YIELD CRITERIA FOR PLASTIC DEFORMATION OF GLASSY HIGH POLYMERS IN GENERAL STRESS FIELDS

by

S. S. Sternstein and L. Onchin
Materials Division
Rensselaer Polytechnic Institute
Troy, New York

INTRODUCTION

Glassy high polymers are known to exhibit two distinct modes of plastic deformation, namely normal stress yielding (crazing) and shear yielding. There is evidence that both forms of yielding are dependent on both the isotropic and deviatoric components of the stress tensor. In a previous study of yielding, Sternstein, Onchin, and Silverman (1) noted that there existed a minimum, or threshold major principal stress which was required to propagate a craze. It was also noted that curvilinear craze growth could be effected in a non-homogeneous stress field, and that the direction of craze growth was such that the advancing craze tip was always oriented perpendicularly to the major principal stress. However, due to the experimental procedure employed, there was some ambiguity as to whether the stress level required to propagate the craze was best expressed as a major principal stress or, alternatively, as a threshold first stress invariant. The experiments reported here clearly resolve the stress field requirement for craze propagation in PMMA, and are believed to be generally applicable to glassy polymers.

Shear yielding (or yielding resolvable to a shear plane) is also believed to be dependent on the isotropic component of the stress tensor. In the previous work (1), it was noted that the yield stress of PMMA obtained in a simple shear device was higher than one-half of the yield stress observed in uniaxial tension. This result suggested that the dilatational stress associated with simple tension effectively lowered the shear stress which was required for yielding. Andrews and coworkers (2) have reported that the observed yield stress of glassy polymers in simple compression is higher than that which is observed in simple tension. They have suggested that the normal stress which acts across the yield plane may effectively influence the yield stress, a tensile normal stress serving to lower the shear stress required for yielding. Our simple shear studies corroborate this viewpoint, but it remains to establish the general yield criterion. The results reported in the present work define the yield criterion and are consistent with previous observations on simple shear, simple tension, and simple compression.

It is shown below that the dependences of crazing and shear yielding on the first stress invariant are distinctly different, and suggest a mechanism for a stress field induced brittle-ductile transition. The reader is referred elsewhere (1) for a general discussion of the background for the present study.

EXPERIMENTAL PROCEDURE

The apparatus used for obtaining general biaxial tension is shown in Figure 1 (refer to references 3,4,5,6,7). The sample consists of a thin walled cylinder with integral threads for mounting in the jaws. The jaws are mounted in an Instron tensile tester which is used to apply the axial load component, whereas the tangential stress component is obtained by internal pressure applied to the cylinder with a silicone fluid and an externally controlled pressure source and monitor.

The sample dimensions shown in Figure 1 are a compromise of several factors in the design. Since the inner surface of the cylinder is subjected

*Present Address: Union Carbide Plastics Co., Bound Brook, New Jersey.

Polymer Preprint, vol. 10, no. 2, Sep 68
to the hydrostatic fluid while the outer surface is at ambient pressure, there exists a radial stress gradient in the sample. The radial stress can be made small relative to the tangential stress by using a small wall thickness to mean diameter aspect ratio. The variation of tangential stress from inner to outer surface is also made small by the same aspect ratio. However, machining tolerances and the capacity of the pressure system and tensile tester serve to determine the absolute dimensions of the sample. For the dimensions shown in Figure 1, the variation of tangential stress from inner to outer wall is about 5%, the internal pressures required to achieve the necessary range of tangential stresses are of the order of 300 psig or less, and the radial stress component is a decade (or more) lower than the tangential stress component.

The samples were machined from cast solid cylinders of PMMA which were previously annealed at 120°C for 24 hours. The gage sections were polished lightly with a fine buffing compound. For the samples used in the crazing studies, an additional machining step was involved. The tubes were axially tapered slightly on the outer surface (with a minimum cross section at the center) so that a stress gradient could be established. The variation in tangential stress was about 15% from the center to the outer edges. In this way, it was possible to avoid tedious repetitions of the experiment to ascertain the crazing stress. Instead, the sample was simply loaded to approximately the correct stress level, and then examined to determine the point on the taper at which crazes ceased to appear. The shear yielding samples had uniform cross section.

