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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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To cite this Article Kinloch, A. J.(1979) 'Interfacial Fracture Mechanical Aspects of Adhesive Bonded Joints—A Review', *The Journal of Adhesion*, 10: 3, 193 – 219

To link to this Article: DOI: 10.1080/00218467908544625

URL: <http://dx.doi.org/10.1080/00218467908544625>

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Interfacial Fracture Mechanical Aspects of Adhesive Bonded Joints—A Review

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(Received April 21, 1979; in final form May 15, 1979)

A serious limitation frequently encountered in the use of structural adhesives is the deleterious effect moisture has upon the strength of a bonded component, especially when the component is also subjected to conditions of relatively high stress and temperature. It is generally recognised that while the locus of failure of well prepared joints is invariably by cohesive fracture in the adhesive layer, after environmental attack it is via failure in the interfacial regions. This interfacial locus of failure focuses attention on interfacial fracture mechanical considerations. This paper reviews mechanisms of environmental failure and considers techniques for estimating and increasing the service-lifetimes of bonded components. Particular emphasis is given to the contribution from the application of continuum fracture mechanics concepts to the study of environmental attack on structural adhesive joints.

INTRODUCTION

Adhesives are being increasingly used in structural engineering applications but a problem frequently encountered is that the mechanical properties of the bonded component may rapidly deteriorate upon exposure of the joint to its normal operating environment. Unfortunately for the adhesion scientist one of the most harmful environments for adhesive joints is water and this paper reviews mechanisms of failure, predictive techniques for estimating service-lifetimes and methods for increasing durability, with particular emphasis on the contribution from workers who have employed a continuum fracture mechanics approach to study environmental attack.

GENERAL OBSERVATIONS

It is of interest to distill from the many outdoor and accelerated laboratory trials some general observations on the parameters which influence joint durability and the mode of joint failure.

Firstly, the obvious statement, namely, that after exposure to hostile environments there have been observed unexpected, premature failures of bonded components or, alternatively upon subsequent testing of adhesive joints considerable reductions in their load-bearing capability have been recorded. The extent of the problem is illustrated in Figure 1 which shows the loss of strength of epoxy-polyamide/aluminium-alloy joints after exposure to a hot-wet tropical environment, while the hot-dry climate has little effect.^{1,2}

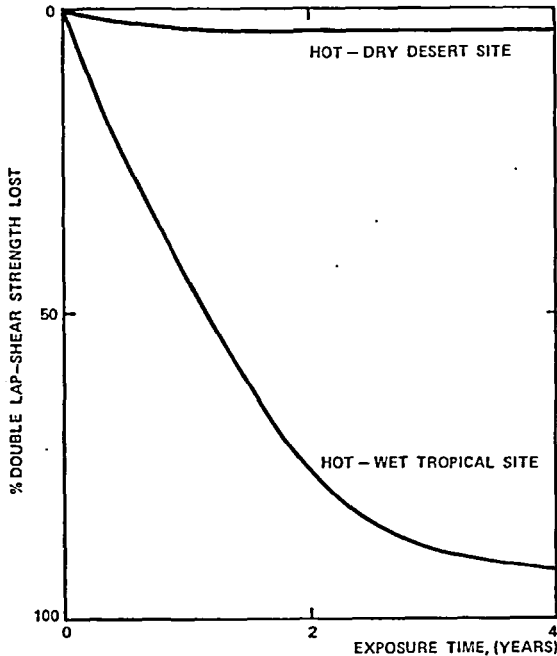


FIGURE 1 Effect of outdoor weathering on the strength of epoxy-polyamide/aluminium-alloy (chromic-sulphuric acid-etch surface pretreatment) joints.

Secondly, while the locus of joint failure of well prepared joints is invariably by cohesive fracture in the adhesive layer, after environmental attack it is by apparent interfacial failure between the adhesive (or primer) and the substrate. This interfacial locus of failure means that interfacial fracture mechanical aspects of adhesive joints become of vital importance.

Thirdly, the following parameters affect joint durability:

Environment The presence of an hostile environment is, of course, the essence of the problem and water, as mentioned above, is undoubtedly the most harmful and most commonly encountered environment.

Adhesive type It is well known that the older phenolic-based structural adhesives generally impart superior joint durability than the more modern epoxide-based adhesives.¹⁻⁴ However, the latter type are now preferred on the basis of their lower cure-temperature/pressure requirements and generally superior peel strengths.

Substrate Joints to metallic substrates present the main problem, *i.e.*, steels, aluminium and titanium and their alloys. Joints to plastics, glass- and carbon-fibre reinforced plastic are far less susceptible to environmental attack; this is not to say that such joints never suffer from environmental attack but when this does occur it is usually the substrate, *e.g.*, the composite material, which is itself attacked more readily and rapidly than the adhesive/substrate interface.

