

Very Slow Crack Growth during Osmosis in Epoxy and in Polyester Resins

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Synopsis

It has been demonstrated that osmotic pressure filled cracks in both epoxy and polyester resins are elastic cracks. Use of classical formulas for elastic cracks has enabled estimates to be made of the time dependence of Young's modulus for both resins. Use of linear elastic fracture mechanics formulas has enabled stress intensity factors to be determined from measurements of crack profiles. Radial crack growth rates are small, in the range 10^{-12} – 10^{-9} ms⁻¹ for hot water tests, and remain constant over a wider range of stress intensity factor, from 0.3 to 0.8 MPa·m^{1/2}. To a first approximation, constant radial growth rate is compatible with a diffusion controlled mechanism. However, analysis of the data indicates an activation energy of ~50 kcal. Some evidence is presented for concluding that, in polyesters at least, the true nature of crack propagation can be by way of slip/stick.

INTRODUCTION

Load transfer at matrix/fiber interfaces is fundamental to the principle of fiber reinforcement. The efficiency of load transfer is impaired during service, and one important mechanism for this is osmosis.¹ Water from the surrounding environment diffuses through the matrix resin, dissolves water-soluble material at the interface, and thereby generates osmotic-pressure-filled pockets which take the form of cracks propagating into the adjacent resin. Examples of resin cracks at fiber interfaces in a C-glass/polyester composite are shown in Figure 1.

To fully understand loss of load transfer, it is evidently necessary to investigate the nature of osmotic-pressure-filled cracks in resin matrix materials. Such an investigation has been carried out for both epoxy and polyester systems.

Of particular interest is the justification for using linear elastic fracture mechanics (LEFM) to describe accelerated test observations and to interpolate such descriptions to weathering in the field. With this in mind, experiments have been carried out to establish that osmotic-pressure-filled cracks are essentially elastic cracks, i.e., cracks which can be treated by LEFM.

MATERIALS

Representatives of commercially available materials were used for the present studies. These were an anhydride-cured DGEBA epoxy resin identified as MY 750 and supplied by Ciba-Geigy, PLC, and an MEKP-cured general purpose polyester resin identified as SR 18979 and supplied by BXL Plastics, PLC. In the epoxy case, it was necessary to artificially add a solute (0.5 wt % of finely ground KCl) in order to promote internal cracking.

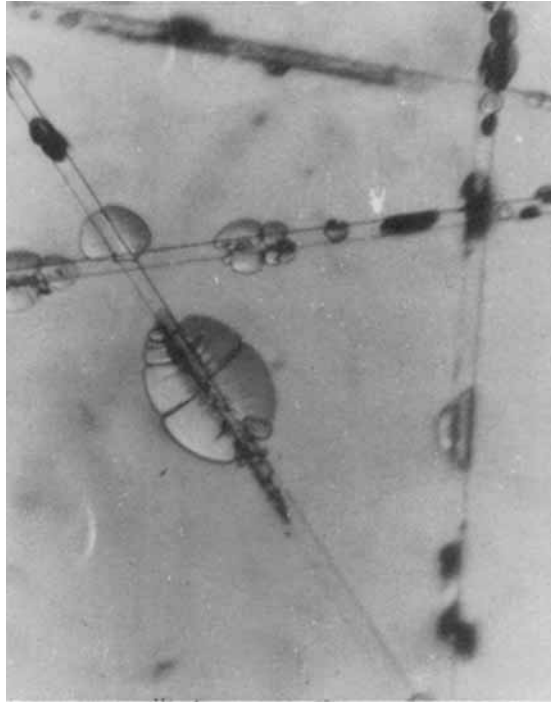


Fig. 1. Resin cracks accompanying loss of load transfer in a C-glass/polyester composite; C-glass contains 9.6 wt % Na_2O . Specimen immersed in boiling water for 20 hr.

EXPERIMENTAL STUDY OF OSMOTIC-PRESSURE-FILLED CRACKS

Elastic Nature of Resin Cracks Observed in Accelerated Tests. To demonstrate the elastic nature of osmotic-pressure-filled cracks in epoxy and polyester resins, and in particular to demonstrate the absence of any permanent (i.e., plastic) contribution to the crack opening displacement, a number of cracks have been photographed and rephotographed after drying by annealing in air. This treatment causes the crack faces to come into contact with each other [Figs. 2(a) and (b) and 3(a) and (b)]. Seen face-on, such cracks in dried samples generate interference patterns [Figs. 4(a) and (b)]. By counting the fringes, the very close proximity of the crack faces can be measured (Fig. 5). Many of the cracks in dried resin are connected to the atmosphere by surface seeking cracks; a surface seeking crack is indicated by an arrow in Figure 4(b). The small residual space between the crack faces is attributed to obstruction by solute deposit after drying (see Fig. 4 in Ref. 2).

