The effect of temperature on the fracture of polycarbonate

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The fracture toughness of polycarbonate was obtained over the temperature range 20 to -120° C. There is a strong thickness dependence which is described in terms of plane stress and plane strain values which are insensitive to temperatures above -40° C but the plane stress value increases below this temperature. This change is associated with the β transition and stable crack growth was observed in this region with accompanying instabilities arising from adiabatic heating at the crack tip.

1. Introduction

The use of fracture mechanics to describe the process of crack growth in polymers has advanced considerably in recent years, e.g. [1-5]. It is now possible to determine fracture toughness with considerable precision for a wide range of different conditions with some confidence. This paper uses the methods of fracture mechanics to investigate the rather complicated behaviour of polycarbonate over a range of temperatures and a simple basic pattern emerges which is consistent with that of other polymers.

The fracture toughness of polycarbonate shows a strong dependence on sheet thickness and a previous paper [6] showed that at 20° C this could be explained in terms of a plane stress fracture toughness K_{C2} and a plane strain value K_{C1} $(\leq K_{C2})$. These two parameters are determined here for the temperature range -120 to 20° C. Work on PMMA (for which there is no appreciable thickness effect [5]) has shown that stable slow crack growth can be produced in the temperature range of the β transition. Only small amounts of slow growth were found at 20° C in polycarbonate [6] but more would be expected at temperatures below -40° C where the β transition occurs [7]. Double torsion tests were used as in [5] in the range -120 to -40° C to examine the slow crack growth and the subsequent onset of crack instabilities.

2. Thickness effects

The apparent fracture toughness K'_{C} of a high © 1975 Chapman and Hall Ltd. Printed in Great Britain. toughness material consists of contributions from K_{C1} , the plane strain fracture toughness and K_{C2} (> K_{C1}), the plane stress fracture toughness. In a single edge notch specimen the crack tip near the free surface is in plane stress while the inner regions are in plane strain. The fracture will, therefore, initiate from the inner region, which has the lower resistance to fracture. This initiation will be arrested by the plane stress region with the high resistance to fracture unless the specimen thickness is large compared with the plane stress region. The plane stress penetration is determined by the plastic zone radius r_{v2} which is [6]:

$$r_{y2} = \frac{1}{2\pi} \frac{K_{C2}^2}{\sigma_y^2}$$
(1)

where $\sigma_{\rm y}$ is the uniaxial tensile yield stress.

Irwin [8] suggested that $2r_{y2}$ should be smaller than half the thickness of the specimen, H, in order that a plane strain situation should exist in the central region, i.e.

$$2r_{y2} < \frac{H}{2}$$

In this situation $K'_{\mathbf{C}}$ can be determined by apportioning the $K_{\mathbf{C}}$ values [6] so that

$$HK'_{C} = K_{C1}(H - 2r_{y2}) + K_{C2}2r_{y2} \qquad (2)$$

or

$$K'_{\mathbf{C}} = K_{\mathbf{C}1} + \frac{K^2_{\mathbf{C}2}(K_{\mathbf{C}2} - K_{\mathbf{C}1})}{\pi o_{\mathbf{y}}^2 H}.$$
 (3)

In the absence of available thick material this



Figure 1 Geometry of surface notch specimens.

effect may be investigated by a surface notch in the shape of an arc as shown in Fig. 1. An equivalent thickness for this kind of notch can be approximated to the width of a crack of uniform depth, d, and the same area [6]. For a circular cutter with radius R, b can be determined from:

$$b^2 = d(2R - d) \tag{4}$$

and the equivalent thickness will be:

$$H' = \frac{4b}{3} \quad \text{for} \quad b \ll R. \tag{5}$$

The stress intensity factor for a semi-ellipse has been approximated by Irwin [9] as:

$$K^2 = Y^2 \sigma^2 d \tag{6}$$

where

$$Y^{2} = \frac{1.21\pi}{\phi^{2} - 0.212 \left(\frac{\sigma}{\sigma_{y}}\right)^{2}}$$
(7)

and

$$\phi = \int_{0}^{\pi/2} \left[1 - \left(\frac{b^2 - d^2}{b^2} \right) \sin^2 \theta \right]^{\frac{1}{2}} d\theta \qquad (8)$$

2.1. Test procedure

Tension tests with both single edge notch and surface notch specimens were performed on an Instron testing machine fitted with a temperature controlled box containing heating elements and a liquid nitrogen vapourizing system. By incorporating a "Eurotherm" control unit into the system it was possible to obtain temperatures between +20 and -120° C to an accuracy of $\pm 1^{\circ}$ C.