Substrate surface pretreatment This is an extremely important factor. To

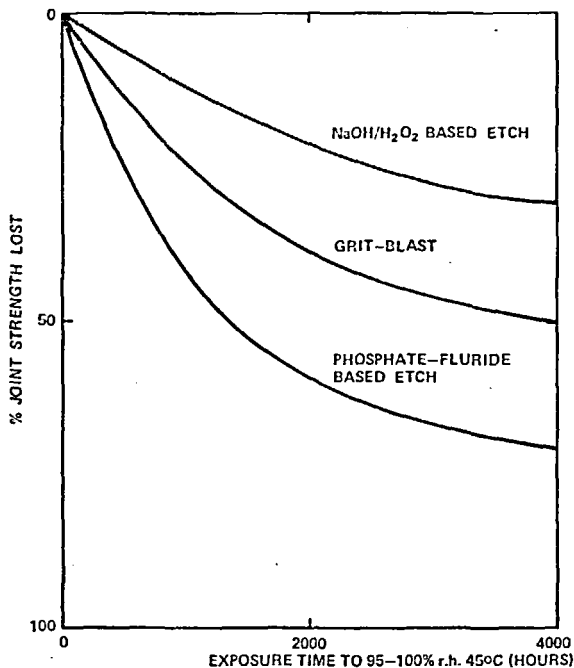


FIGURE 2 Effect of substrate surface pretreatment on the durability of epoxy/titanium joints.

ensure initially strong joints it is usually sufficient to remove surface contamination, weak oxide layers, *etc.*, but to produce durable joints it is also necessary to form stable oxides which are "receptive" to the adhesive and, also, frequently to employ a specially developed primer. The effects of various surface pretreatments on the durabilities of epoxy/titanium² and epoxy/aluminium-alloy⁵ joints are shown in Figures 2 and 3 respectively and clearly demonstrate the importance of selecting an adequate pretreatment. The effectiveness of a pretreatment is often also dependent on the actual alloy type and manufacturing process employed.

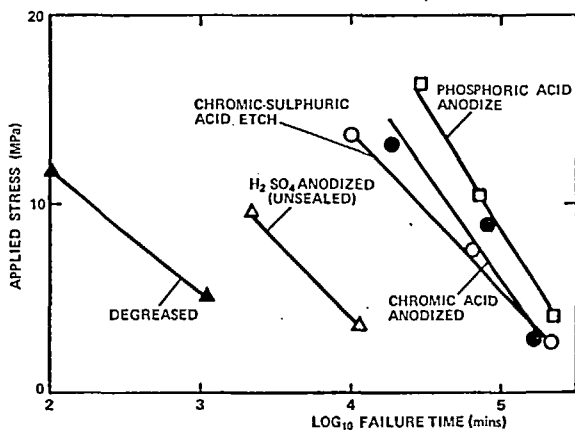


FIGURE 3 Applied stress versus failure time for nitrile-epoxy/aluminium-alloy joints exposed to 100% RH, 52°C.

Temperature Increasing the temperature increases the rate of strength loss.

Applied stress The presence of an applied stress decreases the joint's service-life, and this is illustrated in Figure 3.

Joint design Since it is the interface region which is the failure site after environmental exposure a joint design which has a relatively high stress concentration at, or near, the interface will tend to reveal durability effects more readily, *e.g.*, the Boeing wedge-test⁶ or peel test have greater sensitivities towards environmental attack than, say, the conventional lap-joint.

The use of a continuum fracture mechanics approach to the study of environmental failure has contributed considerably to our understanding of the rôle of applied stress and the effects of joint design. Indeed, the fracture mechanics studies have directly led to the introduction, and now widespread use, of the Boeing wedge-test to rank adhesives and surface pretreatments as to their environmental resistance.

MECHANISMS OF FAILURE

As stated above, the locus of joint failure after environmental exposure is usually at, or very close to, the interface. Thus, while the adhesive, especially if moisture sensitive, may suffer some loss of modulus⁷ and some loss of strength when tested at elevated temperatures near its glass transition temperature due to plasticisation by water, it is the interfacial regions on which our attention must be focused if the mechanisms are to be identified. Essentially, two mechanisms which are complementary rather than exclusive, have been proposed to account for the above observations: one examines the stability of the adhesive/metal oxide interface from a thermodynamic standpoint and the other considers the stability of the metal oxide.

Interface stability: thermodynamic considerations

The thermodynamic work of adhesion, W_A , required to separate unit area of two phases forming an interface may be related to the surface free energies by the Dupré equation. In the absence of chemisorption, interdiffusion and mechanical interlocking the reversible work of adhesion, W_A , in an inert medium may be expressed by:

$$W_A = \gamma_x + \gamma_y - \gamma_{xy} \quad (1)$$

where γ_x and γ_y are the surface free energies of the two phases and γ_{xy} is the interfacial free energy. In the presence of a liquid (denoted by the suffix 'L'), the work of adhesion, W_{AL} , is:

$$W_{AL} = \gamma_{xL} + \gamma_{yL} - \gamma_{xy} \quad (2)$$

For a typical organic adhesive/metal oxide interface the work of adhesion, W_A , in an inert atmosphere, *e.g.*, dry air, usually has a large positive value, indicating thermodynamic stability of the interface. However, in the presence of a liquid, the thermodynamic work of adhesion, W_{AL} , may well have a negative value, indicating the interface is now unstable and will dissociate. Thus, calculation of the terms W_A and W_{AL} may enable the environmental stability of the interface to be predicted.

