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Craze Growth and Void Coalescence in PMMA Round Notched Bars

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Synopsis

A study of the kinetics, failure mechanism, and fracture surfaces of PMMA/methanol crazes has been made on notched circular bar specimens subjected to constant tensile loads. Failures were by void growth and coalescence inside the craze away from the notch tip and near to the specimen center. Two distinct features of void coalescence were observed; the first a cluster of very small voids (each of the order of 3.4×10^3 Å) and the second, separate larger voids which usually caused final failure.

An analysis of craze growth, based on fracture mechanics concepts in conjunction with simple flow analysis, suggests that the growth is controlled mainly by the ability of the environment to flow through the voided structure of the craze. Good agreement has been obtained between predicted behavior and experimental data.

INTRODUCTION

The nature of fracture processes in plastics has become of considerable importance in recent years as these materials are used in increasingly demanding situations. The environmental resistance of many plastics is often good under situations where the loadings are low but can change if the materials are required to sustain high stresses.

There are two main categories into which the environmental attack of polymers may be divided. The first of these, "stress cracking," can occur in polymers subjected to low stresses with or without chemical reactions, for example, the behavior of polyamides in some metallic salts[1] dissolved either in water or in organic media, and the behavior of polyethylene in detergents.[2] The second category is known as "solvent crazing" and occurs mainly in amorphous polymers such as polycarbonate,[3] polystyrene,[4] and poly(methyl methacrylate) (PMMA).[5] The problems of environmental stress cracking and crazing have been studied, and a considerable amount of data is available for assessing the environmental crack growth characteristics of plastics.[2]

Crazes usually initiate at inherent surface flaws, then grow perpendicularly to the direction of maximum stress, and they are normally planar and highly reflective like true cracks grown in uniaxial tensile stress in transparent specimens. The study of crazes has received great attention because they initiate and propagate at low stresses and may cause failure by subsequent void coalescence within the craze.

The concepts of fracture mechanics have been used to describe the craze growth behavior in single edge notched (S.E.N.) specimens of PMMA subjected to stress in a methanol environment.[5] A model for craze formation and propagation for that type of craze was proposed based on simple flow equations and a crack opening displacement "C.O.D." approach, assuming the craze to be a porous system and craze propagation to be governed by liquid movements within the craze. That study has been extended to craze growth under cyclic loads[6] in an effort to outline the differences in behavior which might be expected in practice.

The present work is part of a program designed to extend the study of a range of materials, environments, and frequencies using various fatigue test methods. One of the most common test techniques in fatigue is the use of a

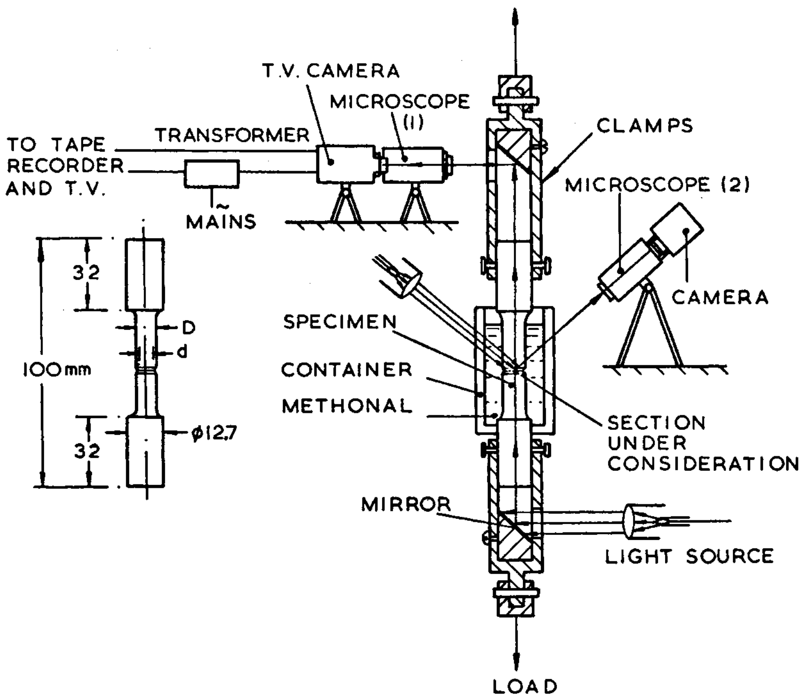


Fig. 1. (a) Test specimen geometry. (b) Schematic diagram of apparatus for viewing void coalescence and craze growth in round bar in tension.

rotating bend test to provide S-N data for the prediction of long-term behavior. There already exists a body of knowledge on the fatigue of plastics in air using this technique,[7] and it therefore seemed logical to extend these data by including environmental attack.

The present paper represents a study of the failure mechanisms and craze growth mechanics for environmental attack in PMMA using notched circular bar specimens (such as those used in the rotating bend tests) in an effort to provide a model background for the explanation of environmental crazing phenomena with this particular geometry.

