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Caustics observations for a study of environmental crack-craze stress fields

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The method of caustics is applied to a study of the environmental crack-craze stress field in polymethylmethacrylate during craze growth in methanol and later during a drying procedure in air. In the presence of methanol non-uniform stress with a maximum level at the craze tip was observed. The concept of a "critical equivalent stress intensity factor" below which no craze growth occurs in liquid is defined. During the drying procedure the location of the maximum stress shifted dramatically from the craze tip to the crack tip.

1. Introduction

Crazes have been considered to be a precursor of fracture in linear glassy polymers. In the presence of plasticizing liquids, crazes can be extended to considerable lengths even under a low level of loading, while the crack itself remains stationary. The growth behaviour of such crazes has been investigated using the fracture mechanics concept by Williams and co-workers [1, 2]. They observed that the craze growth behaviour depends on the level of the initial stress intensity factor $K_I(C)$. A uniform stress distribution along the craze is assumed in the Dugdale–Barenblatt (D–B) model [3, 4]. Williams and Marshall [2], and later Passaglia [5], employed the concept of the D–B model to account for the relaxation effect in the craze material.

Recently a two-step stress distribution concept was introduced to consider the plasticization effect along a craze [6]. Non-uniform craze surface stresses were evaluated by Kramer and co-workers [7, 8] using the craze surface opening profile determined by holographic interferometry, on the basis of the same mathematical line as Knight [9]. A similar stress field was calculated for crazes by Verheulpen-Heymans and Bauwens [10], based on the method of Muskhelishvili [11]. All these works suggest that more detailed examinations of the local stress system around the crack are necessary for characterizing the motion of long crazes.

In this paper the environmental crack-craze stress field was experimentally studied by using the method of caustics. The method was originally based on an elastic assumption [12, 13] and later was applied to materials displaying a large amount of plasticity [14] as well as strain hardening [15]. The present work was carried out to see whether the method could be applied to a long environmental crack-craze system to obtain some quantitative information on the stress distribution along a craze. The experiment was performed during both environmental craze growth and a drying process thereafter.

2. Experimental procedure

Single-edge cracked polymethylmethacrylate (PMMA, Acrylite S) tensile specimens with dimensions of 200 mm length, 40 mm width and 2 or 5 mm thickness were prepared as described previously [16]. The middle part of the specimen containing a crack was immersed in methanol as shown in Fig. 1. Specimens were placed under a constant load condition at 20° C. The craze growth was observed with a travelling optical microscope. Caustics were displayed on a screen plate behind the specimen in a transmitted-light system [17]. This caustic is generated from a very small imaginary curve, the initial curve, on the surface of the specimen [14]. The average size of the initial curve was about 1 mm in radius in the present experiments. Light deflection caused along this curve forms caustic patterns on a screen plate. While the craze length was measured by the microscope, the caustic patterns were simultaneously photographed.

The value of $K_I(C)$ was obtained from the linear fracture mechanics formula [18]. The caustic theory, on the other hand, correlated the value of the stress intensity factor $K_I(S)$ to the caustic diameter ϕ and the specimen thickness d as follows [12, 13]:

$$K_I(S) = A\left(\frac{\phi^{5/2}}{d}\right) \qquad (1)$$

where A is a constant depending on the optical properties of the material and the test conditions. For a PMMA crack containing a small craze the agreement between $K_I(C)$ and $K_I(S)$ is satisfactory [19]. In this case the D–B model predicts the average craze stress $\sigma_{c,av}$ as

$$\sigma_{c,av} = \left(\frac{\pi}{8}\right)^{1/2} \frac{K_I(S)}{R^{1/2}} \qquad R/a \ll 1 \qquad (2)$$

where R and a are the craze length and the crack length, respectively. As the craze becomes larger, however, σ_c may no longer be expressed by Equation 2.

