

The fracture behaviour of uPVC at both ambient and high hydrostatic pressures

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Fracture measurements have been made using a high pressure technique on three batches of uPVC corresponding to distinct levels of gelation. K_c values correlate with methylene chloride attack in the established manner, but are low in comparison with room pressure values measured at comparable strain rates. This is linked with the presence of stress whitening on the fracture surface at room pressure, its absence at high pressure, and its diminution at room pressure when testing speed is increased, when low K_c values are also recorded. The results are successfully interpreted in terms of a multiple craze slow crack growth model, in which cracking in the tests at room pressure and slow speed is assumed to start at the K_c measured at high pressure, and slow crack growth follows as the load on the specimen continues to increase until the specimen fails catastrophically. A reasonable choice of parameters then gives a good prediction of the observed collapse loads.

1. Introduction

There is considerable interest in the fracture behaviour of uPVC, arising largely from its extensive use in pressure-pipe applications [1-5]. It is generally true that values of K_c for uPVC correlate positively with its resistance to attack by methylene chloride (and hence the degree of "gelation" or fusion of the polymer grains) [4], thus enabling fracture toughness to be used as a quantitative quality control factor. The fact that K_c values depend on the rate of testing [1, 3, 4] increases the complexity of the problem.

In this paper, we report K_c measurements of uPVC obtained in an environment of high hydrostatic pressure (250 to 700 MPa). These values are seen to correlate in the expected way with methylene chloride immersion tests; tougher materials are attacked less. They are considerably lower than those obtained at similar testing speeds at room pressure, corresponding more closely to results from higher speed measurements. We attribute this to the presence of stress-whitened zones on the fracture surfaces of room pressure specimens, which decrease in size as testing speed is increased, and which are absent in the high pressure specimens.

These stress-whitened zones are believed to correspond to regions of slow crack growth. Evidence is presented to support the view that the values obtained at high and room pressures are compatible, provided that the latter are interpreted in terms of a slow crack growth model.

2. Materials

Extruded uPVC rod was supplied to us by BP Chemicals Ltd, Barry. (We are indebted to Dr Alan Gray for his kind co-operation in this regard.) Using a twin-screw extruder, three batches of rod were prepared under conditions designed to give three distinct levels of gelation. A rheometry-based method was used to assess the fusion of the material [6]. The extrusion parameters and estimated levels of fusion are given in Table I; Batch 3 is of the highest and Batch 1 of the lowest level of gelation. The conditions are such as to give material in a range comparable with that of typical pipes.

Methylene chloride tests were carried out on a specimen from each batch. Pieces of rod were cut at a small angle to the axis, thus exposing a surface of length ~ 140 mm of the 27 mm

TABLE I

Batch	Extrusion pressure (kPa)	Melt temperature (°C)	% Fusion
1	255	177.7	61
2	284	185.5	81
3	310	193.9	100

diameter rod. The cutting was done by hand, sufficiently slowly to produce no appreciable heating of the cutting tool so as not to form a skin of well-gelled material at the surface. The specimens were immersed in methylene chloride and attack on the exposed surfaces was observed. Batch 1 was readily distinguishable from the other two batches in this way, showing visible attack after 1 h. Batches 2 and 3 showed little sign of attack after 16 h. These tests tend to show that all three batches were of quite well-gelled material.

3. High pressure measurements

3.1. Test conditions and analysis

The high pressure tests were carried out using the same techniques as used previously for polyethylenes [7]. The mode of testing was torsional, using solid cylindrical specimens containing surface notches oriented at $\pi/4$ to the specimen axis. A mathematical analysis of this test has been reported [8]. The notches were made by pressing a new razor blade into each specimen using a jig compressed in a testing machine. The specimens were nominally of 31 mm gauge length and 8 mm diameter. The testing temperature was 20°C and the shear strain rate at the specimen surface was $1.7 \times 10^{-3} \text{ sec}^{-1}$. The hydrostatic pressure was transmitted to the specimens via a medium of deionized water.

Irwin's analysis [9] of a semielliptical surface notch was used to calculate the values of K_c ; justification for the use of such a method has been given previously [8]. The stress intensity K is given by

$$K^2 = \frac{1.2\pi\sigma^2 a}{\phi^2 - 0.212(\sigma/\sigma_y)^2} \quad (1)$$

where a is the elliptical notch depth, σ the applied remote stress and σ_y the yield stress. ϕ is an elliptic integral governed by the ellipse geometry. In practice the notch is assumed to be

equivalent to a semiellipse of the same depth and surface area. The term involving σ/σ_y is a plastic zone correction term; here the value of σ_y used is that obtained in shear (i.e. with an unnotched torsion specimen). This is considered more appropriate than a tensile value, for reasons similar to those discussed elsewhere in relation to the testing of polyethylenes [10]. The value of remote stress σ is determined from Nadai's analysis of a cylinder in torsion [11].

