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On criteria for craze initiation in glassy polymers

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The previous published data on biaxial critical stresses for craze initiation on the surface of cylindrical specimen of glassy polymers have been reexamined. A new interpretation is presented for the trend of crazing stress near pure shear state in the second quadrant of principal stress space which was observed in air at elevated temperatures. That is, an increase in the tensile stress for crazing with an increase in the magnitude of the compressive stress is interpreted not to be followed by a decrease in the dilatational stress but by development of shear yielding. On the basis of this interpretation, a new empirical criterion for craze initiation is proposed by considering the stress concentration due to surface scratch. The theoretical crazing locus accorded with the previous experimental results, except for the data near the shear yield locus in the second quadrant, which were considered to be affected by shear yielding. It was also indicated in the calculation that the shape and direction of surface scratch exert a considerable influence on the trend of biaxial crazing stress.

1. Introduction

Crazing and shear yielding are known as two distinct modes of plastic deformation in glassy polymers. Macroscopic criteria for shear yielding are given by either the modified Tresca or the modified von Mises law [1], whereas that for crazing remains to be established. This is probably due to fewer experiments being carried out under multiaxial states of stress and also to considerable differences in the manner of crazing observed under different conditions.

Previous biaxial experiments on poly(methyl methacrylate) (PMMA) [2] and polycarbonate (PC) [3] revealed that air crazing does not occur under pure shear as already discovered by Sternstein *et al.* [4], while environmental crazing can take place not only under pure shear but also in a wide stress field where the hydrostatic component is compressive. In the light of the criterion of Sternstein *et al.* [5] which assumes the dilatational component of the applied stress to be essential for craze initiation, a possible explanation for this conflict may be that the environmental agent yields additional negative pressure required for craze initiation. However, Matsushige *et al.* [6, 7] observed that in simple tension under hydrostatic pressure crazing can occur on the specimen surfaces of PMMA and polystyrene (PS) covered with a silicon rubber which prevents the pressure medium (silicon oils) from wetting. This observation seems to contradict the above explanation and furthermore casts doubt on whether the dilatational component of applied stress is essential to craze initiation.

In this paper, the experimental results which have so far been obtained under biaxial states of stress and current criteria based on them are re-examined with particular regard to the significance of the dilatational stress in craze initiation. In addition, an empirical equation considering the stress concentration caused by the surface scratch of specimen is proposed and also compared with previous published data of biaxial experiments.

2. Re-examination of the results of biaxial experiments

The full scale biaxial experiments on craze initiation were first performed by Sternstein and coworkers [4, 5]. They investigated the crazing behaviour on the surface of thin-walled and solid cylinders of PMMA under combined loadings of tension–internal pressure and tension–torsion at elevated temperatures (50, 60, and 70° C) in air. On the basis of the experimental results, they suggested that the dilatational component of the applied stress is essential to craze initiation. Argon and Hannoosh [8] measured the critical stress for craze initiation on the surface of an hourglass type specimen of PS. Their experiments were made under constant tension–torsion loading at room temperature in air. They pointed out in their microscopic model for craze initiation that not only a dilatational component of the applied stress but also a shear (deviatoric) stress are required for craze initiation. The authors [2, 3] also investigated craze initiation on the surface of thin-walled cylindrical

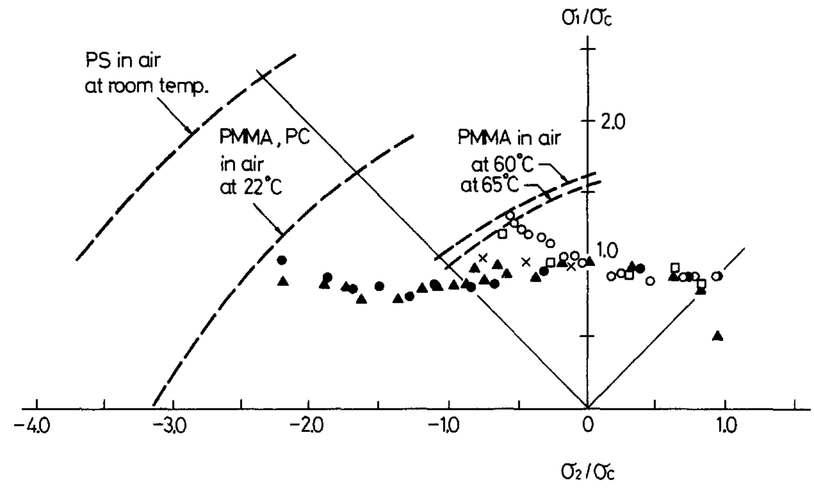

Figure 1 Data of critical biaxial stress for crazing normalized by the critical crazing stress under simple tension σ_c. Broken curves show the theoretical loci for shear yielding calculated by the modified von Mises equation. (○) PMMA in air at 60° C [4], (□) PMMA in air at 65° C [2], (▲) PMMA in kerosene at 22° C [2], (●) PC in kerosene at 22° C [3], (×) PS in air at room temperature [8].