Some examples of values of W_A and W_{AL} are shown in Table I⁸⁻¹⁰. A similar approach has been adopted by Kaelble.¹¹

The change from a positive to negative work of adhesion provides a driving force for the displacement of adhesive on the metal oxide or glass surface by water. It is therefore to be expected that if a joint is subjected to a humid environment there will be a progressive encroachment into the joint of debonded interface. This will have the effect of progressively reducing the joint strength and also of progressively changing the locus of failure from cohesive within the adhesive to interfacial between adhesive and substrate. This is exactly what has been observed in practice.

TABLE I
Values of W_A and W_{AL} for various interfaces

Interface	Work of adhesion	
	Inert medium, W_A (mJ/m ²)	In water, W_{AL} (mJ/m ²)
Epoxy/ferric-oxide	291	-255
Epoxy/silica	178	-57
Epoxy/aluminium-oxide	232	-137
Epoxy/carbon-fibre-reinforced plastic (cfrp)	88→90	22→44

However, for the epoxy/cfrp interface both W_A and W_{AL} are positive indicating greater stability of the epoxy/cfrp interface compared to those between epoxy and highly polar substrates such as glass and metal oxides. This stability is reflected in the locus of failure for cfrp/epoxy/metal joints, after environmental ageing, invariably being at the epoxy/metal interface or within the cfrp substrate.

This thermodynamic approach may also be employed to predict the stability of any interface in any liquid, providing chemisorption and interdiffusion across the interface are absent. Indeed, thermodynamic considerations predict that an epoxy/ferric-oxide interface will be stable in ethanol but dissociate in formamide and this has been experimentally confirmed.⁸

Finally, it should be noted that the thermodynamics as stated in Eqs. (1) and (2) take no account of interfacial adhesion forces arising from primary, chemical bonds or mechanical interlocking. Further, they provide no information on the expected service-life of joints upon being stressed in hostile environments. For this data the thermodynamic analysis needs to be combined with either a stress-biased activated rate theory, as developed by Zurkov and co-workers,^{12,13} and used in joint fracture studies by Levi *et al.*,¹⁴ or a continuum fracture mechanics approach and such approaches should be considered as complementary rather than mutually exclusive.

Locus of failure

Confirmation that the epoxy/mild-steel joints (*i.e.*, the epoxy/ferric-oxide interface) did indeed fail exactly at the interface after environmental attack, as predicted, was obtained by employing modern surface analytical techniques such as Auger and X-ray photoelectron spectroscopy.¹⁵ The direct examination of surfaces and contaminants on them has recently become

possible by the use of Auger electron and X-ray photoelectron spectroscopy (AES and XPS respectively). These two techniques are extremely useful in adhesion studies in that both enable the composition of the outer 1 to 5 atomic layers of the surface of a solid to be analysed. The basic technique in AES consists of bombardment of the surface with a beam of electrons in the range of 1–5 keV and analysis of the energies of the ejected electrons, which usually provides only an elemental analysis. In XPS, photoelectrons (and Auger electrons) are generated when the surface is flooded with soft X-rays; the photoelectrons have discrete binding energies whose values depend upon both the element and its state in the atomic matrix in the surface. Therefore it is possible to determine both the concentration and chemical state in the surface. The two techniques are in many ways complementary. AES gives good spatial resolution since a narrow (1–50 μm) electron beam is used while with XPS such spatial resolution cannot as yet be obtained, since it depends on X-ray photons to excite photoelectrons. The advantage of XPS is, however, that charging effects are minimized and surfaces of insulators can be more easily analysed. The usefulness of these techniques is illustrated by the results shown in Table II which are for the XPS analysis of carbon on mild-steel substrates (i) prior to bonding using an epoxy adhesive, (ii) after bonding and “dry” fracture and (iii) after bonding, exposure to a hot/wet environment and then fracture. To prevent the fresh, fracture surfaces being contaminated by atmospheric contaminants the fracture experiments were conducted inside the ultra-high vacuum system of the X-ray photoelectron spectrophotometer. As may be seen the substrate control, although freshly prepared, is covered by a carbonaceous layer and the 1s carbon photoelectron peak at 285.0 eV may be associated with elemental carbon or hydrocarbon. On ion bombardment the carbon concentration decreases indicating removal of the carbonaceous contamination. As an aside it is interesting to note that any effective adhesive must displace (the thermodynamics would be favourable for this) and absorb this contamination during the wetting process. After joint preparation and fracture, without joint immersion in water, the locus of joint failure was visually assessed as cohesive-in-adhesive and this was “confirmed” by the XPS analysis. The carbon 1s peak at 286.4 eV was considered to be indicative of polymeric carbon in intimate contact with the substrate and on ion bombardment the polymer was degraded to lower molecular-weight carbonaceous species. Finally, after joint preparation and fracture after joint immersion in water the mild-steel substrate surface had virtually no carbonaceous material present. This demonstrated that no significant amount of epoxy adhesive remained on the oxide after “wet” joint fracture and, since analysis of the other (apparently adhesive) fracture surface showed no traces of oxide, the locus of failure for these joints after environmental attack was considered to be truly interfacial.

TABLE II
XPS analysis for carbon on mild-steel substrate surfaces

Sample	Chemical State			Comments
	Initially	After ion erosion of		
		50 Å	130 Å	
Substrate control, prior to bonding	285.0 eV; 19.7%	284.8 eV; 8.5%	284.5 eV; 4.2%	Hydrocarbon contamination from atmosphere—disappears on ion erosion
After "dry" joint fracture	286.4 eV; 26.3%	284.0 eV; 20%	284.3 eV; 20.1%	Polymeric carbon which degrades on ion erosion. Indicates failure in adhesive
After "wet" joint fracture	284.7 eV; 2%	—	—	Negligible hydrocarbon contamination. Indicates failure at interface

Note: Binding energy in electron volts; atomic percentage present.