EXPERIMENTAL

Material and Specimen Preparations

The circular-cross-section notched specimen used in these tests is shown in Figure 1a. The specimens were prepared from 12.7-mm-diameter rods machined from PMMA cast sheets and machine notched with a sharp lathe tool to give a root radius of approximately 00.01 mm. All the specimen surfaces were polished to allow the transmission of light through them (Fig. 1b). Similar specimens having different notch depths and diameters were also prepared.

Test Procedure

The specimens were pin loaded in single-lever rigs which maintained the load constant throughout the test. As illustrated in Figure 1b, each clamp contained a plane mirror inclined at 45° to the axis of the specimen to reflect the light transmitted through the specimen, and microscope 1 was used to observe the surface of the craze formed at the notched section. A closed-circuit television camera was attached to the microscope, and the process of void coalescence within the craze was recorded on video tape. A transparent container was used to maintain the methanol around the notched section and to allow the light from a second source to be reflected at the craze. This light was received by microscope 2, to which an ordinary camera was attached for the purpose of taking photographs at intervals. Craze growth measurements were taken from these photographs.

Specimens with different notch depths and diameters were subjected to various constant loads to give different initial stress intensity factors K_0 (evaluated using the gross stress and initial crack length).

RESULTS AND DISCUSSION

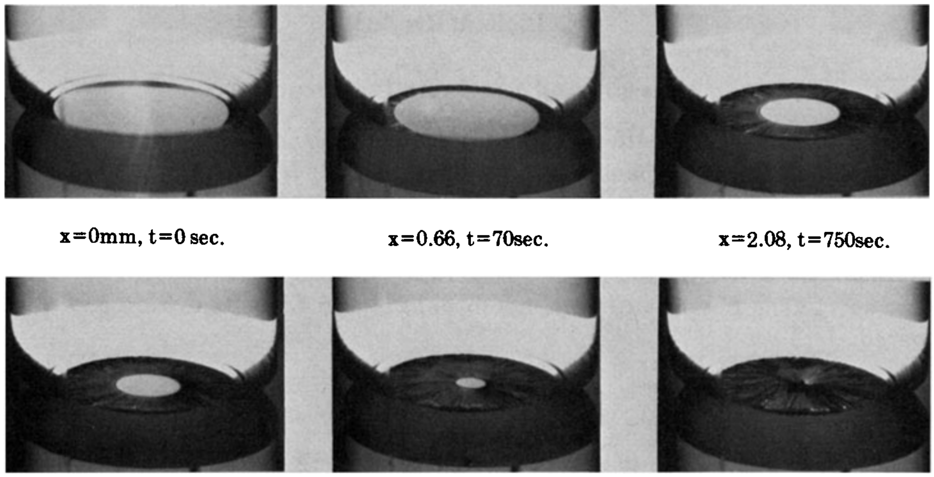
Craze Growth

For craze growth measurements, only tests which gave a symmetrical radial craze growth with respect to the specimen axis as shown in Figure 2a were considered. Measurements of the radial craze growth with time were taken from these photographs, which were enlarged using a projector and the average radial craze length x was determined from

$$x = \frac{d}{2}\left[1 - \frac{1}{2}\left(\frac{b}{B} + \frac{a}{A}\right)\right] \qquad \text{(Fig. 2b)}$$

where d is the notch diameter.

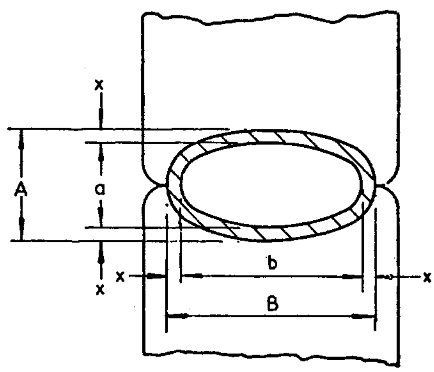
Typical curves obtained for radial craze growth with time for specimens subjected to different initial stress intensity factors K_0 are shown in Figure 3. In some cases, there was a tendency for the craze to accelerate as it approached the center of the specimen (Fig. 3), possibly due to early void coalescence in the craze which may cause a further increase in the K value.



x=0mm, t=0 sec. x=0.66, t=70sec. x=2.08, t=750sec.

x=2.406, t=960sec. x=3.13, t=1380sec. x=3.74, t=590sec.

(a)



(b)

Fig. 2. (a) Radial craze growth in PMMA round notched bar. (b) Schematic representation of craze measurements.

Void Coalescence

It is now known that crazes are a network of small voids interconnected by ligaments. The failure of these links allows the small voids to coalesce and hence grow larger. The stresses carried by the material within the craze increase with time owing to two factors: (1) the craze growth itself which reduces the material at the crazed section carrying the original load on the specimen, and (2) the softening action caused by the diffusion of liquid in the craze. Such softening causes unequal stresses in the ligaments of the material in the craze, i.e., the less softened ligaments in the newly formed part of the craze carry more load and thus are more likely to fail than the more softened ones in the older part of the craze.

