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Some observations on the craze growth kinetics of a cross-linked poly(methylmethacrylate)

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The kinetics of craze growth have been investigated in a commercial cross-linked poly(methylmethacrylate). A method has been developed for measuring the growth of a craze during flexural creep loading, and allows the variation of load during the growth measurements. Crazes were initiated using a 1:1 isopropanol/water vol:vol mixture as the test fluid, and the time dependence of their growth showed that the process is diffusion controlled. The effect of stress on the growth rate was determined for individual crazes, and was found to be a linear function under the conditions of the experiment. Thus the increase in length with time could be modelled by a three parameter equation, but these parameters were found to depend on the pre-conditioning of the plastic.

1. Introduction

The subject of crazing (and cracking) of polymers has received much scientific attention during recent years. The work leading to the current state of knowledge is quite extensive and has been reviewed by several authors [1–5].

The technological importance of crazing is usually associated with changes that occur in the mechanical properties of the material, such as toughness. Crazes appear to be very fine cracks and are easily detectable in glassy polymers since they scatter light. In transparency applications this scattering can cause the material to seem opaque under certain lighting conditions where the scattered light is much brighter than the transmitted light. At this stage of craze development visual rather than mechanical properties determine the replacement of the transparency. Though conditions for initiation of crazes are well known they are not necessarily the same as those required for growth. It is these latter conditions which may determine transparency service-lives.

The purpose of this paper will be to describe the development of a method to measure the kinetics of craze growth in transparent plastics under a flexural creep load. The effects of solvent, thermal treatment, environment (exposure to moisture) and level of stress are also discussed, and a simple empirical model is presented, which can be used to predict the service-life of the material under certain conditions.

2. Method and materials

2.1. Preliminary observations

A standard test method [6] has been developed to evaluate the aggressiveness of "liquid or semi-liquid compounds" towards given types of acrylic sheet under a flexural creep loading. Standards [7–8] have also been established for the resistance of acrylic materials to given solvents under similar test conditions. A "test method similar to [6]" has been used to determine the lowest stress required to craze a cross-linked poly(methylmethacrylate) (PMMA) for a variety of solvents [9]. Since no method could be found in the literature to measure craze kinetics under creep load in flexure, it was decided to extend the standard cantilevered beam test method for this purpose. A drawing of the text fixture and specimen dimensions are given in reference [6]. Specimens of 8 mm thick Plexiglas-55, a commercial cross-linked PMMA (Rohm and Haas) were used throughout this investigation.

Crazing kinetics can be considered as two

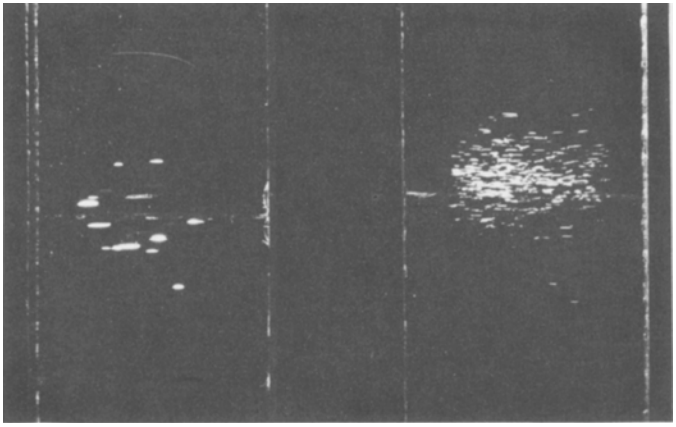

Figure 1 The difference in craze density typically observed for opposite sides of the same sheet of Plexiglas-55 tested at the same maximum outer fibre stress.

separate processes – nucleation and growth – and by monitoring the experiments with a video recorder it was hoped that both processes could be studied. Unfortunately problems associated with focusing on the curved specimen surface, making measurements from the "grainy" display, and parallax precluded the accurate determination of either nucleation or growth of more than a few of the many crazes which were present. For this reason, the technique was abandoned in favour of measurement of individual craze growth with a travelling microscope.