Kinetics of failure

The work on the epoxy/mild-steel joints also provided an insight into the kinetics of the failure mechanism. From measuring the rate of interfacial debonding at different temperatures an activation energy for the displacement of adhesive by water of 32 kJ/mol was deduced. This value is similar to that for the diffusion of water through an epoxy resin, namely 16 to 38 kJ/mol as reported by other workers^{17,18} and suggests that the rate of interface debonding is controlled by the availability of water at the interface which in turn is governed by diffusion of water probably through the adhesive. Assuming Fickian and two-dimensional diffusion the rate of water penetration into the adhesive may be calculated.¹⁹ For this particular adhesive the value of the diffusion constant at 60°C was approximately 18.1×10^{-9} cm²/s and employing this value the relations between water concentration and distance into adhesive, shown in Figure 4, were deduced. Since at 60°C the joints had lost almost all their original strength after a three months immersion in water, the attainment of the equilibrium, water-saturation concentration in the adhesive was obviously not necessary. On the other hand a critical, minimum water concentration in the adhesive would appear to be

a requirement; below about 50% relative humidity storage these joints apparently suffered no environmental attack, even though of course the adhesive still absorbed water up to an equilibrium concentration, although naturally of a lower value.

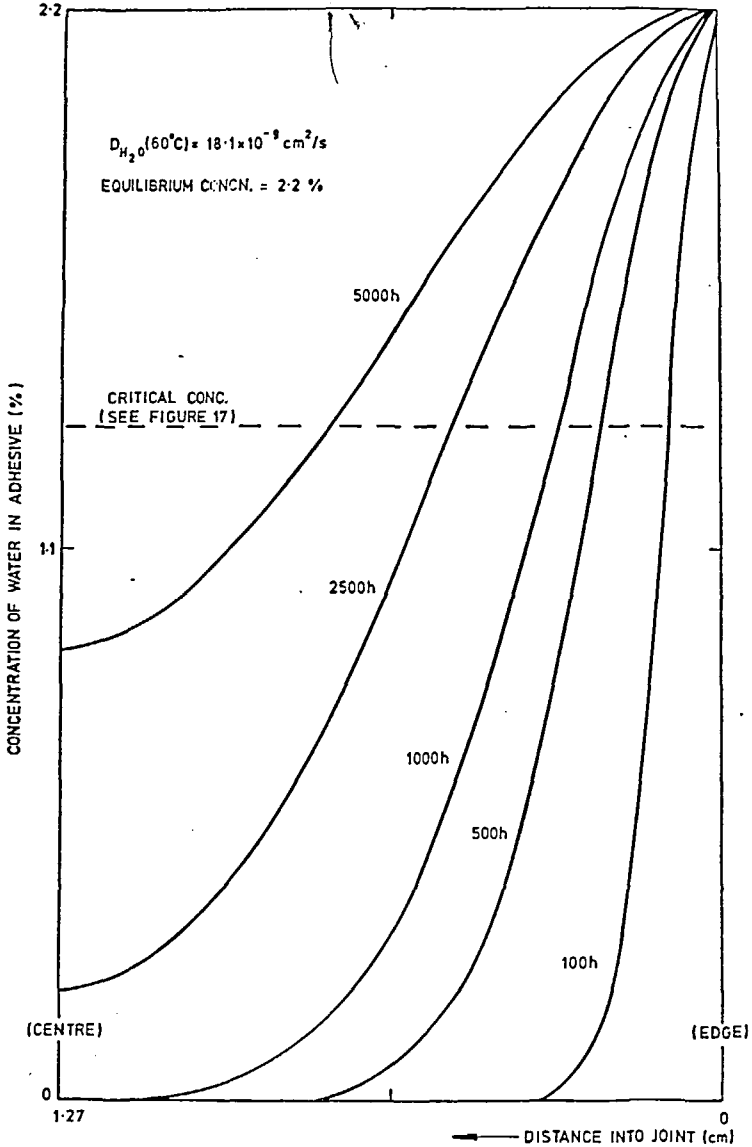


FIGURE 4 Water concentration in adhesive as a function of distance into joint and time.

Oxide stability

Noland²⁰ has reported that the oxide produced on aluminium alloys by a chromic-sulphuric etch is unstable in the presence of moisture and has postulated that the oxide changes to a weaker, gelatinous type which is hydrated and is "gelatinous-boehmite". His evidence for the change in oxide structure comes from X-ray photoelectron spectroscopy analysis of the oxide surface before and after ageing and Figure 5 shows that change in binding energy observed for the aluminium 2p peak position, indicating a change in oxide structure. Noland examined epoxy/aluminium-alloy joints after exposure to hot, humid conditions and reported that, although interfacial failure had visually occurred, in fact the locus of failure was in the weak, gelatinous-boehmite oxide layer. Sun *et al.*²¹ have employed AES to characterise acid-etched aluminium-alloy and suggested that it is the accumulation of certain elements, such as copper and magnesium at the oxide/metal interface or in the oxide layer, which are detrimental to oxide stability and joint durability.

