The Fracture Toughness of Epoxy-glass Bead Composites

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The plane strain fracture toughness of epoxy resins and glass bead filled epoxy composites has been investigated. It was found that the energy required for fracture depended primarily on the ability to dissipate energy in the polymer phase. At low temperatures, where the epoxy was relatively brittle, the addition of glass beads increased the fracture energy and induced roughness in the otherwise smooth fracture surface. At higher temperatures and/or increased catalyst concentration, the unfilled epoxy became more ductile, its fracture surface became rougher, and its fracture energy was increased. When the epoxy was ductile, the addition of beads tended to decrease the fracture energy because of a reduction of the amount of polymer on the fracture surface.

Adhesion of the matrix to the glass beads was only important when the polymer was ductile. Improved adhesion permitted the beads to constrain polymer flow and decrease the fracture energy. Poor adhesion permitted flow around the beads which required additional energy for crack propagation. At low temperatures, where the matrix was brittle, the additional constraints caused by adhesion appeared to make little difference.

Water absorption resulted in plasticizing the polymer, destroying the interface, and probably destroying the polymer near the interface. Short term immersion increased the toughness because of the additional ductility. Long term immersion tended to reduce the toughness. An effective coupling agent minimized this reduction, thereby showing that improved adhesion can improve the environmental stability and extend the useful life of the material.

INTRODUCTION

Fillers and reinforcing agents, acting as stress concentrators, often increase the brittleness of composite materials. In particular, when there is little or no adhesion between phases, microcavitation and debonding can result in cracks of considerable size. Designing against brittle failure in composites is, therefore, of critical importance.

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Irwin has developed the concept of "fracture toughness" as an index of brittleness.[1] It is a measure of the amount of energy required to propagate catastrophically a crack through a material. This concept can be applied to "quasi-isotropic" composites in order to systematically investigate the effect of different variables on the brittleness. The purpose of this investigation was to study the effects of filler concentration, temperature, amount of curing agent, adhesion of polymer to filler and exposure to water on the fracture toughness of particulate filled epoxy materials.

The fracture toughness parameter (γ) for a double edge notched tensile specimen is defined by Irwin[1] as:

$$\gamma = \frac{\sigma^2 W(1 - \nu^2)}{2E} \left[\tan \frac{\pi(a+r_y)}{W} + 0.1 \sin \frac{2\pi(a+r_y)}{W} \right]$$

where σ is the gross section stress at onset of catastrophic fracture, based on the original cross-section, W is the sample width, E is Young's modulus, ν is Poisson's ratio, a is the half crack length at onset of catastrophic fracture, and r_y is Irwin's plastic zone correction factor, given by:

$$r_y = \frac{\gamma E}{\pi(1 - \nu^2)\sigma_y^2}$$

where σ_y is the yield strength of the material. The Poisson's ratio for a composite was computed by the rule of mixtures, (i.e., a volume fraction average) with $\nu = 0.35$ for the epoxy and $\nu = 0.22$ for the glass beads.

The glass beads were Class IV Uni-Spheres, number 4000, diameter range of 1 to 30 microns, purchased from Microbead Division, Cataphote Corporation. To enhance adhesion, the beads were treated with either Union Carbide's A-1100 (gamma-aminopropyltriethoxysilane) or A-187 (gamma-glycidoxy-propyltrimethoxysilane). Both of these are compatible with a diglycidyl ether-bisphenol A type epoxy. In principle, the oxy-silane end of the molecules are capable of chemical reaction with the glass surface while the free amino groups (A-1100) or the free glycidoxy groups (A-187) are capable of chemically reacting with the epoxy resin. Thus, covalent bonding between phases is possible. There is considerable disagreement in the literature as to whether chemical bonding actually occurs, but it is clear that adhesion between phases is improved. To prevent adhesion, the beads were treated with Union Carbide's A-156 (dimethyldichlorosilane). In this case the chlorinated end of the molecules reacts with the glass, leaving the slightly polar methyl groups exposed. This surface is non-wetting with respect to the epoxy, thereby destroying the adhesion between phases. Beads left untreated were used for a fourth composite system.

