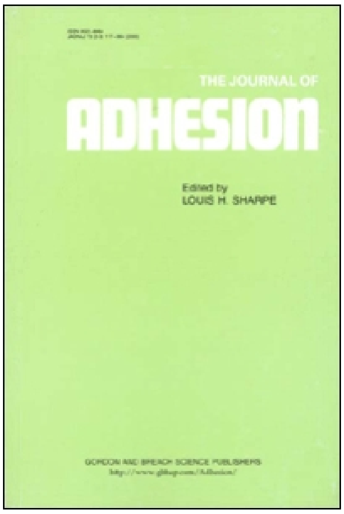

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A Review of Certain Recent Work on the Durability of Aluminium Alloy Bonded with Epoxide and Phenolic Adhesives†

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Single lap joints of aluminium alloy, bonded with a number of structural adhesives, have been aged at 100% or 50% relative humidity (r.h.) at 50°C for up to 10000 hours. The adhesives used have included a simple epoxide and some modified phenolics and epoxides. Whilst joints are not significantly weakened on exposure at 50% r.h., significant weakening occurs at 100% rh. There is an initial fall in strength in the early stages of exposure, but after this period joints remain fairly stable, retaining approximately 40–60% of the strengths they had before exposure. Water diffusion coefficients in the adhesives have been obtained from experiments on the mass uptake of water by films of the adhesives. Water concentration profiles and overall levels of water in adhesive joints have been calculated from diffusion coefficients, and these show that the initial fall in strength is controlled by water diffusing through the adhesive layer. Joint strengths recover significantly when they are dried out. The behaviour of joints can be interpreted by there being ion-pairs at the interface. Water reduces the interionic force by raising the permittivity of the surroundings, and this is reversed when the water is removed.

KEY WORDS Aluminium; durability; epoxide adhesives; phenolic adhesives; ion-pairs; recovery.

INTRODUCTION

One major problem which limits the use of adhesives, and also the safe loads to which adhesive joints can be subjected, is their susceptibility to environmental water. There are many cases in the literature[1,2,3] of adhesive joints with metallic adherends and rigid adhesives being weakened by exposure to wet surroundings, and the common feature is the shape of the joint strength *versus* time plots. Joint strength falls most rapidly at the beginning, and eventually slows down to a very low rate. Although the shapes of curves are similar, there are variations in the initial rates of strength loss and in the fraction of strength which is retained at long exposure times and one factor which has an important effect on these is

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surface treatment of the adherends. Indeed, for some time, effective surface treatment has been seen as an important way of giving joints maximum durability to water.

We have been investigating this problem for a number of years, and the purpose of this paper is to review this work. The approach has been to test lap joints after exposure to warm moist air, and to compare strengths with the rate of water diffusion into the adhesive layer. Diffusion coefficients of water in the adhesives were measured by following the mass uptake of films immersed in water or water vapour. A range of adhesives and surface treatments have been employed but the same aluminium adherend has been used throughout.

Further details of all aspects of the investigations can be found in the original papers.[4–10]

EXPERIMENTAL

The adherend used was aluminium alloy clad with a thin layer (0.08 mm) of pure (99.90%) aluminium of type L65/T6 (formerly BS3L73).[11] Surface treatment has mainly been by etching in chromic acid, but there has been some supporting work with solvent wiping, sandblasting and phosphoric acid anodising. Panels of the metal measuring 450 mm × 75 mm were bonded together in jigs with 12.5 mm overlap along the length. After curing under conditions appropriate for each adhesive, they were cut into individual lap joints with a band saw, using an air jet as a coolant. These were either 12.5 × 12.5 mm single lap joints, or in the cases of FM1000 and BSL 312 adhesives 25 × 12.5 mm double lap joints. These relatively small joints were chosen in order to reduce the time scale needed for water diffusion into the adhesive layers. Joints were exposed in an environmental chamber at 50°C and 100% relative humidity (r.h.), and control specimens were either stored in the laboratory or at 50°C and 50% r.h. over a saturated potassium carbonate solution. Joint testing was in a Monsanto Tensometer using a crosshead speed of 4.8 mm min^{-1} or in a Mayes MPU 500 servohydraulic instrument at a loading rate of 10 kN min^{-1}. Failure of dry joints was mainly cohesive, becoming increasingly interfacial on aging at 100% r.h.

The adhesives used were the modified epoxides BSL 312 (Ciba-Geigy)[7] and FM1000 (Cyanamid)[6,8] and the diglycidyl ether of bisphenol-A cured with 32.5 parts per hundred by weight of di(1-aminopropyl-3-ethoxy)ether (DGEBA/DAPEE).[4,5] Also two nitrile phenolic adhesives (here described as NP1 and NP2) and a vinyl phenolic adhesive (VP) have been used;[9,10] NP2 has also been used with a primer.

