The effect of environmental water on the craze growth rate of atactic polystyrene

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The effect of water at standard temperature and pressure on the rate of craze growth in polystyrene was studied with an elapsed-time photography method. Water was found to be a mild crazing agent for polystyrene, increasing the craze velocity by somewhat more than an order of magnitude at room temperature. The craze length was found to increase proportional to the square root of time, as is expected for transport-limited solvent crazing. The interface convolution model for craze growth and thickening was found to account well for the stress dependence of the craze front velocity in both the "dry" and the "wet" states, and for the total effect of water on the craze velocity. The stress dependence of the craze front velocity implies that craze fibrils grow by surface drawing and that water molecules interact only with the plastically deforming fringing layer of polymer at the craze borders.

1. Introduction

Early in the study of crazing, it was established that craze initiation and propagation depend strongly on the environment [1]. In a systematic study of craze initiation, it was found that the critical stress for initiation decreased dramatically in the presence of various organic vapours and liquids, especially in the case of good solvents [3, 4]. However, even in the case of very poor solvents, measurable decreases of the critical stress for craze initiation have been observed [3]. Furthermore, the collection of agents for environmental crazing has been extended to include agents with very small molecules, such as gases. At thermodynamically favourable conditions for solution, at low temperatures and/or high pressures, gases like CO_2, N_2 and O_2 have all been found to be crazing agents [5, 6].

Water, as an abundant compound of intermediate molecular weight between gases and organic liquids, is known to be a mild plasticizer for many glassy polymers; therefore, it is also possible that water could be a mild crazing agent. However, the effect of water on the crazing behaviour of hydrophobic polymers such as polystyrene is not known. The reason for this is that the removal of small amounts of sorbed water, especially from hydrophobic polymers, needs special experimental provisions.

Here, we report the results of a study of the effect of water on the crazing behaviour of atactic polystyrene, a relatively hydrophobic polymer. Specifically, the craze growth kinetics of atactic polystyrene in "dry" and "wet" conditions was measured by means of a prototype experimental apparatus. In this apparatus, crazes in polystyrene could be grown alternatively in a high vacuum without the interference of environmental water, or in a wet environment. It was found that environmental water is a mild crazing agent for polystyrene, and that in the presence of water the craze growth rate increases by at least an order of magnitude at room temperature

These new results are in apparent contradiction with the early qualitative observations of Hsiao and Sauer [7]. Possible explanations of those early observations are also discussed.

2. Experimental details
2.1. Material and sample preparation

An atactic polystyrene (Styron), manufactured by Dow Chemicals, with molecular weights of $M_w = 3.36 \times 10^5$, $M_n = 8.9 \times 10^4$, free of mineral oil, dyes and anti-oxidants was used[†]. Flat specimens with narrow gauge sections were machined from compression-moulded and previously well-annealed blocks of material. The specimen surfaces were metallographically polished to fine perfection in three stages. First, the specimens were thinned down to final thickness by hand grinding with a 600 grit constantly wetted silicon carbide abrasive paper. Then, the samples were polished with emery paper, wetted with a solution of 1/1000 parts of Photo-flow (Kodak) in distilled water. Finally, the samples were polished to final perfection with 0.05 μm alumina suspended in distilled water with 1/1000 parts of Photo-flow solution, on a metallographic polishing wheel. In the final polished state, the residual birefringence of the samples was checked with a Berek compensator technique on a Leitz Panphot metallograph, and was found to be negligible.