Some modification must be introduced to correlate the craze stress to the caustic size [15]. In the present study the craze stress is assumed to be a function of ϕ as a first approximation:

$$\sigma_c(x, t) = F(\phi) \qquad x \approx 0,\ \phi = \phi_{\text{crack}} \qquad (3)$$
$$x = R,\ \phi = \phi_{\text{craze}}$$

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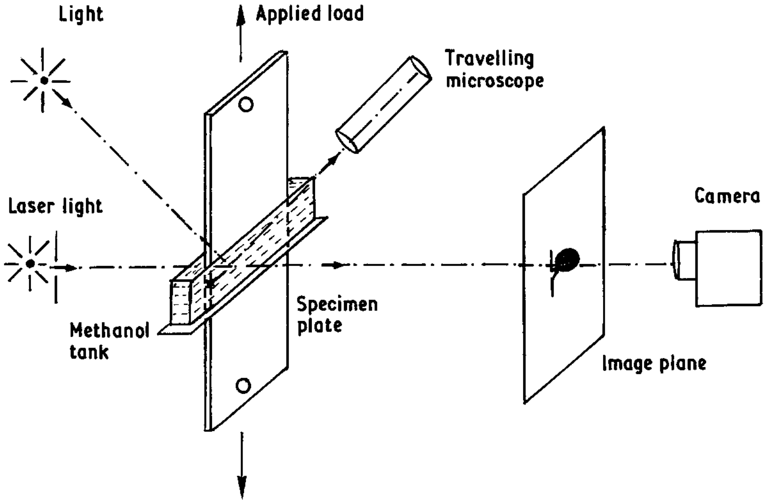

Figure 1 Schematic drawing of the experimental set-up.

where x is distance from the crack tip, t is the total elapsed time from the application of loading, and ϕ_{crack} and ϕ_{craze} are caustic diameters at crack and craze tips. This assumption is based on the fact that the caustic patterns contain information on stress levels, particularly at the crack and craze tips, since the magnitude of the light deflection (or the caustic size) can be correlated with the magnitude of the stress concentration.

An optical effect of immersing the specimens in a liquid on the caustic size was examined, using water which is a fairly weak agent for craze growth and has virtually the same refractive index as methanol. Calibration was performed on the caustic size as stated below.

3. Results and discussion

3.1. Caustic measurement during craze growth

Fig. 2 shows the caustic patterns obtained from a cracked specimen in air (A_{00}) and in water (A_0) under the same applied load. The crack was preceded by no detectable craze at this low level of loading. Both patterns are similar in shape but different in size, reflecting the effect of the liquid. This effect was corrected in later experiments so that the real caustic size (see A_{00}) could be obtained. Fig. 3 shows an example of the measured craze length against time under a comparatively low level of $K_I(C)$ until equilibrium was reached. Similar craze growth data were reported previously [1, 2]. Fig. 4 shows caustic patterns for the same specimen with different craze lengths, corresponding to the stages marked in Fig. 3. For a small craze (A and B) a round caustic curve was formed around the crack-craze tip, while for a longer craze (D to G) two caustic curves tend to be formed, one originating at the crack tip and the other at the craze tip.

In Figs. 5 and 6 values of ϕ at the craze tip under different levels of $K_I(C)$ were plotted against the craze length for different specimen thicknesses of 2 and 5 mm, respectively. The change of ϕ may be divided into three stages. First, as the craze increases in length the value of ϕ decreases to a certain level designated as ϕ_m. Second, crazes continue to grow with this ϕ_m until their length reaches an equilibrium value which depends on the level of $K_I(C)$. The tendency of craze growth to proceed with almost the same caustic size ϕ_m is more clearly seen with thicker specimens as shown in Fig. 6. Finally, the value of ϕ at the craze tip begins to increase without noticeable change of the craze length. It ceases to increase for lower $K_I(C)$. On the other hand for higher $K_I(C)$ the crazes continue to grow (see Fig. 6, $K_I(C) = 0.37\,\text{MN}\,\text{m}^{-3/2}$).

