Scanning electron microscopy of epoxy–glass laminates exposed to humid conditions

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Glass–epoxy laminates were exposed to high relative humidities at temperatures up to 80° C for long periods. The degradation processes (notably fibre–resin debonding, cavitation, and crack formation) were observed by scanning electron microscopy. Cracks were eventually induced, especially at high temperatures (a) near the surfaces, (b) between plies, (c) within plies. The second and third classes of crack were generally found to initiate from regions of cavitation. It is proposed that the cavities were formed by dissolution of embedded particulate residues. Evidence is presented that these residues consisted of unreacted dicyandiamide curing agent. Microscopic observations suggested that the breakdown of fibre–resin adhesion was substantially reversible. Large decreases in shear strength were found on hygrothermal ageing, but reversed completely by slow, careful drying. Small decreases in flexural modulus were also reversed, but the flexural strength was decreased permanently, presumably because of defect formation.

1. Introduction

In recent years, there have been many investigations of the degradation of fibre–resin composites under hygrothermal conditions. Attention has been focused on quantitative aspects such as the extent of change in mechanical properties [1–3], the extent of lowering of the matrix T_g [4, 5] and the kinetics of moisture absorption [6–8].

This paper now provides electron microscope evidence concerning some of the most important degradation processes responsible for the observed changes in laminate mechanical properties. Attention is directed chiefly to (1) interface breakdown and recovery, (2) cavity formation, and (3) internal cracking. Some of the features described are probably specific to the unidirectional glass-epoxy material and processing procedure used, but others are of general applicability to fibrous composites.

## 2. Experimental details

2.1. Materials

The resin matrix was a mixture of a difunctional bisphenol A epoxy resin with tetraglycidyl 4, 4′ diaminodiphenyl methane. There was also a small quantity of a thermoplastic additive, and the curing agent was dicyandiamide, used in conjunction with a tertiary amine accelerator.

The laminates were made from prepreg. Plies were stacked to make 2 and 5 mm sheets, and cured in an autoclave under contact pressure for 2 h at 90° C and 1 h at 120° C. A glass bleed cloth was used, which transferred an impression to the laminate surfaces. These laminates were C-scanned to check void content, and glass content was determined gravimetrically to be 72 to 76% wt/wt.

2.2. Hygrothermal exposure

Parallel-sided strips were cut by means of a diamond wheel to three sizes: 100 mm × 13 mm × 5 mm, 90 mm × 25 mm × 2 mm, and 10 mm × 12 mm × 2 mm. The strips were dried over silica gel, weighed, and placed on stainless steel racks in glass containers within commercial humidity chambers at 80, 45 and 24° C. The relative humidity was measured by wet and dry bulb hygrometers and found to be more than 95%.
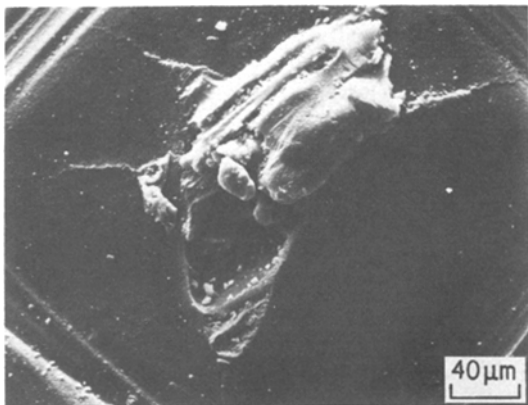
Figure 1 Surface cavity in one of the depressions caused by the bleed cloth. Note the exposed fibre and the loose resin fragments. (Control specimen, × 158.)

After hygrothermal exposure, the specimens were either examined by scanning electron microscopy while still wet, or dried very slowly by first storing at 45° C for two weeks over silica gel, and then storing over phosphorous pentoxide at 45°C until constant weight was achieved after about a year. Extensive experience in this and other laboratories has suggested that wet crosslinked epoxy resins do not undergo microcracking if dried at temperatures below 50° C.

2.3. Scanning electron microscopy
The instrument was a Cambridge 600 Model. Specimens were coated with gold using a Polaron E500 coating unit. Three kinds of surface were examined:

1. the major, outer sufaces of the specimens;
2. inter-laminar cross-sections, obtained by slowly breaking 10 mm × 12 mm × 2 mm strips in three-point bending, and gently pulling the layers apart;
3. trans-fibre cross-sections, obtained by cutting across the width of the strips and polishing with diamond polishing paste.

