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The kinetics of surface craze growth in polycarbonate exposed to normal heptane

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A variable radius of curvature strain-bending apparatus has been used to investigate the propagation of surface crazes in polycarbonate exposed to n-heptane. It was found that for crazes growing in a zone free of other crazes, the growth rate was linear at constant temperature and exponentially dependent upon temperature. An activated-state theory was developed to describe the kinetics of growth in terms of two parameters, B^{-1}, a characteristic strain constant that was independent of test variables, and A', a characteristic growth-rate parameter that varied exponentially with temperature. A strain–temperature equivalence principle was adopted to predict the crazing behaviour over a range of temperatures and strains. A critical strain was defined in terms of a maximum allowable craze growth rate.

1. Introduction

Almost all linear thermoplatic polymers are susceptible to environmental stress-cracking when exposed to a combination of stress and organic liquids. Under certain conditions, crazes will nucleate and grow at a stress well below that necessary to cause homogeneous shear yielding, and are thus the precursors of crack propagation and failure. Since crazing can also be a source of toughness in glassy polymers, the phenomenon is the subject of a large number of published studies. Research has been concentrated on the microscopic structure of crazes, the influence of stress and the effects of environment on the nucleation and growth of crazes, and the effects of crazing on the macroscopic properties of these materials. Review articles by Rabinowitz and Beardmore [1] and by Kambour [2] provide information on the present state of knowledge. The various methods of studying crazing are reviewed by Brown in a more recent article [3]. The criteria for craze initiation and growth have been defined by a number of investigators; among the most widely referenced are the theories of Sternstein and co-workers [4, 5], Oxborough and Bowden [6], Matsushige [7], Marshall, Culver and Williams [9], Andrews *et al.* [9, 10] and Argon *et al.* [11]. It is generally agreed that there is either a critical stress or a critical strain below which crazing does not occur, at least within the time-frame of the usual laboratory experiments. The techniques of fracture mechanics have been used to study the kinetics of craze growth from a sharp notch [8–10, 12], and growth rates have been correlated to the stress intensity factor at the edge of the notch. It is also clear that the temperature and stress dependence of the rate of nucleation and the rate of craze growth can be represented by the rate equations of activated state theories [13–15]. Furthermore, the rate processes are strongly dependent upon the contacting liquid.

Crazes are usually initiated at the surface of a polymer at points of stress concentration, such as notches, voids, embedded second phases, holes and scratches. Internal crazes can also be generated when internal stress concentrations are sufficiently high, as is the case for rubber–particle modified glassy thermoplastics. Crazing occurs in inert atmospheres, but occurs more readily when the material is in contact with certain solvent liquids.

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In models for predicting the initiation and growth of crazes, it is assumed that a liquid or gaseous agent is adsorbed on the surface of the material, and is preferentially adsorbed at points of stress concentration. The effect of plasticization under stress is to induce localized yielding phenomena that lead to the elastic–plastic expansion of voids [10], the repeated nucleation of pores [8, 10], or to unstable material-flow processes that cause the polymer surface to break up into the interconnected pore network characteristic of craze matter [11].

Since glassy thermoplastics are widely used in applications where the materials are exposed to both stresses and solvent environments, it becomes important to define criteria for environmental stress cracking. Many authors have attempted to define a critical stress or strain for a material exposed to a pure liquid or liquid mixture [16–21]. Failure is thus minimized by maintaining the level of stress or strain on the material below the critical value for a particular liquid environment. One of the most popular tests for determining critical strain (popular because of the simplicity of the test), has been to flex the material over an elliptical bending form, immerse it in a liquid environment for a fixed period of time, and measure the minimum strain at which crazes appear on the flexed strip [21–23]. In general, it is found that critical strain levels can be correlated with the physical properties of the polymer and liquid, such as solubility parameters, surface tension or molecular characteristics [2].

It is the purpose of this work to quantify the results that can be obtained from a strain bending apparatus, using the rate equations of a simple activated-state theory. Using our own results on the propagation of crazes in polycarbonate exposed to normal heptane, and also the results of Argon and Salama [11] for the crazing of polystyrene in air, it will be shown that the development of crazes with time can be predicted from a minimum of experimental data. Also, rather than reporting a static or "equilibrium" value of critical strain, we will define a "critical strain" at a specified value of the rate of craze growth, which we feel is a more meaningful parameter for correlation with the lifetime of a material in service.