The latter case may be compared with the case given by Marshall *et al.* for continuous craze growth to fracture. In the first stage the decrease in ϕ may be caused by craze growth, which reduces the craze tip stress. As a result the growth rate should be reduced as shown in Fig. 3. The second stage of craze growth with the same ϕ_m may be explained using Fig. 7. While the value of ϕ at the craze tip is kept almost constant (ϕ_m), that at the crack tip continues to decrease, probably due to a plasticization effect in the craze. This effect should tend to relax the stress along the craze, resulting in a higher stress concentration at the craze tip which should then be a source of further craze growth.

The increase of ϕ in the final stage might be caused by the unavailability of softening liquid near the craze tip, which should sharpen the tip. Kramer *et al.* [8] observed a very small craze opening displacement

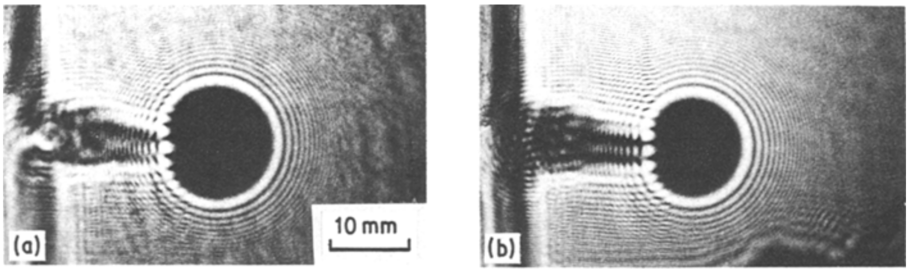

Figure 2 Caustic patterns for a cracked specimen (a) in air (A_{00}) and (b) in water (A_0) under the same load. $K_I(C) = 0.31\,\text{MN}\,\text{m}^{-3/2}$.

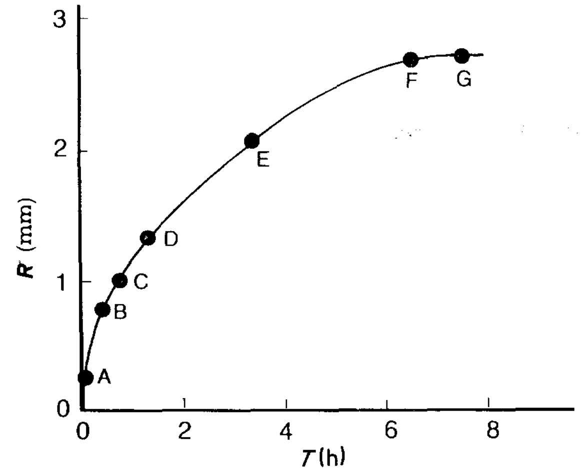

Figure 3 An example of the variation of the craze length (R) with time (T) under the same load. $K_I(C) = 0.31\,\mathrm{MN\,m^{-3/2}}$.

profile at the craze tip as the craze reached its terminal length. Because plasticization continues to take place, especially nearer to the crack tip, the stress level at the craze tip should be raised under the same loading condition. Another possibility for interpreting this increasing stage might be to assume that the onset of the out-of-plane anelastic deformation takes place at the craze tip without enhanced stress intensity. The material in this case might be locally softened, which could lead to the increase of ϕ. The change of ϕ at G on unloading (Fig. 7) should give information on this process. Observations on another specimen revealed that elastic deformation was largely responsible for the caustic in this stage, although a slight indication of plastic deformation was left on unloading. Further examination is required for detailed investigation of this stage.

For specimens with the same thickness the value of ϕ_m seems to be nearly constant, independent of the value of $K_I(C)$ and the craze length. Moreover, even for specimens with different thicknesses, when one takes the value of $\phi_m^{5/2}/d$ (see Equation 1) it can be shown to be almost constant. This means that one may define the concept of "critical equivalent stress intensity factor" $K_I(S)_{c,eq} = A(\phi_m^{5/2}/d)$ at the craze tip. The value of $K_I(S)_{c,eq}$ for the present material is given as $0.15\,\mathrm{MN\,m^{-3/2}}$. This value may be compared with the minimum value of $K_I(C)$, presently obtained as $\approx 0.1\,\mathrm{MN\,m^{-3/2}}$, below which no environmental craze growth would occur, and that given by Marshall *et al.* [1] as $0.06\,\mathrm{MN\,m^{-3/2}}$. We may have a possibility that ϕ_{craze} can be used at all other growth stages of an environmental craze in order to evaluate an "equivalent stress intensity factor" ($K_{I,eq}$) at the craze tip. From the craze tip the stresses may be assumed to go as $\sigma \sim K_{I,eq}/(2\pi r)^{1/2}$ until close to the tip as a first approximation, where r is the distance from the tip.

