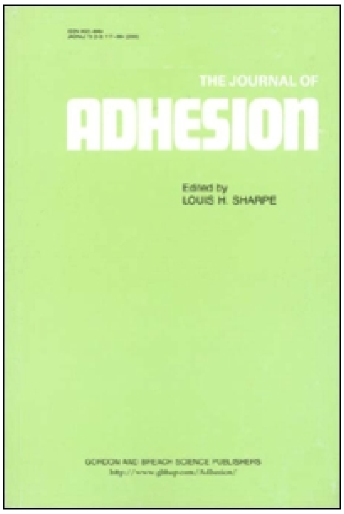

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The Effect of High Humidity on the Dynamic Mechanical Properties and Thermal Transitions of an Epoxy-polyamide Adhesive

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Exposure of a cured epoxy–polyamide adhesive to high humidity resulted in a substantial decrease in the complex dynamic tensile modulus of the material. The effect could be reversed and the original modulus essentially regained by drying the adhesive. Thermal transitions in the dry adhesive were displaced by approximately 40°C to lower temperatures in the wet material; this effect could be reversed by drying.

Strength losses experienced by aluminium joints bonded with this adhesive on exposure to humid conditions could not be regained by removal of water from the joints. The mode of failure of these joints changed progressively from wholly cohesive to predominantly adhesive on exposure to high humidity.

It is concluded that the primary role of water in joint degradation is to displace adhesive from its metal substrate and not to induce cohesive failure of the adhesive.

INTRODUCTION

Numerous reports[1-8] exist describing the performance of adhesive bonded aluminium exposed to natural environments. They confirm that a tropical (hot–humid) climate is more damaging to metal-to-metal joints than either a hot-desert or temperate environment and emphasise the importance of surface preparation on joint durability. Additionally, they reveal the particularly adverse effect that high humidity has on clad aluminium bonded to epoxy–nylon adhesives.

The present work, which is part of a programme designed to improve the durability of adhesive bonded structures exposed to adverse environments, was undertaken to throw some light on the processes involved in the degradation of bonded joints under laboratory controlled conditions by examining the effects of high humidity on the mechanical properties and thermal transitions of cured films of a moisture sensitive epoxy–polyamide adhesive and to attempt to relate these effects to the performance of the adhesive in a metal-to-metal bonded joint. In addition, a brief account is given of the effects o certain metal pretreatments on the strength retention properties of bonded aluminium joints.

EXPERIMENTAL

Materials

An epoxy–polyamide unsupported film adhesive (FM1000), supplied by American Cyanamid, was used to fabricate bonded aluminium test coupons. The adhesive was cured at 175°C.

Clad aluminium panels of BS2L73 alloy (2.03 mm thick) were used to provide standard single overlap test specimens (218.4 mm long, 25.4 mm wide and 12.7 mm overlap).

Surface pretreatments

1) *Vapour degrease* This involved vapour degreasing alclad panels with trichloroethylene followed by washing with methyl isobutyl ketone and, finally, washing and scrubbing in trichloroethane. Degreased panels were dried in an oven at 60°C for about 1 hour.

2) *Chromic-sulphuric acids etch* After vapour degreasing panels were etched in a solution of chromium trioxide in sulphuric acid for 20 minutes at 62°C according to specification DEF STAN/03–2/1. Panels were then washed in running cold tap water for 20 minutes and finally dried in an oven at 60°C for about 1 hour.

3) *Alkaline etch* Vapour degreasing was followed by etching for 20 minutes in an alkaline solution (P3–T6657) supplied by Henkel and Cie GmbH Dusseldorf; panels were then washed in cold running tap water and scrubbed, to remove black deposit formed during etching, before they were dried in an oven at 60°C. Experiments were conducted to determine the optimum time of immersion in the etch solution to give the maximum initial joint strength, and it was found that etching for 6 minutes resulted in a mean strength of 15.2 kN whereas etching for 12 minutes and 20 minutes resulted in mean strengths of 16.6 kN and 17.6 kN respectively. Strength values, obtained with single overlap joints bonded with FM1000 adhesive, were a mean of fourteen determinations in each case.

4) *Phosphoric acid etch* After vapour degreasing panels were etched for 5 minutes at 75°C in a 5.5% phosphoric acid based solution (T6618–1) supplied by Henkel and Cie. They were then washed in cold running tap water and finally dried in an oven at 60°C for 1 hour.

Testing

Single overlap specimens were tested in tension until failure using a Denison T42U tensile test machine.

