JOURNAL OF MATERIALS SCIENCE 5 (1970) 302–307

The Fracture Energy of Some Epoxy Resin Materials

R. GRIFFITHS, D. G. HOLLOWAY
Department of Physics, University of Keele, Keele, Staffs, UK

The double cantilever beam technique has been used to measure the fracture energy of a series of cured epoxy resins. A range of materials was produced by varying the proportion of resin to hardener agent (Araldite CT200 and hardener HT901 – phthalic anhydride, CIBA Ltd) and by adding silica flour or aluminium powder as a filler.

The fracture energy for crack initiation in the cured epoxy resins ranged from approximately 10^3 to 10^5 erg cm^{-2}, and in the "filled resins" from 10^4 to 5×10^5 erg cm^{-2}, as the proportion of hardener increased. The fracture energy for crack arrest was somewhat lower at the higher hardener contents and particularly for the Al-filled material.

1. Introduction

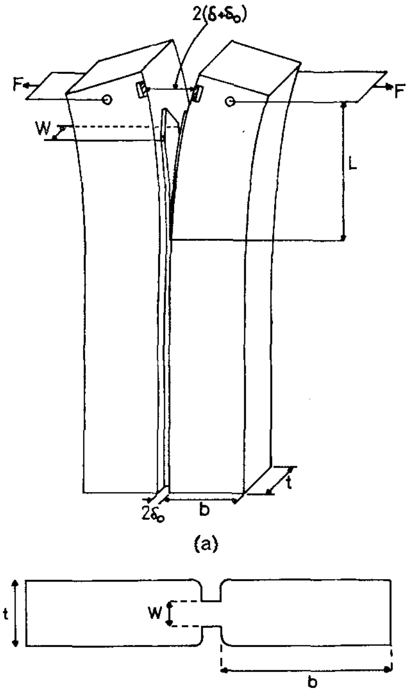
The fracture energy, γ, of a brittle material can be defined as the mechanical energy expended during an infinitesimal extension of a crack per unit area of newly created surface, i.e. $\gamma = -\partial U/\partial A$ where U is the stored elastic strain energy in the material and A is the area of the fracture surface. The fracture energy is simply related to the critical crack extention force, G_{IC}, and the critical stress intensity factor, K_{IC}, of fracture mechanics [1]. While there are a wide variety of experimental procedures available for the determination of these fracture toughness parameters, there are particular advantages to using a procedure which allows controlled incremental propagation of the crack. One such technique using a double cantilever beam (DCB) specimen is now well established and in this work we have used, following Berry [2], DCB specimens with side grooves to maintain the lateral stability of the crack in the isotropic material. Using the approximation that the stress distribution in the DCB specimen is equivalent to that in two simple cantilever beams of the same length as the crack, the following expressions are readily obtained for γ in terms of the specimen dimensions and either the crack opening displacement, 2δ, or the applied force, F. Thus

$$\gamma = \frac{3Etb^3\delta^2}{8wL^4} \qquad (1)$$

or

$$\gamma = \frac{6F^2L^2}{Ewtb^3} \text{ (see e.g. Gilman [3])} \cdot \qquad (2)$$

Some of the effects are neglected in the simple beam approximation, the more important ones being shear and the non-ideal fixing conditions



(a)

(b)

Figure 1 (a) Double cantilever beam specimen and (b) detail of cross-section.

at the ends of the cantilever arms. These have been considered analytically by Gillis and Gilman [4] and they proposed appropriate correction terms to the simple equations. Gross and Srawley [5] carried out a detailed numerical analysis for the critical stress intensity factor for DCB specimens using boundary collocation; the numerical results fitted well a modified form of the simple equations. These take the form

$$\gamma = \frac{3Etb^3\delta^2}{8wL^4}\left[\frac{\left(1 + 0.7\frac{b}{L}\right)}{1 + 2.1\frac{b}{L} + 1.5\left(\frac{b}{L}\right)^2}\right]^2 \tag{1a}$$

and

$$\gamma = \frac{6F^2L^2}{Ewtb^3}\left(1 + 0.7\frac{b}{L}\right)^2 . \tag{2a}$$

Wiederhorn *et al* [6] have established the equivalence of the corrected expressions above and those proposed by Gillis and Gilman.

In this paper we report the measurements of the fracture energy of a cross-linked epoxy resin. The extent of cross-linking has been varied and "model" composites have been examined using two traditional filler materials in the resin matrix.

2. Experimental Procedure

2.1. Specimen Preparation

Cross-linked polymer specimens were produced using a solid epoxy resin (epoxide content 2.2 to 2.5 equivalents per kg) and phthalic anhydride (Araldite CT200 and hardener HT901, products of CIBA Cambridge Ltd). The extent of cross-linking produced during the curing process is determined by the proportion of resin to hardener although the details of the mechanism are apparently uncertain [7].