specimens of PMMA and PC under combined loadings of tension–internal pressure, tension–compression and also torsion–compression. The experiments were carried out both at 65° C in air and at room temperature in an environment of kerosene. They found that environmental crazing can occur in a wide stress field where the hydrostatic component is compressive and air crazes are never observed.

The data of the critical biaxial stress for craze initiation obtained from the above experiments are normalized by the critical crazing stress under simple tension σ_c for each experiment. These data are collected in Fig. 1, where the data of Sternstein and coworkers are restricted to those obtained at 60° C because the data at other temperatures also show the same trend. In addition the critical stress loci for shear yielding are also presented. They are drawn theoretically from the modified von Mises law given by Equation 1 so as to connect several data points

$$S_0\sigma_c = \{\tfrac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]\}^{1/2} + \frac{\mu}{3}(\sigma_1 + \sigma_2 + \sigma_3) \quad (1)$$

where S_0 and μ are constants. The values of σ_c, S_0, and μ for each experiment are shown in Table I. In the first quadrant of the two-dimensional principal stress space, a good correspondence is found between the crazing stress data on PMMA obtained in air at elevated temperatures (Sternstein *et al.* at 60° C and the authors at 65° C) and those in kerosene at room temperature. However, in the second quadrant there exist several features as follows.

(1) The tensile stress σ_1 for crazing on PMMA measured at elevated temperatures in air rises with an increase in the magnitude of the compressive stress σ_2. The level required for crazing is not so low as the stress level required for shear yielding, and is attained in the stress field of dilatation ($\sigma_1 + \sigma_2 > 0$).

(2) The tensile stress σ_1 for crazing on PS measured at room temperature in air (the result of Argon and Hannoosh) is significantly lower than the shear yielding locus, and almost constant irrespective of the compressive stress σ_2. In this case a craze–shear yielding transition is not found.

(3) The experiments of the authors on PMMA and PC made under the action of kerosene at room temperature indicate that the tensile stress σ_1 required for crazing is below the shear yielding locus obtained in air, and initially shows a slight decrease and then increases so as to reach the shear yielding locus.

From only the first feature mentioned above may it be interpreted as usual that dilatational stress is required for craze initiation. If this interpretation is reasonable, an additional dilatational stress induced by the action of the environment must be provided in order to explain the crazing behaviour in the stress field where the hydrostatic component is compressive (under a combined loading of compression and torsion). However, Matsushige *et al.* [6, 7] revealed that in simple tension under hydrostatic pressure crazing could occur on the surface of PS and PMMA solid cylinders although they were covered with silicon rubber which prevents contact with a pressure medium (silicon oils). Since in their experiments the specimen is subjected to compressive hydrostatic stress, the specimen surface is not wetted with silicon oils. This result seems to contradict the above interpretation of crazing behaviour.

Thus it seems necessary to provide an alternative explanation consistent with the features of Fig. 1 and the other experimental results. Now we pay attention to the levels of critical stress required for crazing and

TABLE I The values of σ_c, S_0, and μ in Equation (1) for the previous experimental results

Polymer	Temperature (° C)	σ_c (MPa)	S_0	μ	Reference
PMMA	60	24	1.08	0.17	[4]
PMMA	65	17	1.00	0.15	[2]
PMMA	22	25[a]	1.66	0.15	[2]
PC	22	22[a]	1.65	0.15	[3]
PS	Room temperature	22	2.27	0.25[b]	[8]

[a]These values are obtained in kerosene. The others are obtained in air.
[b]This value is quoted from [1].

