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The Mechanical Properties of an Epoxy Resin with a Second Phase Dispersion

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The mechanical strength of an anhydride-cured epoxy resin was studied by means of tensile tests as a function of particle size and volume fraction of an alumina trihydrate particulate-dispersed phase. These results and those of the microscopic examination imply that the poor strength of the system may be attributed to the intrinsically low strength of the dispersion. The tensile strength can be maximised by correct formulation on the basis of either particle size or volume fraction of the dispersed second phase. The modulus increases with increasing volume fraction, but is unaffected by particle-size variation at a constant volume fraction. The addition of a silane coupling agent increases the modulus of the composite, while having a negligible or adverse effect on the other properties.

1. Introduction

The use of a dispersed second phase in epoxy resin systems serves two main purposes; firstly, to reduce the cost of a component by incorporating a high percentage of low-cost material; and secondly to impart some desired property to the system.

Although many inorganic second phases are incorporated into epoxy resins, few data are available for alumina trihydrate dispersions. Alumina trihydrate ($Al_2O_3 . 3 H_2O$ or $Al(OH)_3$) has a monoclinic crystal structure with four molecules per unit cell, and exhibits perfect cleavage on $\{001\}$ planes. In the powder form, the particles have a platelike structure. No mechanical property data are available, but the reported hardness is between 2.5 and 3.5 on the Mohs scale. The physical and crystallographic properties are summarized by Newsome *et al* [1].

Alumina trihydrate is an important material commercially, and filled-epoxy resins are particularly useful in electrical applications (for example, high voltage bushings) owing to their improved arc and track resistance. However, their main disadvantage, inherent to most other particulate filled epoxies, is that although the modulus increases with volume fraction of dispersion, the tensile strength is reduced considerably [2]. In order to try to overcome this limitation, a research programme was initiated to study the mechanical properties of such a system and to ascertain whether the low tensile strength is due to poor bonding between the dispersion and the resin, or due to the inherent low strength of the dispersion.

In order to promote the bonding between a dispersed phase and the epoxy matrix, coupling agents are employed, often with substantial gains in strength [3-5]. The reported uses of coupling agents usually refer to silica dispersions, but similar enhancements in strength have been found with other inorganic dispersions [5]. The effect of a silane coupling agent was studied in this investigation.

This paper reports the tensile strength and elastic modulus data of an alumina trihydrate*-epoxy composite system with variation in (*a*) particle size at constant volume fraction, and (*b*) volume fraction at constant particle size. Fractographic evidence is also reported. The resin system was a liquid diglycidyl ether of bisphenol A† cured with hexahydrophthalic anhydride.‡ Dimethylaminomethyl phenol§ was used as accelerator. The silane coupling agent

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*Aluminium Company of America: α-alumina trihydrate.
†Union Carbide – ERL 2774.
‡Allied Chemical – HHPA.
§Rohm and Haas – DMP 10.

TABLE I Mechanical properties of the composite system

Particle size (μm)	Vol fract.	Modulus (psi × 10^5)		Poisson's ratio		Tensile strength (psi)	Plastic strain (%)	Fracture energy (in lb. in^{-2})	
		RT	77°K	*RT*	77°K			*RT*	77°K
Unfilled	0	5.51	15.02	0.25	0.39	11010 ± 11.6%	2.20	0.627	0.923
1	0.03	—	—	—	—	9300 % 2.5%	—	0.766	0.509
	0.10	—	—	—	—	8410 ± 5.9%	—	0.743	0.640
	0.215	—	—	—	—	6750 ± 7.1%	—	0.383	0.531
	0.295	10.00	22.04	0.18	0.34	4750 ± 15.1%	0.21	0.384	0.398
2	0.295	10.40	21.46	0.29	0.29	3660 ± 27.7%	0.11	0.428	0.474
5	0.295	10.77	17.69	0.27	0.32	4810 ± 8.1%	0.17	0.705	0.914
8	0.10	6.00	16.53	0.18	0.37	4320 ± 5.6%	0.70	1.038	1.193
	0.215	8.00	17.55	0.27	0.32	4870 ± 6.9%	0.25	1.176	0.976
	0.295	9.50	22.04	0.26	0.35	6520 ± 19.0%	0.22	1.008	0.850
(+ Silane)	0.295	—	—	—	—	6330 ± 14.3%	0.75	—	—
	0.43	12.99	23.35	0.23	0.31	5550 ± 15.2%	0.17	0.649	0.761
(+ Silane)	0.43	21.46	41.62	0.28	0.30	5390 ± 15.0%	2.80	0.377	0.537
12	0.10	—	—	—	—	3940 ± 9.2%	—	1.383	1.080
	0.215	—	—	—	—	6940 ± 7.2%	—	1.606	1.160
	0.295	9.50	22.04	0.27	0.34	5080 ± 16.3%	0.40	1.119	0.908
	0.43	—	—	—	—	5550 ± 13.3%	—	0.714	0.726
Quartz	0.295	10.50	23.06	0.19	0.33	7.140 ± 8.6%	0.47	0.782	0.952