Water uptake studies involved preparing thin films (≤0.5 mm) of the adhesives and immersing them in thermostatted distilled water. Periodically films were removed, dried between paper tissues, weighed and returned to the water. Some uptake studies were from the vapour phase and employed a recording vacuum microbalance.

JOINT STRENGTHS

The manner in which joint strengths change when they are exposed to the various aging conditions is illustrated in Figure 1 and, although this is for a vinyl phenolic adhesive, it is typical of the joints which have been studied. The salient features of Figure 1 are as follows.

(i) On exposure to air at 100% r.h. and 50°C joint strengths initially fall, typically by 40–60%, but then tend to level out.

(ii) Little or no weakening takes place when joints are aged at 50% r.h. and 50°C.

(iii) When joints which have been exposed at 100% r.h. for 5000 h are then stored for a further 5000 h at 50% r.h., a significant part of the strength is recovered.

The use of a primer with NP2 adhesive had a marked improvement on dry and humid aged strengths.

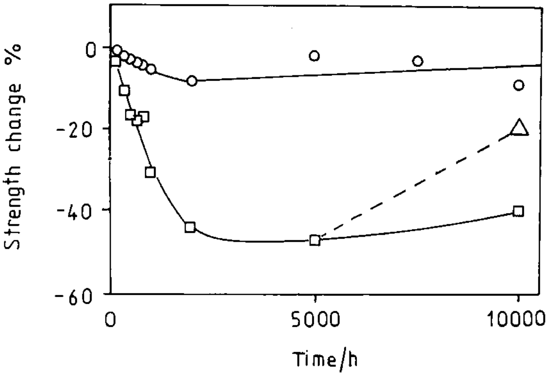

FIGURE 1 Strengths of joints with vinyl phenolic adhesive after exposure to wet air. ○ = 50% r.h., □ = 100% r.h., △ aged for 5000 h at 100% r.h. and then 5000 h at 50% r.h. (Ref. 9).

WATER UPTAKE BY FILMS OF ADHESIVES

Figure 2 shows an uptake plot for a nitrile phenolic adhesive immersed in water at 50°C. This is an example of Fickian diffusion,[12] in that the initial uptake region is linear and this leads to equilibrium uptake. This type of behaviour is commonly observed for water uptake by films of structural adhesives,[13] but the exceptions which sometimes take place are, firstly, that mass can decrease after the initial uptake stage and, secondly, there can be a second uptake stage. Some of the adhesives used here showed the first of these effects, and the instances are indicated in Table I.

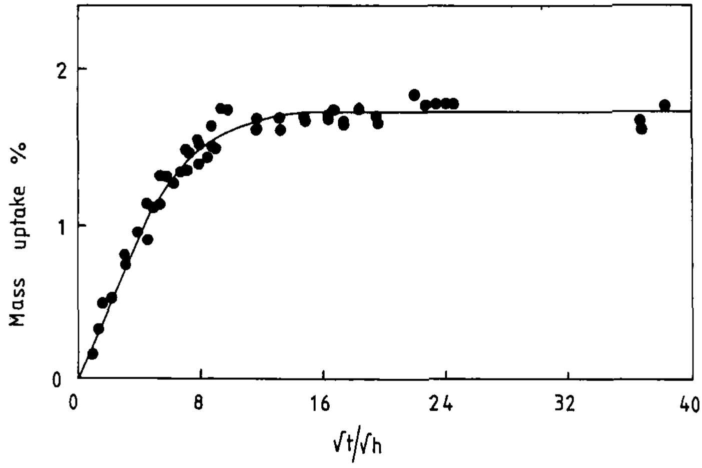

FIGURE 2 Mass uptake of water by a film of NP2 adhesive at 50°C. (Ref. 10).

TABLE I
Water uptake properties of adhesive films and the type of relationship between joint strength and fractional water uptake

Adhesive	M_∞ %	$10^{12}D/\mathrm{m}^2\,\mathrm{s}^{-1}$	Film-uptake plot^{+}	Strength-uptake plot
BSL 312*	2.2	1.8	Fickian	Linear
FM1000	(13.4)	3.2	Max	Initially linear then falls
DGEBA/DAPEE	5.4	0.93	Fickian	Linear**
NP1	(4.5)	4.7	Max	Sigmoid
NP2	1.72	3.2	Fickian	Linear
NP2(primed)	(1.50)	6.8	Max	Linear
VP	8.6	2.3	Fickian	Sigmoid

* From saturated water vapour. Other data are from the liquid.

