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Bonding of Aluminium Alloy with some Phenolic Adhesives and a Modified Epoxide Adhesive, and Strength Changes on Exposure to Moist Air at 50°C

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Single lap joints of aluminium alloy bonded with three phenol-based and one modified epoxide adhesive have been aged at 100% relative humidity (r.h) or at 50% r.h. for up to 10,000 hours at 50°C. Whilst joints are not significantly weakened on exposure at 50% r.h., at 100% r.h. strength falls over about 2000 h and then tends to remain steady. This fall in strength is controlled by the rate at which water enters the adhesive layer. Some joints were exposed firstly at 100% r.h. for 5000 h., and then at 50% r.h. for a further 5000 h whereupon some recovery of strength took place. The effect of moisture on joint strengths can be interpreted in terms of water, by virtue of its high permittivity, weakening ion-pairs at the interface.

X-ray photoelectron spectroscopy has been used to examine fracture surfaces at all stages, showing that visual inspection can lead to false conclusions about the mode of failure.

KEY WORDS Aluminium; durability; epoxide adhesives; ion-pair theory; phenolic adhesives; strength recovery.

INTRODUCTION

Durability in wet environments is a property of prime importance in adhesively bonded metal structures, and this is especially true of

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aircraft structures. While the nature of the substrate and the pretreatment used are known to have an important effect on the durability of joints in aluminium and its alloys, the type of adhesive used is also important.¹ At the commencement of this investigation, which was funded by the Royal Aircraft Establishment (Ministry of Defence), there was evidence² which indicated that metal joints bonded with nitrile-phenolic or vinyl-phenolic adhesives had superior wet resistance over other adhesives such as epoxides, and our intention was to see if this could be substantiated by laboratory durability trials, and possibly to seek the underlying causes.

The general approach has been to expose joints to hot, humid air for various times, and then to examine the fracture surfaces by X-ray photo-electron spectroscopy (XPS).

EXPERIMENTAL

Substrates

The substrate employed was aluminium alloy³ L165/T6 (previously designated as BS3L73) which is clad with a layer (approximately 0.08 mm thick) of 99.90% aluminium. The core has a composition by weight of Al 91.9%, Cr 0.3%, Cu 4.3%, Fe 1.0%, Mg 0.7%, Mn 0.8%, Si 0.8% and Zn 0.2%.

Alluminium alloy panels measuring 450 mm × 75 mm were pre-treated by the following chromic-sulphuric acid etch which is based on a British Standards Institution Code of Practice.⁴

- i) Wipe with a tissue soaked in butanone.
- ii) Immerse in a commercial alkaline degreasing agent (P33-Almeco 18, 30 g dm⁻³) at 64°C for 10 minutes.
- iii) Rinse in a tank of cold tap water for 1½ minutes.
- iv) Immerse in an etching solution of distilled water containing concentrated sulphuric acid (179.5 cm³ dm⁻³), chromium trioxide (68.5 g dm⁻³), copper sulphate (0.39 g dm⁻³) and stearate-free aluminium powder (5 g dm⁻³) at 62°C for 20 minutes. This solution was allowed to age before use.⁵
- v) Rinse in a tank of cold tap water for 1½ minutes.
- vi) Rinse in cold running tap water for 20 minutes.

- vii) Dry in an oven at 60°C for 20 minutes.
- viii) Bonding was carried out within 30 minutes of treatment.

Adhesives

The following film adhesives were used:

Two nitrile phenolic adhesives designated NP1 and NP2.

A vinyl phenolic adhesive (VP).

A modified epoxide adhesive (ME) was used for the purpose of comparison.

NP2 was used both with and without a primer; when used, this was applied with a forward and reverse pass of air brush 30 minutes before application of the adhesive film. Panels were bonded at one edge with an overlap of 12.5 mm, using jigs which we have previously described.⁶ Packing pieces and shims were used to control bondline thickness. Bonds were cured in a hydraulic press under the following conditions which were recommended by the manufacturers:

NP1 at 178°C and 1.03 MPa for 60 minutes

NP2 at 178°C and 0.69 MPa for 60 minutes

VP at 150°C and 0.69 MPa for 30 minutes

ME at 120°C and 0.17 MPa for 30 minutes

Bonded panels were allowed to cool overnight in the press, and were then cut into 28 individual single lap joints, each with 12.5 mm × 12.5 mm overlap. These relatively small joints were chosen to reduce the time scale for water ingress. Cutting was by a band saw with compressed air acting as a coolant. The band speed was 2.5 m s⁻¹ and there were 6 teeth per 10 mm; the panels were fed to the blade fairly slowly.

Testing

Joint strengths were measured on a Monsanto Tensometer 2000 with a crosshead speed of 4.9 mm min⁻¹, and strength of six joints taken from each panel were immediately measured. Only panels with a standard deviation of less than about 5% for strength scatter were accepted. Glue line thicknesses were monitored using an

optical microscope to examine smoothed joint edges; only panels with a value of 0.1 ± 0.005 mm were accepted.

