

NOTES

Toughening of Epoxies by Thermal Expansion Mismatch

Epoxy resins are ideal engineering adhesives and matrices for fiber composites because of their relatively high stiffness, strength, corrosion resistance, and glass transition temperature. However, they are generally brittle and this has severely restricted their wider application as engineering materials. Hence, various methods have been employed to overcome the tyranny of the Griffith equation in this class of materials. Essentially, these methods are based upon attaining a dispersion of second phase particulates in the epoxy matrix which may be either rubbery¹ or rigid² in nature, or both.^{3,4} Substantial enhancement of fracture toughness has been achieved, particularly in the hybrid system.

Various mechanisms of toughening have been proposed for the rubber-modified epoxies.⁵⁻⁹ Many of these are based on the mechanisms observed in rubber-toughened thermoplastics. Examples of these include: crazing,⁷ shear yielding,¹ shear banding,⁸ and rubber stretching and tearing.⁹ Each of these theories has inadequacies and cannot explain satisfactorily the microstructure-property-mechanics relations. This note attempts to highlight an alternative toughening mechanism by virtue of the thermal expansion mismatch between the rubbery particles and the epoxy matrix. Its implication on the failure processes is also discussed.

Under suitable conditions, the shrinkage stresses resulting from the thermal expansion mismatch in short fiber composites may contribute to enhance the work of fracture. These stresses if compressive can considerably increase the pullout stress of debonded fibers.¹⁰ The high values of strength and toughness observed in the partially stabilized zirconia (PSZ) ceramics^{11,12} have also been attributed to the presence of compressive stresses in the vicinity of the crack tip. These stresses arise from the volumetric expansion of metastable ZrO₂ particles during the phase transformation. Residual stresses in brittle ceramics and composites may also be harnessed to improve their fracture resistance.¹³

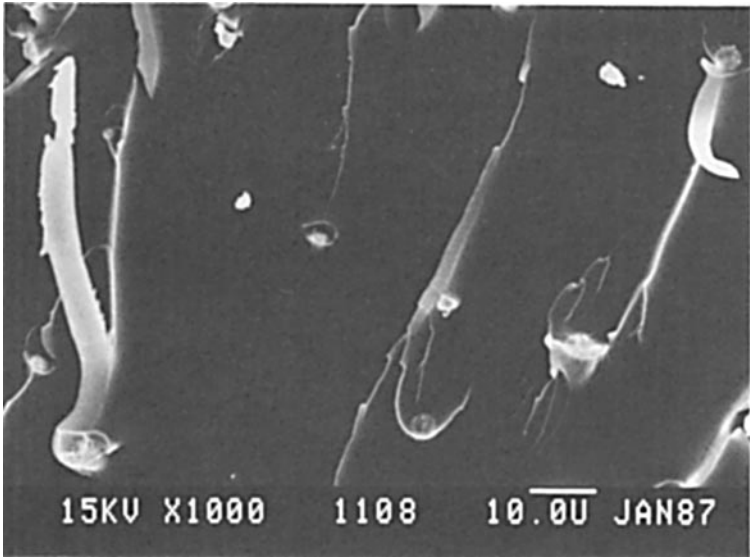
The differential thermal expansion is a very important parameter in any composite system since it determines the residual stress-strain distributions after fabrication and can have significant effects on the resultant mechanical and fracture properties. When the differential thermal expansion ($\Delta\alpha$) between that of the matrix (α_m) and that of the filler (α_f) is negative, toughening of the composite may occur. This arises particularly when the filler-matrix interface is strong enough to support the resulting radial tensile stresses on cooling from the fabrication temperature. Under such condition, the surrounding matrix will be subjected to tangential compressive stresses; this will increase the overall strain required to initiate failure. The composite is thus toughened. If however, $\Delta\alpha$ is positive, induced tangential tensile stresses may weaken and cause embrittlement of the matrix. If the differential is large enough, the failure strain of the matrix may be exceeded and a network of fine microcracks will develop. The magnitude of these radial (σ_r) and tangential (σ_t) stresses may be estimated from¹⁴

$$-\sigma_r = 2\sigma_t = \frac{\Delta\alpha \Delta T}{(1 + \nu_m/2E_m) + (1 - 2\nu_f/E_f)} \quad (1a)$$

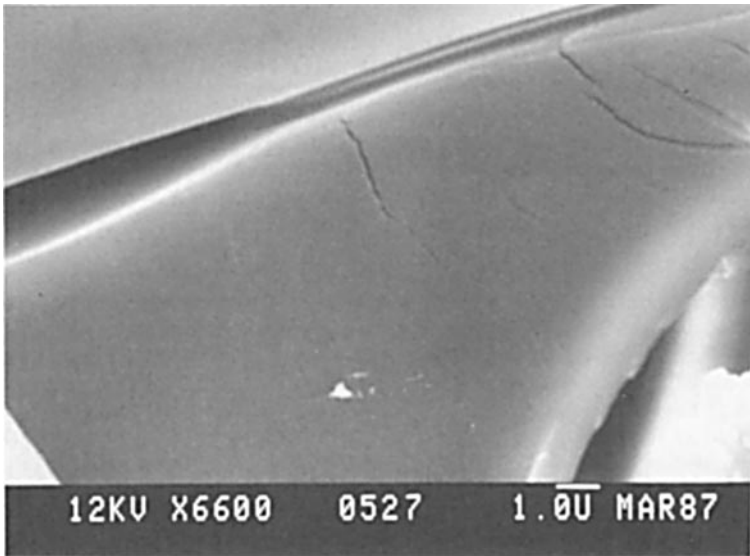
$$\simeq \Delta\alpha \Delta T E_m \quad (1b)$$

where α , T , ν , and E are the linear thermal expansion coefficient, temperature, Poisson's ratio, and elastic modulus, respectively. The subscripts refer to the matrix (m) and filler (f).