3.2. Results and discussion

Tests were carried out at 250, 300, 400, 500 and 700 MPa on each batch of material. For each batch at each pressure, a series of notch depths a were tested, and K_c obtained using Equation 1 with $K = K_c$ and $\sigma = \sigma_f$, σ_f being the fracture stress, and linear least squares fitting. Some of the experimental results analysed in this way are shown in Fig. 1.

The K_c values are plotted as a function of pressure in Fig. 2. As we would expect for notches which are not infinitely sharp, K_c increases with increasing pressure [12, 13]. Measured yield stresses of the materials were observed to increase linearly with pressure, and, as argued previously [7], so should K_c . The calculated slopes were found not to differ significantly, and the three regression lines are plotted at the same (mean) slope. The intercepts are such that Batch 1 gives a significantly lower extrapolated room pressure K_c value than do Batches 1 and 2, which do not differ significantly (though Batch 3 is slightly tougher than Batch 2, as we would expect from the processing data of Table I). When the data from Batches 2 and 3 are combined, the intercept value for the resulting aggregate differs significantly from that of Batch 1 at the 5% level. This is in line with the expected correlation between K_c and resistance to methylene chloride attack. The final values of K_c , extrapolated to room pressure, are 1.53, 1.63 and 1.66 $\text{MN m}^{-3/2}$ for Batches 1, 2 and 3, respectively. These values are low in comparison with room pressure measurements at comparable strain rates reported elsewhere for well-gelled uPVC [4, 5], where values quoted are in the region 3.5 to 5 $\text{MN m}^{-3/2}$; however, they differ less markedly from the 2.4 $\text{MN m}^{-3/2}$ reported at impact speeds [3]. These discrepancies are explored further in the remainder of the paper.

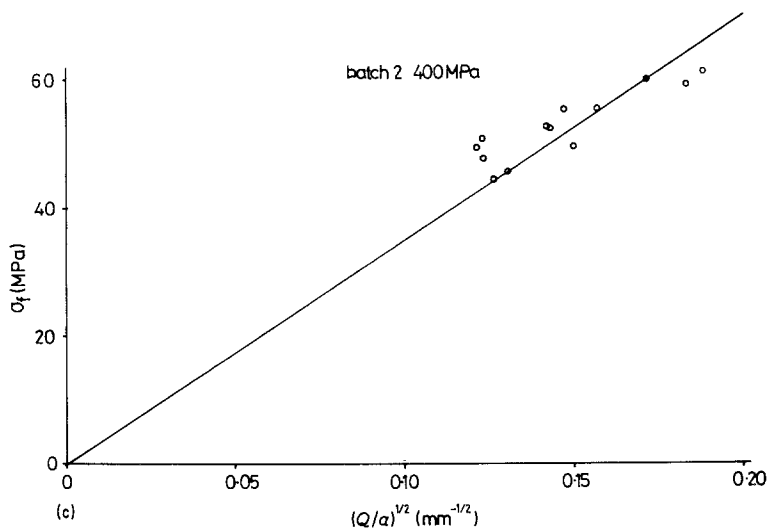
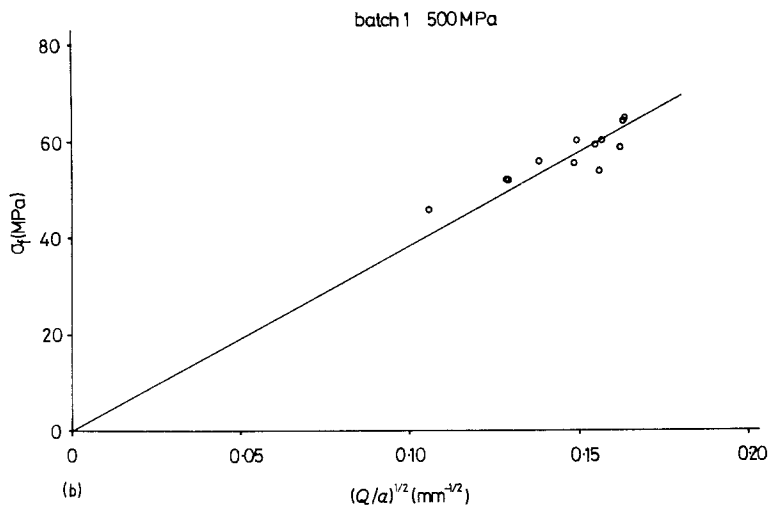
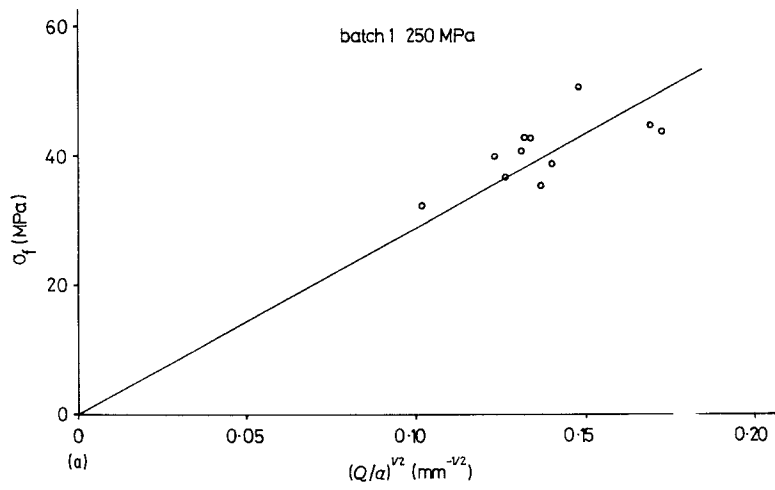