Time Dependence of Young's Modulus. Elastic cracks, i.e., Griffith cracks, are elliptic in nature. This elliptic form has been reexamined by many authors including Sack,³ Sneddon,⁴ Elliott,⁵ and Westergaard.⁶ The specific case of pressure-filled elastic cracks was considered by both Sack³ and Sneddon.⁴ Expansion of Westergaard's equation (4.6) gives

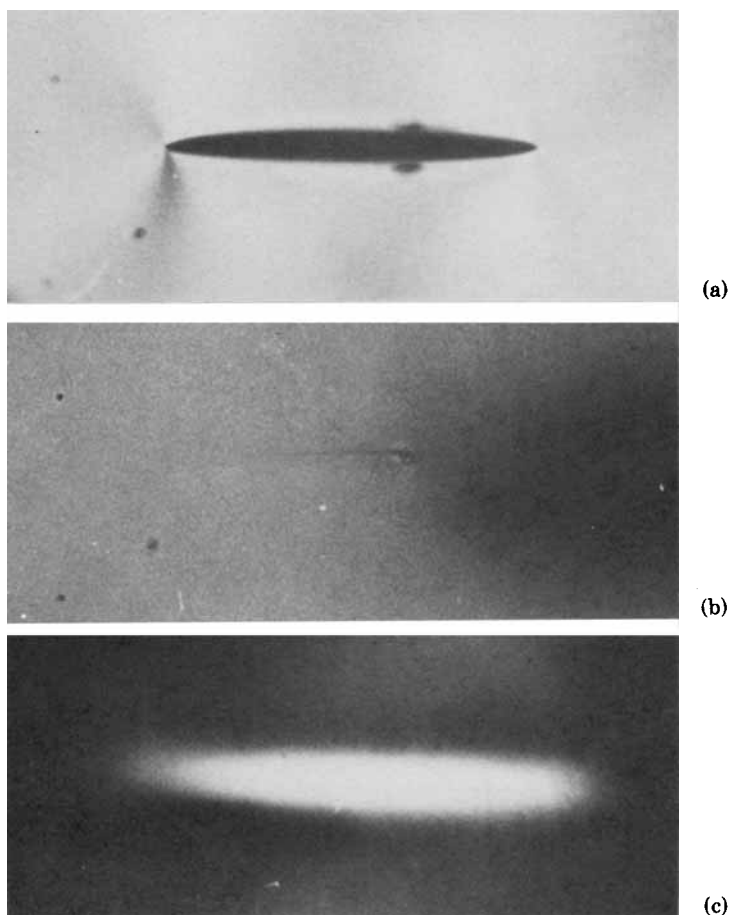
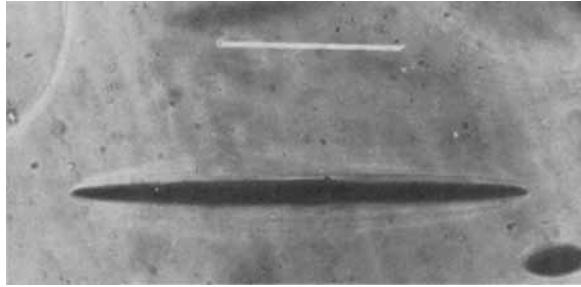


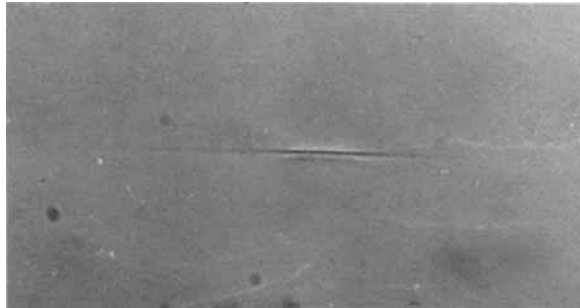
Fig. 2. (a) Penny-shaped crack in KCl-doped epoxy resin photographed edge-on, 140 h immersion in water at 94°C. (b) Same crack after drying in air for 1 h at 100°C. (c) Same as (b) with polarizers crossed. The flare of bright contrast is attributed partly to change of polarization of light reflected by the crack faces and, more importantly, to permanent molecular orientation in resin immediately adjacent to the crack.

$$\eta_0^2 = \frac{-4(1 - \nu^2)^2 p^2 x^2}{E^2} + \frac{4(1 - \nu^2)^2 p^2 a^2}{E^2} \quad (1)$$

where η_0 = half crack opening displacement, x = distance measured from the crack center, a = length of semiminor axis of the crack, ν = Poisson's ratio, and E = Young's modulus. When formed, osmotic-pressure-filled cracks often contain resolvable undissolved solute. Undissolved solute can be seen at the center of the crack shown in Figure 4 of Ref. 2, for example. The water solution within such cracks is evidently saturated with solute. The osmotic pressure, estimated in Ref. 2 for the saturated hot water solution identified in cracks inside the polyester resin system, designated system A in that reference, is 473.3 bars. Some of the present accelerated test data were obtained using the same resin in water immersion tests at 70°C, 80°C, and 94°C. Since osmotic pressures for



(a)



(b)

Fig. 3. (a) Edge-on view of penny-shaped crack in polyester resin designated A in Ref. 1. The marker is 0.1 mm. (b) Same crack after drying.

