Effect of carriers on the performance of aluminium alloy joints bonded with an epoxide–polyamide adhesive

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The introduction of a carrier fabric into an epoxide nylon adhesive lowered the initial shear strengths of lap joints, the effect being more severe with a close knitted carrier. The close knitted carrier led to a large additional decrease in joint strength after exposure to warm humid conditions. Stressing at 20% of the dry lap shear strength sometimes led to complete failure of the joints; this effect was much more marked in the presence of the close knitted carrier. Freeze–thaw cycling after exposure to water did not cause further reduction in joint strength. Drying unsupported adhesive joints after exposure to high humidity resulted in recovery to 80% of the initial dry strength. The total amount of water in a lap joint, calculated from the diffusion coefficient, was found to be linearly related to joint strength.

INTRODUCTION

Structural adhesive bonding in aircraft offers several advantages over mechanical fastening such as weight saving, improved aerodynamics and reduced stress concentrations. Despite these important advantages, the use of adhesives in structural applications has been modest, mainly because of doubts regarding environmental stability, particularly the effect of water. However, with improved adhesives and surface pretreatments, structural bonding is likely to be much more important in new aircraft.

Because of their unique combination of properties, epoxides are usually the basis of structural adhesives, which for convenience and reliability[1] are normally in film form. In recent years fabrics, known as carriers, have been incorporated in these adhesives to improve handling properties and to assist in controlling glue line thickness. The fabrics may be woven, knitted or in the form of rovings. Glass fibres were originally used but polyester and nylon fibres are now preferred.

It is clearly important that carriers do not have an adverse effect on other properties. In this paper the effect of two carriers on the environmental stability of an epoxide–polyamide adhesive, American Cyanamid FM 1000, was examined using an accelerated test. FM 1000 was chosen because it gives very high peel and lap shear strengths with aluminium. Accelerated tests were necessary as the anticipated life of current aircraft may be as long as 30 years. The recovery of joint strength on drying and the effect of freeze–thaw cycling were also examined. In an attempt to understand the effect of water on carried and uncarried adhesives, water uptake experiments were carried out.

EXPERIMENTAL

Materials

FM 1000 is an unsupported polyamide–epoxide adhesive produced by American Cyanamid. FM 1000/EP 15 is the same adhesive except it contains a tightly-knitted nylon carrier. For comparison, an open knitted nylon carrier was incorporated into FM 1000 by applying a pressure of 0.25 MN m^{-2} for 5 min at 100°C; we designated this adhesive FM 1000/OKN.

The adherends were of clad aluminium alloy BS3L73 (2.03 mm and 4.06 mm thickness).

Preparation and Testing of Double Lap Joints

The alloy was cut into panels 450 mm x 100 mm with a guillotine and locating holes 3 mm in diameter were drilled at either end by means of a purpose-built jig. The aluminium panels were surface-treated by the chromic–sulphuric etching method based on method O in the British Standard Code of Practice[2]. Specifically the following pretreatment procedure was adopted:

(i) surface grease and paint removed with methyl ethyl ketone;
(ii) immersed in a mild alkaline degreasing agent Stripalene* 532 (conc. 37g dm^{-3}) at 64°C for five min;
(iii) rinsed in hot tap water to remove excess Stripalene;
(iv) immersed in an etching solution of distilled water containing concentrated sulphuric acid (179.5 cm^3 dm^{-3}), chromium trioxide (68.5g dm^{-3}), copper sulphate (0.39g dm^{-3}) and stearate free aluminium powder (5g dm^{-3}) at 62°C for 30 min;
(v) washed in cold, running tap water for 20 min;
(vi) dried at 60°C for 20 min;
(vii) bonding was carried out within 3 h of surface treatment.

As nylon epoxides tend to absorb water prior to cure[1], the adhesives were dried for 30 min at 90°C. The surface treated aluminium panels and strips of adhesive were laid up on an aluminium baseplate by means of the locating holes to give a double lap configuration of overlap 12.5 mm. Pack-

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ing pieces and metal shims were used to control the glue line thickness. Panels were cured at 170°C and 0.35 MN m^{-2} for 60 min in a hydraulic press. They were allowed to cool overnight in the press, and were then cut into 16 individual specimens (25 mm wide) using a band saw with compressed air acting as a cutting coolant. Curing of long panels of joints in this manner gives greater reproducibility. Each joint was individually labelled and one in every four joints across the panel were tested as initial controls to give the mean initial dry strength of the joints. Testing was carried out on a Mayes MPU500 tensile testing instrument at a fixed loading rate of 10 kN min^{-1} in accordance with DTD5577[3].

The remaining twelve joints from each panel were mixed together and one set of six placed in the environmental chamber (50°C and 100% r.h.) and a second set of six stored at ambient temperature and humidity (approximately 20°C and 45% r.h.). Each set of six joints in the environmental chamber was either unstressed or stressed to 20% of the mean initial dry strength for the appropriate time interval. On removal from the chamber the joints were immersed in water at room temperature and tested between 10 and 40 min later. The joints stored at ambient conditions for the same time interval were also tested.

The extent of joint strength recovery on drying was investigated for FM1000 in the following manner. Four from each panel were tested as initial controls, three were stored in a laboratory environment (approximately 20°C and 45% r.h.) and 9 were placed in the environmental chamber unstressed. After 1000 h these were removed, 3 were tested to destruction and the remaining 6 together with the laboratory-stored specimens were placed in an oven at 50°C. After a further 1000 h they were removed and allowed to cool to room temperature before destructive testing.