In the shear yielding study, the samples were internally pressurized and immediately subjected to a constant axial strain rate of 0.0125 min⁻¹, until the yield point (zero slope) was reached. For the crazing study, the tapered tubes were pressurized, brought to a given level of axial load, and held in this state of biaxial stress for ten minutes. Since occasional machining marks were present in the tangential direction, the tangential stress was generally maintained higher than the axial stress so that the crazes would grow in the axial direction. Well polished sample surfaces gave consistent results and, therefore, we do not consider surface scratches to be a significant factor in the results obtained. Combinations of biaxial stress ranging from uniaxial tension to equal biaxial tension were used in both the crazing and shear yielding studies.

**CRAZE FORMATION IN BIAXIAL STRESS FIELDS**

The principal stress requirements for craze formation in PMMA at three temperatures are shown in Figure 2. These curves represent normal stress yielding envelopes in that a stress state which is below the appropriate temperature curve will not produce visible crazing, whereas a stress state on or above the envelope produces visible crazing. As will be shown later, these results are distinctly different from the yielding envelopes for shear yielding (or yielding resolvable to a shear plane).

The uniaxial tension results ($\sigma_z = 0$) obtained in this study agree well with previous results obtained using a completely different sample geometry (1). In the previous study, the craze threshold stress was obtained from the no-craze boundary in the vicinity of a stress concentrating hole. Since the minor principal stress was about a decade lower than the major principal stress, those results were approximately uniaxial. The data presented in Figure 2 are for crazes which formed perpendicular to the $\sigma_1$ principal axis. Since the samples used were isotropic, the yielding envelopes would show symmetry about the equal biaxial line. Accordingly, we have shown this symmetry in Figure 2. However, it should be noted that stress fields which lie below the 45 degree line would produce crazes perpendicular to the new major principal stress, which is now $\sigma_1$. Clearly, an instability condition wherein the craze plane rotates by 90° is present.
as the equal biaxial stress line is crossed.

The mechanism of normal stress yielding which we propose is illustrated in Figure 3. The general biaxial stress state is considered in terms of its isotropic component, as designated by the first stress invariant \( I_1 \):

\[
I_1 = \sigma_1 + \sigma_2 + \sigma_3
\]  

(1)

where \( \sigma_3 \) is zero in the present experiment, and a stress bias (or orientation stress) \( \sigma_b \) which in magnitude is given by

\[
\sigma_b = | \sigma_1 - \sigma_2 |
\]

(2)

and in direction by the greater of \( \sigma_1 \) or \( \sigma_2 \).

Considering the chain conformational mobility to be a function of both temperature and first stress invariant, then at constant temperature mobility would be expected to increase with increasing \( I_1 \), which is effectively a measure of the dilatational driving force in a given stress field. At some particular level of mobility, localized orientation by normal stress yielding can occur. However, the molecular orientation will be in the direction of the stress bias, with the resultant craze plane perpendicular to the stress bias. Mobility considerations suggest that as \( I_1 \) increases, the magnitude of the stress bias required for the orientation process should decrease, much the same as the effect of increased temperature.

The mechanism proposed has been suggested qualitatively in a previous paper (1), where it was noted that \( I_1 > 0 \) is a necessary condition for craze formation since the deformation is intrinsically dilatational when two planes of material separate normal to each other. Furthermore, the condition of positive first stress invariant is in keeping with the absence of crazing in shear and compression stress states. Therefore, to be consistent with this requirement, we consider the stress bias to be proportional to the reciprocal of \( I_1 \); since a linear decreasing function with \( I_1 \) would not display the required behavior. Thus, at a given temperature,

\[
\sigma_b = A(\tau) + \frac{B(\tau)}{I_1}
\]

(3)

The data of Figure 2 have been replotted according to equation 3, and are shown in Figure 4. This figure is quite sensitive to the shape of Figure 2. For example, a horizontal line drawn through the points of Figure 2 would appear with marked curvature on Figure 4. We conclude that equation 3 and the proposed model are valid.

