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Craze Growth in PMMA under Cyclic Loads

G. P. MARSHALL and J. G. WILLIAMS,
Department of Mechanical Engineering,
Imperial College of Science and Technology, London, S.W.7, England

Synopsis

A series of tests have been conducted to measure the effects of fatigue loading on environmental stress crazing in PMMA. Testing in methanol has shown that long crazes are grown prior to fracture in the same manner as previously observed for constant-load conditions. An analytical model which had been used to describe craze kinetics in terms of environmental flow within the craze for static loads has been amended to account for the variable loads and gives excellent prediction of craze speeds under numerous types of loading. The correlation of theory and experimental data for this second case suggests that environmental crazing is controlled mainly by the way in which the hostile environment is able to flow through the voided structure of the craze. A brief description of the effects of varying the cyclic frequency is also given in an attempt to provide guidelines for future research.

INTRODUCTION

Applications in which plastics may experience fatigue failure due to the effects of cyclic loading are now becoming quite common as these materials are used more frequently as load-bearing members. As it is also known that the presence of organic media is often the instigator of brittle failure at times and stress levels far below expectation, it would seem likely that the simultaneous combination of both cyclic loading and environment would result in a further acceleration of failure. It is therefore surprising to find that an examination of the literature reveals that virtually no work has been published on this combination of effects. The only reference to fatigue and environment in plastics is by Pringle,[1] who tested PMMA in distilled water. (The considerable scatter in the data in this case, however, makes the work difficult to assess.) Various commercial laboratories have attempted to conduct fatigue tests in different liquid environments but have, in general, reverted to tests in air, daunted by the inconsistency of the traditional S-N data. The effects of the corrosion fatigue has been ignored because it is also argued that there have not been many applications of plastics where this type of failure has arisen. This may well be true at the present time but will become increasingly less so.

In metals testing it has been found that the measurement of crack growth per cycle as a function of loading condition provides a rational basis for assessing the relative effects of different material/environment combinations. Recent studies have led to the suggestion of a simple, quantitative method for estimating the effects of aggressive environments on fatigue crack growth in some high-strength steels. Wei and Landes[2] have suggested a model which proposes that the rate of crack growth in a corrosive environment is considered to be the algebraic sum of the rate of growth in an inert reference environment and that of the aggressive component computed from load profile and sustained crack growth data obtained in an identical environment, viz.,

$$\frac{da}{dN} \text{ (corrosion fatigue)} = \frac{da}{dN} \text{ (env.)} + \frac{da}{dN} \text{ (fatigue no env.)}$$

where da/dN is the crack growth per cycle. This simple result has been shown by Wei's experiments to be substantially correct.

With plastics, a similar general criterion of failure would be difficult to construct and apply because one is not always sure of obtaining the same type of behavior in air and liquid environments. For example, PMMA fails in air by continuous cracking through a small craze ($\sim$20 μ) which is formed at the crack tip,[3] whereas in many liquid environments very large crazes ($\rightarrow$20 mm) form before crack growth occurs.[4] Also, special care must be taken in interpreting the results of fatigue experiments because the material properties are extremely sensitive to both time and temperature and hysteresis effects may be significant. Any study of the dynamic fatigue of plastics involves consideration of variables such as cyclic frequency, the use of continuous or discontinuous loading, the level of the applied stress, and whether cycling is at variable stress or strain. Different loading wave forms, e.g., sinusoidal, square wave, saw tooth, etc., can all affect the results.

A previous project using notched specimens had been successful in explaining craze propagation in PMMA in methanol at constant load,[4] and a model for describing craze propagation had been proposed. Because of the lack of data on fatigue in environments, it was felt that a study of crack and craze kinetics in PMMA loaded in methanol could provide a useful basis for understanding the cyclic loading process in plastics.

A brief review of the previous constant-load work is now given so as to familiarize the reader with the background to the effects of methanol on stressed PMMA.

PMMA IN METHANOL AT CONSTANT LOAD

In the constant-load investigation of PMMA in methanol,[4] rectangular prenotched specimens had been tested in tension and it had been found that crazes would grow for loading conditions far below those sufficient to promote cracking in air.[5] Depending on the level of applied stress and/or the size of the induced flaw, single crazes would either grow almost all the way across the specimen at constant speed before eventual failure by crack propagation or would stop after a few millimeters of growth. The

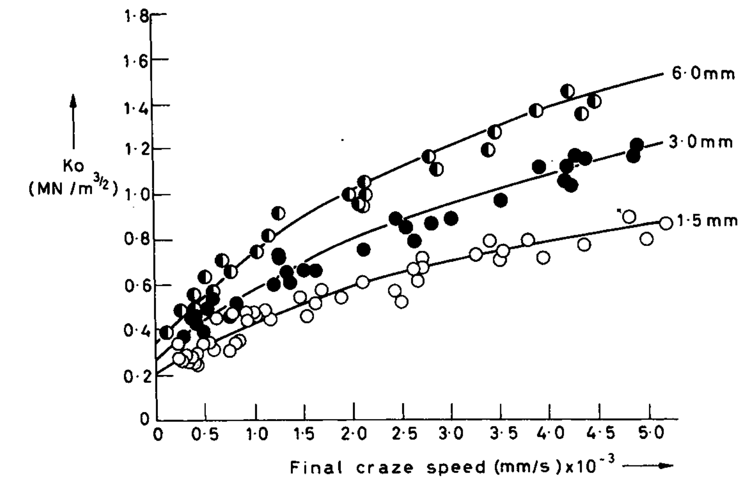

Fig. 1. Variation of final craze speed with initial stress intensity factor: PMMA in methanol, constant load (Marshall et al.[4]).