The process of void coalescence in the present tests was clearly shown on the T.V. screen. There are two distinct features of void coalescence; the first is the clusters of very small voids, of the order of 3–4 × 10^3 Å as measured

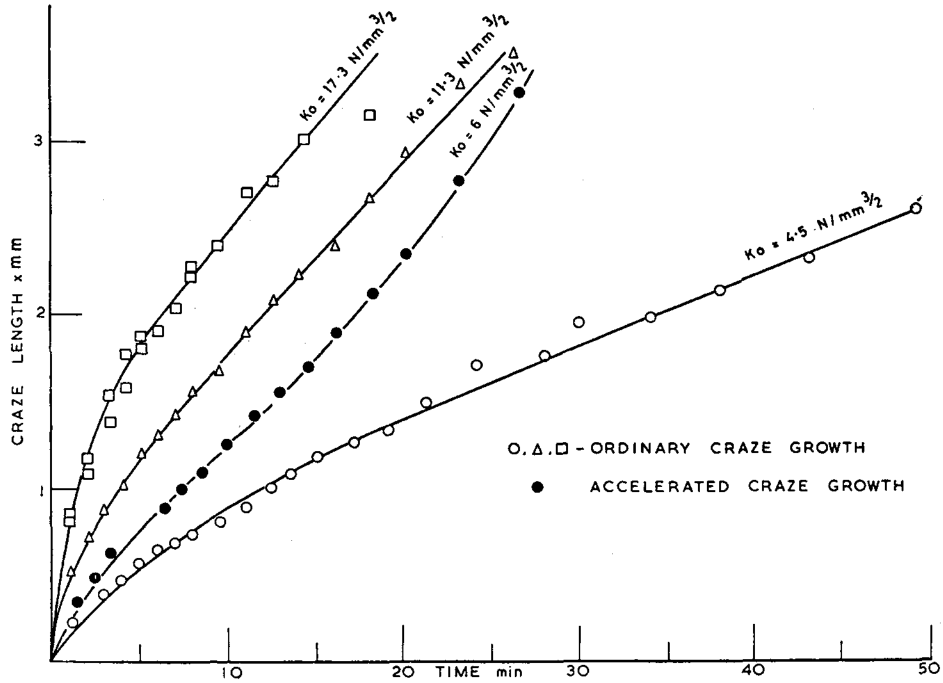


Fig. 3. Variation of craze length with time for different K_0.

from the fracture surface (Fig. 4), appearing as dark areas in the craze (Fig. 5b); and the second is the separate voids which grow much larger than the first type and appear in the craze at different points (Fig. 5c). Once the local failure process started, it continued to give either one of the previously mentioned void forms or resulted in both void features in one craze (Figs. 5d and 5e). Voids usually started to form (Fig. 5a) when the craze had almost completely covered the whole cross section of the specimen; but when the loading was high, early void coalescence started. Final failure was caused by void growth and coalescence eventually leading to complete separation (Fig. 5j). It was usually observed that the large voids grew faster and caused final failure before coalescence occurred between the clusters of small voids if the two patterns were found in one craze.

The pressure inside the voids is low, which allows part of the methanol to evaporate, and voids are thus full of methanol and methanol vapor (Fig. 5h). The movement of methanol vapor bubbles was clear when the large voids grew in size and coalesced, the bubbles of methanol vapor moving to join each other (Fig. 5h), forming one larger bubble filling the space above the methanol in the void.

Some tests of unloading and reloading the crazed specimens which contained the larger voids with the bubbles inside have emphasized the existence of the two phases of methanol in the void. When the specimen was unloaded, the craze relaxed, the two surfaces of the void approached each other, the pressure increased, and the bubbles became progressively smaller until they disappeared. When the specimen was reloaded, the pressure in the void decreased, and there was a delay of approximately 5 min and then the bubbles suddenly reappeared.