2. Experimental procedure

Experiments were conducted on a variable radius of curvature strain-bending apparatus, fashioned after that designed by Stolki and Haslett [23]. Rectangular test specimens, 250 mm by 50 mm, of Lexan polycarbonate, were cut from 4 mm thick sheets, and then annealed and dried at 100° C for 24 h under vacuum. The strain-bending apparatus is shown in Fig. 1. A test specimen was flexed over the surface of the apparatus and attached to the metal block with a pair of grips, as shown. The strain, ϵ, in the test specimen at any point is given by

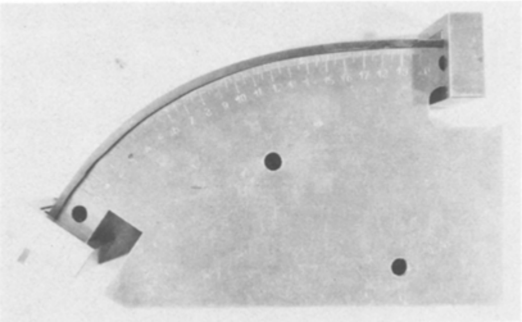

Figure 1 The strain-bending apparatus

$$\epsilon = d/R, \qquad (1)$$

where d is the half-thickness of the specimen and R is the radius of curvature at the neutral axis of the flexed sample. In order to obtain the most accurate values of strain as a function of position along the surface, a calibration was carried out using HBM 3/120 LY58 strain gauges, glued at each point of measurement to a 0.35 mm thick strip of steel mounted in the same manner as a test specimen. A millimetric scale was etched on one edge of the apparatus adjacent to the mounting surface, and the strain was measured as a function of position along the surface. The calibration curve thus obtained is shown in Fig. 2, in terms of per cent strain of the calibrated specimen as a function of position along the curved surface. To use the calibration curve, the ordinate must be multiplied by the ratio of the thickness of the test specimen to the thickness of the calibration specimen (i.e., $2d/0.35$).

The strain-bending apparatus, with test specimen mounted, is placed in an open glass vessel containing the solvent at the temperature of the test. A cover is placed over the top of the vessel to minimize evaporation losses. To maintain a constant temperature, the vessel containing the apparatus is placed in a thermostatically controlled water bath, also of glass, so that the water nearly

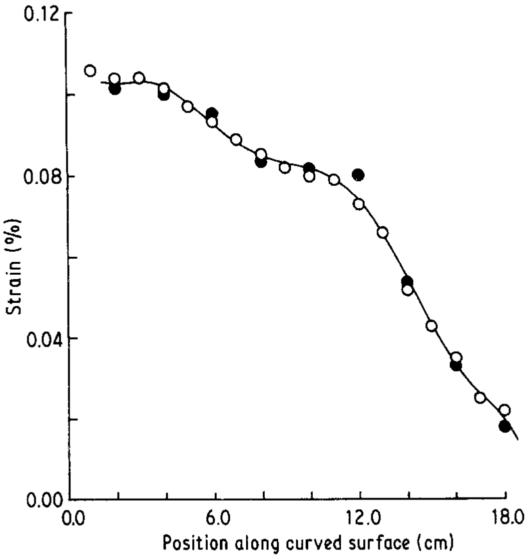

Figure 2 Calibration curve for the strain on the surface of a test specimen 0.35 mm thick.

reaches the top of the immersed vessel. The test apparatus is positioned in such a manner that the crazes forming on the surface of the test specimen can be seen and photographed. A typical photograph is shown in Fig. 3. Crazes appear at one end of the specimen surface, having started from the cut edges. The craze-front moves up the surface, and thus both the movement of the front and the growth of crazes can be recorded as a function of time. In some tests, the cut edges were coated with an epoxy resin to prevent solvent contact, thus forcing the crazes to nucleate on the surface, away from the edges. The rate of craze growth can be determined by measuring the length of an individual craze as a function of time, using a cathetometer.