Rectangular specimens of "Makrolon" polycarbonate 150 mm by 50 mm and of 3 mm and 5 mm thickness were used for both single edge notches and surface notches and the cracks were induced by machining with a dead sharp fly cutter (tip radius < 0.5 μ m). The cutter radius for the surface notches was about 17 mm. For single edge notches a large radius was used in order to obtain an almost square crack tip. $K'_{\rm C}$ did not show any appreciable rate dependence and the results reported here are all at a cross-head rate of 0.5 cm min⁻¹.

2.2. Results of 5 mm specimens

Both single edge notch (SEN) and surface notch (SN) specimens exhibited brittle fracture* in the temperature range +20 to -120° C. Crack initiation in SEN specimens had the same characteristics at all temperatures in that the crack front started bowing prior to uniform growth leading to fracture. $K_{\mathbf{C}}$ at this initiation was determined by taking the load at crack initiation and the original crack length, and its value was almost constant at $K_{\text{initial}} = 2.2 \text{ MN m}^{-3/2}$ for all temperatures. The variation with temperature of the average K'_{C} determined at final fracture for about six specimens at each temperature for both SEN and SN is shown in Fig. 2. There is a similar trend in both sets of data with a minimum around -40° C with the SN data below those for SEN.

2.3. Results of 3 mm specimens

SN specimens exhibited brittle fracture in the temperature range of 0 to -120° C whilst SEN specimens only showed this behaviour in the range of -100 to -120° C. SEN specimens were completely ductile above -40° C and were semi-brittle between -60 to -80° C. Semi-brittle refers to fractures with pronounced ductile characteristics



Figure 2 Fracture toughness for 5 mm specimens.

but not as complete as in a total ductile failure. A $K'_{\rm C}$ value may often be found but it is higher than the true value. Below 20° C, however, there was a pronounced notch "pop-in" in ductile specimens which has already been described [6] and $K'_{\rm C}$ was determined when this occurred. For semi-brittle specimens there is no pronounced "pop-in". An initiation value $K_{\rm initial} = 2.2 \,\mathrm{MN}\,\mathrm{m}^{-3/2}$ over the whole temperature range was again observed. The variation of $K'_{\rm C}$ with temperature is shown in Fig. 3 for both specimen types and a similar pattern to the 5 mm data is evident.



Figure 3 Fracture toughness for 3 mm specimens.

2.4. Discussion

The lower $K'_{\mathbf{C}}$ values found for the SN specimens is a clear indication of the thickness effect. The 5 mm specimens had an equivalent thickness H' of 10 mm while those of 3 mm were 8 mm. By using Equation 3, therefore, it is possible to determine K_{C2} and K_{C1} if σ_{y} is known. In this case, σ_{y} was determined separately and is shown in Fig. 4 for 5 mm sheet for a strain-rate of 0.026 sec^{-1} . For a 3 mm sheet it was found to be about 5% higher and due account was taken of this in the analysis. Although K_{C2} and K_{C1} can be determined in this way the form of Equation 3 is such that the computed value of K_{C1} is subject to large changes because of small variations in the $K'_{\mathbf{C}}$ values. The calculated values of K_{C1} are about 2 MN m^{-3/2} for all temperatures and it is reasonable to suppose that K_{initial} is, in fact, K_{C1} since it represents



Figure 4 The variation of yield stress with temperature at 0.026 sec^{-1} .

fracture in the central region arrested by the plane stress region. If $K_{C1} = 2.2 \text{ MN m}^{-3/2}$ is assumed for all temperatures, K_{C2} may be computed from the four sets of data using Equation 3 and these values are shown in Fig. 5. They show good consistency giving a constant value for temperatures above -40° C and a linear relationship below -40° C. There is evidence of shear lips forming above -60° C and these reduce in size as the temperature falls. At all temperatures they are substantially smaller (< 0.1 mm) than the calculated r_{y2} (~ 1 mm).