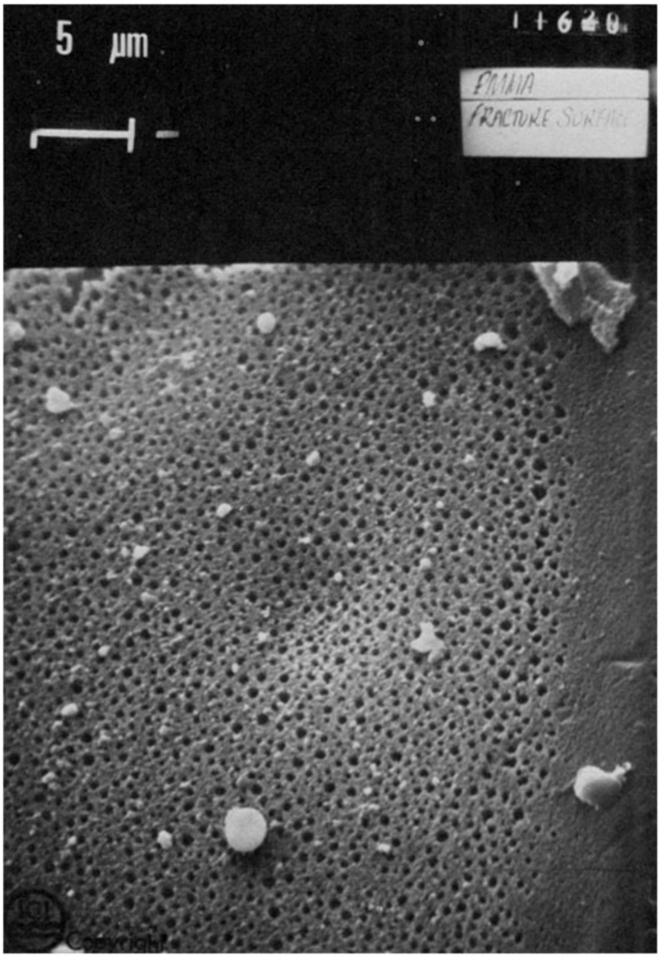
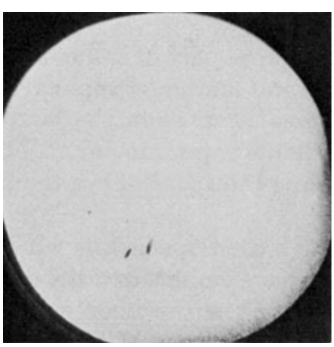


Fig. 4. Clusters of small voids as they appear on the fracture surface.



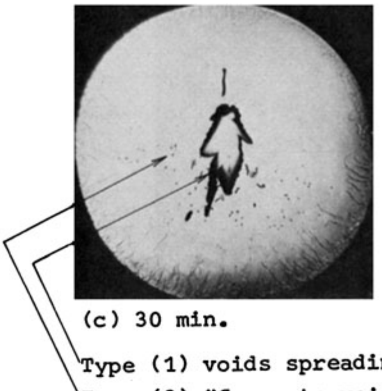
(a) 22 min.*

Start of void coalescence

(b) 26 min. 30 sec.

Type (1), clusters of very small voids

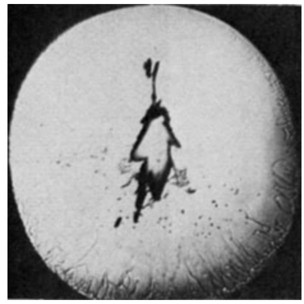
Fig. 5 (*continued*)



(c) 30 min.

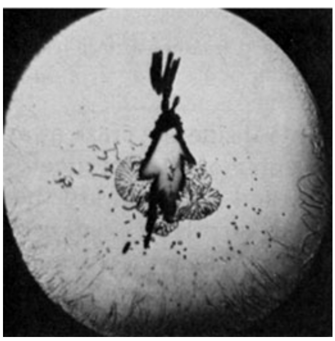
Type (1) voids spreading

Type (2) "Separate voids" appearing



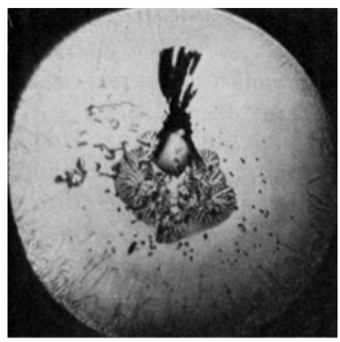
(d) 32 min.

Growth of type (2) voids



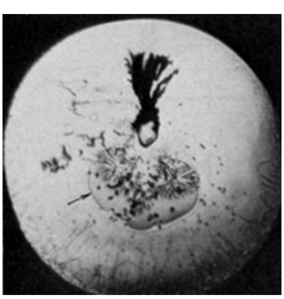
(e) 34 min. 50 sec.

Continuous spreading of type (1), growth of type (2)



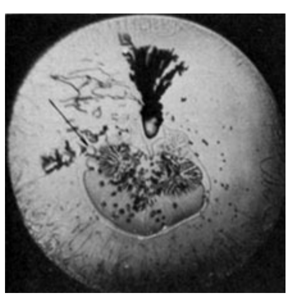
(f) 35 min. 35 sec.

Coalescence of type (2) voids



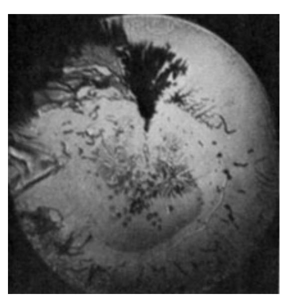
(g) 35 min. 55 sec.

Bubble of methanol vapour inside coalesced voids



(h) 36 min. 10 sec.

