JOURNAL OF MATERIALS SCIENCE 13 (1978) 1093–1098

Growth criteria for solvent crazes

EDWARD J. KRAMER, HEIDER G. KRENZ, DIETER G. AST
Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, New York 14853, USA

Single methanol crazes are grown from sharp cracks in polymethylmethacrylate. Double exposure holographic interferometry is used to determine the sequential strain energy release rates G and opening displacement profile of the craze from the initiation of growth to its cessation. The craze stress profile is determined at various points in its growth from the opening displacement profiles using a Fourier transform method. The rapid increase in G observed just before the craze ceases to grow demonstrates that craze growth criteria based on the concept of a constant critical total strain energy release rate cannot be correct. Similarly, the large stress concentration which develops just behind the craze tip at growth cessation is incompatible with the assumption that the craze grows to a length that just eliminates a stress singularity at its tip (Dugdale model). This feature, however, would be expected if sufficient methanol cannot reach the fibrils just behind the tip of the craze to plasticize them fully.

1. Introduction

Solvent crazes grown from cracks normally cease to grow when they reach a length which depends on the applied stress, crack length, temperature, solvent and polymer molecular weight. Various criteria for the cessation of craze growth have been proposed. Kambour [1] has suggested that craze growth ceases because the polymer becomes oriented by the competing process of plastic (shear) flow ahead of the craze. Williams [2] has proposed that growth stops when enough debris (e.g., broken craze fibrils) accumulates within the craze that the flow of solvent to the craze tip is choked off. Graham *et al.* [3] have advanced the hypothesis that the craze stops when it reaches the length l predicted by the Dugdale model [4], i.e.,

$$\frac{a_0}{a_0 + l} = \cos \frac{\pi\sigma}{2\sigma_f}$$

where σ_f is the flow stress of craze material (assumed to non-strain hardening) and a_0 is the crack length. Andrews and Bevan [5] have proposed that growth ceases when the strain energy release rate of the craze falls below a critical value, the minimum plastic work and surface energy that must be supplied to generate a craze.

To check these criteria, especially the latter two, it is necessary to be able to measure craze displacement profiles, craze stress profiles and craze strain energy release rates. We have shown previously that holographic interferometry can be used to determine these parameters [6, 7]. We report here the first measurements using this technique of the sequential strain energy release rates and opening displacements of growing solvent crazes from the initiation of craze growth to its cessation.

2. Experimental

Methanol crazes were grown from sharp cracks in polymethylmethacrylate (PMMA). With this system, for which the kinetics of craze growth have been extensively investigated [8, 9], it is possible to initiate and grow a single craze to a terminal length of several mm. The PMMA is a commercial grade (with $M_W = 941\,000$ and $M_N = 231\,000$) which was purchased from Westlake Plastics Co. in the form of 0.76 mm thick sheet. A sharp starter crack was grown from a notch in the edge of a 15 mm wide strip by stress cracking with *n*-butylacetate. After stress cracking the strip was vacuum annealed just below the glass transition temperature to remove residual stress cracking agent and to heal out any small crazes at the crack tip.

The specimen was painted white to enhance its reflectivity in the holographic experiment. Since the crazing liquid can interact with the paint causing blistering, a narrow path along the crack (and expected craze propagation) direction was masked during the painting process by covering it with tape. The strips were placed in a tensile strain frame under zero load and methanol was introduced to the crack base using a wick. Since the cooling produced by methanol evaporating from the wick can introduce thermal displacements and thus spurious fringes in the hologram, the strip was allowed to come to a steady state temperature distribution which was achieved after about a 3 min waiting period. The strip was then quickly extended in tension and the grips were fixed for the remainder of the experiment. A sequence of double exposure holograms then were recorded as the craze grew from the crack. The position of the craze tip for each hologram exposure was determined using a telemicroscope. The real and virtual images of the specimen could be reconstructed from the holograms and photographed. Details of the hologram recording and reconstruction steps have been published elsewhere [7, 10].

