Crazes in solvent vapours at very low pressure: activation volume of fibril growth and breakage

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The fracture toughness and craze shape of a propagating single crack–craze in poly(methyl methacrylate) have been measured in very low-pressure toluene and cyclohexane gas environments by means of optical interferometry. In toluene, below a velocity of 0.01 mm s^{-1} the craze size increases to up to four times its value in air, whereas the fracture toughness remains almost identical to its value in air. Above 0.01 mm s^{-1} the crack–craze behaves as it does in air. The results have been analysed in terms of a stress-activated process, and activation volumes have been calculated. It has been shown that craze fibril growth and breakage mechanisms derive from the same activated process in air, but not in solvent vapours. The diffusion coefficient of the solvent vapour in the craze fibrils has been calculated from the critical velocity of 0.01 mm s^{-1}.

(Keywords: craze; poly(methyl methacrylate); interferometry; environment; gas)

INTRODUCTION

The influence of environment on the crazing and fracture properties of polymers is of major importance in the practical uses of these materials. There are many ways for the environment to induce fracture: by means of stress cracking, stress crazing, chain scission, chain crosslinking, etc. Therefore, environmental fracture has been widely studied, especially from the experimental point of view. A review of environmental cracking of polymers is given by Kramer[1]. Most work on environmental crazing has been done in liquid environments[2–4] (solvents and non-solvents of the material) or high-pressure gas environments, near the condensation pressure[5–7] (liquid nitrogen, argon, etc.). There are several categories of problems related to environmental effects, namely the influence of the environment on (i) craze nucleation, (ii) craze growth and (iii) craze fibril rupture. The crazing/rupture mechanism can be governed by the environment, depending on some parameters like the solubility coefficient of the liquid environment, its viscosity, or the sample loading conditions. It is now generally admitted that the environment acts on the craze fibrils like a plasticizer, enhancing fibril extraction from the bulk and the additional creep. Several experimental techniques have been used: the most common one uses simple standard fracture samples, with or without notches, and performs standard fracture tests in the studied environment. No measurements are made at the very tip of the crack, and only fracture toughnesses are recorded. More sophisticated techniques are required to study isolated crazes or the craze at a crack tip. Craze initiation has been followed optically by light reflection on the craze surface[8], and stress concentrations at the craze tip and crack tip have been measured by shadow optics[9], whereas the craze shape and structure have been measured by means of small-angle X-ray scattering (SAXS)[10], transmission electron microscopy (TEM)[11] and even holography[12]. Each of these techniques has some limitations: SAXS applies only to multiple crazes or to very large single crazes, TEM and low-angle electron diffraction (LAED) must be performed under vacuum, and holography applies only to very large crazes.

This paper will focus on the effects of very low solvent gas pressure on a single craze at the tip of a propagating crack, followed by means of optical interferometry. As a matter of fact, the experimental method is extremely sensitive and is able to detect much smaller environmental influences than other measurements of macroscopic fracture properties.

EXPERIMENTAL

Optical interferometry

The measurements shown below were performed by means of the well known optical interferometry technique. An attempt to use this technique for environmental crazing has been made earlier[13] with ethanol liquid crazes. The technique allows the measurement in real time of the craze shape at a running crack tip in a controlled environment. Compared to the other techniques, the advantages are the following: (i) the craze can be very short, (ii) its growth velocity can be as high as 0.1 mm s^{-1}, and (iii) the measurement is done on a single crack–craze system (easy micromechanics) in the environment. The weakness of the method lies in its poor resolution: the inner structure of the craze is not directly visible. The general principles of the method have been described elsewhere[14]. *Figure 1* shows the principle of the measurement.

The compact tension sample is introduced into a small environmental chamber having a window allowing microscopic observation (this chamber is usually used in the experiment to control the temperature during crack

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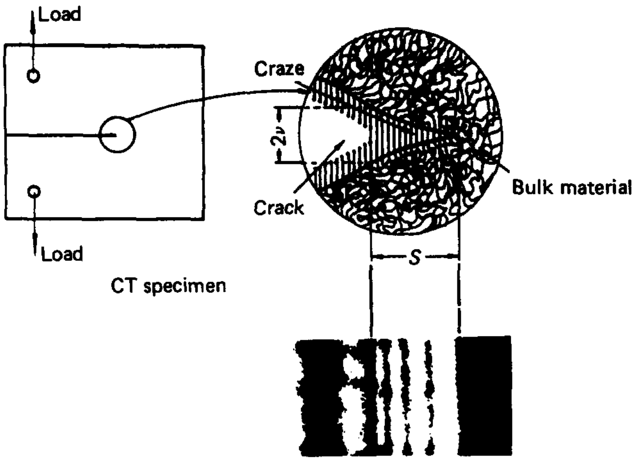

Figure 1 Principle of optical interferometry for crazes

propagation). A drop of the liquid mixture is introduced into the chamber, and the saturated vapour of the liquid is reached within a few minutes. Then the sample is loaded as usual in the experiment, and the craze propagation is observed as described earlier[15].