The gauge sections of the stress-free samples were indented slightly for controlled nucleation of crazes. A
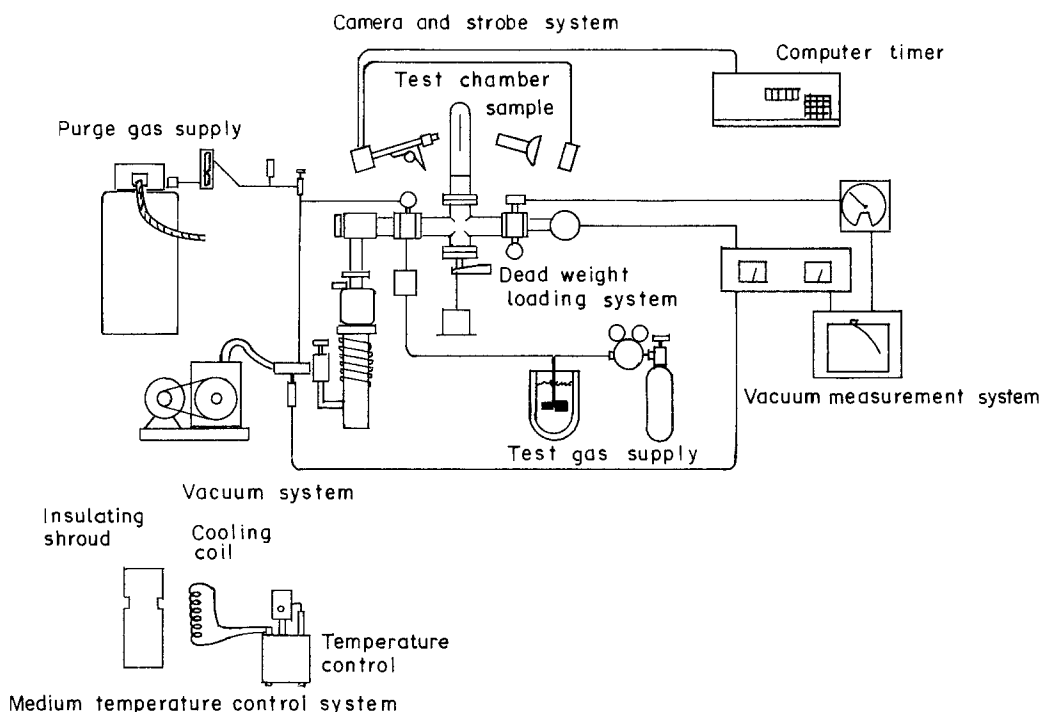
Figure 1 Apparatus for craze growth rate measurement.

diamond indentor of a Leitz microhardness tester was used for this purpose to create pyramidal indentations with a diagonal length of 30 μm and a depth of 6 μm. A series of indentations was made along the tensile axis of the specimen, 300 μm apart from each other. After the indentations, the specimens were left in laboratory air for 12 h. During this time, the residual stress resulting from the indented material misfit caused craze nucleation at the four corners of the indentation. Since no further growth of the crazes was observed after 24 h, it was concluded that these crazes removed nearly all of the initial residual stresses.

2.2. Craze growth test apparatus

The craze growth test apparatus (Fig. 1) was specially built by Hawkins [10] for an earlier investigation to control the environment around a sample crazing under constant stress. The sample was inserted into a slender loading frame and attached to it by means of two pins. The whole loading frame with the sample was enclosed in a high-vacuum glass chamber equipped with an optical window. Dead loads could be applied to the lower part of the specimen by means of a lever system that penetrated into the vacuum chamber through a bellows near the fulcrum point of the lever. A computer-controlled camera viewing the specimen through a microscope (magnification × 350) through the optical window was placed facing the flat indented gauge section of the sample. At specified time intervals, the computer triggered the camera and a strobe light to photographically record a series of pictures of the advancing craze with time. The precise length of the crazes was measured later from the negative by means of a low-power cathetometer (12 ×).

Constant temperature in each experiment was maintained by an annular thermal blanket placed around the glass vacuum chamber, through which a constant-temperature fluid was circulated. The temperature of the blanketing fluid was controlled by a Haake liquid-flow temperature controller. For temperatures around 4° C, an ice and water mixture was circulated through the thermal blanket instead of the oil.

2.3. Removal of environmental water

In order to remove environmental water, a special thermal cycle was utilized prior to the craze growth tests. For reasons to be explained, this cycle will be termed as "vacuum treatment". In this cycle the sample was placed in the vacuum chamber and was kept at 80° C for 24 h under a dynamic vacuum of 10^{-7} torr. Then, the sample was brought back to room temperature in the high-vacuum chamber. The physical ageing of the sample during this cycle was assessed separately, and will be discussed elsewhere [11], where it is demonstrated that it decreases the craze velocity by less than a factor of two.