transition between the two types of behavior and the rates of craze propagation were found to be controlled by the value of the stress intensity factor K_0, based on the level of applied stress and size of initial crack and defined by

$$K_0 = \sigma\sqrt{\pi a_0} \tag{1}$$

where σ is constant applied stress and a_0 is original crack size. (N.B.: This solution is for an infinitely wide plate; for the small specimens used (50 mm wide), π is replaced by a correction factor which is a function of the crack length/plate width.[1])

In those tests where craze propagation led to eventual specimen failure, it was found that the rate of craze propagation was a function of K_0, as shown in Figure 1. The transition craze arrest/craze growth was defined by a critical value K_N, as indicated in Figure 1. The observed craze response to this type of loading was explained in terms of a fluid-flow model which proposed that the rates of craze growth were controlled by the rate at which the environment could flow down the interconnected voids within the craze to continue the attack on the highly stressed, uncrazed material at the craze tip. In particular, the craze arrest histories were shown to be caused by fluid flow down the length of the craze ("end flow") and the constant speed histories by attack from the sides of the specimen ("side flow"), as is shown in Figure 2.

By considering the void area in terms of the crack opening displacement (COD), a relation predicting the rate of environmental flow and hence final craze speed in terms of K_0 was given as

$$\frac{dx}{dt} = C(K_0^2 - K_N^2) \tag{2}$$

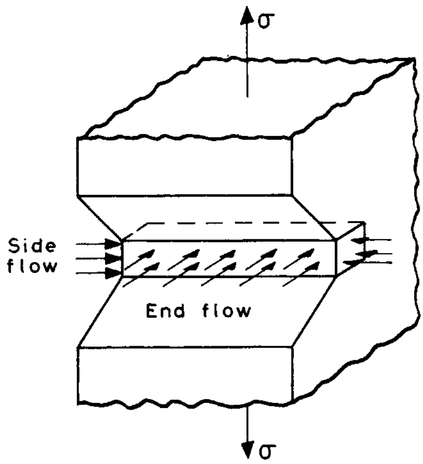

Fig. 2. Environmental flow at a crack/craze tip.

where dx/dt = craze growth rate, C = constant, and K_N = critical value of K_0 for transition from craze arrest to constant speed propagation. This simple equation was found to provide an excellent description of the experimental results (as shown in Fig. 1), and it was hoped that a suitable modification of the model to accommodate varying loads could provide an avenue of approach for the prediction of craze propagation rates under cyclic tensile loads.

EXPERIMENTAL

For all the tests now reported only single-edged specimens (SEN) were used, the dimensions being 150 mm × 50 mm × (1.5 or 3 mm). Initial cracks were induced by notching with a razor blade (see ref. 5), the induced cracks having lengths in the range of 2–12 mm. The only machine available which could control the low loads expected with these small specimens was an Instron Universal TT-D machine, and this restricted the range of testing frequencies which could be employed. Most of the tests were performed on this machine at frequencies of 5×10^{-4} to 3×10^{-1} Hz, although a small number of specimens were tested on a prototype energy cycling machine at 30 Hz (courtesy Instron Ltd.).

All experiments were carried out in a temperature-controlled laboratory at 20 ± 0.5°C and 50 ± 5% relative humidity.

A few preliminary tests on the standard Instron soon showed that at low frequencies, tensile cyclic loads produced the same type of craze growth as had been observed in the constant load tests, i.e., a single craze of considerable dimensions was grown at the crack tip, the crack remaining stationary for the majority of the test.

Before modifying the model for craze growth under constant loads to accommodate a varying load history, it was necessary to have some information on the response of craze propagation rates to a more simple type of varying load than the ramp system imposed by the Instron. Accordingly, a short series of variable load tests was conducted on constant load machines, using square-wave loading cycles.

CRAZE GROWTH UNDER VARYING LOADS

Varying K_0 Tests

The general test procedure was to load a notched specimen at a given K_0 value ($>K_n$) and then allow the growth rate to settle at a constant speed. Having accurately measured this speed (allowing at least 3 mm of growth at constant speed), the load was changed to give a different K_0 value and hence a different speed which was again measured. The K_0 value was then changed once more, and so on. Three main K_0 variation patterns were used, viz.,

(i) $K_0 = 0.4, 0.5, 0.6, 0.8, 0.3, 0.6, 0.5$ MN/m$^{3/2}$

(ii) $K_0 = 0.8, 0.6, 0.5, 0.4, 0.3, 0.4$ MN/m$^{3/2}$

(iii) $K_0 = 0.3, 0.8, 0.6, 0.4, 0.5, 0.6$ MN/m$^{3/2}$

Each loading pattern was repeated twice, using specimens with different initial notch lengths, all the specimens being 1.5 mm thick.