3. Results and discussion
3.1. Effects of coating and SEM examination
Many defects were observed in the hydrothermally exposed samples, although absent from the controls. The question arises whether specimen heating during coating and SEM examination could contribute to the formation of microcracks by inducing rapid water loss. It has been shown recently that subjection to a small number of brief thermal

spikes does not induce damage in wet epoxy–carbon samples [9] and in our case, the heating was confined to the surface regions. The kinetics of moisture loss from crosslinked polymers is such that long periods would be required to dry the interior, even under vacuum. In any case, the evidence for one feature, i.e. gross cracking, is not confined to a study of SEM specimens, since in the most severe cases, the naked eye is sufficient. Therefore, it seems probable that the defects observed were induced by hygrothermal exposure.

3.2. Surface appearance of the controls
The bleed cloth imparted an appearance reminiscent of that of woven roving laminates. Close examination showed that there were numerous surface scratches within the many depressions caused by the bleed cloth. There were also deeper scratches revealing exposed fibres. The deeper ones were often associated with resin fragments, which had become almost completely detached. Fig. 1. shows a detail of the bleed cloth impression, with a broken surface region, loose resin fragments, and an underlying fibre.

3.3. Surface deterioration
Water accumulated in the surface depressions caused by the bleed cloth, and entered surface scratches, causing detachment of loosely bound resin fragments, exposing fibres. Two surface features, namely (1) the weft and warp markings from the bleed cloth, and (2) the depressions in the rectangles caused by the fabric pattern on the surface, acted as crack initiators. Cracks such as those shown in Fig. 2 propagated from a part of
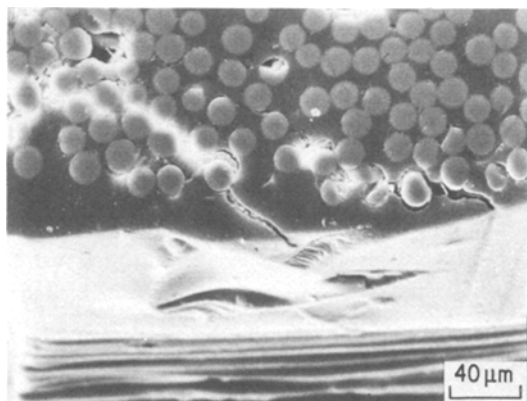
Figure 2 Cracks in hygrothermally exposed sample, originating from surface marks introduced by the bleed cloth. The cracks start at (1) the weft or warp marking of the cloth, (2) the depressions in the surface. × 310

the surface well covered with resin. They could accelerate water absorption.

3.4. Cavitation

A previous, brief communication [10] described the SEM examination of samples which had not been gold-coated. Particles of an additive were found in the samples, and they could be washed out by exposure to 80° C/95% RH for about 2 h, leaving cavities of the same characteristic shapes as the additive particles. The original particles were beam-sensitive and were found in many parts of the matrix phase, especially the regions between plies. The decision not to coat the specimens was to facilitate washing out. The nature and origin of the particles can be explained as follows. The curing agent, dicyandiamide, does not completely mix with the matrix resin phase at the autoclave dwell temperature of 90° C. Tiny, phase-separated particles would therefore soon become surrounded by an impenetrable skin of crosslinked resin, preventing further reaction. Dicyandiamide is readily soluble in hot water, but not very soluble in the cold, so exposure to 80° C/95% RH would be expected to produce much more rapid and extensive cavitation than exposure at 45° C or ambient temperatures. Dicyandiamide also undergoes chemical reaction with water at 80° C, slowly forming ammonia, and other products. The presence of ammonia was confirmed with Nessler's reagent, and its characteristic smell was evident in some of the containers holding the soaked laminates. White deposits appeared on the surface of all specimens exposed at 80° C after a long time. These deposits were carefully collected, and their mass spectrum and infra-red spectrum obtained. Both spectra were consistent with the deposits being dicyandiamide.

