

Crazes in solvent vapours at very low pressure: craze stress and craze structure

R. Schirrer

Institut Charles Sadron, 4 rue Boussingault, F-67000 Strasbourg, France

(Received 30 September 1987; revised 2 May 1988; accepted 27 May 1988)

The shape and size of the single craze at a running crack tip in poly(methyl methacrylate) has been measured in a very low pressure toluene gas environment by means of optical interferometry. It has been shown in a previous paper that there is a critical crack velocity below which the craze becomes up to 4 times longer than in air, whereas the fracture toughness remains almost identical to the toughness in air. It has been carefully examined to what extent the craze shape recorded by means of optical interferometry may give information upon the craze stress distribution along the craze boundary and upon the inner structure of the craze. It has been found that the craze stress distribution and the craze fibril volume fraction remain similar in the toluene gas craze as in air, even at low crack velocity when the size of the toluene gas craze is much larger than that of the air craze.

(Keywords: craze; PMMA; environment; gas; interferometry)

INTRODUCTION

Environmental cracking and crazing is one of the most important features of polymers in practical use. In many cases, the failure of the material is preceded by crazing, so the effect of the environment on the properties of the material in the craze is of great interest. In a previous paper¹, it has been shown how optical interferometry may be used to detect the influence of very low pressure solvent gas on the craze shape. An interpretation in terms of activation processes has been given.

This paper will focus on the interpretation of the experimental data from the previous paper¹ in terms of craze surface stress distribution, $S(x)$, along its boundary and in terms of craze fibril volume fraction, v_f , in the craze. In fact, v_f is the inverse of the fibril extension.

The calculation of $S(x)$ along the craze surface has been studied by several authors, using finite element methods²⁻⁵ or Fourier transform⁶⁻⁸. The finite element method needs very specialized computer programs, whereas the Wang and Kramer method has the advantage of leading to simple computer programs. The simple equation given in reference 8 yields:

$$S(x) = (E^*/4\pi) \int_{PZ} dx_1 (x/x_1)^{1/2} \alpha(x_1)/(x-x_1) \quad (1)$$

where E^* is the 'plane strain' tensile modulus of the bulk material $E^* = E/(1-\nu^2)$, E is the tensile modulus, ν is the Poisson's ratio and PZ is the plastic zone, and

$$\alpha(x) = -\frac{\partial}{\partial x} [T(x)(v_f(x) - 1)]$$

where $T(x)$ is the craze width profile.

Some attempts have been previously made to use the craze shapes recorded by means of optical interferometry to calculate the craze stress distribution^{2,3}. As will be discussed later, there are severe restrictions on the use of

craze shapes obtained by optical interferometry for the evaluation of $S(x)$. Nevertheless, interferometry is probably the only technique allowing the measurement of craze profiles in the case of a small craze at a running crack tip in a gaseous environment in a real time experiment. This justifies the careful examination of all the information that can be obtained from the experiment.

EXPERIMENTAL

The experimental procedure and results have been extensively detailed in a previous paper¹. Hence, they are only briefly recalled.

Procedure

A small compact tension specimen of poly(methyl methacrylate) (PMMA) is introduced into an environmental chamber incorporated in the optical interferometry set-up. The single crack-craze system is first initiated and propagated under cyclic loading in air to get a single sharp notch. Then the crack-craze is propagated under static loading at a controlled velocity (from 0 to 0.1 mm s⁻¹) in a very low pressure toluene vapour (1.4 hPa). Photographs of the interferometrical fringe pattern were taken during the propagation, and all the experimental parameters were recorded simultaneously (load, crack length, sample geometry, etc.).

Results

The experimental parameters allow the calculation of the fracture toughness K_{Ic} versus crack velocity, and the plot of the craze length versus velocity. Some of these results are shown¹ in Figure 1. The most striking result is that the craze becomes up to 4 times longer in toluene gas at low velocity, whereas the toughness remains almost the same. Figure 2 shows the optical craze profile for an air craze and a craze in toluene gas at a velocity of

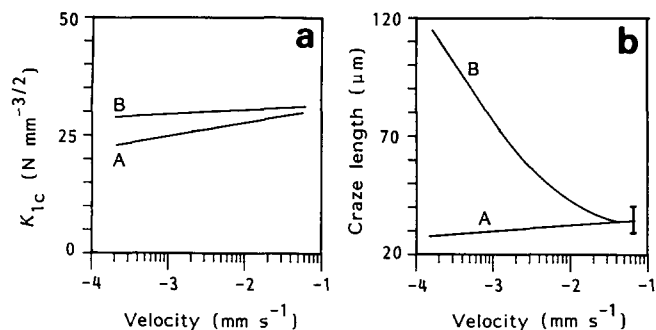


Figure 1 (a) Fracture toughness versus crack tip speed for PMMA (1.4 hPa pressure). (b) Craze length measured at the same time as the fracture toughness. (A) In air, (B) in toluene vapour

