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Craze and yield zones in the fracture of rigid PVC

H. R. BROWN, TAN HEA CHIN*
Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

Two techniques have been used to examine the reported discrepancy between the measured fracture toughness of rigid PVC and that calculated from its crack tip craze. The use of a generalized model of a cohesive zone produced no better agreement between calculation and experiment than the Dugdale model used previously. The discrepancy was probably caused by the coexistence with the craze of a yield zone which was observed by optical and scanning electron microscopy.

1. Introduction

The brittle failure of a number of amorphous glassy polymers, in particular PMMA, polystyrene, polycarbonate and PVC, has been shown to occur by a crazing mechanism [1, 2]. PVC is known to show also a non-crazing failure mode [3, 4]. The shape of crack tip crazes has been examined for PMMA and shown to be an accurate fit to the Dugdale model [5, 6] and the stress intensity factors from the crack tip craze displacements using the Dugdale model also agree well with experimental values. This is not the case for crack tip crazes in PVC however; both Mills and Walker [2] and also Brown and Stevens [4] found that in this material the crack tip crazes were much more wedge shaped than would be predicted by the Dugdale model, and also that the stress intensity factors calculated from the craze parameters using the Dugdale model were less than half of those observed experimentally. Mills and Walker suggested that this discrepancy might be caused by the existence of plastic yielding above and below the craze whereas Brown and Stevens thought the use of the Dugdale model for the wedge shaped crazes might be the problem. A fairly similar discrepancy has been observed by Fraser and Ward [7] in polycarbonate. In this case shear lips were plainly visible on the sides of the specimen and they analysed their data on the assumption that the failure energy of the shear lips was higher than that of the craze. Kambour *et al.* [8] have however noted the existence of plane strain plastic zones as well as crazes in low speed failure in polycarbonate at room temperature.

The purpose of the current work is to attempt to discover which, if any, of these suggestions is correct for PVC. This has been approached in two ways, firstly by optical and scanning electron microscopic observation of fracture in a commercial grade of clear rigid PVC and secondly by recalculation of stress intensities from crack tip crazes by use of Smith's [9] generalized model of the "cohesive zone". Smith has proposed a generalized model for a cohesive or yielded zone at a crack tip in which the stress across the zone is not assumed to be constant. Using this model it is possible to calculate stress intensity factors from craze shapes with no assumptions about the magnitude of the stress across the craze and so find directly whether the failure energy is all going into this crack tip craze.

2. Theory

Smith assumed the existence of an infinite elastic body which contains a centre slit of length $2c$ on the axis, $y = 0$, the solid experiencing a remote stress $p_{yy} = \sigma_0$ such that it deformed in plane strain. A small cohesive zone of length R ($\gg c$) was assumed to exist near the crack tip and the co-ordinate system was chosen such that $x = 0$ at the tip of the cohesive zone. He showed that the stress $p(s)$ across the cohesive zone at a position $x = s$ is given by

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*Present address: Esso Australia Ltd, Sale, Victoria 3850, Australia.

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$$p(s) = \frac{\mu}{\pi(1-\nu)}(R-s)^{\frac{1}{2}} \int_0^R \frac{(\mathrm{d}v/\mathrm{d}t)\mathrm{d}t}{(t-s)(R-t)^{\frac{1}{2}}} \tag{1}$$

where $v(x)$ is the y component of the displacement of the surface of the cohesive zone, t is a variable on x axis, μ is a Lamé constant and ν the Poisson's ratio. He also showed that the smooth closure condition, the requirement that $\mathrm{d}v/\mathrm{d}t = 0$ at $x = 0$ and that no stresses become infinite, gives

$$\sigma_0 = \frac{\mu}{\pi(1-\nu)}\left(\frac{2}{c}\right)^{\frac{1}{2}} \int_0^R \frac{(\mathrm{d}v/\mathrm{d}t)\mathrm{d}t}{(R-t)^{\frac{1}{2}}} \tag{2}$$

As it is assumed that the cohesive zone length is small with respect to the crack length, the normal small scale yielding approximation, then,

$$K_\mathrm{I} = \sigma_0 \sqrt{(\pi c)}$$

$$\therefore \quad K_\mathrm{I} = \frac{E}{(1-\nu^2)}\frac{1}{(2\pi)^{\frac{1}{2}}} \int_0^R \frac{(\mathrm{d}v/\mathrm{d}t)\mathrm{d}t}{(R-t)^{\frac{1}{2}}} \tag{3}$$

Stress intensity factor can hence be calculated directly from craze (cohesive zone) displacements if the modulus and Poisson's ratio of the material are known.

The theory described above assumes a large specimen and constant remote stress σ_0 whereas the experiments, to be described later, were done by wedging open a crack. If the plastic zone is small enough with respect to the specimen dimensions then on the basis of St Venant's principle we can assume these situations to be equivalent.