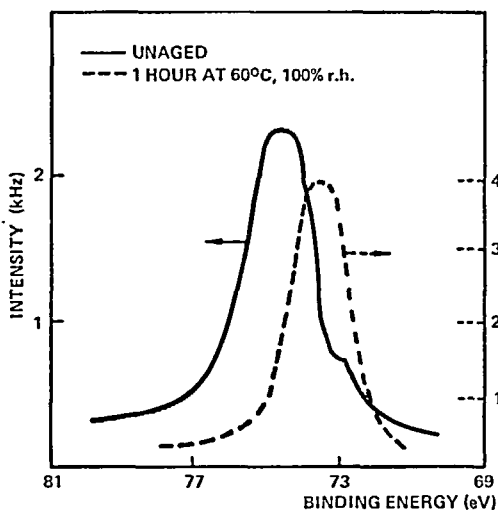


FIGURE 5 XPS analysis of chromic-sulphuric acid etched aluminium-alloy surface (Al₂p) before and after etching.

As mentioned previously, clad aluminium-alloys may present a particular problem and the reasons for this have been considered by Riel.¹⁶ With clad aluminium alloys the electrode potential is generally higher than the base alloy. This choice is deliberate in that the clad material is selected to be anodic with respect to the base alloy so that in a corrosive environment the cladding will be consumed, thus protecting the base alloy. This mechanism

is very effective in protecting the structure from surface corrosion such as pitting and Figure 6 is a sketch showing how pitting penetration is restricted on clad aluminium, as compared to the same alloy without cladding. On the clad alloy pitting is less likely to occur due to the nature of the alloy and where pits do form and penetrate the clad surface, its anodic nature will cause the pit to grow laterally once the base alloy is reached; instead of penetrating into the base alloy. However, while this mechanism of corrosion inhibition may be effective for exposed aluminium-alloy structures, if one considers the mechanisms concerned whereby clad aluminium-alloy achieves its corrosion resistance then the clad layer is actually undesirable in the context of adhesive bonding. The sketch in Figure 7 shows how a galvanic cell may be established between cladding and substrate with the progressive

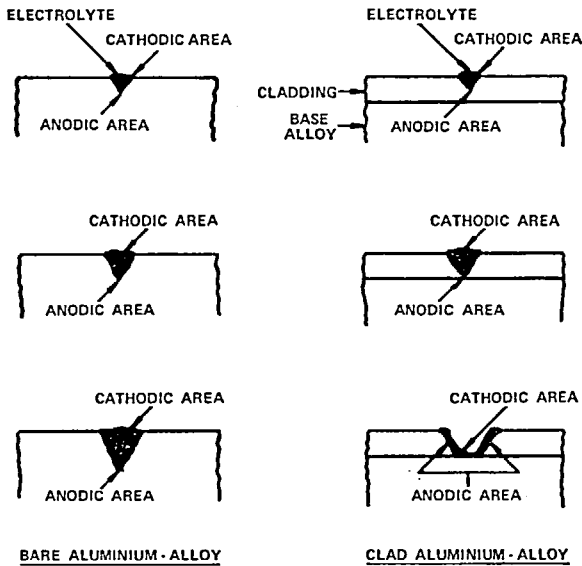


FIGURE 6 Progressive pitting of bare and clad aluminium-alloy in a corrosive environment.

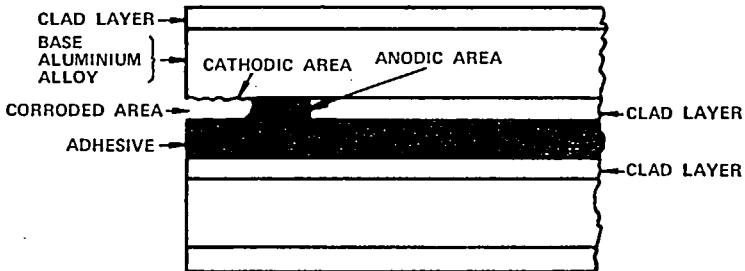


FIGURE 7 Corrosive delamination of adhesive-bonded clad aluminium-alloy.

destruction of the interfacial regions. Once this galvanic action starts, the acidity and oxygen concentration factors come into play and progressive delamination occurs. Bascom and Patrick²² have commented that in general the attachment of the adhesive to a layer of metal which is anodic with respect to the rest of the metallic system is always undesirable from the standpoint of corrosion resistance. Also, chemical components in the adhesive may diffuse into the "electrolyte" area and, *e.g.*, if the adhesive is an amine-cured epoxy any unreacted amine diffusing into the region of corrosion could affect or even control the pH of the electrolyte solution. Indeed, certainly in the United States, the trend is away from adhesive bonding to clad aluminium-alloys^{2,23,35} but where unclad alloys are bonded and used in areas exposed to corrosive environments any non-bonded, exterior surfaces must be protected by appropriate means in order to limit surface corrosion.