Some preliminary experiments were done with a variety of solvents to establish conditions which would lead to the growth of a few large crazes, rather than a large number of small ones. During this phase of the experimentation, two interesting effects were observed. The extent of crazing produced by a solvent at a given level of stress did not appear to be reproducible. In certain instances only a few large crazes would be formed, while in others a large number of very fine crazes would be obtained, as can be seen in Fig. 1. This difference was eventually traced to which side of the commercial sheet was being tested at that time. Another lot of material was tested, and similar results were obtained. Though this phenomenon did not indicate a difference in resistance to crazing all specimens were tested on a common side. In addition, the crazes obtained were not straight. It is generally agreed upon in literature [1, 2] that crazes grow in a direction perpendicular to the principal stress. We therefore expected with this type of loading to obtain straight crazes which could be measured easily. Experimentation revealed that the specimens had to be annealed by a procedure similar to that in [7] to obtain linear growth, and for this reason all specimens were annealed by this procedure after machining.

A mixture of 1:1 isopropanol/water by volume was selected from a series of liquids as the test solvent since it seemed to produce a small number of well-formed crazes. More aggressive liquids were found to produce larger numbers of smaller crazes.

During the measurement of preliminary test specimens, further problems became apparent. At the stress levels required to produce crazes within an acceptable nucleation time, individual crazes could easily be detected and measured. However, at relatively short time intervals, other crazes were found to nucleate and grow in the vicinity of the craze under study. Not only did these crazes have the potential to retard or stop the growth of the craze of interest, but they may also interfere optically in the measurement. In several cases fracture of the specimen occurred as well. These problems significantly reduced the amount of data that could be obtained from a given specimen. The effects of craze interactions on growth [10] and fracture [11] have been investigated and reported in the literature. It was decided for this type of study that the interactions caused by additional craze growth only complicated the problem and would be best avoided. Therefore, it would be desirable to further limit the nucleation of crazes. Since the test solvent had been selected as that which produced the minimum number of crazes, a reduction in the level of stress appeared to be the best method to attack the problem.

The kinetics of craze growth have generally been measured under a constant applied load, or local stress intensity where the crazes were grown from defects. Only in a few cases, for example in the work by Murray and Hull [12], was the load increased with time. In no case were we able to find that the load had been intentionally reduced during craze growth. A scheme was therefore devised in which the craze growth would be measured at reduced levels of stress. Not only would the technique reduce the occurrence of unwanted crazing but the dependence of craze growth upon stress would be obtained as well.

2.2. Test procedure

The test specimens as 25.4 mm × 180 mm bars were annealed at 120° C for 2 h, then cooled slowly to room temperature over a further 2 h. After annealing, the specimens were kept in a desiccator at 25° C, or conditioned at 25° C and 50% r. h. for a period before testing [7, 13].

Specimens were loaded to produce the desired outer fibre stress at the fulcrum of the test fixture [6], and after 10 min, solvent was applied to the surface and timing commenced. A thin sheet of Mylar film (0.03 mm) was used to cover this surface to prevent evaporation, and hence cooling, while still allowing the crazes to be visible. After the test solvent had been applied the specimens were observed at an angle with the aid of a high intensity light to determine the onset of crazing. As soon as the first craze was observed, weights were removed to lower the level of stress in the specimen. After some practice, bars could be produced with only one or two crazes growing in them. The maximum length of the craze parallel to the surface was measured as a function of time. If the craze did not grow above the fulcrum of the loading fixture, the outer fibre was calculated by linear interpolation between the maximum stress at the fulcrum and zero stress at the point where the bar was loaded [14]. The craze growth did not appear to be influenced by the presence of another craze in the specimen if separated by at least 2 mm.