Assuming that the dispersed particles were chemically the same as the white deposits on the surface (and no other water-soluble substance could be envisaged from a knowledge of the matrix phase) then they would be expected to dissolve readily at 80° C and the cavities formed would therefore contain an aqueous solution of dicyandiamide together with several of its hydrolysis products, including ammonium hydroxide. An osmotic cell would be set up [11, 12] with the matrix as semi-permeable membrane between cavities containing solutions of different concentrations. Osmotic pressure can rupture resins [13] and it semms probable that some of the inter-ply and
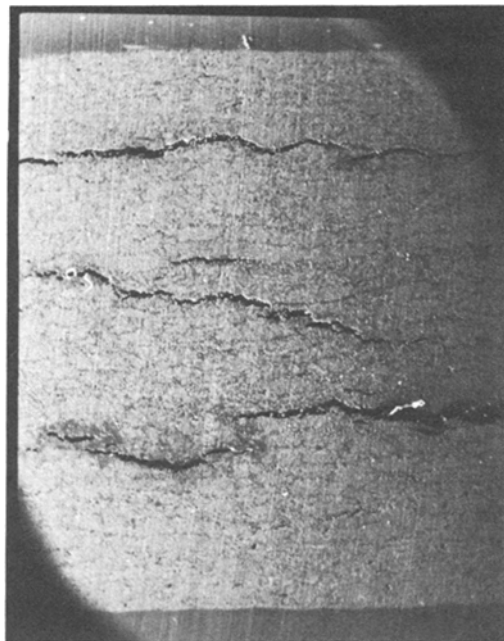

Figure 3 Gross interlaminar cracking (delamination cracking) after several months at 80° C. The whole specimen thickness of 2 mm can be seen. × 38

intra-ply cracks initiated from the edges of cavities containing aqueous solutions. These cracks are discussed below.

3.5. Cracks associated with cavitation

Cavities were formed extremely slowly at 24° C, more quickly at 45° C, and rapidly at 80° C. They were most plentiful in the inter-ply regions. Cracks eventually appeared in these regions, running parallel to the major surfaces along ply boundaries. Fig. 3 shows a low magnification micrograph covering the entire 2 mm thickness of a laminate strip. The cracks in this sample could be observed with difficulty without a microscope, and were formed only after prolonged exposure for several months at 80° C/95% RH. Their widths often exceeded 50 μm. Close examination showed that these delamination cracks were associated with severe cavitation.

Much finer cracks propagated from regions of moderate cavitation within a single ply. An example of an intra-ply crack is shown in Fig. 4a and a typical cavitation region in Fig. 4b. Such cracks propagated around the contours of the fibre–resin interface, with some jumps across resin-rich regions.
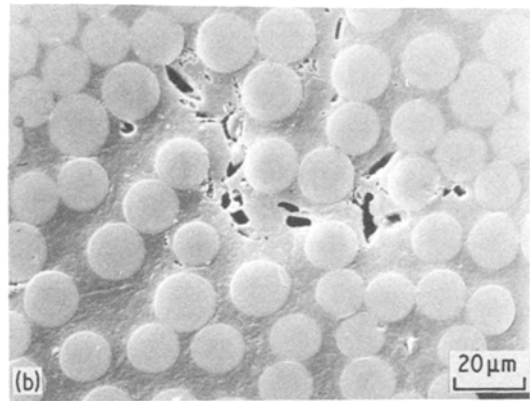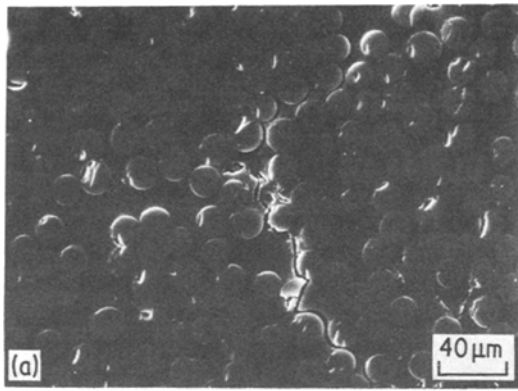
Figure 4 (a) Intra-ply crack originating from a cavity, × 340; (b) Intra-ply cavitation, × 620.

3.6. Fibre—resin debonding

There was a sharp contrast between the appearance of inter-laminar sections from control samples (Fig. 5), in which adhesion was good, with nearly all the fibres showing resin fragments attached to them, and that of analogous sections from samples which had experienced prolonged hygrothermal exposure, as in Fig. 6. The latter sections showed substantially clean fibre surfaces, with only a few resin fragments attached to the fibres. Debonding would be expected to result in a lower short-beam shear strength for the composites. The shear strength was therefore measured by ASTM-D-2344. The decrease in shear strength was large, i.e. about 50% after 2.5% water absorption at 80° C, and about 60% after 4.0% water absorption which took 21 days.