The test conditions consisted of storage at 50°C and either 100% or 50% relative humidity. These were obtained in desiccators containing either distilled water or a saturated solution of potassium carbonate⁷ which were contained in a large oven. Joints were removed at chosen intervals and their strengths measured; six joints were used for each experimental condition.

Some surfaces were examined by X-ray photoelectron spectroscopy within 24 hours of fracture. A VG Escalab 5 instrument, located at Loughborough University of Technology, was employed using AlK_{α} X-rays.

RESULTS AND DISCUSSION

Joint strength

The strengths of freshly prepared and unexposed joints are shown in Figure 1 (error bars are standard deviations), where the superior strength of the modified epoxide adhesive can be clearly seen. All these joints exhibited failure within the adhesive, although with primed NP2 this was close to the primer layer in some areas. The strengths of joints exposed to wet air are shown in Figures 2–6. In these Figures, circular points are used for data at 50% r.h., square points at 100% r.h., and triangles for joints exposed firstly at 100% r.h. for 5000 h., and then at 50% r.h. for a further 5000 h in the expectation that they might recover in strength. All adhesives show a decline in strength after prolonged exposure at 100% r.h., although there are significant differences with the different materials. After 2000 h and 10 000 h the percentage strength losses are:

	NP1	NP2	NP2 (primed)	VP	ME
2000 h	54	37	14	45	30
10,000 h	44	35	16	40	34

This clearly shows the advantages of using a primer with NP2, but otherwise strength changes of the joints are fairly similar. With NP1

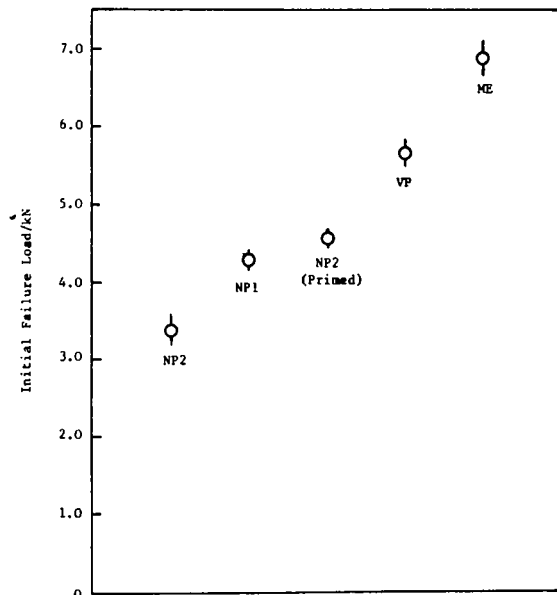


FIGURE 1 Strengths of freshly prepared joints.

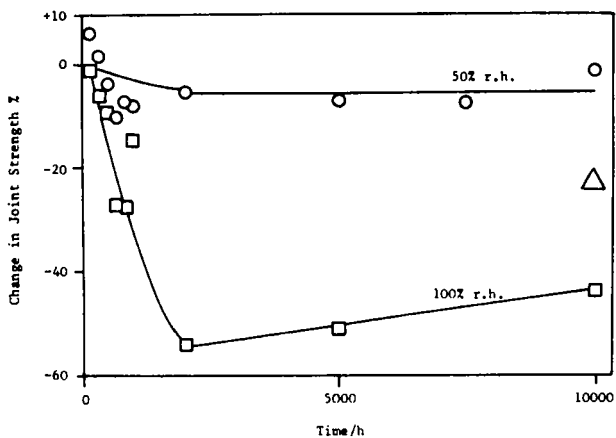


FIGURE 2 Strengths of joints with NP1 adhesive after exposure to wet air at 50°C.

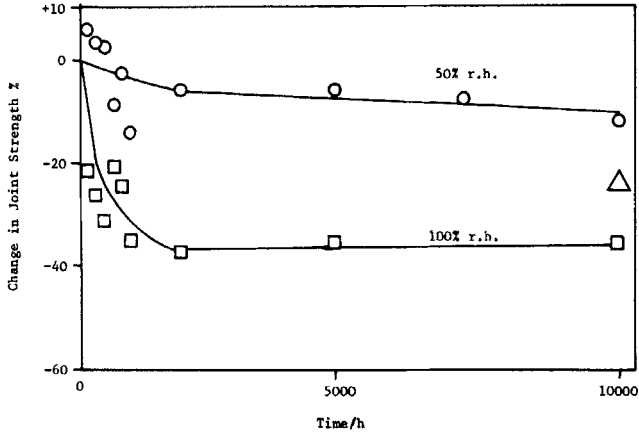


FIGURE 3 Strengths of joints with NP2 adhesive after exposure to wet air at 50°C.

and VP, there is a substantial loss of strength over the first 2000 hours, followed by a slight recovery of strength.

Strength reductions with NP2 (primed) are quite small but with the unprimed surfaces, and with ME, a substantial weakening occurs during the first 2000 hours at 100% r.h. After this strengths remain stable.

