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The fracture of particulate–filled epoxide resins

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The double torsion test technique was used to investigate the fracture properties of two commercial epoxide resins filled with glass beads. The influence of varying the volume fraction of glass, the mean particle size and the pre-treatment of the glass surface on the stress intensity factor have been determined. A correlation has been found between the compressive yield strength and the stability of fracture in these composites, similar to that found for unfilled epoxide resins.

1. Introduction

In a previous publication [1] the fracture of epoxide resins filled with silica, alumina and dolomite particles was described. In this paper we report the effect of glass beads on the fracture properties of these resins. Glass beads have been widely used as a model system for the roughly shaped mineral particles frequently employed in plastic mouldings. There are several advantages in using glass beads owing to the regular particle shape and the fact that they are readily available in a wide range of particle sizes. High volume fractions may be incorporated into most resins.

The purpose of this work was to evaluate whether these spherical particles indeed act as an effective model system or whether different mechanisms may intervene from changing the shape and nature of the particles.

2. Materials and experimental

Two epoxide resins were used for this investigation which were both products of Ciba-Geigy. The first (resin A) was solid at room temperature and based on the diglycidyl ether of bisphenol-A, cured with phthalic anhydride. The second (resin B) was an epoxide based on dimethyl hydantoin which was also anhydride cured. The details of the curing conditions and specimen preparation have been described previously [1].

The resins were filled with varying volume fraction of glass beads of type 2429 (diameter 50 to 100 μm) and 2400 (0 to 50 μm). The beads were supplied in untreated form and treated with CPO3 "coupling agent". In addition, work was carried out on beads treated in our laboratory. Three silane compounds were used to change the adhesion between the resin and the filler. The first chlorotrimethyl silane (CTMS) was intended to reduce the adhesion. The other two silanes were commercial "coupling agents", γ-aminopropyltriethoxysilane (A1100*) and γ-glycidoxytrimethoxysilane (A187*), in order to improve the interfacial bonding. The filler particles were treated using a method based on that suggested by Trachte and DiBenedetto [2].

In addition, a set of specimens was prepared using hollow silica spheres. These were obtained from Emerson and Cumings and has a mean

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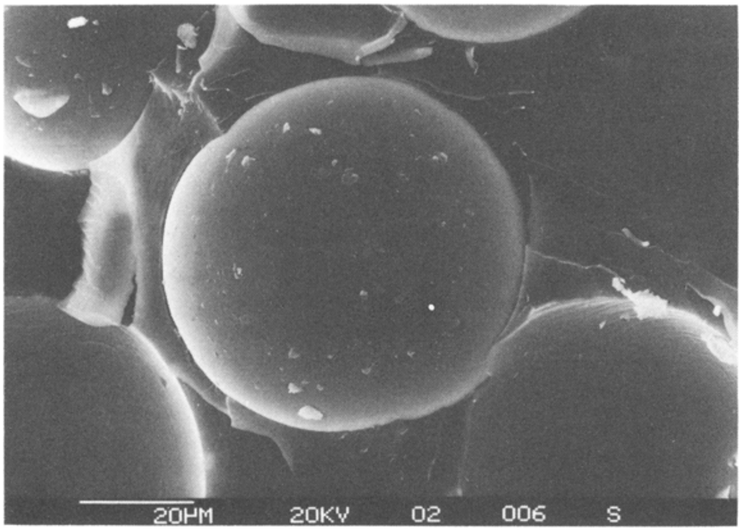

Figure 1 The fracture surface of resin B filled with untreated glass particles.

diameter of 80 μm with a wall thickness of 1.5 μm.

The double torsion test technique was used to measure the stress intensity factor (K_{Ic}) for these composites, as described previously [1]. After failure the two sections of the double torsion specimen were polished. These were then used to measure the flexural strength in three-point bending or the yield stress in plane strain compression. The latter test was developed by Williams and Ford [3]. Hence, the values of K_{Ic}, yield stress and flexural strength could be directly compared on the same specimen.

In all cases the fracture surfaces were examined under the scanning electron microscope.