A typical craze-growth history obtained from part of one of these tests, using variation pattern (ii), is shown in Figure 3. It can be seen that there is a distinct response in the growth rate to varying K_0 values. The constant speeds obtained at each K_0 value were measured and found to be entirely consistent with the values obtained in the conventional static load tests.[4] There was no noticeable difference produced by changing the load variation pattern; a given K_0 value always gave the same speed (within

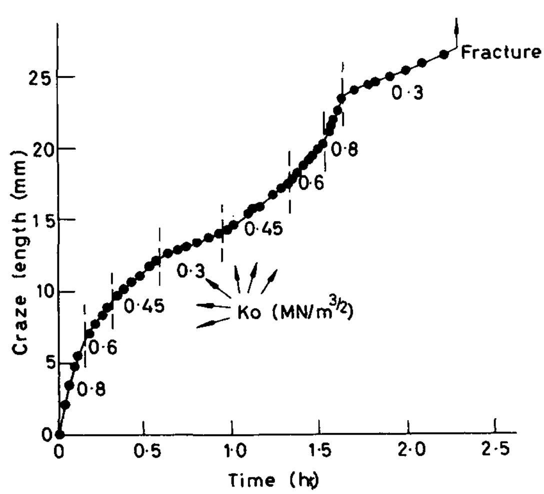

Fig. 3. Effect of Varying K_0 on craze-propagation rates

± 8%), irrespective of whether the test was run after an increase or decrease in the loading condition.

On changing the K_0 values, although the response of the craze growth rate was almost immediate, there was usually a short delay before a steady-state speed was achieved (as shown in Fig. 3). In considering an analysis of a ramp loading test, these short delays would tend to be self-compensating on the loading and unloading cycles, and it is thought that their effect would be small at low test frequencies.

The explanation of the changes in velocity with K_0 changes is clearly that the void area (ψ) is still determined by the current K_0 value and that the observed speed changes are merely responses to changes in the void area. Changes in K_0 simply produce different craze tip deflections and hence different void areas.

Load/Unload Tests

As a further test on craze growth recovery, a number of ancillary tests were conducted. In the first tests, specimens with crazes growing at a constant rate were unloaded, left to stand in the methanol for short periods, and then reloaded again at the same K_0 condition. For unloading periods of less than 23 min, the craze maintained its silvery appearance (even though the relaxations within the craze must have been "squeezing" alcohol out of the voids), and on reload the craze started to grow once more at the same speed as before (shown in Fig. 4). Unloading for longer than 20 min allowed for much more complete evacuation of the alcohol, and the craze began to lose its silver-like appearance, e.g., unloading for 30 min produced a time lag of 20 min in craze reinitiation.

To investigate the effects of long periods of unloading and complete alcohol evacuation, specimens which had been maintaining constant speed growth were removed from the loading stations and allowed to stand un-

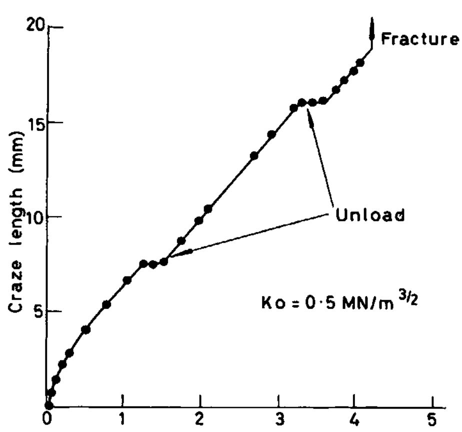

Fig. 4. Effect of unloading on craze-propagation rates.

loaded for periods of up to ten weeks, when they were again reloaded. In most of the cases it was found that the main craze gradually regained its silvery appearance over a 2–3-hr time period, the time depending on the craze length. The only exceptions to this form of "recovery" were two specimens in which the crazes had been grown to extreme lengths ($\simeq$0.8 width) before load removal. After 20 hr in the methanol, no recovery was observed, and since it was thought that soaking effects would have distorted the behavior by this time, the tests were discontinued.

In general, then, it would appear that the deflection at the craze tip (which controls the growth rate) responds in an essentially elastic manner to quite drastic changes in both loading variations and load removal. This does not infer that all the deflections down the main craze are necessarily recoverable since the extensions which are imposed during craze propagation will almost certainly produce permanent "plastic" deformation, on top of that which exists as a virtue of the existence of the craze. The response of these deflections to changes in loading will be a function of the craze stress/strain behavior; and to date, no information is available on this subject for a "wet" craze, although Kambour et al.[6] have given some results for a *dry* polycarbonate craze, showing that permanent deformations were produced by comparatively small craze thickness extensions.

As a whole, however, the elastic-like response of the craze-growth rate to changes in load gave good hope that a simple modification of the model, derived for constant-load behavior, could be used to accommodate a constant rate of change in load and hence provide some insight into the effects of cyclic fatigue on craze propagation in PMMA in methanol. The analysis of a ramp-load input cycle is now given.

ANALYSIS OF CRAZE GROWTH—CYCLIC LOADING

The tests on the constant-load machines have shown that the craze speed in a varying-load test remains a function of the K_0 level. In deriving an analysis for predicting the craze speed, it is presumed that the environmental attack occurs, as before, by either side or end flow and that the equations derived previously for static loads are valid at any instant in time. It is also presumed that the K_m and K_n limitations on craze initiation and final craze propagation to fracture (via the side flow) will again be operative, and the analysis is derived for the particular case of zero minimum load and the more general case where the lower limit ($\check{K}_0$) is any value of $K_0 > K_n$.

Cyclic Craze Growth for $\check{K}_0 = 0$

The loading history is as illustrated in Figure 5 with zero initial load. For a ramp load input,

$$\sigma = At \tag{4}$$

where σ is the gross stress and t the loading time.