** Linear relationship observed with etching, anodising, solvent degreasing and sandblasting as surface treatments. In other cases, adherends were etched in chromic acid.

† This column indicates whether the uptake plot was Fickian or showed a maximum which was followed by weight loss. In the latter case the bracketted values in the M_∞ column indicate the values used in calculating D.

MATHEMATICS OF WATER UPTAKE BY ADHESIVE FILMS AND SQUARE ADHESIVE GLUELINES

The solution to Fick's second equation[14] for the case of an initially dry, thin film of adhesive of thickness l immersed in water, or water vapour at a constant partial pressure, is given by Eq. (1).

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

The origin of coordinates is at the centre of the film, and water concentrations (C) are at points distance x from the centre of the film; C, is the concentration at equilibrium, D is the diffusion coefficient and t is time. Equation (1) assumes that equilibrium is instantaneously established at the faces of the film. By integrating Eq. (1) we obtain Eq. (2), which gives the total mass uptake of water by the film at time t.

$$\frac{M_t}{M_\infty} = 1 - \sum \frac{8}{(2n+1)^2\pi^2} \exp \frac{-(2n+1)^2\pi^2 Dt}{l^2} \tag{2}$$

At short times Eq. (2) simplifies to Eq. (3).

$$M_t/M_\infty = 4(Dt/\pi)^{1/2}/l \tag{3}$$

In these equations M_t is the mass of water absorbed at time t and M_∞ is the mass absorbed at equilibrium. The ratio M_t/M_∞ is known as the fractional uptake, which we will now represent by the symbol U. Thus Eq. (3) indicates that a plot of mass uptake against the square root of time should be initially linear and of slope $4M_\infty(D/\pi)^{1/2}/l$. Some diffusion coefficients which have been obtained from the slopes of water uptake plots, by using this relationship, are shown in Table I; equilibrium uptake levels are also shown.

Equations (1) and (2) apply equally well to thin films and to thick slabs if their dimensions are such that diffusion into the edges can be neglected. If two slabs intersect at right angles (one on the x-axis and the other on the y-axis), then concentrations at points in the prism of intersection are the same as in the adhesive layer of a rectangular lap joint. The fractional uptake ($U_{x,y}$) of water in the adhesive layer can be determined from the fractional uptakes (U_x and U_y) in the two slabs, by using Eq. (4).

$$(1 - U_{x,y}) = (1 - U_x)(1 - U_y) \tag{4}$$

In the case of a square lap joint $U_x = U_y$ whence

$$(1 - U_{x,y}) = (1 - U_x)^2 \tag{5}$$

Equations (4) and (5) can thus be used to calculate overall levels of water uptake in adhesive joints. In doing this it is assumed that metallic adherends are impermeable to water, and water enters adhesive joints by diffusion in the adhesive layer. There are a number of ways by which joint strengths can be compared with the amount of water taken up by the adhesive layer.

One way is to compare simultaneously, on the same graph, joint strengths and water uptake levels. This is done for some joints with an epoxide adhesive in Figure 3. Although the scales of the two ordinates have been adjusted to give a best fit, there is nevertheless an excellent comparison between the points, which are for measured joint strengths, and the line which is the calculated water level.

A second way is to plot joint strength against the fractional water uptake and this is illustrated for a nitrile-phenolic adhesive in Figure 4. It can be seen that there is a linear relationship between strength and water level, and the same relationship has been observed in the majority of cases which we have examined.

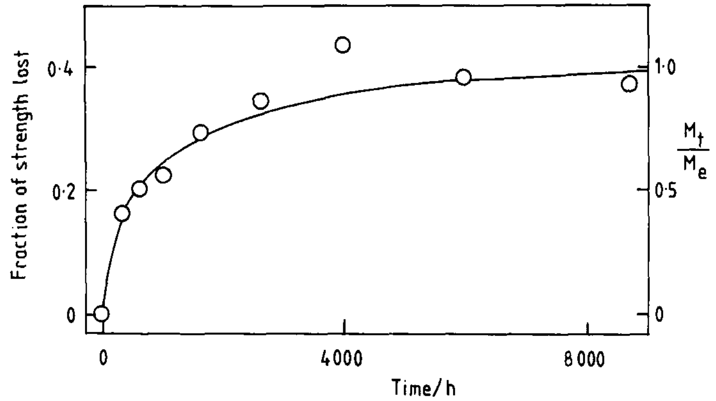

FIGURE 3 Comparison of the strengths of joints with DGEBA/DAPEE adhesive (experimental points) with uptake of water (calculated line). (Ref. 4).