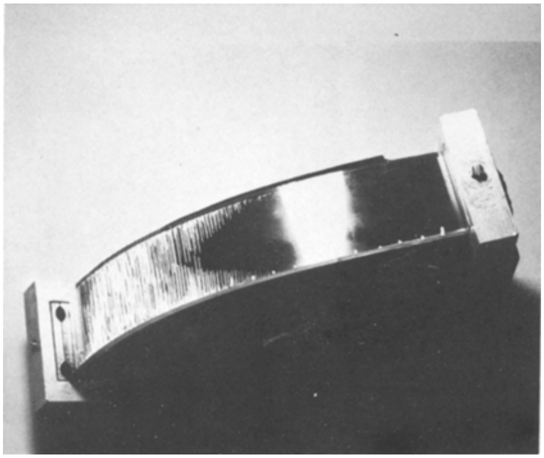

Figure 3 The envelope of crazes on a polycarbonate specimen exposed to n-heptane.

3. Theoretical analysis

When a polymeric solid is flexed and the surface under tension is exposed to a solvent, crazes nucleate at the cut edges of the solid and at other sites of stress inhomogeniety, and, subsequently, grow to macroscopic dimensions in a direction perpendicular to the imposed tensile load. When the distance between crazes is sufficient, the nucleation and growth of a surface craze is not affected by the presence of others. Under such conditions, it has been shown that both the nucleation rate and the growth rate of the "non-interfering" crazes are linear [11, 13] and can be represented by one-dimensional models [14]. In a previous paper, Nicolais and DiBenedetto [15] assumed that the initial nucleation rate and the growth rate were activated processes that could be represented by Arrhennius-type equations. Following the lead of Zhurhov *et al.* 13], they used the following rate equations:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 \exp\left(-\Delta E_\mathrm{n}/RT\right) \sinh\frac{(n-1)\sigma}{\sigma^*}, \quad (2)$$

where $\mathrm{d}N/\mathrm{d}t$ is the nucleation rate, N_0 is a constant, ΔE_n is the activation energy for nucleation, $(\sigma^*/n-1)$ is a characteristic stress constant, and σ is the maximum imposed tensile stress, and

$$\frac{\mathrm{d}G}{\mathrm{d}t} = G_0 \exp\left(-\Delta E_\mathrm{G}/RT\right) \sinh \sigma/\sigma^*, \quad (3)$$

where $\mathrm{d}G/\mathrm{d}t$ is the craze growth rate, G_0 is a constant, ΔE_G is the activation energy for the one-dimensional growth process, and σ^* is a characteristic stress constant.

When the cut edges of the test specimen are exposed to solvent, it can be observed that nucleation occurs preferentially (exclusively at low enough deformation) from the cut edges. Furthermore, it is observed that the crazes grow perpendicular to the direction of the applied stress. It is reasonable to assume that the time required from an edge, at any given level of strain, is negligible compared to the time required for the craze to grow to optically visible dimensions. Under these conditions, and at constant temperature, Equation 3 may be integrated to give

$$G(t) = G_0 \exp\left(\frac{-\Delta E_\mathrm{G}}{RT}\right) \int \sinh\frac{\sigma(t)}{\sigma^*}\,\mathrm{d}t, \quad (4)$$

where $G(t)$ is the craze length at time t. In a strain-bending apparatus, the deformation is held constant and the stress relaxes with time. For glassy polymers well below their glass transition temperatures, the relaxation times tend to be long relative to the time scale of a typical test, and a constant average value of the stress $\sigma(t) \sim \langle\sigma\rangle = E_0\,\epsilon$, may be used in the integrand of Equation 4. Integration of Equation 4 yields

$$G(t) = G_0 \exp\left(-\frac{\Delta E_G}{RT}\right) \sinh\left(\frac{E_0 \epsilon}{\sigma^*}\, t\right). \quad (5)$$

Measured from the instant of immersion of the specimen in the solvent, the time required for a craze initiated at an edge to reach the mid-point of the specimen is defined as $\bar{t}$. The length of the craze when it reaches the mid-point is $G(t) = G_M$. Equation 5 may be rearranged into the following form:

$$\epsilon = (B^{-1}) \sinh^{-1}\left(\frac{G_M}{A'\bar{t}}\right) = (B^{-1}) \ln\left[\frac{G_M}{A'\bar{t}} + \left(\frac{G_M^2}{A'\bar{t}} + 1\right)^{1/2}\right], \quad (6)$$

where

$$A' = G_0 \exp\left(-\frac{\Delta E_G}{RT}\right) \quad (7)$$

and

$$(B^{-1}) = (\sigma^*/E_0). \quad (8)$$

The quantity A' has the dimensions of length per unit time, and may be interpreted as a characteristic growth-rate constant for a given polymer–solvent system. It depends exponentially on temperature, so that the activation energy for craze growth, ΔE_G, may be calculated from a plot of $\ln A'$ against T^{-1}.