The effect of freeze–thaw cycling on double lap joints with FM1000 was also examined. A standard panel of 16 joints of FM1000 was prepared and 4 specimens tested as initial controls. 3 were stored in ambient laboratory conditions and 9 were immersed in distilled water at 50°C in a thermostatic water bath. After 1000 h, 3 of the latter set were tested to destruction and the remainder were subjected to a series of ten 24 h freeze–thaw cycles (–20°C to +20°C) and then tested together with the 3 laboratory-stored specimens.

Environmental Chamber

It was necessary to build an environmental chamber in which double lap joints could be stressed to 20% of their breaking load and exposed to a relative humidity of 100% at a temperature of 50°C. Links of adhesive joints were suspended vertically under load in a chamber through which hot wet air was circulated. The load was set to the predetermined value by the compression of disc washers. Some stress relaxation occurred, almost entirely during the first 24 h, and this was compensated for by readjustment of the load to the set value. Details of the environmental chamber are given elsewhere[4].

Preparation and Testing of Peel Joints

Aluminium alloy BSL152 (3.56 mm) was used for the backing and BS3L61 (0.55 mm) for the flexible member. The alloy was cut into panels 250 mm x 200 mm using a guillotine. The pretreatment procedure and curing conditions were those used for the double lap joints. A 25 mm tag was left unbonded at one end. Two panels were cured simultaneously and then each was sawn into 7 individual specimens 25 mm wide. Six were tested to give the mean initial dry peel strength and the remaining 8 were placed in the environmental chamber unstressed. The 90° peel test was carried out using an Instron 1026 in accordance with DTD5577[3]. The peeling rate used was 100 mm min^{-1}, and the maximum, minimum and mean peel strengths were recorded.

Diffusion Studies on Cured Films of FM 1000

Cured films of FM1000 were prepared by cutting the film adhesive into strips (25 mm x 150 mm) and drying in an oven at 90°C for 30 min. The film was then cured in the hydraulic press between sheets of PTFE at 170°C and 0.35 MN m^{-2} for 60 min. Once cured, the strips were cut into squares (15 mm x 15 mm) and their thickness measured with a micrometer. The film samples were kept dry by storing in a desiccator over silica gel. The initial dry weight was measured and then samples were placed in screw-capped glass jars containing distilled water. Water uptake was followed at 1°C, 25°C and 50°C by immersing the glass jars in thermostatic water baths for the two higher temperatures and a refrigerator for the lower temperature. After certain time intervals the films were removed from the jars, blotted with tissue to remove surface water and weighed twice. The samples were then immediately returned to the water to minimize losses by desorption.

Measurement of Glass Transition Temperature

Cured film samples of FM1000 were prepared as described above. One sample of each film was stored over silica gel and one sample immersed in distilled water at room temperature for sufficient time to reach equilibrium. The glass transition temperatures of the wet and dry adhesive was measured on a Du Pont 900 thermomechanical analyser using the instrument in the penetrometer mode. Scanning was carried out from well below the expected transition temperature, cooling with liquid nitrogen; the heating rate was 10°C min^{-1} and a 10 g weight was placed on the probe. On removal from the water the 'wet' adhesive samples were blotted with tissue to remove surface water, cut to the required size and immediately placed in the penetrometer sample holder.

RESULTS

The effect of carriers on the failure loads of joints bonded with FM1000 is given in *Table 1*; the results are for the initial dry strengths and those for joints exposed to various aging conditions. The effect of these warm humid conditions on the lap shear strengths for FM1000 and FM1000/EP15, as a function of time, are given in *Figures 1* and *2* respectively. The laboratory-stored specimens did not show a significant change in strength compared with the initial control specimens.

The failure modes of the initial controls were as follows:

FM1000 apparent interfacial failure with crack jumping from one surface to the other. Permanent deformation of the thinner adherends was apparent and in some places tearing of the cladding was evident on the fracture surface;

Table 1 Effect of carriers on the failure loads obtained using FM1000

Adhesive	Conditions	Time (h)	Mean failure load (kN)
FM 1000 Unstressed	Initial controls	0	42.4 ± 1.3
	Laboratory stored	1003	42.7 ± 0.7
	50°C, 97–100% r.h.	1003	28.0 ± 1.5
FM 1000 Stressed to 20% of initial dry strength	Initial controls	0	42.2 ± 0.9
	Laboratory stored	1009	40.8 ± 0.5
	50°C, 97–100% r.h.	1009	28.5 ± 0.9
FM 1000/EP15 Unstressed	Initial controls	0	26.9 ± 1.3
	Laboratory stored	1007	26.4 ± 0.6
	50°C, 97–100% r.h.	1007	16.1 ± 3.1
FM 1000/OKN Unstressed	Initial controls	0	37.5 ± 0.9
	Laboratory stored	1003	37.3 ± 0.8
	50°C, 100% r.h.	1003	23.2 ± 0.7

