high pressures to a yielding process without crazing, the reduction in crazing stress in the presence of certain liquids and vapours and, to some extent, for the effects of temperature and pre-orientation. These theoretical predictions are found to be in reasonably satisfactory agreement with experiment. In view of the limited number of adjustable parameters in the theory (the principal one being the stress-magnification factor associated with a typical nick or flaw), this general agreement over a wide range of experimental conditions and variables suggests that the proposed mechanism of stress-crazing is basically correct.

1. Introduction

Under stress, and especially in the presence of suitable liquids, many glassy polymers develop crazes perpendicular to the applied tension [1-5]. These crazes consist of thin bands of porous oriented matter, capable of bearing stress. They may be distinguished from true cracks by this feature. If the stress is maintained, cracks form preferentially in the weaker crazed material, and thus crazes are generally a cause of premature fracture. Such fracture is termed "brittle" because the overall deformation is small, even though the material within the craze has undergone a large extension of 100% or more.

A hypothetical mechanism of craze formation is given below in terms of a stress-activated transition at the tip of a flaw from a glassy to a softer rubbery state, followed by cavitation of the transformed material under the hydrostatic tension component of tensile stress in the tip region. This hypothetical mechanism is shown to be capable of accounting qualitatively, and to some extent quantitatively, for a number of different aspects of craze formation:

(i) Craze formation is prevented by the application of large hydrostatic pressures [6, 7]. For example, polystyrene at room temperature under a hydrostatic pressure greater than about 2 kbar is ductile rather than brittle, yielding and drawing in tension without the formation of crazes [6].

(ii) The crazing stress depends markedly on temperature, decreasing as the test temperature is increased towards the glass transition temperature [8, 9].

(iii) The tensile stress at which crazes form is much lower in the presence of certain active liquids and vapours [10-13]. These craze-promoting fluids are characteristically rather poor swelling agents for the polymer, being neither fully compatible nor completely incompatible.

(iv) Crazes do not form in materials with pronounced molecular orientation in the direction of the applied tension, but form readily when

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the orientation direction is perpendicular to the applied tension [8, 14].

The proposed mechanism of crazing is closely similar to that put forward by Knight [15] in terms of a stress-induced "fibrillation" at the tip of a flaw. Indeed, a quantitative criterion for "fibrillation" emerges from the present treatment. The proposed mechanism is also closely related to that proposed by several authors [16-19] for yielding in glassy plastics, in terms of a stress-induced transition to the rubbery state. However, the importance of stress concentrations in this process does not appear to have been pointed out before, nor has its possible role in crazing been discussed previously to the author's knowledge.

2. Theoretical Considerations

2.1. Stresses at the Tip of an Edge Flaw

A small region at the tip of a sharp flaw is subjected to a tensile stress σ substantially higher than the overall applied tensile stress $\bar{\sigma}$. The stress concentration factor k is given by the Inglis relation for linearly-elastic solids [20],

$$\sigma/\bar{\sigma} = k = 1 + 2(l/r)^{\frac{1}{2}} \qquad (1)$$

where l is the length of an edge flaw and r is the tip radius. The most severe edge flaws which might occur by chance in smooth machined surfaces would be about 10^{-3} cm long and about 10 Å in tip radius, corresponding to a value for k of about 200. On the other hand, for a smooth circular hole in a thin sheet k has the value 3. Thus, values for k in the general range 10 to 50 seem physically reasonable for edge flaws in normal tensile test-pieces.

Any applied hydrostatic pressure P also acts at the flaw tip, of course, so that the triaxial tension D at that point is given by the difference between the dilatant action of the tensile stress σ, i.e. $\sigma/3$ [21], and P,

$$D = \frac{\sigma}{3} - P, \qquad (2)$$

neglecting tip stresses, if any, arising from lateral constraints.