On the basis of Equation 3 and the sizes of the caustics at both crack and craze tips, the stress distribution along a craze was assumed as shown in Fig. 8. It is suggested in the figure that (i) the maximum stress ($\sigma_{c,\max}$) exists at the craze tip while the minimum ($\sigma_{c,\min}$) is at the crack tip, and that (ii) during craze growth (A_0 to F) both $\sigma_{c,\max}$ and $\sigma_{c,\min}$ decrease with a larger rate for the latter. The probable stress field

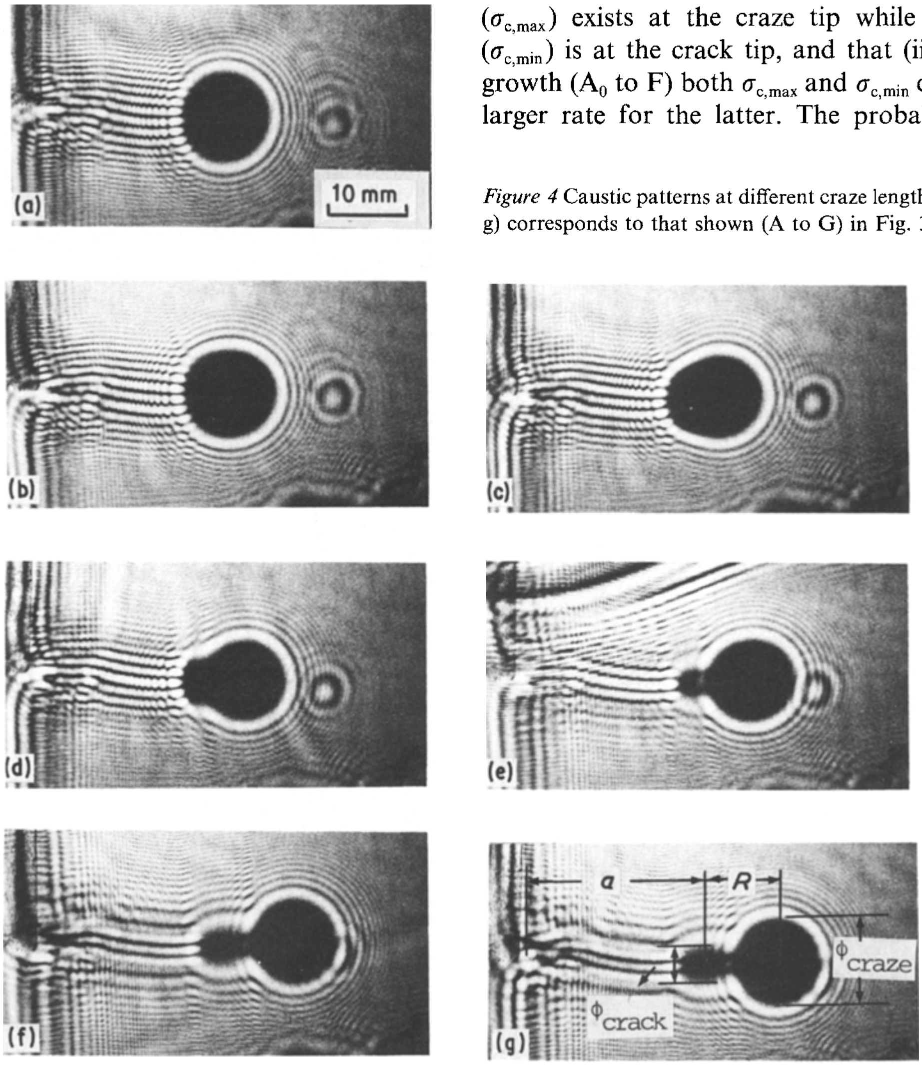

Figure 4 Caustic patterns at different craze lengths. Each stage (a to g) corresponds to that shown (A to G) in Fig. 3.

