The growth rates of diamond cavities in polycarbonate

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An attempt to quantify post-yield fracture in polymers has been made by examining the growth rates of diamond cavities in cold-drawn polycarbonate. The application of the basic principles of fracture mechanics show that the growth rate is extremely stress sensitive. Also, a simple Eyring equation, based on the net section stress, appears to fit the available data. The "activation volumes" derived from the crack growth and neck propagation are of the same order which suggests that the rate of simple shear yielding adjacent to the cavity controls the growth rate.

1. Introduction

In a recent paper [1] it was shown that there was a common post-yield fracture process in many polymers. The characteristic feature of this process is the slow-stable growth of a straight-sided crack while adjacent areas of the matrix shear plastically with a direction of shear parallel to the tensile axis. Depending on the loading conditions and the specimen geometry, complete failure may be entirely in this mode or a fast brittle fracture may be initiated from the straight-sided crack. In un-notched tensile specimens of many cold-drawing polymers the growing cracks are lozenge-shaped and consequently have been termed "diamond" cavities or simply "diamonds". Diamond cavities have been studied in some detail for rigid PVC [2, 3]. However, these studies were essentially qualitative and in this paper we have attempted to apply the principles of fracture mechanics to this crack growth process.

When plastic flow occurs in a localized area such as in a thin notched tensile specimen, there is a non-uniform cross-section and the calculation of stresses in the vicinity of the growing cavity is difficult. For this reason this study is restricted to the growth rates of diamond cavities in a cold-drawing polymer. Polycarbonate (bis-phenol A) was chosen because, unlike PVC, it provided drawn material with a uniform cross-section and a reproducible draw-ratio. Also, having attained an equilibrium draw-ratio, the drawn material did not appear to creep appreciably over the period of each test.

In the experiments described below diamonds were initiated in the cold-drawn section of tensile specimens while drawing was taking place. Since the drawing load is a function of the neck velocity, the applied stress on the drawn section was pre-determined by selecting the cross-head speed of the testing machine. Complications caused by relaxation while loading and unloading were thereby avoided.

2. The application of fracture mechanics to diamond cavities

Generally the onset of growth or the growth rate of a crack is related to some parameter such as the path-independent integral, J, derived by Rice [4], or more commonly Irwin's stress intensity factor, K [5]. In the case of diamond cavities, it was shown [2] that very small defects initiate growth as soon as the surrounding matrix deforms plastically. Therefore, we are more concerned with the factors which control growth rather than initiation. Unfortunately, we cannot calculate a meaningful value of K, since the plasticity is not well contained, and the matrix certainly is not isotropic. Similarly, the J integral cannot be evaluated with any confidence because the J integral is only applicable for reversible non-linear strains and the deformation adjacent to a diamond is mostly plastic. In the absence of a single par-

ameter applicable to diamond growth, initially we are restricted to assessing the separate influences of crack length, a, and stress, σ, on the rate of growth, da/dt.

However, slow-stable crack growth followed by catastrophic failure is a well established phenomenon in brittle polymers [6–8]. In some cases [7, 8], the best fit to experimental data is obtained by a stress-biased Eyring treatment [9] and given by an equation of the form

$$\frac{da}{dt} = A_1 \exp\left(\frac{-U}{2kT}\right) \exp\left[\frac{\gamma f(a)g(\sigma)}{4kT}\right] \quad (1)$$

where A_1 is a frequency factor, γ is a constant, k is Boltzmann's constant, T is absolute temperature and U is a potential barrier for bond rupture. The two functions f and g are included to account for the effects of crack length and applied stress. In brittle materials f and g can be replaced by a function of K. For example, Atkins et al. [7] substituted K^2 for these two functions, while Weiderhorn [8] simply used K.

For the reasons mentioned above, K has little physical meaning for diamond cavities and we are reduced to empirically determining f and g. If an Eyring model is applicable then the effect of temperature will be significant. Since there are large areas adjacent to a diamond deforming plastically in simple shear, heat will be liberated which may enhance further growth. It was therefore necessary to estimate the temperature rise near a diamond tip and it was proposed to do this by using infra-red photography.

