The toughness of epoxy polymers containing microvoids

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This work has demonstrated that microvoids a micrometre or so in diameter, with a volume fraction of ~ 17%, would appear to give a significant increase in the toughness of a thermosetting epoxy polymer.

(Keywords: toughness; epoxy polymers; microvoids)

Introduction

Recent studies[1–6] have provided a detailed description of the toughening mechanisms involved in the fracture of rubber-modified crosslinked epoxy polymers. They include: (i) localized shear yielding, or shear banding, in the epoxy matrix which occurs between the rubbery particles; (ii) plastic void, or hole, growth in the epoxy matrix which is initiated by cavitation or debonding of the rubbery particles; and (iii) bridging of rubber particles behind the crack tip.

Further, recent work[7] has suggested that the mechanisms involving localized shear yielding, or shear banding, in the epoxy matrix which occurs between the rubbery particles and plastic void, or hole, growth in the epoxy matrix do not require the rubbery particle to be well-bonded to the matrix. On the other hand, it does appear that the rubber-bridging mechanism is only operative if the rubbery particles are chemically bonded to the matrix. For example, rubbers have been employed which contain no chemically reactive, functional end groups. However, providing the volume fraction and size of the dispersed rubbery particles which phase separated were relatively unaffected compared to that obtained using the reactive rubbers, it was found that the unreactive rubbers were still able to significantly toughen the epoxy matrix. Nevertheless, the fracture energies, G_{Ic}, of such rubber-toughened epoxies were somewhat lower than that observed when a typical bifunctional, and hence reactive, rubber was employed; and this small decrease could be quantitatively attributed to the rubber-bridging mechanism being inoperative when using the unreactive rubbers.

The relatively high toughness observed for the rubbers which possessed no chemically reactive, functional end groups raises the question of how an epoxy polymer simply containing holes, or voids, would behave. The previous problem in conducting this experiment has always been preparing such materials with a representative volume fraction and size of holes or voids. However, Waddill[8] has suggested a way of preparing epoxy polymers containing holes and proposed that such materials may exhibit an improved toughness. The present paper describes a study of such epoxy polymers and examines the toughness and toughening mechanisms of the materials.

Experimental

The formulations used are given in *Table 1*. The epoxy resin employed was a diglycidyl ether of bisphenol A with an epoxy equivalent weight of $\sim 190\ \mathrm{g\ mol^{-1}}$. The curing agent was an amine-terminated polypropylene glycol (Jeffamine D-230, Texaco plc) and the accelerator was an aliphatic amine (Jeffamine 399, Texaco plc). The microvoiding agent was a urea-terminated polyether amine (Jeffamine BuD 2000, Texaco plc). The curing schedule used was 7 days at 22°C but the curing reaction was accompanied by an appreciable exotherm which significantly raised the temperature of the reactants. As may be seen from *Table 1*, a 'control' specimen was prepared together with a specimen containing microvoids.

A small, carefully polished specimen of the material was coated with gold, to prevent charging, and was then examined using a scanning electron microscope. The micrographs were then processed using an image analyser to determine the parameters which characterize the microstructure: namely the volume fraction, V_{f}, and the diameter, d_{p}, of microvoids. The values of the glass transition temperature, T_{g}, of the materials were measured using a Du Pont differential scanning calorimeter, at a heating rate of $10^{\circ}\mathrm{C\ min^{-1}}$.

Moulded sheets of the epoxy polymers were cut into compact tension specimens (10.0 × 40.0 × 38.4 mm). The fracture toughness, or stress-intensity at the onset of crack growth, K_{Ic}, was measured according to the procedures outlined in the latest testing protocol[9] and the fracture surfaces were examined using the scanning electron microscope. Plain-strain compression tests[10] were performed to measure the yield stress, σ_{y}, and fracture strain, γ_f, of these materials, and the elastic moduli, E, were measured using the three-point bending flexural test, according to the appropriate ASTM standard[11]. The values of the fracture energy, G_{Ic}, were deduced from the relationship:

$$K_{\mathrm{Ic}}^2 = EG_{\mathrm{Ic}}/(1 - \nu^2) \qquad (1)$$

where ν is the Poisson's ratio of the polymer and was taken to be 0.35.

The surfaces of the fracture test specimens were coated with gold, to prevent charging, and were then examined using a scanning electron microscope.

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Table 1 The formulations and the microstructural parameters of the materials

Material	Epoxy (phr)	D-230 (phr)	BuD-2000 (phr)	Accel. 399 (phr)	V_f (%)	d_p (μm)	ρ (g cm^{-3})
'Control'	100	30	–	10	0	–	1.131
'Voided'	100	30	20	10	17	0.70	1.139

Table 2 Mechanical properties of the materials

Material	Voids (%)	T_g (epoxy) (°C)	K_{Ic} (MPa m$^{1/2}$)	E (GPa)	G_{Ic} (kJ m^{-2})	σ_y (MPa)	γ_f
'Control'	0	50	1.03	3.24	0.29	91.6	0.60
'Voided'	17	50	1.96	2.47	1.36	60.1	0.67

Figure 1 Scanning electron micrograph of a polished surface of the 'voided' formulation