3. Results

A typical reconstructed hologram for incremental craze growth is displayed in Fig. 1. The fringes represent lines of constant displacement along the tensile (strip axis) direction since control holograms taken during the growth increment show no inhomogeneous out-of-plane displacements as a result of craze growth [7]. The increment in displacement from one fringe to the next can be determined from the geometry of the hologram recording step and the wavelength of the laser, taken to be $\Lambda = 0.303\,\mu m$.

3.1. Craze opening displacements

Craze opening displacements can be determined by tracing the fringes to their termini on the craze line. Starting from the zero order fringe at the tip of the craze, the fringe order at every point along both sides of the craze can be found. Multiplying the order of a particular fringe by Λ gives the displacement w of the craze surface at this point. The total craze opening displacement (displacement between points on opposite surfaces of the craze) is $2w$ since the fringes enter symmetrically. Fig. 2 shows the cumulative craze surface displacement from sequential holograms during the growth of a methanol craze from a crack in PMMA. Each hologram gives the increment in displacement from one curve to the next. (Due to the fact that the initial craze growth is relatively rapid, part of the second growth increment (from $z = 1.97$ to $z = 2.30$) was missed during the changing of the holographic plates. In this case the incremental displacement in the region $1.97 < z < 2.30$ was extrapolated smoothly from the data between $z = 2.30$ and $z = 2.52$. For this reason stresses to be subsequently derived

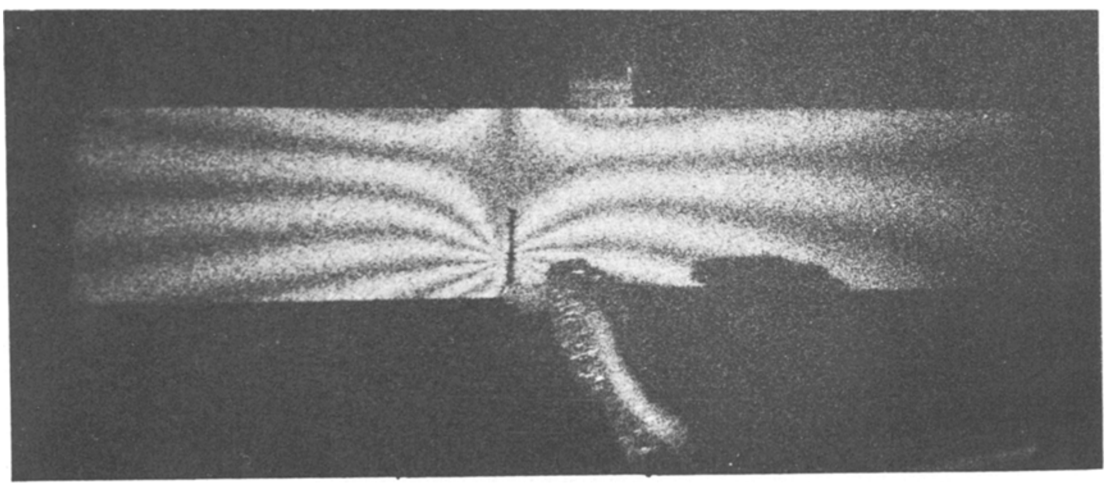

Figure 1 Virtual image reconstructed from a double exposure hologram of a PMMA strip containing a methanol craze which grew 0.35 mm between exposures.

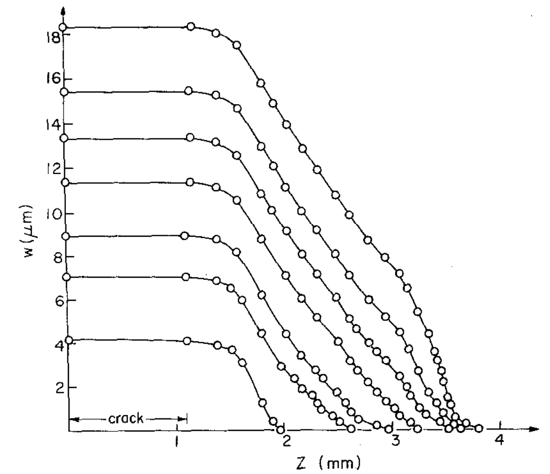

Figure 2 Cumulative craze surface opening displacement profiles of growing craze.

from these data are somewhat suspect near the craze base $z \simeq 1.1$ to 2, but near the craze tip they should be more accurate.) The shape of the craze opening displacement profile at the craze tip changes as the craze reaches its terminal length from a gently curving profile to one which shows very little opening immediately behind the craze tip and then a rapid increase in displacement at a further distance behind the craze tip. This change in craze tip displacement was also observed in other runs at the termination of craze growth and appears to be a general feature of methanol craze growth in PMMA.