2.2. Plastic Yielding at the Flaw Tip

Simple plastic yielding would be expected to occur at the tip of a flaw when the local tensile stress reaches a critical value σ_c. By analogy with the theoretical treatment of yielding in crystalline solids the critical stress σ_c should be somewhat less than Young's modulus E, lying in the range $0.1E$-E. We take here as a reasonable value for σ_c, $E/3$, i.e. about 15 kbar for a typical glassy plastic, corresponding to a maximum elastic strain before yielding of 1/3. The corresponding critical value $\bar{\sigma}_c$ for the applied tensile stress is then given by

$$\bar{\sigma}_c = E/3k. \qquad (3)$$

Assuming reasonable values for k, $\bar{\sigma}_c$ is thus expected to lie in the range 0.3 to 1.5 kbar. When craze formation is prevented by pre-orientation of the polymer [8, 14] or by applying hydrostatic pressure [6, 7], glassy polymers are, indeed, found to undergo plastic yielding at tensile stresses of this order of magnitude. Paterson [22] has drawn attention to the proportionality between $\bar{\sigma}_c$ and E (corresponding to a value for k of about 25 in equation 3) in measurements where both quantities were increased by hydrostatic pressure. Similarly, a decrease in yield stress with increasing temperature [8] would be expected in view of the well-known decrease in Young's modulus with temperature. Thus, qualitatively, and to some degree quantitatively, the onset of plastic yielding can be accounted for in terms of large elastic deformations at the tip of a flaw.

After initiation the yield process will probably develop as a shear slip band to minimise the overall dilation of volume, at least under applied stresses which have no net dilatant effect, for example under compressive or shear stresses. Indeed, the initial yield process could well consist of a shear yield under a critical local shear stress given by the modulus of rigidity. The numerical consequences of such a yield mode would be virtually the same, a critical applied tensile stress $\bar{\sigma}_c$ of 0.3 to 1.5 kbar, because the shear stresses associated with a tensile stress σ have the value $\sigma/2$ and the modulus of rigidity is given approximately by $E/3$. For present purposes, therefore, we do not differentiate between these two similar yield processes.*

2.3. Glass-to-Rubber Transition at the Flaw Tip

We now consider a different mode of deforma-

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*It should be pointed out that the application of an overall shear stress does not necessarily lead to a simple shear stress regime at the tip of a chance flaw. A dilational component of stress will generally be set up in addition. Shear stress criteria for simple shear yielding are therefore not readily deduced when yielding occurs at points of local stress concentration, as proposed here.

tion at the flaw tip.It is proposed that the material at the tip of the flaw is transformed abruptly from a glassy to a softer rubbery state when the dilatant stress D reaches a critical value. The transformation may be regarded as the normal glass-to-rubber transition, taking place at a stress-dependent transition temperature T (D) which becomes equal to the test temperature T when the dilatant stress D reaches a critical value D_c. This stress-induced lowering of the glass transition temperature from T_g to T is attributed to volume dilation of the polymer. Indeed, if it is assumed that molecular motion becomes possible when a critical amount of "free volume" has been attained [16-19] and if the free volume is increased only by volume expansion in excess of that characteristic of the glassy state, then the critical dilatant stress D_c will be given by [23]:

$$D_c = (T_g - T)(\alpha_r - \alpha_g)/(C_r - C_g)\,, \quad (4)$$

where α_r, α_g are the coefficients of thermal expansion in the rubbery and glassy states and C_r, C_g are the corresponding compressibilities.

Measurements of the effect of hydrostatic pressure on the glass transition temperature yield a linear dependence [22, 24] corresponding to

$$D_c = \beta(T_g - T)\,,$$

where the coefficient β is about 50 bar/°C, in reasonable agreement with equation 4. Thus, a local softening to a rubbery state is proposed to occur at a critical value $\bar{\sigma}_c$ of the applied tensile stress, given by

$$\bar{\sigma}_c = 3[\beta(T_g - T) + P]/k\,, \quad (5)$$

from equations 1, 2 and 4.

The softened rubbery material, once formed, is bounded above and below by regions of untransformed glassy polymer which transmit the tip stress σ_c to it. These circumstances enhance the dilatant component of the tip stress from $\sigma_c/3$ to approach the value σ_c when the length of the transformed zone is greater than its thickness [25]. Thus, it appears that the tensile stress required for development of a thin band of softened material is reduced to,

$$\bar{\sigma}_c = [\beta(T_g - T) + P]/k\,, \quad (6)$$

in place of equation 5. Moreover, as the transformed material is much softer than before, the tensile stress at the tip of such a thin band will be maintained at a level sufficient to continue the transformation. We conclude that a softened zone with a thickness of the same order as the diameter of the initial flaw tip will tend to grow across the specimen under an applied tensile stress given by equation 6.