Dynamic mechanical measurements

Tan δ and dynamic force measurements were made on strips of cured FM1000 adhesive of accurately known dimensions (approximately 50 mm long, 2 mm wide and 1.7 mm thick) using a Dynamic Viscoelastometer Rheovibron model DDV–II manufactured by the Toyo Measuring Instruments Company Limited, Japan. Measurements were made at 110 Hz and, except for specimens that had been exposed to high humidity, over five lengths of each specimen. Specimens that had been exposed to high humidity tended to cool and lose absorbed moisture in the rheovibron and thus rendered measurements at more than one test length impracticable. In general, measurements with the rheovibron are made over a range of test lengths of the polymer specimen in order to obtain a correction factor to be applied to the measured value of dynamic force. This procedure allows for the error imposed on the measurement by the modulus of elasticity and displacement of the rheovibron stress gauge and its chuck during passage of a sinusoidal wave. It was determined that dynamic force values obtained from measurements made on a single test length of FM1000 adhesive were, on average, 2.3% greater (mean of 12 determinations) than corrected values obtained over five test lengths.

Using the rheovibron the complex dynamic tensile modulus (E^*) may be computed from the formula:

$$|E^*| = \frac{2L}{S} \times \frac{1}{D} \times 10^9 \text{ dyne/cm}^2$$

where L is the length of sample

S is the sectional area of sample

D is the dynamic force reading.

The dynamic elastic modulus (E') is given by $E' = |E^*| \cos \delta$ and the loss modulus (E'') by $E'' = |E^*| \sin \delta$, where δ is the phase angle. As a check on experimental technique the complex dynamic tensile modulus of a sample of Mylar (polyester film), provided by the manufacturers of the rheovibron, was determined and the value obtained (4.20 GN/m^2) was in good agreement with the value (4.40 GN/m^2) quoted in the instruction manual for the instrument.

Differential scanning calorimetry

Thermal transitions occurring in wet and dry samples of cured FM1000 adhesive were observed on a Dupont 900 thermal analyser equipped with a DSC cell and a thermal mechanical analyser attachment.

RESULTS AND DISCUSSION

Experiments conducted to determine the extent of water uptake by dry samples of cured FM1000 adhesive exposed to high humidity (97% RH, 43°C) revealed that after 1 hour the weight of exposed specimens had increased by 11% (mean of 4 determinations) and after 96 hours' exposure absorbed water corresponded to an increase in weight of 14%.

In order to determine the effect of absorbed moisture on the mechanical properties of FM1000 adhesive tan δ and dynamic force measurements were made on wet and dry samples of the material.

Seven strips were cut from a film of cured adhesive that had been stored in a desiccator over silica gel for 11 days, and the dynamic modulus of each specimen was determined. Six of the specimens were then suspended in a constant humidity chamber, and at specified times one specimen was withdrawn and its modulus determined; it was then dried under high vacuum (1.33 mN/m^2) for 48 hours before its modulus was redetermined. Results of these experiments are summarised in Tables I and II.

Exposure to high humidity resulted in substantial decreases (approximately 82% at 1000 hours exposure) in the modulus of cured FM1000 adhesive; however, the original value of the modulus was essentially restored by removal of water from the adhesive.

The seventh specimen of the adhesive (dry modulus 2.58 GN/m^2) was exposed in the laboratory (34% RH, 20°C) for 2230 hours at which time its modulus had decreased to 1.31 GN/m^2.

In additional experiments, modulus measurements were made on two strips cut from a dry sample of cured FM1000 adhesive. One of the specimens was placed in a high humidity chamber and the other was left exposed to a laboratory environment. The modulus of each specimen was redetermined at specified times, and it was found that the modulus of the specimen exposed to high humidity fell by 80.2% (2.38 GN/m^2 to 0.47 GN/m^2) at the end of 2450 hours' exposure and was essentially at its lowest value (0.41 GN/m^2) after 400 hours' exposure.

Results obtained with the laboratory stored specimen are shown in Figure 1, and although the decrease in modulus is less pronounced than that experienced under conditions of high humidity a fall of about 43% was recorded after 2450 hours exposure.