This pattern is consistent with the occurrence of a β process below -40° C resulting in increases in $K_{\rm C}$ from viscoelastic energy losses. For PMMA a constant crack opening displacement u [5] proved



Figure 5 K_{C_1} and K_{C_2} as functions of temperature.



Figure 6 Variation of K_{C_2} with yield stress.

a good criteria for this type of behaviour. K_C for a line plastic zone is given by [5]:

$$K_{\mathbf{C}} = \sqrt{\frac{u}{e_{\mathbf{y}}}} \cdot \sigma_{\mathbf{y}} \tag{9}$$

where e_y is the yield strain which is reasonably constant for polycarbonate at about 0.02 for this temperature range. Fig. 6 shows K_{C2} plotted versus σ_y and there is a good linear relationship indicating that the viscoelastic effects are additional to K_{C1} . The slope gives a value of u of $37 \mu m$. Transitions to ductile fractures were encountered only in 3 mm SEN specimens which is consistent with the criterion:

$$\frac{H}{r_{y2}} < 4, \quad \text{i.e.} \quad 2\pi H \left(\frac{\sigma_y}{K_{C2}}\right)^2 < 4.$$

The transition at -80° C indicates a value of 5.3 instead of 4 which probably arises from variations in σ_y with rate in this region.

3. Slow crack growth

The variation of $K_{\rm C}$ with crack speed for temperatures below -40° C was determined using the double torsion method as described in detail for PMMA in a previous paper [5]. The double torsion specimen is designed so that cracks may be grown at a constant speed by loading the specimens at a constant displacement rate. The tests were performed using the same temperature box and testing machine as for the tension tests. Specimens of 5 mm and 3 mm thickness with side grooves were used so that the effective thicknesses were about 3 to 4 mm and 2 mm. Single edge notched 1996

instability values for these thicknesses were determined using Equation 3 with the appropriate values of K_{C1} and K_{C2} .

 $K_{\rm C}$ versus crack speed curves were determined over the range 0.15 to 15 mm sec⁻¹ at -60, -80, -100 and -120° C and these are shown in Figs. 7 and 8. When plotted on a log-log basis the data follow quite good parallel straight lines of slope 0.044 which is approximately the tan δ for the β process. The data can also be described quite well by the Arrhenius equation and give an activation energy of 10 kcal mol⁻¹ which is in good agreement with reported values for the β process [7]. The form of these data exactly parallel that obtained for PMMA [5].

The specimens showed the same instability phenomena as PMMA in that it was not possible to obtain stable crack growth above a certain speed at each temperature. These speeds are determined experimentally by extrapolating the $K_{\rm C} - \dot{a}$ curves to the SEN values as shown in Figs. 7 and 8 and good consistency (i.e. reasonably independent of



Figure 7 Variation of fracture toughness with crack speed determined in double torsion, 5 mm specimens.



Figure 8 Variation of fracture toughness with crack speed determined in double torsion, 3 mm specimens.

Temperature (°C)	Experimental \dot{a}_{C} (mm sec ⁻¹)		$\bar{\tau}$ τ (°C)	Developed in (more sea-1)
	H = 5 mm	H = 3 mm	$I = I_0 (C)$	reducted $a_{\rm C}$ (mm sec)
- 60	37	67	23.0	32
- 80	20	27	18.9	20
-100	11	13	14.6	12
-120	6	6	11.0	6

TABLE I

thickness) is obtained at each temperature as shown in Table I.