In the rubber-modified epoxy system, $\Delta\alpha$ is negative ($\alpha_{\text{epoxy}} = 65 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$; $\alpha_{\text{rubber}} > 85 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). It follows from eq. (1b) that radial tensile stresses of about 6 MPa are induced at the rubber matrix interface on cooling from the curing temperature of 120°C. Since the adhesion between the rubbery particles and the epoxy matrix is very strong,¹ the interface can support the resulting radial tensile stresses. The rubbery particles will endeavor to strain the matrix in compression in the *axial* direction. This will invariably increase the fracture resistance of the matrix.



(a)



(b)

Fig. 1. Scanning electron micrograph of an epoxy system reinforced with short Al_2O_3 fibers: (a) fracture of fibers; (b) microcracking in the matrix.

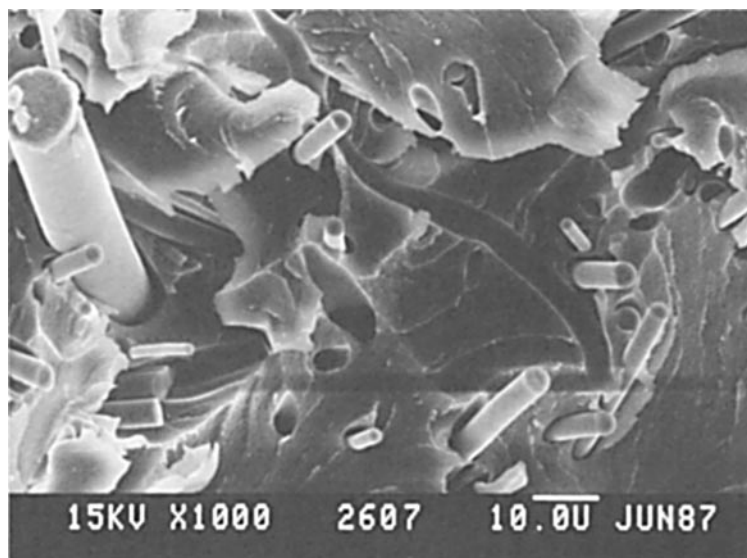


Fig. 2. Scanning electron micrograph showing extensive fiber debonding and pull outs in an epoxy system containing both rubbery particles and short Al_2O_3 fibers.

The addition of a second filler, e.g., short Al_2O_3 fibers⁴ to the rubber-modified epoxy matrix will complicate the above mechanism especially when they have a lower value of α than that of epoxy ($\alpha_{\text{Al}_2\text{O}_3} = 8.5 \times 10^{-6} \text{C}^{-1}$). Under this circumstance, the thermal expansion mismatch effect of the two fillers will be diametrically opposing each other. At the interface between rubber and epoxy, radial *tensile* stresses of about 6 MPa are induced with the concomitant generation of tangential *compressive* stresses at the surrounding matrix. On the other hand, radial *compressive* stresses of about 16 MPa are induced at the fiber-matrix interface in concert with the production of tangential *tensile* stresses in the matrix. In the absence of the interference from the rubbery particles as in the fiber-epoxy system, a very strong bond at the interface can be developed. When this happens, the efficient stress transfer from the matrix to the fiber enables the hydrostatic tensile stresses in the fibers to become large enough for fiber fracture in preference to fiber debonding [Fig. 1(a)]. The formation of microcrackings in the matrix [Fig. 1(b)] results from the endeavor of the fibers in keeping the matrix in tension in the axial direction.

These failure processes are considerably modified in the presence of rubbery particles (Fig. 2). The presence of large radial tensile stresses associated with these particles serves to dilute the magnitude of radial compressive stresses at the fiber-matrix interfaces. The interface bonding is thus effectively weakened rendering poor stress transfer at the interface. Consequently, the fiber will be readily debonded and pull out (Fig. 2). This ease of fibers debonding and cavitation of rubber particles reflect the formation of an extensive stress whitening in these hybrid epoxies.⁴ The concurrent display of extensive fiber pull outs and the presence of tangential compressive stresses in the matrix in the conjunction with various energy dissipating processes⁴ are accountable for the very high fracture toughness being achieved ($K_{IC} \approx 4.0 \text{ MPa m}^{1/2}$).

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I. M. Low

Department of Chemical and Materials Engineering
University of Auckland
Private Bag, Auckland, New Zealand

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