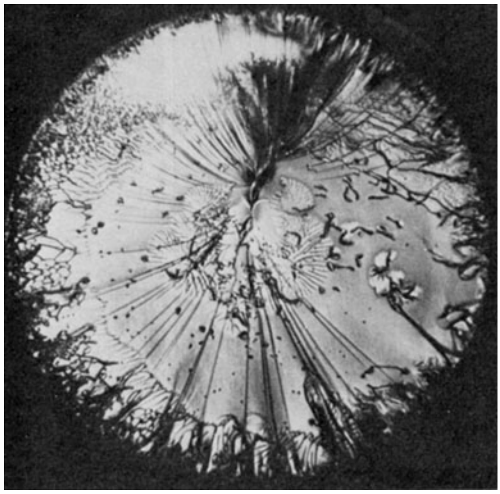
Small bubble of metha-nol vapour joining main bubble



(i) 36 min. 15 sec.

Immediately prior to fracture

Fig. 5 (*continued*)



(j) Fracture Surface

Fig. 5. Void growth and coalescence in the crazed section and fracture surface features after complete separation. (Times were considered from the beginning of the test.)

It has been noticed that void coalescence starts inside the craze away from the original crack or notch and near to the center of the specimen. This means that failure in the craze starts internally and grows toward the notch in a radial direction. It is thought that this rather surprising event occurs because the material within the craze is plasticized by the methanol, and the effect increases with time so that the material is more plasticized in the craze near the notch than in the center. Thus, most of the load is carried by the

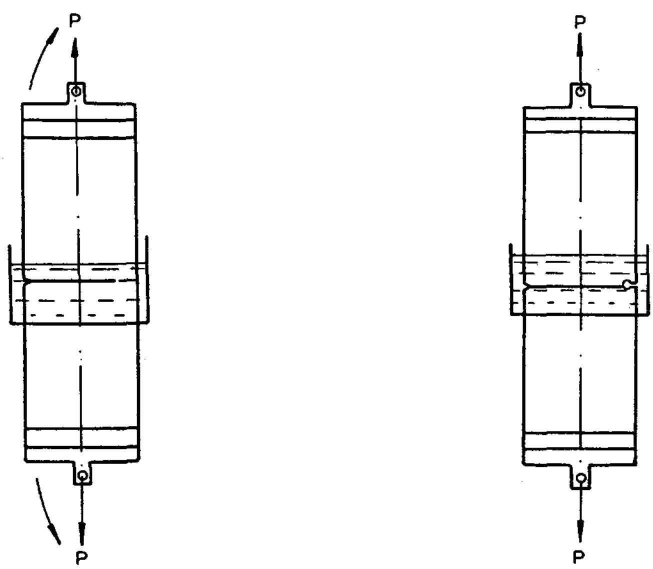


Fig. 6. (a) Craze growth in S.E.N. specimen. (b) Symmetrical loading of crazed S.E.N. specimen.

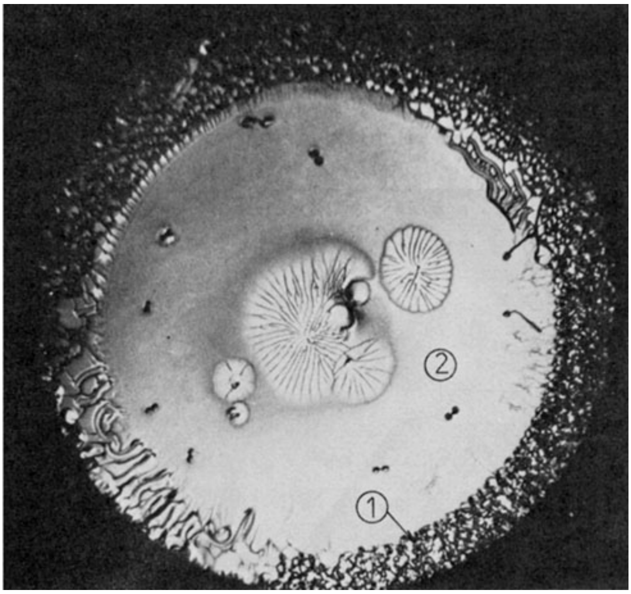


Fig. 7. The two main zones of the fracture surface. (1) The island and crater zone. (2) The featureless zone in which rosette puddles appear.

central section, and if a fault or weak link is present there it will cause void coalescence to start and lead to the final failure.