Fracture mechanics approach

Continuum fracture mechanics is the study of the strength of a material which contains a flaw, usually considered as an elliptical crack. Two main, inter-relatable criteria for fracture are proposed. Firstly, Irwin²⁴ found that the stress field around a crack could be uniquely defined by a parameter named the stress-intensity factor, K , and stated fracture occurs when the value of K exceeds some critical value K_c . Secondly, the energy criterion arising from Griffiths²⁵ and, later, Orowan's²⁶ work, which supposes that fracture occurs when sufficient energy is released (from the stress field) by growth of the crack to supply the requirements of the new fracture surfaces. The energy released comes from stored elastic or potential energy of the loading system and can, in principle, be calculated for any type of test piece. This approach, therefore, provides a measure of the energy required to extend a crack over unit area, and this is termed the fracture energy and is denoted by G_c . When plane-strain and a tensile opening-mode prevails it is denoted G_{Ic} .

The pioneering work in the application of continuum fracture mechanics to the failure of adhesive joints was undertaken by Mostovoy, Ripling and co-workers.²⁷⁻²⁹ They developed the tapered-double-cantilever-beam joint geometry, which is shown in Figure 8 and which is a constant-compliance geometry which results in the adhesive fracture energy being independent of crack length and thus well suited to environmental studies where crack velocity will be a function of the applied load and environment. They found that a specimen containing a cohesive starter-crack, loaded and placed in water, showed interfacial rather than cohesive failure. This interfacial failure occurred within the stress field generated by the original cohesive crack and eventually propagated along the adhesive/metal-oxide interface and a typical relationship between the adhesive fracture energy, G_{Ic} , and resulting

crack velocity, \dot{a} , is shown in Figure 9. As may be seen the value required to cause crack growth in an aqueous environment is much lower than that needed in a relatively dry environment. However, the measured adhesive fracture energies required for these crack growth rates are, of course, much higher than the values for the thermodynamic works of adhesion given in Table I. This is because, under an applied load, mechanical strain-energy is available to assist environmental crack propagation and thus this is reflected in inelastic energy dissipative processes, *e.g.*; plastic flow, occurring in regions of the adhesive around the crack-tip. The values of W_A and W_{AL} do not allow for any such processes.

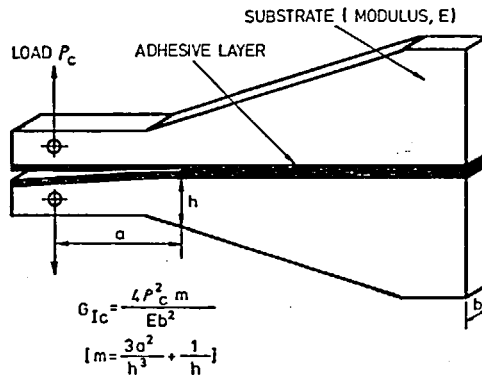


FIGURE 8 Tapered-double-cantilever-beam fracture mechanics specimen.

From data such as that shown in Figure 9 Mostovoy and Rippling concluded that there was a minimum value of G_{Ic} , denoted G_{Isc} , below which slow crack growth would not occur in aqueous environments and such a minimum value implies that there is a stress below which no environmental attack will occur. However, the evidence for such a proposition is conflicting. First, the time-scale over which the experiments were conducted for Figure 9, or in similar experiments on other adhesives,²⁸ is insufficiently long to be able to state with confidence that a true minimum value of G_{Ic} , *i.e.*, a G_{Isc} value, has been attained and plotting the data in the form of Figure 10, with a logarithmic G_{Ic} scale, demonstrates this. Second, it is well established that joints under no externally applied stress[†] may still suffer environmental

† It is of interest to note that Cherry and Thomson^{31,32} have recently also argued that the presence of stress is essential for environmental attack but consider that in the absence of an externally applied stress, internal shrinkage stresses provide the necessary strain-energy requirements. However, this hypothesis has yet to be proven, especially since (i) hot-cure adhesives will have the highest shrinkage stresses but generally result in the most durable joints and (ii) any shrinkage stresses will probably be rapidly diminished by stress relaxation processes in the adhesive, accelerated by plasticisation by water, and swelling stresses due to water absorption.

attack. Thus, whether the presence of stress is essential for environmental attack to occur has yet to be firmly established but it is obvious that stresses, including applied, swelling³⁰ stresses, may accelerate the environmental decay mechanisms.

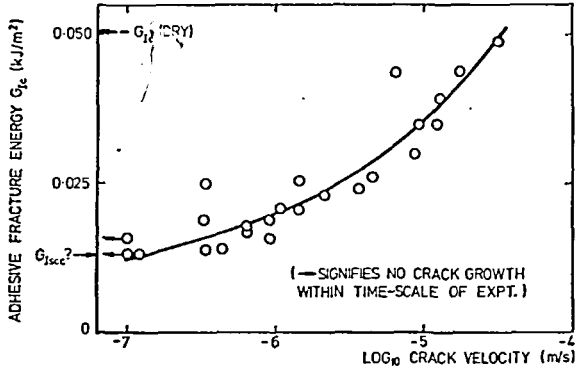


FIGURE 9 Adhesive fracture energy versus crack velocity in water for epoxy-tetra-ethylenepentamine cured/aluminium-alloy joints.