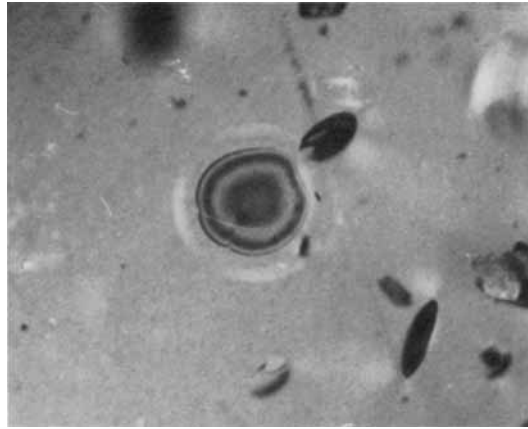
saturated solutions of common inorganic solutes increase only marginally in this temperature range, a constant value of 500 bars was assumed when using eq. (1) to compute the respective magnitudes of E from data such as that shown in Figure 6. Static values for E were determined on the same samples by simultaneous measurements of the longitudinal and transverse sound wave velocities at 5 Mhz; no significant differences from the room temperature value of 4.0 GPa for the dry resin were found. It is therefore concluded that the variations in E obtained from Figure 6 are attributable solely to its time dependence. Figure 7 summarizes the data.

Measurement of Crack Growth Rates. Figures 8(a) and (b) show edge-on views of a penny-shaped crack in epoxy and polyester resin samples photographed after several times of immersion in water at 94°C. Measurements of the crack diameter reveal that the radial crack growth rates are constant at $4.9 \times 10^{-10} \text{ m}\cdot\text{s}^{-1}$ and $1.1 \times 10^{-9} \text{ m}\cdot\text{s}^{-1}$, respectively. The same experiment on cracks in polyester specimens immersed in water at 70°C and 80°C reveal constant crack growth rates of $5 \times 10^{-12} \text{ m}\cdot\text{s}^{-1}$ and $7 \times 10^{-11} \text{ m}\cdot\text{s}^{-1}$, respectively.

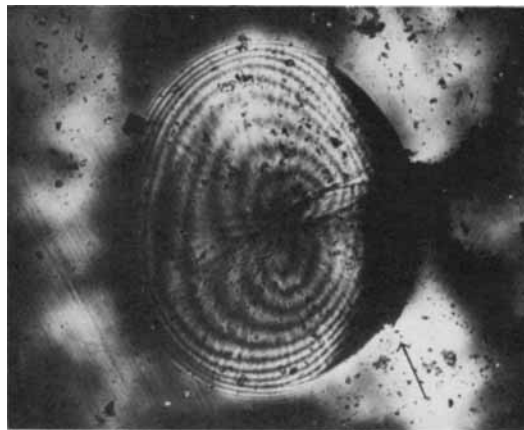
The following argument demonstrates that constant radial growth rate, at a given temperature, is dimensionally compatible with a diffusion controlled mechanism for fracture: The total flux of water entering the crack is

$$J \propto \frac{d(V)}{dt} \quad (2)$$

where V is its volume. If Young's modulus (E) is constant, then, putting $x = 0$ into eq. (1), we see that, at the center of the crack, the crack opening displacement is proportional to the crack radius (a). Hence $V \propto a^3$ and $J \propto a^2 da/dt$,



(a)



(b)

Fig. 4. Face-on views of penny-shaped cracks after drying. Notice the interference fringes: (a) epoxy; (b) polyester resin.

which, since da/dt is found experimentally to be constant, implies that J is proportional to a^2 .

If the fracture process is diffusion controlled then, by Fick's first law, the flux across unit area is

$$j = -D \frac{\partial c}{\partial x} \tag{3}$$

where the diffusion coefficient (D) is a constant. The concentration gradient $\partial c/\partial x$ is also constant since, with undissolved solute always present (refer to the previous subsection), the concentration of water in the electrolyte, as well as that in the environment outside the specimen, is constant. The catchment area across which water entering the crack must diffuse, i.e., the surface area of the crack, is proportional to a^2 . Hence for a diffusion-controlled mechanism we expected $J = j \times \text{catchment area}$ to be proportional to a^2 .