TABLE I

Complex dynamic tensile modulus (E^*) of specimens of cured FM1000 adhesive exposed to high humidity (97% RH, 43°C)

Specimen number	Modulus (E^*) (GN/m^2) dry adhesive	Exposure time (hours)	Modulus (E^*) (GN/m^2) wet adhesive	Modulus (E^*) (GN/m^2) vacuum dried adhesive
1	2.27	142	0.337	2.42
2	2.61	358	0.306	2.75
3	2.30	504	0.333	2.28
4	2.68	844	0.328	2.78
5	2.19	1000	0.374	2.53
6	2.69	2040	0.437	2.45

TABLE II

Tan δ values of specimens of cured FM1000 adhesive exposed to high humidity (97% RH, 43°C)

Specimen number	Tan δ (dry adhesive)	Exposure time (hours)	Tan δ (wet adhesive)	Tan δ (vacuum dried adhesive)
1	0.029	142	0.195	0.007
2	0.038	358	0.270	0.007
3	0.044	504	0.270	0.011
4	0.039	844	0.260	0.009
5	0.041	1000	0.275	0.010
6	0.039	2040	0.272	0.008

The effect of absorbed water on the thermal characteristics of cured FM1000 adhesive was examined by differential scanning calorimetry (DSC), and whereas transitions were observed at 99°C (inflexion) and 141°C with the dry adhesive these were displaced to 50°C and 102°C respectively in adhesive that had been exposed to high humidity for 66 hours. After drying the conditioned adhesive, by outgassing under high vacuum for 41 hours, it was re-examined by DSC and showed an inflexion at 80°C and an endothermic peak at 136°C in its DSC curve.

Experiments with a penetrometer on dry and wet samples of the adhesive revealed, with the former sample, two inflexions (extrapolated onset temperature) close to 35°C and 130°C; whereas with the latter sample only one inflexion was observed at 87°C. However, when the wet sample had been dried two penetration inflexions were restored at 40°C and 131°C. These results showed that thermal transitions (as measured in DSC and penetration experiments) occurring in dry FM1000 adhesive are displaced to lower temperatures by absorbed water, but they can be essentially restored by removing water from the wet adhesive. These findings may be of significance in the natural ageing of stressed FM1000 bonded joints since glue-line temperatures in excess of 50°C have been recorded at Australian test sites,[9] and at such temperatures the effect of plasticising the adhesive with water would tend to change the mode of joint failure from brittle to ductile.

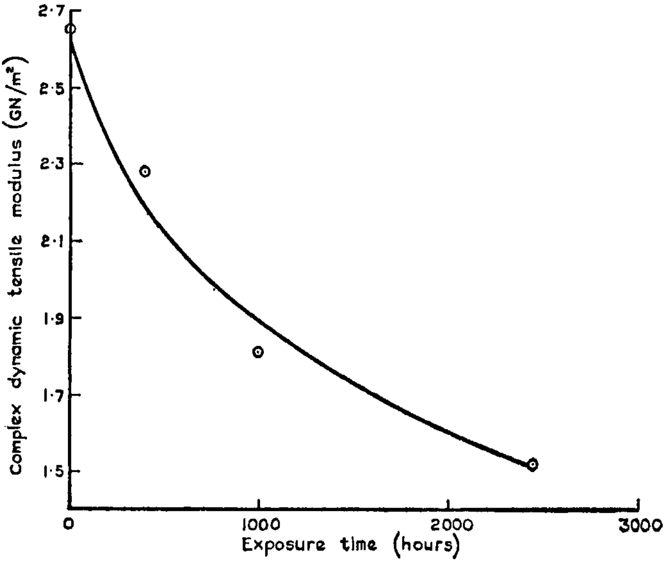

FIGURE 1 Effect of laboratory environment (20°C, 34% RH) on the complex dynamic tensile modulus of an epoxy-polyamide (FM1000) adhesive.

In an attempt to determine if the changes induced in the mechanical properties and thermal transitions of FM1000 adhesive by exposure to high humidity could be related to strength losses experienced by aluminium joints bonded with this adhesive exposed to a humid environment, joints were exposed in a humidity chamber and when their mean strength had fallen by

41% (26.9 MN/m^2 to 15.9 MN/m^2, mean of three determinations) three joints were removed from the chamber and were outgassed under high vacuum for 72 hours to remove moisture from the adhesive. After vacuum treatment, which included warming the joints to 55°C for 2½ hours, the specimens were broken and the mean strength (16.7 MN/m^2) was found not to have increased significantly. In a second experiment, when the mean strength of joints exposed to high humidity had fallen by 34% (26.9 MN/m^2 to 17.7 MN/m^2) three joints were removed from high humidity and were outgassed for 365 hours under high vacuum before they were broken and their mean strength computed to be 14.8 MN/m^2. These results showed that in contrast to the finding that the modulus of dry FM1000 adhesive can be restored by removal of water from the wet adhesive, the decline in strength experienced by FM1000 adhesive bonded joints under tropical conditions cannot be reversed by removal of absorbed water.