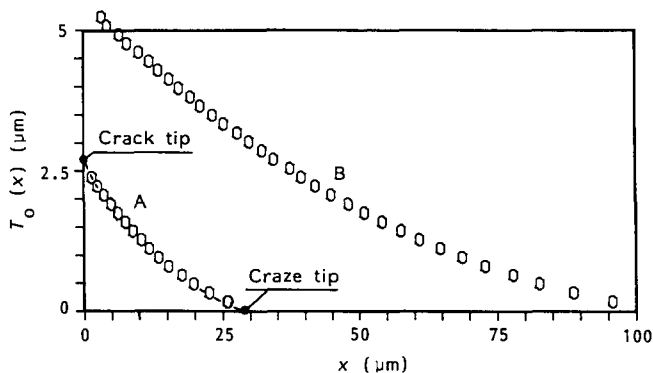


Figure 2 Craze profile (optical width T_0) of two crazes from Figure 1 at the same velocity ($2 \times 10^{-4} \text{ mm s}^{-1}$), obtained from the interferometrical fringe pattern. (A) In air, (B) in toluene vapour, (O) the positions of the fringes. The crack and craze tip positions are not known exactly and must be found by extrapolation

$2 \times 10^{-4} \text{ mm s}^{-1}$. It shows that not only the craze length is larger in toluene gas, but also the craze width.

CALCULATION OF THE SURFACE STRESS ALONG THE CRAZE

Reliability of the calculation

There are at least two problems in the use of the craze profiles obtained by interferometry for craze surface stress calculations.

The first problem is due to the fact that these profiles are 'optical width' profiles, with unknown optical index in the craze. Hence, neither geometrical profiles $T(x)$ nor fibril volume fraction $v_f(x)$ distribution in the craze are known. Both are necessary to calculate absolute values of the craze surface stress⁸. As discussed in references 2, 3, 9 and 10, under certain conditions, valid craze surface stresses may be obtained. If it can be assumed that v_f is constant along the craze, then equation (1) yields:

$$S(x) = (v_f - 1)(E^*/4\pi n) \int_{pz} dx_1 \frac{\partial}{\partial x_1} T_0(x_1)(x/x_1)^{1/2}/(x - x_1) \quad (1')$$

where $T_0(x_1)$ is the optical craze width and n is the refractive index of the craze.

The 'constant craze fibril volume fraction' assumption is rather restrictive, but seems realistic in the case of PMMA. Moreover, if the calculated craze surface stress distribution is constant, then, *a posteriori*, the assumption is correct, because in the case of a craze

growing by means of surface drawing from the bulk (as is the case for PMMA) a constant stress along the craze can hardly generate a variable craze fibril structure (i.e. a variable volume fraction) along the craze.

The second problem is due to the small number of fringes on the interference pattern leading to a small number of points defining the craze profile. So, interpolated points between the experimental points and extrapolated points to find the craze tip and the crack tip must be calculated. For that reason, the influence of these more or less subjective calculations must be carefully estimated. To illustrate these problems, Figure 3 shows several craze profile simulations and the corresponding craze surface stress profile calculated with the Fourier transform method: a perfect Dugdale craze defined by means of 48 theoretical points, and the corresponding calculated craze surface stresses for three different estimations of the crack tip position, followed by a perfect Dugdale craze defined by means of 19 theoretical fringes and 48 interpolated and extrapolated points. The theoretical fringes have been digitized and have undergone the whole experimental process used with real recorded fringe patterns. These simulations allow the following conclusions: the calculated craze surface stress is correct between about 1/6 and 5/6 of the craze length, and is quite sensitive to the crack tip position estimation. Specifically, if a continuous increase or decrease of the craze surface stress is observed from the craze tip towards the crack tip, it can be supposed that the crack tip position has been badly estimated.