It seems that this type of failure is different from that observed in crazed S.E.N. specimens in which the original crack propagates in the craze causing the final failure.[8] However, in the S.E.N. case, the crack may be forced to propagate in that way because the specimen is not completely symmetrical

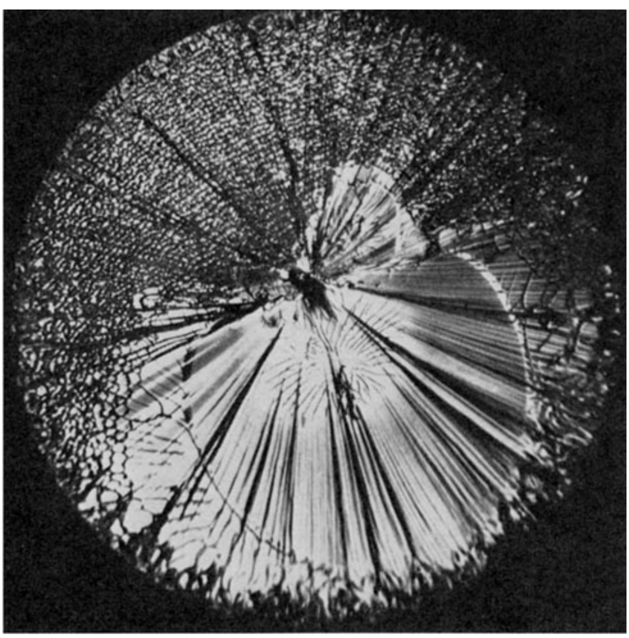


Fig. 8. Fracture surface with its radial marks.

with respect to the loading axis as shown in Figure 6a. This causes bending, which forces the original crack to propagate in the craze. As evidence of this, additional tests were made on S.E.N. specimens. The load in these tests was controlled to allow the craze to propagate to more than three quarters of the specimen width and to leave a length of uncrazed material ahead of the craze

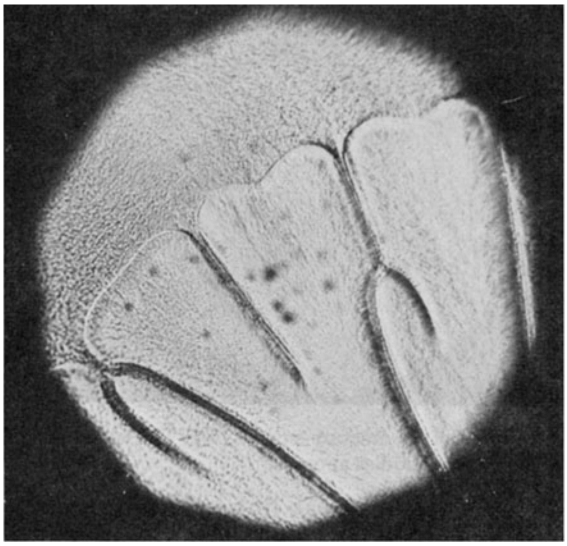


Fig. 9. Definitive boundary of a rosette puddle.

approximately equal to the original crack length; then the material ahead of the craze was removed and the specimen quickly reloaded in methanol but with a smaller load (Fig. 6b). Complete failure of all these specimens was caused by void coalescence in the newly formed part of the craze at the far end from the original crack, and the crack started and propagated from this end while the original crack remained stationary.

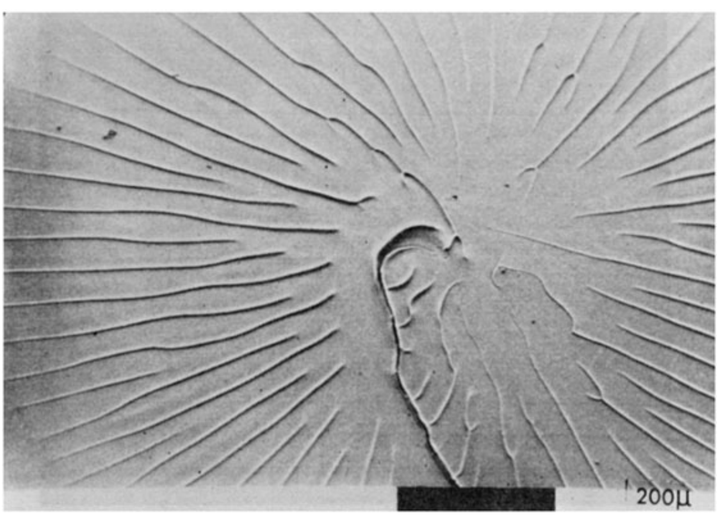


Fig. 10. Central area of a rosette puddle.

Fracture Surface

The fracture surface patterns produced by void coalescence and crack propagation through the wet craze distinguish that sort of failure from others, e.g., fracture in air.

The first distinct zone is the featureless part in which "puddles" appear (Fig. 7). However, in some cases, radial marks appear in this zone pointing to the center of the specimen as shown in Figure 8. The puddles represent the maximum size of the voids before fracture starts, and the radial marks represent the direction of craze propagation. In some cases, these puddles had very definitive boundaries (Fig. 9) and usually had radial marks pointing to the origin of the start of void coalescence (Fig. 10) and showing the direction of void growth. However, these marks have no relation to those showing the direction of craze propagation; they may intersect each other at any angle (Fig. 8).