The experimental conditions were the following: The initial crack–craze system was produced in air under cyclic loading to get a very sharp crack and a single craze at its tip. Propagation in solvent vapour was done under static loading conditions, and recording of the interference pattern was done when the steady state of propagation was reached (no memory effect). Room temperature (no control) was about 20°C.

The samples used were small compact tension (CT) specimens. Each measurement in a given environment consisted of an interference pattern of the running crack–craze, with the following parameters: sample geometry, crack velocity and load applied on the sample. The load and sample geometry give the fracture toughness *versus* crack speed, and the interference pattern gives the craze shape and size *versus* crack speed. These are direct experimental results. The use of some craze micromechanics model applied on the craze shape gives the craze surface stress distribution[16]. The craze surface stress is the stress required to pull new material out of the bulk to allow fibrils to grow. After a certain time under stress, the fibrils may break, and the lifetime of the fibrils may be easily defined as the craze length divided by the crack velocity[15]. All these indirect experimental results may be subjected to criticisms related to the validity of the craze micromechanics. In the case of poly(methyl methacrylate) (PMMA), the simple 'constant craze surface stress' model (Dugdale model) works quite well. The craze surface stress distribution will be examined in a following paper, which will confirm the validity of the constant stress on the craze surface in PMMA even under a solvent gas environment.

Choice of the solvent vapour

It is well known that the nature and pressure of the environmental gas is quite important. In an unclosed system, the highest obtainable pressure of the gas is the saturated vapour pressure (or condensation pressure) of the liquid. To reach lower pressures, the liquid must be mixed with another liquid having a much lower saturated vapour pressure; the second liquid should not influence the crazing. Here silicone oil was used to reduce the pressure of the active gas. Henry's law gives the vapour pressure of a mixture of two liquids:

$$P_X = P_0 C_X$$

where P_X = partial pressure of X in the mixture, P_0 = saturated vapour pressure of pure X and C_X = concentration of X in the mixture (in weight).

The choice of the vapour pressure was made in the following way. First the craze was propagated under saturated solvent pressure. In this case, the craze is extremely long (several millimetres) and the crack–craze cannot be propagated and observed under the microscope. The solvent pressure is then decreased until the craze length reaches a value that is convenient from the experimental point of view (1–4 times longer than an air craze). The corresponding partial vapour pressures for toluene were found to be:

pure	29 hPa, good solvent of PMMA
5% solution	1.4 hPa
0.5% solution	0.14 hPa

(Note: 1 hPa = 100 Pa; atmospheric pressure = 1000 hPa).

To elucidate the influence of the chemical structure of the gas, another gas having a comparable physical molecular size, but a quite different structure and solubility in PMMA, has been used, namely cyclohexane.

There are two ways to create comparable situations for two gas environments: either by using the same absolute pressure, or by using the same relative pressure (relative to the condensation pressure). The cyclohexane has been used at 1.4 hPa, which is the same absolute pressure as for toluene and corresponds to a relative pressure between those of toluene at 1.4 and 0.14 hPa. The partial vapour pressures for cyclohexane are:

pure	86 hPa, bad solvent of PMMA
1.6% solution	1.4 hPa

Experimental results

There are two kinds of values derived from the experiment: first, direct experimental values, obtained without the use of any theoretical model, like craze length, craze width, crack velocity and fracture toughness; secondly, local material properties, obtained from the preceding results and the use of some models for the crack–craze tip micromechanics.

Direct experimental values. Some of these results have been published in a previous paper[17]. They will be presented here in addition to some new results, on the same plots.

(a) *Fracture toughness.* The values of K_{1c} as a function of the crack velocity can be easily measured by means of the apparatus. The crack–craze system must be propagated under the gas environment until the craze has reached its stationary size and shape. Then, the direct experimental values may be measured. *Figure 2* shows the fracture toughness *versus* crack velocity for various vapour pressures. In view of the usual scatter in K_{1c} measurements, the values of the fracture toughness can be estimated as being the same for all the environments shown on the plots. This is not surprising, because the vapour pressure of the active gas is very low. The only noticeable effect could be a very small increase of K_{1c} in the case of very slowly propagating cracks in the 5% toluene mixed vapours.