The resin, hardener and any filler powder were heated, mixed in the required proportions, poured into individual steel moulds coated with silicone grease and then cured at about 135° C for 16 h to produce specimens 30 cm long, from 2 to 5 cm wide and of the cross-section shown in fig. 1b. After curing, the specimens were removed from the moulds, holes were drilled and a slot, terminating in a "swallow tail" was cut in the plane of the grooves (fig. 1a). Finally the specimens were annealed before testing. The annealing routine was varied according to the specimen composition since the softening temperature increases with hardener content. Specimens containing 5 parts by weight of hardener to 100 parts by weight of resin (denoted 5 pph) and those containing 2 pph of hardener were annealed at 50°C for 3 h and slowly cooled to room temperature; specimens with hardener contents of 8 pph and above were annealed at 90° C for 4 h before slowly cooling to room temperature.

2.2. Testing

Specimens were cleaved on a simple machine consisting of a rigid metal frame supporting a fixed and a movable chuck, the latter driven by a hand crank through a worm gear. The test specimen hung vertically in the machine supported by steel pins passing through the holes drilled in the ends of the cantilever arms and the chucks. The crack opening displacement, 2δ, and the crack length, L, were measured with a cathetometer.

For each specimen a series of crack propagations was examined within the range of crack lengths from $L \sim 7$ to 23 cm. The value of Young's Modulus was determined for a series of specimens of each composition in a separate three-point bend experiment.

3. Experimental Results

3.1. General Behaviour

With the exception of the unfilled resins with $\leqslant 5$ pph hardener, all the epoxy resins examined in this work exhibited a "crack-jumping" phenomenon, i.e. if L and $2\delta_1$ were the observed values of crack length and crack opening displacement (COD) at a particular position of crack-arrest, then in order to repropagate the crack, the COD had to be increased by a finite amount to, say, $2\delta_2$; the crack then propagated rapidly until again arrested at a new length L_2. It is possible, therefore, to calculate two distinct fracture energies for each specimen, one for crack-initiation using the data corresponding to successive values of L_1 and δ_2 and one for crack-arrest using L_1 and δ_1 etc.

In contrast, the unfilled epoxy resins with $\leqslant 5$ pph hardener exhibited a continuous slow crack propagation i.e. once a crack had been initiated from the original "swallow tail" it continued to propagate down the specimen at constant crack opening displacement. In this case the calculated value of the fracture energy falls with the time which has elasped since the last increase in displacement. The particular fracture energies reported here for these materials are calculated from the crack lengths 2 min after each increase in the COD.

3.2. Preliminary Investigations

A detailed series of experiments was carried out with an unfilled resin containing 15 pph hardener to examine directly the significance of the deviations from simple beam behaviour. Separate estimates of the fracture energy based on equations 1 and 1a were obtained from the recorded values of successive COD's and the crack lengths corresponding to δ_1 and L_1 for each of a series of specimens. The values of the fracture energy were calculated using the slope of the straight line obtained by plotting either δ versus L^2 for equation 1 or $\delta\{[1 + 0.7(b/L)]/[1 + 2.1\ (b/L) + 1.5\ (b/L)^2]\}$ $(= \delta_{\text{corr}})$ versus L^2 for equation 1a. Typical examples of the straight lines obtained with the data from a relatively wide specimen ($b = 3.45$ cm) are shown in fig. 2 where it is clear that the deviations from simple beam behaviour are reflected mainly as an intercept.

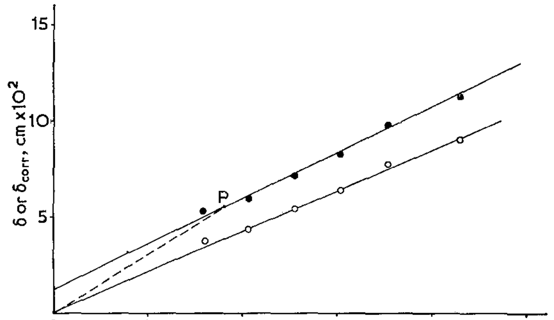


Figure 2 Relationship between crack opening displacement and crack length in a specimen with $b = 3.45$ cm. The filled circles represent δ and open circles represent δ_{corr} (see text).