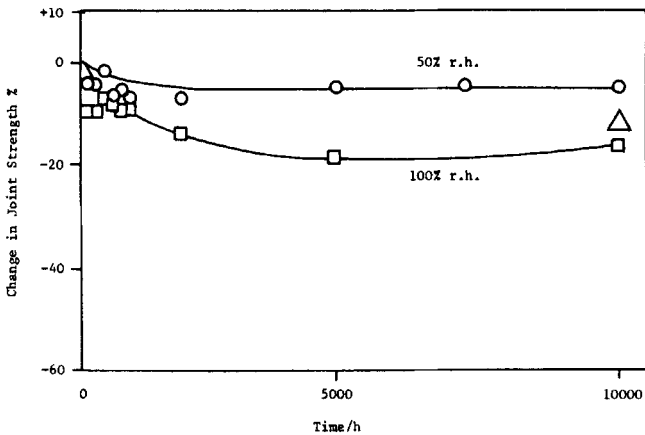


FIGURE 4 Strengths of joints with NP2 (primed) adhesive after exposure to wet air at 50°C.

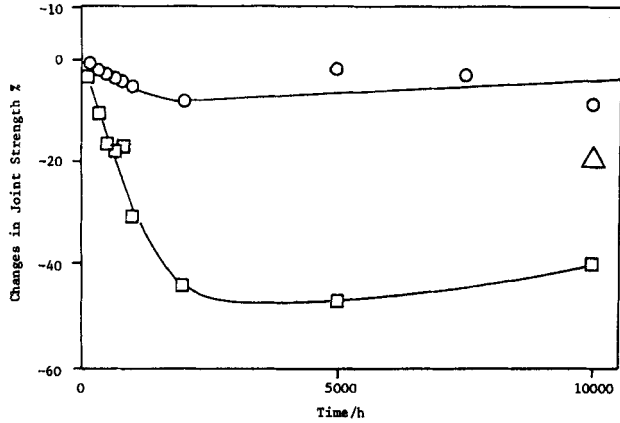


FIGURE 5 Strengths of joints with VP adhesive after exposure to wet air at 50°C.

After 5000 h exposure at 100% r.h., some joints were stored for a further 5000 h under drier conditions; the resulting joint strengths are the triangular points in Figures 2-6. In all cases, some recovery of strength occurs. This drying was not complete but to assume that further drying would cause increased recovery is clearly speculation.

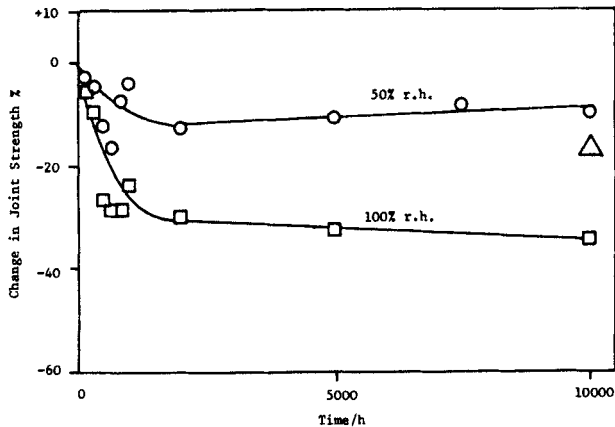


FIGURE 6 Strengths of joints with ME adhesive after exposure after exposure to wet air at 50°C.

Fracture surfaces—visual

Visual inspection of fracture surfaces showed areas of bare metal after 1000 hours exposure. This was slight with NP1 but with ME it increased to over 50% of the total area at 10,000 hours. Both primed and unprimed NP2 showed apparent interfacial failure at all times. VP only showed bare metal after 5000 hours.

On drying out joints which had been exposed to saturated air for 5000 hours, no changes occurred in the locus of fracture with NP1, NP2 and NP2 (primed), whilst ME showed less bare metal and no bare metal was evident with VP. Joints bonded with ME showed cohesive failure with the crack jumping from one surface to the other. This has been noted before in this adhesive⁸ and, according to Bascom and Cottingham,⁹ is the result of a propagating crack being deflected at the interface. Because of the high strength of this adhesive (Figure 1), a distinct bending of the adherent was visible before fracture, which would introduce a significant cleavage stress to the joints.

Fracture surfaces—XPS

Results of XPS analyses of fracture surfaces with NPI adhesive are shown in Table I. The most significant feature is the total absence of aluminium, even from areas which appeared to be bright metal. All fracture surfaces are essentially covered with adhesive, as is shown by the similar levels of C, N and O on both sides of the broken joint. 100% r.h. leads to the appearance of a small amount of zinc, and silicon appears after 10,000 h at 100% r.h.