However, when the local stress σ_c at the flaw tip is sufficiently large to cause significant deformation of the glassy polymer, i.e. when σ_c is of the order of $E/3$ say, then the transformed material can no longer be considered to lie between two relatively rigid regions and the dilatant effect of the tip stress is no longer enhanced by their restraining effect. Under these circumstances, it seems likely that a thin band of softened material will not form, but rather a general plastic yielding will take place of the kind treated in the previous section. Thus, a transition from thin-band softening at a tensile stress given by equation 5 to plastic yielding at a stress given by equation 3 is postulated to occur when the tip stress σ_c becomes comparable with one-third of Young's modulus E.

The tip stress for softening is increased by the action of a hydrostatic pressure, equation 5, so that a transition from thin-band softening to general yielding is predicted to occur at a critical pressure P_c given by

$$P_t = \frac{1}{9} E - \beta(T_g - T)$$

from equations 3 and 5. In agreement with this, craze formation is found to be prevented by the application of sufficiently high pressures [6, 7], and the polymer then undergoes yielding. (It is shown in the following section that crazing is the inevitable consequence of thin-band softening.) Indeed, the observed relation for brittle fracture stress of polystyrene [6], assumed here to be related to the crazing stress, was of the general form of equation 5,

$$\bar{\sigma}_c(\text{kbar}) = 0.4 + 0.15\,P\,,$$

a transition to yielding without crazing taking place when the applied pressure P reached a value of 2.5 kbar.

It is interesting to compare these experimental results with those given by the preceding theoretical treatment. We assume as reasonable values: $k = 20$, $\beta(T - T_g) = 3$kbar, and $E =$ 50kbar. Equation 5 then becomes

$$\bar{\sigma}_c\,(\text{kbar}) = 0.45 + 0.15P\,,$$

and the transition pressure P_t is predicted to be 2.5 kbar. Thus, agreement with experiment is achieved by means of the proposed crazing mechanism, using quite reasonable values for the principal parameters: k, E and β. Indeed, only the magnitude of the stress-concentration factor k is uncertain to any significant degree, the other terms being known to within rather narrow limits. This agreement is therefore regarded as quite satisfactory.

Similar agreement is obtained for the crazing stress of polycarbonate as a function of hydrostatic pressure. The experimental results take the form

$$\bar{\sigma}_c(\text{kbar}) = 0.9 + 0.1\,P\,,$$

a transition to ductile yielding being observed at a pressure of about 2 to 3 kbar [7]. Assuming as before that $k = 20$ and $E = 50$ kbar and putting $\beta(T - T_g) = 4$ kbar (increased in accordance with the higher glass transition temperature of polycarbonate), equation 5 becomes

$$\bar{\sigma}_c(\text{kbar}) = 0.6 + 0.15P\,,$$

and the transition pressure P_t is predicted to be 1.5 kbar. Both of these predictions are again in satisfactory accord with experiment.

2.4. Cavitation of the Transformed Phase

Under sufficiently large hydrostatic tensions, soft highly-elastic materials undergo cavitation. This process may be regarded as the unstable expansion of pre-existing microvoids by rupture of the surrounding material at a critical level of dilatant stress [25]. If the initial voids are relatively large in diameter, 10^{-5} cm or more, the critical stress is small, of the order of Young's modulus E for rubbers, i.e. about 20 bar. If they are much smaller, then the critical dilatant stress is correspondingly larger, approaching 1 kbar for voids of molecular dimensions, about 10 Å in radius [26]. It is found experimentally that profuse cavitation occurs in soft rubbery solids under stresses of the order of 1 kbar [27] and lesser number of larger holes are produced at lower stresses, down to a threshold stress of the order of E [28].

It is now proposed that cavitation occurs when a softened phase forms at the flaw tip, under the action of the same dilatant stress that brought about the softening. When the temperature difference $T_g - T$ exceeds about 20° C (assuming $\beta = 50$ bar/°C), the critical dilatant stress D_c will be greater than 1 kbar, equation 4, and hence quite sufficient to cause profuse cavitation in a rubbery material. We therefore propose that craze formation in glassy plastics occurs first by local transformation to a soft rubbery phase and then by its inevitable cavitation under the diltant stress responsible for its formation. Only when the dilatant stress is unusually small will the softened material be able to support it without cavitation.