Figure 1 (a) to (f) Fracture plots based on Equation 1 for the three materials at various pressures: $Q = \phi^2 - 0.212 (\sigma_f/\sigma_y)^2$.

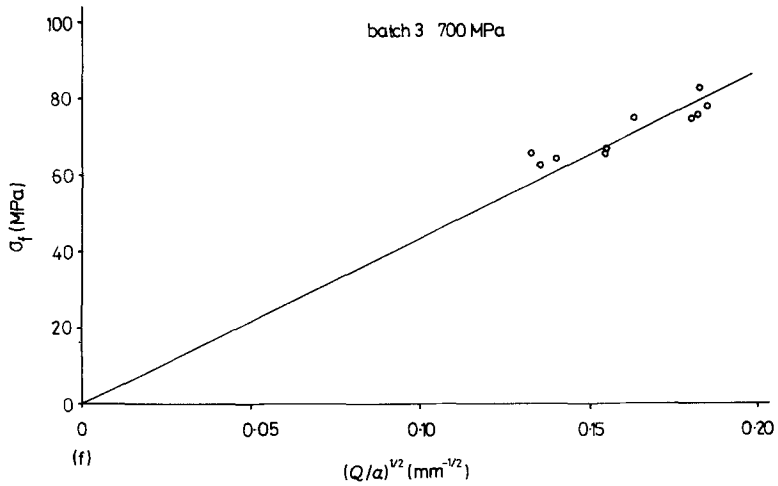
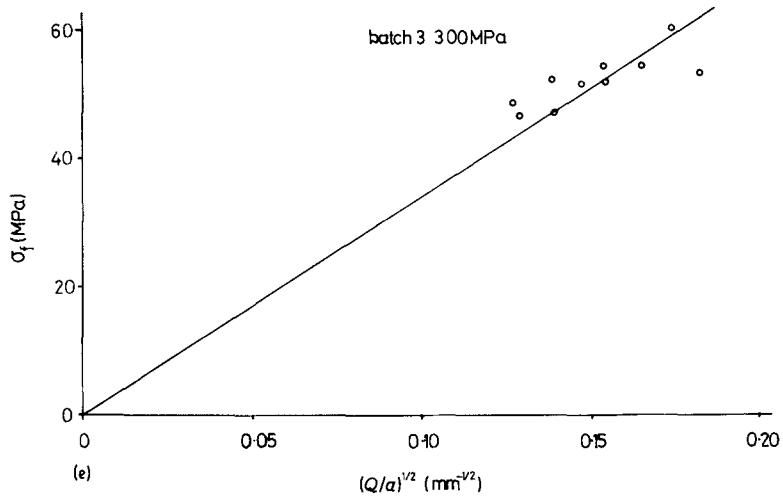
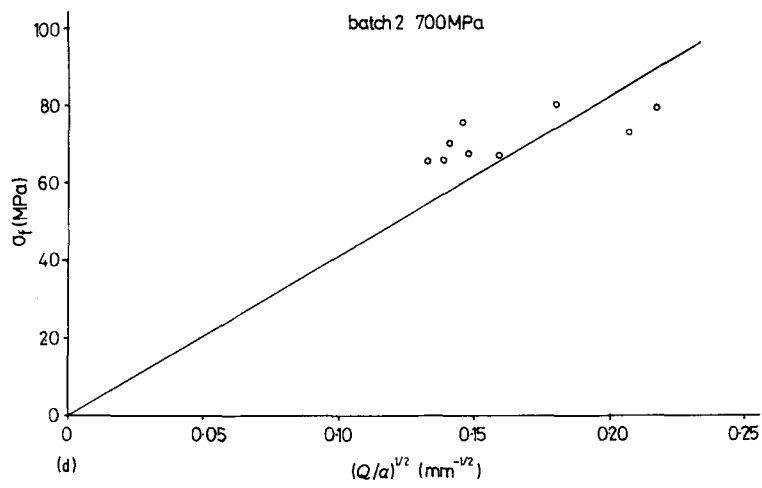