The reciprocals of the intercepts on the abscissa of Figure 4 can be considered as defining a critical first stress invariant, \( I_1^\ast \) which is seen to decrease with increasing temperature. For all stress fields with \( I_1 > I_1^\ast \), the stress bias for crazing is zero. This implies the existence of a critical mobility, induced by a dilatational stress, for which a differentially small deviation from equal biaxial stress (see equation 2) is sufficient to result in a preferred orientation direction. This is consistent with both the symmetry and instability conditions of the equal biaxial stress state discussed above in reference to Figure 2.

The results of Figure 4 are expected to vary somewhat with the timescale of observation. However, previous results (1) have shown that the craze threshold stress is independent of timescale for load application times ranging from ten minutes to several hours. Also, Mordvin and Sternstein (8) have observed the existence of craze threshold stresses for samples of PMMA immersed in various liquid environments, but with
significantly lower threshold values than in air.

**SHEAR YIELDING IN BIAXIAL STRESS FIELDS**

The yield points obtained using the sample geometry shown in Figure 1, are given at one temperature in Figure 5 in terms of the principal stresses. For comparison, the Von Mises criterion is shown also. In terms of the octahedral shear stress, equation 4, Von Mises criterion is a statement that yielding occurs when \( \tau_{oCT} \) reaches a particular value for a given material and temperature.

\[
\tau_{oCT} = \frac{1}{3} \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2}
\]  

(4)

It can be shown that a constant \( \tau_{oCT} \) at the yield point is equivalent to a constant distortional strain energy (refer to ref. 9 for a general discussion). Thus, Von Mises criterion is based upon the deviatoric stress tensor only, and therefore is not dependent on the isotropic component of the stress tensor. Accordingly, a plot of \( \tau_{oCT} \) versus mean normal stress \( \sigma_m = \frac{1}{3} \sum \sigma_i \) would give a horizontal line (zero slope).

The data of Figure 5 along with two additional temperatures are shown in Figure 6 as \( \tau_{oCT} \) versus \( \sigma_m \). The slopes of the three lines are approximately the same and equal to 0.15. Thus, it would seem that the isotropic component of the stress tensor influences the observed shear yield stress, a dilatation serving to lower the yield stress.

From equations 1 and 4, it is easily shown that uniaxial tension is represented in Figure 6 by a straight line of slope \( \sqrt{2} \) and uniaxial compression by a straight line in the second quadrant (not shown) of slope \( -\sqrt{2} \). Also, the ordinate of Figure 6 is the pure shear condition, since \( \sigma_m = 0 \) for this stress state.

Extrapolation of the curves in Figure 6 to the condition \( \sigma_m = 0 \) gives the pure shear yield stress versus temperature. These results are in excellent agreement with the simple shear values obtained directly (1). The pure shear extrapolations are about 54% higher than the simple shear measurements, which is to be expected due to the second order mean normal stress in the latter (1). The ratio of (extrapolated) uniaxial compressive to uniaxial tensile yield stress is obtained directly by the intercept ratio on the lines of the slope \( \sqrt{2} \) and \( -\sqrt{2} \), respectively, and this ratio is 1.3. This is also in good agreement with measured values of 1.3 to 1.4 (see ref. 2 and 10). The effect of mean normal stress on shear yielding as shown in Figure 6 is consistent with data obtained in simple compression, simple tension, simple shear and, in the present work, biaxial tube specimens.