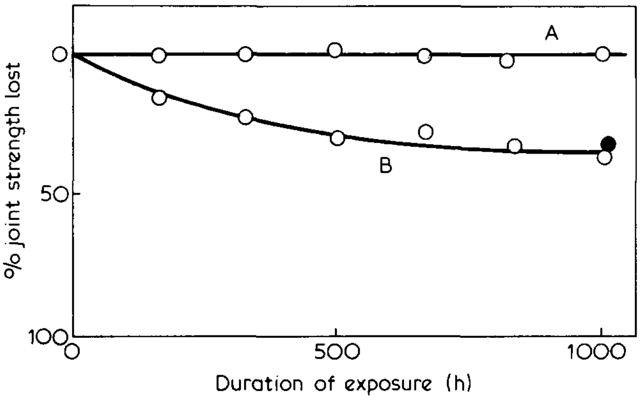

Figure 1 Effect of high humidity at 50°C on double lap joints of FM 1000. ○, unstressed joints; ●, joints stressed to 20% of initial dry strength. A, stored in ambient conditions; B, stored at 50°C, 100% r.h.

FM1000/EP15 failure occurred along the carrier fabric, which was usually left torn with half adhering to each fracture surface;

FM1000/OKN failure was about 50% cohesive and 50% apparent interfacial, the pattern of the carrier knit being clearly visible on the fracture surface. The carrier itself was torn between the two fracture surfaces and fibres were visible adhering to each surface. In some cases permanent deformation of the thinner adherend was observed.

The failure modes of joints subjected to the hot humid conditions (unstressed) were as follows:

FM1000 apparent interfacial failure in the main but for specimens exposed for longer than 500 h cohesive failure around the edges was observed; this amounted to about 25% after 1000 h;

FM1000/EP15 failure occurred straight along the carrier as for the unexposed samples;

FM1000/OKN the failure was 50% cohesive and 50% apparent interfacial. The failure for the stressed joints was the same as just described. The extent of joint strength recovery on drying at 50°C for FM1000 and FM1000/EP15 is shown in *Table 2*.

The effect of freeze–thaw cycling on joints of FM1000 is shown in *Table 3*. Immersion in water at 50°C caused a loss in bond strength of 40%, slightly higher than that caused by exposure to high humidity. The subsequent freeze–thaw cycling did not appear to cause any further loss in bond strength. Failure for the controls and laboratory stored specimens was mainly apparent interfacial but those immersed in water, and specimens immersed and then frozen and thawed, showed mainly cohesive failure.

The dry peel strengths for FM1000 and FM1000/15 are given in *Table 4*. These show that the carrier has very little effect on the peel strength.

Water uptake by FM1000 at 50°C is shown in *Figure 3*; the data for 25°C and 1°C are given in *Figure 4*.

M_0 is the initial dry weight of the sample;
M_t is the weight at time t;
l is the sample thickness.

The initial stiffness of the FM1000 film rapidly gave way to flexibility upon water immersion. With FM1000 a maxi-

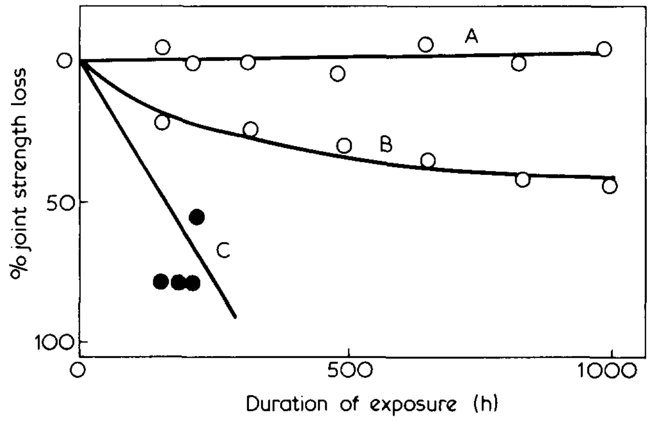

Figure 2 Effect of high humidity at 50°C on double lap joints of FM 1000/EP 15. ○, unstressed joints; ●, joints stressed to 20% of initial dry strength. A, stored in ambient conditions; B, stored at 50°C, 100% r.h.; C, stored at 50°C, 100% r.h. The three lowest points (●) represents time to failure at 20% stress level

Table 2 Recovery of joint strength on drying, after exposure to 100% r.h. at 50°C (unstressed)

Adhesive	Conditions	Time (h)	Mean failure load (kN)
FM 1000	Initial controls	0	42.3 ± 0.7
	50°C, 100% r.h.	1004	27.2 ± 0.7
	50°C, 100% r.h.	1000	
	then 50°C drying	1006	33.7 ± 2.0
	Laboratory stored,	1004	
	then 50°C drying	1006	40.3 ± 0.5
FM 1000/EP15	Initial controls	0	27.6 ± 1.0
	50°C, 100% r.h.	1000	16.1 ± 3.1
	50°C, 100% r.h.	1000	
	then 50°C drying	1000	25.9 ± 0.5
	Laboratory stored	1000	
	then 50°C dried	1000	31.9 ± 0.3

Table 3 Effect of freeze–thaw cycling on failure load

Conditions	Mean failure load (kN)
Initial controls	39.4 ± 1.1
Distilled water at 50°C for 1000 h	24.1 ± 2.7
Distilled water at 50°C for 1000 h and 10 x 24 h freeze–thaw cycles	23.3 ± 1.2
Laboratory stored for 1240 h	39.9 ± 0.6