3. Results

The micrographs of the fracture surface are shown in Figs. 1 to 3. These suggest that the adhesion was modified in the manner desired. The values of K_{Ic}, at a crosshead displacement rate of 0.1 mm min^{-1} are given in Table I. For both resins filled with untreated beads and those treated with CTMS the crack propagation was stick-slip. In the case of resin A, beads treated with A187 and A1100 also gave stick-slip crack propagation, whereas with resin B improved bonding led to stable crack growth. These latter results parallel the phenomena observed for these resins in the unfilled state [1]. Resin A showed stick-slip propagation at low cross-

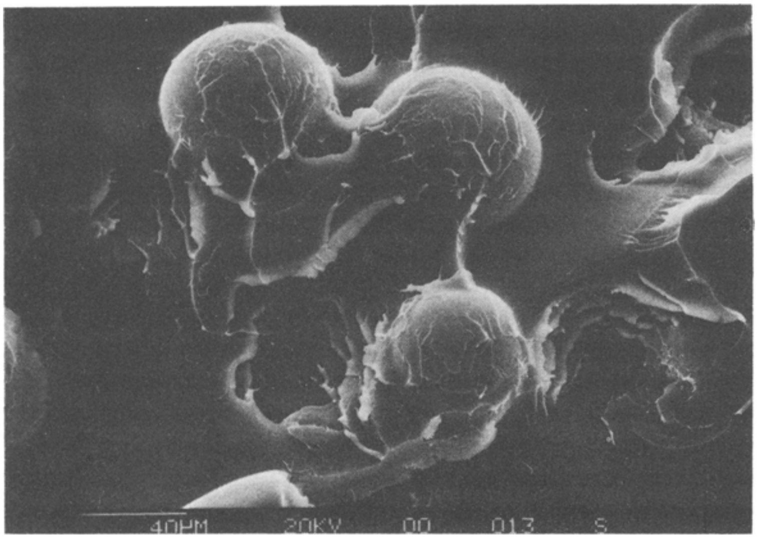

Figure 2 The fracture surface of resin A filled with A187 treated glass particles.

TABLE I The effect of surface treatment on the stress intensity factor of glass bead composites (40% by volume beads, type 2429)

Resin	Treatment	Mean value K_{Ic} (MN m$^{-3/2}$)	
		Initiation	Arrest
A	none	1.88	1.52
	CTMS	2.26	1.37
	A187	1.89	1.74
	A1100	1.96	1.73
B	none	1.57	1.35
	CTMS	1.75	1.21
	A187	1.45	
	A1100	1.48	

TABLE II The effect of surface treatment on the flexural strength of glass bead composites (three point bending)

Resin	Treatment	Flexural strength (MPa)
B + 40% glass	none	59.8
	A187	69.8
	A1100	86.6

head displacement rates (below 0.5 mm min^{-1}) and resin B showed stable crack growth over the whole range of crosshead displacement rates.

For resin B filled with glass beads, treated with coupling agent, the relationship between K_{Ic} and the volume fraction was found to be linear, as shown in Fig.4. No difference was observed by changing the mean particle size by using the 2400 and the 2429 beads. A similar linear correlation was found for this resin filled with alumina and silica particles although the slope was different.

The influence of the filler surface treatment and the volume fraction on the yield stress of the composites is shown in Fig. 5. Treatment with a "coupling agent" increased the yield stress as compared to the unfilled resin, whereas non-treated beads and those treated with CTMS had a yield stress inferior to that of the resin.

The change in flexural strength of resin B with surface treatment of the glass is shown in Table II.

4. Discussion

Kinloch and Williams [4] have recently proposed a theory concerning the stability of crack propagation in epoxide resins. They related the amount of crack tip blunting to the yield stress of the epoxide resin. For resins with a low yield stress (100 MPa appeared to be a critical value for a wide range of epoxides) polymer material in the vicinity of the crack tip may flow giving a blunt crack. The specimen must be loaded further to re-initiate a sharp crack, and the crack propagation is hence unstable. If the yield stress is sufficiently high this plastic flow at the crack tip does not occur, and the crack propagation is stable.

It has already been observed with silica and alumina filled resins that conditions which reduce the yield stress, for example, elevated temperatures but which were still well below T_g, gave rise to unstable crack growth [1]. In all cases where crack propagation was unstable the yield stress of the material was lower than that of the unfilled resin. Exactly the same behaviour has been observed for these glass bead filled systems. Only in the case of resin B filled with glass beads treated with coupling agent was the yield stress superior to that of the unfilled resin (see Fig. 5).