(b) *Craze size* (length and width). *Figures 3* and *4* show the craze length and width as obtained from the interference pattern recorded during the propagation. As opposed to the fracture toughness, the craze size is drastically affected by the 5% toluene mixture vapour at

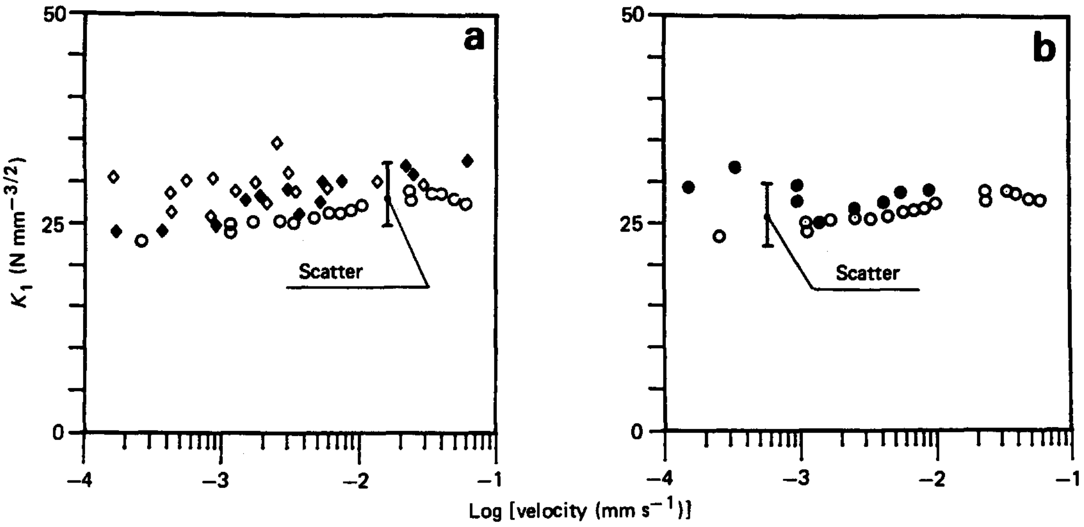

Figure 2 The fracture toughness of PMMA *versus* crack speed. (a) Toluene: (○) craze in air; (◆) 0.14 hPa; (◇) 1.4 hPa. (b) Cyclohexane: (○) craze in air; (●) 1.4 hPa. The scatter of K_1 values is usually rather high. Small scatter means that the measurements have been performed on the same sample

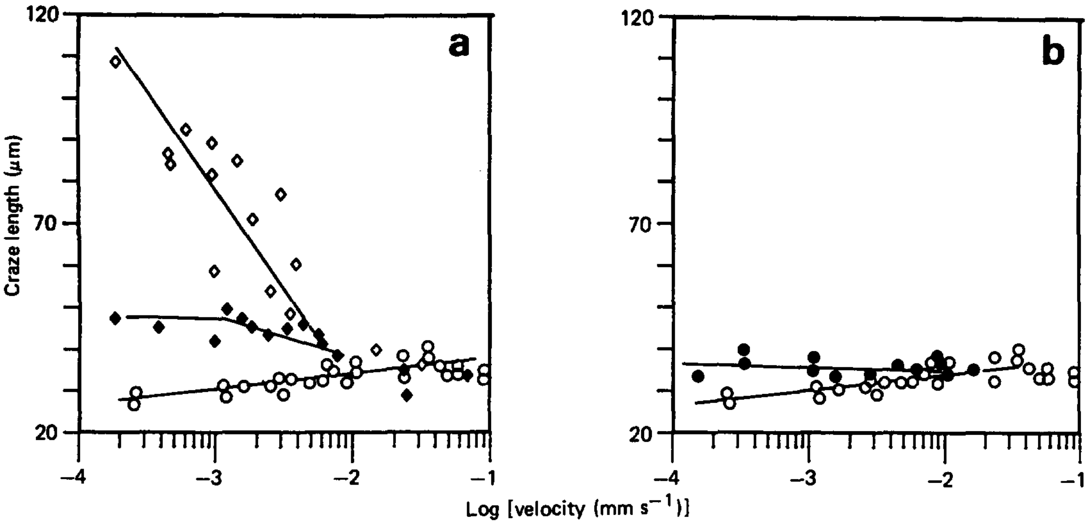

Figure 3 The craze length at the crack tip *versus* crack speed. (a) Toluene: (○) craze in air; (◆) 0.14 hPa; (◇) 1.4 hPa. (b) Cyclohexane: (○) craze in air; (●) 1.4 hPa