The quantity B^{-1} has the dimensions of strain (i.e., is dimensionless), and may be interpreted as a characteristic strain constant for a given polymer, It should be relatively independent of temperature, well below the glass transition temperature of the polymer.

Thus, the time required for a craze to reach the mid-point of a test sample surface (i.e., $\bar{t}$) for different values of ϵ (i.e., at fixed positions along the strain bending apparatus surface), can be measured and then Equation 6 can be used to evaluate the characteristic constants A' and B^{-1}. By repeating the experiments at different temperatures, the activation energy for craze growth, ΔE_G, can be evaluated.

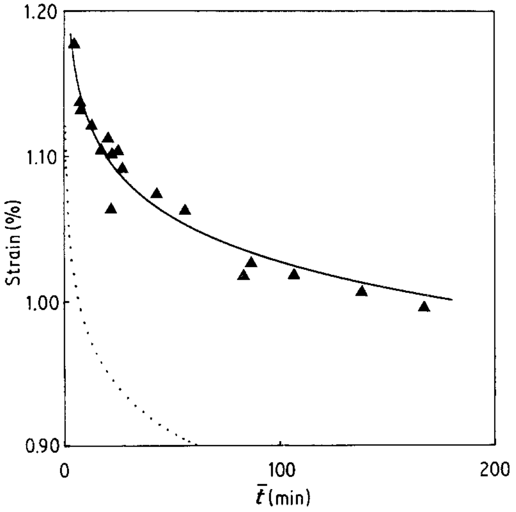

Figure 4 A plot of per cent strain against the time necessary for a craze to reach the centre of the test specimen for polycarbonate in n-heptane at 300 K, (Solid Curve) and 308 K (Dotted Curve).

4. Experimental results

The experiments were carried out on Lexan polycarbonate immersed in n-heptane at temperatures of 300, 304, 308, 313 and 318 K.

A typical set of experimental values of $\bar{t}$ at various levels of strain, for a specimen with the cut edges exposed to solvents, is illustrated in Fig. 4 for a temperature of 300 K. The dotted curve is a trace of the data at 308 K, and illustrates the strong effect of temperature on the craze growth rate. When $(G_M/A') \gg \bar{t}$, and $(2\,G_M) = 50$ mm, the width of the test specimen, Equation 6 may be rewritten as:

$$\epsilon \sim B^{-1} \ln \frac{50}{A'} - B^{-1} \ln \bar{t}. \quad (9)$$

A linear regression analysis may be used to calculate the values of the parameters A' and B. The solid line drawn through the data at 300 K is the calculated curve, using $A' = 2.8 \times 10^{-12}$ cm min^{-1} and $B = 2200$.

Another method of calculating A' and B at constant values of both temperature and strain, ϵ, is to measure the craze growth as a function of time at various points along the test specimen. Equation 3 may be rewritten in terms of A' and B, as:

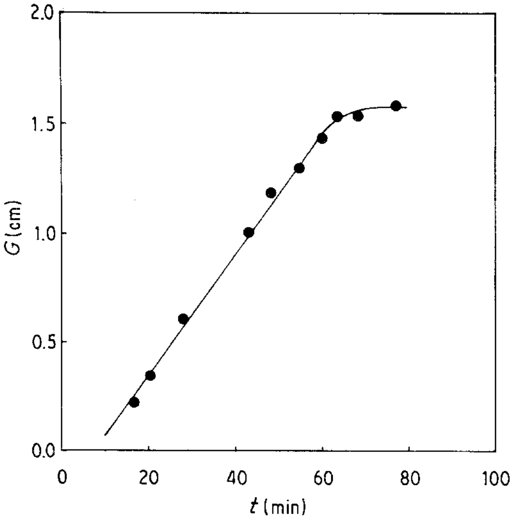

Figure 5 Craze length as a function of time for polycarbonate in n-heptane. The linear portion shows non-interfering craze growth. The logarithmic portion shows the effect of craze interaction.