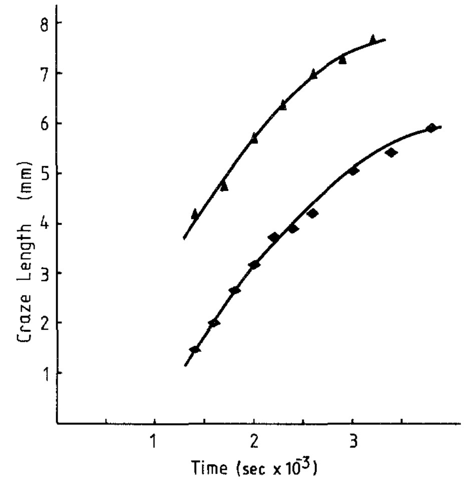

Figure 2 Variation of craze length with time for two crazes grown at different outer fibre stresses. ▲ 29.0 MPa, ♦ 26.1 MPa.

3. Results and method of analysis

The data for two crazes grown at two different levels of stress are given in Fig. 2. As can be seen from the data, the craze growth becomes non-linear in both cases. These experimental data were fitted by use of linear regression analysis [15] to several models which have been used to describe creep and craze behaviour in plastics. The results can be seen in Table I: L is the length of the craze in millimetres, t is the time in seconds, m and b are the parameters obtained from the regression analysis, and r is the correlation coefficient. The magnitude of this coefficient can have values from zero to one, and indicates the goodness of fit: the closer it is to one, the better the fit to the model.

As can be seen from the results in Table I, the data seems to be best fit with logarithmic and root time models, and a plot of craze length against root time is given in Fig. 3. For reasons discussed in a later section, the data were plotted against

TABLE I Parameters obtained from the fit of craze growth data in Fig. 2 to different models

Model	Stress (MPa)	m	b	r
exponential	29.0	3.42×10^{-4}	2.73	0.97
$L = be^{mt}$	26.1	5.15×10^{-4}	1.00	0.93
logarithmic	29.0	4.41	−27.8	0.99
$L = m \ln t + b$	26.1	4.41	−30.4	1.0
power curve	29.0	0.763	1.68	0.99
$L = bt^m$	26.1	1.30	1.51	0.97
root time	29.0	0.189	−2.87	0.99
$L = mt^{1/2} + b$	26.1	0.180	−5.00	0.99

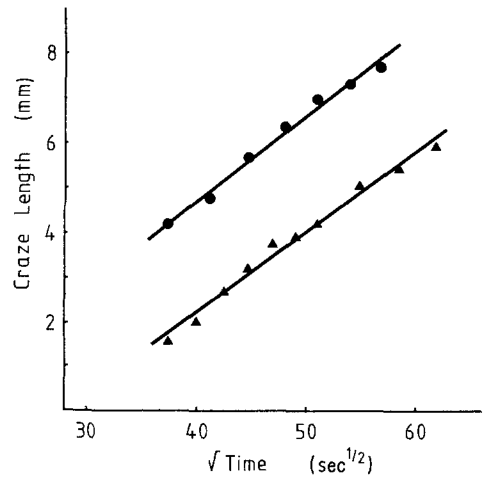

Figure 3 Craze length plotted against root time for two crazes grown at different stresses. ● 29.0 MPa, ▲ 26.1 MPa.

root time, rather than log time in subsequent analyses.

Since it was desired to determine the effect of stress upon the craze growth, the method was extended to incorporate successive reductions in load upon the specimens. Fig. 4 shows the type of data obtained by this technique. After 5 or 6 data points were obtained, the load was further reduced. As can be seen in moving from one section to the next on the graph, the craze appears to have stopped and then start again. This phenomenon was thought to be due to creep recovery in the specimen when the sample was unloaded, so creep measurements were made on a separate test specimen under identical unloading conditions. Once growth data had been obtained at this lower stress,

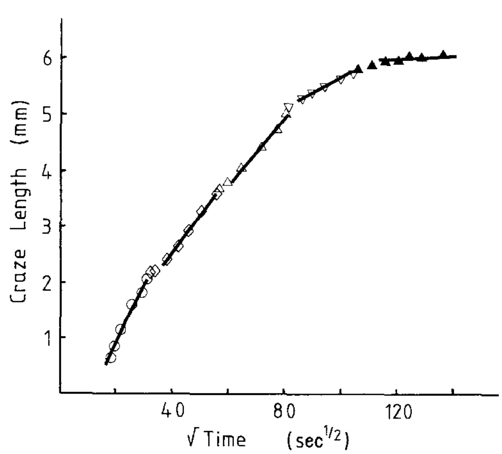

Figure 4 Variation of craze length with time for a single craze grown at different stresses. ○ 24.5 MPa, ◇ 20.9 MPa, △ 17.6 MPa, ▽ 14.3 MPa, ▲ 11.1 MPa.