An exception is the epoxide-polyamide adhesive FM1000 (Figure 5) where there is a clear deviation from the straight line at high water content. This was accompanied by the onset of corrosion on the metal from within the broken joints. A second type of exception is the sigmoid curve shown in Figure 6, where there is a sharp drop in strength at about $U = 1/2$. The type of curve followed by each adhesive is indicated in Table I.

MECHANISM OF ADHESION

The major features of the joint strengths are (1) joints at most are only slightly weakened on exposure at 50% r.h., (2) exposure at 100% r.h. leads to partial loss of strength and (3) on reconditioning at 50% r.h. there is some recovery.

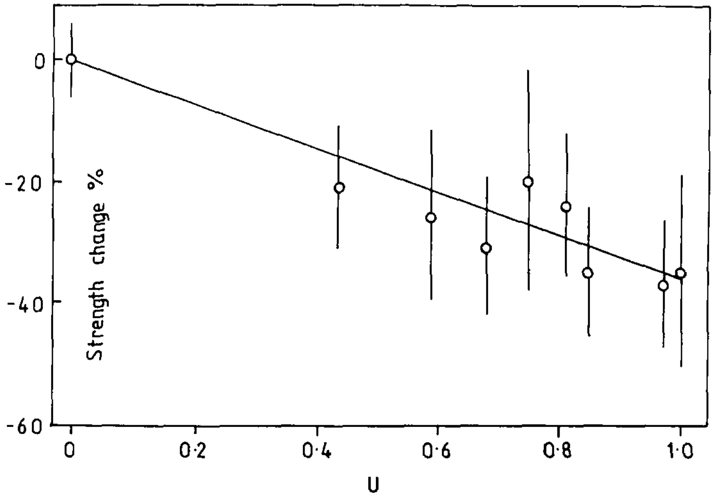

FIGURE 4 Dependence of joint strength on water content for joints with NP2 adhesive. (Ref. 9).

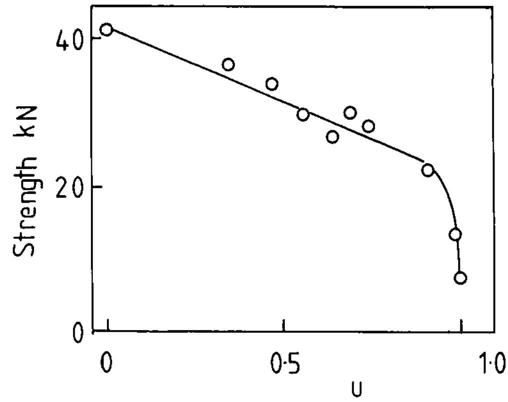

FIGURE 5 Dependence of joint strength on water content for joints with FM1000 adhesive. (Ref. 8).

Available experimental evidence on the uptake of water vapour by structural adhesives is that the isotherms (plots of equilibrium mass uptake against r.h. or some other measure of partial pressure) are straight lines or gentle curves;[13] the sorption isotherm for DGEBA/DAPEE is shown in Figure 7. The consequence of this is that at 50% r.h. the adhesive layers in metal joints would be expected to absorb significant amounts of water. This led Gledhill, Kinloch and Shaw[15] to propose that there must be a critical water concentration, below which weakening does not occur. The data presented here shows this is probably the case for phenolic and epoxide adhesives.

The initial loss of joint strength at 100% r.h. is controlled by the rate at which water diffuses into the adhesive layer. Once within a joint, there are several

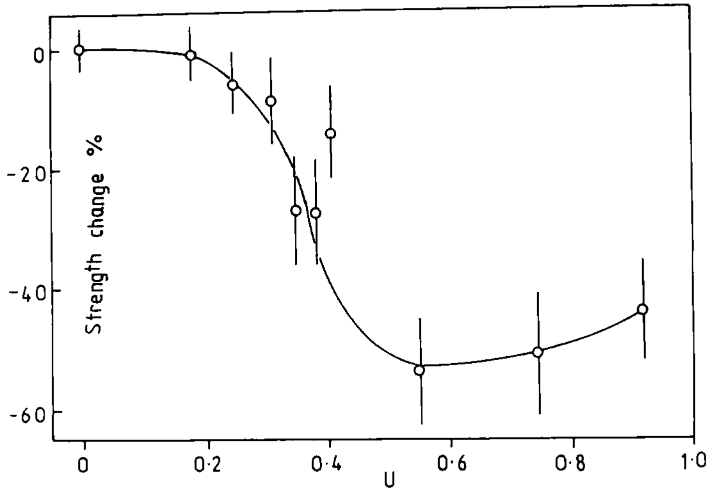

FIGURE 6 Dependence of joint strength on water content for joints with NP1 adhesive. (Ref. 9).