3. Experimental method and result

3.1. The material

The material used was a clear rigid PVC sheet, ICI Darvic 110, which had a thickness of 6 mm. No information was available on the lubricant and stabiliser systems; the molecular weight distribution of the polymer was examined in a Du Pont liquid chromatograph and the weight average molecular weight M_w was found to be 1.1×10^5. The elastic modulus of the material was measured and found to be 3.4 GPa at a strain of 0.1%. The fracture toughness was examined using compact tension specimens and a cross-head speed of 10^{-2} cm min^{-1}. Stable crack growth was not observed in this material and the instability fracture toughness, K_IC was found to be 1.30 ± 0.15 MN m$^{-3/2}$. Shear lips were again not observed. The calculations described in Section 4 were made on results obtained by Brown and Stevens on slightly plasticised PVC compounds whose preparation has already been described [4].

3.2. Optical measurements

The crack front was observed in reflection and transmission optical microscopy in a manner similar to that described previously [4]. The crack was propagated in a horizontal plane by wedging its base open with a razor blade and was observed using approximately monochromatic green light. As stable crack growth was not possible in this material, the crack was initially grown unstablely for about 10 mm from a saw cut. This ensured the existence of a sharp crack front well away from the razor tip. As the aim of the work was to observe the crack and craze just before crack propagation, the craze was loaded by pushing the razor into the crack and a photograph was taken of the fringe pattern. It was then unloaded and the unloaded fringe pattern recorded. This was repeated for small and slowly applied incremental loads until the crack propagated in an unstable manner.

A number of photographs taken using this technique are shown in Fig. 1. It is clear from these pictures that the craze is growing in a fatigue manner on each loading cycle. The most intriguing feature however is the way that, on loading, a new craze is sometimes formed some distance beyond the old craze, with a dark band between them. As these are reflection micrographs this dark band must consist of material which does not reflect light and so is probably not crazed. The most likely explanation is that the dark band is a yield zone which is formed in front of the pre-existing craze on unloading or reloading. The new craze then forms in front of this yielded zone giving two craze fringe patterns with a dark line between them.

It can be seen from the photographs that on fatiguing both craze and yield zones break down gradually to a rough structure which shows no fringes.

3.3. Scanning electron microscope observation

A fracture surface of a specimen similar to that studied optically was examined in a scanning electron microscope. The surfaces were coated with gold in a vacuum evaporator before examination to reduce specimen charging. The fracture

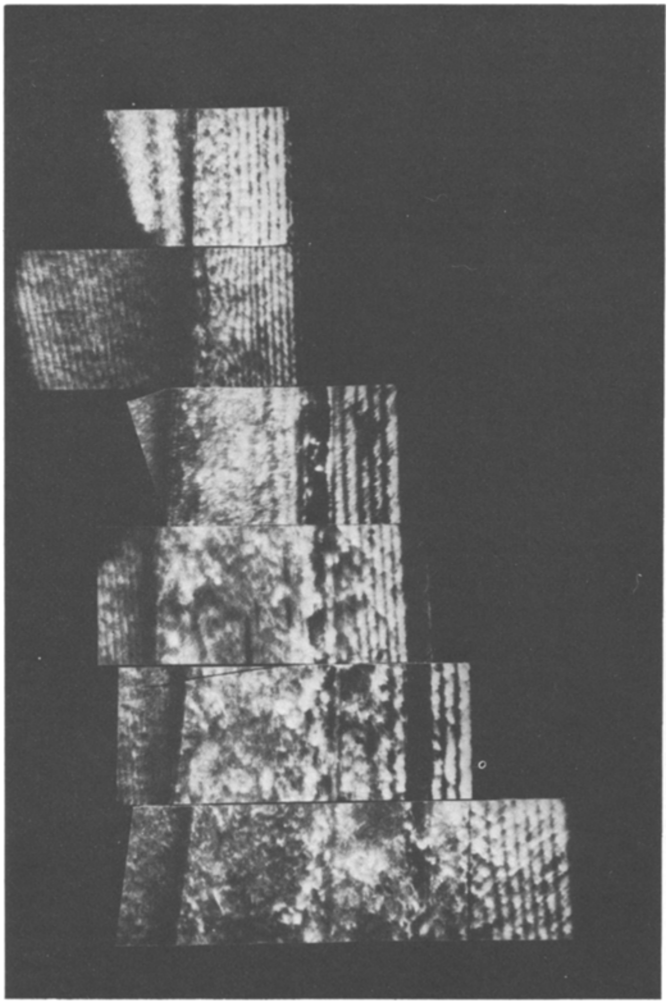

Figure 1 Reflection optical micrographs of an unloaded craze taken after successive fatigue cycles. The top two crazes have lengths of 90 μm.

surface is shown in Fig. 2 with the prominent band at high magnification in Fig. 3. These pictures can be considered as more evidence for the existence of yielded zone between crazes. The width of the highly drawn region in Fig. 3 is similar to that of the dark bands in the optical micrographs so it seems probable that the dark bands consisted of yield regions which were drawn out on failure to a greater extent than the craze either side.