Table 4 Peel strengths for the FM1000 and FM1000/EP15 systems

	Peel strength (kNm^{-1})		
Adhesive	Maximum	Minimum	Mean
FM 1000	22.4 ± 0.5	17.3 ± 2.0	20.0 ± 1.2
FM 1000/EP 15	21.9 ± 0.5	19.3 ± 0.8	20.8 ± 0.4

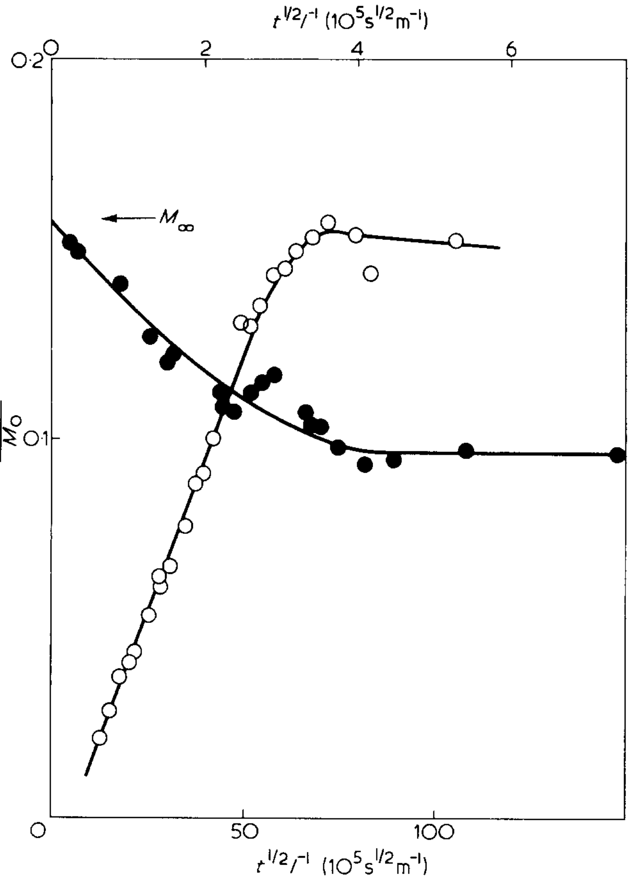

Figure 3 Uptake of water by FM 1000 at 50°C. ○, short time scale, upper abscissa; ●, long time scale, lower abscissa

mum occurred in the uptake profile at all three temperatures after which the weight slowly decreased until an equilibrium was reached. The sample, kept at 50°C, was dried out and the sorption repeated. The second sorption attained equilibrium without the film passing through a weight maximum, the solubility at equilibrium being the same as for the first sorption. The reason for this effect is probably due to low molecular weight material leaching out from the resin during the first sorption.

Sorption by FM1000 containing a non-woven polyester carrier at 50°C was the same as that shown by the unsupported adhesive.

The glass transition temperature of dry FM1000 as measured by thermomechanical analysis is 34°C. This value is close to that measured by the torsion pendulum technique[5,6], but we are unable to account for the much higher value of T_g given by Butt and Cotter[28] using differential scanning calorimetry. However, they do observe a transition close to 35°C using t.m.a. The transition for the wet adhesive was found to be –32°C.

Diffusion coefficients (D) have been estimated from the tangents of the uptake regions at $(M_t - M_0)/M_0 = 0.1$ in *Figures 3* and *4*. The relationship between the time dependent water uptake M_t, water uptake at equilibrium M_∞, time t, and film thickness l for a semi-infinite film in a infinite bath at short times, is[19]:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2},$$

hence the tangent slope $=4(D/\pi)^{1/2}$.

The intercept on the ordinate (illustrated in *Figure 3*) was used for M_∞. The values of D so obtained which have an accuracy of about ±30% are:

$$D = 7.5 \times 10^{-14}\ \text{m}^2\ \text{s}^{-1} \text{ at } 1°\text{C}$$

$$D = 1.1 \times 10^{-12}\ \text{m}^2\ \text{s}^{-1} \text{ at } 25°\text{C}$$

$$D = 3.2 \times 10^{-12}\ \text{m}^2\ \text{s}^{-1} \text{ at } 50°\text{C}$$

The energy of activation for diffusion ΔH_D was obtained by plotting the logarithms of these values against reciprocal temperature ($1/T$). The three points fitted well to a straight line and gave the value of ΔH_D as 57 kJ mol^{-1}. It is probable that this value represents the value of ΔH_D appropriate to the adhesive in its leathery state.