$$\frac{\mathrm{d}G}{\mathrm{d}t} = A' \sinh B\,\epsilon. \tag{10}$$

Specimens with their cut edges covered, were immersed, and the craze growth observed using a cathetometer. A typical growth curve is illustrated in Fig. 5. Initially, the craze length is a linear function of time. It was found that whenever an isolated craze was able to grow without interference of other crazes, the growth was always linear. As a growing craze encountered crazes coming from the other direction, or when a new craze developed near other crazes (for example, see Fig. 3), the growth rate decreased markedly and did not follow a linear law. The change from linear growth for the specimen used (illustrated by Fig. 5) occurred after about 60 min, which was the time at which the craze approached the centre of the sample and encountered crazes coming from the other direction. During the period between 50 and 80 min, the growth was logarithmic, and quite analogous to that found by Wales [24]. The slope of the initial portion of the curve can be used to determine the growth rate, $\mathrm{d}G/\mathrm{d}t$, for the "non-interfering" case.

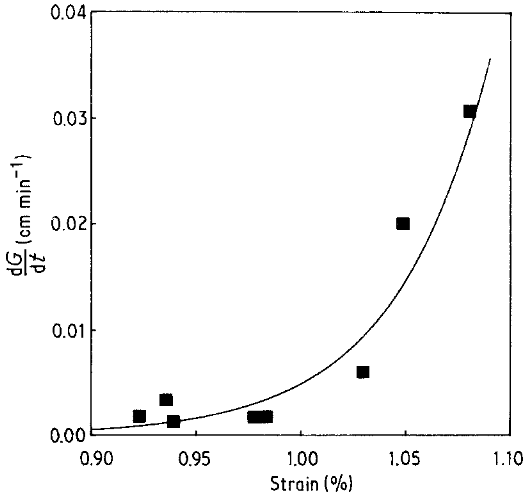

Figure 6 Craze growth rate as a function of per cent strain for polycarbonate in n-heptane at 300 K.

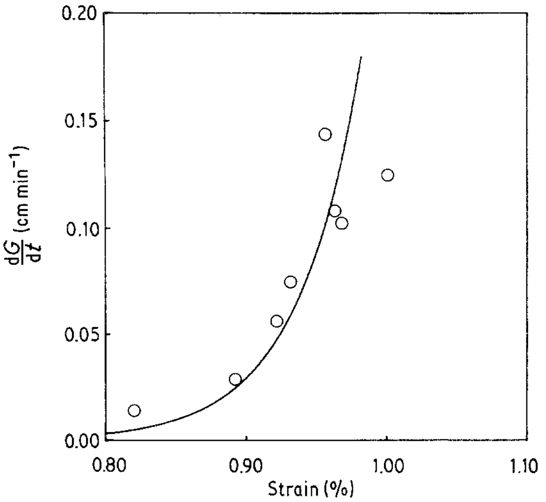

Figure 7 Craze growth rate as a function of per cent strain for polycarbonate in n-heptane at 318 K.

Values of $\mathrm{d}G/\mathrm{d}t$ as a function of strain, ϵ, are illustrated in Figs 6 and 7, for temperatures 300 and 318 K, respectively. For the rage of variables studied, the minimum value of $(B\epsilon)$ was of the order of 18, so the hyperbolic sine function is well approximated by an exponential and Equation 10 may be rewritten as:

$$\ln\left(\frac{\mathrm{d}G}{\mathrm{d}t}\right) = \ln\frac{A'}{2} + B\,\epsilon. \tag{11}$$

A linear regression analysis may be used to evaluate A' and B at each of the temperatures used. The solid curves drawn through the data in Figs 6 and 7 are obtained using the best-fit values of A' and B at the respective temperatures.

A constant value of $B = 2200$ was used for all values of temperature. Using a value of $E_0 = 2200$ MPa for the modulus of polycarbonate, a value of $\sigma^* = 1$ MPa for the value of the characteristic stress constant for polycarbonate is found. The growth rate parameter A' for the polycarbonate–