Note 1 psi = 6.895×10^3 N.m^{-2} = 6.895×10^4 dyne. cm^{-2}
1 in lb. in^{-2} = 1.762×10^2 J. m^{-2} = 1.762×10^5 ergs. cm^{-2}

studied was beta 3, 4 (epoxy cyclohexyl) ethyl trimethoxy silane.||

Quartz-dispersed resins usually have high strengths, similar in value to unfilled material [2], and comparison of the alumina trihydrate results is made with those of a similar resin system with a quartz particulate dispersion.

2. Experimental

2.1. Specimen Preparation

Filled and unfilled batches of epoxy were made with the composition ratio ERL 2774:HHPA: DMP 10 = 100:80:0.18 and cast into tensile specimens using a mould conforming to ASTM standard D638, type I, with gauge length dimensions 5 cm long by 1.3 cm wide. In order to study the effect of particle size on the properties of the epoxy, batches were prepared using alumina trihydrate with average particle sizes of 1, 2, 5, 8 and 12 μm at a constant volume fraction of 29.5 vol %. The effect of volume fraction of dispersion was studied by testing the following additional compositions: with 8 μm and 12 μm powder, batches with 10, 21.5 and 43 vol % were prepared. Using 1 μm powder, specimens with 3, 10 and 21.5 vol % were made; loadings higher than 29.5 vol % were not possible owing to the viscosity of the uncured system. Each of these filled resins was mixed at 100°C for several hours and de-aired in a heated vacuum-desiccator at 100°C before casting. Castings were cured overnight at 100°C and post-cured for 6 h at 135°C.

The effect of adding a silane coupling agent to the composite was investigated, using specimens with 43 and 29.5 vol % of 8 μm powder. The amount of silane added was 2.5 parts per hundred parts of resin.

For comparison with the alumina trihydrate-filled epoxy, specimens containing 29.5 vol % of a dried and reground quartz particulate dispersion (average particle size 6.3 μm) were also prepared.

In this research, the densities of the resin and the alumina trihydrate were taken as 1.17 and 2.47 g.cm^{-1}, respectively. The density of the quartz was taken as 2.65 g.cm^{-1}.

2.2. Measurements

Tensile tests were made on all compositions at room temperature and 77°K (liquid nitrogen

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||Union Carbide – A186.

temperature). Young's modulus and Poisson's ratio were also measured, and the fracture surfaces were examined both optically and with the scanning electron microscope. The effect of the silane coupling agent on the mechanical properties and the rate of water adsorption was studied.

Also in this research, fracture energies and fracture toughness data were obtained for all composites using a double-beam cantilever technique. The results of these investigations are reported elsewhere [2]. Table I summarises all of the mechanical properties.

3. Results

Figs. 1 and 2 show the effect of the dispersion on the modulus of the composite. At constant particle size (fig. 1) the modulus increased with volume fraction (V) and above about 5% filler the relative modulus (E filled/E_0 unfilled) could be expressed by the following equations:

$$\frac{E}{E_0} = 0.925\,(1 - V)^{-5/3} \text{ at room temperature,}$$

$$\frac{E}{E_0} = 0.955\,(1 - V)^{-1} \text{ at } 77^\circ\text{K}$$

Addition of the silane coupling agent increased the modulus by a factor of 1.5 to 2 at both temperatures. At constant volume fraction (fig. 2) the modulus did not vary with particle size. However, all the values were higher than for the unfilled resin.