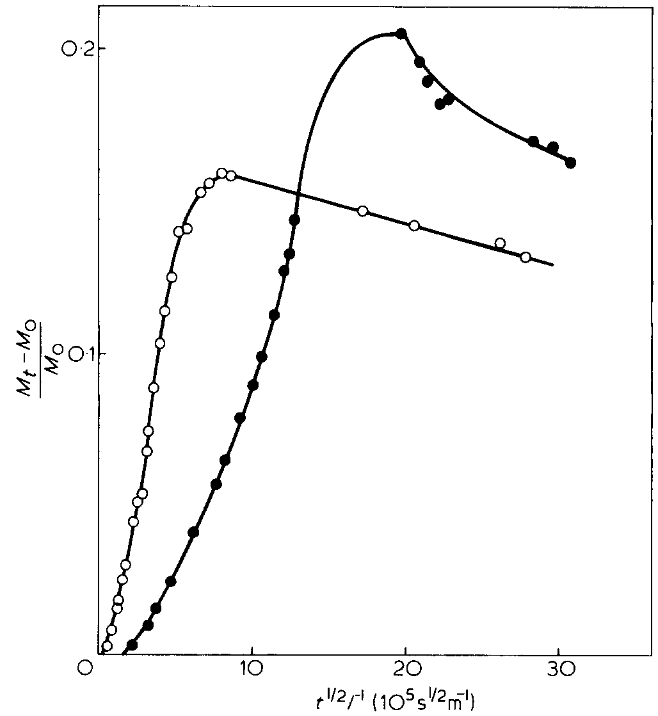

Figure 4 Uptake of water by FM 1000. ●, 1°C; ○, 25°C

The vapour uptake experiment at 50°C gave a value of $D = 3.4 \times 10^{-12}\ \mathrm{m^2\ s^{-1}}$ ($\pm 16\%$) which is in good agreement with the value from liquid uptake, taking regard of the uncertainty in the latter result caused by there being no clear value for M_∞ in liquid uptake experiments. The vapour value has been used in subsequent calculations.

DISCUSSION

The results in *Table 1* show that carriers can reduce the lap shear strength obtained with FM1000. However, the magnitude of the reduction depends on the nature of the carrier, being 30% with a close knitted nylon carrier, but only 10% with an open knitted nylon.

The weakening of an adhesive joint by the presence of a carrier is at first sight surprising because it might be expected that a carrier would reinforce the adhesive. However, though this might be achieved by the use of carriers made from stiff strong fibres such as glass or carbon, those currently used are much weaker and more flexible, and hence unable to reinforce. The carriers appear to act as inert fillers, reducing the strength of the adhesive by an amount similar to the volume fraction present. There is also the possibility that the carrier encourages the trapping of air bubbles. It should be noted that no adverse effect on peel strengths was observed (*Table 4* and ref 7).

The weakening effect of a carrier has been noted by other workers. Hughes and Rutherford[8] studying the mechanical properties of adhesives in joints found that the presence of a nylon carrier in an epoxide system reduced the effective tensile modulus. Seago[9] investigating cyclic creep properties under ambient conditions found unsupported adhesives superior to carried adhesives. Two of the adhesive systems Seago used were FM1000 and FM1000/EP15. His tests were intended to simulate a helicopter rotor blade start–stop cycle by 1 h (20.7 M $\mathrm{Nm^{-2}}$) followed by 15 min unload cycle. This type of very slow cycle fatigue has since been found to be more damaging to adhesive joints than cycling at higher frequencies[10]. FM1000 survived Seago's tests 1800 h without breaking whereas FM1000/EP15 failed after several hours.

The main reason for the low strength and durability of FM1000/EP15 is probably the construction of the carrier, the knit being so close that the adhesive cannot penetrate the fabric causing an inherent weakness. Three joints of FM1000/EP15 stressed at 20% failed within 220 h and the residual strength of the remaining 3 from a string of 6 was 60% lower than their dry strength. However, joints of FM1000 and FM1000/OKN stressed to 20% did not fail until more than 3000 h; with the former adhesive, failure occurred at 3265, 3252 and 3465 h while with FM1000/OKN failure occurred after 3603, 3420 and 3741 h. This shows that carriers may or may not have a detrimental effect on joint strength durability depending on the nature of the carrier.

The change in failure mode for FM1000 from apparent interfacial failure to partial cohesive on exposure to moisture is probably due to plasticization of the adhesive by water. When dry, the strength of the adhesive is such that failure occurs at the interface. The strength of cured films of FM1000 has been found to be greatly reduced on exposure to moisture[5]. Thus when adhesive joints are exposed to moisture the cohesive strength is lowered and hence cohesive failure becomes increasingly apparent.

At low temperatures epoxide–nylon adhesives, like FM1000, show good retention of bond strength provided that peeling forces are minimized[12]. Hertz[13] reported little change in bond strength when a nylon epoxy was thermally cycled between −267°C and 25°C. However, it was suggested that if joints were allowed to absorb water prior to thermal cycling, ice crystals might develop in the adhesive on freezing which could cause damage. However, the results presented in *Table 3* show that if ice crystals do form in the adhesive they are of insufficient size to affect the bond strength.

The measurement of the water content of an adhesive joint and the time taken for a glue line to become saturated should help considerably in understanding the adverse effect of water on epoxide–metal joints. In an attempt to be able to predict these quantities water diffusion studies were carried out on cured films of unsupported FM1000. With FM1000 the T_g of the dry adhesive (34°C) is only just above room temperature; thus at 50°C it is in the leathery state. The water uptake curves show Fickian diffusion at 50°C and non-Fickian at 1°C and 25°C. The reader is referred to a paper by Fujita[14] for a discussion of Fickian and non-Fickian diffusion. At these lower temperatures a discontinuity is observed in the uptake profile when the glassy polymer absorbs enough sorbant to pass through its glass transition. Once in the leathery state uptake occurs more rapidly. The glass transition temperature of FM1000 which had been saturated with water at 25°C is −32°C.