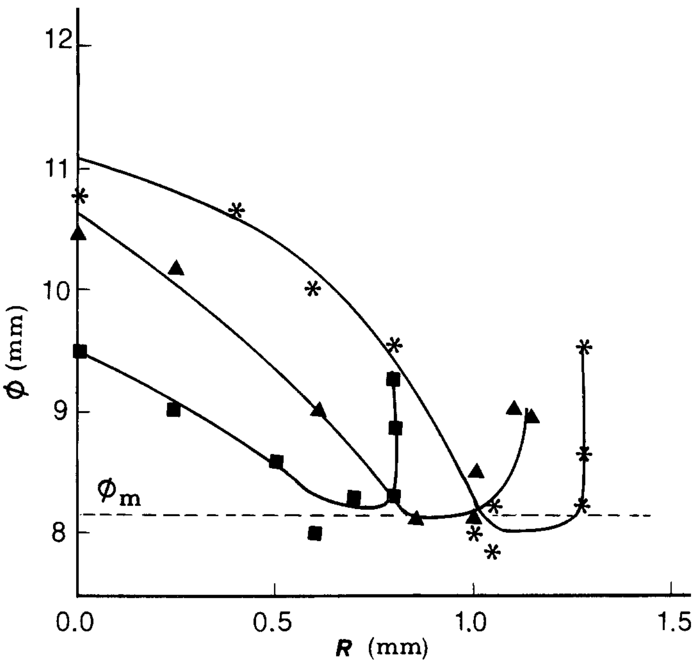

Figure 5 The value of ϕ at the craze tip against R for a specimen thickness of 2 mm under different levels of $K_I(C)$: (■) 0.23, (▲) 0.28, (*) 0.29 MN m$^{-3/2}$.

shown in Fig. 8 agrees with the result of Kramer *et al.* [8] on PMMA in that the stress field along the environmental craze is not uniform but has the maximum at the craze tip, and that the maximum stress level decreases with the craze length. According to Kramer *et al.* [8], the craze tip stress increases again just before the craze ceases to grow, which agrees with our result if we consider that the increase of ϕ in the final stage (Figs. 5, 6 and 7) is due to a real re-enhanced stress intensity. It should be noted here that their experimental conditions differ from ours in the value of $K_I(C)$, the type of loading, the method of liquid supply and the specimen thickness.

3.2. Drying procedure

Caustics measurements were carried out further for specimens undergoing a drying procedure. After the caustic ceased to grow, the methanol tank was removed from the specimen while the same load was still applied. The specimen was left to dry in air at room temperature without noticeable change either in the crack length or in the craze length. Fig. 9 shows the changes in the caustics at different drying times. A dramatic change of the caustic size was observed: the caustic size at the craze tip was decreasing, while increasing at the crack tip. This reverse process seems to continue until evaporation of the plasticizing liquid is completed. The variation of ϕ at both crack and craze tips with drying time is shown in Fig. 10.

The effective drying procedure seems to end at a time of about 1 h. The change of the stress level along the craze in this case is schematically assumed in Fig. 11. It is shown that (i) the stress field changes as a function of time in the drying procedure, and that (ii) the location of the maximum stress moves from the craze tip to the crack tip during the procedure. This rearrangement of the stress field upon drying may be due to a variation in the plasticization effect [20] and in the surface tension of the craze fibrils [21]. The result suggests that for a normal dry craze the stress intensification at the crack tip can be larger than that at the craze tip.