Results for air and toluene crazes

The preceding considerations concerning the validity of the craze surface stress calculation from the interference pattern suggest that the results should be used for relative comparison between different crazes rather than to obtain absolute values of the stress. Also,

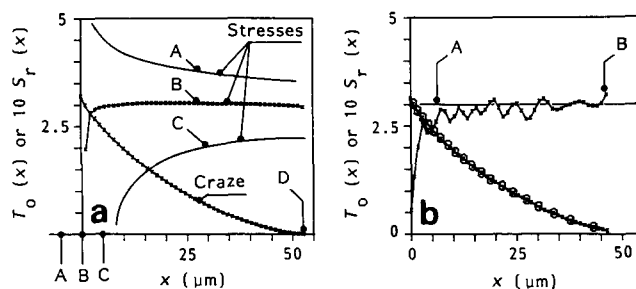


Figure 3 (a) Perfect Dugdale craze profile (optical width T_0) with its tip at D, defined by 48 theoretical points. B (at the coordinate origin) is the right crack tip position and the corresponding surface stress (curve B) is calculated with the Fourier transform method and the computer program. The value of the stress should be constant and equal to 3 along the whole craze length. In fact, the numerically calculated distribution B is equal to 3 but has a slight curvature and drops sharply at the crack tip. A and C at the origin coordinate are under- and over-estimations of the crack tip position. They simulate experimental scatter of the crack or craze tip positions which are often difficult to determine. Curves A and C show that the calculated stress is very sensitive to the estimation of these positions. (b) Same perfect Dugdale craze defined by 19 theoretical fringes which have been digitized and processed like real recorded fringes (48 points have been interpolated and extrapolated from the fringes). The calculated stress exhibits the scatter due to the fringe processing. The crack tip position and craze tip position being unknown, the stress exhibits systematically a continuous small drop from the craze tip to the crack tip and a peak at the craze tip. Therefore, the calculation is assumed to be correct between the limits A and B, that is, over the whole craze length (except for 15% at the tip and end)

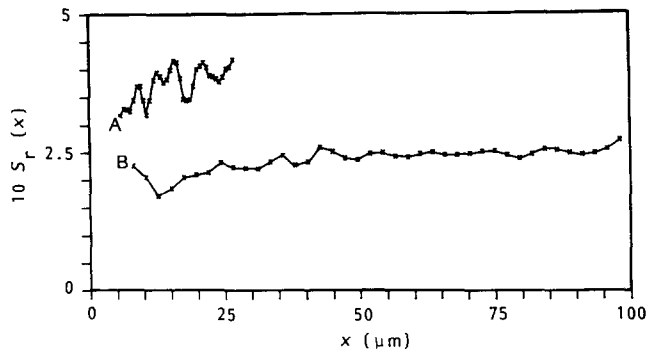


Figure 4 (A) Surface stress calculated for the craze in air, and (B) for the craze in toluene vapour shown in *Figure 2*. B is rather constant along the craze length, whereas A drops steadily from craze tip to crack tip, which corresponds probably to a very little crack tip position overestimation. Since craze A is much shorter than B, the stress A is much more sensitive to an error for the crack tip position. The error is in the order of 2–3 μm for both A and B. As shown in a previous paper¹, the craze surface stress is lower in the case of toluene vapour

only large variations of the stress distribution between different cases should be considered as relevant. *Figure 4* shows two typical sets of experimental data for a craze in air and a craze in toluene gas at a low propagation velocity where the toluene gas craze is 3–4 times longer than the air craze. Volume fraction of the craze fibrils and tensile modulus of the bulk being unknown, the reduced value of the stress has been plotted:

$$S_r(x) = S(x)/S_c = \int_{\text{PZ}} dx_1 \frac{\partial}{\partial x_1} T_0(x_1)(x/x_1)^{1/2}/(x-x_1) \quad (2)$$

where $S_c = E^*(1-v_f)/4\pi n$ will be called the ‘craze structural parameter’ because it includes v_f explicitly and implicitly in n . No absolute values for v_f and E are given at this stage. The next section will discuss the calculation of v_f and the value of E^* .

The plots show that in both cases the craze stress $S_r(x)$ is almost constant (noted S_r) along the craze, and is about 40% lower for the toluene gas craze. There is a contradiction between this result (in air) and those shown in references 2 and 3, where it was found that the craze stress increases steadily from the craze tip to the crack tip. This discrepancy can be due to material differences, or more likely to crack tip position estimation. As noted previously, it is rather unlikely that a craze growing by means of surface drawing from the bulk may have simultaneously a constant v_f (i.e. a constant optical index as assumed in refs. 2 and 3) and a stress steadily varying along its boundary. The fibril drawing is some kind of natural necking phenomenon which remains identical to itself as long as it is predominant and makes plausible constant drawing stress, and constant fibril structure along the craze. At the craze and crack tips, other fibril growing mechanisms may be involved and lead to changes in v_f and surface stress as shown by many other authors who found constant craze surface stress except at crack and craze tips⁶.