TABLE I
XPS analyses of fracture surfaces with adhesive NP1

Exposure		Si	C	Atomic %		Zn	Na
				N	O		
Nil		—	89.3	5.0	5.8	—	—
2000 h/100% r.h.		—	87.8	2.4	7.7	1.0	1.2
10,000 h/50% r.h.	Adhesive	—	89.9	3.9	5.8	—	—
	'Metal'	—	86.2	5.0	8.0	—	—
10,000 h/100% r.h.	Adhesive	1.7	84.1	2.5	9.3	0.3	—
	'Metal'	1.4	84.1	4.0	8.9	0.7	—
5000 h/100% r.h. then 5000 h/50% r.h.	Adhesive	—	88.0	4.0	7.0	1.0	—
	'Metal'	—	80.2	4.5	6.3	1.0	—

TABLE II
XPS analyses of fracture surfaces with adhesive NP2

Exposure		Al	S	Atomic %			Zn	Na
				C	N	O		
Nil		—	0.4	88.4	7.8	3.4	—	—
168 h/100% r.h.	Adhesive	—	—	85.6	6.7	7.3	—	0.3
	'Metal'	—	—	82.5	0.7	7.3	—	0.3
1000 h/100% r.h.	Adhesive	1.1	0.4	81.3	4.4	11.7	0.7	0.4
	'Metal'	15.5	0.3	44.5	2.4	31.7	1.0	0.5
10,000 h/50% r.h.	Adhesive	—	0.4	88.3	8.6	2.8	—	—
	'Metal'	—	0.5	87.9	9.0	2.4	—	—
10,000 h/100% r.h.	Adhesive	1.2	1.0	76.2	5.4	13.8	1.7	0.8
	'Metal'	3.3	1.6	68.6	5.7	17.7	1.9	1.1
5000 h/100% r.h. then 5000 h/50% r.h.	Adhesive	0.5	0.5	84.9	8.3	5.7	0.2	—
	'Metal'	1.0	0.3	83.9	8.8	5.9	0.1	—

XPS analyses with NP2 appear in Table II. Aluminium appears on the fracture surfaces after 1000 h at 100% r.h. and is seen in lesser quantities after 10,000 h at 100% r.h. and also after drying. Also, whenever aluminium appears, zinc appears as well, although zinc was not detected on the metal surface at any stage of the pretreatment process.

The sampling depth in XPS is around 5–10 nm,¹⁰ so the detection of an element may only mean that it resides within this depth of the surface rather than at the actual surface. Nevertheless, the figure of 15.5% Al observed after 1000 h at 100% r.h. represents quite a

TABLE III
XPS analyses of fracture surfaces with adhesive NP2 (primed)

Exposure		Al	Si	S	Atomic %			Zn	Na
					C	N	O		
Nil		—	—	0.5	87.4	7.6	4.5	0.1	—
168 h/100% r.h.	Adhesive	—	—	0.6	88.1	8.4	2.7	0.2	—
	'Metal'	0.5	—	0.5	86.5	8.7	3.6	0.2	—
1000 h/100 r.h.	Adhesive	0.6	—	0.4	85.4	8.9	4.5	0.1	—
	'Metal'	0.3	—	0.5	85.1	9.6	4.3	0.2	—
10,000 h/50% r.h.	Adhesive	—	0.3	—	86.3	7.1	6.3	—	—
	'Metal'	—	0.3	—	83.6	9.6	6.1	—	0.3
10,000 h/100% r.h.	Adhesive	6.7	—	—	64.4	4.8	22.3	1.5	0.3
	'Metal'	8.0	—	—	64.4	5.2	20.9	1.0	0.5
5000 h/100% r.h. then 5000 h/ 50% r.h.	Adhesive	6.9	—	0.8	64.7	5.3	20.8	1.1	0.5
	'Metal'	12.4	0.4	0.4	54.8	3.6	26.8	1.1	0.5

TABLE IV
XPS analyses of fracture surfaces with adhesive VP

Exposure	Al	Si	Atomic %		O	Na
			S	C		
Nil	0.6	—	—	72.7	26.6	—
1000 h/100% r.h.	1.2	—	0.2	72.4	24.6	1.7
10,000 h/50% r.h.	Adhesive	—	—	73.1	26.9	—
	'Metal'	—	—	73.5	25.1	—
10,000 h/100% r.h.	Adhesive	0.9	3.3	—	72.4	23.0
	'Metal'	3.8	4.1	—	69.5	23.6
5000 h/100% r.h.	Adhesive	—	2.2	—	71.0	25.7
then 5000 h/50% r.h.	'Metal'	—	2.3	—	71.5	26.2

large amount of aluminium in the sampling depth (pure Al_2O_3 would give a figure for Al = 40%), and this probably represents a significant level of interfacial failure or failure in the oxide layer.

Table III shows that aluminium is present in significant quantities in the recovered sample of NP2 (primed). Aluminium appears after only 168 h at 100%, but again does not appear even after 10,000 h at the lower relative humidity of 50%. Zinc is now more apparent and now may occur without aluminium. With VP (Table IV) a small amount of aluminium is seen with the initial dry joints and also appears on exposure at 100% r.h. After 10,000 h at saturation, some silicon appears and this is also seen in the recovered samples.