The method of caustics has been shown to give valuable information as to stress distribution along a PMMA craze in methanol. A quantitative theoretical analysis is now being made for caustics on the basis of

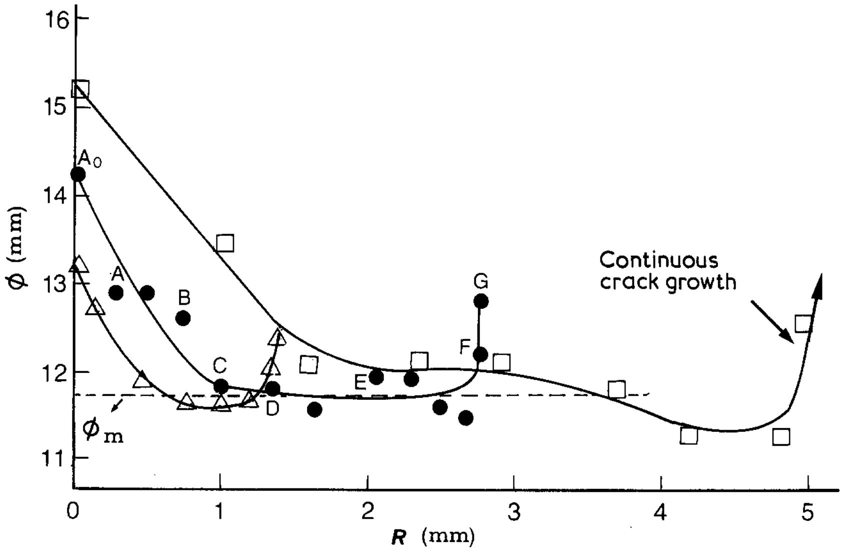

Figure 6 The value of ϕ at the craze tip against R for a specimen thickness of 5 mm under different levels of $K_I(C)$: (△) 0.28, (●) 0.31, (□) 0.37 MN m$^{-3/2}$.

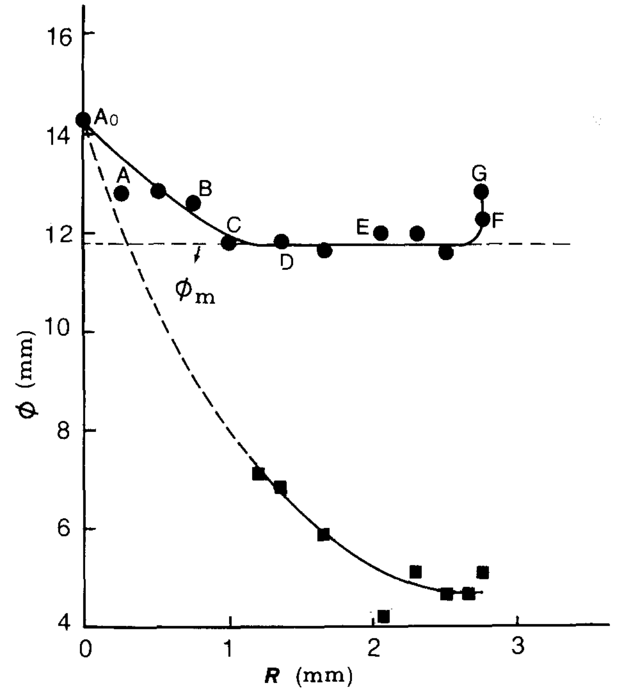

Figure 7 The value of ϕ at (●) craze tip and (■) crack tip against R. $K_I(C) = 0.31\,\mathrm{MN\,m^{-3/2}}$, $d = 5\,\mathrm{mm}$.

an elastoplastic theory to correlate the caustic pattern with the stress distribution along a long environmental craze.