The resin used was Shell's Epon 828, a diglycidyl ether-bisphenol A type epoxy. The curing agent was catalyst Z, a liquid eutectic mixture of aromatic

amines. Catalyst concentration was varied from 10.38 to 26.65 parts by weight Catalyst Z per hundred parts by weight epoxy. Optimum properties were obtained at 20 parts by weight Catalyst Z per hundred parts by weight epoxy, so this concentration was chosen for most of the experiments. The curing cycle for the systems was 24 hours at room temperature, 24 hours at 60°C, 24 hours at 100°C, and 12 hours at 130°C, followed by slow cooling. The samples were machined, further conditioned by annealing at 100°C for 12 hours and then stored in desiccators over silica gel until testing. The specimens used for the water immersion studies were immersed in distilled water at room temperature for the specified time. The fracture toughness was measured using a double edge notched tensile specimen as described previously.[2]

RESULTS

The results for the dry epoxies are summarized in Table I and Figures 1 to 12. The postulated explanations of the observed phenomena are based primarily on scanning electron microscope photographs of the fracture surfaces, tensile strengths and Young's moduli. Table I presents the overall effect of a given

TABLE I

Summary of fracture toughness data for dry epon 828/catalyst Z epoxy composites (20 pph catalyst unless stated otherwise, curing cycle of 24 hr at 20°C, 24 hr at 60°C, 24 hr at 100°C, 12 hr at 130°C)

Material	Parameter	Effect on γ of increase in parameter	Reason	Evidence
Unfilled epoxy	Curing agent concentration (catalyst Z concentration varied from 10.38 to 25.65 pph)	Increase	Incompletely reacted curing agent plasticized epoxy	Decrease in strength and modulus, increase in fracture surface roughness
Unfilled epoxy	Temperature (varied from −20°C to 130°C)	Increase	Increase in ductility	Decrease in strength and modulus; Increase in fracture surface roughness
Glass bead/ epoxy composites at 25°C (composition range: 0–30% by volume glass)	Adhesion (varied by using A-1100 A187 and A156)	None	Constraints on polymer flow due to adhesions are not important when polymer is very brittle	Fractographic plus toughness data

Table continues

TABLE I—*continued*

Material	Parameter	Effect on γ of increase in parameter	Reason	Evidence
Glass bead/ epoxy composites at 100°C, and 130°C (composition range 0–30% by volume glass)	Adhesion (varied by using A-1100 A-187 and A156)	Decrease	Adhesion at interface constrains polymer flow and significantly reduces energy absorbing ability of polymer	Fractographic plus toughness data
A-156 silane treated glass bead-epoxy composites at 25°C, 100°C and 130°C	Glass bead concentration (varied from 0–30% by volume)	Increase	Increase in total polymer fracture surface due to increase roughness plus unconstrained polymer flow around beads at fracture surface	Fractographic
Untreated, A-1100 silane treated, and A-187 silane treated glass bead-epoxy composites at 25°C	Glass bead concentration (varied from 0–30% by volume)	Increase	Increase in polymer fracture surface roughness counterbalances the supplanting of polymer by beads. Polymer ductility is not a dominant factor	Fractographic
Untreated, A-1100 silane treated and A-187 silane treated glass bead/epoxy composites at 100°C and 130°C.	Glass bead concentration (varied from 0–30% by volume)	Decrease	Increase in total polymer fracture surface is counteracted by constraint of polymer flow near beads	Fractographic

parameter, holding the others constant, on the fracture toughness γ. Increases in the curing agent concentration and the temperature are the most effective ways of increasing the fracture toughness. In both cases it is at the expense of strength and modulus, which leads one to the speculation that the flow properties of the resin phase are the most important factors in controlling the

toughness. A lower yield strength increases the ability to dissipate energy in the polymer phase, thereby increasing the resistance to crack propagation. Changes in the degree of adhesion and the filler concentration had a relatively minor effect except at high temperatures where the polymer was relatively ductile. This also tends to strengthen the above speculation. These factors may be examined in greater detail with the help of Figures 1 through 12.

The increase of the fracture toughness with increasing curing agent concentration and temperature is shown in Figure 1. Apparently, incompletely reacted curing agent served as plasticizer, lowered the glass transition temperature, and thereby enhanced viscous flow during fracture. Similarly, higher temperatures caused a corresponding enhancement of ductility and polymer flow, and thus increased the fracture toughness. These increases in ductility were apparent in the fracture surface morphology as illustrated in Figures 2 and 3. The increase in temperature had a greater effect than did the increase in curing agent concentration. The concurrent decreases in Young's modulus and tensile strength are shown in Figures 4 and 5 respectively.