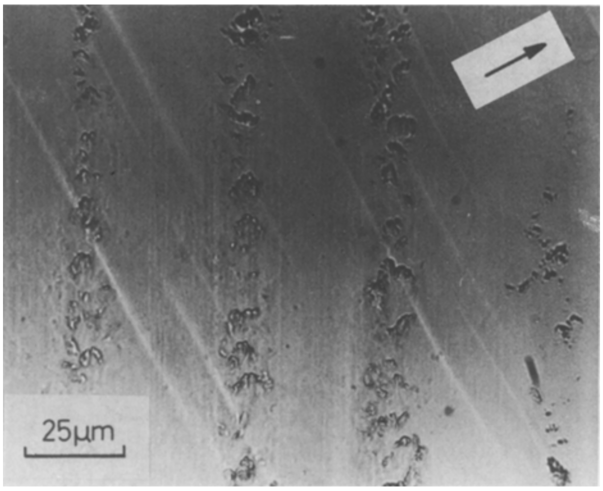

Figure 2 Optical micrograph of crazes initiating at the surface scratch of PMMA specimen exposed to kerosene at 22° C. Arrow denotes the direction of maximum principal stress.

shear yielding. It is indicated that in the second quadrant the tensile stress σ_1 required for crazing increases with an increasing magnitude of the other (compressive) stress σ_2 in the stress field near the shear yielding locus. It is well known that when shear yielding takes place it is followed by the formation of a shear band, which acts as a "craze-stopper" [9]. Consequently, it is suggested that an increase in σ_1 for craze initiation with increasing magnitude of σ_2 in the neighbourhood of the pure shear state ($\sigma_1 + \sigma_2 = 0$) is not an essential of the dilatational stress required for craze initiation but rather means that initiation and growth of crazes are prevented by the progress in shear yielding. From this view point, a basic feature of the critical stress for craze initiation in the second quadrant of principal stress space will be given by the experiments of Argon and Hannoosh and those of the authors performed in the environment of kerosene.

3. On the effect of surface scratch on craze initiation

As has been pointed out by Argon and Hannoosh [8], Koguchi and Hori [10], and Kramer [11], the effect of surface scratch on craze initiation should be considered in the examination of crazing criteria. Fig. 2 is an optical micrograph of crazes initiating at the surface scratch. This figure was obtained from authors' experiment on PMMA under combined torsion and tension ($\sigma_1 = 22.7$ MPa, $\sigma_2 = -8.5$ MPa) in the environment of kerosene at room temperature. An arrow in the figure denotes the σ_1 direction. The figure shows that the surface scratch participating in craze initiation consists of grooves and pits. This situation is schematically illustrated in Fig. 3. These types of scratch cause a stress concentration at their bases. The stress concentration by the groove is directional, while that by the pit is isotropic. Therefore, the applied stress required for craze initiation is apparently affected both by the fraction of each type of scratch and by the orientation of the groove with respect to the stress axis. Such effects of surface scratches on crazing will be discussed in detail elsewhere.

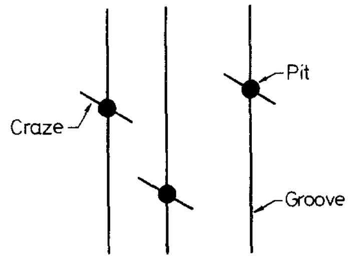

Figure 3 Schematic illustration of the situation of craze initiation at the surface scratch.

4. New criteria for craze initiation

Wellinghoff and Baer [12] revealed in the observation of the surface of PS film by transmission electron microscopy that a microscopic shear-yielded region acts as a precursor of craze nucleation. Recently, Koguchi and Hori [13] investigated stress- and time-dependences of craze density (number of crazes per unit surface area) on PMMA specimen surface, at elevated temperatures (50–70° C) in air and showed that craze density increases with increasing loading time and then attains a saturated value, which is a function both of applied stress and of the shear yield stress. If the microscopic shear yielding dominates the process of craze nucleation, criteria for crazing will be given by either the modified Tresca or the modified von Mises law. However, the biaxial experiments shown in Fig. 1 gives results which fit neither of them, rather the maximum principal stress criterion which Matsushige *et al.* have proposed.

Under the situation mentioned above it is proposed that in the process of craze initiation both shear yielding and drawing take place simultaneously in a microscopic region. Under multiaxial states of stress, shear yielding and drawing are considered to be dominated by either the maximum principal shear stress τ_1 or the second invariance of the deviatoric stress J_2 and by the maximum principal stress σ_1, respectively. Thus two types of expression in which either τ_1 or J_2 and σ_1 simultaneously participates are proposed as criteria for crazing. The first type is given by the sum of them as

$$\sigma_1 + C_1\tau_1 = C_2 \tag{2}$$

or

$$\sigma_1 + C_1 J_2^{1/2} = C_2. \tag{3}$$

The second type of criterion is the form of the product of them written as

$$\sigma_1\tau_1 = C \tag{4}$$

or

$$\sigma_1 J_2^{1/2} = C, \tag{5}$$

where

$$J_2^{1/2} = \{\tfrac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]\}^{1/2}, \tag{6}$$

and C_1, C_2, and C are constants. The hydrostatic stress-dependent term of shear yielding is not considered here for convenience. In these expressions the maximum principal stress σ_1 is required to be positive