Exposure at 45° C did not produce such high water absorption, but at 20% uptake, the shear strength had fallen by about 25%. This took 150 days using small shear specimens measuring 10 mm × 12 mm × 2 mm.

Figs. 5 and 6 are photomicrographs of sections prepared by carrying out three-point bend tests, as described in Section 2.3. They demonstrate that hygrothermal exposure weakened the fibre—resin interface. There was also another indication. White lines began to appear and develop progressively on specimen surfaces during the exposure period, always parallel with the fibres. Sections through the affected areas revealed interfacial damage.

Figs. 7 and 8 show two adjacent areas of a trans-fibre section through a specimen exposed at 45° C for 90 days. The feature marked "C" is common to both figures. The inter-ply boundary region shown as "A" in Fig. 7 was unaffected by hygrothermal ageing. This region was also free of delamination cracks of the kind observed in more severely exposed cases. The debonding crack at B travelled through one of the fibres instead of
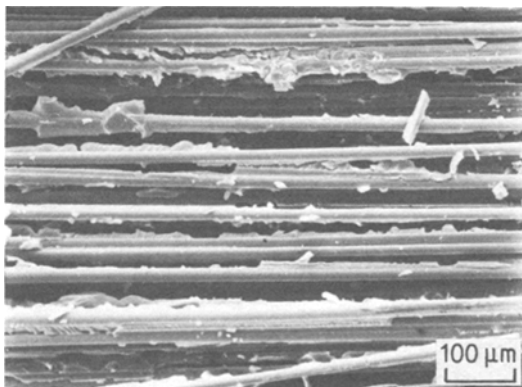

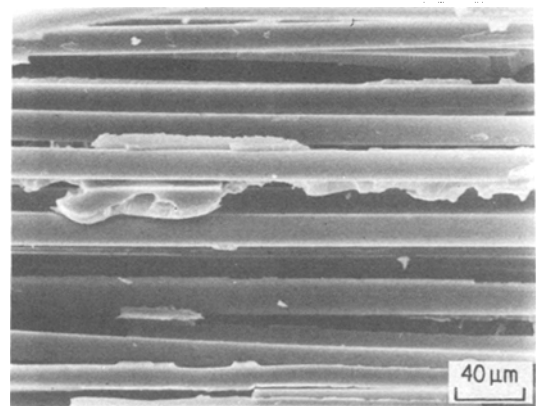*Figure 5* Inter-laminar section, showing good adhesion between fibres and resin. (Control specimen, × 122.)

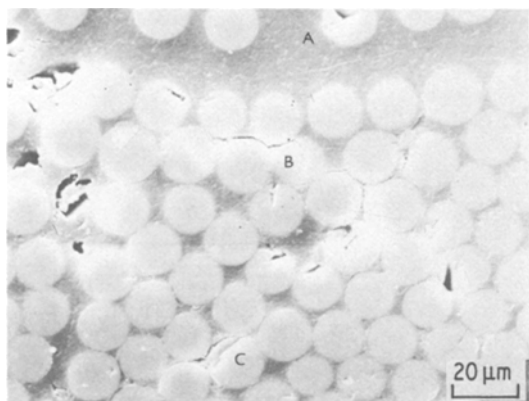*Figure 6* Interfacial weakening in a 2 mm thick specimen exposed in a humidity chamber at 80° C for 30 days. × 291

Figure 7 Interfacial breakdown in a specimen exposed at 45°C for 90 days. Fig. 8 shows an adjacent region. The letters are explained in the text. × 589

around it, and could be seen to connect with the debonding crack on the other side of the fibre cross-section circumference. This is quite different, and easily distinguished from, the scratch marks at C and F, believed to be caused during sample preparation.

Examples of interfacial weakening were apparent at fibre-rich zones B, C and D, and also at resin-rich zones such as E. After long periods of exposure, when water uptake had reached about 1.4% wt/wt the debonding cracks propagated around the circumferences of several fibres, to travel considerable distances (Fig. 9).