Addition of glass beads to the brittle epoxy (Epon 828/20 phr Z) resulted in increased fracture toughness at room temperature as shown in Figure 6. As is evident from comparing Figure 7 with 2, the addition of beads resulted in increased roughness in the fracture surface, and probably increased the total
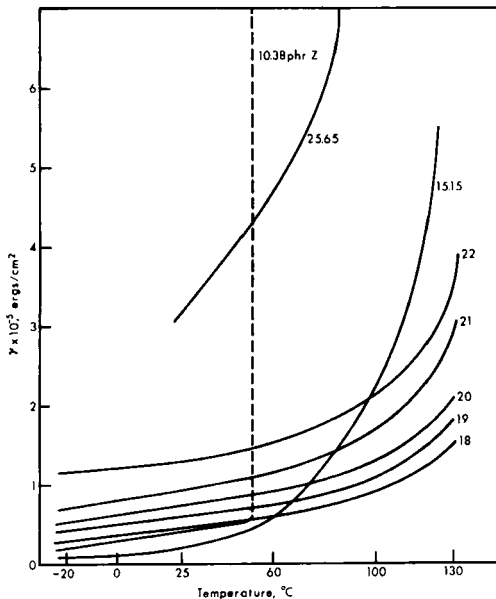

FIGURE 1   Effect of temperature and catalyst Z concentration on gamma-fracture toughness of unfilled epon 828 epoxies.
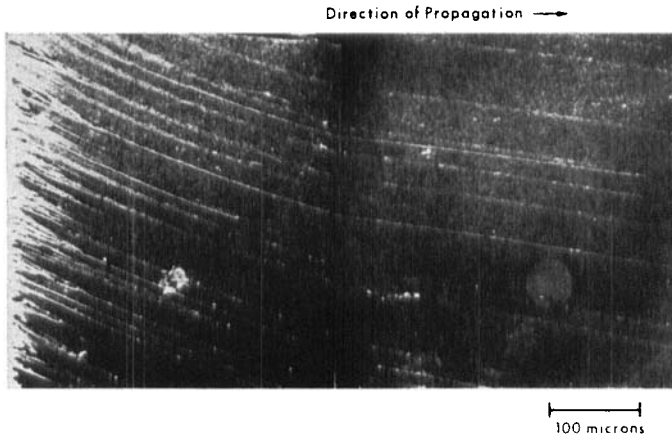
Direction of Propagation ⟶

100 microns

FIGURE 2   Fracture surface of unfilled epon 828 epoxy cured with 20 pph catalyst Z—Fractured at room temperature.

Velocity Transition

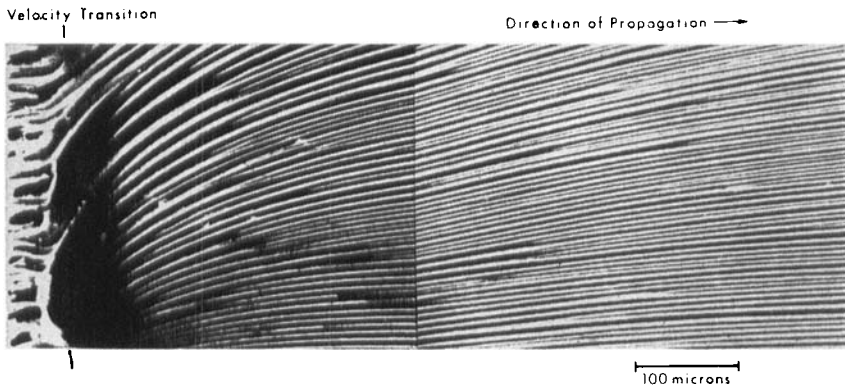Direction of Propagation ⟶

100 microns

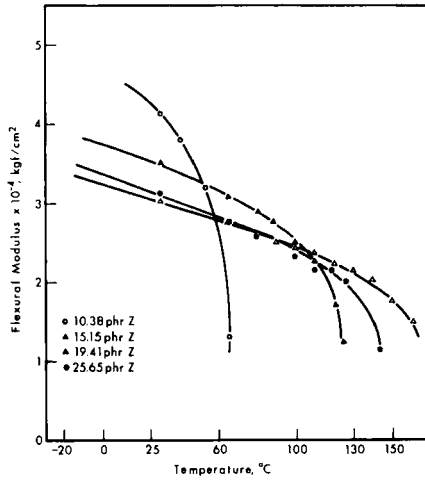FIGURE 3   Fracture surface of unfilled epon 828 epoxy cured with 20 PHR catalyst Z—Fractured at 100°C.