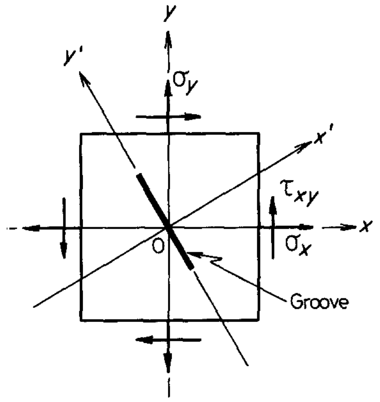

Figure 4 Schematic illustration of a small region including a groove.

(tensile) to correspond with the experimental results shown in Fig. 1. However, this restriction is mathematically inherent for the latter Equations 4 and 5. Therefore they seem superior to the former Equations 2 and 3. In addition, since choosing whether τ_1 and $J_2^{1/2}$ concerned with shear yielding does not have substantial importance, it is adequate to adopt $J_2^{1/2}$ of which the form is not changed in the first and the second quadrants in two-dimensional principal stress space. Consequently, Equation 5 is the most reasonable of the four expressions presented above. Equation 5 resembles in form either the criterion of Argon and Hannoosh [9] for an ideally smooth surface free of flaw written as

$$(I_1 + X)J_2^{1/2} = Y \tag{7}$$

or that so far presented by the authors [2] of the form

$$I_1(J_2^{1/2} - S_i + I_1) = C_3, \tag{8}$$

where I_1 is the first invariant of the stress tensor, and X, Y, S_i, μ and C_3 are constants. Equations 7 and 8 are introduced from a microscopic physical and a semi-empirical models, respectively. These criteria require, in common, I_1 to be positive (dilatational). However, as discussed in the previous section, this requirement does not seem necessary for craze initiation process. A physical model corresponding to Equation 5 can not be established until the mechanical behaviour of molecular chains in glassy state can be satisfactorily explained.

In order to account for actual crazing behaviour influenced by scratches on the specimen surface, it is necessary to induce the effect of stress concentration into Equation 5. Thus Equation 5 is rewritten as

$$\hat{\sigma}_1 \hat{J}_2 = C, \tag{9}$$

TABLE II Theoretical values of τ_c/σ_c and σ_{bc}/σ_c calculated from Equations 15 and 16 for two extreme types of surface scratch

Type of scratch	τ_c/σ_c	σ_{bc}/σ_c
Pit	0.76	1.00
Groove (ϕ = 0)	1.14	1.06

where a symbol "^" on each term denotes a concentrating stress. Suppose a small region including a groove shown in Fig. 4, where the x-axis is settled in parallel to the loading axis, then an angle between x axis and normal axis (x'-axis) of the groove is called an "orientation angle ϕ". Two-dimensional components of applied stress (σ_x, σ_y, τ_{xy}) are given in the x'y' plane by

$$\left.\begin{aligned} \sigma_{x'} &= \sigma_x \cos^2\phi + \sigma_y \sin^2\phi + \tau_{xy} \sin 2\phi \\ \sigma_{y'} &= \sigma_x \sin^2\phi + \sigma_y \cos^2\phi - \tau_{xy} \sin 2\phi \\ \tau_{x'y'} &= \tfrac{1}{2}(\sigma_y - \sigma_x) \sin 2\phi + \tau_{xy} \cos 2\phi \end{aligned}\right\} \tag{10}$$

At the bottom of the groove, these components are amplified to

$$\hat{\sigma}_{x'} = \alpha_1 \sigma_{x'} \quad \hat{\sigma}_{y'} = \alpha_2 \sigma_{y'} \quad \hat{\tau}_{x'y'} = \alpha_3 \tau_{x'y'} \tag{11}$$

where α_1, α_2, and α_3 are stress concentration factors. The maximum and the minimum principal stresses at the base of the groove are given by

$$\hat{\sigma}_1 = \tfrac{1}{2}\{\hat{\sigma}_{x'} + \hat{\sigma}_{y'} + [(\hat{\sigma}_{x'} - \hat{\sigma}_{y'})^2 + 4\hat{\tau}_{x'y'}^2]^{1/2} \tag{12a}$$

and

$$\hat{\sigma}_2 = \tfrac{1}{2}\{\hat{\sigma}_{x'} + \hat{\sigma}_{y'} - [(\hat{\sigma}_{x'} - \hat{\sigma}_{y'})^2 + 4\hat{\tau}_{x'y'}^2]^{1/2} \tag{12b}$$

respectively. The second invariance of the deviatoric stress is rewritten in this case as

$$\hat{J}_2 = \tfrac{1}{12}[3(\hat{\sigma}_1 - \hat{\sigma}_2)^2 + (\hat{\sigma}_1 + \hat{\sigma}_2)^2]. \tag{13}$$

