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Effect of stress and temperature on dry craze growth kinetics during low-stress creep of polycarbonate

Part 1 *Experimental*

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Craze growth kinetics in polycarbonate are studied over a wide range of stress and temperature. The delay time for appearance of crazing is found to vary with stress and temperature following a rate process equation. Activation energy and activation volume are smaller for crazing than for shear-resolvable yielding.

1. Introduction

It is a well-documented fact that apparently brittle fracture of glassy polymers is associated with the previous growth of crazes and the ductile fracture of one of them [1–19]. Also, as the subsequent fracture of the specimen is extremely rapid, the major part of its lifetime is taken up by craze growth [20]. A thorough study of craze formation and growth kinetics would, therefore, be a useful start towards a better understanding of the brittle fracture process in glassy polymers. However, it appears from a literature survey that work is mostly concerned with crazing in an active environment [21–28]. Studies of dry crazing kinetics have only been carried out over narrow ranges of test temperatures and stresses or strain-rates [20, 29–31].

The present work is concerned with crazing kinetics of dry polycarbonate submitted to creep over a wide range of temperatures and strain-rates.

2. Experimental

Creep tests were conducted on polycarbonate specimens at five temperatures ranging from room temperature to 100° C. Such tests were preferred to tensile tests for the following reasons. Firstly, as crazing kinetics are very sensitive to stress level [20, 21, 29–33], it was felt that creep tests would be easier to interpret than tensile tests. Secondly, loading conditions in practice are closer to low-stress creep than to the relatively high strain-rate conditions encountered during a tensile test. Thirdly, it was necessary to use rather low stress levels in order to observe craze growth easily, even during the rapid growth stage following initiation. The highest applied stress at any temperature was approximately 90% of the tensile yield stress at a deformation rate of $10^{-5}\,s^{-1}$.

Polycarbonate was chosen as the test material because its high transparency, together with the possibility of formation of large crazes, make craze growth easy to follow. A commercially available polycarbonate (Makrolon, Bayer), in 2 mm thick sheets was used. Samples with flared ends and a variable cross-section, allowing several stress-levels to be studied during the same test (Fig. 1), were cut out of the sheet. In order to avoid craze or crack initiation from the machined edges, these were polished down to grade 000. Groups of two light scratches 2 mm apart were used as bench-marks for strain measurements, and to enable recognition of particular areas of the samples.

Specimens were not submitted to any thermal

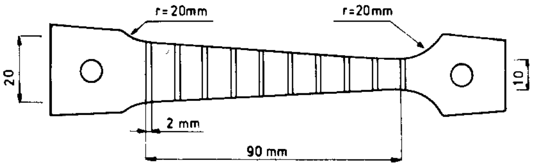

Figure 1 Creep specimen with variable cross-section.