TABLE II Coefficient of determination values for constants fitted to different models

Model	r
linear $m = a\sigma + b$	0.98
power curve $m = a\sigma^b$	0.97
hyperbolic sine $m = a \sinh(b\sigma)$	0.95

m is the regression coefficient from Equation 1, σ is stress.

the load was reduced in further increments as indicated in the figure until the craze was found to stop growing. As can be seen in Fig. 4, the data show good root time behaviour for each load interval. The slopes (m) from the root time regression analysis for different stress levels were fitted to three simple functions of stress often used to describe creep and craze data. The correlation coefficients (r) for the fit of these functions are shown in Table II. From the results it can be seen that dependence of the regression coefficient (m) upon stress is best described by a linear function at these low levels of stress near which the craze can stop growing.

In performing the above analysis on the data it became apparent that the regression coefficient (m) was also dependent on the history of the specimen. Accordingly, specimens were tested after annealing and conditioning for various periods at 25° C and 50% r.h. Both parameters in the linear function relating m to stress varied with the conditioning period.

Since PMMA is viscoelastic, as evidenced by its creep behaviour, it was suspected that the results obtained may be influenced by load history through strain hardening. In a separate experiment. the load was reduced immediately upon craze nucleation to that of the final load in the previous experiment. Again the craze stopped growing. The sample was kept wet with test liquid for 72 h and no further craze growth was obtained. In a further test of how the craze growth process could be interrupted, a specimen was crazed for a period of time, sufficient load was removed for 3900 sec to stop the craze growth and then reloaded. As can be seen in Fig. 5, when the data were plotted as though no interruption had been made, the craze growth rate appeared to be constant over the entire time period. Thus, it appeared that the craze

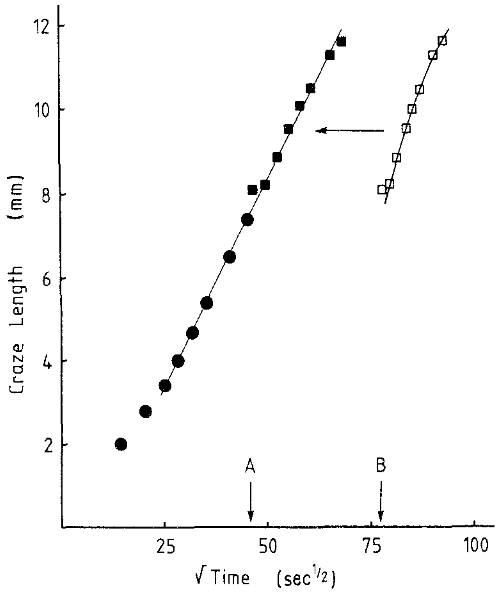

Figure 5 Effect of interrupting the growth of a craze on its growth rate. • grown at 28.6 MPa until time A; □ grown at the same stress from time B. Between A and B the craze length was constant at a stress of 15.7 MPa. ▪ calculated points allowing for the delay AB.

could be interrrupted for short time periods to obtain any desired load history.