In the featureless region (Fig. 7), mating surfaces are identical. It is thought that the crack was propagating slowly through the center of the craze

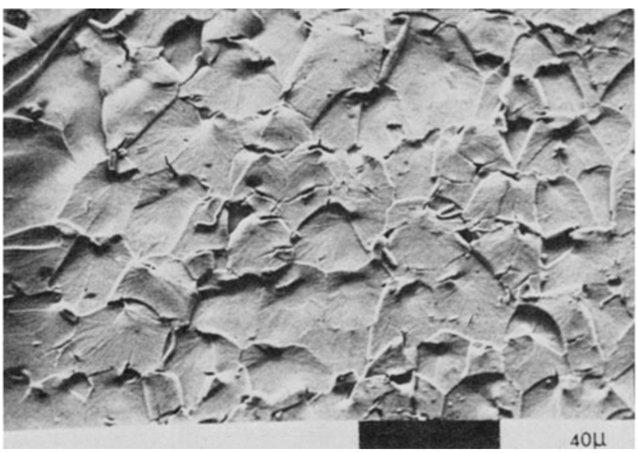


Fig. 11. Island and crater structure.

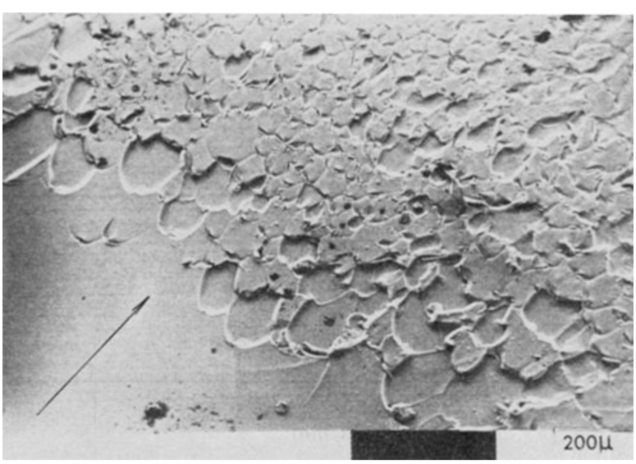


Fig. 12. Transition region between the two zones of the fracture surface. (Arrow indicates direction of radial crack propagation.)

which would give two identical surfaces with hills and valleys of the order of 300 Å, the average spacing between the sites of inhomogeneities in the material. This feature would be difficult to see, however, even with a powerful microscope. Alternatively, it is thought that any microfeatures which might have been formed in this region were masked by the relaxation of the highly stressed craze.

It was noticed that the clusters of small voids which appear as dark areas in the craze before failure did not usually leave any feature on the fractured surface. However, in some cases, when these clusters were formed in that part of the craze where fast crack propagation occurred, the features were seen on the fracture surface, e.g., Fig. 5j; and when compared with Figure 5e and Figure 5i, this shows that some of these clusters have disappeared on the fracture surface where there was slow crack propagation while some are still visible where there was fast crack propagation.

The second distinct zone is the island structure (Fig. 11) with its definitive type of island and crater features which may give an indication of the discontinuous propagation along the craze/matrix interface, i.e., the crack transferring across the craze thickness in an irregular manner. The transition to this

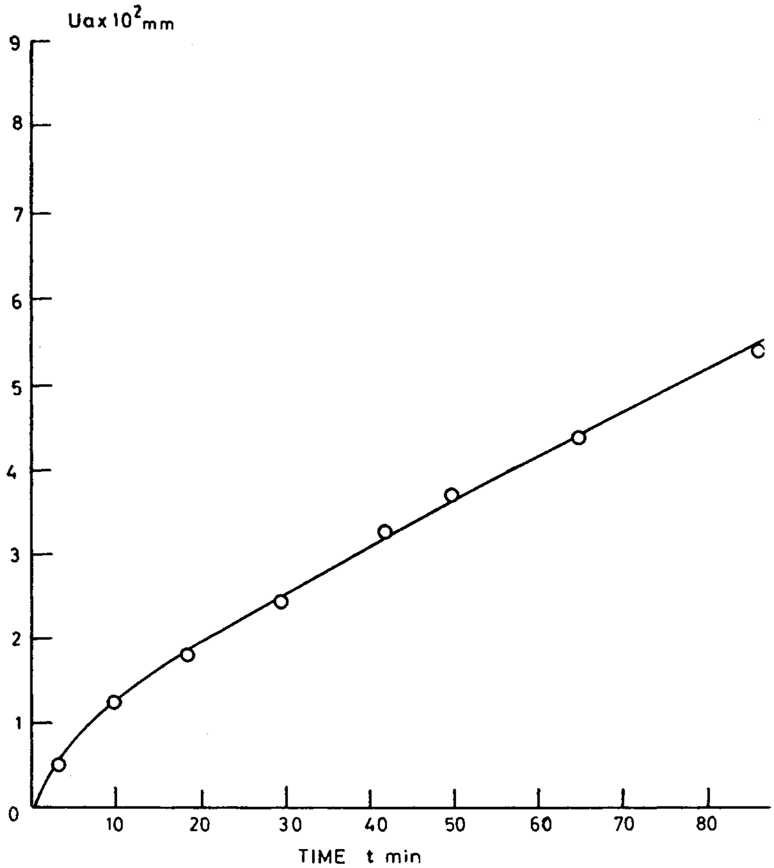


Fig. 13. Variation of crack opening displacement (U_a) with time in S.E.N. specimen K_0 = 15.4 N/mm$^{3/2}$.