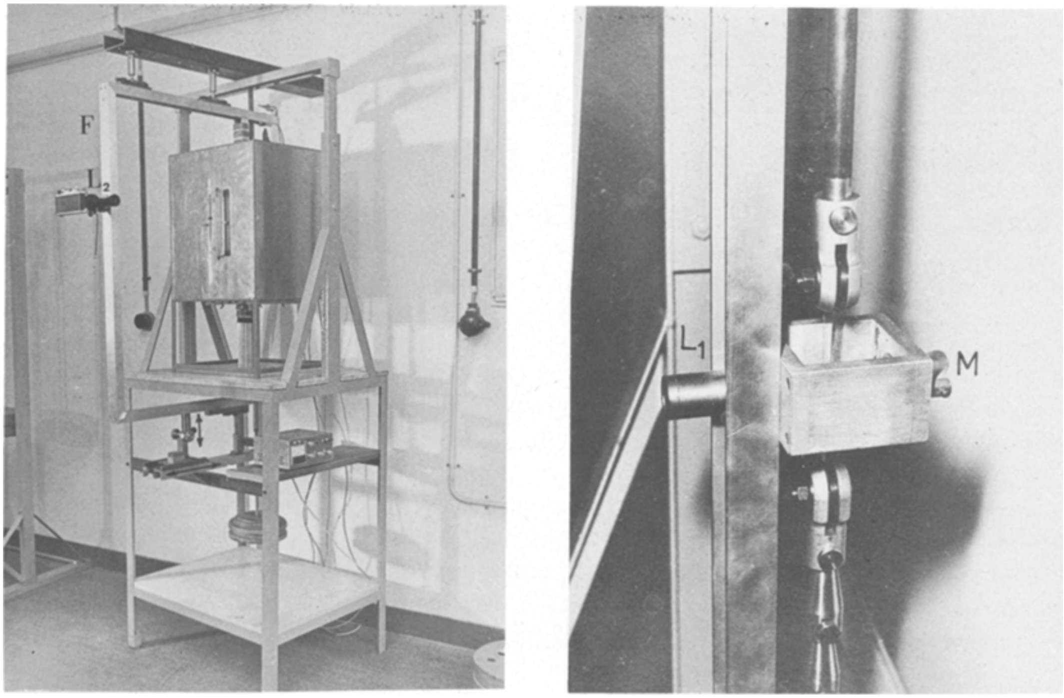

Figure 2 Apparatus for loading and observation of specimens.

treatment prior to testing, as it was felt that ageing might then occur during the test, affecting craze kinetics. Results of only one specimen at each temperature are given, as it was found that use of several specimens led to increase, rather than decrease, of data scatter.

The apparatus shown in Fig. 2 was used to load and photograph samples inside an environmental chamber. These were viewed in transmitted light, by means of an objective lens L_1 near the sample and an ocular L_2; lighting was ensured by a source S outside the environmental chamber and a mirror M behind the sample. Movement of the frame F holding the mirror and lenses was possible in two directions: horizontal for focusing and vertical to enable viewing of predetermined areas of the sample.

Photographs were taken of each area at times determined by a logarithmic time-scale of ratio 1.5 to 2. Tests were generally stopped after 4 to 6 weeks, after which time craze growth became extremely slow. Individual lengths of all crazes in each area were measured as a function of time from photographs such as those in Fig. 3. If craze density was high, no more than eight non-interfering crazes were measured.

Surface replicas of samples were made after unloading, and were examined in transmission electron microscopy. The replicating agent was polyvinyl alcohol, and the second-stage replicas were carbon with chromium shadowing. A few samples were examined in the scanning electron microscope. Owing to charging, samples could not

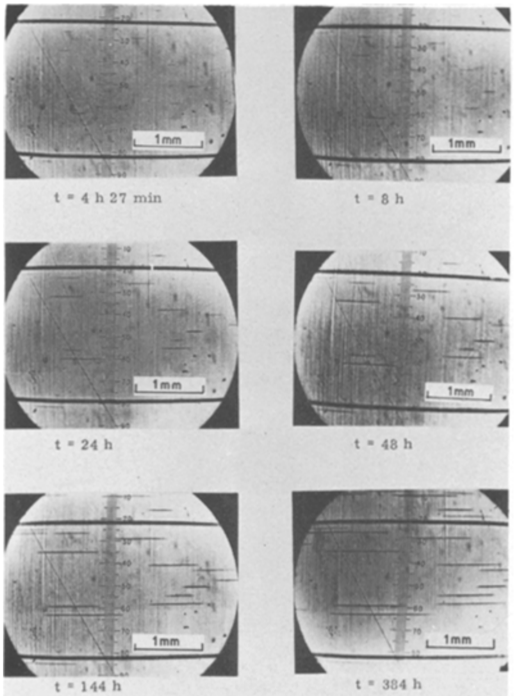

Figure 3 Series of photographs showing craze propagation. The thick horizontal lines are bench marks (see Fig. 1). Testing conditions $\sigma = 3.36\ \mathrm{kg\ mm^{-2}}$; $T = 60°\ \mathrm{C}$.

be examined directly, even after coating with aluminium, and it was preferred to use aluminium-coated one-stage gelatin replicas. Some gelatin replicas of specimens under stress were also examined, in an attempt to observe thickness variation during craze growth.

3. Results

3.1. Observations of craze growth

Individual craze lengths (l) were plotted against log time for various testing conditions. Such plots were generally linear (Fig. 4a) except occasionally during the initial stage of growth (Fig. 4b). Craze stabilization, such as has been observed by Sato [31], seldom occurred at the stress levels used in our tests; when it did, it could in all cases be attributed to onset of general yielding.