4. Calculations using Smith's model

The shapes of crack tip crazes in five grades of rigid PVC were examined by Brown and Stevens and the fracture toughness calculated by fitting the craze length and craze opening displacement to a Dugdale model [4]. In this work a constant refractive index of 1.30 was assumed for the unloaded crazes so that the actual displacements of the unloaded craze could be calculated. In no case were shear lips observed in these specimens. Fracture toughnesses have now been recalculated from these craze shapes by numerical solution of Equation 3. The results obtained are given in Table I.

5. Discussion and conclusions

It can be seen from results in Table I that the K_I obtained by use of the Dugdale model was in all cases larger than that obtained using the actual craze displacements and Smith's model. The measured K_I values were considerably larger than those obtained by either technique so the use of the Dugdale model in [4] was not the reason for the discrepancies observed between measured stress intensities and those calculated from the shape of the crack tip crazes.

It seems probable that crazes and yielded but non-voided zones co-exist at crack tips in some grades of PVC. The existence of the yield zones is the most likely explanation for the discrepancies

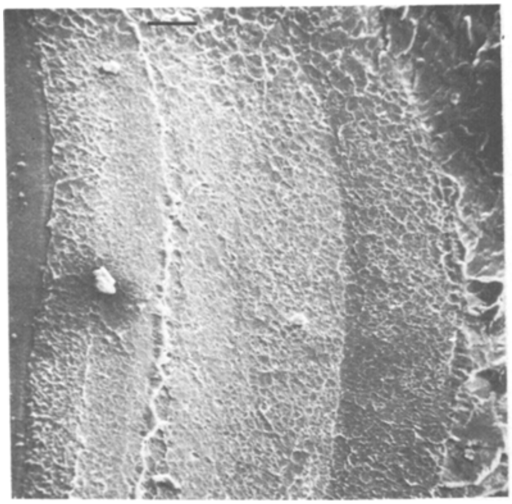

Figure 2 SEM picture of fracture surface. Scale bar = 50 μm.

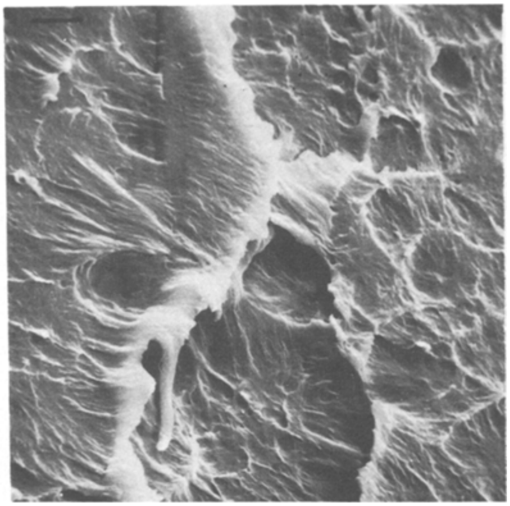

Figure 3 The prominent band on Fig. 2 shown at higher magnification. Scale bar = 5 μm.

shown in Table I. The materials used in those calculations cover a plasticizer range of 3 to 15 p.h.r. and hence they are representative of most commercial materials which contain lubricants if not plasticizers in this concentration range. The yield zones are probably above, below and, maybe, in front of the craze as suggested by Mills and Walker. Because of their existence it is not valid to use Equation 1 to calculate the stresses across the craze.

In a particular grade of clear PVC, Darvic 110, unloading and reloading the crack tip caused the craze to renucleate beyond the craze tip yielded zone. In one case the new craze actually appeared on unloading so it seems likely that the resistance of the yield zone to reverse yielding causes a stress concentration on unloading. This dilational stress must be large enough to form a small craze. This effect is very convenient in that it makes the yield zone "visible". This craze tip zone may itself be formed on unloading, as in continuous loading the yield might be only above and below the craze.

The co-existence of crazing and yield zones in PVC is not surprising as a ductile, non-crazing failure mode has been shown to exist in some grades of this material [3, 4]. Also Vincent [10] showed that the impact strength varies rapidly with notch tip radius in PVC, a phenomenon which is normally associated with yielding rather than crazing failures at large tip radii.

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TABLE I Measured and calculated K_I values

Material PVC+	Measured K_I (MN m$^{-3/2}$)	Dugdale K_I (MN m$^{-3/2}$)	Equation 3 K_I (MN m$^{-3/2}$)
3% DIOP	1.6	0.51	0.36
5% DIOP	2.6	0.67	0.47
7% DIOP	2.6	0.76	0.52
10% DIOP	3.0	0.79	0.57
15% DIOP	2.4	0.73	0.69