It has been suggested [10] that in the plastic material localized in crazes, the material separates by molecular disentanglement. If the material at the tip of the diamond separates in this way, then higher growth rates may be found in low molecular weight material. On the other hand, if varying the molecular weight has no effect, then a bond rupture mechanism is favoured. Consequently two commercial polycarbonate samples at opposite extremes of the available molecular weight range were examined.

TABLE I Molecular weight characteristics of polycarbonate samples

Sample designation	Number average ($\times 10^{-3}$ mol wt)	Weight average ($\times 10^{-3}$ mol wt)	Poly-dispersity
A	12.5	27.0	2.2
B	35.0	74.0	2.2

3. Experimental procedure

Two grades of commercial polycarbonate (trade name Makrolon) were obtained in the form of granules. The molecular weight characteristics of the two polymers are shown in Table I. The dried granules of each polymer were formed into nominally 0.8 mm thick sheets by compression moulding at 220° C for sample A and 280° C for sample B. Although the press could be cooled rapidly by circulating water, the low molecular weight polymer aged appreciably during cooling. This ageing was removed by holding the sheets of sample A in an oven at 160° C for 4 h. Differential scanning calorimetry showed that quenching from this temperature produced negligible ageing and also that the shift in T_g due to the difference in molecular weight did not alter appreciably after the pressing treatment. In identical experiments the two unaged polymers had similar yield stresses and draw stresses.

From the pressed sheets, conventional dumbbell specimens (narrow section 25.4 mm × 4 mm) were cut. A grid was imprinted on the surface of each specimen by evaporating gold–palladium alloy through a fine mesh placed on the surface of the specimens. The squares of deposited metal were 63.8 μm across. In the drawing process the squares were elongated by a factor of 1.69 ± 0.02. It has been noted [2] that the spacing of the grid lines does not alter appreciably in the vicinity of an edge diamond, and it was decided therefore to use the number of grid lines traversed as a measure of the crack length. This greatly facilitates crack length measurement especially at high growth rates.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The specimens were extended on an extensometer designed specifically for these experiments and which was fitted to the stage of a Leitz Epivert microscope. The extensometer was of the conventional type with one fixed grip attached to a load cell and a grip on a moving cross-head. The cross-head could be driven at constant speed in the range 0.002 to 5 cm min^{-1} and loads of up to 50 kg could easily be attained. The load–displacement curves produced by this extensometer compared favourably with those obtained from commercial machines. As a diamond grew, its progress was recorded by means of a TV camera fitted to the microscope and a video-tape recorder (VTR). While the recording proceeded a time-date generator produced a digital time
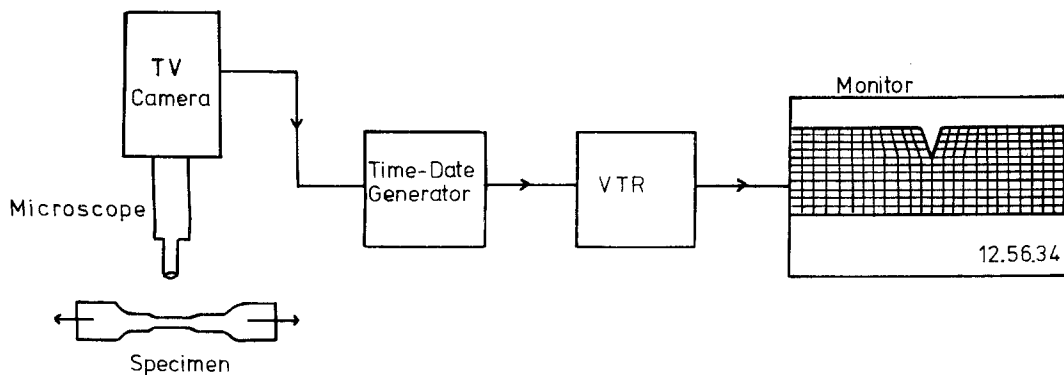
Block diagram of the apparatus used to determine the growth rates of diamonds.

Figure 1 A schematic diagram of the apparatus used to determine growth rates.

display which was mixed with the signal from the camera. In each recorded frame there was therefore a time display accurate to 1/100 sec. However, the time increments could only be resolved to 1/50 sec since that was the frequency of the frames generated by the camera.