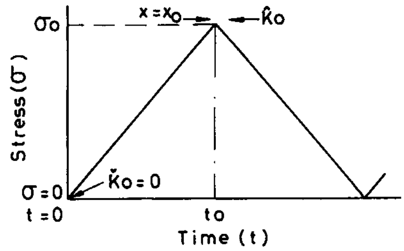

Fig. 5. Loading pattern for $\check{K}_0 = 0$.

At maximum stress, let $\sigma = \sigma_0$ and $t = t_0$. Hence,

$$A = \sigma_0/t_0$$

and

$$\sigma = \sigma_0 t/t_0. \tag{5}$$

Using eq. (5) together with the fact that at any time

$$K_0^2 = \sigma^2 Y^2 a$$

where Y is a correction factor introduced to account for finite plate effects, cf. eq. (1), gives

$$K_0^2 = \frac{\sigma_0^2 Y^2 a_0 \cdot t^2}{t_0^2} = \frac{\hat{K}_0^2 t^2}{t_0^2} \tag{6}$$

where $\hat{K}_0$ is the maximum value of K_0 in any cycle of loading.

From the constant-load analysis, eq. (3), the craze-growth rate for side-flow conditions (dx/dt) is given by

$$dx/dt = C(K_0^2 - K_n^2) \tag{7}$$

where C is a constant.

Substituting for K_0 from eq. (6) in eq. (7) gives the growth rate under cyclic loading, $(dx/dt)_{\text{cyclic}}$, as

$$(dx/dt)_{\text{cyclic}} = C[\hat{K}_0^2(t^2/t_0^2) - K_n^2]. \tag{8}$$

Now it will be assumed that constant-speed growth only occurs for $K_0 > K_n$, i.e., when $t > t_n$.

Integrating eq. (8) and using the condition $x = 0$ until $t = t_n$ and that a mean craze speed per cycle is defined by

$$\frac{d\bar{x}}{dt} = x_0/t_0$$

(x_0 as in Fig. 7) gives

$$\frac{d\bar{x}}{dt} = C\left(\frac{\hat{K}_0^2}{3} - K_n^2 + \frac{2}{3}\frac{K_n^3}{\hat{K}_0}\right) \tag{9}$$

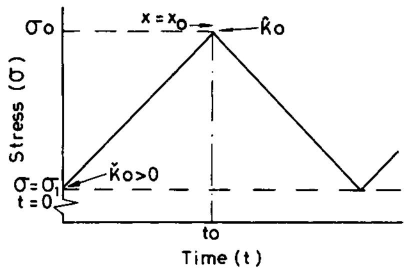

Fig. 6. Loading pattern for $\hat{K}_0 > K_n$.

where $d\bar{x}/dt$ is the average speed over a complete loading cycle. Now let

$$\frac{d\bar{x}}{dt} = C(\bar{K}_0^2 - K_n^2) \tag{10}$$

where $\bar{K}_0$ is the "equivalent" K_0 value which gives a speed $d\bar{x}/dt$ in a *constant-load* text.

From eqs. (9) and (10),

$$\bar{K}_0 = \frac{\hat{K}_0}{\sqrt{3}}\left(1 + 2\left\{\frac{K_n}{\hat{K}_0}\right\}^3\right)^{1/2}. \tag{11}$$

Cyclic Craze Growth for $\check{K}_0 \geq K_n$

In any given test, presume cycling between stresses σ_1 and σ_0 (σ_0 = maximum stress in cycle, at $t = t_0$, and σ_1 = minimum stress, Fig. 6); i.e.,

$$(\sigma - \sigma_1) = A't.$$

At $\sigma = \sigma_1$, $t = 0$, and at $\sigma = \sigma_0$, $t = t_0$, whence

$$\sigma = \sigma_1 + (\sigma_0 - \sigma_1)t/t_0$$

i.e., at any time,

$$K_0 = \check{K}_0 \frac{t_0 - t}{t_0} + \hat{K}_0 \cdot \frac{t}{t_0} \qquad (\check{K}_0 = \min K_0). \tag{12}$$

As before, combining eqs. (7) and (12) and using the boundary condition $x = 0$ at $t = 0$ gives

$$\frac{d\bar{x}}{dt} = C\left(\frac{\check{K}_0^2}{3} + \frac{\hat{K}_0^2}{3} + \frac{\check{K}_0\hat{K}_0}{3} - K_n^2\right) = C\,(\bar{K}_0^2 - K_n^2)$$

where $d\bar{x}/dt = x_0/t_0$ as before, i.e.,

$$\bar{K}_0 = \frac{1}{\sqrt{3}}\,(\check{K}_0^2 + \hat{K}_0^2 + \check{K}_0\hat{K}_0)^{1/2}. \tag{13}$$

Thus, an analysis of this form allows for the comparison of constant-load and cyclic-load tests. By choosing the K_0 limits from eqs. (11) and (13), it is possible to run cyclic tests at $\bar{K}_0$ values for which results are available from constant-load tests, and the rates of craze growth can be compared. To enable such a comparison to be made, two test series were conducted, using both zero and nonzero minimum loads.

RAMP LOADING TESTS

Very Slow Cycling Rates (5×10^{-4} Hz)

In order to examine the craze-growth pattern in detail, an initial series of tests was performed (using the SEN specimen) at very low cycling rates (viz., 5×10^{-4} Hz) on the Instron. The load was varied from zero to some positive tensile value (at which $K_0 = \hat{K}_0$) and then decreased again, giving a ramp cycle of K_0 values as shown in Figure 7, which also illustrates the craze growth behavior for $\hat{K}_0 = 1.0$ MN/m$^{3/2}$. During the loading half of each cycle, the craze growth rate gradually accelerated, as expected, until the maximum K_0 value was reached, the growth rate decreasing thereafter until the craze eventually stopped growing at $K_0 =$ 0.24 MN/m$^{3/2}$. The cycle was then repeated as shown.