2.5. Effect of Stress-crazing Liquids and Vapours

Swelling by compatible liquids causes a pronounced decrease in the glass transition temperature T_g and consequently lowers the stress level necessary to cause devitrification at the flaw tip, equation 5. Although the degree of swelling is increased by a dilatant stress [29], all surface regions of the sample are likely to be swollen highly by compatible liquids. Relatively incompatible liquids and vapours, on the other hand, undergo a remarkable increase in swelling power under the action of a dilatant stress, as shown below. In this case, therefore, material at the tip of a flaw is likely to undergo selective swelling, and hence softening, because of the high local dilatant stress. These considerations are now employed to account for the craze-promoting action of certain liquids.

We assume for simplicity that the swelling liquid is an "ideal" plasticiser with zero viscosity, so that the glass transition temperature T_g' of the swollen material is given by

$$T_g' = \nu_2\,T_g$$

where ν_2 is the volume fraction of polymer in the swollen gel [30]. From equation 5, the applied stress necessary to cause softening at the flaw tip then becomes

$$\bar{\sigma}_c' = \bar{\sigma}_c - 3\beta T_g \nu_1/k\,,$$

where $\nu_1(= 1 - \nu_2)$ is the volume fraction of swelling liquid in the swollen gel, and $\bar{\sigma}_c$ is the crazing stress of the dry polymer at the test temperature. Assuming reasonable values for $\beta T_g\,(= 18$ kbar) and k $(= 20)$, this relation takes the form

$$\bar{\sigma}_c' = \bar{\sigma}_c - 2.7\,\nu_1\,(\text{kbar})\,. \qquad (7)$$

The degree of swelling ν_1 depends on the dilatant stress. If the polymer is regarded as a rubbery molecular network swollen to equilibrium, the degree of swelling is given approximately by the Flory-Huggins relation, which takes into account entropy of mixing, energy of mixing, and elastic strain energy changes on swelling. In the presence of a dilatant stress D, this relation takes the form [29]):

$$\ln(1 - \nu_2) + \nu_2 + \mu\nu_2^2 + \frac{\rho V_1}{M_c}\left(\nu_2^{\frac{1}{3}} - \frac{\nu_2}{2}\right) = \frac{DV_1}{RT}, \qquad (8)$$

where μ is the polymer-solvent interaction parameter, denoting the (unfavourable) heat of mixing, ρ is the density of the polymer, M_c is the molecular weight of a network chain molecule, V_1 is the molar volume of the swelling liquid, and R is the gas constant. We take as representative values; $V_1 = 100$ ml/mole, $\rho = 1$ g/ml, $T = 300°$ K and $M_c = 10^4$ g/mole. This last quantity is a not unreasonable value for the effective molecular weight of a network chain in a physically-entangled polymer network [30]; no permanent network is envisaged here. In any case, the term in equation 8 involving M_c is so small in most of the calculations described below that it can generally be omitted altogether without affecting the conclusions.

The predictions of equation 8 are shown graphically in fig. 1. The equilibrium degree of swelling represented by ν_1 is plotted against the dilatant stress D for various values of the interaction parameter μ. Compatible liquids with values for μ of 0.5 or less are predicted to swell highly even under zero stress (and infinitely highly under quite small dilatant stresses). On the other hand, relatively incompatible liquids with values for μ of 2 to 10, say, are predicted to swell by only a few per cent under zero stress, but to an infinite extent under a critical dilatant stress, of the order of 0.1 to 1 kbar.* Thus, swelling by relatively-incompatible liquids is particularly dependent on the dilatant stress level and will be largely restricted to the region at the tip of a flaw, where the dilatant effect of small applied stresses is magnified.