3.2. Craze stress profile

We have shown previously that the craze stress profile along a line parallel to the craze but displaced from it can be approximately determined directly from the fringe pattern by measuring the spacing between fringes [7]. For the present purposes this procedure lacks the resolution necessary to determine accurately the stress over the spacing between fringes. We have adopted a Fourier transform procedure outlined by Sneddon [11] for converting crack opening displacement profiles to the surface stress σ_y necessary to maintain this displacement; Knight [12] was the first to apply this method to crazes but he used arbitrarily chosen opening displacements which are rather far from those observed. The stress σ_y is given by

$$\sigma_y(z) = -(2/\pi)\int_0^\infty \bar{p}(\xi)\cos(\xi z)\,d\xi\sigma_{yy}{}^\infty \quad (1)$$

where $\bar{p}(\xi)$ is

$$\bar{p}(\xi) = (\xi E/2)\int_0^a w(z)\cos(\xi z)\,dz \quad (2)$$

The latter integral is over the distance a from the base of the crack to the tip of the craze. The initial stress $\sigma_y(z)$ before craze growth is taken to be that of the double-ended crack with the same stress intensity factor, $K_I = 0.515\,\mathrm{MN\,m^{-3/2}}$, as our single edged precrack in our finite specimen. The changes in $\sigma_y(z)$ determined from the opening

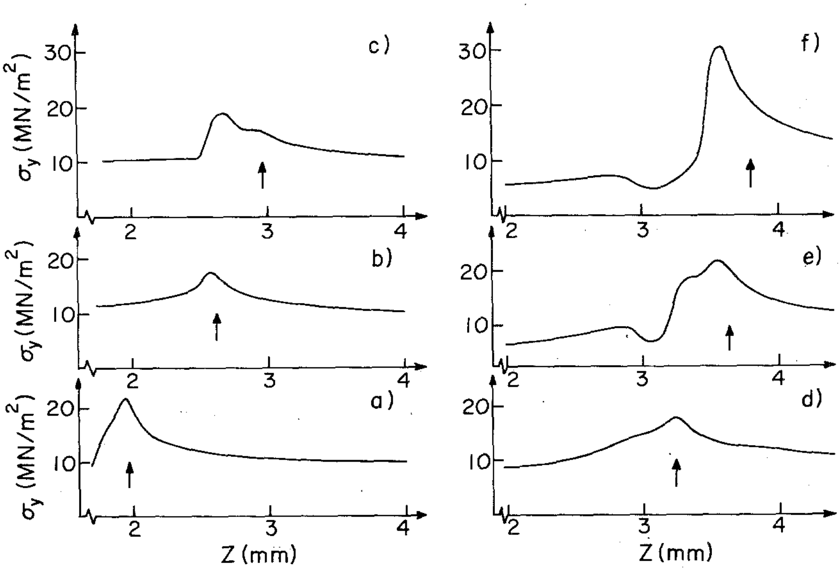

Figure 3 Stress normal to the craze versus distance along the craze. Arrows represent the positions of the craze tip.

displacements after each growth increment are added to the initial $\sigma_y(z)$. The results corresponding to some of the displacement profiles in Fig. 2 are displayed in Figs. 3a to f. The arrows in each of these figures represent the craze tip position determined optically.*