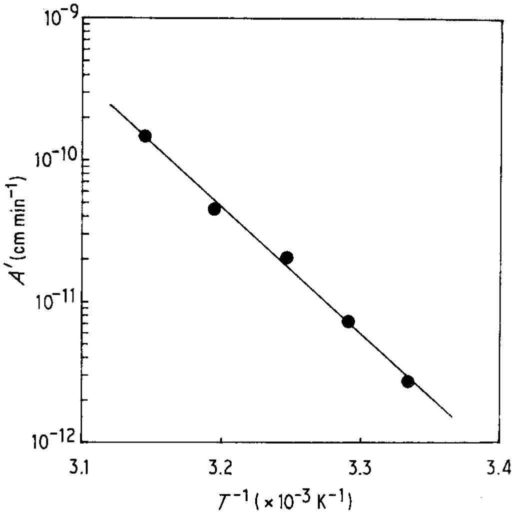

Figure 8 Semi-logarithmic plot of the craze growth rate parameter as a function of T^{-1} with $\Delta E_G = 167\,000$ J g-mol^{-1} for polycarbonate in n-heptane.

n-heptane system varied exponentially with temperature (Equation 7). The results are illustrated in Fig. 8, as a semi-logarithmic plot of A' as a function of T^{-1}. From the slope of this plot, a value for the activation energy of $\Delta E_G = 167\,000$ Joules gram mol^{-1} may be calculated.

Using Equations 5 and 9, with the measured values of A' and B, the position of the craze boundary (Fig. 3) as a function of time can be predicted, as shown schematically in Fig. 9. The present authors found the calculated craze fronts matched the experimental data within the precision of the measurements.

5. The equivalence of strain and temperature

A master curve for the craze growth rate at a reference temperature may be calculated by recognizing the equivalence of strain and temperature as they affect the growth rate. Equating two values of $\mathrm{d}G/\mathrm{d}t$ at two temperatures T and T_R,

$$\left(\frac{\mathrm{d}G}{\mathrm{d}t}\right)_T = \left(\frac{\mathrm{d}G}{\mathrm{d}t}\right)_{T_R} \sim G_0 \exp(-\Delta E_G/RT + B\epsilon_T)$$

$$= G_0 \exp\left(\frac{-\Delta E_G}{RT_R} + B\epsilon_{T_R}\right) \qquad (12)$$

is obtained, which may be rewritten as

$$\epsilon_T = \epsilon_{T_R} \frac{-\Delta E_G}{RB} T_R^{-1} - T^{-1} . \qquad (13)$$

Thus, $(\mathrm{d}G/\mathrm{d}t)_{T_R}$ may be plotted at any given reference temperature, T_R, as a function of the strain, ϵ_{T_R}. The master curve may be used at any other temperature, T, by recalculating the strain to the "equivalent" values, ϵ_T, using Equation 12. The data reported previously at the five temperatures used were shifted in this manner to a reference temperature of $T = 294$ K. The result is shown in Fig. 10.

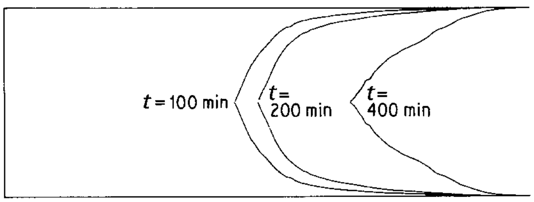

Figure 9 Calculated craze envelopes at various times.

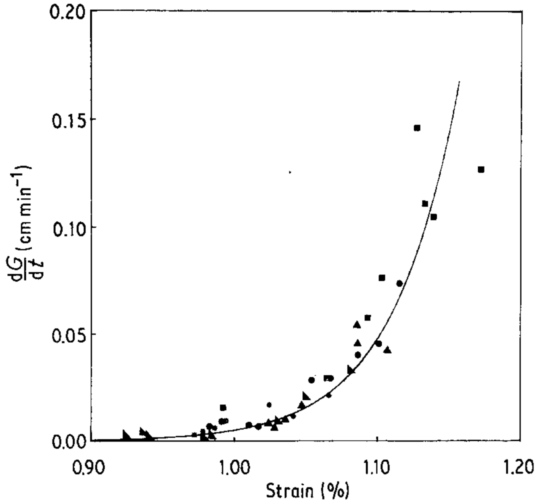

Figure 10 Master curve of craze growth rate as a function of per cent strain for polycarbonate in n-heptane. Reference temperature is 294 K.