For example, consider simple loading types; torsion, tension, and equal biaxial tension. The critical states of stress for craze initiation for each case are given by

$$\left.\begin{array}{lll} \sigma_x = \sigma_y = 0 & \tau_{xy} = \tau_c & \text{for torsion} \\ \sigma_x = \sigma_c & \sigma_y = \tau_{xy} = 0 & \text{for tension} \\ \sigma_x = \sigma_y = \sigma_{bc} & \tau_{xy} = 0 & \text{for equal biaxial tension} \end{array}\right\} \tag{14}$$

respectively, where τ_c, σ_c, and σ_{bc} indicate the critical crazing stress for each loading type. Substituting them into Equations 9–13 can provide ratios τ_c/σ_c and σ_{bc}/σ_c as

$$\left(\frac{\tau_c}{\sigma_c}\right)^2 = \frac{\alpha_1 \cos^2\phi + \alpha_2 \sin^2\phi + [(\alpha_1 \cos^2\phi - \alpha_2 \sin^2\phi)^2 + \sigma_3^2 \sin^2 2\phi]^{1/2}}{(\alpha_1 - \alpha_2) \sin 2\phi + [(\alpha_1 + \alpha_2)^2 \sin^2 2\phi + 12\alpha_3^2 \cos 2\phi]^{1/2}}$$
$$\times \frac{\{3(\alpha_1 \cos^2\phi - \alpha_2 \sin^2\phi)^2 + 3\alpha_3^2 \sin^2 2\phi + (\alpha_1 \cos^2\phi + \alpha_2 \sin^2\phi)^2\}^{1/2}}{\{[3(\alpha_1 + \alpha_2)^2 + (\alpha_1 - \alpha_2)^2] \sin^2 2\phi + 12\alpha_3^2 \cos^2 2\phi\}^{1/2}} \tag{15}$$

$$\left(\frac{\sigma_{bc}}{\sigma_c}\right)^2 = \frac{\alpha_1 \cos^2\phi + \alpha_2 \sin^2\phi + [(\alpha_1 \cos^2\phi - \alpha_2 \sin^2\phi)^2 + \alpha_3^2 \sin^2 2\phi]^{1/2}}{2\alpha_1[3(\alpha_1 - \alpha_2)^2 + (\alpha_1 + \alpha_2)^2]^{1/2}}$$
$$\times \{3(\alpha_1 \cos^2\phi - \alpha_2 \sin^2\phi)^2 + 3\alpha_3^2 \sin^2 2\phi + (\alpha_1 \cos^2\phi + \alpha_2 \sin^2\phi)^2\}^{1/2} \tag{16}$$

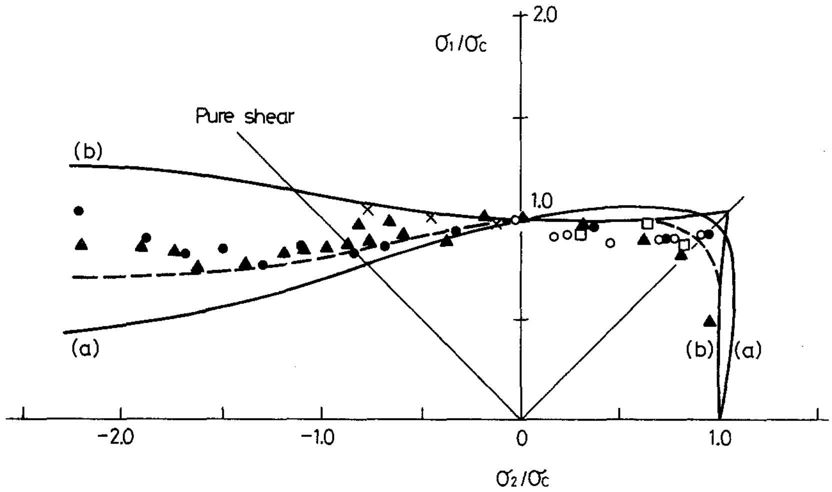

Figure 5 Data of critical biaxial stress for crazing normalized by σ_c, which are regarded to be relieved from the influence of shear yielding. (○) PMMA in air at 60° C [4], (□) PMMA in air at 65° C [2], (▲) PMMA in kerosene at 22° C [2], (●) PC in kerosene at 22° C [3], (×) PS in air at room temperature [8]. Solid and broken curves are theoretical loci for crazing.