With the epoxide adhesive (Table V), we have the only case where aluminium is evident after an exposure at 50% r.h., and again aluminium can reach the relatively high level of 11.2% after 10,000 h at 100% r.h.

TABLE V
XPS analyses of fracture of surfaces with adhesive ME

Exposure	Al	Si	Atomic %			
			C	N	O	
Nil	—	—	81.0	3.7	15.3	
1000 h/100% r.h.	8.5	—	54.9	6.4	30.2	
10,000 h/50% r.h.	Adhesive	1.3	—	75.5	8.8	14.4
	'Metal'	1.7	—	75.5	7.7	14.5
10,000 h/100% r.h.	Adhesive	3.1	1.2	73.9	4.4	17.4
	'Metal'	11.2	0.2	49.5	2.1	36.0
5000 h/100% r.h.	Adhesive	2.4	—	73.9	9.1	14.5
then 5000 h/50% r.h.	'Metal'	4.6	—	68.0	8.1	19.3

TABLE VI
Ash analyses of adhesives and primer

Adhesive	Total residue % by wt.	% Composition of total weight Insoluble		
		Zn	Mg	Ash
NP1	2.00	0.91	5.98×10^{-3}	0.72
NP2	2.64	1.95	5.05×10^{-3}	—
VP	0.03	—	—	—
ME	1.99	3.98×10^{-4}	2.58×10^{-3}	1.83
Primer	5.70	1.82	3.64	—

Visual inspection of fracture surfaces can clearly lead to false conclusions about the mode of failure.

To explore the possibility that the adhesives, or primer, were the sources of silicon and zinc, they were ashed at 770°C and the residues analysed by atomic absorption spectroscopy. Results appear in Table VI. Zinc occurs in appreciable quantities in NP1, NP2 and the primer, and the insoluble ash in NP1 and ME is probably silicon dioxide. The zinc and silicon compounds may well be mobile in the adhesive under conditions of high humidity, and collect to form a weak layer. Wake¹¹ has stated that some metals, of which zinc is a notorious example, react with organic acids present in paint formulations or with rosin acid impurities in tackifiers in adhesive formulations to form soaps which easily fail cohesively.

Joint strengths and water uptake

We have undertaken a study of the uptake of water by cured films and full details of this will appear subsequently.¹² The results of this study are summarised in Table VII; in all cases Fickian uptake¹³ was observed. Previous results from these laboratories compared the strengths of lap joints with the total amount of water to have entered joints and observed in almost every instance a linear relationship between the two parameters. The amount of water in joints was calculated from the water diffusion coefficient in films of the adhesives, and linearity was observed with aluminium lap joints for an aliphatic amine cured epoxide adhesive (di(1-aminopropyl-3-ethoxy)ether with the diglycidyl ether of bisphenol A) using five

TABLE VII
Diffusion coefficients and equilibrium water uptake of water in cured adhesive films

Adhesive	Equilibrium	
	water uptake %	$10^{12}D \text{ m}^2 \text{ s}^{-1}$
NP1	4.5	4.7
NP2	1.72	3.2
NP2 (Primed)	1.50	6.8
VP	8.6	2.3
ME	3.6	7.2

different surface treatments¹⁴ and a rubber-modified epoxide adhesive with chromic acid etched adherends in double lap joints.⁸ With the epoxide-polyamide adhesive FM 1000,^{6,15} however, strengths were linear up to about 90% of saturation, whereupon larger losses took place.

The results of examining the current adhesives in this manner are shown in Figures 7-11. The linear relationship is upheld with both

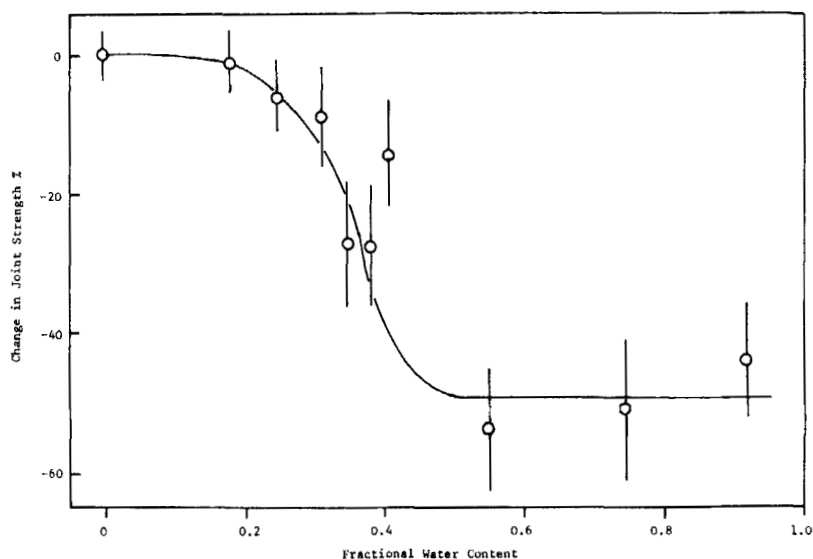


FIGURE 7 Dependence of joint strength on calculated water content of the adhesive layer for NP1.