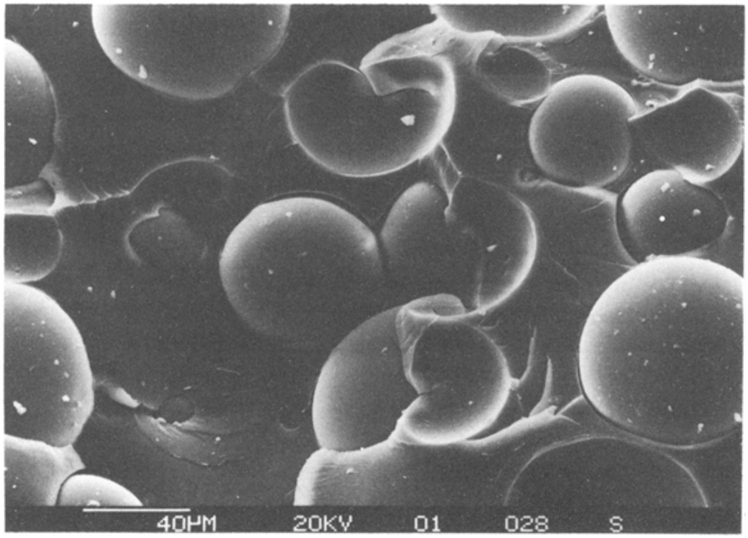

Figure 3 The fracture surface of resin A filled with CTMS treated glass particles.

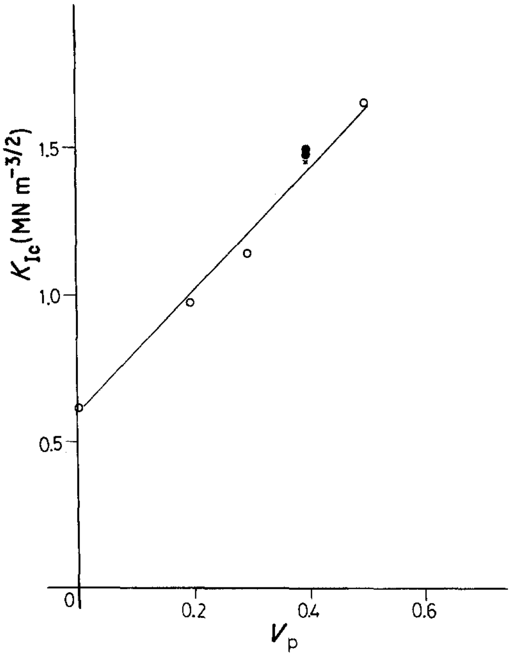

Figure 4 The variation in the stress intensity factor with the volume fraction of glass particles. Resin B: ○ beads 2400 treated with CPO3, X beads 2429 treated with CPO3, ● beads 2429 treated with A187.

For resin B filled with 40% untreated beads the yield stress was only 83 MPa. It might be expected that the yield stress would be decreased as if the system were filled with voids. Ishai and Cohen [5] have evaluated the yield stress for epoxide resins with varying volume fractions of voids. The stress at yield was related to the volume fraction as follows:

$$\sigma_{y\,\mathrm{comp}} = \sigma_{y\,\mathrm{resin}}\left(\frac{1}{1-1.2V_p^{2/3}}\right) \tag{1}$$

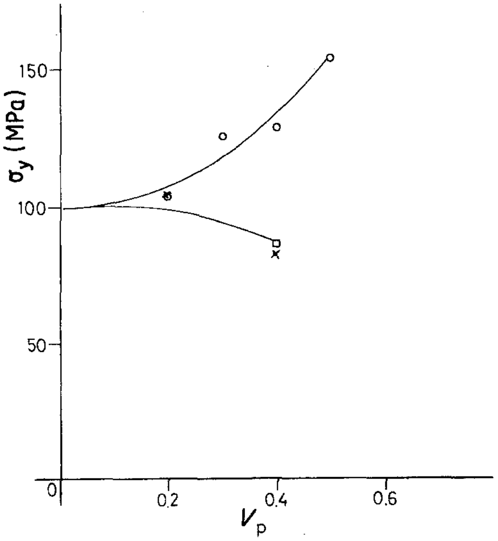

Figure 5 The variation in the yield stress with volume fraction of glass beads. Resin B: X untreated beads, ○ CPO3 treated beads, □ CTMS treated beads.

where $\sigma_{y\,\mathrm{comp}}$ and $\sigma_{y\,\mathrm{resin}}$ are the yield stresses of the composite and the unfilled resin respectively, and V_p is the volume fraction of voids.