3. Experimental results

In "vacuum-treated" samples, subsequently cooled down to room temperature, it was expected that any previously sorbed water would have been substantially removed. In samples prepared in this manner, the increase in craze length as a function of time was measured at room temperature at several different constant stress levels, in a vacuum of about 10^{-7} torr. A typical set of measurements is shown in Fig. 2 as the time interval A′–A. At Point A, laboratory air was let into the chamber to bring the sample to atmospheric pressure. No perceptible change in the craze growth rate under continued constant stress was found during the time interval A–B. This was in accordance with previous results where the samples were left to craze in dry air for much longer periods. Within this period of about 500 sec, although some gases were expected to have been sorbed by the surfaces of the specimen, no significant amount of water was expected to have been
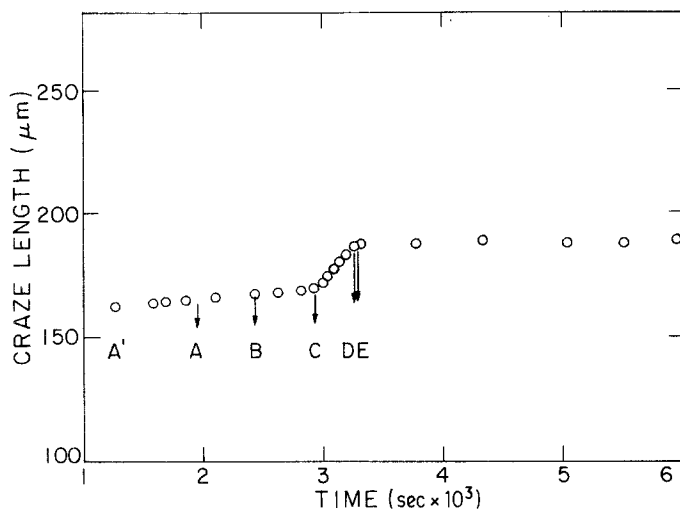
sorbed by the polymer as a whole, due to the low partial pressure of water and the short time. In order to study the effect of water it was introduced directly on the surface, by wetting it with a cotton swab dipped in distilled water (see Point B in Fig. 2). After an elapsed time of 500 sec, a sharp increase in the craze growth was recorded (see C–D in Fig. 2). Accelerated growth of the observed craze was stopped after 320 sec by removing the stress from the sample (Point D). Then, the sample was vacuum-treated once more to remove the water introduced. After cooling to room temperature, the same stress was re-applied to the sample and the craze growth against time was measured (D–E of Fig. 2). The rate of growth of the craze returned to its initial value prior to the exposure to water.

To further establish the above phenomenon a sample was given the same vacuum treatment, then the craze growth rate was measured for three stress levels at room temperature in a vacuum. The stress dependence of the craze growth rate under these conditions is shown by the filled circles in Fig. 3. After that, the sample was removed from the test chamber and dipped in distilled water, the excess water being removed with a paper towel. The craze growth rate was again measured for two stress levels at atmospheric pressure. The growth rate for the water-treated sample is shown by the open circles in Fig. 3. Although the craze growth rate decreases slightly in air with time, care was taken so that the error in the measurement was minimal, taking measurements after a standard elapsed time.

To examine the effect of temperature on the craze growth rate, the above experimental procedure was performed with an identical sample which was cooled down to 4.5° C. The closed and open triangles in Fig. 3 correspond to the "dry" and "wet" states, respectively, at this temperature. From Fig. 3, it is clear that the presence of water affects the rate of growth of craze in polystyrene at least by one order of magnitude, and that the temperature dependence of the craze growth rates in the "dry" and the "wet" states are almost of the same type.