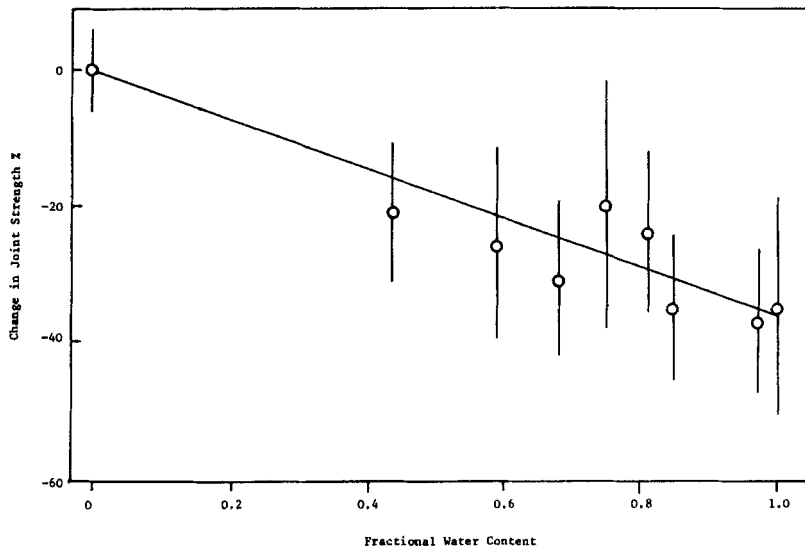


FIGURE 8 Dependence of joint strength on calculated water content of the adhesive layer for NP2.

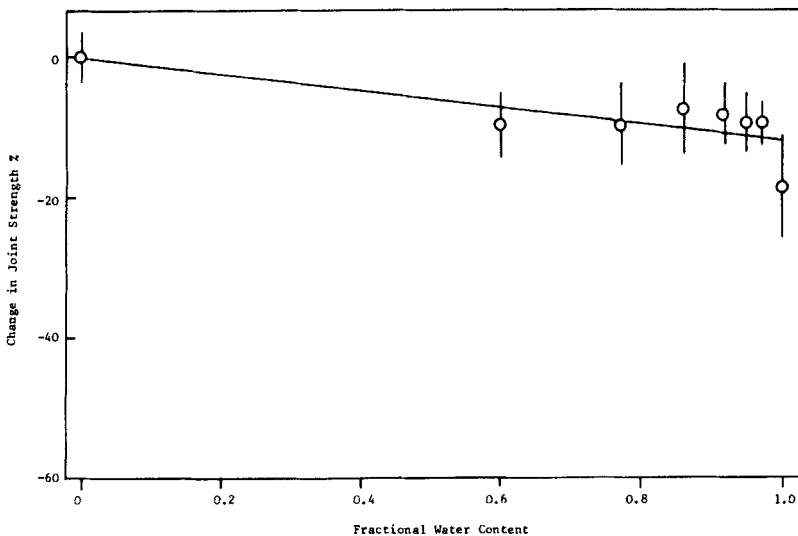


FIGURE 9 Dependence of joint strength on calculated water content of the adhesive layer for NP2 (primed).

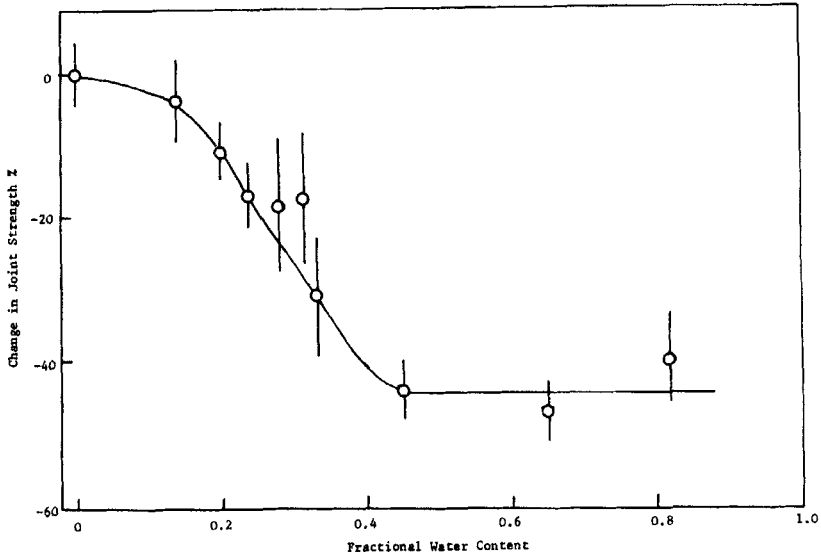


FIGURE 10 Dependence of joint strength on calculated water content of the adhesive layer for VP.