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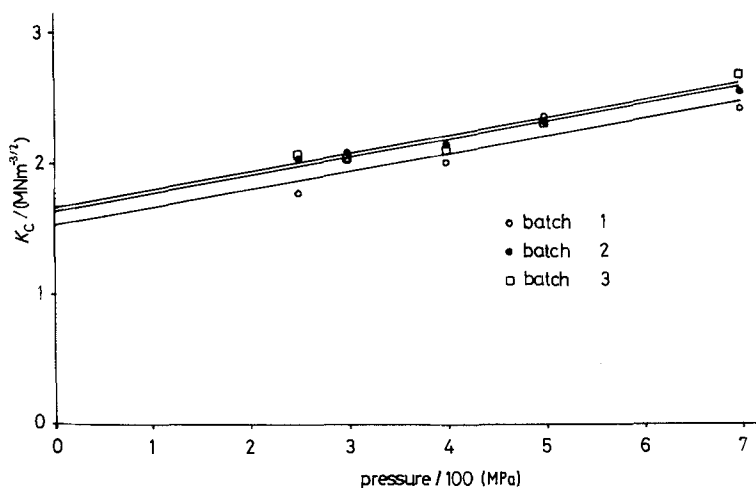


Figure 2 K_c as a function of pressure for the three materials.

4. Room pressure testing

4.1. Method of test

Specimens of rectangular cross-section 22 mm \times 13 mm were made from the Batch 3 material. They were notched in the 13 mm width surfaces and tested in three-point bend using a knife-edge span of 100 mm, at speeds of 5, 100 and 200 mm min⁻¹. The lowest speed gives a strain rate approximately equivalent to the shear strain rate used in the high pressure tests. The tests were carried out in air at a temperature of 20° C.

The notches for these bend specimens were made with a fly-cutter to a maximum depth of 10 mm. The notch tips were examined using optical microscopy and the notch tip radii were found to be in the range 10 to 30 μ m. This should be small enough to give K_c values for uPVC which are independent of notch sharpness [4]. In the low speed tests discussed below (i.e. at 5 mm min⁻¹), the notches of half of the total number of specimens were sharpened by pushing new razor blades up into the tips of the fly-cut notches; this tended to reduce the tip radius by a factor of about 2. Results from the sharpened specimens did not appear to differ significantly from those obtained with the unsharpened ones, indicating that the crack tip radii are so small that their effects are dominated by other crack-blunting mechanisms. We therefore conclude that the notch sharpness of the bend specimens is such as to justify comparison of toughness values with those obtained using razor-notched torsion specimens.

4.2. Results and discussion

K_c values were calculated using the boundary

collocation results quoted by Rooke and Cartwright [14] for three-point bend testing. Results at the different testing speeds are given in Fig. 3 as graphs of σ_f against $1/Y(pa)^{1/2}$. K_c values were calculated at 5.44, 2.54 and 2.23 MN m^{-3/2} for the 5, 100 and 200 mm min⁻¹ testing speeds, respectively. The low speed value is comparable with values obtained by Marshall and Birch [4] at strain rates of the same order, whereas the high speed tests give results resembling those reported for impact speeds [3], and are more comparable with the 1.66 MN m^{-3/2} high pressure value. It should be noted that our values are calculated on the assumption that the peak stress in the bend test is equal to the stress at crack initiation. We do not believe this assumption to be correct, and this consideration lies at the heart of the discrepancy between the room and high pressure results; it forms the subject of Section 5.

Moore *et al.* [3] also note a decrease in K_c with increasing testing speed which resembles that reported here but at generally higher testing speeds. Toughness also decreases with decreasing testing speed at speeds much lower than those reported by us [3], so that K_c actually peaks at around the strain rate corresponding to our 5 mm min⁻¹ speed. However, this lowering of toughness is probably due to an entirely different mechanism, perhaps associated with creep effects, from that responsible for the decrease in toughness with increasing speed at higher testing speeds which concerns us here. It is not therefore relevant to the present discussion.

There are obvious differences in appearance between the fracture surfaces obtained at room

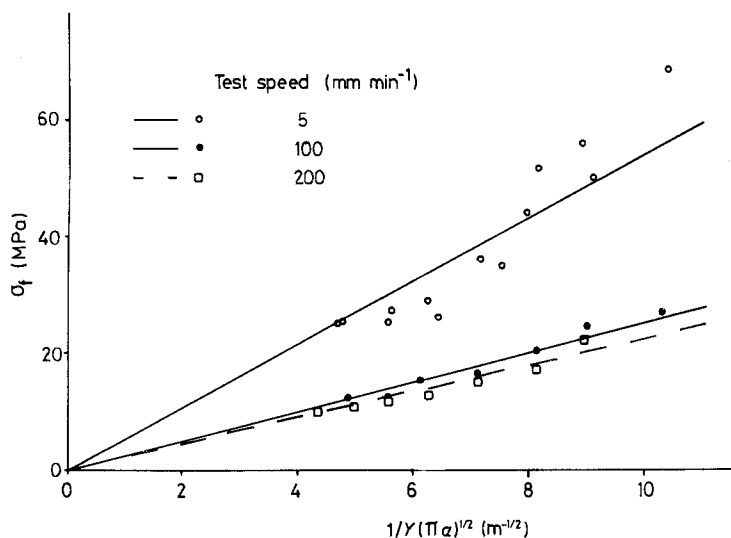


Figure 3 Fracture plots of bend tests at room pressure on Batch 3 material.

pressure at the high and low speeds and at high pressure. Photographs in Fig. 4 show that there are clearly visible stress-whitened zones adjacent to the notch tips in the room pressure specimens, of length ~ 6 mm at the 5 mm min^{-1} speed, and ~ 2 mm long for the 100 and 200 mm min^{-1} speeds. None of the high pressure specimens stressed at 250 MPa and above showed any such feature. Stress-whitened zones have been associated with slow crack growth in high toughness (i.e. well-gelled) uPVC [4].