type of feature (Fig. 12) may be the result of the crack within the craze reaching its instability condition causing a transition from slow to fast crack propagation. The parabolic markings at the zone boundary are similar to those found for fast crack propagation in a craze in air in PMMA[9] and are thought to represent the intersection of an expanding void in the craze and a radial crack moving at high speed.

ANALYSIS OF THE CRAZE GROWTH

In all the tests, measurements had been made of the rate of craze growth across the specimens, a typical example of craze length-versus-time curve having been shown previously as Figure 3. Such data had been obtained at different loading levels, and an analysis was made of the data to provide a basis for predicting growth rates.

A previous model for craze formation and growth[5] in PMMA had shown that the K_0 dependence of growth rates was due to variations in the displacements in the craze. At high K_0 values, large deflections occur since the crack opening displacement (COD) U_a is given by $U_a = K_0^2/\sigma_y \cdot E$, where σ_y is the yield stress and E is the modulus, and the void area is increased. Basing an analysis in terms of fluid flow rates within the pores of the craze had given an equation of the form:

$$\Delta = AK_0 t^{1/2}$$

where Δ is the craze length, t is time, and A is a constant based on void dimensions and fluid properties.

A refinement of this analysis[10] has been proposed to account for viscoelas-

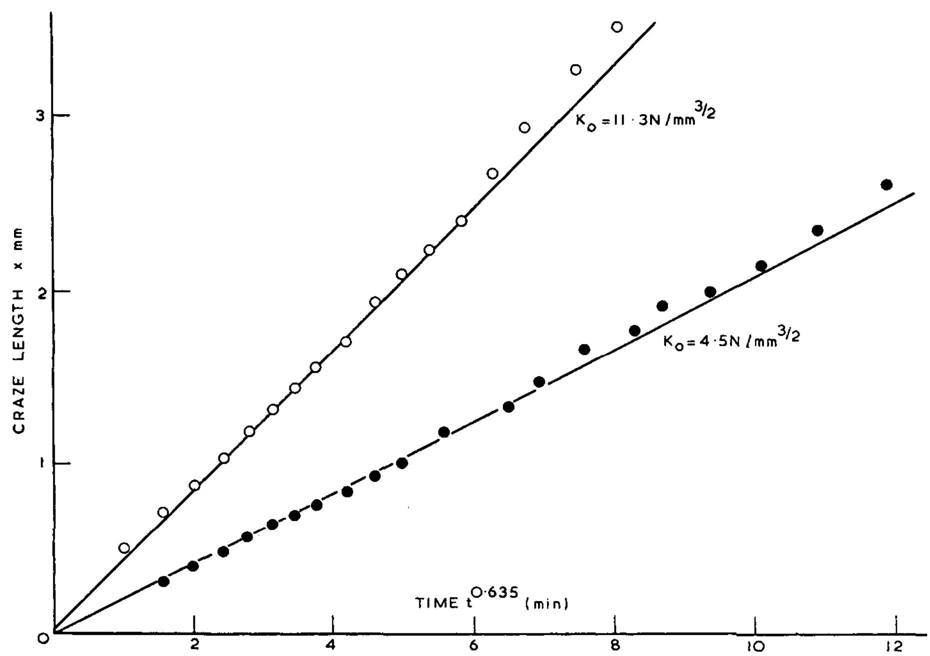


Fig. 14. Variation of craze length with (time)$^{0.635}$.

tic effects since both the yield stress and modulus of PMMA are time dependent and the COD (U_a) changes with time, as shown in Figure 13.

Assuming a power law dependence of the form

$$\sigma_y = \sigma_0 t^{-m} \text{ and } E = E_0 t^{-n}$$

gave $\Delta \alpha K_0 t^{1/2+(m+n/2)}$.[10] Such an assumption is not a perfect fit to modulus and yield data for PMMA,[11] and if an equation is fitted to the data, a more precise solution can be obtained. Also the solution evaluates an equivalent K value for the case of a crack with long extended zone instead of K_0. The analysis has been conducted (available on request); but because of the complexity of the mathematics, only the general result is given, viz.,

$$\Delta \alpha K_0 t^{0.635}$$

The approximate solution above gives an exponent of 0.6.

The craze growth data from the present tests were plotted on such a power law basis, and, as can be seen from the examples shown in Figure 14, the results are well represented by a straight line. It would thus appear that the same fluid flow controls considered in other geometries are applicable to the circular notched specimen and provide an excellent basis for future prediction of growth rates and failure times in fatigue tests.

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