Results

The evidence for the formation of microvoids in the formulation containing the BuD 2000 in the paper by Waddill[8] was obtained from scanning electron micrographs of the fracture surfaces. However, it is now clearly recognized that voids may develop during the crack growth process. Therefore, in the present work, in order to establish conclusively that microvoids were formed, the specimens were examined prior to fracture testing. The transparent control formulation contained no second phase particles. However, the opaque, water-white, 'voided' formulation was found to contain holes, or voids, as may be clearly seen from *Figure 1*. It should be noted, that whilst some of the holes are shallow and might have been formed by rubbery particles extracted during the polishing operation, many of the holes are deep and it seems most unlikely that the gentle polishing employed could have extracted rubber so deeply embedded in the epoxy polymer. Indeed, other work[7] has shown that careful polishing of rubber-modified epoxy polymers with known poor particle/matrix adhesion does not remove the rubbery particles from the epoxy matrix. Further, it may be seen from *Figure 1* that some of the voids contain material, and there are no signs of this material being the remains of removed rubber particles. Therefore, such micrographs support the earlier conclusions of Waddill. Namely, that a rubbery phase resulting from the addition of a urea-terminated polyether amine has phase separated during the curing process. However, due to differential thermal strains, the rubbery phase so-formed has debonded from the matrix or internally cavitated and formed the microvoids which may be observed in *Figure 1*. The density, ρ, values for the 'control' and 'voided' materials are very similar and this supports the proposed routes for the formation of the microvoids. The volume fraction and size of the microvoids were determined from a large number of micrographs and are given in *Table 1*.

The values of T_gs for the epoxy matrix are given in *Table 2*, and are the same for both materials. This supports the suggestion that the urea-terminated polyether amine has virtually completely phase separated during the curing process.

The mechanical properties of the materials are given in *Table 2*. The modulus of the 'voided' material is ~20% lower than for the 'control' and this is about the same level of decrease as observed when a similar volume fraction of rubbery particles are present[7]. The value of σ_y is appreciably reduced by the presence of the microvoids and γ_f is somewhat higher. Thus, the changes in both of these properties reveal that the 'voided' polymer can more easily undergo plastic deformation than the 'control' material. This is reflected by a significant increase in K_{Ic} at fracture from 1.03 to 1.96 MPa m$^{1/2}$ arising from the presence of the microvoids. The modulus, E, has, as expected, decreased due to the introduction of the microvoids. This factor, together with the increase in K_{Ic} [see equation (1)], leads to a major increase in G_{Ic} from 0.29 to 1.36 kJ m^{-2}. Hence, the introduction of microvoids, of a similar size and volume fraction to that observed for the typical rubbery phase in rubber-toughened epoxy polymers, has clearly increased the crack resistance of the epoxy material.

Indeed, the fracture surface of the 'voided' material shown in *Figure 2* is very reminiscent of that of a rubber-toughened epoxy, but in the case of a rubber-toughened epoxy the voids are formed *during* the crack growth process. However, the voids seen on the fracture surface of the 'voided' material are somewhat larger in size than the original microvoids, due to plastic hole growth of the epoxy polymer.

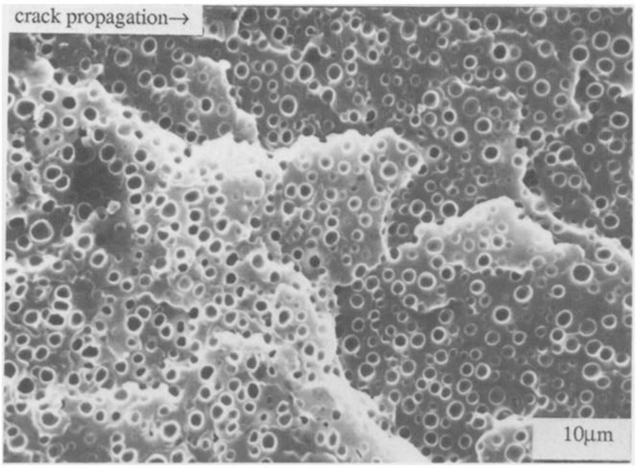

Figure 2 Scanning electron micrograph of the fracture surface of the 'voided' formulation

Conclusions

The present detailed study has confirmed the earlier work of Waddill[8] and shown that, if microvoids of a micrometre or more in diameter, are present at a volume fraction of ~17% in a relatively ductile epoxy, then they can significantly increase the toughness of the thermoset epoxy polymer.

These studies also strongly support recent work[7] on the role of interfacial adhesion in the rubber-toughened epoxy polymers. This work has demonstrated that, providing the second phase microstructure can be generated, then reactive functional groups do not have to be present on the rubber molecules and that interfacial adhesion forces arising from secondary, van der Waals, forces would appear to be sufficient to give a significant increase in the toughness of such multiphase thermosetting polymers. Nevertheless, it should be noted that the maximum toughness values are invariably observed when a reactive rubber is employed, which phase separates and results in particles which are chemically bonded to the matrix.

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References

1 Kunz-Douglass, S., Beaumont, P. W. R. and Ashby, M. F. *J. Mater. Sci.* 1980, **15**, 1109
2 Kinloch, A. J. in 'Rubber-Toughened Plastics' (Ed. C. K. Riew), Advances in Chemistry Series 222, American Chemical Society, Washington DC, 1989, p. 67
3 Kinloch, A. J., Shaw, S. J. and Hunston, D. L. *Polymer* 1983, **24**, 1355
4 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1986, **21**, 2475
5 Huang, Y. and Kinloch, A. J. *J. Mater. Sci.* in press
6 Huang, Y. and Kinloch, A. J. *J. Mater. Sci. Lett.* in press
7 Huang, Y., Kinloch, A. J., Bertsch, R. J. and Siebert, A. R. 'Rubber-Toughened Plastics' (Eds A. J. Kinloch and C. K. Riew), Advances in Chemistry Series, American Chemical Society, Washington DC, in press
8 Waddill, H. G. 11th National SAMPE Tech. Conf., Boston, 13–15 November, 1979
9 European Group on Fracture Task Group 'Testing Protocol' (Ed. J. G. Williams), Imperial College, London, 1990
10 Williams, J. G. and Ford, H. *J. Mech. Eng. Sci.* 1964, **6**, 7
11 ASTM Standard D790M 'ASTM Annual Handbook', ASTM, Philadelphia, 1986