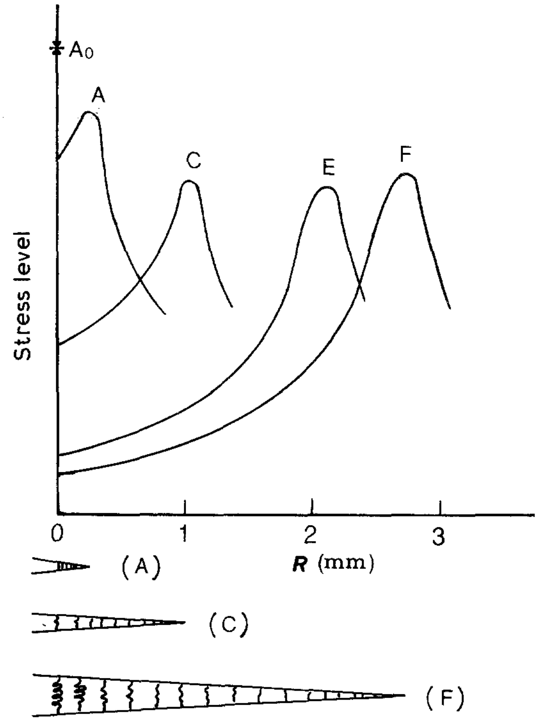

Figure 8 Probable stress field along a growing craze in methanol predicted by the result in Fig. 7. Expected craze profiles are also shown.

4. Conclusions

The method of caustics can give us valuable information on the local stress field along environmental crack-crazes in glassy polymers. The change of the caustic size with craze growth in methanol under different levels of $K_I(C)$ has three stages; the first linearly decreasing stage, the second constant stage

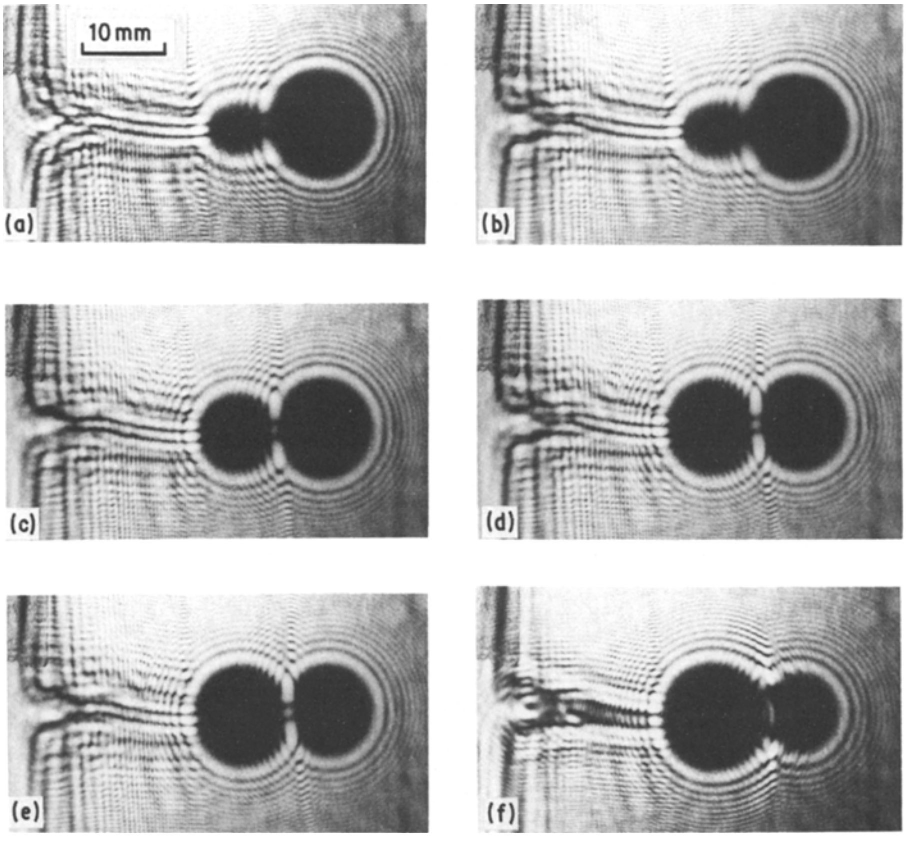

Figure 9 The change of the caustic patterns at different drying times. (a) Stage G*, 6 sec; (b) Stage H, 5 min; (c) Stage I, 10 min; (d) Stage J, 15 min; (e) Stage K, 25 min; (f) Stage L, 10^3 min. Stage G* follows G in Fig. 4g. [It should be noted that the load was removed partly ($\simeq 3/4$) after Stage K to avoid the creep effect, and returned to the inital value in 10^3 min (Stage L)].