Poisson's ratio varied between 0.18 and 0.28 at room temperature and between 0.29 and 0.39 at 77°K.

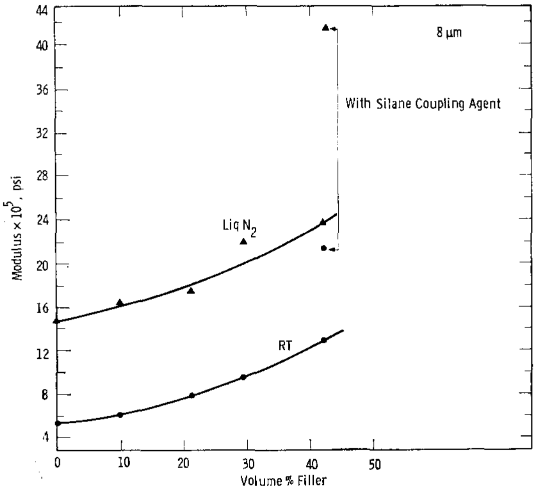

Figure 1 Variation of tensile modulus with volume fraction at constant particle size.

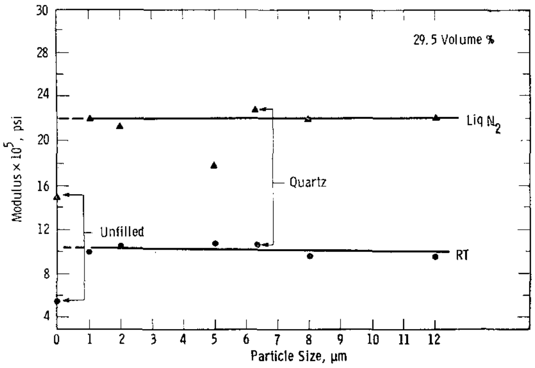

Figure 2 Variation of tensile modulus with particle size at constant volume fraction.

Addition of the second phase to the resin produced large variations in the tensile strengths, as seen in figs. 3 and 4. Fig. 3 shows that for the 8 and 12 μm particles, a maximum occurred at a critical volume fraction of dispersion; for the 1 μm particles, the strength progressively decreased with increasing volume fraction. All composites, however, exhibited lower strengths than the unfilled resin. At constant volume fraction, the strength varied according to the dispersed particle size (fig. 4). The effect of the silane coupling agent was negligible.

The plastic strain prior to fracture decreased with increasing volume fraction of dispersion and a slight increase was found with increasing particle size at constant volume fraction. Both

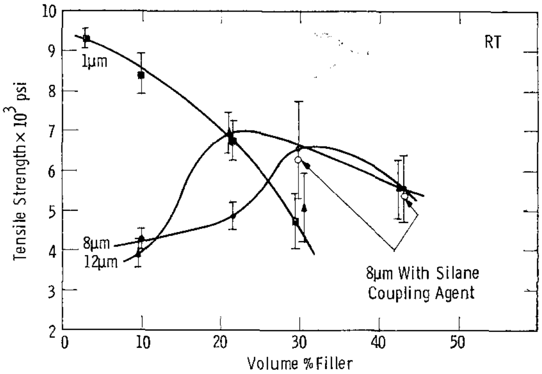

Figure 3 The relation between the room temperature tensile strength and volume fraction at constant particle size.

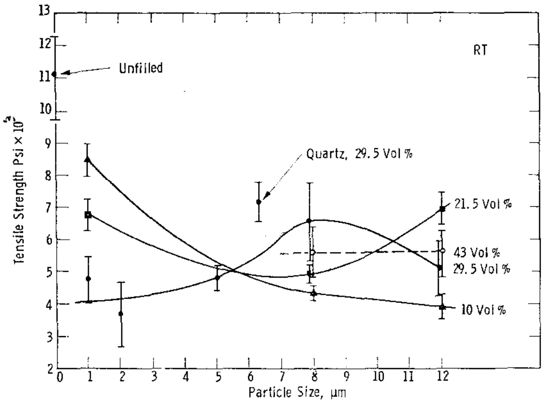

Figure 4 The relation between the room temperature tensile strength and particle size at constant volume fraction.

the unfilled specimens and those with the silane coupling agent exhibited much higher strains prior to fracture.