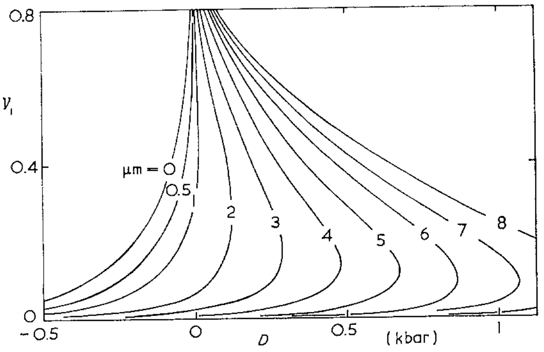

Figure 1 Equilibrium volume fraction ν_1 of swelling liquid versus dilatant stress D, calculated from the modified Flory-Huggins swelling relation, equation 8.

The dilatant stress D at a flaw tip is given by equations 1 and 2 in terms of the applied stress $\bar{\sigma}$,

$$D = \frac{k}{3}\bar{\sigma} - P. \qquad (9)$$

The critical applied stress $\bar{\sigma}_c'$ for crazing in the presence of a liquid or vapour is assumed to be that which gives rise to a critical value of dilatant stress D_c' at the flaw tip,

$$\bar{\sigma}_c' = 3(D_c' + P)/k, \qquad (10)$$

from equation 9, where the critical value D_c' is that at which the corresponding polymer/liquid mixture, whose composition is assumed to be given by equation 8, has a glass transition temperature equal to the test temperature. This condition is represented by equation 7. Thus, equations 7, 8 and 10 constitute a set of simultaneous equations for the crazing stress of a glassy plastic as a function of the swelling power of the crazing fluid (represented by the interaction term μ), the pressure P, and the test temperature and the glass transition temperature of the polymer, in so far as these parameters govern the crazing stress $\bar{\sigma}_c$ of the dry polymer, equations 5 and 7. These theoretical predictions are compared below with observation.

In order to calculate the crazing stress in various fluids, the degree of swelling ν_1 necessary to lower the crazing stress to a particular value $\bar{\sigma}_c'$ was calculated from equation 7, Then the corresponding dilatant stress D_c' was computed from equation 10, for the case when no hydrostatic pressure acts, i.e. $P = 0$. Finally, the value of the interaction parameter μ for which these values of ν_1 and D_c' are mutually consistent was calculated from equation 8. Relations between crazing stress and solvent power obtained in this way are shown in fig. 2.

They are in good qualitative agreement with

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*Dual solutions are obtained for the degree of swelling under a dilatant stress greater than zero, fig. 1. This feature is due to the diminished importance of the heat of mixing term, involving μ, at high swelling ratios. Although it is a major term at low degrees of swelling when v_2 is close to unity, it decreases more rapidly with increasing swelling than the other terms in equation 8 so that all the swelling relations converge at infinite dilution. The larger swelling ratios at a given stress thus correspond to unstable states when the stress is maintained. Only the lower values are used in the present analysis.

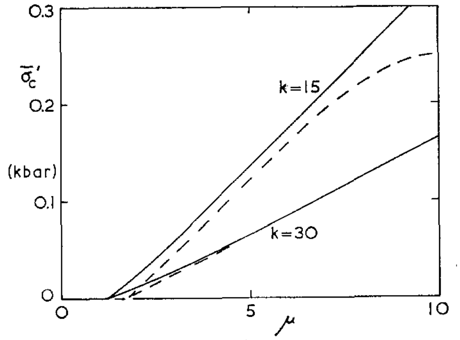

Figure 2 Critical tensile stress $\bar{\sigma}_c'$ for craze formation in a fluid environment versus polymer-fluid interaction parameter μ. The full curves correspond to a dry crazing stress of 1 kbar and the broken curves to one of 0.25 kbar.

observation [13]. The calculated crazing stresses are much smaller than for the dry polymer, being reduced to less than 10 bar for relatively compatible fluids. Even for fluids which do not swell the unstressed polymer significantly, the crazing stress is reduced to a small fraction of its original value. Changes in the value chosen for the dry crazing stress $\bar{\sigma}_c$ do not greatly alter the calculated crazing stress in a fluid environment, indicating a relatively minor dependence on temperature (although possible changes in polymer-fluid compatibility with temperature have not been taken into account). Recent measurements show little dependence of the crazing stress on temperature, above a critical value [31].

Thus, one of the most striking features of stress-induced crazing, namely, the powerful effect of weakly swelling fluids, is accounted for qualitatively, and to some degree quantitatively, by the proposed crazing mechanism.