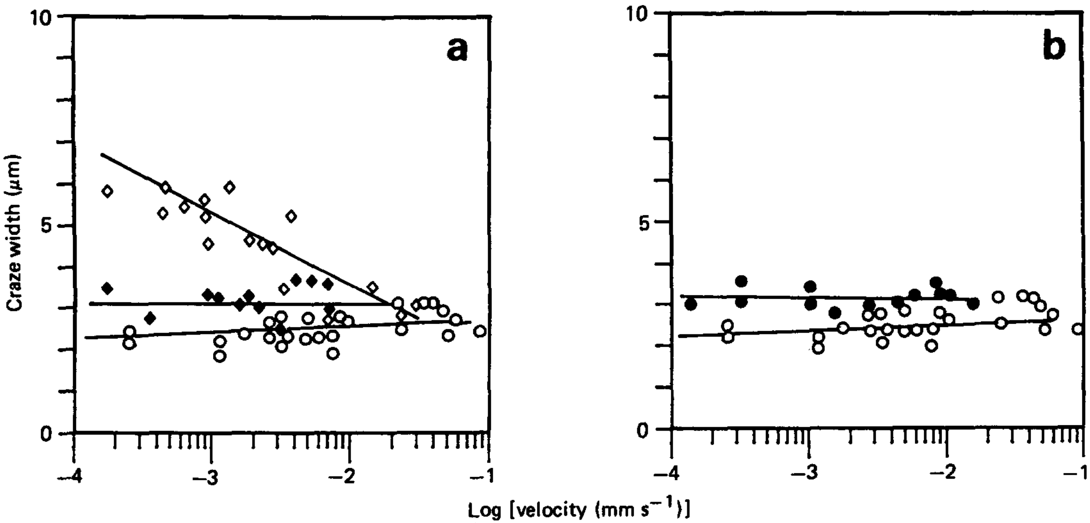

Figure 4 The craze width at the crack tip *versus* crack speed. (a) Toluene: (○) craze in air; (◆) 0.14 hPa; (◇) 1.4 hPa. (b) Cyclohexane: (○) craze in air; (●) 1.4 hPa

low crack propagation velocity. The craze size can be three times larger. The most obvious result of these figures is that the crack propagation velocity is one of the most critical parameters affecting the efficiency of the vapour. The vapour pressure of toluene is also an important parameter, as well as the nature of the gas: the influence of cyclohexane is negligible and that of toluene is important, at the same pressure. Nevertheless, the critical velocity of 0.01 mm s^{-1} seems to remain the same for both toluene pressures.

As mentioned earlier, for higher pressures of toluene, the increase of the craze size may be so dramatic that it never reaches a stationary length, preventing any meaningful measurements during propagation.

Craze material properties. As noted previously, some craze material properties may be inferred from the craze shape. The plots showing these properties are much more meaningful than the direct experimental values plotted previously. Nevertheless, they are calculated by means of some models whose validity might be discussed. In this paper it is assumed that the craze stress is constant along the craze boundary. This has been shown to be true for PMMA crazes grown in air. In a further paper, the craze surface stress profile will be analysed in detail, and the results show that it still remains constant along the craze boundary even in the case of solvent gas crazes.

(a) *Craze stress.* The craze grows (at least partially) by pulling new material out of the bulk. This mechanism requires a certain stress at the junction between the craze fibril and the bulk. This is sometimes compared to the propagation of a neck in a tensile test on ductile material. The value of the craze stress calculated here is actually a mean value over the whole interface between the craze and the bulk, neglecting the fact that the sum of the fibrils' cross-sectional areas is smaller than the craze boundary surface.

Figure 5 shows the craze stress *versus* craze propagation velocity. The fibrils' diameter being unknown, the lower mean stress on the craze surface does not necessarily mean a lower stress in the fibrils, whose diameter might be lower as well, but it may be understood as an important modification in the fibrils' extraction mechanism.

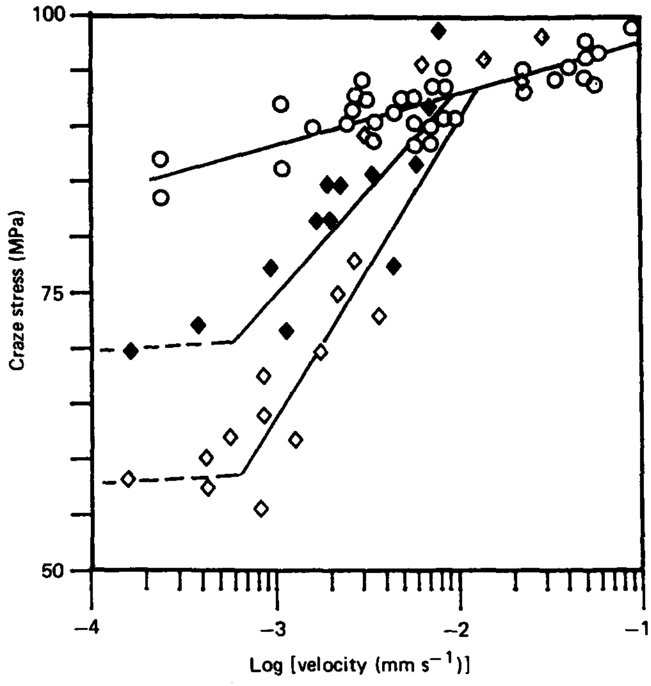

Figure 5 The craze surface stress calculated from the 'constant craze stress' model *versus* crack velocity in the case of toluene gas: (◇) 1.4 hPa; (◆) 0.14 hPa; (○) air