As shown in fig. 5, the water adsorption was very small (about 0.5% after 100 h); however, the adsorption with the silane coupling agent added was more serious, being above 0.5% in 30 h.

Examination of the surface topography of fractured specimens revealed two distinct types of fracture. With large volume fractions, i.e. for volume fractions giving maximum tensile strength and higher, the fracture surfaces appeared similar to those found in polycrystalline materials. The surfaces were rough and irregular and the particles and the matrix were almost indistinguishable (fig. 6). For smaller volume fractions, i.e. approaching the maximum tensile strength, the dispersed particles were clearly visible, and characteristic surface steps were associated with each particle (fig. 7). For compositions close to the maximum in tensile strength, a combination of both types of fracture patterns was observed, but the particles were more closely spaced and the steps intersected neighbouring particles.

When macroscopic flaws were present, the fracture pattern showed a mirror-like ring around the flaw with a rough area around the

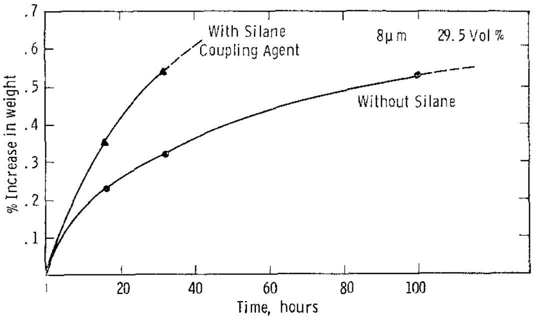

Figure 5 The percentage increase in weight of tensile samples with time of boiling in water.

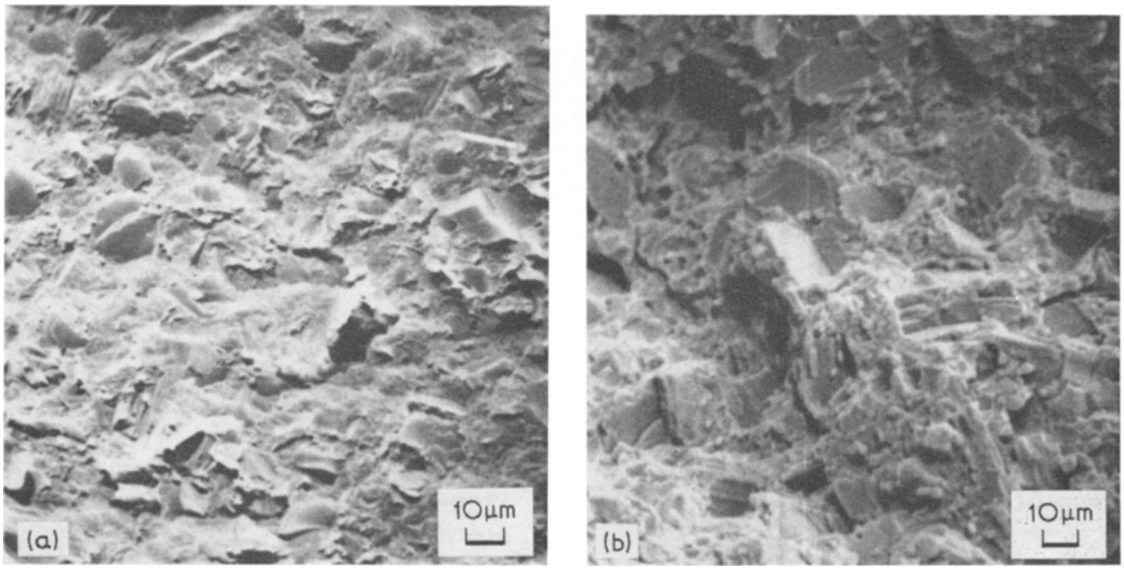

Figure 6 Scanning electron micrographs of fracture surfaces of alumina trihydrate filled specimens tested at room temperature. (a) 8 μm, 0.43 volume fraction. (b) 8 μm, 0.295 volume fraction + silane coupling agent.