Plasticization by water can be examined using the Fox equation[15]:

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_A}{T_{gB}}$$

where T_g is the glass transition temperature of the mixture; T_{gA} and T_{gB} are those of dry adhesive and water respectively; W_A and W_w are weight fractions of water and adhesive in the mixture. The sample examined had absorbed water for 12 days and $W_A = 0.100$. This gives a value of 82K for the glass transition temperature of water compared to the accepted value of about 132K[16]. This implies that all sorbed water is contributing to plasticization of the epoxide and that none is prevented from this function by being isolated in clusters. If there were no clusters then no damage due to freeze–thaw cycling would be expected (see *Table 3*).

Solubility of water in FM1000 is higher at lower temperatures, although the dependence of solubility on temperature is not great, that is the system has a small exothermal heat of sorption.

The reason why FM1000 behaves differently to certain other epoxide systems[17] is probably the nylon component. The values of diffusion coefficient and solubility of water in FM1000 are more characteristic of a nylon than of an epoxide[17,18].

Having obtained figures for diffusion coefficients of FM1000 system it was possible to calculate theoretical values for the fractional water content at points in the joint at time t. The following equation which is a solution of Fick's Second Law for a slab[19] was used:

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-D(2n+1)^2\pi^2 t/4l^2\right) \times \cos\left((2n+1)\pi x/2l\right)$$

where C_0 is the initial concentration within the slab, C_1 is the surface concentration, C is the concentration at time t, D is the diffusion coefficient, and $2l$ is the thickness of the slab.

For uptake of water by a lap joint, this equation can be applied in x- and y-directions which are in the plane of the glue line; it was assumed that no diffusion occurred in the perpendicular z-direction. The coordinate system used is shown in *Figure 5*. The concentration of water at any point (x, y) could then be found from the product of the concentrations relative to the x and y slabs[20]. The adhesive layer was a normal section of a rectangular prism, the prism being formed at the intersection of two slabs at right angles. The adhesive layer consisted of four identical quadrants, and thus the values of relative concentration needed only to be calculated in one quadrant. This was done in the quadrant

$$0 \leqslant x \leqslant l_1, \qquad 0 \leqslant y \leqslant l_2$$

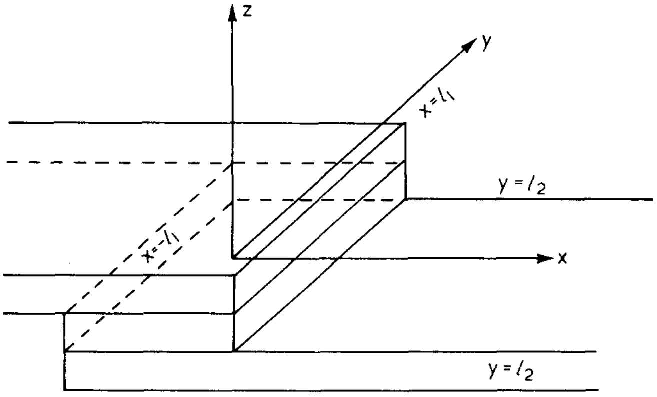

Figure 5 Coordinate system for a lap joint

A computer programme was set up to obtain solutions to the equation and give relative water concentrations in a lap joint. The series in the equation converges so rapidly that only the first few terms needed to be considered[21]. The fractional water content at points within a quadrant of a 25 mm × 12.5 mm lap joint bonded with FM1000 calculated in this manner for a time of 1003 and 10 000 h is given (*Table 5*).

The following equation was used[19] to determine the total water taken up due to diffusion firstly in the x-direction and then in the y-direction. The product of these two was taken as the total water uptake in the joint:

$$\frac{M_t - M_\infty}{M_\infty - M_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-D(2n+1)^2\pi^2 t/4l^2\right)$$

Here

$$\frac{M_t - M_\infty}{M_\infty - M_0}$$

is the fractional uptake of water by the joint.

The computer programme permits the evaluation of water distribution in the x- and y-direction. However, it is also possible that water may have a distribution in the z-direction, and that this may be influenced by the surface treatment given to the adherend. This would possibly provide an explanation for the frequently observed fact that joints bonded with the same adhesive, but with adherends which have been given different surface treatments, have different strengths after exposure to water.

This was applied to FM1000 and the resulting fractional uptake is compared with joint strength in *Figure 6*. This Figure illustrates a linear dependence of the strength of double lap joints on fractional water uptake. A similar

Table 5

(a) Fractional water content at points within a quadrant of a 12.5 x 25 mm lap joint of FM 1000 after 1003 h at 50°C (using $D = 3.4 \times 10^{-12} \mathrm{m^2 s^{-1}}$)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.1	.442	.462	.496	.542	.599	.667	.743	.825	.911	1.000
0.2	.452	.472	.505	.550	.607	.673	.747	.828	.913	1.000
0.3	.470	.490	.522	.566	.620	.684	.756	.834	.916	1.000
0.4	.500	.519	.549	.590	.642	.702	.770	.843	.920	1.000
0.5	.545	.562	.589	.627	.674	.728	.790	.857	.927	1.000
0.6	.606	.620	.644	.677	.717	.765	.818	.876	.937	1.000
0.7	.684	.695	.715	.741	.773	.811	.854	.901	.949	1.000
0.8	.779	.786	.800	.818	.841	.868	.898	.930	.964	1.000
0.9	.886	.890	.897	.906	.918	.932	.947	.964	.981	1.000
1.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