As is obvious from equations 1 and 1a large errors can arise if the equation based on the simple beam approximation is used to evaluate γ from the data for a single position of the crack; this is equivalent in fig. 2 to using the slope of a line through the origin such as OP rather than that of one of the continuous lines. However, for narrow specimens, ($b \leqslant 2.5$ cm), the difference between the slopes of the continuous lines through the points representing a series of crack positions in a given specimen (and thus the difference between the values of γ obtained using equations 1 and 1a) was not much larger than the variation in the value of γ between specimens. Moreover preliminary experiments indicated that very large changes in fracture energy occur over the range of hardener concentrations so that, for the more detailed survey, the values of fracture energy were obtained by using graphical averaging to find (δ/L^2) and the simpler equation 1. Fig. 3 summarises the values obtained for Young's Modulus for the range of compositions used. The loads used in the three-point bend experiments were such that for each material the maximum curvature of the beam exceeded that in the cantilever arms of the corresponding DCB specimens.

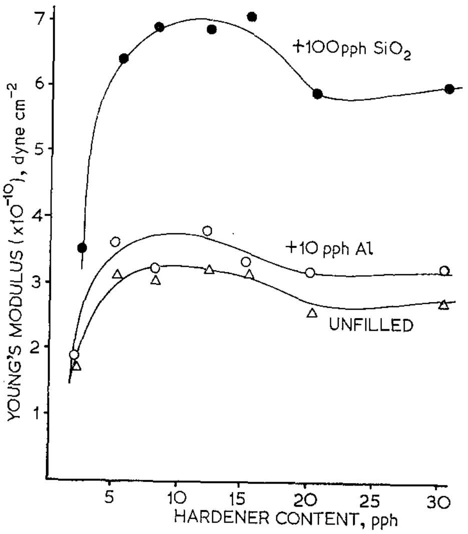


Figure 3 Young's Modulus as a function of hardener content.

3.3. Fracture Energies of Araldite Compositions

Figs. 4 and 5 illustrate the changes observed in the fracture energy for crack-initiation and for crack-arrest in Araldite CT200 with increasing proportions of hardener HT901 and with 100 pph silica flour (i.e. 100 parts by weight of silica flour to 100 parts of CT200 resin) or 10 pph aluminium powder. The individual points on these graphs represent mean values obtained from at least two different specimens. Larger numbers of specimens were tested at selected compositions and in these cases the standard error of the mean was between 5 and 10%. For

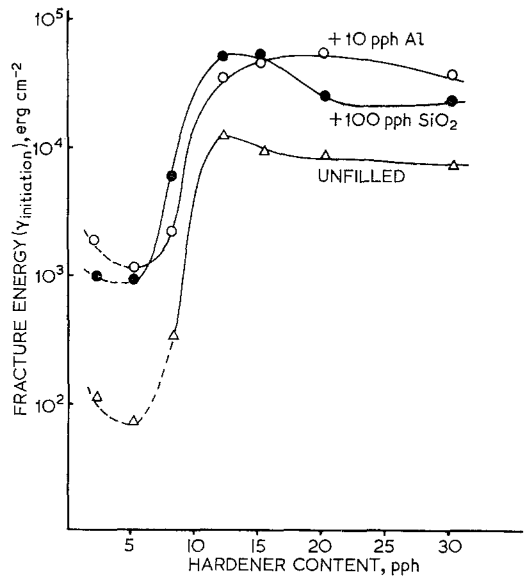


Figure 4 The fracture energy for crack-initiation as a function of hardener content.

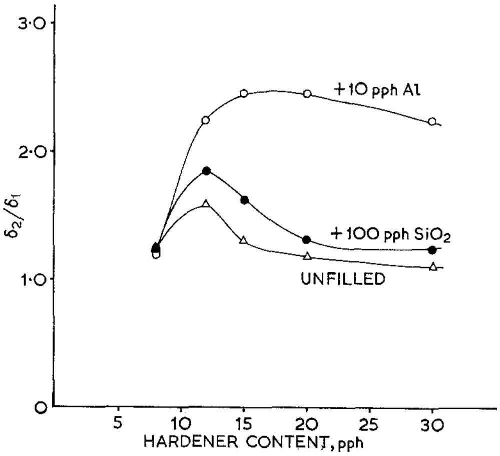


Figure 6 Variation with composition of the ratio of the limiting values of the COD corresponding to initiation-arrest at a given crack length.