4. Discussion

It is evident from the experimental results in Fig. 3 that water acts as a crazing agent in polystyrene at

standard temperatures and pressures. For strong crazing agents, the kinetics of craze growth at constant stress are time-dependent. This is due to the transport-controlled interaction of the agent with the material. Although the specific action of the crazing agent on the craze matter is not always clearly understood, in environmental crazing the craze length c usually follows a general square-root law of time [12], expressed as

$$c = \alpha t^{1/2} \qquad (1)$$

where α is a stress- and temperature-dependent proportionality constant and t is the elapsed time. The increasing length of a wet craze was recorded for a
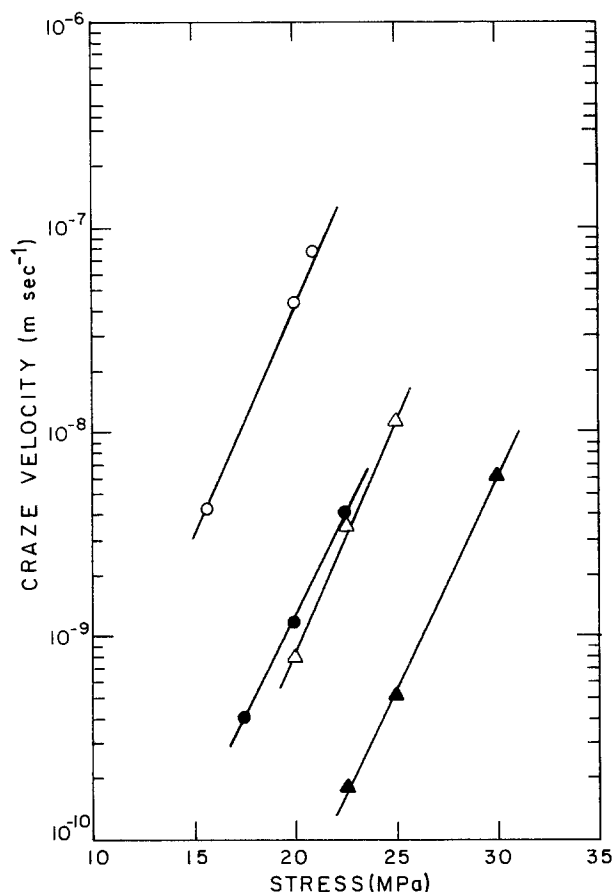

Figure 3 Stress dependence of craze growth rate for dry conditions (△) at 25° C, (▲) at 5° C, wet conditions (○) at 25° C, (●) wet conditions at 4.5° C.
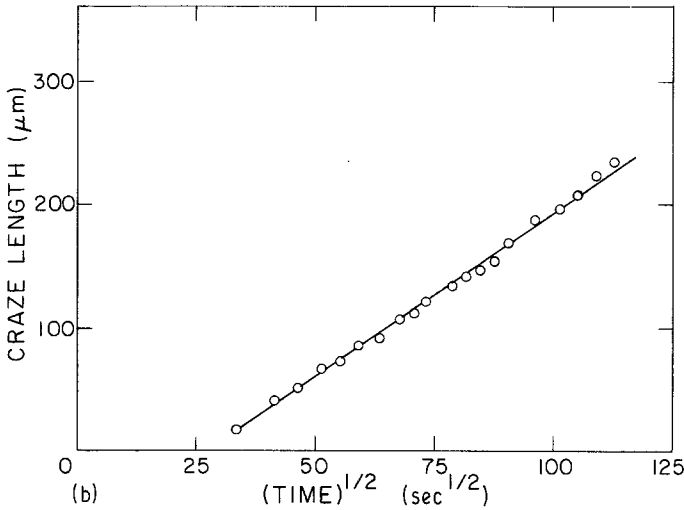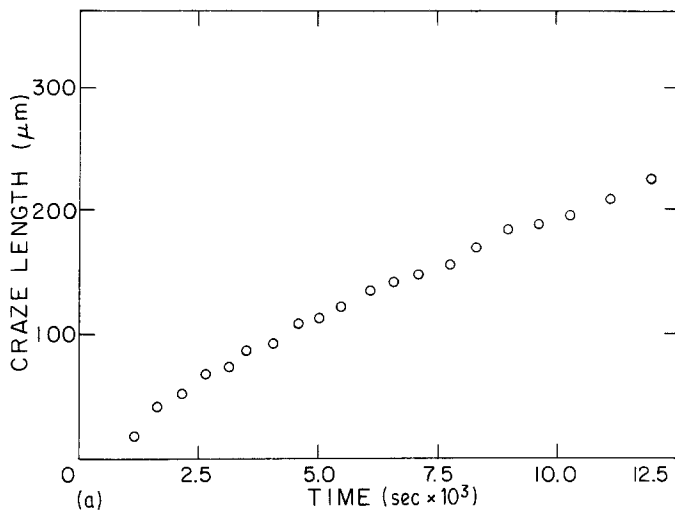
Figure 4 (a) Craze extension as a function of time under a stress of 20 MPa; (b) same craze extension as a function of square root time.