However, in the case of uncoupled glass beads the yield stress is not diminished to the extent predicted by this equation. This is probably because of the finite resistance of the glass beads in compression as compared to a void.

For resin B filled with well-bonded glass beads there was a linear relationship between K_{Ic} and the volume fraction. However, the increase in K_{Ic} was lower than that observed for silica and alumina composites. There are various possible mechanisms for the increase in toughness by the inclusion of second phase particles. These mechanisms have been reviewed by Green [6]. Firstly, the fracture energy may be increased by an augmentation in the surface area of fracture as follows:

$$\gamma_{\mathrm{comp}} = \gamma_{\mathrm{resin}}\left(\frac{A_t}{A_p}\right) \tag{2}$$

where γ_{comp} and γ_{resin} are the fracture energies of the composite and resin respectively; A_t is the true surface area and A_p the planar surface area. However, this effect is too small to account for the observed increases in toughness.

Secondly, the fracture energy may be increased by the creation of fracture surface steps. These arise when the crack front is divided and is forced into different planes. "River" markings have been observed frequently on the fracture surfaces of two phase materials [7]. The additional energy depends on the volume fraction of the second phase (V_p) and the height of the fracture steps:

$$\gamma_{\mathrm{comp}} = \gamma_{\mathrm{resin}}(1-V_p) + S\left(\frac{h}{dc}\right) \tag{3}$$

where S is a constant, h the step height and dc the centre-to-centre interparticle spacing.

Thirdly, the fracture toughness may be increased by a bowing of the crack front between the particles. This mechanism was originally suggested by Lange [8] and is analogous to the line tension concept used in dislocation theory. This mechanism was analysed further by Evans [9] who calculated the increased energy required to bow

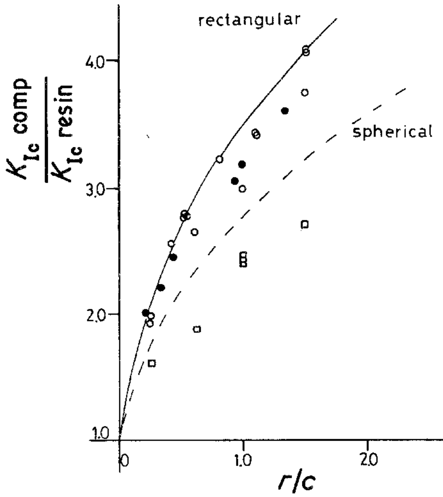

Figure 6 The increase in the stress intensity factor required to move a semi-circular crack through a series of obstacles. —— theoretical curve for rectangular obstacles, – – – theoretical curve for spherical obstacles. Resins A and B: ○ silica particles, ● alumina particles, □ glass beads treated with A187.

the crack in terms of the ratio of the particle size to the particle spacing (r/c^{*}). We have used this mechanism to explain the increase in the stress intensity factor for epoxide resins filled with silica and alumina particles [1]. Good agreement was obtained between the theoretical and experimental results as shown in Fig. 6. These particles were assumed to be rectangular, and their length twice their width. Green [10] has also calculated the increase in stress intensity factor for spherical particles, and this is plotted in Fig. 6. The measured values of K_{Ic} for resin B filled with well-bonded glass beads are somewhat lower than predicted, the reason for this is unclear at present.

A fourth possible mechanism for the increase in toughness by particulate inclusions is a decohesion of the particles from the matrix ahead of the crack tip giving rise to crack tip blunting. Owen [11] has conducted a microscopic study of the fracture of a glass bead-filled epoxide resin and observed such a decohesion ahead of the crack. Broutman and Sahu [12] have also given evidence of decohesion in glass bead-epoxide composites from water uptake studies. This mechanism may explain the difference in behaviour of the poorly bonded and well-bonded beads. In the case of composites prepared from poorly-bonded beads the yield stress is lower than that of the matrix, and as the crack propagates the particles become debonded giving rise to crack tip blunting. The specimen must be re-loaded to initiate a sharp crack and thus unstable fracture is observed. For the composites prepared from well-bonded beads the yield stress is superior to that of the matrix and crack propagation is stable.