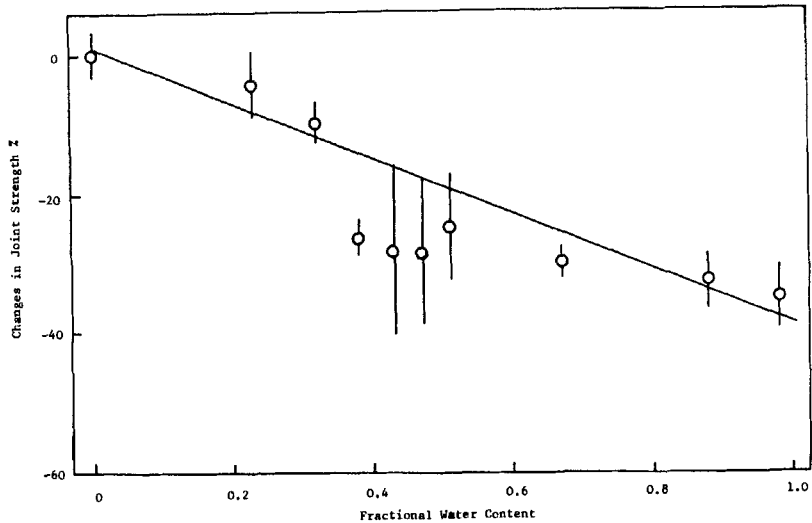


FIGURE 11 Dependence of joint strength on calculated water content of the adhesive layer for ME.

primed and unprimed NP2, and with ME (our earlier experiments with this adhesive used double lap joints,⁸) but there are distinct deviations from linearity with NP1 and VP. Here, joint strengths fall to a minimum when the fractional water content reaches about 0.5, and any increases in strength at higher water levels are considered to be insignificant. The abscissae on these plots are fractional water content, such that at 0 the joint is free from water whilst it is saturated at 1.0.

Mechanism of adhesion

The major features of the data presented in Figs. 2–6 are (1) most joints are only slightly weakened by exposure to air at 50% r.h., (2) exposure at 100% leads to a partial loss of strength over about the first 2000 h and after this strengths remain fairly stable, and (3) joints recover some strength on reconditioning at 50% r.h.

The humidity of laboratory air in England remains fairly static at about 45–55% throughout the year and there have been several reports that joints are not weakened by exposure under such conditions. These have included work by Kinloch *et al.*¹⁵ who exposed butt joints with an epoxide adhesive at 55% r.h. for 2500 h., and Comyn *et al.*^{6,8,14,16} who exposed joints with modified epoxide adhesives in laboratory air for up to 10,000 h. From abroad, De Lollis¹⁷ has referred to some epoxide-aluminium joints which showed no loss of strength after exposure to laboratory air for up to 11 years.

Available experimental evidence on the uptake of water vapour by structural adhesives is that the isotherms (plots of equilibrium water uptake against r.h. or some other measure of partial pressure) are straight lines or gentle curves;¹⁸ in other words, adhesive layers in metal joints would be expected to absorb significant amounts of water at 50% r.h.

This led Kinloch *et al.*¹⁵ to propose that there must be a critical water concentration in the adhesive layer, below which weakening does not occur; the current work demonstrates that this is probably the case for phenolic-based as well as epoxide adhesives.

The initial loss of strength over the first 2000 h at 100% r.h. is controlled by the rate at which water diffuses into the adhesive layer and this can be demonstrated in the following manner. If a long

metal-adhesive-metal sandwich of width $2l$ is exposed to water vapour then the water concentration (C) at points across the adhesive layer at time t is given by the following solution to Fick's second law of diffusion.¹⁹

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

Here, C_1 is the water concentration at equilibrium, and x is the space coordinate across the adhesive layer with origin along the centre line of the sandwich and D is the diffusion coefficient. Diffusion into the ends of the sandwich is neglected. Some values of C/C_1 at the centre of the sandwich (where $x=0$ and hence the cosine term in Eq. (1) is unity) are shown as a function of Dt/l^2 in Figure 12.

Now, if two such long sandwiches intersect at right angles, the intersecting zone represents a square lap joint. Diffusion into this would be from all four sides and the concentration at the centre of the joint is given by Eq. (2).¹⁸

$$\left(1 - \frac{C}{C_1}\right)_{\text{joint}} = \left(1 - \frac{C}{C_1}\right)_{\text{sandwich}}^2 \quad (2)$$

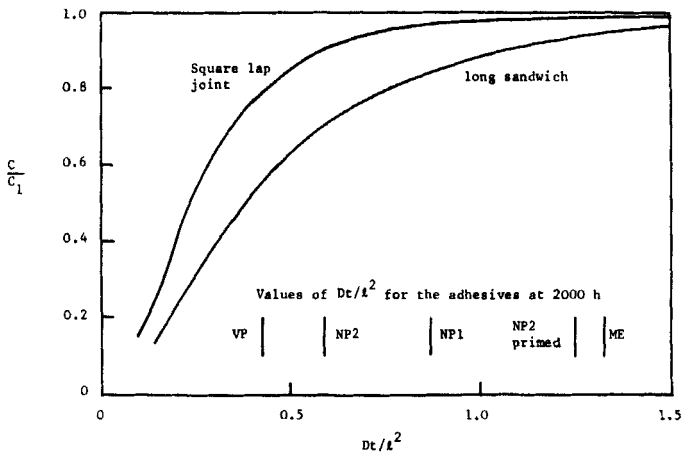


FIGURE 12 Calculated water concentrations at the centre-line of a long sandwich and at the centre point of a square lap joint.