The initiation and arrest points were somewhat difficult to define precisely, since the microscope had to be rezeroed (on the tip of the original crack) before each reading, because the specimen tended to move slightly in the grips during loading. Nevertheless, sufficient readings were obtained to show that the craze initiation and arrest condition were tolerably close to the value of K_n (e.g., $K_0 = 0.24$ MN/m$^{3/2}$ for arrest here and $K_n =$ 0.21 MN/m$^{3/2}$ from constant load tests).

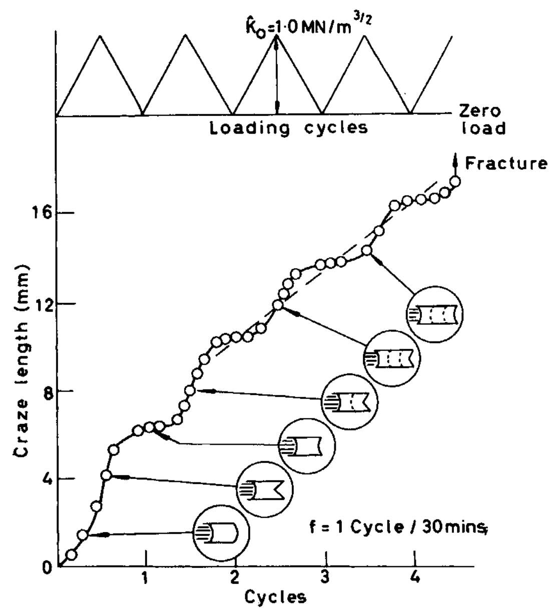

Fig. 7. Craze growth pattern: very low cyclic frequency, $\hat{K}_0 > K_n$.

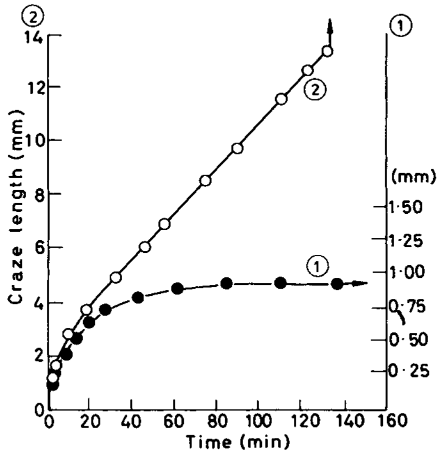

Fig. 8. Typical craze length-vs.-time curves: $f = 10^{-1}$ Hz.

The insert sketches show the form of the craze front profile, and it can be seen that the typical side flow "vee" pattern becomes pronounced as K_0 increases and then less apparent as K_0 decreases. When fracture eventually occurred, where was no obvious change in the craze growth behavior, and the process took place without any visible warning sign.

Cyclic Loading at 10^{-1} Hz

Most of the cyclic loading tests have been performed at 10^{-1} Hz since this was a reasonably convenient frequency for the Instron to maintain for long time periods. The two main test series involved testing a large number of specimens at both zero and nonzero minimum loads. Equations (11) and (13) were then used to deduce equivalent static K_0 values, $\bar{K}_0$.

As in the constant-load tests, there were two types of craze-growth history produced, depending on the level of K_0, and these are shown in Figure 8. For $\hat{K}_0 < K_n$, craze growth started at a high rate and then eventually slowed until it ceased altogether (curve 1 in Fig. 8). In the second type ($K_0 > K_n$), the growth rate eventually settled to a constant value, as before, in the constant load tests (curve 2 in Fig. 8).

If it is assumed that the craze velocity is fixed by the current value of K_0 at any given time, then clearly $\dot{x}$ will decrease as observed and the crazes will stop for $\hat{K}_0 < K_n$. For any value of K_0, local variations in craze-growth pattern, shown in Figure 7, would not be apparent at the present cycling frequency (10^{-1} Hz), and only the average form of curve, shown as the dotted line in Figure 7, would be apparent (as in Fig. 8).

Craze Appearance

In broad terms, the crazes grown under cyclic-loading conditions were very similar in appearance to those grown in the constant-load tests. For

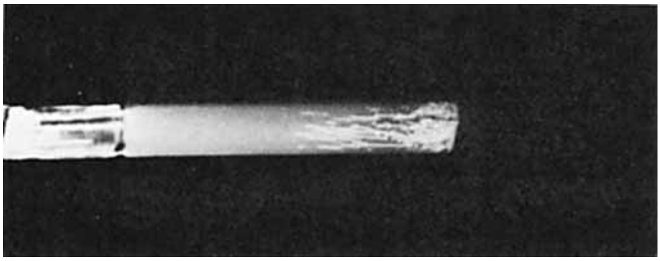

Fig. 9. "Grain" markings at slow craze speeds.

values of $\hat{K}_0 < K_n$, there was no sign of the inverted "vee" front associated with side flow, hence lending support to the assumption that once again this behavior is caused by end flow alone. At the craze arrest condition however, it was noticed that the craze front became very irregular and small line markings gave the front a nonuniform appearance. It would appear that the craze propagates in a most irregular manner in the last few minutes of true growth, indicating some degree of heterogeneity in the craze tip region.