respectively. The value of constant C in Equation 9 is assumed to be held constant irrespective of difference in loading types. If all the scratches on the specimen surface are pit-like, the stress concentration factors α_1, α_2, and α_3 approximately take the same value α_0. On the other hand, in the case that the surface scratches are always groove-like and lying in the direction of the circumference of the cylindrical specimen, the orientation angle ϕ equals zero and the three stress concentration factors take different values. If the groove is approximated to a circumferential notch with a sectional shape of semi-circle, the values of α_1, α_2, and α_3 are given by 3, 1, and 2, respectively, which correspond to the case when a notch radius is satisfactorily small compared with the diameter of the cylinder. The values of the ratios τ_c/σ_c and σ_{bc}/σ_c for the two extreme cases mentioned above are summarized in Table II. The table indicates that as the fraction of the groove in the surface scratches increases both τ_c/σ_c and σ_{bc}/σ_c increase, and that τ_c/σ_c becomes greater than unity when all the scratches consist of grooves.

5. Comparison with the data

The biaxial stress data on crazing are again shown in Fig. 5, normalized by the critical crazing stress under simple tension σ_c for each experiment as before. However, the data in the second quadrant of principal stress space are restricted to those which seem to describe the fundamental characteristics of crazing behaviour relieved from the influence of shear yielding. Accordingly the data of Sternstein *et al.* and of the authors obtained for PMMA in air at elevated temperatures are excluded from the figure. The solid curves (a) and (b) and the broken curve denote the theoretical crazing loci obtained in the following way. Under the assumption that all the scratches on the surface of cylindrical specimen are pit-like, Equation 9 with the stress concentration factors α_1, α_2 and α_3 of the same value α_0 gives the solid curve (a). Since the stress concentration factor of the pit is not directional, the crazing locus normalized by σ_c is the same as that for an ideally smooth surface. The curve (a) in general exhibits relatively large upward curvature but gradually shows slight downward curvature with increasing magnitude of the compressive stress σ_2. In contrast the curve (b) calculated from Equation 9 with $\alpha_1 = 3, \alpha_2 = 1$, and $\alpha_3 = 2$ corresponding to the case in which all the scratches are groove-like exhibits downward curvature as a whole and particularly is of the cusp type in the first quadrant as shown in the experimental results of Sternstein *et al.* [4]. In addition, the critical tensile stress σ_1 for crazing increases with an increase in the magnitude of the compressive stress σ_2 in the second quadrant. Since the actual surface scratches are made by mixing the pit and the groove, the experimental data will be positioned in and/or near the curves (a) and (b). The figure shows this prediction to be adequate.

The broken curve in the figure represents the calculated results for the case in which the orientation angle of the groove ϕ is 30°. The values of the stress concentration factors are the same as those for curve (b). The general trend of this curve resembles that of curve (a) rather than (b). The figure shows that a comparative small inclination of the groove exerts a considerable influence on the trend of the crazing stress.

6. Concluding remarks

In this paper the data of the biaxial crazing stress so far obtained by the experiments performed in air or in liquid environment using thin-walled or solid cylindrical specimens are reexamined and a new interpretation for them is presented which is evidently different from the current one. This interpretation is that near the pure shear state in the second quadrant of principal stress space an increase in the critical tensile stress for crazing with an increase in the magnitude of the compressive stress is not followed by a decrease in the dilatational stress but by development of shear yielding. On the basis of this interpretation and the other observations, an equation expressed by the product of the maximum principal stress and the second invariance of the deviatoric stress at the base of the surface scratch is proposed as a criterion for craze initiation. When the data which seem to be affected from shear yielding are excluded, the results calculated from the proposed equation can provide a good agreement with the experimental results for a wide range of biaxial stress. The equation indicates that the craze initiation stress is strongly influenced by not only the shape of the surface scratch but also the inclination of the groove-like scratch. It seems necessary to investigate precisely the relation between crazing and shear yielding in order to provide a solid foundation to the hypothesis presented in this paper.

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