3.7. Recovery on drying

Specimens 10 mm × 12 mm × 2 mm were hygro-thermally exposed at 80°C/95% RH until they had increased in weight by 2.5%. They were then thoroughly re-dried as described in Section 2.2.
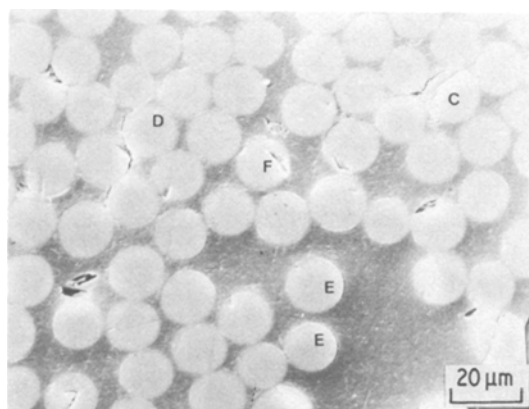

Figure 8 Interfacial breakdown in a specimen exposed at 45°C for 90 days. Fig. 7 shows an adjacent region. The letters are explained in the text. × 589

TABLE I Recovery of the short-term shear strength on drying

Exposure temp. (°C)	Exposure time (days)	% weight gain	% recovery of original strength on drying
45	37	0.8	110.3 (4.2)*
45	93	1.5	110.9 (2.3)
45	150	2.0	112.7 (4.1)
80	1	1.0	116.0 (2.5)
80	2	1.5	111.6 (5.1)

*Standard deviations.

Interlaminar sections of the dried specimens showed resin adhering to the fibres almost as extensively as in the control specimens (compare Fig. 10, a re-dried sample, with Fig. 5, control, and Fig. 6 a wet sample). Similar results were found after drying specimens previously exposed to 45°C/95% RH for 90 days. Interfacial recovery was also reflected in the trans-fibre sections, even in regions close to permanent damage features such as cavities.

Further evidence for an improvement in fibre–resin adhesion is provided by measurements of the short-beam shear strength after drying. Table I shows complete recovery of the original shear strength.

Changes in flexural strength and modulus in three-point bending were also observed, using ASTM-D-790. Fig. 11 shows the decline in these properties consequent upon hygrothermal exposure at 80°C/95% RH. Flexural modulus levelled off at slightly more than 85% retention while flexural strength fell below 60% of its original value when the material had absorbed 3.0% water.

On drying, the recovery in flexural modulus was almost complete (Table II). This is consistent with the theory that the lowering of modulus is mainly a reversible effect related to matrix plasticization and debonding. Flexural strength was not completely restored on drying, as it is affected by the introduction of cracks and cavities.

TABLE II Recovery of flexural strength and modulus on drying

Exposure time at 80°C (days)	% weight gain*	% retention of flexural	
		strength	modulus
10	0.8	93.5 (5.5)†	99.0 (1.0)†
20	1.9	91.0 (3.6)	97.3 (2.5)
45	2.4	81.3 (5.0)	94.0 (2.5)

*The weight gains differ from those given in Table I because of specimen geometry.
†Standard deviations.
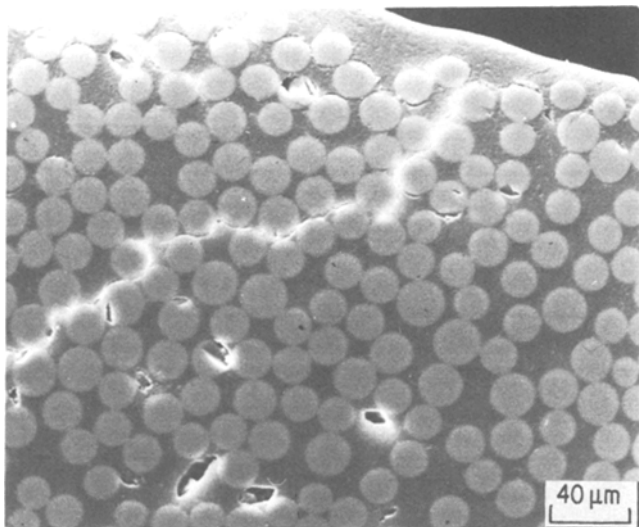
Figure 9 Debonding crack in a specimen exposed at 45°C until a 1.4% weight increase had occurred. A second crack, nearly parallel to the edge, can also be seen. × 408

4. Conclusions

1. Extensive debonding was induced in the glass-epoxy laminates by exposure to hot, wet atmospheres. According to SEM evidence, fibre—resin adhesion was apparently substantially restored on slow, careful drying to constant weight, and the shear strength also recovered. Flexural modulus was only slightly (and reversibly) lowered, but flexural strength underwent a permanent reduction.