In those tests growing to failure (i.e., $\hat{K}_0 > K_n$), the general craze appearance was as before—the inverted "vee" pattern asserted itself during the constant-speed history. However, at slow speeds ($<4\times10^{-4}$ mm/sec), the "grain" markings, which had been noticed at such speeds in the constant-load tests, once again appeared (see Fig. 9). Under cyclic conditions, this graininess was far more pronounced and widespread and did not disappear as in the constant-load tests. It would appear that these marks are caused by the craze being heterogeneous and that cyclic loading enhances the effect because of the disturbances to the microstructure caused by the continual load reversals.

No Side Flow Tests

The observed craze arrests when $\hat{K}_0 < K_n$ (e.g., curve 1 in Fig. 8) and the craze front patterns produced all suggest that once again this type of craze growth is controlled by the flow of the environment down the length of the craze as opposed to fluid flow through the sides of the specimens. To provide a conclusive check, a short series of tests in which the side flow was cut off by greasing the specimen surfaces was conducted. In all cases, the crazes stopped growing after a short time, irrespective of the value of K_0. It is therefore concluded that the processes involved in craze growth under cyclic loading in PMMA in methanol are controlled by the flow processes and that the transposition of the constant load model is valid.

CRAZE BREAKDOWN

The onset of ultimate craze failure was more readily apparent under cyclic loading at 10^{-1} Hz. In the constant load tests, the crack growth

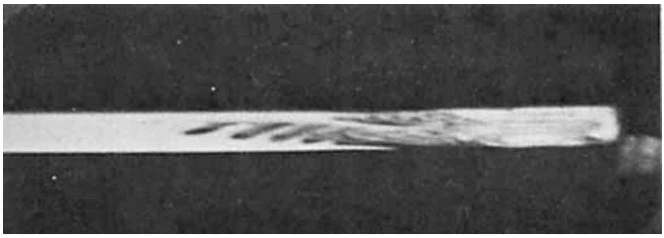

Fig. 10. Void coalescence immediately prior to specimen fracture: $f = 10^{-1}$ Hz.

through the craze was normally smooth and continuous and rather difficult to discern when the craze was viewed from above. Also, the crack growth period was usually a small fraction of the total testing time. In the cyclic tests, failure occurred by a more random mechanism of void coalescence within the craze. The first signs of failure were the appearance of small dark "finger" markings growing from the crack tip. These markings, representing regions of local void coalescence, would grow in a rather haphazard manner and did not usually spread across the whole section. Instead, other "dark" regions would appear some way ahead of the crack, and the various regions eventually moved toward one another, as shown in Figure 10.

Eventually, the regions would coalesce to spread straight across the specimen thickness, and failure would occur almost immediately—by fast crack propagation. It is almost certain that the dark regions shown in the photographs are regions of void coalescence, since in some cases, when the regions had started to join together, alcohol could be seen "bubbling" in and out of the regions as the load was cycled. Also, photographs taken from the side showed that at this stage, considerable crack extension had taken place. In some cases, this process would take as long as 40 min to occur, and there was a marked effect on the craze growth rate, especially during the later stages when the voids had coalesced across the section, hence increasing the effective $\bar{K}_0$ value.

The fracture surfaces of the slowly cycled specimens showed ample evidence of the void coalescence. A typical example is shown in Figure 11. The outline of the "puddles" formed by the void coalescence are clearly visible. The repeated ripple markings on the surfaces indicates the gradual progression of both the primary and the secondary cracks. These marks are typically observed on the fracture surfaces of specimens which have failed by fatigue. In metals, it has been observed that the crack growth/cycle occurs as a repetitive process of crack tip blunting followed by resharpening, it being this process which causes the characteristic marks on the surface. A similar process of blunting and resharpening is thought to occur in the present case, although from the appearance of the islands of material left on the surface it would appear that the crack-growth path is rather tortuous, the crack probably branching between the craze/matrix interfaces and the center of the craze.

Fig. 11. Fracture surface of specimen cycled at 10^{-1} Hz in methanol.

MODELING THE RESULTS

The cyclic model was found to give a most satisfactory prediction of the growth rates in these tests; Figure 12 shows a typical curve from a cyclic loading test ($\Delta K_0 = 0 \rightarrow \hat{K}_0$) and the experimental points obtained from a constant load test conducted at the equivalent $\bar{K}_0$ value deduced from eq. (11). Figure 12 also shows the curve obtained when the mode of loading was changed from constant load at $K_0 = 0.45$ MN/m$^{3/2}$ to cyclic load at 10^{-1} Hz, the cyclic limits as indicated giving $\bar{K}_0 = 0.45$ MN/m$^{3/2}$ (i.e., the same predicted condition). In both these cases, the agreement is excellent.

The comparison of the results from the main body of tests, with their constant-load counterparts, is shown in Figure 13 where the equivalent

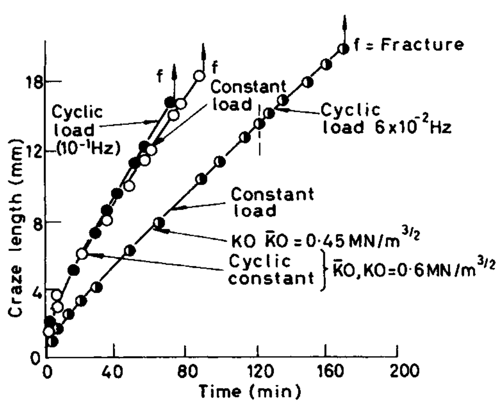

Fig. 12. Comparison of craze growth due to constant and cyclic loading.