The linear parts of plots such as those of Figs. 3 and 4 can be defined by two parameters, the slope l_0 and the time-axis intercept or delay time for crazing t^*, which is not necessarily identical to the initiation time t_i (Fig. 4b). It was found that l_0 was slightly larger at longer delay times, whereas no significant variation with temperature was found. An average value was 250 μm. On the other hand, delay times were found to rise with decreasing stresses and temperature. This variation was systematic, although somewhat clouded by the scatter which is characteristic of crazing phenomena. It was therefore felt that the Eyring theory of rate processes could be applied to the data, using the following equation:

$$\frac{\sigma}{T} = A\left(\frac{Q}{RT} + \ln 2C - \ln t^*\right) \qquad (1)$$

where Q is the activation energy, C a characteristic time constant and A is proportional to reciprocal activation volume. A plot of the ratio of applied stress to absolute temperature, σ/T, against log t^* is given in Fig. 5 for a test temperature of 20° C.

Values of A, Q and C were determined in the following manner. At each temperature, a straight line was fitted to the data by the least-squares method. The average value of the slopes of these lines was taken as A. A set of parallel straight lines of slope A was then fitted by the least-squares

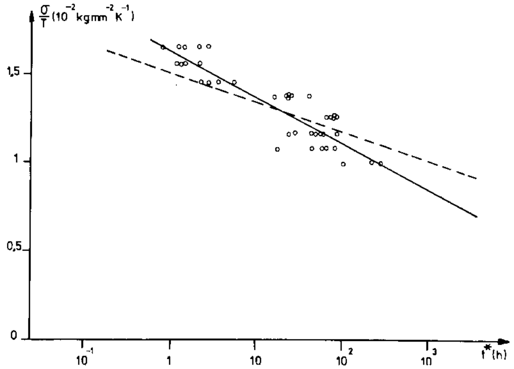

Figure 5 Variation of delay time for crazing with ratio of applied stress to temperature at 20° C. Dotted line: best fit to data. Full line: best fit to data having $A = 7.34 \times 10^{-4}$ kg mm^{-2} K^{-1}.

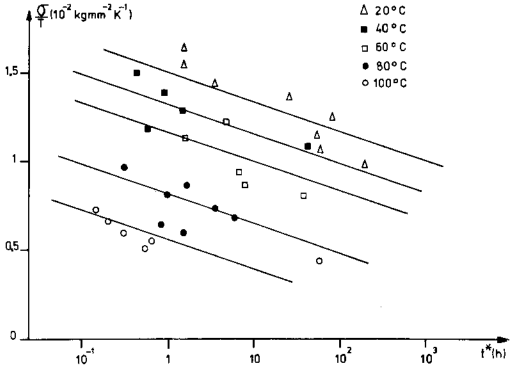

Figure 6 Variation of delay time for crazing with ratio of applied stress to temperature. Straight lines are best fit to data having $A = 7.34 \times 10^{-4}$ kg mm^{-2} K^{-1}.