(b) Fractional water content at points within a quadrant of a 12.5 x 25 mm lap joint of FM 1000 after 10 000 h at 50° C (using $D = 3.4 \times 10^{-12} \mathrm{m\,s^{-1}}$)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.1	.999	.999	.999	.999	.999	.999	1.000	1.000	1.000	1.000
0.2	.999	.999	.999	.999	.999	.999	1.000	1.000	1.000	1.000
0.3	.999	.999	.999	.999	.999	.999	1.000	1.000	1.000	1.000
0.4	.999	.999	.999	.999	.999	1.000	1.000	1.000	1.000	1.000
0.5	.999	.999	.999	.999	1.000	1.000	1.000	1.000	1.000	1.000
0.6	.999	.999	.999	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.7	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.8	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.9	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

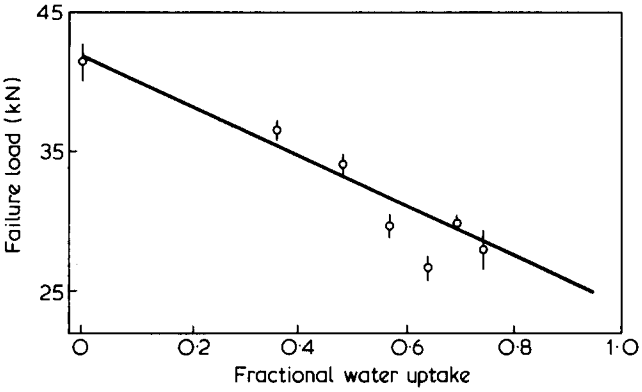

Figure 6 Dependence of the strength of adhesive joints with FM 1000 on water uptake

relationship has been reported between loss of joint strength of carbon fibre composite bonded joints and the amount of water taken up by the composite[22].

However, the above theory assumes that ingress of water into an adhesive joint occurs by means of diffusion through the resin, and the results shown in *Figure 6* provide some evidence in favour of this mechanism. However, other possible mechanisms are a process of wicking along the interfaces (epoxide–aluminium oxide, epoxide–carrier) or diffusion through the aluminium oxide layer*. In an attempt to discover whether diffusion through the resin is the operative mechanism, an experiment has been set up to follow the diffusion of tritiated water into an adhesive joint. The experiment is still in progress at the time of writing but should yield a pattern of water uptake across the joint with time which can then be compared with the calculated results. An experiment is also being conducted using a carried adhesive to determine the effect of the carrier.

At present the mechanism by which an adhesive joint loses strength on exposure to water is not clear; several theories have, however, been put forward. One suggestion[23–25] is the occurrence of hydrolysis of covalent bonds in the cured adhesive. These workers subjected aluminium–epoxide adhesive joints to high humidity and moderately elevated temperatures. The joints were found to drop in strength by 40% after 20 days. The specimens were then dried out and, similar to data reported here, were found to recover to 85% of the original bond strength. The amount of strength recovered was ascribed to the reforming of hydrogen bonds within the network and the permanent damage to breaking of covalent bonds. It is interesting that complete recovery in the mechanical properties of films of FM1000 after drying has been observed[5,28].

Other workers have suggested[26,27] that the cause of the weakening of aluminium–epoxide joints is due to hydration of the oxide surface, i.e. the oxide becomes mechanically weaker and causes premature failure. Bethune[26] reported that phosphoric acid anodizing lead to much improved durability in warm humid conditions and failure of joints was cohesive. He argued that the success of the pretreatment was due to the elimination of a weak oxide layer. Further evidence was given showing that corrosion resistant primers gave improved durability.

The loss of strength of bonded components in humid environments has also been explained[28–30] by the displacement of the adhesive on the substrate surface by water. Calculations were reported[30] of the thermodynamic work of adhesion (*WA*) for aluminium–epoxy bonds both dry and after exposure to water. In a dry atmosphere *WA* was found to be positive (+232 mJ m^{-2}) indicating a stable surface; but in a wet atmosphere *WA* is negative (–137 mJ m^{-2}), indicating that debonding is favoured thermodynamically. It has been suggested[29] that the rate of debonding of epoxide adhesives from mild steel is controlled by the availability of water diffusing through the resin. Gettings *et al.*[31] using e.s.c.a. and Auger techniques found that the iron oxide thickness increased from 10 nm when dry to 60 nm after a joint had been exposed to moisture.

Some mechanisms of joint strength degradation are reversible (e.g. water plasticization) whereas others are irreversible (e.g. formation of weak metal oxide). The recovery of joint strength is therefore an important criterion in establishing the mechanism. The results in *Table 2* show substantial but incomplete recovery. Desorption is usually slower than sorption and may be incomplete; therefore no firm conclusions can be drawn from these results. However, experiments involving more rigorous desorption are being carried out.

At present the mechanism for the degradation of adhesive joints on exposure to moisture is not clear. As can be seen from the theories outlined above, there is considerable debate as to whether it is primarily the metal substrate, the interface or the adhesive that is attacked by water.

The regions a few nanometres either side of the interface are of particular importance and these have been very difficult to study quantitatively until recently. However, some of the newer analytical techniques for studying surfaces look very promising, in particular e.s.c.a.[31], Auger[31] and inelastic electron tunnelling[32]. These techniques should shed more light on the mechanisms of joint strength deterioration and enable surface treatments and adhesives to be selected on a more rational basis.