Some values of water concentration at the centre of the square lap joint are shown in Figure 12, where the values of Dt/l^2 for each adhesive system at 2000 h also appear. With the exception of VP, all adhesives have attained a fractional water content above 0.9 at the centre after 2000 h. VP would require a little longer, about 2700, to reach this level. The rate at which water enters a joint is thus a prime factor in controlling the rate of strength decline.

Once within a joint, there are several possible ways by which water may cause weakening. These have recently been reviewed by Comyn¹⁸ and include reversible (*e.g.*, plasticization, the introduction of swelling stresses and weakening of ion-pair interactions) and irreversible processes (*e.g.*, cracking, crazing or hydrolysis of the adhesive and surface displacement of the adhesive by water). In all cases studied, there are significant increases in strength when joints aged for 5000 h at 100% r.h. are then reconditioned at 50% r.h. for a further 5000 h., and this clearly indicates the occurrence of reversible processes. A reversible process which can account for the observed behaviour is the effect of water on ion-pair interactions at the interface. If ion-pairs contribute to the interfacial force, the force between an ion-pair is given by the expression:

$$F = \frac{q_1 q_2}{4\pi\kappa\epsilon_0 r^2} \quad (3)$$

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 the relative permittivity (dielectric constant) 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 the water would restore F to the original value.

The relative permittivities of mixtures of water with organic solvents are approximately linear with composition, examples being water-dioxan and water-methyl cellosolve mixtures.^{20,21} If this is the case for water-adhesive mixtures and the relative permittivity of the adhesive reasonably represents that at the interface, then using $\epsilon_0 = 5$ for adhesives and ϵ_0 (water) = 80 we would obtain, using Eq.

(3), the following strength reductions:

	NP1	NP2	NP2 Primed	VP	ME
Predicted Fall in Strength (%)	40	20	18	56	35
Actual Fall in Strength at 2000 h (%)	54	37	14	45	30

The following calculation illustrates how the figure of 40% is reached in the case of NP1. The ionic charges are unaffected by water uptake and we will assume that the interionic distance is also unchanged. Hence, Eq. (3) may be used to compare the interionic force in wet and dry joints, thus:

$$\frac{F(\text{wet})}{F(\text{dry})} = \frac{\epsilon_0(\text{dry adhesive})}{\epsilon_0(\text{wet adhesive})} \quad (4)$$

But

$$\begin{aligned} \epsilon_0(\text{wet adhesive}) &= C_1 \epsilon_0(\text{water}) + (1 - C_1) \epsilon_0(\text{adhesive}) \\ &= 0.045 \times 80 + 0.955 \times 5 = 8.37 \end{aligned}$$

Thus

$$\frac{F(\text{wet})}{F(\text{dry})} = \frac{5}{8.37} = 0.60$$

which represents a 40% reduction in strength. We have taken the value of C_1 from Table VII and assumed $\epsilon_0(\text{adhesive}) = 5$ and $\epsilon_0(\text{water}) = 80$.

This agreement is regarded as good, and deviations between predicted and actual figures may be due to an uneven distribution of water, possibly due to the isolation of some water in droplets¹⁸ which are often referred to as clusters.

This approach allows partial weakening of joints in the presence of water, with recovery when the joints are dried. This is in contrast to the physical adsorption theory^{18,22} which predicts the reduction of joint strength to zero as water displaces adhesive from the metal oxide, and no recovery as a crosslinked adhesive would have

insufficient molecular mobility for it to establish intimate contact with the substrate.

Clearly, interfacial ion-pairs can arise in with phenolic adhesives by phenol groups being adsorbed as the phenolate ion, and Comyn has proposed a route for their formation with amine-cured epoxides.¹⁸

CONCLUSIONS

1) Strengths of all joints decline over a period of about 2000 h at 100% r.h. and 50°C and then remain relatively static. The rate of fall is controlled by the rate of water diffusion into the adhesive layer.

2) The levels of weakening on exposure at 50% r.h. are low.

3) All joints show some recovery in strength on reconditioning at 50% r.h.

4) For the systems studied, phenolic adhesives show no advantages in durability over the epoxide.

5) The use of a primer with the nitrile-phenolic adhesive gives much improved durability.

6) Visual inspection of fracture surfaces can incorrectly indicate the occurrence of interfacial failure.

7) The decline of joint strength on exposure at 100% r.h. is a linear function of fractional water uptake for NP2 and ME adhesives, but not with NP1 and VP.

8) The water durability data can best be explained in terms of the weakening effect which water has on ion-pairs at the interface; the partial recovery in joint strength on reconditioning at 50% r.h. can be explained likewise.

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