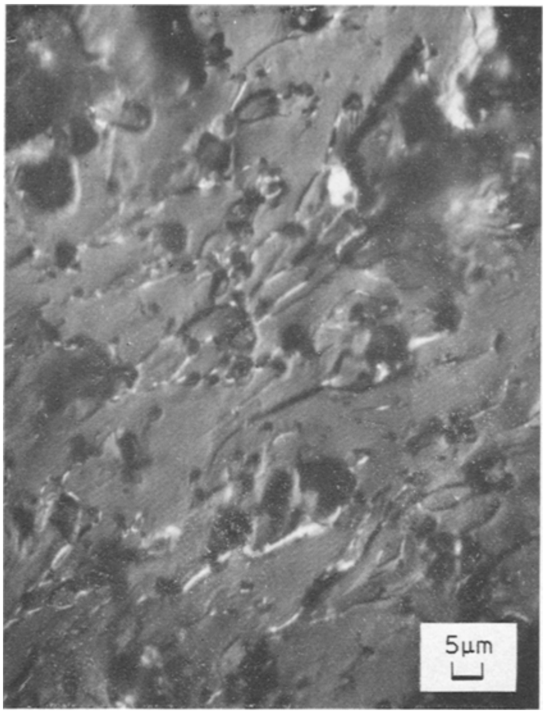

Figure 7 Optical micrograph of 12 μm, 0.10 volume fraction specimen fractured at room temperature, showing characteristic surface steps associated with each filler particle.

ring. Fig. 8 shows two such fracture patterns with fracture initiating at air bubbles trapped during specimen manufacture.

4. Discussion

The increase in modulus with the addition of a high-modulus dispersion to a low-modulus matrix is expected, and agrees with both experimental observations and theoretical analyses reported in the literature [2, 7]. Similarly, the decrease in tensile strength of the epoxy resin when a second phase is added agrees with the reported results of other composite epoxy systems [1].

The tensile properties indicate that a relationship exists between strength, particle size, and volume fraction of the dispersed phase. Fracture energy measurements made by Lange and Radford [6] showed that maxima occurred at a particular particle size and volume fraction of the dispersed phase (the data are listed in table I). Since the tensile strength is related to the fracture energy $\gamma(\sigma \propto \sqrt{(\gamma E)/c}$, where E is the tensile modulus, c the intrinsic crack size), it is reasonable to expect a maximum also to exist in the tensile strength as a function of volume fraction.