If we accept that the stress whitened zone is the result of microvoiding or crazing, then this immediately gives a reason for its absence in the high pressure test; it would require a tensile zone to exist in the interior of the specimen, and this is not possible to any significant extent because the specimen interior is in a state of hydrostatic compression [12]. Thus, slow crack growth would be avoided in the high pressure test and the peak stress should correspond to the stress at crack initiation. On this basis, the high pressure test should give a true value of K_{Ic} which is not confounded by slow crack growth effects. The small differences between K_{Ic} values measured for the different batches using the high pressure technique may indicate that methylene chloride testing correlates more with resistance to slow crack growth than it does with K_{Ic} .

It might be suggested that the differences in fracture surfaces between those resulting from bend and those resulting from torsion tests might be due to different test geometries rather

than the application of high pressure. This possibility was explored by doing torsion tests at relatively low pressures (100 and 150 MPa) which, while too low to give valid fracture mechanics measurements on specimens of this size, were high enough to produce fracture surfaces. Small stress whitened zones were observed adjacent to the notch tips on these fracture surfaces, confirming that the different appearances were due to difference in pressure.

The information available is insufficient to allow a rigorous discussion of the dependence of the room pressure measurements on the rate of testing. We may envisage that, the slower the speed of test, the more time would be available for a craze zone to grow, and that its resulting greater size would allow it to dissipate more energy, thus postponing the onset of catastrophic failure. The viscoelastic nature of the material might also play a role, as might the increased importance of dynamic effects at higher speeds. The experimental evidence alone shows that large stress whitened zones are associated with high failure loads, and suggests that the reduction in size of the zones by whatever means lessens the degree of slow crack growth and the resulting delay between crack initiation and specimen collapse. A simple model of slow crack growth is given in the next section as an attempt to demonstrate the compatibility of the high pressure and room pressure results.

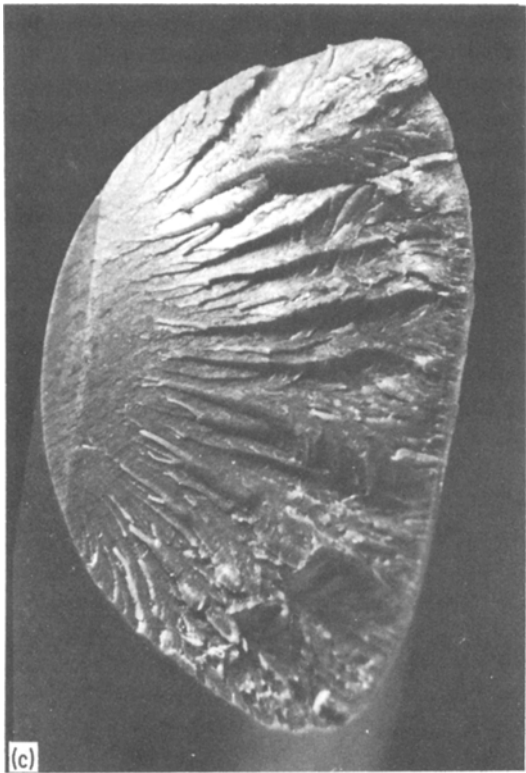
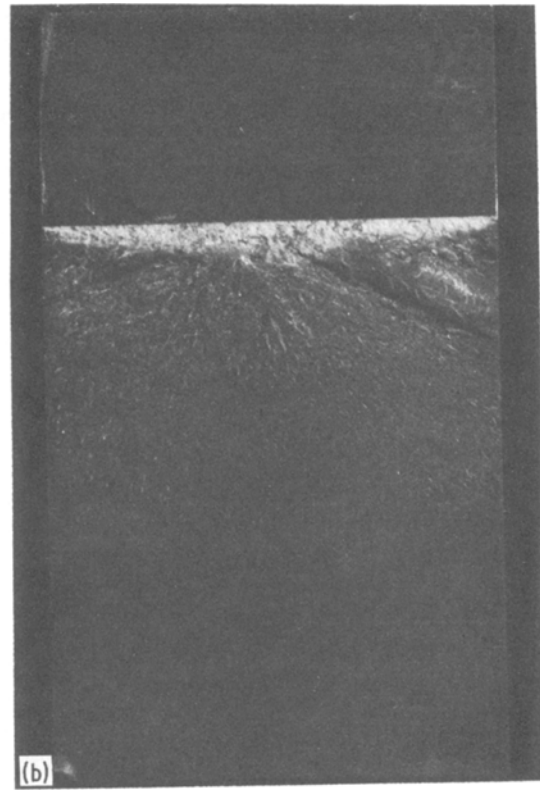
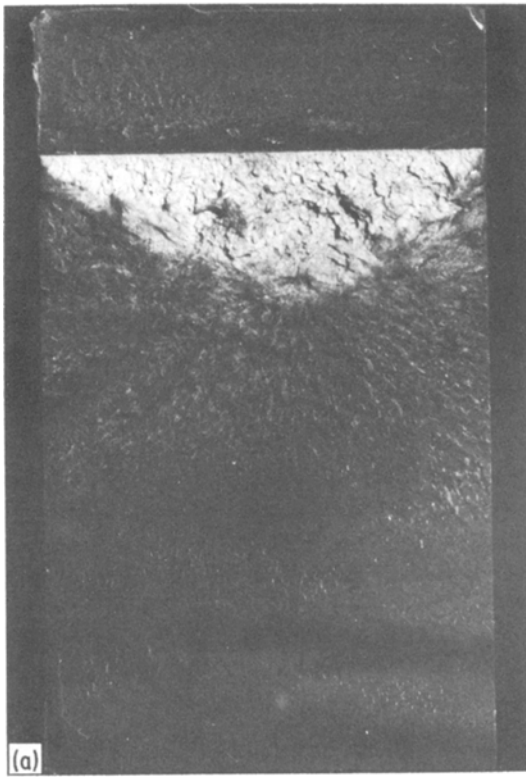