FIGURE 4   Effect of temperature and catalyst Z concentration on the flexural modulus of epon 828 epoxies.
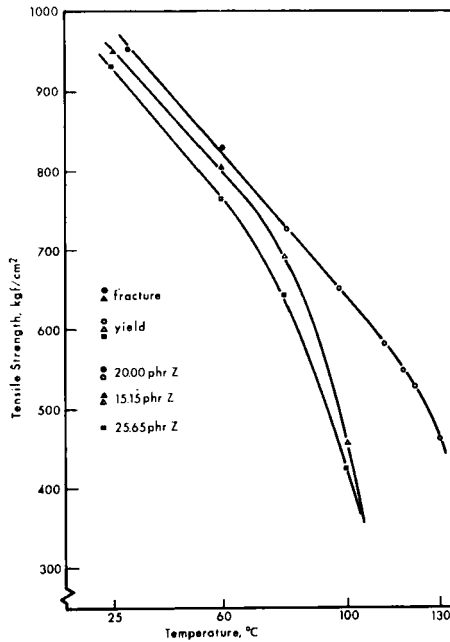
FIGURE 5   Effect of temperature and catalyst Z concentration on the tensile strength of unfilled epon 828 epoxies.
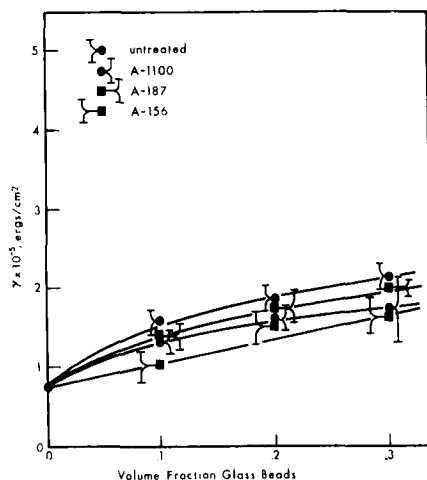
FIGURE 6   Effect of volume fraction glass beads and bead surface treatment on the gamma-fracture toughness of epoxy composites at 25°C.
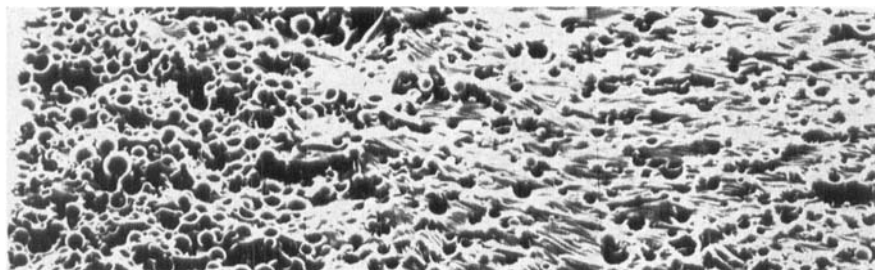

FIGURE 7   Fracture surface of 0.3 volume fraction A-1100 silane treated glass bead-epoxy composite—Fractured at room temperature.

amount of polymer surface per unit area of cross-section. This additional polymer on the surface required more energy dissipation per unit area, thereby increasing the fracture toughness. Only insignificant changes due to glass bead surface treatment were observed at room temperature.