However, unstable crack propagation was not observed for these resins filled with alumina particles which were also poorly bonded. The aspect ratio of the particles appears to play an inportant role here. For spherical particles there is always one part of the interface that is subject to the maximum normal stress giving rise to a zone of decohesed particles. Evidence in favour of this explanation has been given by Su and Suh [13] who studied void cavitation in a glass bead-filled epoxide resin. They found that cavitation began at locations near the two poles of the beads in the tensile direction. In the case of epoxides filled with roughly-shaped mineral fillers such as silica and alumina void nucleation is more difficult. This is reflected in the flexural strength in that the glass bead composites had strengths considerably lower than either the alumina or silica filled resins [1].

A set of experiments was also performed using hollow silica spheres at a constant volume fraction of 30%. The stress intensity factor was found to be identical to that of the unfilled resin that is $0.6\,\mathrm{MN\,m^{-3/2}}$. The fracture surface, shown in Fig. 7, was rather different from that of the glass bead-filled resins as there was no evidence of plastic deformation of the matrix. The crack front is normal to the tangent of the spheres and many of the particles have been fractured. This may be contrasted with the fracture surfaces of the glass bead-filled resins in Figs. 1 to 3 where there is considerable evidence of crack bowing between the particles.

5. Conclusions

Epoxide resins may be toughened by the addition of rigid particulate fillers. However, the maximum increase in toughness may only be obtained under certain conditions.

1. The particles must be more resistant than the matrix. Particles like the hollow silica micro-

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[*] The particle spacing has been calculated on the basis of the mean free path. Green [6] has suggested that this may not be valid and a better method should be by calculating the nearest neighbour spacing. However predicted increases in toughness are considerably greater than the measured values if this latter definition of interparticle spacing is used.

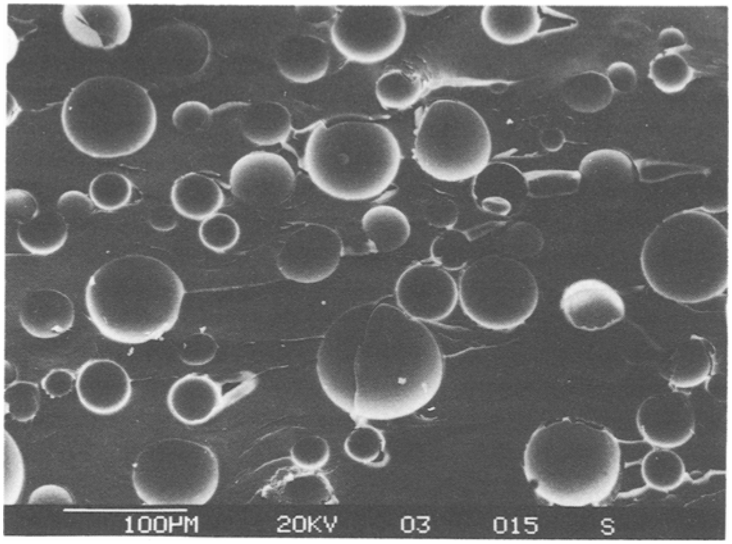

Figure 7 The fracture surface of resin B filled with hollow silica spheres.

spheres give rise to composite with a toughness equal to that of the resin. The mere presence of interfaces is insufficient to promote increased toughness. Fillers like dolomite [1] and aluminium hydroxide [14] give some increase in K_{Ic} but above a certain volume fraction transparticle fracture occurs, and there is no further toughening.

2. A certain minimum adhesion between the filler and the resin is necessary for toughening by crack bowing. For the resins filled with decoupled glass beads the yield stress of the composite was lower than that of the matrix. In this case unstable crack propagation occurs presumably due to blunting at the crack tip. The toughness of these composites is high but this is to the detriment of the strength which is lower than when the particles are well-bonded.

3. The particle shape plays an important role in determining the toughness of the composite. The theoretical work of Green and the experimental results presented here show that spherical particles are less effective increases in toughness by particles. Spherical glass beads do not give composites with the same fracture properties as roughly shaped mineral fillers and care should be exercised in extrapolating results from tests on resins filled with glass beads to other filler systems.

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