long period of time in an experiment at room temperature. In Figs 4a and b the length of the craze is plotted first as a function of time, and then as a function of the square root of time. A straight-line correlation was found with the square root of time, as is clear from Fig. 4b. This suggests strongly that water interacts with the craze matter in polystyrene, similar to the action of other crazing agents, with a time-dependent, transport-controlled mechanism.

Argon and Salama [9] have derived an expression for the rate of growth of dry crazes, by an interface convolution process occurring at the craze tip. According to this model, the craze velocity is proportional to the steady-state rate of advance of the craze tip, which in turn is a product of the plastic strain rate $\dot{\varepsilon}$ at the prevailing average craze traction and the steady-state opening displacement δ at a point behind the craze tip, where the craze tuft structure has just become established. In this model, the craze velocity is independent of time and is given as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\delta}{6} \dot{\varepsilon} \qquad (2)$$

The plastic strain rate $\dot{\varepsilon}$ is given in turn by the theory for plastic flow of glassy polymers by Argon [13]. Substituting the stress dependence of $\dot{\varepsilon}$ from the above theory in Equation 2, we get

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\delta}{6} \dot{\varepsilon}_0 \exp\left\{-\frac{A}{T}\left[1 - \left(\frac{Y}{\hat{Y}}\right)^{5/6}\right]\right\} \qquad (3)$$

where

$$A = \frac{3\pi\mu\omega^2 a^3}{16(1 - v)k} \qquad (4)$$

and

$$\hat{Y} = \frac{0.133}{(1 - v)} \mu \qquad (5)$$

In Equations 3 to 5, ω is the angle of rotation of a segment of a molecule or cluster of molecules having a radius a, constant for a given polymer; $\dot{\varepsilon}_0$ is a pre-exponential constant which varies little from polymer to polymer, k is Boltzmann's constant and μ, v are the shear modulus and Poisson's ratio, respectively. In Equation 3, Y is the yield stress of the polymer that must prevail at the tip of the craze, and is assumed to be equal also to the flow stress of drawn fibrils. Thus, in a long craze growing at a steady state, for which the average craze traction must be equal to the applied stress σ_∞, $Y = \sigma_\infty \lambda_n$ where λ_n is the effective extension ratio of the fibrils incorporating the effect of orientation hardening in the fibrils [9, 14].

Substituting the known parameters in Equation 3 we get, in a linearized approximation,

$$\ln \dot{c} = \ln\left(\frac{\delta\dot{\varepsilon}_0}{6}\right) - 0.942\frac{A}{T} + 6.5\left(\frac{\omega^2 a^3}{kT}\right)\lambda_n\sigma_\infty \qquad (6)$$

where we have applied a Taylor expansion to the

stress-dependent term and evaluated coefficients at a stress of 23 MPa, in the middle of the range of the data in Fig. 3. Equation 6 then gives a linear stress dependence for the logarithm of the craze growth rate with a level

$$L = \ln\left(\frac{\delta}{6}\dot{\varepsilon}_0\right) - 0.942\,\frac{A}{T} \qquad (7)$$

and a slope s of

$$s = 6.5\left(\frac{\omega^2 a^3}{kT}\right)\lambda_n \qquad (8)$$

It is interesting to note that although the slope s is independent of the elastic constants, the level L depends linearly on the shear modulus.