Figure 4 Fracture surfaces at (a) room pressure and 5 mm min^{-1} , (b) room pressure and 200 mm min^{-1} , (c) high pressure (500 MPa).

5. Modelling of slow crack growth

List of symbols

- a notch depth
- a_0, a_1 coefficients in creep compliance function
($C(t) = a_0 + a_1 t$)
- c crack length
- C creep compliance function
- E elastic modulus
- K stress intensity
- K_c critical stress intensity
- K_c^{app} apparent critical intensity (calculated assuming no growth)
- R craze zone length
- R_c as defined in Equation 4
- t time
- x co-ordinate in direction of crack
- Γ fracture energy
- δ length of primary craze zone
- Δu displacement discontinuity across crack
- ν Poisson's ratio
- σ_c craze stress

Dean *et al.* [15] have proposed a model of slow crack growth in uPVC which takes account of multiple crazing ahead of the crack tip and is based on McCartney's [16] study of crack growth in a viscoelastic material. A Griffith-type energy balance approach is adopted, and the energy balance carried out over a region of primary crazes, of length δ , ahead of the crack tip. There are also secondary crazes ahead of the primary crazes which act as a crack blunting mechanism but are less directly involved in the crack growth process. In physical terms, it is assumed that the material in the secondary crazes is too distant from the crack tip for the approximation of instantaneous energy transfer between plastic zone and crack tip inherent in an energy balance equation such as Equation 2 below to be valid; the work done on the secondary zone is dissipated as heat. In both primary and secondary zones, the stress is a constant σ_c , the craze stress. The stress field is therefore similar to that of Dugdale's strip zone model [17]. The material is elsewhere assumed to be linear viscoelastic.

The energy balance takes the form

$$\int_{c(t)}^{c(t)+\delta} \sigma_c \frac{\partial \Delta u(s, t)}{\partial t} dx = 2\Gamma \dot{c}(t) \quad (2)$$

This equation has been solved, for $\delta \ll R$, to give

$$\begin{aligned} \frac{1}{2} \ln (R_c/R) &= (R/\dot{c}) \int_0^1 \frac{\dot{C}[R(1-\mu^2)/\dot{c}]}{C(0)} \\ &\times \ln [(1+\mu)/(1-\mu)] \mu d\mu \end{aligned} \quad (3)$$

where R is a function of t and R_c is defined as

$$R_c = \frac{\delta}{4} \exp \left[\frac{\pi \Gamma}{2\sigma_c^2 C(0) \delta} - 1 \right] \quad (4)$$

In deriving Equation 3 from Equation 2, use was made of the expression for Δu for the Dugdale stress field in a linear viscoelastic material

$$\Delta u(x, t) = 4\pi \int_{-\infty}^t C(t-\tau) \frac{\partial \Omega(x, \tau)}{\partial \tau} d\tau$$

where on the assumption of small-scale yielding Ω is defined by

$$\begin{aligned} \pi^2 \Omega(x, \tau) &= 2\sigma_c R(\tau) \left\{ \lambda - \frac{1}{2}(1-\lambda^2) \right. \\ &\left. \times \ln [(1+\lambda)/(1-\lambda)] \right\} \end{aligned}$$

with $\lambda^2 = 1 - [x - c(\tau)]/R(\tau)$.