The activation energy (Q) for this mechanism may be estimated from the rate as follows:

$$\text{rate} \propto e^{-Q/kT} \tag{4}$$

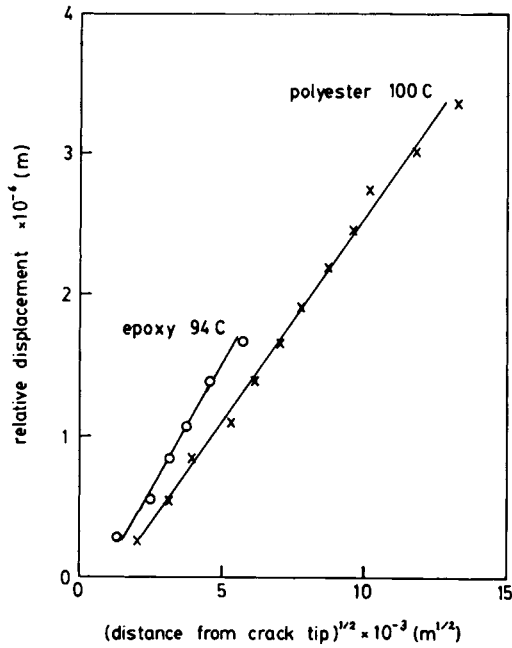


Fig. 5. Data from profiles of penny-shaped cracks after drying.

$$\log_e(\text{rate}) = \frac{-Q}{kT}$$

$$\frac{d}{dT}(\log_e(\text{rate})) = \frac{Q}{kT^2}$$

$$Q = kT^2 \frac{d}{dT}(\log_e(\text{rate})) \tag{5}$$

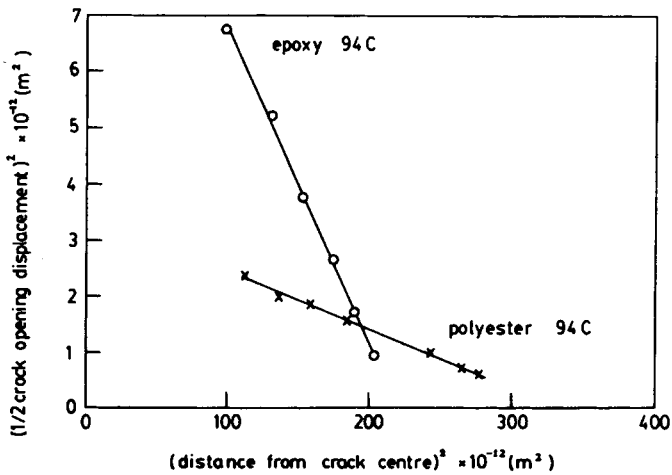


Fig. 6. η_0^2 vs. x^2 data from profiles of penny-shaped cracks in epoxy and polyester resin.

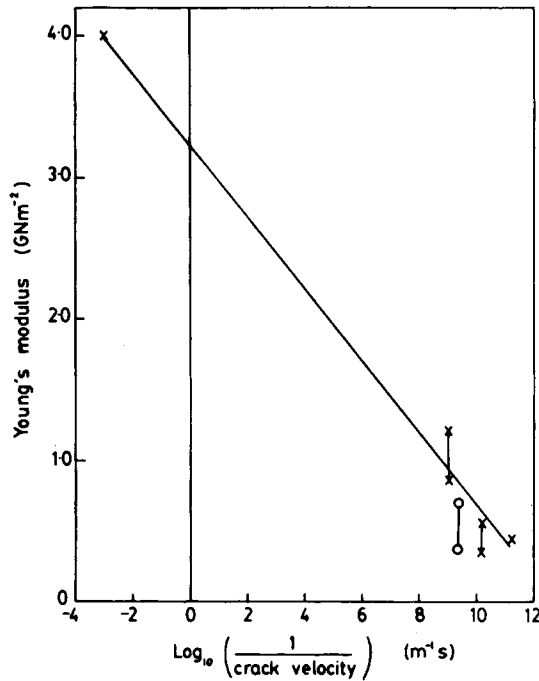


Fig. 7. Time (proportional to 1/crack velocity) dependence of Young's modulus for epoxy and polyester resins. Note the approximation to exponential behavior.

For polyester resin, the rate of radial crack growth increases by one order of magnitude between 70°C and 80°C
Hence,

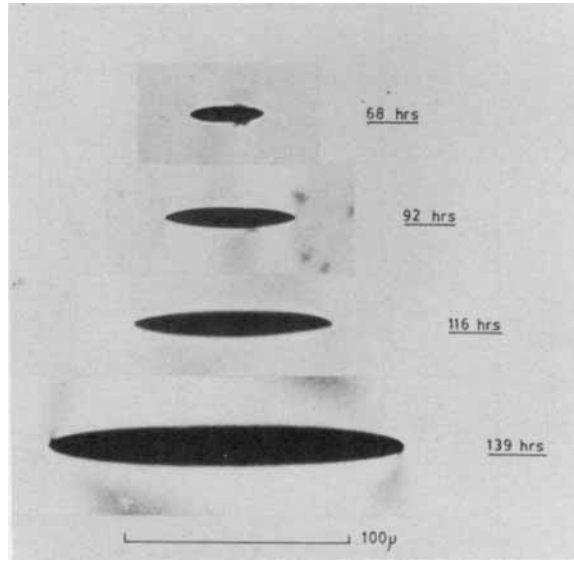
$$\begin{aligned}
 Q &= 2(350)^2 \times 2.3 \times 10^{-1} \text{ cal} \\
 &= 0.5 \times 10^5 \text{ cal} \\
 &= 50 \text{ kcal}
 \end{aligned}$$

This is a somewhat high value for the activation energy for diffusion of water in resins.