Two different possibilities for the action of water on craze growth must be distinguished. The first possibility is fibril creep, where sorbed water is expected to interact primarily with craze fibrils and not to affect the polymer in bulk. Fibril creep, under constant craze traction, would then result in craze thickening and a coupled increment of the steady-state tip-opening displacement, and consequently in an increase in the craze velocity. In the second possibility, the sorbed water interacts primarily with the bulk polymer in the border layer between craze matter and the surrounding bulk polymer. Localized plasticization or reduced surface tension would then change δ and/or A, and consequently the craze velocity. In the accentuated fibril creep mechanisms, the effective extension ratio λ_n is expected to increase, but in the plasticization mechanism involving accentuated drawing of fibrils out of the craze flanks, λ_n should be constant [2, 14].

From the identical slopes of wet and dry crazes in Fig. 3 and Equation 8 it is evident that λ_n remains constant, within experimental error, for both types of environment. Therefore, the mechanism of craze thickening involves the drawing of fibrils out of the craze flanks, irrespective of whether it occurs under wet or dry conditions. This is in accordance with many direct experimental observations [2, 15]. Even in strongly plasticizing environments of both liquid [16] and gaseous form [5], e.g. CO_2, crazes in polystyrene were found to thicken by enhanced drawing of fibrils out of craze flanks.

The mechanism of fibril drawing implies that water interacts with the fringing layer of bulk polymer at the craze borders, and not the drawn fibrils themselves. In this case, water molecules can either simply reduce the surface energy by adsorption on the craze surfaces or produce localized plasticization in the fringing polymer layer. In the first case, δ should actually decrease in proportion to an expected decrease in the inter-fibril spacing, and L should shift slightly downwards in proportion to $\ln\delta$, according to Equation 7. In the second case, δ is expected to increase and A is expected to decrease. The observed experimental change in L reflects a 1.6 decade change in craze velocity between dry and wet conditions. In support of the second possibility, dry crazes were observed to thicken substantially after the introduction of water. Measurement with a light microscope of the thickness of the craze, just behind the tip of the already photographed crazes,

gave roughly a ratio $b_{\mathrm{wet}}/b_{\mathrm{dry}} \simeq 4$. This change alone cannot account for the observed shift in L. Therefore, A and hence the shear modulus μ, must also have changed due to local sorption, which then directly results in local plasticization. Although the actual solubility of water in unstressed polystyrene is usually considered negligible, it is quite possible that the dilated and plastically flowing fringing layers of polymer at the craze borders are affected much more directly by the water, which permits slight penetration of the water and thus plasticization of the deforming layer only. This is in keeping with the known rejuvenation behaviour of aged polymers when they are brought to the state of plastic flow, where a flow-induced increase in free volume is expected to occur [17]. This can be further "catalysed" by the presence of a mild solvent.

A quantitative estimate of the required change in modulus to account for the craze acceleration would be of interest. It is easy to demonstrate that the required fractional decrease in the modulus $(\mu_1 - \mu_2)/\mu_1$, where μ_1 is the initial "dry" modulus and μ_2 is the "wet" modulus, can be obtained from Equations 7 and 8 as

$$\frac{\mu_1 - \mu_2}{\mu_1} = \frac{(L_2 - L_1)\lambda_n}{0.122\,s\mu_1} = \frac{8.2\,\lambda_n\ln(\dot{c}_2/\dot{c}_1)}{\mathrm{d}(\ln\dot{c})/\mathrm{d}(\sigma/\mu_2)} \qquad (9)$$

The slopes in Fig. 3 give $\mathrm{d}(\ln\dot{c})/\mathrm{d}(\sigma/\mu_2) = 646$. Thus, for an effective extension ratio $\lambda_n = 1.8$ [9] we determine that the fractional change in the shear modulus between "wet" and "dry" states of the craze need only be 0.0228, to account for the observed increase in craze velocity.