At 100°C and 130°C (illustrated for 130°C in Figure 8), the fracture toughness of the composites containing the non-adhering (A-156 silane treated) beads was significantly greater than the fracture toughness of the other epoxy composites. A close examination of the fracture surfaces reveals that when there is no adhesion, the polymer tends to flow away from the filler interface leaving a large smooth crater within which the particle sits (Figure 9). On the other hand, when there is adhesion, the polymer tends to be constrained by the
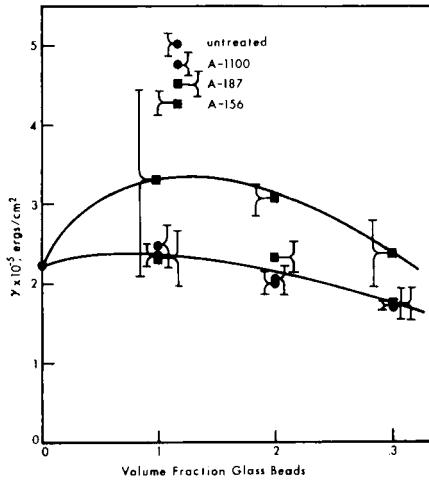
FIGURE 8   Effect of volume fraction glass beads and bead surface treatment on the gamma-fracture toughness of epoxy composites at 130°C.
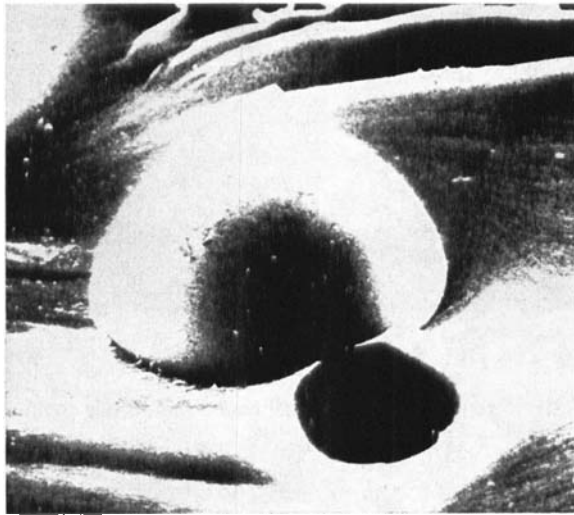

FIGURE 9   Fracture surface of A-156 silane treated glass-epoxy composite—Fractured at 100°C.

rigid filler surface and in a region of about 1/4 to 1/2 micron around the filler surface there is a tendency for cavitation of the polymer rather than gross yielding (Figure 10). The same situation exists in PPO-glass composites,[2] but to even a greater extent. The constraint on flow and the supplanting of the polymer by the addition of beads are probably the primary factors that cause the decrease of the fracture toughness for these composites. The tensile strengths and Young's moduli are illustrated in Figures 11 and 12. Below the glass transition temperature, Young's modulus was not affected by bead surface treatment. At these temperatures, the particulate glass filler is always in compression because of the greater thermal contraction of the polymer. Since the measurement of initial Young's modulus is conducted at relatively low deformation, there is not sufficient dilation to cause an interface separation. Thus, the degree of adhesion does not noticeably affect the initial modulus.
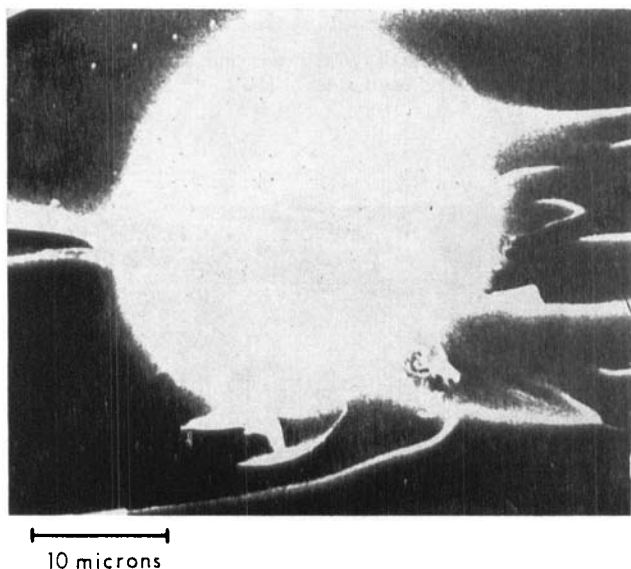

10 microns

FIGURE 10   Fracture surface of A-187 silane treated glass-epoxy composite—Fractured at 100°C.