Fibril volume fraction

As previously noted, v_f is not known from experiment. With the craze surface stress being constant, it may be calculated by means of the Dugdale equation¹¹:

$$S_d = K_1(\pi/8S)^{1/2} = S(x) = \text{constant value} \quad (3)$$

where S_d is the Dugdale craze stress, S is the craze length and K_1 the stress intensity factor.

Using equations (2) and (3) the numerical value of the ‘craze structural parameter’ S_c is experimentally known:

$$S_c = S(x)/S_r(x) = S_d/S_r \quad (4)$$

Figure 5 shows the evolution of S_c versus the craze length in both environments. The craze length is the most sensitive ‘image’ of the influence of the toluene gas under different propagation conditions. In air, the craze length and the value of S_c are almost constant at all velocities (see *Figure 5*). In toluene gas, the craze length is quite sensitive to the propagation velocity, whereas the value of S_c remains in the same scatter band as in air ($S_c = 210 \pm 30$ MPa). It can be concluded that the structure of the craze represented by S_c is not affected by the toluene gas.

On the other hand, n may be expressed as a function of v_f by means of the Lorentz–Lorenz equation:

$$(n^2 - 1)/(n^2 + 2) = v_f(1.5^2 - 1)/(1.5^2 + 2)$$

where 1.5 is the optical index of bulk PMMA. Then, $n^2 = (1 + 0.6v_f)/(1 - 0.3v_f)$ and S_c yields:

$$S_c = E^*(1 - v_f)(1 - 0.3v_f)^{1/2}/4\pi(1 + 0.6v_f)^{1/2} \quad (5)$$

Figure 6 shows S_c taken from equation (5) versus v_f . It shows that S_c is quite sensitive to v_f , and is therefore a good means to evaluate v_f with the numerical values of *Figure 5*. It can be estimated that the tensile modulus E^* of the bulk PMMA is not affected by the very low pressure toluene gas environment during the short duration of the experiment. Unfortunately, the numerical value of E^* may vary from 2000 to 4000 MPa, depending on strain and strain rate¹². Hence, the choice of E^* has a considerable influence on both the numerical value of $S(x)$ (equation (1)) and on the calculated v_f . It seems more realistic to proceed in the opposite way: the optical craze index in PMMA in air without load is known¹³, $n_c = 1.32$, which corresponds to $v_f = 0.6$. From optical interferometry, it is known that the craze just before

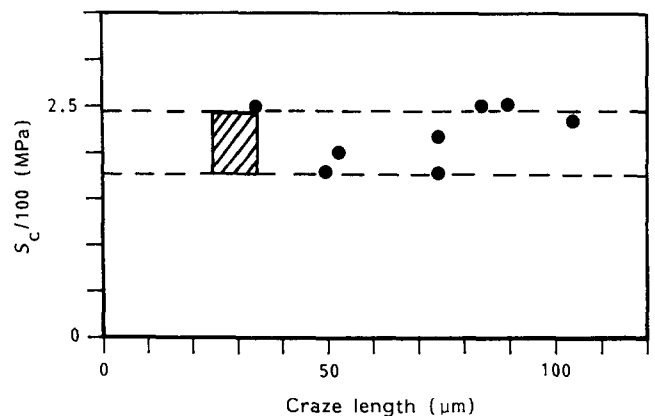


Figure 5 ‘Craze structural parameter’ as defined by equation (2) and as determined by equation (4). This parameter includes the craze fibril volume fraction and the tensile modulus of the bulk. The shaded area encloses the values of S_c for all the crazes in air shown in *Figure 1*, whereas the symbols correspond to the crazes in toluene shown in *Figure 1*. The craze length has been used as a variable because it is the most evident craze parameter which is extremely sensitive to the toluene vapour. In air, it is well known that the craze length is almost constant whatever the velocity of the crack