6. Application of theory to data of Argon and Salama

Equation 3 for the craze growth rate is quite general and should be applicable to other experimental conditions. Argon and Salama [11] have measured craze growth rates of commercial polystyrene under constant uniaxial tension, in air at 253 and 293 K. Their data have been correlated using Equation 2. Values of $\sigma^* = 3.3$ MPa, $A' = 2{,}76 \times 10^{-11}$ and 1.22×10^{-9} cm min^{-1} at 253 and 293 K, respectively, and a value of $\Delta E_G = 54\,400$ Joules gram mol^{-1} (based on two temperatures), were calculated. The results are summarized in Figs 11 and 12.

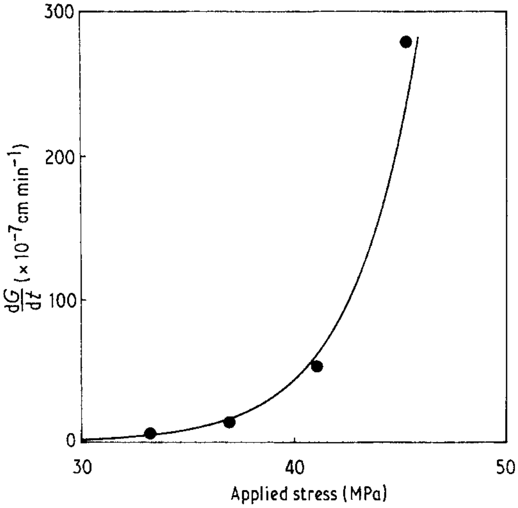

Figure 11 Craze growth rate at various constant stresses. Data of Argon and Salama [11] for commercial polystyrene in air at 253 K.

7. A definition for critical strain based on craze growth rate

The experiments in which the cut edges of the test samples were protected from the solvent, seem to indicate that there exists a value of deformation below which nucleation of crazes does not occur, at least within the experimental time-frame of days. However, the experiments conducted with specimens whose cut sides were exposed to solvents, seem to indicate that crazes are present even at deformations below the critical values reported in the literature. At very low strains, the crazes do not grow rapidly enough to be measured during the time devoted to the experiment, but extrapolation of the growth-rate equation would, nevertheless, indicate a finite growth rate.

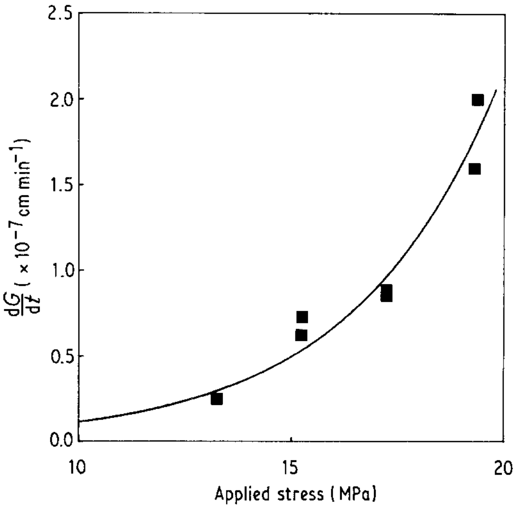

Figure 12 Craze growth rates at various constant stresses. Data of Argon and Salama [11] for commercial polystyrene in air at 293 K.

TABLE I Variation of critical strain with temperature for polycarbonate in n-heptane

ϵ_c (%)	T (K)
0.43	300
0.39	304
0.34	308
0.30	313
0.26	318

TABLE II Variation of critical strain with temperature for polystyrene in air

σ_c(MPa)	ϵ_c (%)	T (K)
23.1	1.0	253
11.5	0.5	293

A more conservative definition of critical strain could be based on the growth-rate equation by setting a criterion of a maximum allowable craze growth rate. We propose the criterion that a nucleated craze should grow, for example, no more than 1 mm in 10 years at constant strain and temperature. The calculated linear growth rate is

$$\left(\frac{dG}{dt}\right)_{\text{critical}} = 1.903 \times 10^{-8} \text{ cm min}^{-1}. \quad (14)$$

With the parameters calculated above for polycarbonate in n-heptane, the values for the critical strain, ϵ_c, given in Table I are obtained.

These are lower than the value of 0.94 to 1.02 at room temperature, reported by Kambour [2].

Using an equivalent definition at constant stress, the value of 2200 MPa for the modulus of polystyrene, from the data of Argon and Salama can be obtained the values of ϵ_c for polystyrene in air given in Table II.

The values reported here are lower than numbers previously reported in the literature because they are based on the growth rate of pre-existing crazes emanating from flaws.

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