In each test, when sufficient drawn material had been obtained, a defect was introduced in the side of the specimen midway between the propagating necks by touching with a scalpel. An edge diamond was always initiated and the slow-stable crack growth was recorded. Using the slow-motion and still frame facilities of the VTR, it was possible to calculate growth rates which were too rapid to be measured at the time of the test. Fig. 2 shows a typical image which was produced on the monitor although, because of the difficulties in obtaining still pictures from a monitor, this

photograph is a representation constructed with a 35 mm camera.

The applied stress σ was calculated by assuming affine deformation. The reduced area of the drawn material is then the original area divided by the draw ratio, λ, observed under load. Dividing the draw load by this reduced area gives a value for σ.

Infra-red photography [11] has shown that the energy dissipated in the propagating necks can produce a temperature rise of a few tens of degrees. For the case of polycarbonate the temperature rise is only insignificant when the neck velocity, v_n, is below $1 \, \text{cm} \, \text{min}^{-1}$. Since the polycarbonate samples produced λ close to 1.7, the cross-head speed, v_c, was restricted to a maximum of $0.2 \, \text{cm} \, \text{min}^{-1}$. so as to avoid thermal softening.

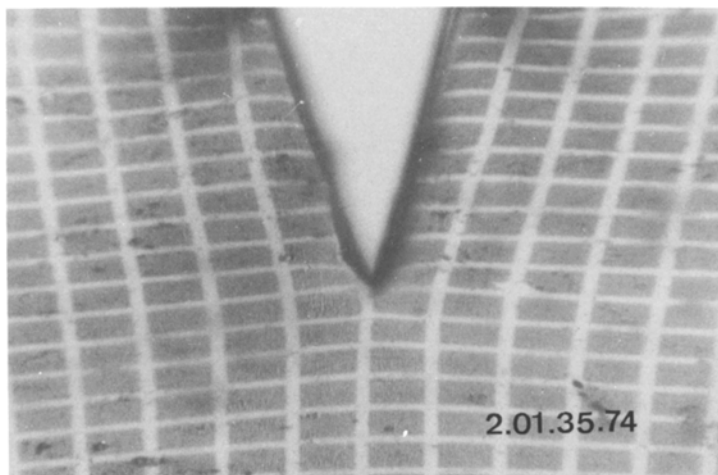The technique used to assess temperature increases in propagating necks was also employed

Figure 2 A representation of a typical image observed on the monitor.

here to investigate whether the plastic shear deformation enhances crack growth via thermal softening. For this purpose, diamonds in large (narrow section 50 cm × 10 cm) specimens of commercial Makrolon sheet were examined with a Thermovision infra-red camera. This instrument has the facility to produce contours of equal temperature.

4. Results and discussion

Initially the growth rates observed in each test were plotted on logarithmic axes against a/W where W is the specimen width. Some typical results are shown in Fig. 3. The curves appear to be separated according to applied cross-head speed and therefore the applied stress (v_c and σ are not directly equivalent because of slight variations in the nominal thickness). The slope of each plot is seen to increase with a/W and this may be attributed to the finite specimen dimensions. In fracture mechanics, correction factors for specimen geometries are generally close to unity at small crack lengths so that by taking the initial slopes of the plots we estimate that the growth rate varies as $(a/W)^{1.5-3.0}$.

The sensitivity of the growth rate to changes in stress can be assessed by plotting da/dt against σ at constant a/W. Unfortunately, at low cross-head speeds there was a drop in the load when the cavity reached a certain size. Presumably the movement of the cross-head is more easily accommodated by the increased compliance due to the opening of the cavity rather than by continued propagation of the neck.

As v_c was increased the load drop occurred at progressively higher a/W values until at $v_c = 0.2$ cm min^{-1} the load drop was insignificant. In assessing the influence of stress we require data from all values of v_c and are therefore restricted to values of a/W less than 0.25. Fig. 4 shows the plot of da/dt against σ on log axes for $a/W = 0.1$ and 0.2. The slopes of the two plots are similar and from least squares fits are put in the range 30 ± 3. Since v_c is the only independent variable, straight line fits in this study were either regression lines on that variable or, as in Fig. 4, the bisector of the two regression lines of each variable on the other. There appears to be a large amount of scatter but it is evident that small errors in the calculations of σ will produce large deviations from the regression lines. Assuming the deviations from the lines are produced mainly by errors in σ, the maximum error in that variable is around 5% while for the majority of the points the error is less than 2%.