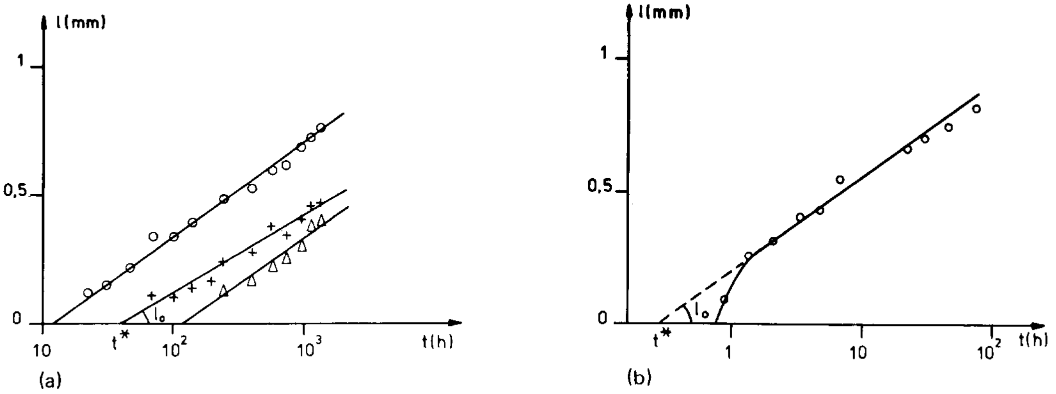

Figure 4 Craze propagation in polycarbonate. (a) $\sigma = 2.69$ kg mm^{-2}, $T = 60°$ C; (b) $\sigma = 2.24$ kg mm^{-2}, $T = 80°$ C.

method to the data obtained at all temperatures. On Fig. 5, the best fit to the data is shown as a dotted line, and the best fit having slope A as a full line. The horizontal shift between these lines gave values of the activation energy, and C was found from the log t^* axis intercept. Individual and average values of A, Q and C are given in Table I. Fig. 6 shows data obtained at all temperatures, together with the set of parallel straight lines defined above.

It should be pointed out that, because of the wide data scatter, it is not proven that appearance of crazing is due to an activated rate process, but only that it is consistent with Equation 1.

TABLE I (a) Parameters for crazing in polycarbonate

T (°C)	$10^4 A$ (kg mm^{-2}K^{-1})	Q (k cal mol^{-1})	$2C$ (sec)
20	11.64	22.6	2.2×10^{-8}
40	5.25	22.1	2.1×10^{-8}
60	8.21	56.5	2.1×10^{-8}
80	6.12	46.3	1.1×10^{-27}
100	5.44		1.5×10^{-27}

Average values: $A = 7.34\ 10^{-4}$ kg mm^{-2}K^{-1}

$$\left.\begin{array}{l} Q = 22.4 \text{ k cal mol}^{-1} \\ C = 10^{-8} \text{ sec} \end{array}\right\} \quad T \leqslant 60° \text{ C}$$

$$\left.\begin{array}{l} Q = 51.4 \text{ kcal mol}^{-1} \\ C = 0.65 \times 10^{-27} \text{ sec} \end{array}\right\} \quad T > 60° \text{ C}$$

(b) Parameters for yielding in polycarbonate (from [36])

$A_y = 4.16 \times 10^{-4}$ kg mm^{-2}K^{-1}
$Q_y = 75.5$ kcal mol^{-1}
$C_y = 10^{-31}$ sec

3.2. Electron microscopy

A transmission electron micrograph of a surface replica of a crazed polycarbonate specimen is shown in Fig. 7. Penetration of replicating agent into large cavities in the craze caused a row of "stalactites" to build up along the midline of the craze. This confirms work by Beahan *et al.* who observed a row of cavities along the midline of crazes in polystyrene thin films [34].

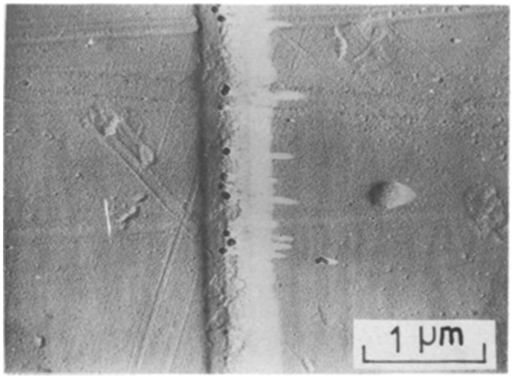

Figure 7 Transmission electron micrograph of a replica of a polycarbonate craze. Testing conditions: $\sigma = 2.20$ kg mm^{-2}, $T = 100°$ C.

Thickness of short crazes was found to grow slightly with craze length. Typical values were 0.18 μm for a craze length of 30 μm, and 0.4 μm for craze lengths greater than 200 μm. For longer crazes, no systematic variation of thickness with length was observed. Testing conditions were not found to influence craze structure nor thickness, in contrast with the variation with fracture stress of the thickness of the craze in which fracture occurs, observed in polystyrene by Murray and Hull [35]. However, this variation might be due to dependence of residual craze strain after fracture on fracture stress, rather than to variations in craze thickness prior to fracture.