4. Discussion

Various workers have reported different types of craze growth. Argon and Salama [16] found that the growth of crazes on polystyrene (PS) was linear with time when exposed to air under a variety of multi-axial states of stress. Priori *et al.* [17] also reported linear craze growth at constant temperature in polycarbonate (PC) exposed to a homologous series of *n*-hydrocarbons under constant strain in flexure. In contrast to this, many authors have reported that the growth rate decreased with time. Thus, Sato [18] reported that the length of crazes was proportional to the logarithm of time when PC film was stretched in air. Miltz *et al.* [19] also found that the craze length was proportional to the logarithm of time when the crazes were grown from a central hole in a plate of PC under stress in ethanol. Their results indicated that the solvent crazing process was controlled by diffusion (end flow) through the craze into the material. Marshall *et al.* [20] found, for crazes grown from razor blade notches in PMMA under load in methanol, that the craze length was proportional to root time under end flow conditions. However, for unnotched specimens of PMMA under load in methanol, Williams *et al.* [21] found that the craze growth was linear with time (constant speed) and was controlled by side flow of the liquid in which the diffusion distance remains constant during the growth.

In the current study of the surface crazing of PMMA in 1:1 isopropanol/water under flexural load, the craze growth was non-linear with time as can be seen in Fig. 2. Four models (Table I) were fitted to the length–time data, and the logarithm time and root time models were found to give the best results. During the experimentation, it was noted that the craze growth along the surface of the specimen appeared to be intermittent. The ends of the craze would seem to have periods of rapid growth to produce the shape in Fig. 6 and then of slow growth while the rest of the craze filled in to form the commonly observed semi-elliptical shape. Opfermann and Menges [11] have reported similar behaviour of craze growth for constant length at the surface. Once the regular shape of the craze had reappeared, the process

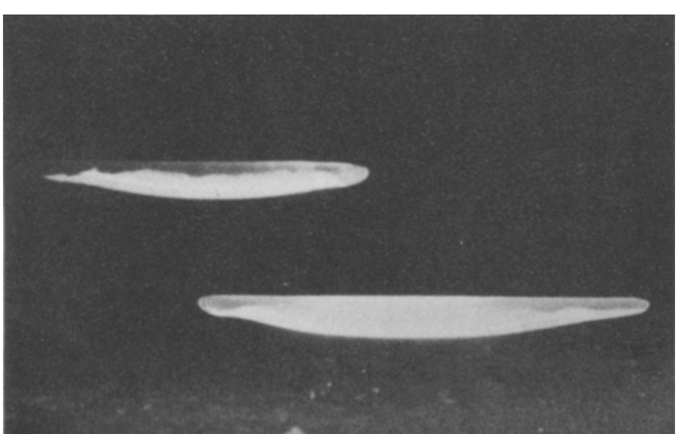

Figure 6 Craze showing the ends jutting out and distorting the semi-elliptical shape. Approximate maximum dimensions: parallel to the surface 5 mm; perpendicular 0.7 mm; craze separation 3 mm.

would repeat itself causing the oscillation of the data about the model as can be seen in Fig. 3, where the craze length is plotted against root time, and gives further evidence that the process is diffusion controlled. The models proposed by Williams *et al.* [21] for side and end flow of a fluid into a surface notch may explain this behaviour. For growth only along the surface, constant-speed growth is predicted, while for penetration, i.e. growth at constant length at the surface, root time behaviour would be expected. In addition, the craze growth occurred as long as the stress concentration at the craze tip exceeded the yield stress [22, 23]. Thus even crazes grown in flexure should show root time dependence for penetration, until the remote, applied tensile stress becomes too small, when growth would cease. From our observations, it appears that the overall process is controlled by the penetration of the craze into the material. For this reason we chose to plot craze length against root time rather than log time.

When the data were plotted against root time, linear behaviour was observed and the length can be represented by

$$L = m(t^{1/2} - A) \tag{1}$$

in which A^2 can be considered to be an induction time, while the regression coefficient m is equivalent to a growth rate constant.