2. Permanent damage was also induced. Many regions of the matrix phase became subject to cavitation. It is suggested that the cavities arose by removal of unreacted, water-soluble curing agent (dicyandiamide). Cavitation was much more noticeable at high exposure temperatures (80° C/95% RH) than at ambient temperatures.

Figure 10 Inter-laminar section showing good interfacial recovery on drying, after exposing at 80° C until a weight increase of 2.5% was reached. × 372

3. Cavitation zones were mainly in the inter-ply, resin-rich regions, where they became associated with relatively large delamination cracks. Less severe cavitation, within plies, led to the formation of finer cracks, which travelled considerable distances, but with no preferred direction.

4. The identity of the unreacted dicyandiamide was confirmed by chemical means. Dicyandiamide underwent hydrolysis to give ammonia, which would be expected to accelerate the degradation of the glass reinforcement by increasing the pH of the solutions contacting the fibres.

5. Minor blemishes were apparent on the laminate surfaces. They were apparently caused by the bleed cloth during fabrication, and led to the propagation inwards, from the surface, of cracks which could accelerate water ingress.

6. The hygrothermal stability of the material could be much improved by: (a) reducing or eliminating the phase-separated dicyandiamide; (b) avoiding the bleed cloth impression; (c) reducing the width of the inter-ply boundaries. It should be stressed that the damage features mentioned were induced by severe test conditions. They were caused by exposure for extensive periods at 80° C and 95% RH. Subjection to less severe conditions resulted in very much slower deterioration.
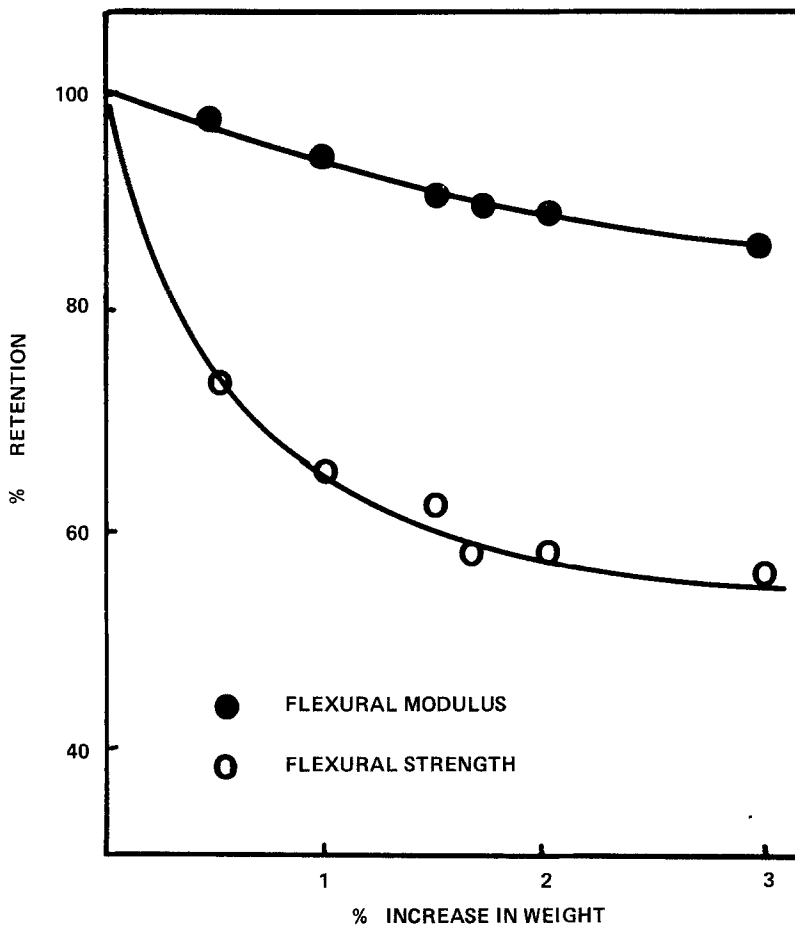
Acknowledgements

Figure 11 Effect of hygrothermal exposure at 80° C/ 95% RH on the flexural strength and modulus in three-point loading.

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