In addition, it was observed that the mode of failure of FM1000 adhesive bonded joints exposed to humid conditions progressively changed from wholly cohesive to predominantly adhesive. These findings are in accord with a primary role for water in joint degradation of displacing the adhesive from its metal substrate and not that of inducing cohesive failure of the adhesive. Most probably the hygroscopic nature of the epoxy–polyamide adhesive aids the transport of moisture through the adhesive to the interfacial regions.

The mechanism of failure of mild steel joints, bonded with an epoxy adhesive, exposed to high humidity can be predicted from thermodynamic considerations and has been shown to involve displacement of adhesive on the metal oxide surface by water.[10]

In contrast, other workers who exposed aluminium joints bonded with an epoxide adhesive to high humidity reported[11] that although the mean strength of the joints decreased by about 86% during 10 days' exposure, almost 80% of the initial strength was regained by drying the joints in vacuum at 90°C. The partial recovery in strength of the coupons was attributed to the reforming of hydrogen bonds while the permanent loss in strength (about 20%) was ascribed to covalent bond rupture.

The present work shows that attempts to improve the durability of structures bonded with FM1000 adhesive must be directed to increasing the moisture resistance of the interface by use of surface pretreatments and primers capable of rendering the metal surface less susceptible to attack by moisture, and by use of adhesion promoters whose primary role would be to increase the extent of covalent bond formation between adhesive and its metal substrate.

Strength retention curves (Figure 2) for the humid ageing of FM1000 adhesive bonded aluminium test coupons treated with either chromic-sulphuric acids, degreasing solvents, alkaline or phosphoric acid based formulations (see experimental section) clearly demonstrate the importance of pre-bonding surface preparation and the decided superiority of chromic-sulphuric acids in imparting improved durability characteristics to joints bonded with a moisture sensitive adhesive.

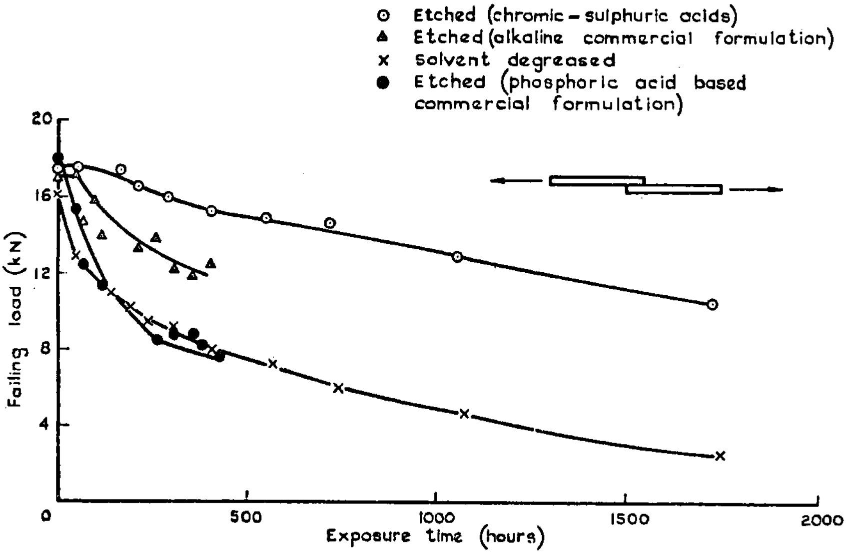

FIGURE 2 Effect of high humidity (43°C, 97% RH) on the strength of aluminium joints bonded with an epoxy-polyamide (FM1000) adhesive.

CONCLUSIONS

a) Dry specimens of cured FM1000 adhesive exposed to high humidity absorb an equilibrium 14% of water.

b) Exposure of the adhesive to humid environments results in substantial decreases in its complex dynamic tensile modulus; however, this effect can be reversed and the original value of the modulus restored by removal of water from the adhesive.

c) Thermal transitions observed by differential scanning calorimetry in dry specimens of the cured adhesive are displaced, by approximately 40°C, to lower temperatures during exposure to humid conditions but are essentially restored by removal of water from the adhesive.

d) In contrast to the reversible changes induced in the dynamic mechanical properties and thermal characteristics of FM1000 adhesive by absorbed water, strength losses experienced by bonded joints aged in humid conditions cannot be restored by removal of water from the adhesive.

e) The mode of failure of joints bonded with FM1000 adhesive changes progressively from wholly cohesive to predominantly adhesive on exposure to high humidity.

f) The primary role of water in the degradation of strength of aluminium joints bonded with FM1000 adhesive is to disrupt bonds at the interface between adhesive and metal.

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