To determine the effect of stress, a scheme was devised in which a craze could be nucleated at a high level of load, and then the load would be reduced in successive intervals during which the craze length would be measured as a function of time. Experiments showed that the craze growth could be interrupted for short periods of time without any detrimental effect upon the craze growth process. The craze length as a function of root time over five successive reductions of stress can be seen in Fig. 4. The initiation load for this growth was 28 MPa, which is the same as the minimum stress to craze this PMMA which has been annealed and conditioned for 2 days at 25° C and 50% r.h. Thus it can be seen in Fig. 4 that the craze can continue to grow at far lower stresses than those required to initiate it as might be expected for an activated process [17]. When the stress was reduced to 11.1 MPa, the craze stopped growing. The linear segments for each loading were analysed by linear regression to obtain values for m (Equation 1).

The dependence of the regression coefficient m upon stress was determined by fitting three models to the experimental data. The results in Table II indicate that the data are best fit with a linear model. Hence Equation 1 can be written as

$$L = k_\sigma(\sigma - \sigma_c)(t^{1/2} - A) \tag{2}$$

where σ_c would be the stress below which craze growth stops. Other workers have used the hyperbolic sine [16, 17] to describe the stress dependence and the method of fitting the model is given in reference [24]. The results reported in this paper were obtained at loads lower than that required to initiate crazing (i.e. those used by the other researchers), and these low loads in turn would reduce the applicability of the assumption used in [24] to obtain the regression analysis.

Since the results indicate that the craze growth depends linearly on stress, then the Boltzmann Superposition Principle [25] should apply, at least under conditions of continuous growth and at low stress levels. From Equation 2, the variation in length with time during which the load is changed will be given by:

$$L = k_\sigma [(\sigma_i - \sigma_c)(t^{1/2} - A) + (\sigma_1 - \sigma_i)(t - t_1)^{1/2} + (\sigma_2 - \sigma_1)(t - t_2)^{1/2} + \ldots]$$

where σ_i, σ_1, σ_2 etc. are the intial load and the other growth loads at times t_1, t_2 etc., when the loads were changed. Fig. 7 shows the fit to a data set by linear regression. The values of the parameters k_σ, σ_c and A derived from this analysis were also close to those obtained through applying the simpler method described earlier.

Creep data were obtained for a specimen which experienced the same history as that in Fig. 7. The variation with time of the deflection of the cantilever under the initial load was fitted to the Nutting equation [25]

$$\epsilon = B\sigma_i t^n.$$

Using the superposition principle, the deflections at the other loads were predicted and this is shown in Fig. 8. This shows that the experiments have been performed under conditions where the PMMA is a linear viscoelastic material. The interesting fact is that the cantilever did not stop deflecting with time when the craze stopped growing, nor stop growing when the deflection had apparently ceased due to the unloading. This result is similar to that reported by Mills [10] for poly(vinyl chloride). Mills discussed the point that if

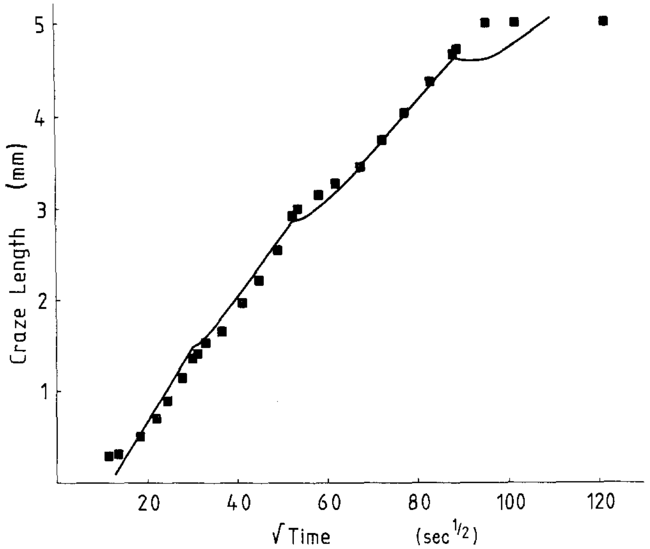

Figure 7 Calculated craze length plotted against root time using the Boltzmann Superpositional Principle. ■ experimental data.

craze growth were directly linked to the creep process then the kinetics of the two processes should be quite similar. The results of this investigation add further evidence that this does not appear to be the case.