The assumption that Young's modulus (E) is constant is, however, not valid. Using eq. (1), the crack volume $V \propto (a/E)^3$ which since E increases with volume gives $V \propto a^{<3}$. Experimentally, we find $V \propto a^{2.6}$ for both resins, from which it is concluded that water diffusion alone is not rate-determining.

Crack Surface Topography. In the case of polyester samples close inspection of the crack surfaces has sometimes revealed the presence of more or less concentric steps, i.e., abrupt changes in fracture path. Examples can be seen on the crack surface shown in Figure 9. The steps delineate positions at which the crack was presumably at rest and are assumed to be direct evidence for a slip/stick mode of crack propagation.

Crazing is the precursor to fracture in many polymeric materials, the occurrence of which immediately suggests a model for slip/stick crack propagation. The craze is comprised of highly drawn material and, since the necking-down



(a)

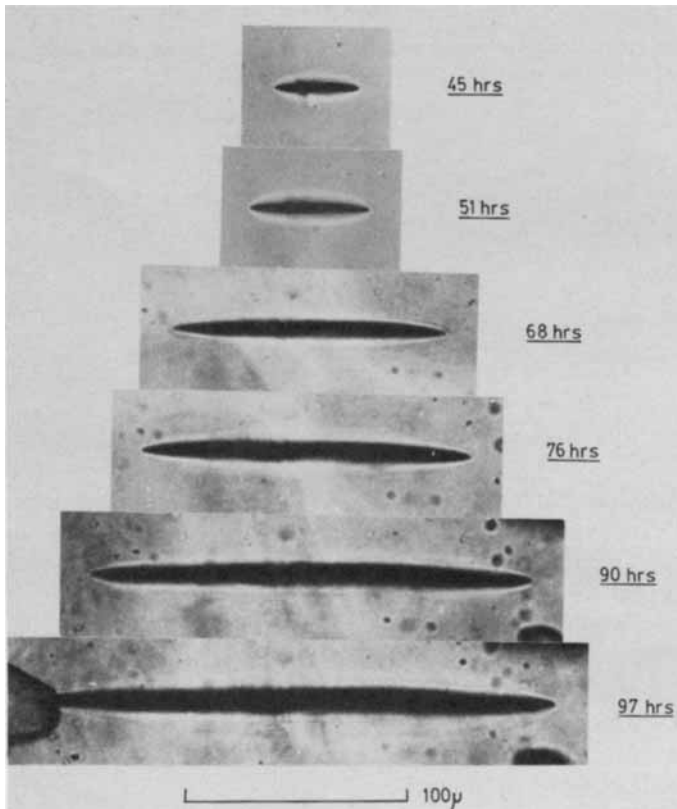


Fig. 8. (a) Edge-on view of growth of single penny-shaped crack ~ 0.2 mm below the surface in epoxy resin; (b) same in polyester resin.

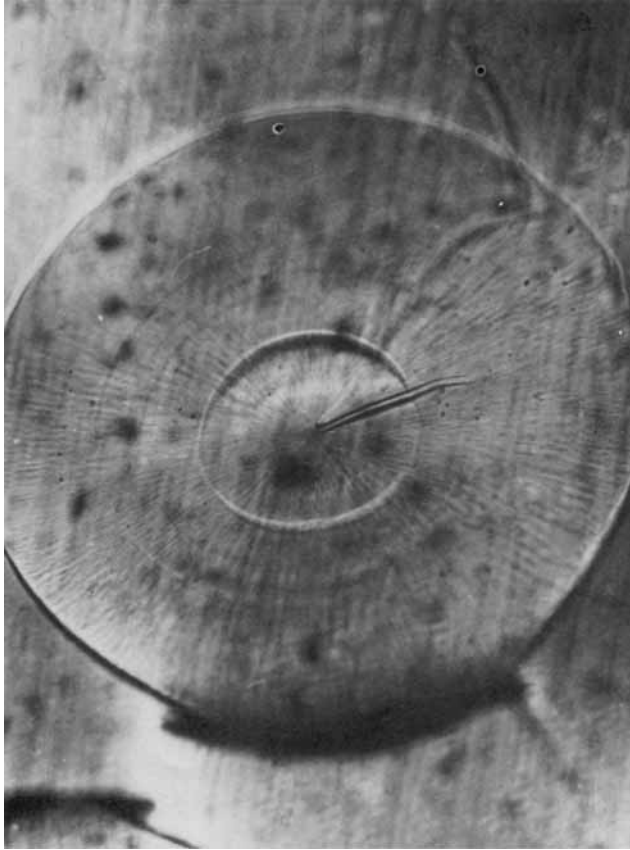


Fig. 9. Crack showing concentric growth ring structure.