Equation 3 was simplified and used to analyse the results of the slow bend tests reported in Section 4. The following assumptions were made.

1. Since the experiments to be modelled are of short duration (~ 40 sec), the creep compliance was assumed to be a linear function of time, $C(t) = a_0 + a_1 t$. For a realistic behaviour at short times, a_0 must be assigned a value corresponding to impact speed testing, estimated as $a_0 = 2 \times 10^{-4} \text{ m}^2 \text{ MN}^{-1}$. a_1 is chosen so as to give the correct creep strain after 100 sec at the assumed craze stress (35 MPa) and 20°C according to published data on pressure pipe uPVC [18]. This gives $a_1 = 2.2 \times 10^{-6} \text{ m}^2 \text{ MN}^{-1} \text{ sec}^{-1}$.

2. The craze length was calculated on the assumption that the craze is equivalent to a yielded plastic zone, using the finite element results of Larsson and Carlsson [19]; thus,

$$R = 0.15(K/\sigma_c)^2 \quad (5)$$

3. δ was assumed to be a fixed proportion of R ; this proportion was arrived at by trial and error to give the best representation of the experimental data. As a result, it was assumed that $\delta = 0.2R$.

4. A value of the craze stress σ_c of 35 MPa was assumed. This compares with a tensile yield stress of 53 MPa. The assumption is consistent with the observation that σ_c is of the same order as the yield stress, but somewhat less as crazing takes place in preference to yielding during crack growth.

5. K_c was assumed to be the value derived using the high pressure technique of $1.7 \text{ MN m}^{-3/2}$.

6. The fracture energy Γ was assumed to be equal to half the strain energy release rate at crack initiation. For a plane strain test, the appropriate expression is $\Gamma = K_c^2(1-\nu^2)/2E$ where ν is Poisson's ratio and E the elastic modulus. Numerically, $E = 1/a_0$ and $\nu = 0.35$.

As a result of Assumption 1, Equation 3 reduces to

$$\dot{c} = \frac{2Ra_1}{\ln (R_c/R)a_0} \quad (6)$$

Both Equations 3 and 6 predict that $\dot{c} \rightarrow \infty$ as $R \rightarrow R_c$. This condition corresponds to catastrophic failure, and is taken as representing the final collapse of the bend specimens.

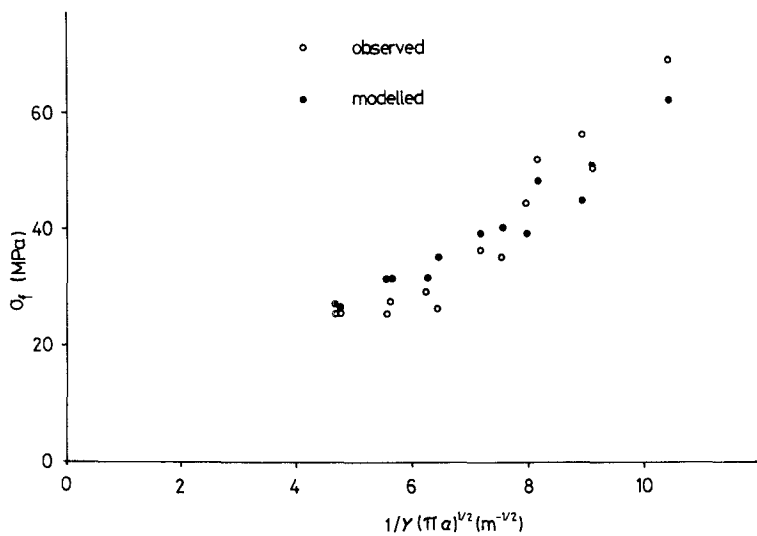


Figure 5 Predicted and observed fracture plots for 5 mm min^{-1} room pressure tests.

Equation 6 was used as the basis of a numerical model in which time was incremented in steps, and at each step the experimentally measured moment applied to a specimen used to calculate K using boundary collocation results [14], and thus R and \dot{c} using Equations 4, 5 and 6. The calculated \dot{c} was used to increment the crack length c for the next time step, and the process repeated until the condition $\dot{c} \rightarrow \infty$ was reached, thus obtaining a prediction of the ultimate collapse load of the specimen. This model was applied to each of the 5 mm min^{-1} bend specimens, using the recorded load–time curves as data; these were extrapolated smoothly past the failure loads so as to give sufficient data for failure to be predicted at either above or below the measured collapse loads.