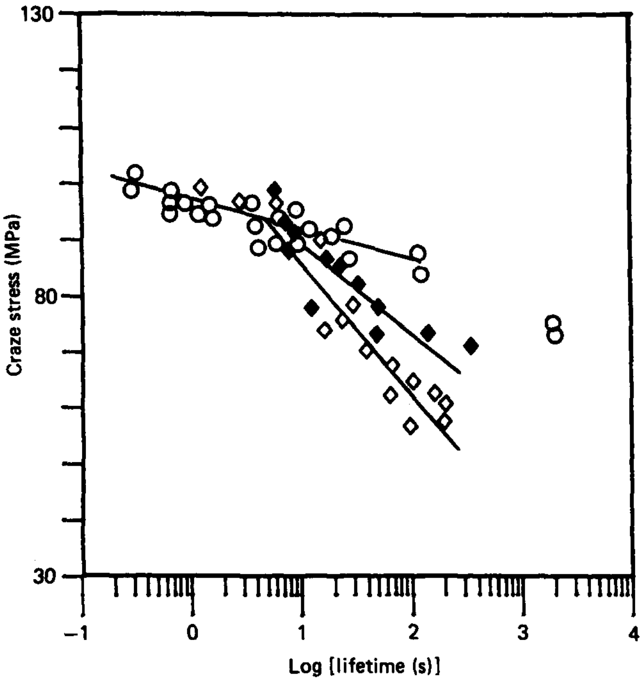

Figure 6 The craze fibril lifetime *versus* the average load applied on the fibrils in toluene gas: (◇) 1.4 hPa; (◆) 0.14 hPa; (○) air

(b) *Lifetime.* For the crack growing into the craze, one important feature of the fibrils is the time it takes them to break under a certain load. As defined in another paper[15], this time may be plotted as shown in *Figure 6*. As previously, toluene considerably affects the lifetime of the craze fibrils above a critical time of about 1 s. In air crazes in PMMA, it is usually admitted that the fibrils' diameter does not change significantly by additional creep before it breaks. In the case where the environment controls the craze size, this point of view might have to be reconsidered. Owing to their very high surface/volume ratio, giving a high efficiency of the solvent vapour, one could expect creep of the fibrils.

INTERPRETATION IN TERMS OF STRESS-ACTIVATED PROCESS

Activation volumes: theory

The effects of the vapours may be separated into two independent parts: first, on the bulk during fibril extraction, and secondly, on the fibrils themselves for additional creep before breakage. Both mechanisms (extraction and fibril creep and breakage) are plastic flow mechanisms. Earlier papers showed that both correspond to stress- and/or temperature-activated processes: the log(lifetime) *versus* temperature or stress as well as the log(craze growth) *versus* time or stress are straight-line plots, at least over a few decades[15,18]. Generally, the fracture velocity *versus* applied load or stress exhibits a threshold stress below which the process stops and above which the process is stress-activated.

Therefore, above the threshold, they may be expressed by means of an Eyring's law equation:

$$\dot{\varepsilon} = B\exp(-\Delta H/kT)\exp(V^{*}\sigma/kT) \qquad (1)$$

where $\dot{\varepsilon}$ may be the fibrils' extraction strain rate, the crack–craze velocity, or the inverse of fibril lifetime, T is the temperature, ΔH is the activation enthalpy, k is the Boltzmann constant, V^* is the activation volume and σ is the stress. This equation reduces to a simpler one:

$$\dot{\varepsilon}=E\exp(-\Delta H/kT)\exp(\sigma/\sigma_0) \tag{2}$$

where

$$1/\sigma_0=V^*/kT \tag{3}$$

will be called the 'normalized activation volume'. As the temperature is constant in this work, the first exponential term is a constant.

Using the same type of notation, the lifetime t (fibril effect) and the crack–craze velocity V_c may be written as functions of stress:

$$t=t_0\exp(-\sigma/\sigma_t) \tag{4}$$

$$V_c=V_{c0}\exp(\sigma/\sigma_v) \tag{5}$$

where $t=S/(\mathrm{d}a/\mathrm{d}t)=S/V_c$ (ref. 15), a is the crack length and S is the craze length.