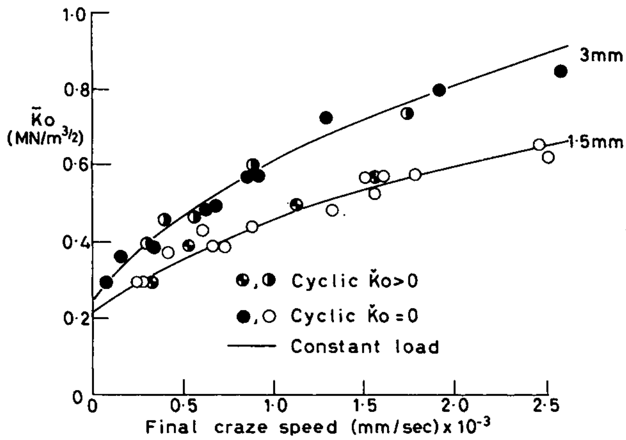

Fig. 13. $\bar{K}_0$ vs. final craze speed: constant load, cf. cyclic load.

static $\bar{K}_0$ values have been calculated from eqs. (11) and (13) and then plotted versus the observed cyclic craze speeds. The results of the previous constant-load tests[4] are shown superimposed on the same graph, and once again the agreement is seen to be excellent for both specimen thicknesses and both types of minimum-load conditions. Thus, knowing the constant-speed behavior of the PMMA craze, use of the simple modifications given in the present analysis allows for the prediction of the craze speed for any type of ramp loading condition at this frequency.

The validity of the assumption that the craze velocity is solely dependent on the current K_0 value was further confirmed by conducting an experiment where the loading condition (i.e., ΔK_0) was changed for set periods during the test so as to observe the effect this would have on the velocity. The resulting growth rate curve is shown as Figure 14, and it can be seen that for each change in ΔK_0 value there was an equivalent change in the craze speed. The changes in velocity were almost immediate, and the

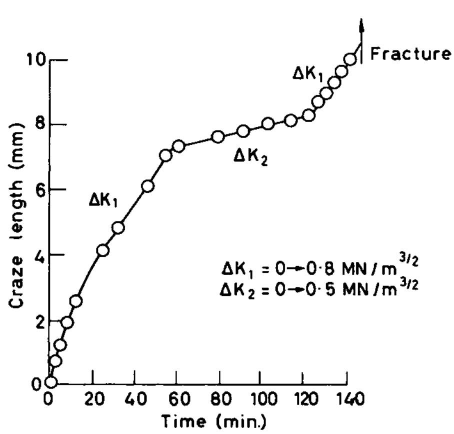

Fig. 14. Effect of changing load amplitude on craze propagation.

speeds were as would have been expected from tests at a single-loading condition. Again, the change in ΔK_0 is seen to reflect changes in the average void area, to which the craze responds as shown.

FREQUENCY EFFECTS

Because of the rate and temperature dependence of the properties of plastics, cyclic frequency can have a considerable effect on the results of tests, crack growth/cycle usually decreasing with increasing frequency although crack initiation occurs at lower K_c values.

Difficulties in cycling at "high" frequency on the conventional Instron (5×10^{-1} Hz is the limit) have allowed only a limited series of exploratory tests to be run so as to assess the possible consequences of varying the frequency of load application. Two brief series have been conducted. In the first case, tests were run as before on the Instron at frequencies of 10^{-1} to 5×10^{-1} Hz; and in the second, a few tests have been made using a prototype Instron "Dynamic Energy Cycler" machine at 30 Hz (using 6-mm specimens since it was difficult to control the machine at low loads).

Tests at Frequencies $10^{-1} \rightarrow 5 \times 10^{-1}$ Hz

All tests used 1.5-mm-thick specimens, and cycling ranges were for $\hat{K}_0 > K_n$. The same type of craze-growth pattern as before was obtained, craze speeds settling at a constant value until final fracture. The effect of test frequency on these final speeds is illustrated in Figure 15, which shows craze length–time curves for three frequencies, all tests being for the same loading condition. The curve for 10^{-1} Hz represents a lower bound since below 1.5×10^{-1} Hz, frequency had no obvious effect on the results (within experimental accuracy). The $\bar{K}_0$ concept discussed previously does, of course, give a satisfactory explanation of the difference between the constant-load and low-frequency results; however, it can be seen that for fre-

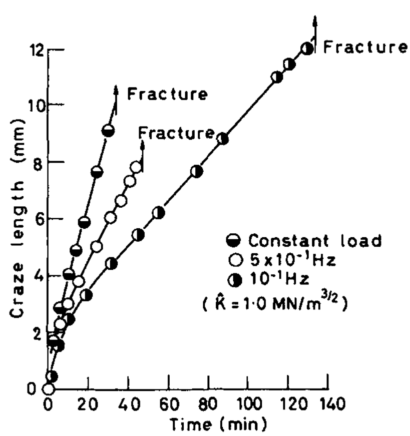

Fig. 15. Effect of frequency on craze growth: $\hat{K}_0$ = constant.