The procedure outlined above is really only rigorous for a double-ended crack and craze in an infinite specimen. Nevertheless, since all components of stress can be computed at any position of the craze plane by taking the appropriate transform of $\bar{p}(\xi)$ [11] it is possible to compare the strain ϵ_{yy} computed from displacements using the double-ended crack model with the strain measured directly from the reconstructed hologram [10]. A comparison of the strain profiles along a line parallel to the craze but displaced from it shows the overall strain level from the double-ended crack/craze calculation is too high by about 20% but that the shape and position of the peak in strain at the craze tip is about the same for both methods [13]. The higher overall strain of the calculated profile is due to the applied tensile stress σ_{yy}^{∞} which must be assigned a higher value for a double-ended cracked specimen than for a single edge notched specimen if the same K_I is to be achieved. Since the precrack length to specimen width ratio of the specimen being analysed is considerably smaller than that on which the comparison was made [13] the overall stress and strain levels computed from the double-ended crack model should be within 15% of those of the actual crack/craze.

One further caution about interpertation of the stresses at the craze tip is in order. The local stress at the craze tip is very sensitive to the local derivative of displacement. A discontinuous derivative of displacement at the craze tip gives rise to a singularity in the stress at that point [14]. Since we can only sample the displacement at a small number of points in that vicinity (corresponding to the fringes on the reconstructed hologram) it follows that the very localized displacement derivatives and thus very local stresses can not be specified with accuracy. It is possible, and in our opinion likely, that the very local stress, within a few microns behind the craze tip, rises to the value close to the stress necessary to craze the dry polymer.

3.3. Strain energy release

The strain energy released ΔU per unit thickness of specimen during a growth increment may be computed using three different methods. In the first method $\Delta U^{(1)}$ is determined from

$$\Delta U^{(1)} = -\frac{\Delta g}{2B}\Delta P \tag{3}$$

where Δg is the original (fixed) grip displacement, B is the sample thickness and ΔP is the change in tensile force due to the craze growth increment [6]. The spacing (parallel to the tensile axis) between fringes is used to establish the average change in tensile strain $\langle\delta\epsilon_{yy}\rangle$ on a cross-section of the specimen far from the craze [6, 7]; ΔP can then be computed from Hooke's law. In the second method the incremental opening displacement at the base of the crack is used to estimate $\Delta U^{(2)}$ approximately following the procedure outlined by Krenz *et al.* [7]. Finally, since both craze surface displacements and stresses have been determined, $\Delta U^{(3)}$ may be computed as

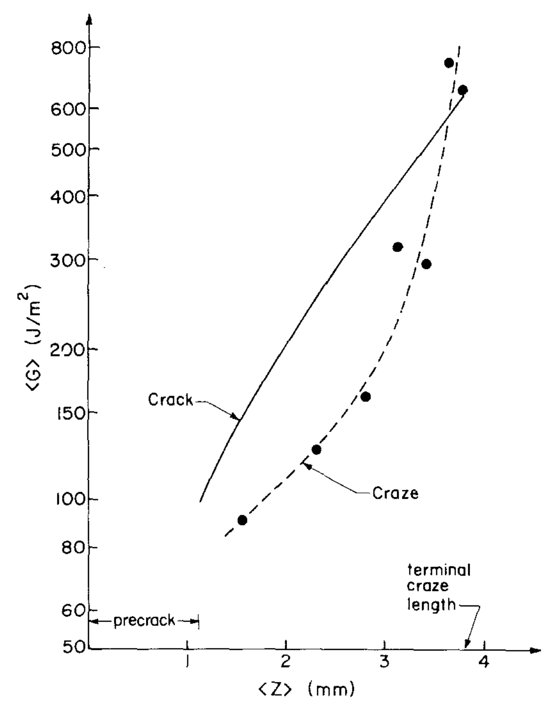

Figure 4 Strain energy release rate of growing craze averaged over the growth increment as a function of craze length. For comparison the average strain energy release rate for a crack growing the same distance is shown.

*The computation procedure was checked using the displacements from the Dugdale model [4] and found to give $\sigma_y(z)$ within 2% of the correct values except very near the discontinuity at the crack tip where it varied smoothly from 0 to the flow stress.