phenomenon which gives rise to high draw ratio is a characteristic of high temperature drawing, it is evident that a zone of high temperature material must exist ahead of the craze. For polymers, room temperature is near the melting temperature so high temperature probably means just a few degrees above room temperature. Intermittent falls in temperature, and hence interruptions of the necking-down process associated with crazing, would be expected to cause crack arrests until the stress is raised sufficiently to reheat the craze leader. The small changes in fracture path each time crack growth resumes is in accordance with Griffith's⁷ evaluation of the tensile stress at the surface of and tangential to an elliptic cavity in a plate subjected to principal stresses σ_1 and σ_2 , respectively, making angle Φ and $\pi/2 - \Phi$ with the major axis of the ellipse. Inglis⁸ considered the case of an elliptic hole in a plate subject to a tensile stress σ applied in a direction making an angle Φ with the major axis of the ellipse [Fig. 10(a)] and found that the tensile stress at the surface of and tangential to the hole is

$$\sigma_{\beta\beta} = \sigma \left[\frac{\sinh 2\alpha_0 + \cos 2\Phi - e^{2\alpha_0} \cos 2(\Phi - \beta)}{\cosh 2\alpha_0 - \cos 2\beta} \right] \quad (6)$$

Referring to Figure 10(b) for $\sigma_2 = 0$ the Inglis solution, with the sense of increasing β reversed, gives

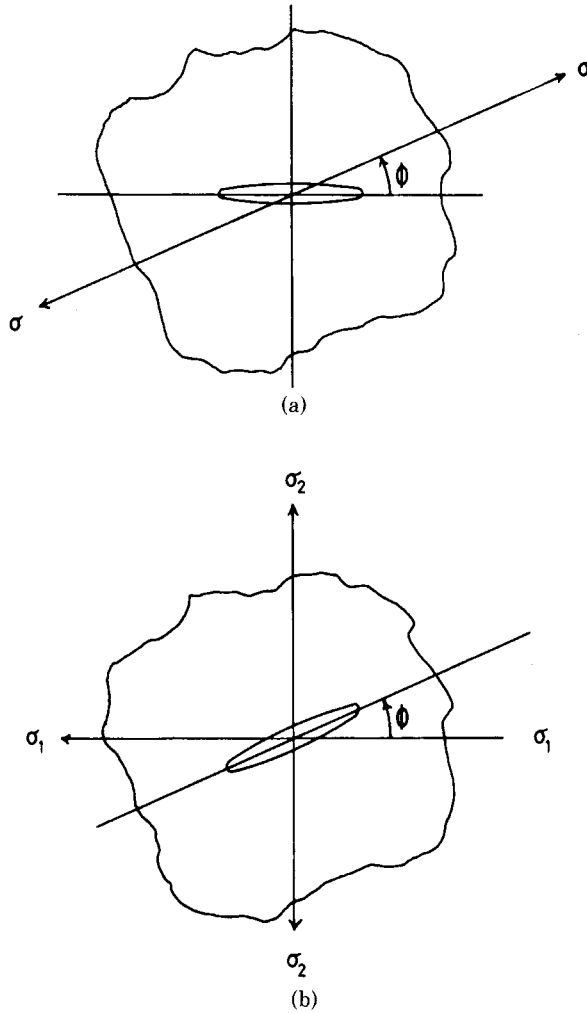


Fig. 10. Diagrammatic representation of the crack and the stress systems. See text.

$$\sigma_{\beta\beta} = \sigma_2 \left[\frac{\sinh 2\alpha_0 + \cos 2\Phi - e^{2\alpha_0} \cos 2(\Phi - \beta)}{\cosh 2\alpha_0 - \cos 2\beta} \right] \quad (7)$$

and for $\sigma_1 = 0$ it gives

$$\sigma_{\beta\beta} = \sigma_1 \left[\frac{\sinh 2\alpha_0 + \cos 2(\pi/2 - \Phi) - e^{2\alpha_0} \cos 2(\pi/2 - \Phi + \beta)}{\cosh 2\alpha_0 - \cos 2(-\beta)} \right] \quad (8)$$

Hence, by superposition,

$$\sigma_{\beta\beta} = \left[\frac{\sigma_1 + \sigma_2}{\cosh 2\alpha_0 - \cos 2\beta} \sinh 2\alpha_0 + \frac{(\sigma_1 - \sigma_2) \{ e^{2\alpha_0} \cos 2(\Phi - \beta) - \cos 2\Phi \}}{\cosh 2\alpha_0 - \cos 2\beta} \right] \quad (9)$$

The values of Φ and β for which $\sigma_{\beta\beta}$ is a maximum are found by differentiation. Putting $\partial\sigma_{\beta\beta}/\partial\beta = 0$ and taking as solution $\sin 2\beta = A\alpha_0 + O(\alpha_0^2)$, it can be demonstrated that $\sigma_{\beta\beta}$ is a maximum at *two pairs of points* on each crack. If