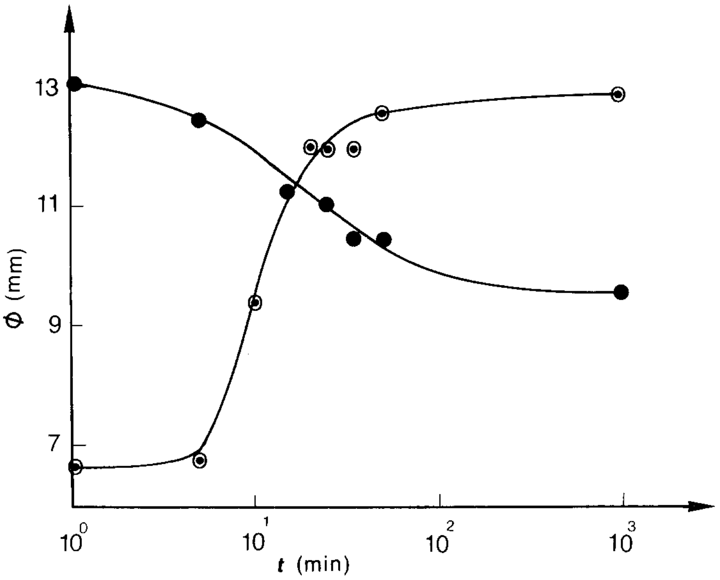

Figure 10 The variation of ϕ at (●) craze tip and (⊙) crack tip with the drying time (t).

with the craze growing, and the third increasing stage without, or eventually with, craze growth. During the first and second growth stages the stress field has its maximum and minimum levels at the craze and crack tips, respectively. Both levels decrease, with a larger rate at the crack tip, as the craze grows at a low $K_\mathrm{I}(\mathrm{C})$. A concept of "critical equivalent stress intensity factor" is defined for craze growth in an environmental liquid. During a drying procedure in air the location of the maximum stress level moves from the craze tip to the crack tip.

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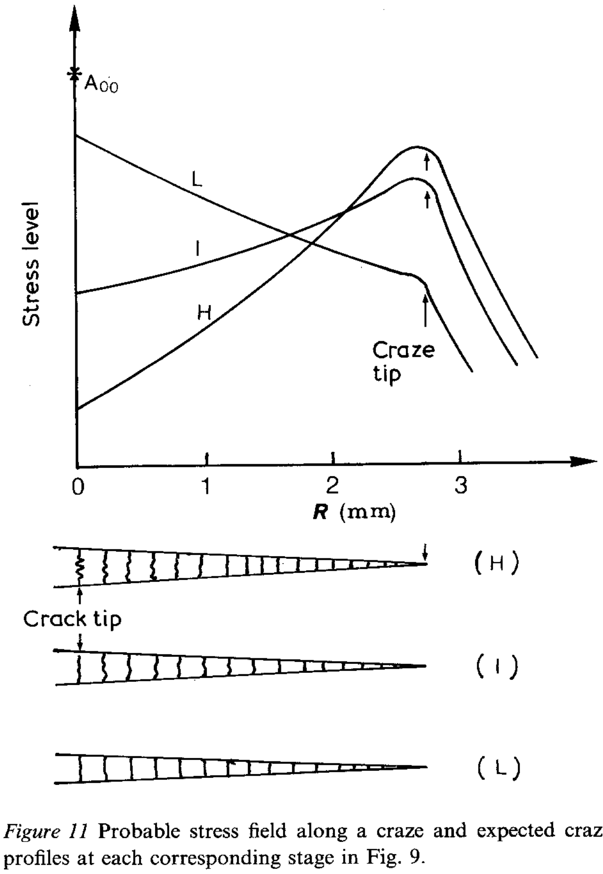

Figure 11 Probable stress field along a craze and expected craze profiles at each corresponding stage in Fig. 9.

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