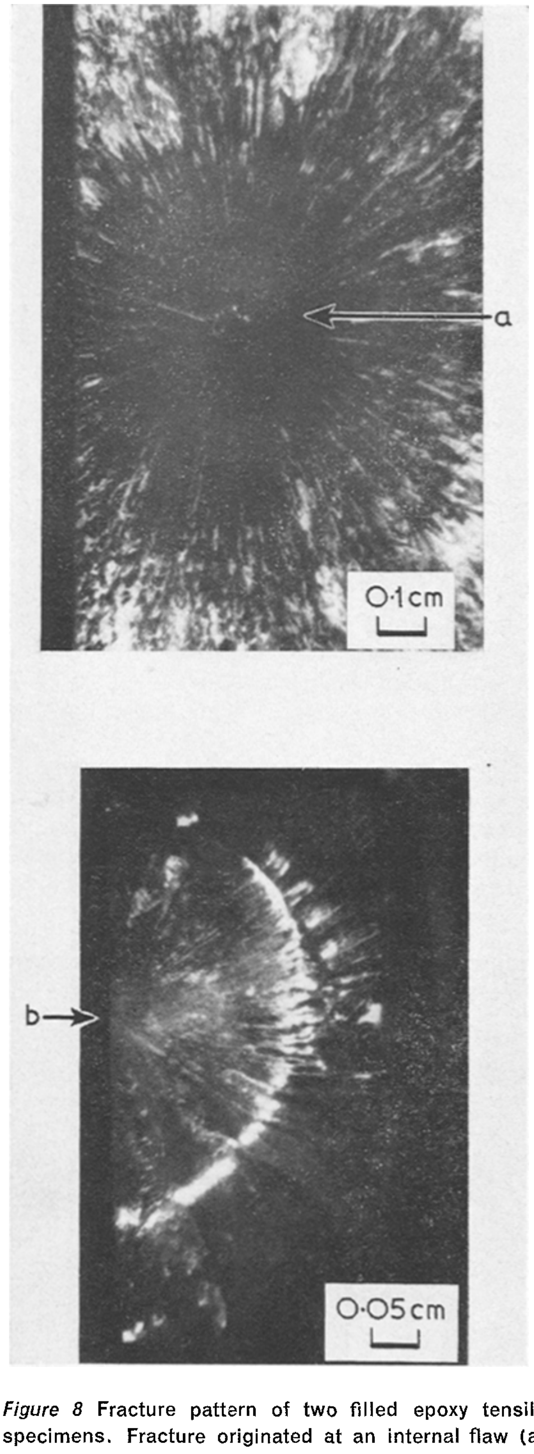

Figure 8 Fracture pattern of two filled epoxy tensile specimens. Fracture originated at an internal flaw (a) and at a surface flaw (b).

The fractographic evidence shows several features. The alumina trihydrate-filled specimens and those with silane coupling agent added exhibit similar fracture surfaces. The particles are evident by their flat cleavage type surfaces, separated by the rough epoxy matrix. Since alumina trihydrate has a plate-like structure in the crystalline form, and also exhibits perfect cleavage on (001) planes, it is uncertain whether cleavage or fracture at the alumina trihydrate-epoxy interface occurred. The silane coupling agent, however, increased the modulus significantly (which implies that a strong interfacial bond was formed), but it did not increase the tensile strength. It appears likely, therefore, that interfacial fracture is not the cause of the poor composite strength.

The quartz-dispersed specimens exhibited fracture energies comparable to those of the alumina trihydrate composites, and the fracture path appeared to propagate within the resin (fig. 9). Since the tensile modulus of the quartz-dispersed specimens is of a similar magnitude to that of the alumina trihydrate specimens, it appears that the greater tensile strengths of the former composites are due to the higher strength of the dispersed phase. The inference from all these observations is that alumina trihydrate particles are inherently weak, and are the primary cause of the low tensile strength values.

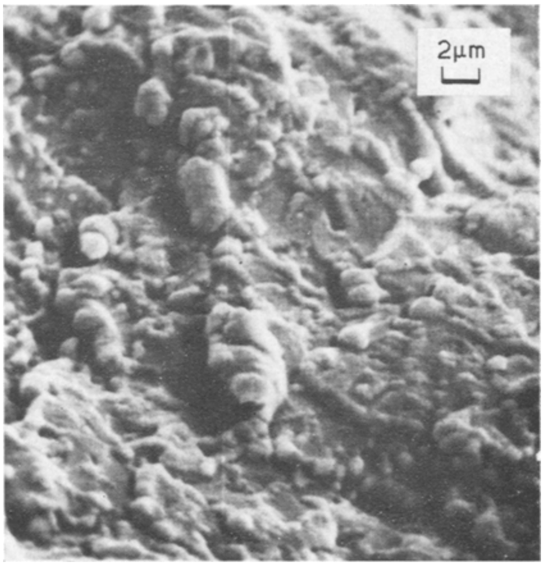

Figure 9 Scanning electron micrograph of a quartz filled specimen fractured at 77° K.

5. Conclusions

(1) The poor tensile strengths exhibited by this composite system can be attributed to the low intrinsic strength of the alumina trihydrate dispersion. Maximum strength can be attained by formulating compositions on the basis of either constant particle size or constant volume fraction of second phase.

(2) The elastic modulus for the 8 μm powder increases with increasing volume fraction V of dispersion. At room temperature the relative modulus can be described by the equation:

$$\frac{E}{E_0} = 0.925\,(1 - V)^{-5/3}\,,$$

and at liquid nitrogen temperature by

$$\frac{E}{E_0} = 0.955\,(1 - V)^{-1}$$

where E_0 is the modulus of the unfilled system.

Both equations are valid for concentrations of second phase above 5 vol %. The modulus is unaffected by particle size variation at constant volume fraction.

(3) The addition of a silane coupling agent does not affect any property significantly apart from the modulus and the plastic strain, which are increased dramatically. Water adsorption is also increased with the silane additive.

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