In summary the simple fracture mechanics approach shows that the growth of diamond cavities is extremely stress sensitive and varies approximately as
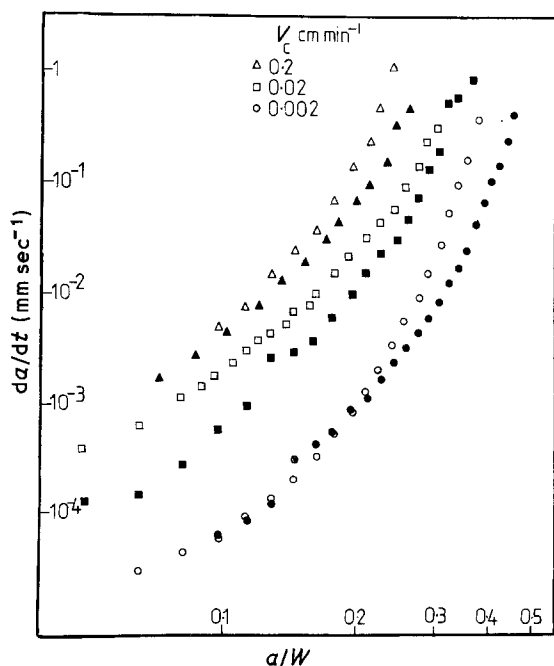

Figure 3 The variation of diamond growth rates with a/W. (Solid symbols represent the lower molecular weight polymer).
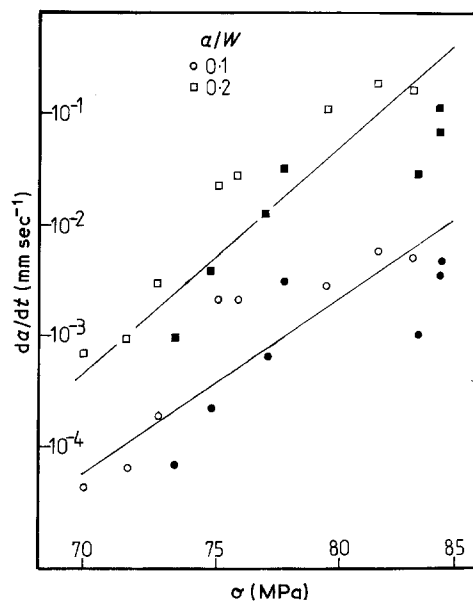

Figure 4 The variation of diamond growth rates with applied stress. (Solid symbols represent the lower molecular weight polymer).

$$\frac{da}{dt} \propto a^{1.5-3.0}\sigma^{27-33}. \qquad (2)$$

If the growth rate were to vary as some function of K, then since $K \sim \sigma(\pi a)^{1/2}$, we would expect the exponent of σ to be twice that of a. As they are widely different we are led to the conclusion that K has no part to play in the plastic fracture of polymers. In particular, as it has been shown that plastic fracture in notched thin sheets is very similar to diamond cavities [1], we suggest that the practice of attributing a value of K to plane stress conditions is not a valid approach. At present the extreme stress sensitivity of the crack growth rate cannot be explained in terms of a fracture mechanism since that has not yet been determined. However, in this study there appeared to be no apparent difference between the two grades of polycarbonates, which would appear to support a theory of bond rupture rather than molecular separation.

Since the stress is controlled by the cross-head speed, v_c, a logical way to eliminate the errors in assessing σ would be to plot da/dt at constant a/W against v_c. Fig. 5 shows such a plot on log–log scales for $a/W = 0.1$ and 0.2. There is some agreement with straight lines whose slopes are calculated to be 0.82 ± 0.11 for $a/W = 0.1$ and 0.97 ± 0.08 for $a/W = 0.2$. Since at $a/W = 0.2$, da/dt can be measured more accurately than at $a/W = 0.1$, we have more confidence in the second plot and it is assumed that da/dt is nearly proportional to v_c. It is well established that the Eyring approach can be used in the tensile yielding of polymers [12–15] and it is suggested that here the neck velocity and hence v_c can be related to the stress via an Eyring equation, i.e.