CONCLUSIONS

(1) The introduction of a carrier fabric into the epoxide–nylon adhesive, FM1000, lowered the initial shear strength of lap joints. The extent to which this occurred depended on the construction of the fabric; the carrier should preferably be light and open in texture to minimize the reduction. Peel strengths obtained with FM1000 were not significantly affected by the addition of a carrier.

(2) An open knitted carrier did not have an additional deleterious effect on the lap shear strength in warm, humid conditions over the unsupported forms of the adhesives. However, the close knitted carrier studied significantly impaired joint durability.

(3) With FM1000 or FM1000/OKN, stressing at 20% of mean dry shear strength in humid conditions did not have an additional effect on strength as compared with joints unstressed in the same conditions up to 1000 h. However, catastrophic failure occurred with these systems after about 3500 h. With FM1000/EP15 (i.e. the system containing a close knitted carrier), complete failure occurred after about 200 h.

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* The observation of identical water uptake plots for FM1000 and for FM1000 with a woven polyester carrier does not mean that the carrier will have no effect on water ingress in a joint. This is because the directions of diffusion are different in the two cases, i.e. normal to the fibres with the detached film, but along the fibres with an adhesive joint, so that wicking along the fibre could make an important contribution in the latter case.

(4) Freeze–thaw cycling of FM1000 after exposure to water was not found to further weaken lap joints.
(5) The drying of unsupported adhesive joints for 1000 h after exposures to high humidity was found to result in 80% recovery of the initial dry strength.
(6) The total amount of water in a lap joint calculated using a theoretical model has been found to be linearly related to joint strength.

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REFERENCES

1 Patrick, R. L. (ed.) 'Treatise on Adhesion and Adhesives', **4**, Marcel Dekker, New York, 1976, Ch 4
2 Br. Std. Inst. 'Code of Practice for Cleaning and Preparation of Metal Surfaces', CP 3012, 1972
3 Ministry of Defence, Specification DTD 5577 (Nov. 1965), 'Heat Stable Structural Adhesives'
4 Brewis, D. M., Comyn, J., Cope, B. C. and Moloney, A. C. *Laboratory Practice,* July 1979, 743
5 Shalash, R. J. A. Unpublished work
6 Althof W. and Brockmann, W. *Adhesives Age,* September 1977, 27
7 Bascom, W. D. and Cottington, R. L. *J. Adhesion,* 1972, **4**, 193
8 Hughes, E. J. and Rutherford, J. L. *Picatinny Arsenal Tech. Rep.* PATR-3744 (August 1968), AD 613745
9 Seago, R. *Nat. SAMPE Tech. Conf.,* 1970, **2**, 135
10 Marceau, J. A., McMillan, J. C. and Scardino, W. M. *Adhesives Age,* April 1978, 37
11 Brewis, D. M., Comyn, J., Cope, B. C. and Moloney, A. C. Unpublished work
12 Bolger, J. C. in 'Treatise on Adhesion and Adhesives', **3**, (R. L. Patrick (ed.)) Marcel Dekker, New York, 1973, Ch. 1
13 Hertz, J. *Adv. Cryogen. Eng.,* 1961, 7, 336
14 Fujita, H. *Adv. Polym. Sci.,* 1961, **3**, 1
15 Fox, T. G. *Bull. Am. Phys. Soc.,* 1956, **1**, 123
16 Tan, Y. Y. and Challa, G. *Polymer,* 1976, **17**, 739
17 Comyn, J., Brewis, D. M., Shalash, R. J. A. and Tegg, J. L. *Adhesion,* 1979, **3**, 13
18 Asada, T. and Onogi, S. *J. Colloid Sci.,* 1963, **18**, 784
19 Crank, J. 'Mathematics of Diffusion', Oxford University Press, 1956
20 Carslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids', 2nd Edn., Oxford University Press, 1959
21 Barrer, R. M. 'Diffusion in and through Solids', Cambridge University Press, 1941
22 Parker, B. M. *Royal Aircraft Establishment Tech. Rep. 77019,* 1977
23 Kerr, C., MacDonald, N. C. and Orman, S. *J. Appl. Chem.,* 1967, **17**, 62
24 Kerr, C., MacDonald, N. C. and Orman, S. *Br. Polym. J.,* 1970, **2**, 67
25 MacDonald, N. C. 'Aspects of Adhesion', 1967, **5**, 123
26 Bethune, A. W. *SAMPEJ,* 1975, **11** (3), 4
27 Reynolds, B. L. *Proc. Army Mater, Tech. Conf.,* 1976, **4**, (*Adv. in Joining Technol*), 605
28 Butt, R. I. and Cotter, J. L. *J. Adhesion,* 1976, **8**, 11
29 Gledhill, R. A. and Kinloch, A. J. *J. Adhesion,* 1974, **6**, 315
30 Kinloch, A. J., Dukes, W. A. and Gledhill, R. A. in 'Adhesion Science and Technology', *9B*, Plenum Press, New York, 1975
31 Gettings, M., Baker, F. S. and Kinloch, A. J. *J. Appl. Polym. Sci.* 1977, **21**, 2375
32 White, H. W., Godwin, L. M. and Wolfran, T. *J. Adhesion,* 1978, **9**, 237