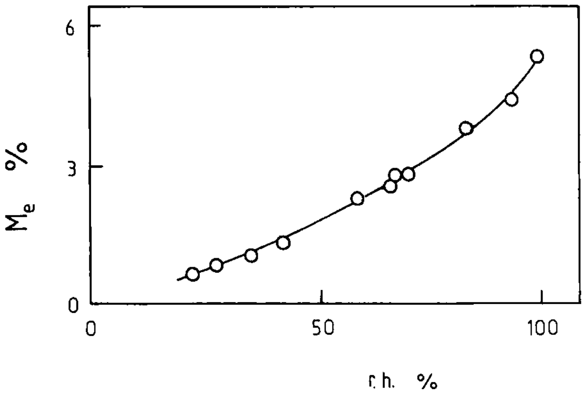

FIGURE 7 Water absorption isotherm for DGEBA/DAPEE adhesive at 50°C. (Ref. 5).

possible ways by which water may cause weakening. These have been reviewed by the author[13] and include reversible (e.g. plasticisation, swelling stresses and weakening of ion-pairs) and irreversible processes (*e.g.* cracking, crazing or hydrolysis of the adhesive and surface displacement of the adhesive by water). Recovery of joint strengths clearly indicates the occurrence of reversible phenomena, and one which can account for the observed behaviour is the weakening of interfacial ion-pairs by water.

If ion-pairs contribute to the interfacial force, the interionic force will be given by Eq. (6).

$$F = q_1 q_2 / 4\pi\kappa\varepsilon_0 r^2 \qquad (6)$$

Where q_1 and q_2 are the ionic charges and r is the interionic distance, ε_0 is the permittivity of a vacuum and κ is the relative permittivity of the medium. Epoxide adhesives have low values of κ $(4-5)$ and phenolics are probably similar, whilst that for water is about 80. Hence a small amount of water entering an adhesive would increase κ and lower F, not to zero, but to a fraction of its original value. Complete removal of water would restore F to its original value.

The relative permittivities of mixtures of water with organic solvents are approximately linear with composition. If this is the case for water-adhesive mixtures and the relative permittivity of the adhesive reasonably represents that surrounding the interfacial ion-pairs, then strength reductions can be calculated. The results of the calculation, using $\varepsilon_0 = 5$ for adhesives and $\varepsilon_0 = 80$ for water are compared with actual falls in strength in Table II. Agreement between the two columns of figures in Table II is considered to be good.

The ion-pair concept allows partial weakening of joints in the presence of water, with recovery when the joints are dried out. This is in contrast to the physical adsorption theory[2,13] which predicts the reduction in strength to zero as water displaces adhesive from the metal oxide and no recovery, because a glassy adhesive (such as those considered here) would have insufficient molecular mobility for it to re-establish intimate contact with the substrate.

TABLE II
Comparison of experimental and calculated falls in joint strengths on aging at 100% relative humidity at 50°C. Chromic acid etched adherends

Adhesive	Fall in joint strength %	
	Experimental	Calculated
BSL 312	50	36
FM1000	78	68
DGEBA/DAPEE	40	45
NP1	54	40
NP2	37	20
NP2 (primed)	14	18
VP	45	56

RECOMMENDATIONS FOR IMPROVEMENTS IN DURABILITY

The diffusion of water is the controlling factor in the initial fall in strengths, when joints are exposed to air at high humidity. There are thus two recommendations for making joints with enhanced durability which arise from this. The first is to make large joints. This will lengthen the diffusion path and increase the times for water uptake. If we consider the case of an infinitely wide lap joint (so that we can neglect diffusion from the sides of the joints) then the times for the centre lines of the adhesive layers to reach half saturation can be calculated from Eq. (1). If we use a value of $1 \times 10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for D then the time for a joint with 1 mm overlap is 10.5 h, rising to 44 d at 10 mm overlap and 120 y at 100 mm.

The ability of an adhesive to transmit water into the joint depends on the permeability coefficient, which can be approximated by the product of diffusion coefficient and equilibrium uptake. The recommendation which follows from this is to choose an adhesive with a low water permeability coefficient.

CONCLUSIONS

1. High humidity weakens adhesive joints, but after an initial fall in strength which is controlled by the rate of water diffusion, there is a levelling out.
2. Joints are not significantly weakened by exposure to air at 50% relative humidity. This indicates a critical water level for weakening.
3. Joints aged at high humidity partially recover their strengths on drying.
4. Falls in strength on aging joints at 100% relative humidity are close to those predicted by the ion-pair theory.

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