$$v_n = \frac{v_c}{(1-1/\lambda)} = A_n \exp\left(-\frac{U_n}{2kT}\right)\exp\left(\frac{\sigma V}{4kT}\right) \quad (3)$$

where A_n is a frequency factor constant, U_n is a potential barrier for the yielding process and V is an activation volume. Since $(da/dt)_a$ and v_c appear to be proportional, we are led to the suggestion that the growth rate at any crack length, $(da/dt)_a$, is related to σ by a similar expression. Moreover the potential barrier and activation volume will be similar in both cases, i.e.

$$\left(\frac{da}{dt}\right)_a = A_2 \exp\left(-\frac{U_n}{2kT}\right)\exp\left(\frac{\sigma V}{4kT}\right) \quad (4)$$

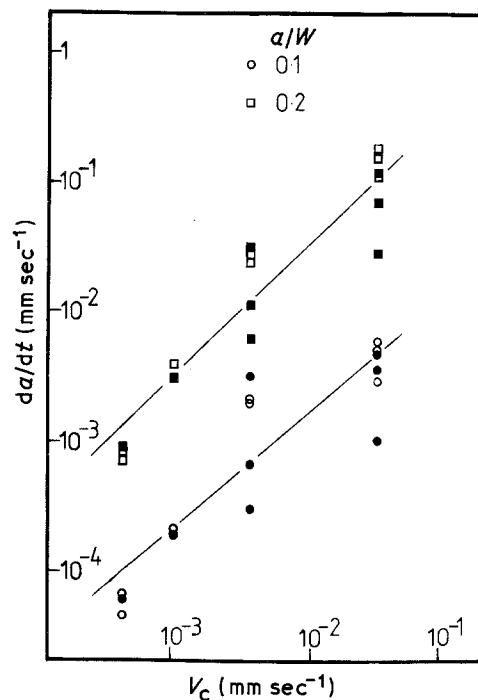where A_2 is a constant. This expression implies that $f(0.1W) \sim f(0.2W) \sim 1.0$. Plots of $\log v_c$

Figure 5 The variation of diamond growth rates with cross-head speed. (Solid symbols represent the lower molecular weight).

against σ and $\log (da/dt)_a$ against σ (Fig. 6a and b) support this suggestion.

However, there are problems in deciding which value of σ to put in Equation 4. Fig. 6a uses the value on the drawn section, but since the yielding process takes place over a tapering cross-section, this represents an upper limit. The lower limit is the stress on the unyielded section which is $1/\lambda$ times σ. The range of activation volumes calculated from the slope and produced by this variation in stress in Equation 4 is 6 to $11.0\,\text{nm}^3$. The results of several previous studies [12–15] have put V in the range 4 to $12\,\text{nm}^3$ so that the values here agree with those previously reported. However, the figures are not exactly comparable because these earlier estimations were made by taking the stress at the onset of yielding, while here we have a steady-state flow stress. Fig. 6b gives activation volumes for the crack growth process of $7.5\,\text{nm}^3$ for $a/W = 0.2$ and $6.0\,\text{nm}^3$ for $a/W = 0.1$. These values are close to those obtained by the yielding process, which therefore supports the use of Equation 4.