The temperature change of approximately $20°\mathrm{C}$ would theoretically change the slope s by only 7%. Experimentally, no change in slope could be observed. However, since δ and A are functions of temperature, a change in L is expected. The observed shift in L is almost the same as the shift due to "dry" and "wet" conditions. This temperature dependence of the craze velocity in the dry condition is a result both of the temperature dependence of the shear modulus appearing in A, and accelerated kinetics due to a change in temperature. Its effect on craze velocity is given by the second and third terms on the right-hand side of Equation 6.

Finally, although $4.5°\mathrm{C}$ is close to the freezing point of water, the increase in craze velocity due to its introduction on the surface is almost as much as that at $20°\mathrm{C}$.

The earlier report of Hsiao and Sauer [7], stating that "water seemed to have a healing effect on cracks" (to be reinterpreted to be crazes), is in apparent contradiction with our measurements reported above. The reason for this might be the fact that the refractive index change between dry crazes and polystyrene is much larger than the corresponding difference for wet crazes. Hence, wet crazes are expected to lose much of their "crack-like" appearance, as Fig. 5 indicates.

5. Conclusions

1. Water at standard temperature and pressure was found to be a mild crazing agent that increases the craze growth rate by an order of magnitude.
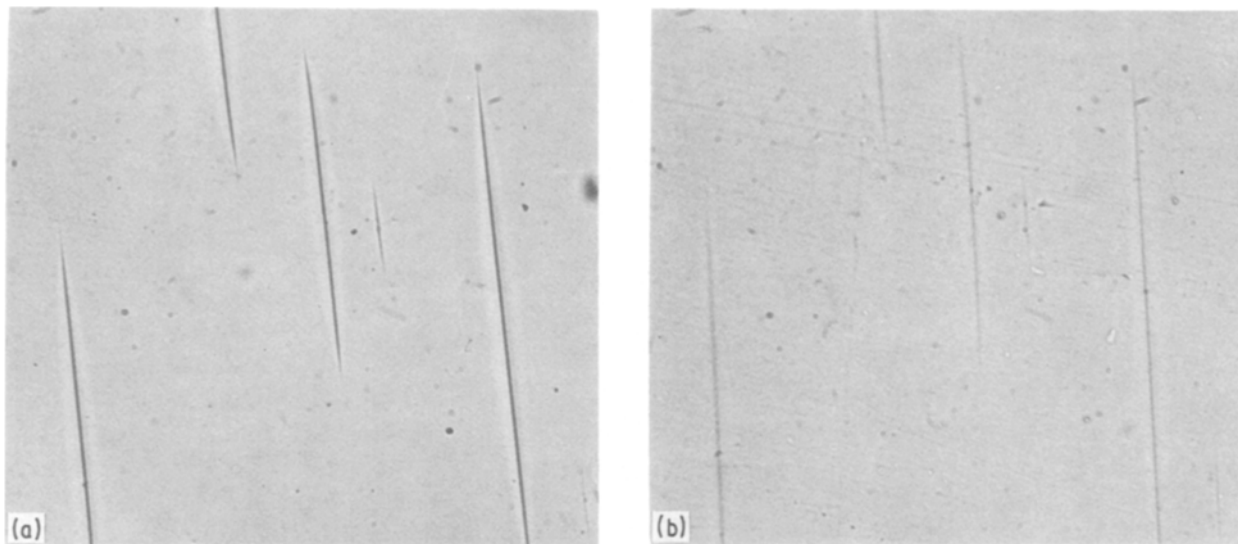
Figure 5 Changed appearance of crazes: (a) when they are dry, and (b) when they have been filled with water.

2. The craze velocity in a wet environment was found to follow an inverse square root law in common with the behaviour of all other solvent crazing phenomena.

3. The established theoretical models for craze growth and thickening by interface convolution indicate that the acceleration of craze growth in the presence of water is a result of a reduced plastic deformation resistance in the fringing layer of the craze, where polymer fibrils are drawn out of the craze flanks. The observed increase in craze velocity can be explained by only a 2.28% reduction in shear modulus in the fringing layer at the craze borders. Such a local effect due to water on the polymer in a state of plastic flow is quite likely.

4. The introduction of water into a dry craze is almost equivalent to a temperature rise of 20° C in its effect on the craze growth rate in polystyrene.

Acknowledgement

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