By replacing t and V_c in $S=V_ct$, the craze length yields:

$$S=t_0V_{c0}\exp(\sigma/\sigma_v-\sigma/\sigma_t) \tag{6}$$

where σ_t and σ_v are the so-called 'normalized activation volumes' and will be the only ones used in further calculations.

By removing the stress in equations (4) and (5), the lifetime and crack–craze velocity may be expressed as a straight line:

$$\ln(t)=A\ln(V_c)+B \tag{7}$$

where $A=-\sigma_v/\sigma_t$ is a constant and $B=\ln(t_0)+(\sigma_v/\sigma_t)\,ln(V_{c0})$ is also a constant.

The above calculation, instead of being made with crack–craze velocity V_c, can be made with a more fundamental parameter, namely the fibril extraction velocity V_e. The Appendix shows the calculation with V_e.

The overall results are mainly the same, V_c being replaced by V_e, the activation volume σ_{ve} of the fibril growth is equal to σ_v. The constant factors are slightly different.

Particular case. If the 'activation volumes' σ_v and σ_t of both phenomena are the same and written as σ_0, the following conclusions can be pointed out from equations (6), (7) and (A7):

$$\ln(t)=-\ln(V_c)+\ln(V_{c0}t_0) \tag{8}$$

which means that the log(V_c) *versus* log(t) plot is a straight line, with a slope of −1 (see *Figure* 7), and

$$\begin{aligned} S&=t_0V_{c0}\\ T_c&=2V_{e0}t_0 \end{aligned} \tag{9}$$

(see Appendix), which means the craze length S and width T_c remain constant at different velocities.

It should be noted that very early experimental work on propagating crack tips in PMMA showed that the craze length at the running crack tip remained almost constant over eight decades of velocity and from −20 to 60°C[14,15]. The reason for that has never been elucidated. The constant craze length over a large velocity (or temperature) range means that the extraction and the breakage mechanisms have the same activation volume (or energy). Many materials exhibit a constant craze length at a running crack tip. Poly(vinyl chloride) (PVC) is a notable exception, showing a craze length decreasing strongly with temperature, and hence having two different molecular processes for fibril extraction and fibril rupture[14].

Independently of whether V_c or V_e is used, the main consequences of these equations are as follows: If the craze length increases with velocity (or equivalently with stress), the 'activation volume' of fibril extraction σ_{ve} or of velocity σ_v is smaller than that of fibril lifetime σ_t, and vice versa. The same conclusion can be deduced from the log(V_c) or log(V_e) *versus* log(t) plot. If the slope is equal to −1 the 'activation volumes' are the same. If the slope is less than −1 the 'activation volume' of the fibril lifetime is larger than that of the fibril extraction, and vice versa.

Activation volumes: discussion of the numerical values

As shown in the preceding paragraphs, the most important plots are craze length or width *versus* log(V_c) and log(V_c) *versus* log(t). Both will show the relative

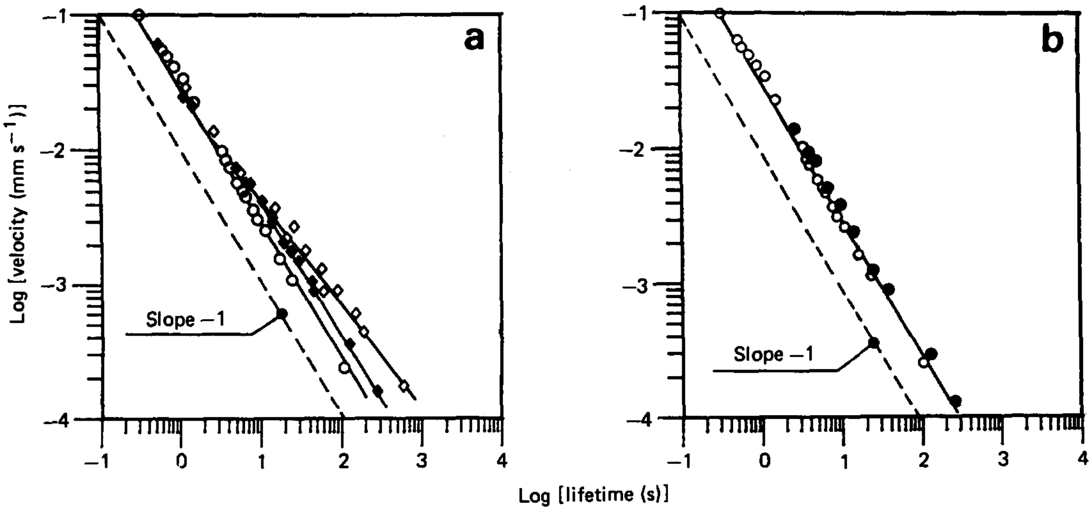

Figure 7 The fibril lifetime *versus* extraction velocity. (a) Toluene: (○) air; (◇) 1.4 hPa; (◆) 0.14 hPa. (b) Cyclohexane: (○) air; (●) 1.4 hPa