In the course of these experiments it was observed that the values of the parameters obtained from the analysis of the stress dependence of the craze growth were dependent on the conditioning time before testing. The rate of growth of a craze, given from Equation 2 by:

$$\frac{\mathrm{d}L}{\mathrm{d}t} = \dot{L} = \tfrac{1}{2} k_\sigma (\sigma - \sigma_c) t^{-1/2} \qquad (3)$$

varied with the conditioning time, while the stress dependence of this rate

$$\frac{\mathrm{d}\dot{L}}{\mathrm{d}\sigma} = \tfrac{1}{2} k_\sigma t^{-1/2}$$

showed that k_σ decreased. During conditioning moisture is absorbed by the specimen, a measure of which is the square root of the conditioning time. Accordingly, the reciprocal of k_σ has been plotted against this in Fig. 9. Apart from the zero time point the others lie on a straight line. Thus the material appears to be more resistant towards craze growth as the water content increases,

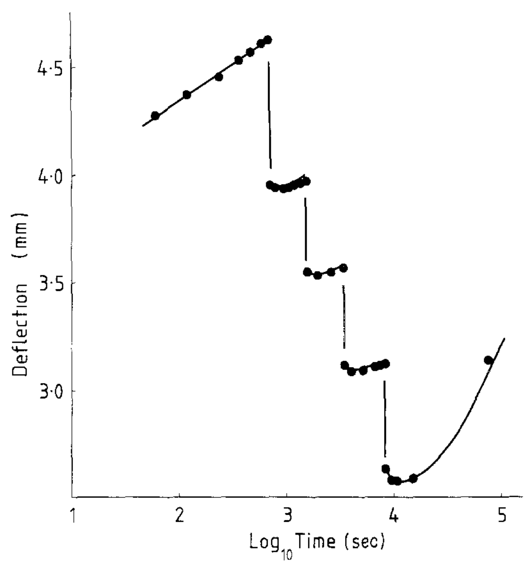

Figure 8 Deflection of the cantilever at different loads predicted by the Boltzmann Superposition Principle from the initial creep data. ● experimental data.

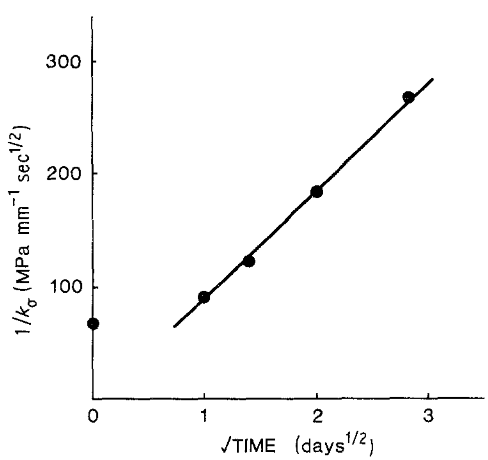

Figure 9 $1/k_\sigma$ (Equation 2) plotted against square root of the conditioning time.

contrasting with a previous observation [9] that the minimum stress to craze this PMMA falls linearly with increase in water content. However, the minimum stress at which the craze will grow also falls with water content, and thus the growth rate (Equation 3) will be greater at the lowest stress levels as this content increases.

5. Conclusions

The method outlined in this paper allows craze growth to be determined for individual crazes growing in the surfaces of transparent plastics at varying levels of stress down to that at which the craze stops growing. The craze length did not increase linearly with time, and since the craze growth appeared to be controlled by its penetration into the material (diffusion controlled) a root time model was chosen to represent the craze kinetics. The effect of stress was found to be linear, however, there is a stress below which the craze ceases to grow.

The effect of exposure to moisture was also found to be time dependent. A reciprocal-k_σ against root time model was found to give a good fit to the data.

Creep data showed that the bulk creep behaviour of the material did not solely control the crazing behaviour, whereas the root time effects seen in the craze growth and effect of exposure indicated that diffusion played an important part in the process.

More experimental work is required to resolve and explain the differences in results that are obtained with different test conditions.

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