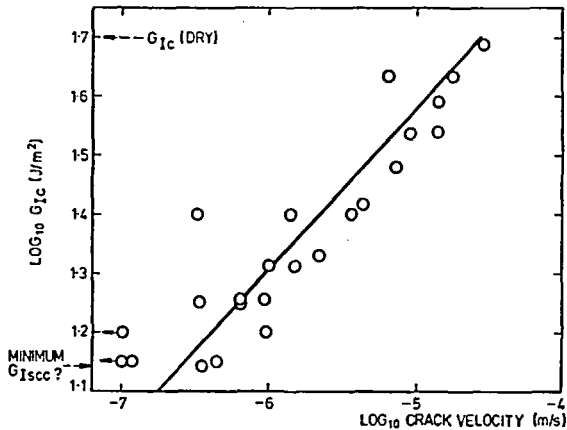


FIGURE 10 Existence of minimum G_{Isc} ? Data from Figure 9 replotted as $\log_{10} G_{Ic}$ versus \log_{10} crack velocity.

Kinloch, Gledhill and Dukes^{9,33} have conducted static fatigue tests employing the tapered-double-cantilever-beam specimen which consisted of aluminium-alloy (grit-blasted surface pretreatment) bonded with a tertiary-amine cured epoxy resin. The value of the adhesive fracture energy, G_{Ic} , imposed and the resulting time taken for specimen fracture is shown in Figure 11 for two environments: 23°C with 56% relative humidity and 23°C

with immersion in water. Considering first fracture in the former, drier environment, then the locus of joint failure was cohesive, in the centre of the adhesive layer and, as may be seen, there is a linear relationship between G_{Ic} and logarithmic time to fracture. Further, the time to fracture represents an induction time; the original, naturally propagated, start crack remained perfectly stationary up to the instant of fracture and it then propagated with a velocity of about 20 m/s; *i.e.*, no relatively slow crack growth region was observed. From considering the crack to be modelled by an elastic-plastic material with a plastic zone at the crack-tip it can be shown that there is a critical value of the plastic zone size at the crack-tip at which fracture occurs. This gives a unique failure criterion for the fracture of these joints over eight decades of time. A value of 16 μm for the critical plastic zone size was calculated for this particular adhesive.^{33,34}

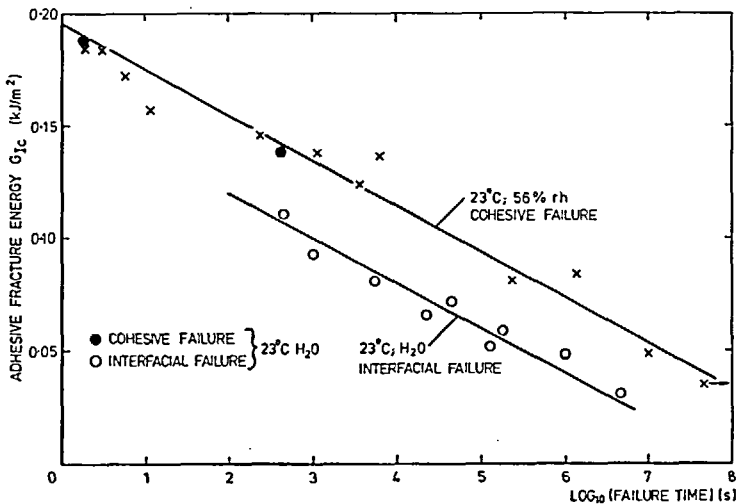
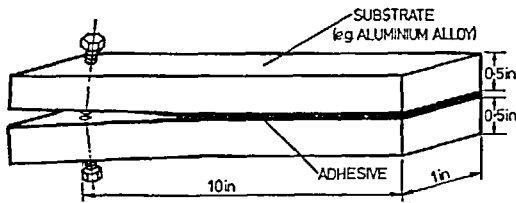


FIGURE 11 Adhesive fracture energy versus time-to-failure for epoxy/aluminium-alloy joints.

The effect of immersion in water on the fracture behaviour of these joints is particularly interesting. The value of the thermodynamic work of adhesion, W_A , in a dry atmosphere is 232 mJ/m^2 (see Table I), and being positive indicates stability of the interface, which is confirmed by the cohesive locus of joint failure observed above. However, when there is an adsorbed layer of water at the interface the thermodynamic work of adhesion, W_{AL} , has a negative value, -137 mJ/m^2 . This predicted instability of the interface is reflected by the locus of joint failure becoming interfacial in the presence of a water environment. Exceptions to this were, however, observed when the applied adhesive fracture energy was relatively high and the time to fracture

short, about 300 seconds or less. Under such circumstances, water has insufficient time to diffuse and penetrate the interface prior to normal cohesive fracture occurring and thus the failure behaviour of the joints under these conditions resembled that of the dry fracture results.

However, apart from such exceptions, the mechanism of environmental failure appeared to be the penetration of water and the displacement of the epoxy/aluminium oxide interface as predicted from the thermodynamic considerations. Thus, as observed by Ripling and Mostovoy, in the region of the interface near the original cohesive starter crack, interfacial debonding occurred. However, in this case an induction time was observed and no significant slow crack growth was recorded up to the instant of fracture when the crack propagated rapidly along the interface. Further, and more importantly, this environmental failure mechanism resulted in times to fracture, at a given value of G_{Ic} , about two decades shorter than those from fracture experiments conducted in the relatively dry environments. Finally in neither the low humidity nor the aqueous environments was there a discernible minimum value of G_{Ic} , below which failure did not occur.