environmental effect on craze breakage and fibril extraction. On the other hand, Kramer proposed a simple model for diffusion-controlled craze growth[1]. Therefore, we shall point out the effect of solvent vapour on craze fibril extraction and their breakage, as well as the numerical values of the diffusion coefficient of the gas in the polymer.

Fibril extraction mechanism versus fibril breakage mechanism. The most interesting point in the comparison is that the mechanisms are the same in the case of a crack–craze system propagating in air, and differ notably in the case of a toluene vapour environment for low velocities.

A linear best fit on the plots of *Figure 5* shows that for craze propagation in PMMA in air:

$$1/\sigma_v = 0.53 \qquad \text{for fibril growth}$$

Figure 6 shows that for the fibril lifetime in PMMA in air:

$$1/\sigma_t = 0.51 \qquad \text{for fibril rupture}$$

This suggests that σ_v and σ_t are similar, and confirms the previous results[14] showing the invariance of the craze length *versus* crack–craze velocity in air.

In toluene vapour at 1.14 hPa pressure, we can make the following points. (i) Above a velocity $V_c = 0.01\ \text{mm s}^{-1}$, both mechanisms remain the same (the slope of *Figure 7* is equal to -1), and the activation volumes remain unchanged, showing that the vapour has no influence on fibril extraction or on breakage. (ii) Below a velocity of $V_c = 0.01\ \text{mm s}^{-1}$, *Figures 5*, *6* and 7 show that the mechanisms differ noticeably, the fibril extraction velocity becoming relatively high, showing a stronger effect of the vapour on fibril extraction than on rupture, and the activation volumes changing in the following way (from *Figures 5* and *6*):

$$1/\sigma_v = 0.083 \qquad \text{for fibril growth (toluene 1.14 hPa)}$$

$$1/\sigma_t = 0.10 \qquad \text{for fibril rupture (toluene 1.14 hPa)}$$

These values should be compared to the values in air: 0.53 and 0.51, respectively.

The difference between the activation volumes of the lifetime and fibril rupture is confirmed by the fact that the craze length and width are not constant in toluene vapours (equation (9)), as shown by *Figures 3* and *4*.

Figure 7 shows remarkably clearly how both mechanisms differ above a velocity of 0.01 mm s^{-1}, which corresponds to $V_e = 0.001\ \text{mm s}^{-1}$. The slope of the plot is quite perfectly -1 in air, -1 in 0.14 hPa toluene gas, notably different from -1 in 1.4 hPa toluene, and still perfectly -1 in 1.4 hPa cyclohexane. *Figure 7* is much more precise than any other plot in the paper: as a matter of fact, the main scatter has its origin in the K_1 values, affecting all further stress calculations. On the other hand, craze length and velocities are rather precise measurements. In *Figure 7*, only craze length and velocities are involved, leading to very low scatter.

Diffusion coefficient of the vapour in the material. Kramer showed in a very simple case the relationship between the craze growth velocity and the diffusion coefficient when the craze growth is diffusion-controlled and due to fibril extraction from the bulk[1].

In the case of a Fickian diffusion, the craze surface velocity yields:

$$V_e = (D/R_0)\ln[C_0/C(S)] \tag{10}$$

where D is the diffusion coefficient of the polymer (cm^2 s^{-1}), R_0 is the fibril radius, C_0 is the equilibrium concentration of the gas in the polymer at the surface, $C(S)$ is gas concentration at the creep zone boundary and $C(S)/C_0 = 0.5$; hence

$$V_e = 3 \times 10^5 D \tag{11}$$

(see ref. 1). *Figures 3–6* show that the limiting crack–craze velocity V_{lim} for showing an effect of the vapour is about 0.01 mm s^{-1}, corresponding to a craze surface velocity V_e of about 0.0001 cm s^{-1} (*Figure 8*). Then, the diffusion coefficient yields (equation (11)):

$$D = 3 \times 10^{-10}\ \text{cm}^2\ \text{s}^{-1} \tag{12}$$

These values (V_{lim} and D) are in good agreement with Kramer's work, and seem to indicate that craze thickening may be diffusion-controlled by the gas in our experiment. A following paper will show that the fibril volume fraction in the craze remains constant even when the gas acts on the propagation. This indicates that in a gas the craze is still thickened by a drawing mechanism rather than a fibril creep mechanism. It should be noted that we assumed a craze fibril radius R_0 without knowing its true value. Moreover, the diffusion model used is rather crude as noted in ref. 1, so the numerical values should be understood as orders of magnitude, rather than true values.