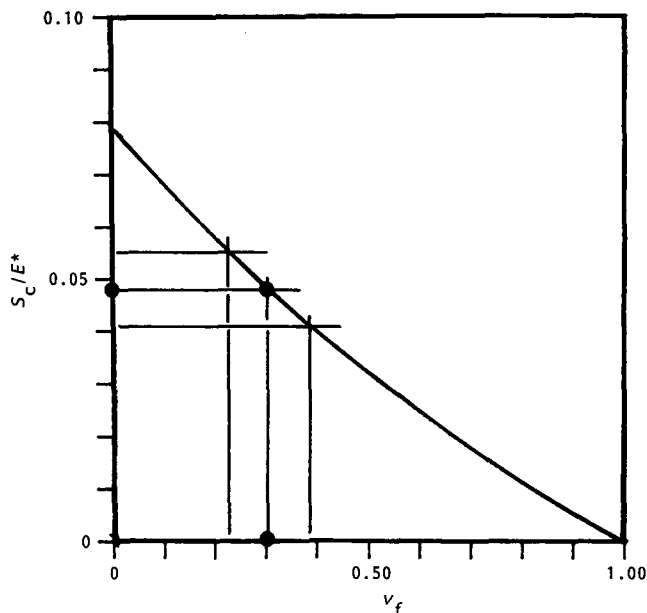


Figure 6 'Craze structural parameter' versus v_f from equation (5). The numerical value of 0.048 ± 0.007 for S_c leads to a value of 0.3 ± 0.08 for v_f

breakage is twice as wide as unloaded ($v_f=0.3$) and hence using the Lorentz-Lorenz equation its optical index is then $n=1.15$. From Figures 5 and 6 it can be concluded that the bulk modulus around the propagating crack is about 4400 MPa, which is a high value in view of the strain rates at a propagating crack tip (10^{-2} – 10^1 s $^{-1}$). Using the scatter displayed by Figure 5, it can be concluded from Figure 6 that v_f is constant ($v_f=0.3$) within a scatter band of ± 0.08 , and is therefore not sensitive to the toluene gas.

This result is consistent with Kramer's results showing that the fibril extension ratio (which is just the inverse of v_f) is equal to the bulk polymer network full extension ratio. It is unlikely that the toluene vapour changes the physical and chemical structure of the bulk: it just makes the fibril drawing 'easier'. It is generally admitted, however, that the fibril diameter multiplied by the craze surface stress is constant⁶. Therefore, the craze surface stress being lower in toluene vapour, the fibrils are

probably thicker. It seems that the influence of the toluene vapour is confined to a pure plasticizing of the polymer (lower flow stress), leading to a larger craze with probably a coarser structure, with no change in the fibril growth mechanism by drawing from the bulk.

CONCLUSIONS

The Fourier transform method has been used to calculate the craze surface stress distribution from craze shapes obtained by means of optical interferometry. The single crazes have been propagated at a crack tip in PMMA in a toluene gas pressure of 1.4 hPa, at velocities between 10^{-4} mm s $^{-1}$ and 0.1 mm s $^{-1}$ under constant loading. The following points have been found: (i) the craze shapes are the same in air and in toluene gas, only their sizes vary; (ii) the craze surface stress is almost constant along the craze boundary; (iii) v_f remains constant in air and in toluene gas over the whole velocity range, despite the fact that at low velocity in toluene gas the craze length reaches 4 times the length in air; (iv) the optical interference set-up may give valuable information on the variation of v_f , but not on its absolute numerical value.

REFERENCES

- Schirrer, R. and Galleron, G. *Polymer* 1988, **29**, 634
- Bevan, L., Doell, W. and Koenczoel, L. *Polym. Bull.* 1986, **16**, 545
- Bevan, L., Doell, W. and Koenczoel, L. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2433
- Bevan, L. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1759
- Bevan, L. *J. Appl. Polym. Sci.* 1982, **27**, 4263
- Kramer, E. J. Microscopic and molecular fundamentals of crazing in 'Advances in Polymer Science', Vol. 52/53, Springer Verlag, Berlin, pp. 16–21
- Wang, W. C. and Kramer, E. J. *Polymer* 1982, **23**, 1667
- Wang, W. C. and Kramer, E. J. *J. Mater. Sci.* 1982, **17**, 2013
- Krenz, H. G. PhD Thesis, Cornell University, 1976
- Kramer, E. J. Environmental cracking of polymers in 'Developments in Polymer Fracture' (Ed. E. H. Andrew) Applied Science Publishers, London, 1979, pp. 81–86
- Dugdale, D. S. *J. Mech. Phys. Solids* 1960, **8**, 100
- Ogorkiewicz, R. M. 'Engineering Properties of Thermoplastics', J. Wiley Interscience, London, 1970, p. 225
- Kambour, R. P. *J. Polym. Sci.* 1964, **A2**, 4159