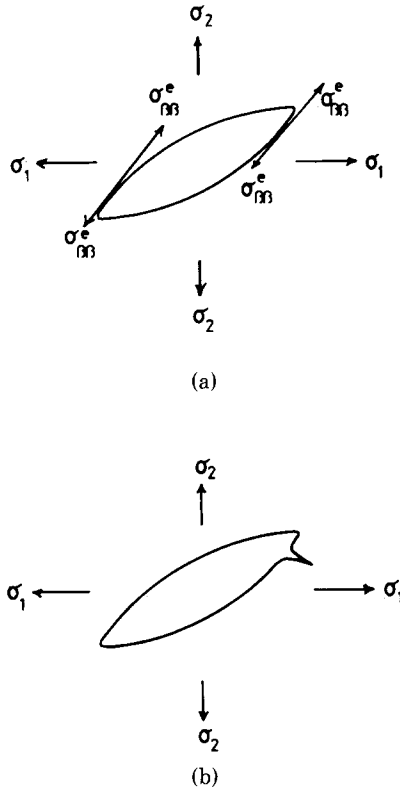


Fig. 11. (a) Locations of maximum tensile stress on an elliptic cavity in a plate subjected to biaxial tension; (b) crack propagation from one such location.

$\Phi = 0$ or $\pi/2$, these points are at the ends of the major and minor axes, respectively. For all other values of Φ both pairs of points are very near the ends of the major axis as sketched schematically in Figure 11(a). The two extremal values of $\sigma_{\beta\beta}$ always have opposite sign. Continuation of fracture from one such point, thereby leaving a step on the fracture surface, is illustrated in Figure 11(b).

The classical crazing material is polystyrene. The fact that the polyester resin studied here contains styrene as monomer may explain the evidence of slip/stick fracture shown in Figure 9. No such evidence was seen on the faces of cracks in epoxy samples.

APPLICATION OF FRACTURE MECHANICS TO OSMOTIC PRESSURE-FILLED CRACKS

Fracture mechanics is concerned with the propagation of atomically sharp cracks. It may well be that, when propagating, osmotic-pressure-filled cracks in polyester resin are indeed atomically sharp. It may also be the case that the periods of propagation are short, in which case the time dependence of elastic modulus may be ignored and *linear* elastic fracture mechanics (LEFM) may be

used to describe the cracks. In the following analysis, both these assumptions are made.

Crack Growth Times. The usual starting point for analysis of crack growth in inorganic glasses⁹ is the parabolic relationship between stress intensity factor (K) and crack length (a):

$$K = \sigma Y a^{1/2} \quad (10)$$

where σ is the tensile stress normal to the crack and Y is a constant determined by the crack geometry.

In resin matrix composite materials, cracks can nucleate and grow in the absence of any externally applied stress; the driving force for fracture is derived from osmosis^{1,2} with each crack containing an internal osmotic pressure (p). p may be substituted for σ in eq. (10) in order to obtain an equation for the stress intensity factor for a pressure-filled crack

$$K = p Y a^{1/2} \quad (11)$$

where the constant Y is of order unity.

Rearranging eq. (11) and differentiating, we get

$$v = \frac{da}{dt} = \frac{2K}{p^2 Y^2} \frac{dK}{dt} \quad (12)$$

Hence the time required for a crack inflated by osmotic pressure to propagate under the action of that pressure is

$$t = \frac{2}{p^2 Y^2 v} \int_{K_{I\text{initial}}}^{K_{I\text{final}}} K dK \quad (13)$$

$$= \frac{1}{p^2 Y^2 v} [K_{I\text{final}}^2 - K_{I\text{initial}}^2] \quad \text{if } v \text{ is constant} \quad (14)$$

Stress Intensity Factors. The cracks described here are elastic cracks, and, if they can be described by linear elastic fracture mechanics, measurements of their profiles can be used to obtain values for stress intensity factor (K_I).

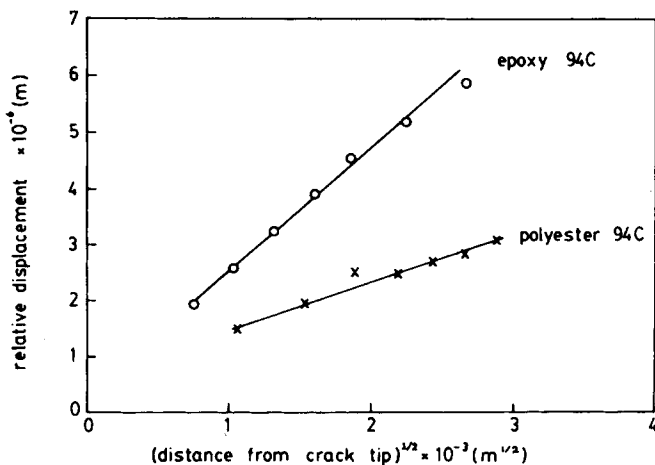


Fig. 12. Δv vs. $r^{1/2}$ data for cracks grown in both epoxy and polyester resin at 94°C.