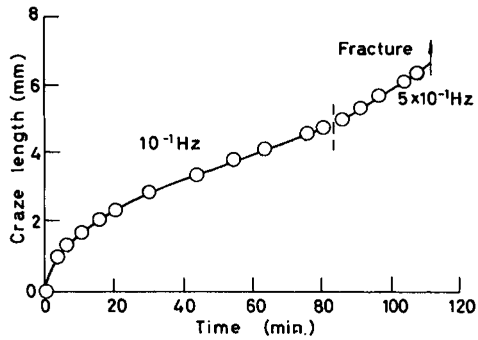

Fig. 16. Effect of changing frequency during a test.

quencies greater than 1.5×10^{-1} Hz there is a pronounced effect, the speeds increasing with frequency, so that the simple theory is inapplicable. The final speed value is still somewhat below that obtained in a constant load test (run at $K_0 = \hat{K}_0$) which could be considered in this context as being run at an infinitely high frequency. The frequency effect which is shown is certainly not due to normal variations in the tests, since the effect was observed in a single test in which the frequency was altered in the middle of the test. The result is shown in Figure 16 and clearly illustrates the increased growth rate produced at higher frequencies.

High-Frequency Tests (30 Hz)

Because of difficulties in obtaining time on a suitable testing machine, only a limited number of tests have been performed. The results on 6-mm-thick specimens showed that for the initial period of the test, the craze growth pattern is as before, the growth rate being greater than any previously noted, as expected from the trends in the lower frequency tests. However, the craze-growth pattern was not maintained for the whole of the test as before. After a few millimeters of craze growth, it could be seen that a crack was growing through the craze. When this crack approached the craze tip (within 300 μ), then, instead of fast fracture occurring—as in all previous tests—the crack and craze proceeded to grow together across the specimen until eventually fast fracture occurred at some undefined instability point.

The nature of the joint crack/craze growth portion of the test history is shown in Figure 17. It can be seen that the growth rate accelerated as the crack transversed the specimen, presumably because of the high ΔK value since the *load*-cycling range was held constant all through the test.

Discussion of Results

From the way in which the craze growth rate responds to changes in loading in both the variable static-load tests and the cyclic tests below 10^{-1} Hz, it appears that there is an apparently elastic responses to deformation of the material at the craze tip.

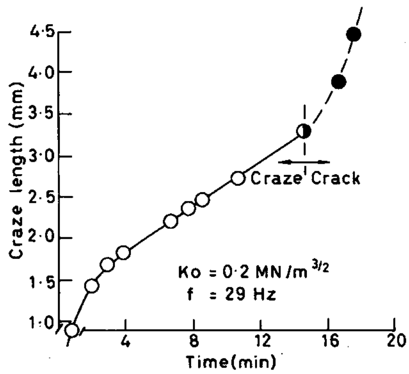

Fig. 17. Crack and craze growth at high frequency: $f = 30$ Hz.

At higher frequencies, it would seem that there is a pronounced viscoelastic response and that the deformations at the craze tip are not fully recoverable during the unloading half of the cycle. As a consequence, it would follow that the average void opening is greater, hence allowing an increased flow rate of the alcohol through the craze, thereby giving a higher craze speed. As the frequency is increased, the effect would be expected to become more pronounced until eventually the deformations are cycled so quickly that there is zero material response and the voids remain permanently open as in the constant-load tests.

A second factor affecting the results could be the effects of viscous damping. Kosten and Zwicker[7] have proposed a model for the viscoelastic behavior of a rubber foam, and they showed that viscous damping at high frequency can alter the flow characteristics of air flowing through the foam. Converting their argument to the case of alcohol flow in a craze it can be postulated that at low cyclic frequencies, the alcohol flow is slow and the viscous damping is correspondingly small. As the deformation frequency rises, the damping increases due to the increased flow of the environment through the craze pores. The viscous resistance increasingly constrains the environment within the craze and the flow rate diminishes, thereby leaving a reservoir of alcohol which is free to attack the unconverted plastic zone. (The decrease in flow rate will reduce the damping once more, and so the pattern would also be cyclic in nature.) Although this argument does have some merits, the two cases are not strictly analogous since the compressibility of the air will affect the results more in the rubber foam case.

It is thought that the viscoelastic response is by far the more important of the two effects.

CONCLUSIONS

The results of both varying static-load and ramp-loading tests at low frequency have shown that craze growth is again the precursor of failure in PMMA in a methanol environment. The effects of cyclic frequency can alter this pattern, but only when loading rates are of the order of 30 Hz, when a mixed mode of continuous crack and craze growth can occur.

At the low frequencies ($<10^{-1}$ Hz), it has been shown that the craze-growth rates are controlled by the "initial" stress intensity factor, K_0, and that the processes of end and side flow again govern craze speeds, as in the constant-load tests. The modified flow model has been shown to give excellent agreement with the rates of craze propagation at different levels of loading, thus lending confidence to the analysis. The fracture through the crazes macroscopically occurs in a slightly different manner under cyclic load, however, since the effects of void coalescence within the craze are much more readily apparent and cracks seem to propagate through the craze in a more irregular and haphazard manner.

Before a complete description of the effects of fatigue and environment can be obtained, much further work obviously needs to be done, in particular on the effects of cyclic frequency. However, as a first step, good progress has been made, and it would appear that there are no fundamental difficulties in interpreting data which cannot be overcome. In examining the effects of craze growth, the most complex situation has been attempted, since failure by crack growth in an environment should be capable of interpretation by the more conventional type of fracture mechanics approach which has been successful in explaining fracture in air. Whether cracking or crazing occurs, the effects of soaking on both the bulk and crack/craze tip material will obviously play an important role since conventional fatigue tests normally run for many times the time scales used in the present tests.

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