On the other hand, although the crack length appears to have little effect, $f(a)$ cannot be insignificant since the ligament area decreases as the crack grows, which must cause it to accelerate. A
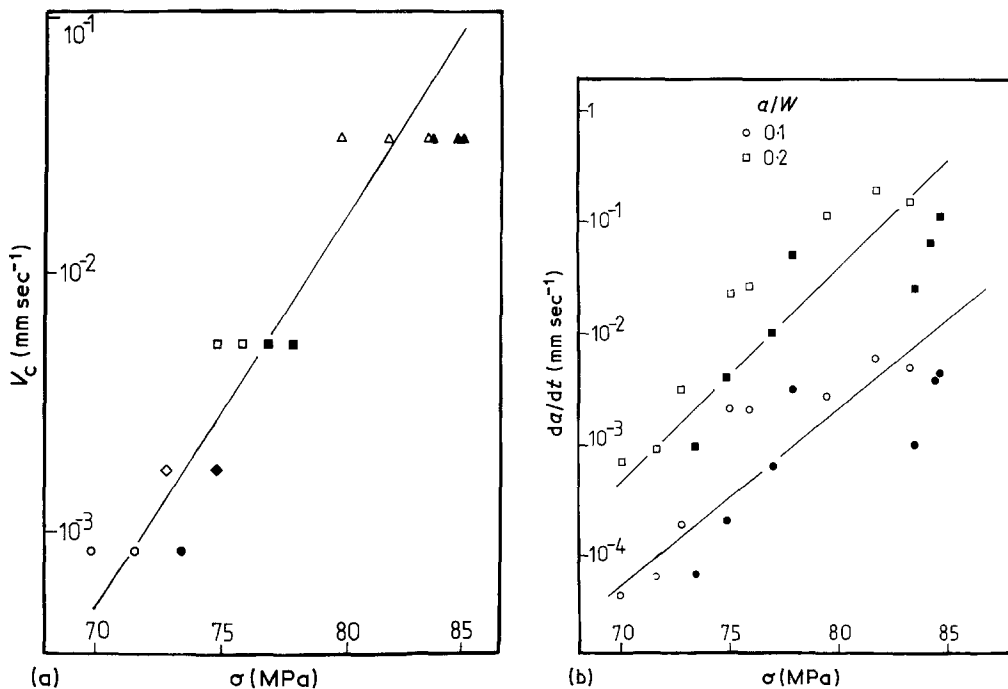
Figure 6 (a) An Eyring plot of cross-head speed against applied stress and (b) An Eyring plot of diamond growth rate against applied stress. (Solid symbols represent the lower molecular weight polymer).

log $(da/dt)_\sigma$ against a plot for several tests (Fig. 7) with $a/W < 0.25$ shows that $f(a)$ is also a linear function. One possible combination of $g(\sigma)$ and $f(a)$ which is favoured by the authors and appears to give a good empirical fit to the data is the net section stress, i.e.

$$\frac{da}{dt} = A_3 \exp\left(-\frac{U_n}{2kT}\right) \exp\left(\frac{\sigma_{net}V}{4kT}\right) \quad (5)$$

where $\sigma_{net} = \sigma/(1 - a/W)$ and A_3 is a frequency factor. Fig. 8 shows the plot of log (da/dt) against σ_{net} for various experimental conditions $(a/W < 0.25)$. The slope of each plot is linear and produces a value for V of $4.6\,nm^3$. The plots appear to be split unsystematically into two groups which suggests the influence of an unconsidered parameter. The segregation may be the effect of temperature fluctuations because although the experiments were carried out a nominally constant temperature of $25°C$, it was observed that a fluctuation of $1°C$ can produce a 6% change in the draw load. It was also observed that the switching of the control heaters caused a $\pm\frac{1}{2}°C$ cycle in the constant temperature room, which may have caused the segregation. Further studies in a more closely controlled temperature environment are proposed so that the parameter U_n can be estab-

lished. Future work should also investigate the growth of small cavities since, if Equation 5 is a good description, then $\sigma_{net} \sim \sigma$ for small a/W and the growth rate should be constant.

The toughness of a material is determined by its ability to blunt sharp defects by localizied yielding. For example, the crazing at the tips of cracks in brittle polymers consumes much more elastic energy than the creation of new surfaces. It has been shown above that the tensile yielding and diamond growth rate in polycarbonate can both be described empirically by an Eyring equation. Consequently we are led to the suggestion that the crack growth rate is controlled by the time-dependent shear deformation adjacent to the diamond. As shown previously [2], as the cavity propagates, the adjacent regions of the matrix are brought into a stress field which causes strain softening and easy plastic flow in the observed simple shear mode. This shear yielding consumes large amounts of elastic energy and effectively blunts the crack. It is observed that a maximum shear strain is attained [2]. If the crack cannot propagate further before the yielding material reaches this strain, then the crack growth rate will depend on the rate at which the shearing occurs. The activation volume obtained from Equation 5
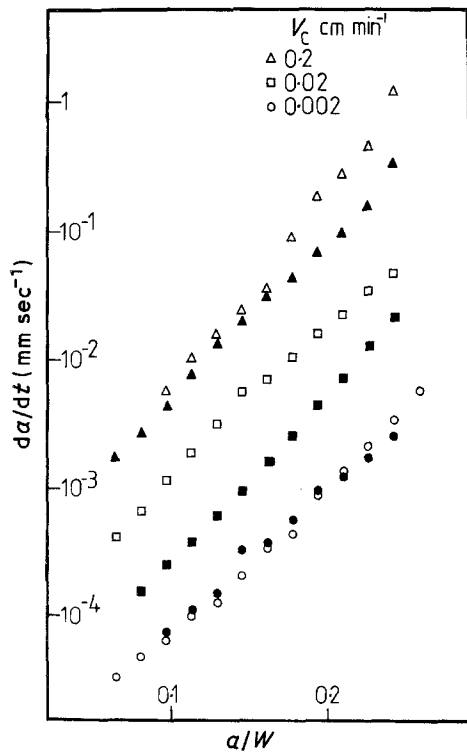
Figure 7 An Eyring plot of diamond growth rate against a/W. (Solid symbols represent the lower molecular weight polymer).