The shear yielding of glassy PMMA, and probably Polystyrene, is consistent with the three dimensional analog of the Mohr-Coulomb criterion

\[
\tau_{oCT} = \tau_s - \mu \sigma_m
\]  

(5)

where \( \tau_s \) is the pure shear yield stress and \( \mu \) is the "bulk" friction factor. It appears from Figure 6 that \( \mu \) is relatively insensitive to temperature. Clearly, the strain rate dependence of \( \tau_s \) and \( \mu \) should be established. Limited information on the strain rate dependence of the simple shear yield stresses (1) has indicated a parallel shift of the yield curves on the temperature axis, as opposed to simple tension yield data, where a shift and change in slope are observed. Thus, it would seem that \( \tau_s \) and \( \mu \) are affected differently by strain rate. This is not unexpected since \( \tau_s \) involves pure shear response only whereas \( \mu \) involves the effect of density change on the conformational mobility of the glassy polymer.

1120
GENERAL DISCUSSION

The two forms of yielding in glassy PMMA have been characterized with respect to their general stress field dependences. Normal stress yielding (or crazing) has been shown to obey equation 3, as evidenced by the data of Figure 4. Shear yielding has been shown to obey equation 5, as substantiated by Figure 6 and its consistency with other observations. A comparison of both yielding envelopes is presented in Figure 7, where equations 3 and 5 have been used as bases for linear extrapolation in general biaxial stress space, for the data obtained at 70°C.

Referring to Figure 7, in the tensile (first) quadrant of stress space, the normal stress yielding envelope is everywhere inside the shear envelope. This implies that all combinations of tensile biaxial stress produce crazes prior to shear yielding. However, the second and fourth quadrants show completely different behavior, due to the significant increase in stress bias required to propagate a craze as the pure shear condition is approached. This effect is to be expected since pure shear is a non-dilatational stress state, and crazing is an inherently dilatational mode of yielding. By contrast, shear yielding is possible in a non-dilatational stress field (1). Thus, at a particular combination of stresses, the two envelopes intersect each other. For all stress fields having \( I_1 \), less than the value of \( I_1 \) at which this intersection occurs, the preferred mode of yielding is shear and not normal stress yielding. It can be argued that the intersection points in the second and fourth quadrants represent a stress field induced brittle to ductile transition. This stress field can be shown to be a simple tension plus a hydrostatic pressure. It is emphasized that both yielding modes are coexistent and the transition is not a material transition, per se, but a transition in the sense of which mode, shear or crazing, is predisposed to occur first in a given stress field.

The analysis of yielding which is presented here has direct application to the mechanism of toughening in rubber modified, brittle polymer systems (11).

ACKNOWLEDGEMENTS

This study was supported by a grant from the National Institute of Dental Research and was performed in the Materials Research Center at Rensselaer Polytechnic Institute, which is funded by the National Aeronautics and Space Administration.

LITERATURE CITED


11. Paterno, J. and Sternstein, S., Rensselaer Polytechnic Institute, work in progress.

FIGURES

![Diagram of sample and jaw fixture for biaxial tension.]

FIGURE 1: SAMPLE AND JAW FIXTURE FOR BIAXIAL TENSION.
FIGURE 2: PRINCIPAL STRESS REQUIREMENTS FOR CRAZE FORMATION IN PMMA.

FIGURE 3: NORMAL STRESS YIELDING MECHANISM.

FIGURE 4: STRESS BIAS REQUIRED FOR NORMAL YIELDING VERSUS RECIPROCAL FIRST STRESS INVARIANT.
FIGURE 5: PRINCIPAL STRESS REQUIREMENTS FOR SHEAR YIELDING OF PMMA AS COMPARED WITH VON MISES CRITERION.

FIGURE 6: SHEAR YIELDING OF PMMA EXPRESSED AS OCTAHEDRAL SHEAR STRESS VERSUS MEAN NORMAL STRESS.

FIGURE 7: COMPARISON OF NORMAL STRESS AND SHEAR STRESS YIELDING ENVELOPES, SHOWING A TRANSITION IN SECOND AND FOURTH QUADRANTS.