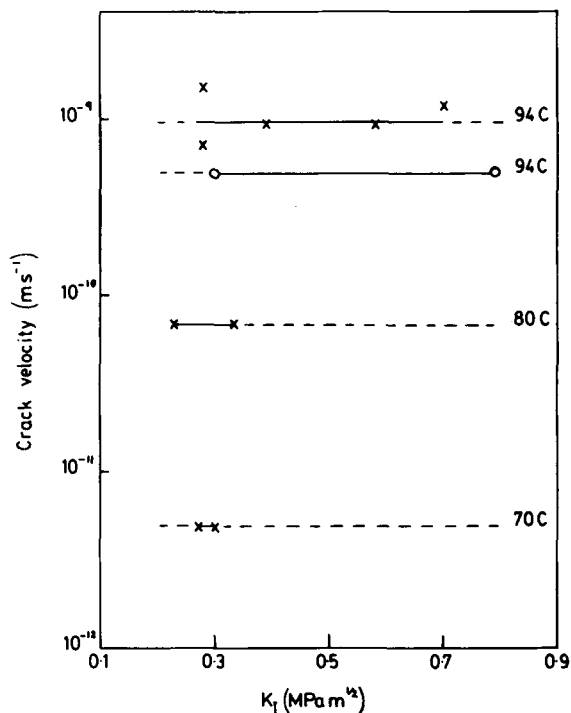


Fig. 13. Crack velocity (v) vs. stress intensity factor (K) for osmotic pressure filled cracks: (O) epoxy; (X) polyester resin.

Eshelby's¹⁰ eq. (2.10) for the parabolic relationship between crack opening displacement (ΔV) and distance from the crack tip (r) is

$$\Delta V = \frac{K_I}{(2\pi)^{1/2}} \cdot r^{1/2} \cdot \frac{8(1 - \nu^2)}{E} \tag{15}$$

Figure 12 shows plots of ΔV vs. $r^{1/2}$ for cracks at 94°C, from the slopes of which, stress intensity factors have been calculated. These and the corresponding crack velocities are presented in the form of V - K relationships in Figure 13. For a given immersion water temperature, the velocity remains constant even when, due to changes in aspect ratio and Young's modulus, the stress intensity factor varies. Table I summarizes the data obtained for the osmotic-pressure-filled cracks.

TABLE I
Summary of Data Obtained for the Osmotic-Pressure-Filled Cracks

Resin	Temp (K)	Young's modulus (GN · m ⁻²)	K_I (MPa · m ^{1/2})	Crack velocity (m · s ⁻¹)
Epoxy	367	0.37 → 0.72	0.30 → 0.79	4.9×10^{-10}
Polyester	343	0.55 → 0.59	0.27 → 0.30	4.9×10^{-12}
	353	0.35 → 0.56	0.23 → 0.33	6.8×10^{-11}
	367	0.86 → 1.22	0.28 → 0.73	1.1×10^{-9}

Figure 13 contains sufficient data to check the validity of eq. (14). Taking just two of the cracks, namely, the epoxy at 94°C and the polyester at 94°C, the maximum predicted times of propagation are, for the epoxy, $t = 4.3 \times 10^5$ s, compared with 2.56×10^5 s actual, and, for the polyester, $t = 1.65 \times 10^5$ s compared with 1.88×10^5 s actual. The agreement is good and lends credence to the approach adopted.

CONCLUSIONS

Measurements of the profile of osmotic-pressure-filled cracks in epoxy polyester resins, generated when immersed in distilled water, have been used to calculate the variation of Young's modulus for very small crack velocities. It has been demonstrated that the cracks are essentially elastic in nature and that linear elastic fracture mechanics can be used to calculate the stress intensity factors.

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References

1. K. H. G. Ashbee and R. C. Wyatt, *Proc. Roy. Soc.*, **A312**, 553 (1969).
2. K. H. G. Ashbee, F. C. Frank, and R. C. Wyatt, *Proc. Roy. Soc.*, **A300**, 415 (1967).
3. R. A. Sack, *Proc. Phys. Soc.*, **58**, 729 (1946).
4. I. N. Sneddon, *Proc. Roy. Soc.*, **A187**, 229 (1946).
5. H. A. Elliott, *Proc. Phys. Soc.*, **59**, 208 (1947).
6. H. M. Westergaard, *J. Appl. Mech.*, **6**, A49, (1939).
7. A. A. Griffith, First International Conference on Applied Mechanics (Delft, 1924, p. 55).
8. C. E. Inglis, *Trans. Inst. Naval Architects*, **55**, 219 (1913).
9. A. G. Evans, *J. Mater. Sci.*, **7**, 1137 (1972).
10. J. D. Eshelby, *Sci. Prog.*, **59**, 161 (1971).

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