Figure 8 An Eyring plot of diamond growth rate against the net section stress. (Solid symbols and + represent the lower molecular weight polymer).

should therefore be that of the shear yielding process. Simple shear tests were performed on drawn Makrolon sheet using the shear rig described in [2]. The activation volume calculated from the yield point was found to be 2.5 nm³, which is of the same order. At a sufficiently high crack growth rate the shear deformation cannot respond quickly enough to absorb the increase in elastic energy and a catastrophic brittle fracture occurs. If the shearing process does control the growth rate, then no difference between the two samples would be expected since the yielding properties of polycarbonate do not vary over this molecular weight range. On this basis the question of whether new crack surfaces are produced by molecular rupture or separation remains unanswered.

As there is no significant plastic deformation in the ligament ahead of a diamond [2] the use of σ_{net} in the Eyring equation has only empirical basis. However, the use of σ_{net} can be justified by considering that as the net section stress increases the elastic stresses at the diamond tip will also increase and the rate of plastic shear flow will accelerate allowing a faster growth rate.

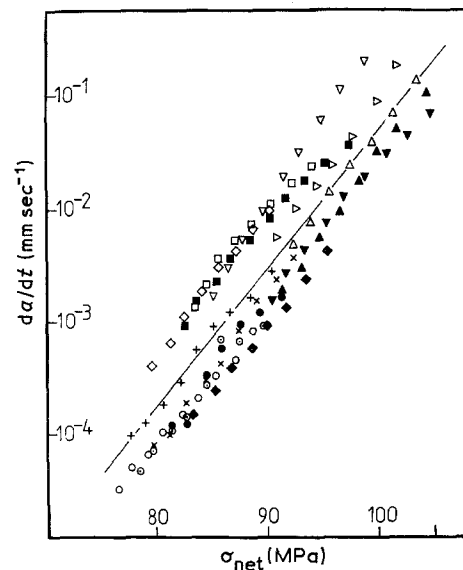Finally, Fig. 9 shows the temperature profile around an edge diamond in a large polycarbonate specimen extended at 0.2 cm min⁻¹. At this point the cavity is approaching the final failure and a temperature rise of 5° C was recorded near the tip. At low crack speeds and for $a/W < 0.2$, the temperature rise was found to be less than 1° C. While admitting that the geometric resolution of the infra-red camera may not detect very small high temperature regions near the tip, it is reasonable to assume that no significant temperature increase was produced by the shearing process.

5. Conclusions

The growth rate of diamond cavities in cold-drawn PVC has been shown by a simple fracture mechanics analysis to be very stress dependent. Although the data are restricted to low crack lengths, it appears that the growth rate can be des-
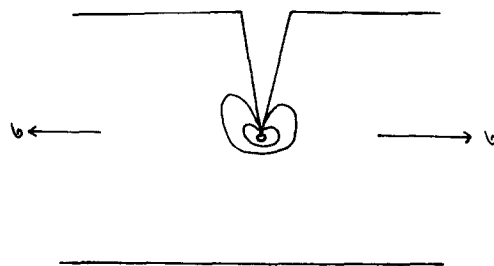

Figure 9 A tracing of a thermogram showing contours of equal temperature increments. Each successive isotherm represents an increase of 1.5° C.

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cribed fairly well by an Eyring equation using the net section stress. Furthermore, the similarity between the activation volumes calculated for the yielding and crack growth processes suggest that the rate of plastic flow in the sheared regions close to the diamond controls its growth rate.

Acknowledgements

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