The fracture toughness of the unfilled epoxy increased significantly upon short term immersion in distilled water at room temperature (Figure 13). Similar increases for untreated bead composites after 100 hours are shown in Table II. However, after 135–160 days in water, the fracture toughness of untreated and A-156 treated materials reverted to slightly lower values than the dry composites. The fracture toughness for composites containing A-1100
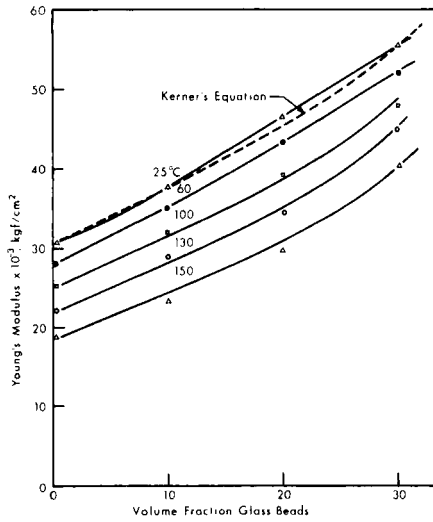
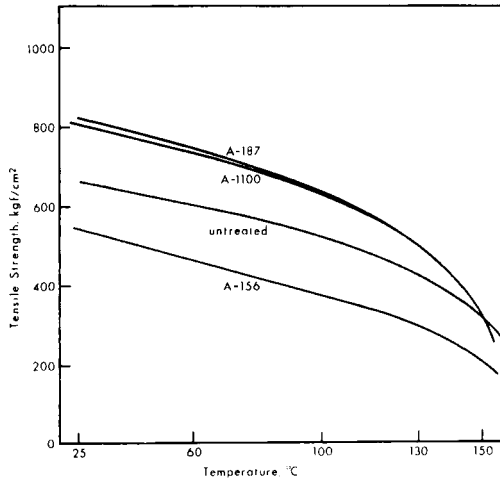FIGURE 11 Effect of volume fraction and temperature on the Young's modulus of glass bead-epoxy composites.

FIGURE 12 Effect of temperature and bead treatment on the tensile strength of glass bead-epoxy composites.

silane treated glass beads continued to increase for longer periods of time as shown in Table II but ultimately reached a fairly constant value. In all cases the water immersion caused decreases in tensile strength ranging from 20 to 50 percent of the dry strength.
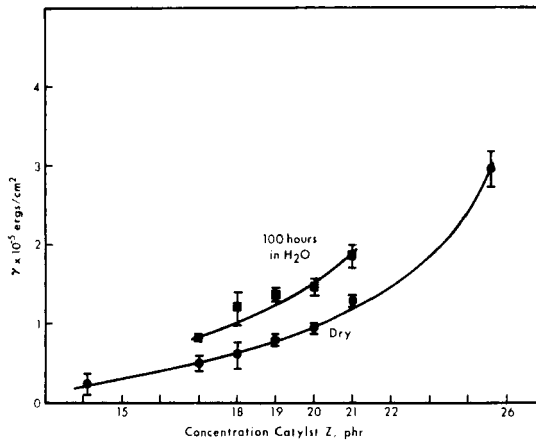
FIGURE 13   Effect of 100 hours of immersion in water on the gamma-fracture toughness for unfilled epon 828 expoxies at room temperature.

The amount of water absorbed per unit volume of polymer in the composites at 25°C is shown in Figure 14. For immersions of the order of 135–160 days, the amounts of water absorbed per unit volume of polymer was greater than for the unfilled polymer when there was no adhesion between polymer and filler (A-156) but was less than for the unfilled polymer when there was good adhesion (A-1100). This clearly suggests that water accumulated at the poorly
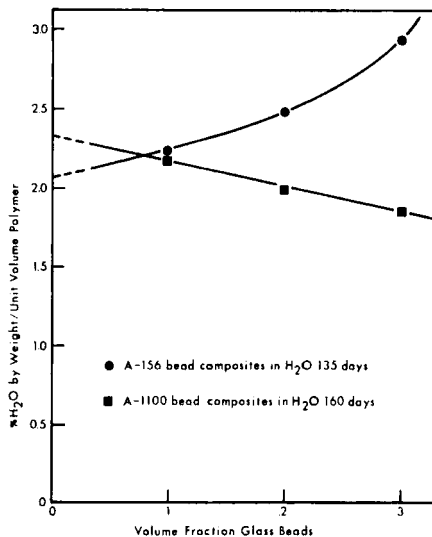
FIGURE 14   Water content per unit volume polymer as a function of volume fraction glass beads for glass-bead epoxy composites at 25°C.