TABLE I

$\bar{a}$ (mm)	ΔU_{crack} (J m^{-1})	$\Delta U^{(1)}_{\text{craze}}$ (J m^{-1})	$\Delta U^{(2)}_{\text{craze}}$ (J m^{-1})	$\Delta U^{(3)}_{\text{craze}}$ (J m^{-1})	$\Sigma\Delta U_{\text{crack}}$ (J m^{-1})	$\Sigma\Delta U^{(1)}_{\text{craze}}$ (J m^{-1})	$\Delta U^{(3)}_{\text{crack}}$ base (J m^{-1})	$\Delta U^{(3)}_{\text{crack}}$ tip (J m^{-1})	$\langle G_{\text{tip}}\rangle$ (J m^{-2})
1.1	–	–	–	–	–	–	–	–	–
1.97	0.125	0.080	0.075	0.070	0.125	0.080	–	0.070	80
2.62	0.167	0.080	0.095	0.081	0.922	0.160	0.057	0.024	37
2.97	0.125	0.055	0.060	0.058	0.417	0.215	0.055	0.003	8
3.24	0.113	0.085	0.085	0.095	0.530	0.300	0.090	0.005	18
3.54	0.156	0.090	0.080	0.084	0.686	0.390	0.080	0.004	13
3.64	0.058	0.075	0.100	0.081	0.744	0.465	0.080	0.0005	5
3.80	0.100	0.105	0.145	0.103	0.844	0.570	0.101	0.0005	3

$$\Delta U^{(3)} = 2\int_0^a \overline{\sigma_y}(z)w(z)\mathrm{d}z \qquad (4)$$

where $\overline{\sigma_y}(z)$ is the average at position z of the stress before, and the stress after, the increment of craze propagation. These three estimates of ΔU are tabulated in Table I together with the position a of the craze tip at the end of the growth increment. It is apparent that there is reasonable agreement among these different methods of determining ΔU. For comparison the ΔU for a crack propagating the same increments as the craze is also tabulated. The average strain energy release rate $\langle G\rangle$ over the growth increment Δa is

$$\langle G\rangle = \Delta U/\Delta a \qquad (5)$$

This quantity is plotted in Fig. 4 versus the average craze tip position $\langle z\rangle$ during the growth increment. The average strain energy release rate for a crack propagating the same distance as the craze is also given as the solid line.

4. Discussion

One intuitively expects that the strain energy release rate for a craze should decrease with increasing craze length until it falls below some critical value at which point growth stops. Fig. 4 shows that just the reverse is true; the strain energy release rate increases rapidly with increasing craze length and achieves its highest values, which *exceed* the strain energy release rate for a crack of the same length, just before craze growth ceases. The apparent paradox is removed if one realizes that the strain energy release rates of a crack and a craze are fundamentally different. For a crack propagating an incremental distance, there is no work done behind the original crack tip ($\sigma_y(z)$ is zero there); however since $\sigma_y(z)$ for a craze is finite behind the original craze tip (the craze base), work is done in opening this section and in fact contributes a major portion of the strain energy released. By breaking Equation 4 up into the sum of two integrals, one over the craze base and one over the incremental distance Δa propagated (craze tip), one can compute the contributions of these two regions to ΔU as follows:

$$\Delta U^{(3)} = \Delta U^{(3)}_{\text{base}} + \Delta U^{(3)}_{\text{tip}} \qquad (6)$$

$$\Delta U^{(3)}_{\text{base}} = 2\int_c^{c+a-\Delta a} \overline{\sigma_y}(z)w(z)\,\mathrm{d}z$$

$$\Delta U^{(3)}_{\text{tip}} = 2\int_{c+a-\Delta a}^{c+a} \overline{\sigma_y}(z)w(z)\,\mathrm{d}z$$

The results, displayed in Table I, show that the craze base contributes over 99% of the strain energy released near the terminal craze length. In fact, it is possible to achieve an infinite strain energy release rate after the craze growth stops since the craze base fibrils can continue to relax, and the craze base to open, even if the craze tip does not advance; Krenz [13] has obtained a hologram of such a craze which opened but did not grow in length. All that is required is that the cumulative strain energy released be less than that of a crack (that this is true in our case is confirmed by a comparison of $\Sigma\Delta U_{\text{crack}}$ with $\Sigma\Delta U_{\text{craze}}$ in Table I); the strain energy release rate of a craze can be much larger than that of a crack.