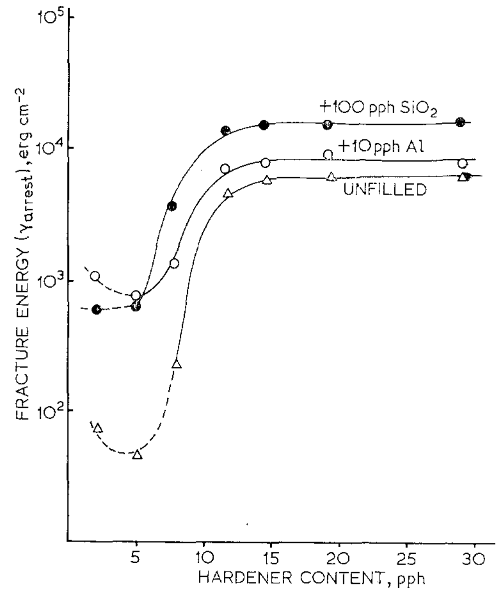


Figure 5 The fracture energy for crack-arrest as a function of hardener content.

some specimens of the filled materials at the high hardener contents only two crack arrests occurred within the sample length and in these cases single average values of $\delta(tb^3/w)^{\frac{1}{2}}L^{-2}$ were obtained by plotting $\delta(tb^3/w)^{\frac{1}{2}}$ versus L^2 using data from several different specimens.

Fig. 6 shows the variation with composition of (δ_2/δ_1) – the ratio of the two extreme values of the COD corresponding to a given crack length. This ratio which is equal to the ratio of the critical stress intensity factors for initiation and arrest and also to $(\gamma_{\text{initiation}}/\gamma_{\text{arrest}})^{\frac{1}{2}}$, gives a quantitative measure of the "crack-jump" tendency. Below 5 pph hardener $\delta_2/\delta_1 = 1$ and the apparent small difference between the fracture energies for initiation and arrest in figs. 4 and 5 arises from the arbitrary choice of the crack length at 2 min for the evaluation of γ_{arrest} for a continuously propagating crack.

Photomicrographs of polished sections of the composite materials are shown in figs. 7 and 8. The silica particles are evidently roughly equiaxed whereas the Al particles are more plate-like. It is also clear that the Al-filled resins have an appreciable bubble content (fig. 8) and it may be that these materials should really be regarded as three-component composites.

4. Discussion

The fracture energies observed with the unfilled epoxy resins are generally far larger than is plausible for the normal free surface energy of the material. By driving a small wedge into a saw-cut in the edge of a flat sheet of the material it is possible to propagate a "through-the-thickness" crack and then to examine at high magnification the profile of the crack tip on the surface of the sheet. For materials with the higher proportions of hardener such crack tips are obviously quite blunt (fig. 9) and it appears

Figure 7 Section of a "silica-filled" araldite specimen (× 250).

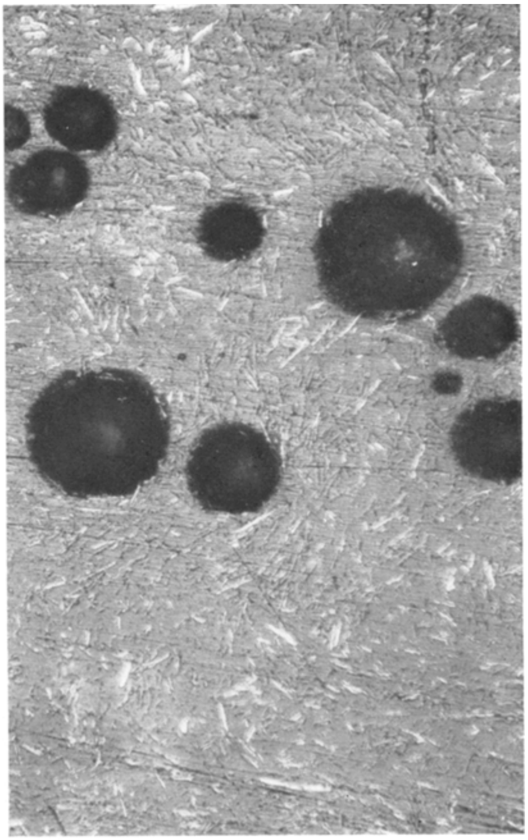


Figure 8 Section of an "aluminium-filled" araldite specimen (× 45).

feasible that the high values of fracture energy are associated with the work done in plastically deforming the material in a zone ahead of the crack tip. To a good approximation at these high energies the surface free energy is negligible and in the absence of sub-surface cracking and marked roughness we can write [8]

$$\gamma = \tfrac{1}{2}\sigma\alpha$$

where σ is the flow stress and α is the extension in an idealised plastic enclave ahead of the crack tip.

The flow stress, calculated from measured diamond pyramid hardness using $H/\sigma = 2$ [9], increases from 5 to 10 kg mm^{-2} as the hardener content increases from 5 to 15 pph and then remains approximately constant from 15 to 30 pph. Thus if the large changes in fracture energy are to be attributed to changes in the work done on a plastic zone ahead of the crack tip, these must be due to changes in the value of α at instability rather than in the flow stress. This is qualitatively consistent with microscope observations of crack-tip profiles; blunt tips can be detected in samples containing 15 or 30 pph hardener, whereas for samples with 5 pph hardener the crack tip cannot be clearly resolved in the optical microscope.