TABLE II

Effect of water immersion of fracture toughness of epoxy systems

Polymer or composite	Time in water	% Water absorbed	% Water per unit volume polymer	% Change in γ
Epon 828 +				
18 phr Z	100 hours	0.37	0.37	+70
19 phr Z	100 hours	0.39	0.39	+67
20 phr Z	100 hours	0.39	0.39	+65
21 phr Z	100 hours	0.39	0.39	+62
22 phr Z	100 hours	0.38	0.38	+60
Epon 828 + 20 phr Z untreated beads				
$v_f = .10$	100 hours	0.42	0.46	+57
.20	100 hours	0.39	0.39	+75
.30	100 hours	0.34	0.49	+100
.30	160 days	2.23	3.18	−7
Epon 828 + 20 phr Z A-1100 treated beads				
$v_f = .10$	150 hours	0.37	0.41	+40
.20	150 hours	0.31	0.39	+40
.10	160 days	1.95	2.17	+67
.20	160 days	1.58	1.98	+62
.30	160 days	1.29	1.84	+53
Epon 828 + 20 phr Z A-156 treated beads				
$v_f = .10$	135 days	2.01	2.23	+45
.20	135 days	1.98	2.47	−17
.30	135 days	2.05	2.93	−50
Epon 815 + 20 phr Z	100 hours	0.45	0.45	+50

bonded interfaces causing a destruction of the interface and a decrease in the physical properties of the system. Good adhesion at the interface, however, caused a barrier to migration of water and in fact promoted a lowering of the solubility of water in the epoxy near the interface, thereby at least temporarily protecting the hydrophilic surfaces from damage. Figure 15 shows the water pickup at 40°C. At the higher temperature, the pickup per unit volume of polymer after 5 days was higher in the composites, indicating an accumulation
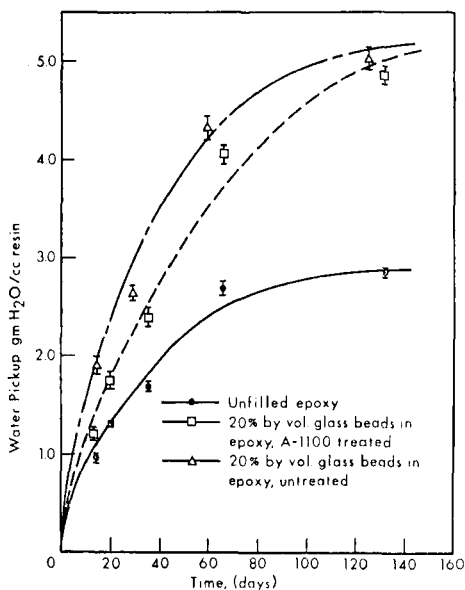
FIGURE 15   Water pickup per unit volume of epoxy during long term immersion at 40°C.

of water at the interface. After 120 days the treated and the untreated materials were indistinguishable.

The tentative explanation for the initial increase in toughness and continual decrease in strength is that the polymer phase is slightly plasticized during the initial stage of water sorption, thereby enhancing the ductility. Continued sorption, however, leads to a migration of the water to the hydrophilic glass surfaces thus causing a degradation of all physical properties. The development of good adhesion at the interface retards this latter phenomenon, thereby improving the environmental stability of the material. Ultimately, long term exposure leads to the same kind of degradation observed in the poorly adhering system.

In conclusion, it has been found that the addition of particulate filler to an epoxy resin does not markedly affect the fracture toughness of the materials. Relatively small increases or decreases can occur because of changes in filler concentration or degree of adhesion between phases. Long term exposure to moisture will result in a degradation of all properties including fracture toughness. One method of improving the resistance to brittle failure is to change the resin matrix by changing the amount or type of curing agent. The fracture energy is a function of the ability of the polymer phase to dissipate energy so that anything that increases the ductility of the basic resin should

also improve toughness. By analogy with polyphenylene oxide composites[3] it is expected that reinforcement with fibres should also cause a significant increase in the fracture toughness.

Acknowledgment

References

1. G. R. Irwin, "Fracture toughness testing of high-strength sheet materials under conditions appropriate for stress analysis". *Naval Research Laboratory Report No.* 5846 (1960).
2. A. Wambach, K. Trachte, and A. DiBenedetto, "Fracture Properties of Glass Filler polyphenylene oxide composites", *J. Composite Materials* **2,** No. 3, 266 (1968).
3. K. L. Trachte and A. T. DiBenedetto, "Fracture Properties of Polyphenylene Oxide Composites", *Intern. J. Polymeric Mater.* (accepted for publication 1971).