Clearly the total strain energy release rate cannot be interpreted as a craze extension force. One is tempted to use the strain energy release rate from the tip section $\langle G_{\text{tip}}\rangle \equiv \Delta U_{\text{craze tip}}/\Delta a$ for this purpose. Unlike the total strain energy release rate $\langle G_{\text{tip}}\rangle$ decreases as the craze lengthens, as shown by the last column in Table I. Nevertheless this decrease in $\langle G_{\text{tip}}\rangle$ occurs not because the stress at the craze tip decreases (Fig. 3) but because the opening displacement just at the craze tip becomes smaller and smaller in response to this stress just before the craze stops (Fig. 2). This feature of the results is in disagreement with the assumptions of the Andrews and Bevan [5] proposal. Just as clearly the stresses in the craze are not approaching the constant value expected from the Dugdale model as proposed by Graham *et al.* [3], but rather a pronounced stress concentration develops *behind* the tip of the craze just before it stops. This feature would be expected if sufficient methanol cannot reach the fibrils just behind the tip of craze to plasticize them fully. It is not necessary, however, that the craze actually clogs with debris as suggested by Williams [2]. It is proposed elsewhere [15] that the solvent craze is actually preceded by a very short length of dry craze that is necessary to achieve mechanical equilibrium, and that the craze stops when the fibril volume fraction v_f in the solvent craze, just behind the short air craze tip, becomes so large that fluid transport through this zone becomes negligibly small. Since the hydraulic permeability of the craze very rapidly decreases as v_f increases, negligible fluid transport occurs when v_f is still less than one, especially when the volume swelling of the fibrils with solvent is taken into account. (The volume fraction of methanol absorbed in PMMA at equilibrium is 25% at room temperature [16]). It may also be that these high stresses at the craze tip in the absence of solvent produced orientational shear flow in a zone ahead of the craze as suggested by Kambour [1], although there is no evidence from our holograms of a large zone (greater than 0.1 mm in diameter) of this type.

Acknowledgements
The financial support of the U.S. Army Research Office at Durham is gratefully acknowledged. This reasearch also benefited from use of the facilities of the Cornell Materials Science Center which is funded by the National Science Foundation. Helpful discussions with the Professor J. G. Williams about his unpublished hypothesis are appreciated.

References
1. R. P. KAMBOUR, *J. Polymer Sci.* 7 (1973) 1.
2. J. G. WILLIAMS, private communication.
3. I. D. GRAHAM, J. G. WILLIAMS and E. L. ZICHY, *Polymer* 17 (1976) 439.
4. D. S. DUGDALE, *J. Mech. Solids* 8 (1960) 100.
5. E. H. ANDREWS and L. BEVAN, *Polymer* **13** (1972) 337.
6. H. G. KRENZ, E. J. KRAMER and D. G. AST, *J. Polymer Sci. Polymer Lett.* **13** (1975) 583.
7. H. G. KRENZ, D. G. AST and E. J. KRAMER, *J. Mater. Sci.* **11** (1976) 2211.
8. J. G. WILLIAMS and G. P. MARSHALL *Proc. Roy. Soc. London.* **A342** (1975) 55.
9. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *ibid* **A319** (1970) 165.
10. T. L. PETERSON, D. G. AST and E. J. KRAMER, *J. Appl. Phys.* **45** (1974) 4220.
11. I. N. SNEDDON, "Fourier Transforms" (McGraw–Hill, New York, 1951) p. 395.
12. A. C. KNIGHT, *J. Polymer Sci.* **A3** (1965) 1845.
13. H. G. KRENZ, Ph. D. Thesis, Cornell University, 1977.
14. N. VERHEULPEN-HEYMANS, *J. Polymer Sci.* **14** (1976) 93.
15. E. J. KRAMER and R. A. BUBECK, to be published.
16. E. H. ANDREWS, G. M LEVY, and J. WILLIS, *J. Mater. Sci.* 8 (1973) 1000.

Received 26 July and accepted 9 September 1977.