CONCLUSIONS

The fracture toughness of PMMA and the craze shape of a propagating single crack–craze has been measured in very low-pressure toluene and cyclohexane gas environments by means of optical interferometry. This is currently the only technique allowing craze shape measurements under such conditions. The pressure has been chosen to be low enough to reach (within the measured velocity range) the point where the craze behaves like a craze in air. The following points have been found.

The craze size may be 1–4 times the craze size in air, depending on the crack propagation velocity.

There is a critical crack–craze propagation velocity (0.01 mm s^{-1}), independent of gas pressure, above which the gas has no effect.

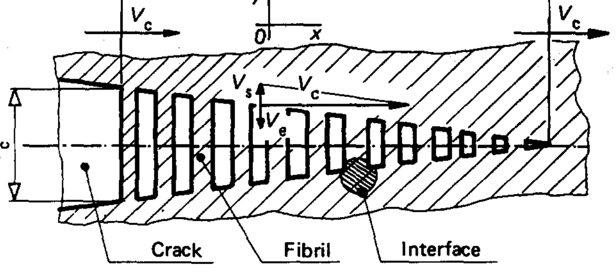

Figure 8 The fibril extraction velocity at the craze–bulk interface. The width-to-length ratio of the craze is usually of the order of 0.1

Over the whole velocity range, the fracture toughness changes only slightly due to the environment, in spite of the great change in craze size.

The lifetime of the craze fibrils and the craze stress required for fibril growth are drastically affected by the environment below the critical velocity.

The influence of the gas on the lifetime and on the fibril growth may be separate, and their activation volumes may be calculated. In air, both mechanisms have the same activation volume.

The critical velocity allows the calculation of the diffusion coefficient of the gas in the fibrils. The craze still seems to thicken by means of a drawing mechanism, diffusion-controlled at low velocity.

APPENDIX

If fibril growth takes place by pulling out new material from the bulk, the crack–craze velocity may be replaced by the fibril extraction velocity. In the case of fibril creep, it could be replaced by the creep rate. It is known that in PMMA the fibrils grow mainly by drawing material out of the bulk. Hence, the calculation will be done using the fibril extraction velocity V_e as shown in *Figure 8*. The subscript e will be used for all fibril extraction parameters.

The activated process yields:

$$V_e = V_{e0} \exp(\sigma/\sigma_{ve}) \qquad \text{(A1)}$$

As the crack–craze system moves steadily along the x axis at a velocity V_c (*Figure 8*), the craze surface moves along the y axis with a velocity V_s. If the fibrils grow by pulling new material out of the bulk, then the fibril extraction rate V_e ($= -V_s$) can be defined as the crack–craze velocity V_c times a constant (the craze shape is assumed to be primarily a triangle):

$$V_c = V_e(2S/T_c)$$

or

$$V_{c0} = V_{e0}(2S/T_c) \qquad \text{(A2)}$$

with T_c = craze width. Therefore, the crack–craze velocity is correlated with the fibril extraction rate. It should be noted that V_e is neither the real shear rate nor any other 'clean' deformation rate at the craze–bulk interface. It is simply a variable proportional to an average value of the field of the deformation rate at the interface. That field depends strongly on the fibril diameter, on the radius of the connecting zone at the interface and on the rheological properties of the material.

Using equations (5), (A1) and (A2), one obtains:

$$\sigma_{ve} = \sigma_v \qquad \text{(A3)}$$

which means that the activation volumes found from the crack–craze velocity plots are identical to those of the fibril extraction mechanism.

Each fibril stays in the propagating craze during a time t, so its final length will be:

$$T_c = 2V_e t$$

Using equations (A1) and (4):

$$T_c = 2V_{e0}t_0 \exp(\sigma/\sigma_{ve}) \exp(-\sigma/\sigma_t) \qquad \text{(A4)}$$

and the log(t) *versus* log(V_e) plot yields:

$$\ln(t) = A \ln(V_e) + B \qquad \text{(A5)}$$

where

$$A = -\sigma_{ve}/\sigma_t$$

and

$$B = \ln(t_0) + (\sigma_{ve}/\sigma_t) \ln(V_{e0}) \qquad \text{(A6)}$$

If both activation volumes are identical and denoted σ_0, then the craze width is constant over the velocity range (equation (A4)):

$$T_c = 2V_{e0}t_0 \qquad \text{(A7)}$$

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