The most direct comparison between theory and experiment is made by plotting observed and predicted failure stresses in the manner conventional for fracture data as used in Fig. 3. This is done in Fig. 5, where it can be seen that the choice of parameters σ_c and δ results in good agreement between the predicted points and the observed ones. The modelled points given a value of K_c^{app} essentially in agreement with the measured value of $5.44 \text{ MN m}^{-3/2}$. The results, in terms of K_c^{app} calculations based on initial crack length, are not sensitive to the value of σ_c , to the extent that varying σ_c between 20 and 50 MPa only results in a variation in K_c^{app} between 5.3 and $5.5 \text{ MN m}^{-3/2}$. This lack of sensitivity is to be expected, in view of the fact that the true K at which the crack speed becomes infinite is for-

mally independent of σ_c . The goodness of fit between the observed and the modelled results is therefore essentially governed by δ ; varying δ between $0.15R$ and $0.3R$ gives a variation in K_c^{app} between 6.0 and $4.8 \text{ MN m}^{-3/2}$. An alternative single-craze crack growth model, discussed by Dean *et al.* [15], for which $\delta = R$, was implemented and gave consistently low predictions for K_c^{app} . This indicates that the basic concept of the multiple-craze model is a useful one, and that a model of this nature can permit a unified interpretation of the high pressure craze-free results and the room pressure results which show stress-whitening.

One implication of this interpretation is that, if crack initiation could be detected accurately, room pressure tests would give the same results as tests at high pressure. Birch *et al.* [5] used optical microscopy to detect initiation, and thus measured a K_c for uPVC of $3.5 \text{ MN m}^{-3/2}$. It is instructive to examine the model predictions of crack growth in order to estimate how sensitive a measurement of crack length would need to be to give a reasonable estimate of K_c . Fig. 6 shows crack growth as a function of applied K (calculated on the basis of initial crack length) from a typical model prediction of a bend test. The numerical results show that the first crack growth of $10 \mu\text{m}$ occurs as K increases from 1.7 to $3.2 \text{ MN m}^{-3/2}$, and the first $1 \mu\text{m}$ occurs as K increases from 1.7 to $2.2 \text{ MN m}^{-3/2}$. This points to a requirement of extreme accuracy of crack measurement for satisfactory estimates of K_c .

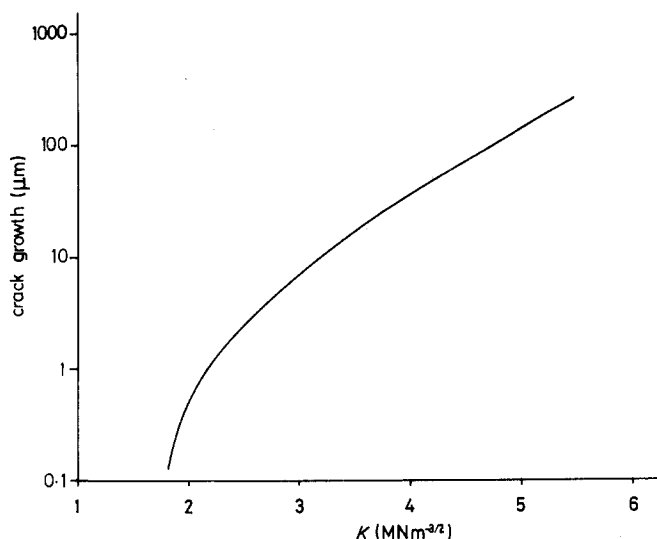


Figure 6 Model prediction of crack growth as a function of K .

That this model is not a complete representation of the fracture of uPVC is apparent from the fact that it does not predict any rate-dependence of the collapse stress; while the high speed results could probably be satisfactorily modelled using a different expression for δ in terms of R , this would not be instructive due to its arbitrariness and the probable inapplicability of a steady-state model to high speed tests. Some independent calculation of δ/R might be added to give a useful generalization of the model used here. However, we believe that, as it stands, it gives a convincing representation of the slow bend experiments.

6. Conclusions

K_c measurements on uPVC carried out using the high pressure technique show the established correlation between toughness and resistance to methylene chloride attack. The K_c values are, however, low in comparison with those measured by us and those reported by others based on room pressure testing. This is associated with the presence of stress whitening at room pressure and its absence at high pressures. The relationship between the stress whitened zone and the toughness measurement is reinforced by the observation that, when testing speed is increased at room pressure, shrinking of the whitened zone accompanies a lowering in K_c . We associate the stress whitening with slow crack growth. A numerical model of slow crack growth is used to support the view that the high and room pressure measurements are com-

patible, in the sense that K_c is the same in both cases, but is followed by slow crack growth at room pressure; at high pressures, the crazes or microvoiding which we hold to be the cause of the slow crack growth are suppressed by the prevailing hydrostatic compressive stress in the interior of the specimen. According to the model predictions, the initial crack speed is very slow, and this has implications for experimental methods of detecting crack initiation.

It could be argued that the true K_c as measured in the absence of slow crack growth is of little practical significance, since in most circumstances slow growth will follow initiation. Then it follows that relatively crude measures of K_c which include a degree of slow crack growth are more relevant. This is equivalent to the assertion that, in terms of resistance to failure of uPVC, resistance to crack growth is more important than the resistance to crack initiation, and this now seems to be the case. The high pressure technique enables initiation and growth to be separated and leads to an improved understanding of the processes involved in the fracture toughness testing of uPVC.

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