It has been shown previously [5] that this instability can be ascribed to the onset of adiabatic heating at the crack tip and consequential softening. The $K_{\rm C} - \dot{a}$ curves may be modelled by:

$$K_{\rm C} = \sqrt{(u.e_{\rm y})} \cdot \left(\frac{\pi e_{\rm y}}{u}\right)^n \cdot E_0 \cdot e^{nH/R(1/T-1/T_0)} a^n$$

where E_0 is the unit time modulus value. *n* is used to describe the modulus data in the form:

$$E = E_0 \cdot t^{-r}$$

and determines the slope of the log $K_{\rm C} - \log a$ curve. The condition for $dK_{\rm C}/d\dot{a} = 0$ is given by:

$$\dot{a}_{\rm C} = \frac{\rho ck}{e_{\rm y}^2} \cdot \frac{(\overline{T} - T_0)^2}{K_{\rm C}^2}$$
$$\overline{\overline{x}} = \frac{\pi}{K_{\rm C}} - \frac{2R}{K_{\rm C}^2}$$

where

$$\bar{T}-T_0 = \frac{2R}{H} \cdot \bar{T}^2,$$

where $\rho = \text{density}$, c = specific heat, and k = thermal conductivity. Using the following values:

$$H/R = 4840 \text{ K}; \ e_y = 0.02; \ \rho = 1200 \text{ kg m}^{-3};$$

 $k = 0.19 \text{ Nm m}^{-1^\circ} \text{C}^{-1} \text{sec}^{-1};$
 $c = 1260 \text{ Nm kg}^{-1} \circ \text{C}^{-1},$

together with the appropriate values of $K_{\rm C}$ gives the theoretical values shown in Table I. The agreement is excellent and provides further confirmation of this hypothesis for instability.

4. Conclusion

The variation of $K_{\rm C}$ with thickness seems to be adequately explained by the concept of a plane strain and a plane stress value. The independence of both values of strain-rate and temperature above -40° C would indicate almost no viscoelastic effects in the fracture process. This is surprising since the yield stress shows significant changes and indeed it is these which result in the apparent change in $K_{\rm C}$ which derives from changes in $r_{\rm y2}$. Small strain viscoelastic data [7] are consistent with this since they indicate very low tan δ values in the range -40 to 20° C. It is possible that σ_y is governed by larger scale molecular motions which are active over a wide temperature range but do not affect the fracture values. Below -40° C the increase in viscoelastic effects associated with the β process produces a pronounced effect on K_{C2} and this becomes proportional to σ_y as in PMMA. K_{C1} , however, does not appear to be affected.

One possible explanation for the results is in terms of the degree of constraint imposed by the test geometry. K_{C1} is under plane strain conditions and the viscoelastic processes may not be as active under these conditions, i.e. volumetric deformations are not strongly viscoelastic and these govern K_{C1} . K_{C2} , on the other hand, is determined substantially by shear processes and these would be expected to show viscoelastic effects.

When the viscoelastic effects are active and produce stable crack growth the behaviour of polycarbonate is very similar to PMMA in every respect. There is a fixed crack opening displacement of about $37 \mu m$ (c.f. 1.6 μm for PMMA) and the variations in K_C reflect changes in the modulus and yield stress. Instability crack speeds correlate very well with the predictions of an isothermaladiabatic transition as in PMMA.

References

- 1. J. P. BERRY, J. Polymer Sci. A1 (1963) 993.
- F. A. JOHNSON and J. C. RADON, Eng. Fract. Mechs. 4 (1972) 555.
- L. J. BROUTMAN and F. J. MCGARRY, J. Appl. Polymer Sci. 9 (1965) 589.
- G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Plastics and Polymers* February (1969) 75.
- G. P. MARSHALL, L. H. COUTTS and J. G. WILLIAMS, J. Mater. Sci. 9 (1974) 1409.
- 6. M. PARVIN and J. G. WILLIAMS, Int. J. Fract., in press.
- N. G. MCCRUM, B. E. READ and G. WILLIAMS, "Anelastic and Dielectric effects in polymeric solids" (Wiley, New York, 1967).

- 8. G. R. IRWIN, J. A. KIES and H. L. SMITH, Proc. ASTM 58 (1958) 640.
- 9. G. R. IRWIN, J. Appl. Mechs. December 29 (1962) 651.
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