For "resin + 15 pph hardener" $\sigma = 10$ kg $\text{mm}^{-2} = 10^9$ dyne cm^{-2} and taking α to be equivalent to the width of the crack tip as in fig. 9 $\sim 1.5 \times 10^{-4}$ cm, then $\tfrac{1}{2}\sigma\alpha \sim 7.5 \times 10$ erg cm^{-2} which is of the same magnitude as the measured fracture energy.

The phenomena of slow crack-propagation and crack-jumping are particularly interesting from a fundamental viewpoint and both have been observed in other materials [10–13]. The information available for the epoxy resins with which we are concerned here is not yet sufficient to justify detailed discussion.

Throughout the whole range of hardener

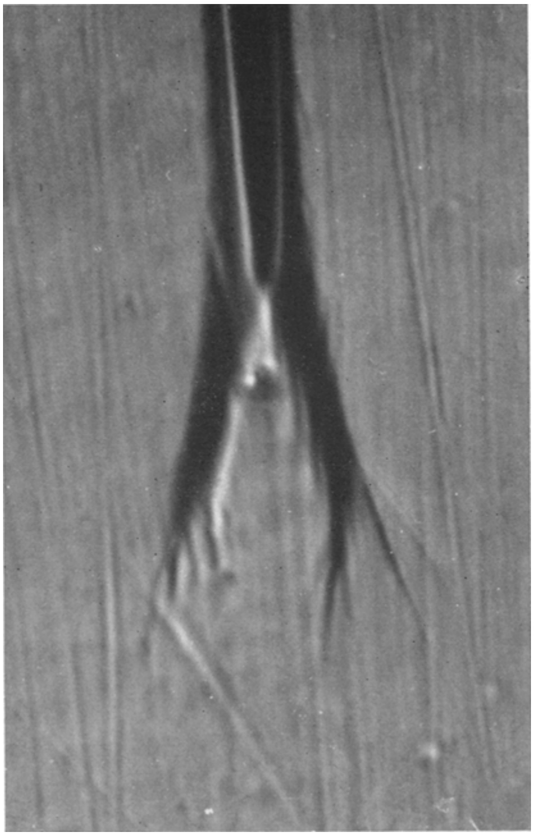


Figure 9 Blunt crack tip in a sample sheet of Araldite with 15 pph hardener (× 2200).

contents used in these experiments the "filled" resins are tougher. The fracture surfaces of the filled materials are complex: the silica-filled specimens showed extensive sub-surface cracking although macroscopically a relatively smooth fracture surface; the Al-filled specimens had very rough fracture surfaces.

It seems doubtful whether the increase in surface area alone is adequate to account for the appreciably higher fracture energy of the filled specimens.

Acknowledgement

The authors are grateful to the Governors of the North Staffordshire College of Technology for the leave of absence granted to R. Griffiths which enabled him to contribute to this work.

References

1. J. D. ESHELBY, "Fracture Toughness" Chapter 3 pub. No. 121 (Iron and Steel Inst., London, 1968).
2. J. P. BERRY, *J. Polymer Sci.* **50** (1961) 107; 313.
3. J. J. GILMAN, "Fracture", edited by A. L. Averbach *et al* (Wiley, New York, 1959).
4. P. P. GILLIS and J. J. GILMAN, *J. Appl. Phys.* **35** (1964) 647.
5. B. GROSS and J. E. SRAWLEY, NASA tech. note D3295 (1966).
6. S. M. WIEDERHORN, A. M. SHORB, and R. L. MOSES, *J. Appl. Phys.* **39** (1968) 1569.
7. B. J. HAYES, "The Plastics Manual" (Scientific Press, 1962) p. 27.
8. A. H. COTTRELL, *Proc. Roy. Soc.* **A282** (1964) 2.
9. D. M. MARSH, *ibid* **A279** (1964) 420.
10. J. J. BENBOW and F. C. ROESLER, *Proc. Phys. Soc.* **B70** (1957) 201.
11. K. R. LINGER, and D. G. HOLLOWAY, *Phil. Mag.* **18** (1968) 1269.
12. S. M. WIEDERHORN, *Mat. Sci. Res.* **3** (1966) 503.
13. R. G. HOAGLAND, *J. Basic Eng. ASME* **89** (1967) 525.

Received 17 November 1969 and accepted 15 January 1970.