2.6. Effect of Pre-orientation

A pre-oriented glassy plastic is markedly anisotropic in elastic behaviour [32, 33]. The value of Young's modulus E_1 in the direction of pre-orientation rises to several times the original value E as the degree of orientation is increased, while the value E_2 for tensions perpendicular to the direction of pre-orientation falls somewhat. The dilatant effect of a simple tensile stress σ in the direction of pre-orientation is therefore no longer given by $\sigma/3$, as for an isotropic solid, but is greatly reduced [34]. Similarly, the dilatant effect of a tensile stress in the perpendicular direction is enhanced. The crazing stress in the direction of orientation will be correspondingly increased, and that in the other direction decreased, in comparison with the crazing stress for the unoriented material, if craze formation follows a free-volume criterion as proposed here. Such changes are observed in practice [8, 35], craze formation being prevented altogether in sufficiently pre-oriented samples of polystyrene, whereas in the perpendicular direction the crazing stress is decreased to about one-quarter of its original value [35].

3. Discussion

A number of characteristic features of craze formation in glassy plastics have been shown to be qualitatively, and to some extent quantitatively, in accord with a particularly simple crazing mechanism, i.e. that the applied tensile stress is magnified by a nick or flaw to such a degree that the dilatant stress component at the flaw tip is high enough to transform glassy material there into the rubbery state. When the local strains become relatively large before the conditions for transformation are reached, yielding is assumed to occur instead of softening and cavitation. This simple criterion for crazing allows several numerical predictions to be made, which are found to be in reasonably good agreement with observation in all cases. Three questions are now considered. Is a glass-to-rubber transition the only possible mechanism of cavitation, and hence crazing? What aspects are not explained by the proposed mechanism? What experiments would help to elucidate the mechanism of crazing further?

Clearly, other mechanisms of void growth and cavitation could occur in place of the specific mechanism proposed here. One may consider, for example, the stability of a void in a general ductile medium under various stress fields [36, 37]. The results of such analyses will be of greater generality than the present solution, of course, but it should be noted that the formation of thin crazes is not a very general phenomenon; it is observed only in glassy polymers capable of transformation to the rubbery state. Moreover, the successful treatment of the effects of hydrostatic pressure and active environments, and the approximate numerical agreement with experiment, strongly suggest that the proposed mechanism is correct.

The different crazing behaviour of different polymers and the effect of temperature on crazing stress, particularly in the presence of active fluids, have not been treated in any detail. This is partly because of a lack of experimental data and partly because of some uncertainty regarding the true stress-dependence of the glass-to-rubber transition temperature. The glassy state is generally regarded as a non-equilibrium one. It has been characterised successfully by a "fictive" temperature, differing from the true temperature, in studies of specific volume and relaxation processes [38], and in treating yielding as a consequence of the glass-to-rubber transition [19]. This concept allows a relatively small stress to cause yielding (as is observed) because the fictive temperature is assumed to be not far below the glass transition temperature. However, a similar result is obtained by considering yielding to be inititiated at points of stress concentration where the applied stress is magnified greatly. Both of these factors should probably be taken into account in a satisfactory treatment; we have employed only the latter one in the present analysis, for simplicity.

Use of the Flory-Huggins relation for relatively-incompatible fluids, and particularly for glassy plastics, is open to considerable criticism. Nevertheless, the qualitative form of the present results, i.e. a greatly enhanced swelling in the presence of a dilatant stress field, is likely to be retained whatever the physical mechanisms of liquid absorption.

The parameter k, representing the stress magnification factor associated with a typical nick or flaw, is the only quantity in the present treatment not easily accessible to experimental measurement. Studies of crazing from well-defined cuts [12] are therefore particularly worthwhile. Investigations of the development of a single craze in this way under general stress fields [39], especially in conjunction with a superimposed hydrostatic pressure [6, 7], are likely to distinguish successfully between dilatant stress and other criteria for crazing. It would also be helpful to study the crazing characteristics of samples of a glassy plastic prepared so that they have different "fictive" temperatures, i.e. are of different specific volume at the test temperature, in order to assess the importance of this feature. Finally, polymers of widely different glass transition temperatures, thermal expansion coefficients and compressibilities would permit the predictions of equations 4 and 5 to be examined experimentally.

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