4. Discussion

Parameters A_y, Q_y and C_y for tensile yielding in polycarbonate, given in Table I, were determined previously [36] from the variation of tensile yield stress σ_y with temperature T and strain-rate $\dot{\epsilon}$, using an Eyring equation:

$$\sigma_y = A_y\left(\frac{Q_y}{RT} + \ln 2C_y\dot{\epsilon}\right). \qquad (2)$$

It can be seen that the slope A is smaller for yielding than for crazing, but that the activation energy is higher. This is in contradiction with the observation by Haward *et al.* that slopes of plots

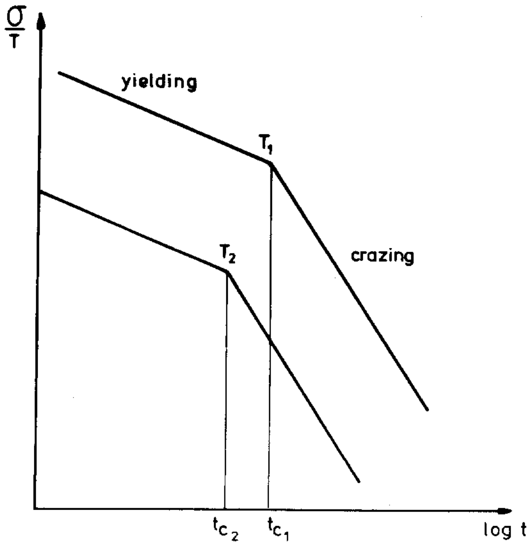

Figure 8 Variation of ratio of crazing or yield stress to temperature with delay time (schematic).

of crazing or yield stress of polystyrene against log strain-rate are identical [37]. However, if this were so, it would not be possible to explain why crazing does not appear before yielding at sufficiently high temperatures [38] or strain-rates [39]. From Fig. 8, which represents schematically the variation of crazing stress and yield stress with log delay time, it can be seen that for delay times shorter than t_c, yielding occurs before crazing, which therefore does not appear. This is possible only if the value of A for crazing is larger than for yielding.

Our values of the activation energy for crazing are close to the value of 37.4 kcal mol^{-1}, found by Sato for craze initiation in polycarbonate [31]. However, the latter is a stress-dependent apparent activation energy and, in fact, analysis of Sato's results using Equation 2 allows a true activation energy for crazing to be found, equal to 95 kcal mol^{-1}. This value is much higher than that which results from our data. However, Sato's tests were conducted at temperatures ranging from 95 to 115° C, and the difference could be due to the approaching glass transition. Our own results seem to indicate a rise in activation energy above 60 or 80° C.

It is possible to interpret the experimental results in this paper, if it is supposed that craze growth is due to creep of craze material [40]. A model, based on this assumption, leads to the following relation between applied stress and delay time for crazing [41]:

$$\frac{\sigma}{T} = sA_c\left(\frac{Q_c}{RT} + \ln 2C_c\frac{E_c}{A_cT} - \ln t^*\right) \quad (3)$$

where $s = \frac{\sigma}{\sigma_c}$; σ_c is the average local stress close to the craze; A_c, Q_c and C_c are parameters for yielding of craze matter, following an Eyring equation such as Equation 2; E_c represents craze material rubber elasticity.

This equation is formally identical to Equation 1, and therefore the activation energy for craze growth is the same as for creep of craze material. Experimental results show that activation energy for yielding of craze matter is much lower than that for uncrazed material. This difference might be connected with a decrease in viscosity of craze filaments, due to their small dimensions, as suggested by Kambour and Kopp [42].

5. Conclusions

Experimental results show that plots of craze lengths in polycarbonate against log time are linear; within the limits of experimental scatter, their slope is barely dependent on testing conditions. Variation of delay time for crazing with applied stress and temperature is compatible with an Eyring rate-process equation, and the values of the parameters A_c and Q_c for crazing, derived from this analysis, are distinct from those for tensile yielding. This must necessarily be so, if crazing only appears before yielding in a limited range of temperatures and strain-rates. It can therefore be stated that crazing is an entirely distinct process from general yielding.

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