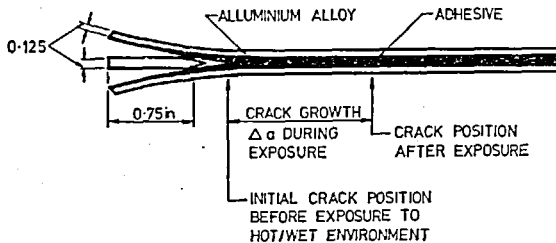


$$G_{Ic} = \frac{y^2 E h^3 [3(a+0.6h)^2 + h^2]}{16[(a+0.6h)^3 + ah^2]^2}$$

y = DISPLACEMENT AT LOAD POINT
a = CRACK LENGTH

h = HEIGHT OF BEAM
E = SUBSTRATE MODULUS

FIGURE 12 Constant displacement, double-cantilever-beam geometry.



TYPICAL EXPOSURE: 1 HOUR AT 49°C; 100%rh Δ a RECORDED IS MEASURE OF DURABILITY

FIGURE 13 Boeing wedge-test specimen for ranking adhesive joint durability.

The specimen geometry and test procedures used for the above experiments are too complex and costly for quality control use in industry and so two modifications have been devised and are shown³⁵ in Figures 12 and 13. Both are constant-displacement specimens rather than constant-load and thus caution must be exercised in interpreting the results since stress-relaxation may occur in the adhesive thereby diminishing the effective stress at the crack tip and lowering the observed crack growth rate. Indeed, crack tip blunting leading to a decrease in crack propagation rate, may be a problem with even the constant-load experiments³⁶ and may account for the often considerable scatter in the reported experimental data. Further, the Boeing wedge test, Figure 13, does not lend itself to stress analysis because of non-linear bending displacements.³⁷ However, the ease and speed of obtaining stressed, durability data make these specimens extremely valuable additions to the range of test techniques.

INCREASING DURABILITY

Now the deleterious effect of water on the joint strength and post-failure corrosion of the substrate could be avoided if the integrity of the interfacial regions could be maintained. Thus, either water must be prevented from reaching the interface in sufficient concentration to cause damage or the intrinsic durability of the interface must be increased.

Decreasing water permeation

All organic polymers are permeable to water and some values of permeability coefficients, P , and diffusion constants, D , for water through various polymers are given in Table III.^{38,39} As may be seen epoxy and phenolic materials are at the low end of the spectrum and whilst there is undoubtedly room for improvement, the other properties of any adhesive, such as wetting/adhesion characteristics, processability, toughness, cost, must be balanced against the need for low values of P and D .

A second approach has been to use sealants (which are usually based upon organic polymers) to coat the edges of the exposed joint. However, while this will obviously slow down water penetration it is often not possible to apply a thick enough layer to be very effective and has other disadvantages such as adding an extra operation and cost to the bonding process.

Increasing the intrinsic durability of the interface use of primers

It has been shown that the environmental resistance of joints consisting of mild-steel substrates bonded with a simple epoxy adhesive may be considerably increased by applying a γ -glycidoxypropyltrimethoxy silane primer

solution to the substrate prior to joint formation.⁴⁰ Previous work⁴¹ had shown that silane primer films are usually polymeric and essentially composed of a polysiloxane network and this was confirmed by using secondary ion mass spectroscopy (SIMS). With this technique ionized particles ejected from the surface by the action of an argon beam are mass analysed. As the current densities used in SIMS are low ($\sim 10^{-10}$ A/cm²) the first one or two monolayers of the surface can be investigated. Either atoms or molecules can be ionized and thus details about the chemical state of atoms in a surface can be inferred. This technique also revealed the presence of Fe SiO⁺ radicals from the primer-coated substrate surface.⁴² This is strong direct evidence for the formation of a chemical bond, probably —Fe—O—Si≡, between the metal oxide and polysiloxane primer. No such radicals were detected from several other silane coated surfaces where there was no improvement in joint durability. Thus only for the silane primer which resulted in improved joint durability was there any evidence for chemical, rather than purely secondary bonding, between the primer and metal oxide and it is postulated that it was the presence of these interfacial chemical bonds which were responsible for the greatly increased durability.

TABLE III

Permeability coefficients (*P*) and diffusion constants (*D*) for water through polymers

Polymer	Temp °C	<i>P</i> × 10 ⁹ ^a	<i>D</i> × 10 ⁹ (cm ² /s)
Vinylidene chloride/acrylonitrile copolymer	25	1.66	0.32
Polysisobutylene	30	7→22	—
Phenolic	25	166	0.2→10
Epoxy	25	10→40	2→8
Epoxy/ <i>tert.</i> amine	20	—	2.4
	40	—	6.5
	60	—	18.1
	90	—	60.7
Polyvinylchloride	30	15	16
Polymethylmethacrylate	50	250	130
Polyethylene (low-density)	25	9	230
Polystyrene	25	97	—
Polyvinylacetate	40	600	150

^a in $\frac{\text{cc S.t.p. cm}}{\text{cm}^2\text{s. cm Hg}}$

Further work, using Auger and X-ray photoelectron spectroscopy¹⁵ has shown that although a silane primer often considerably increases joint durability, and the polysiloxane metal-oxide interface is resistant to water attack, the primer layer itself is now the weakest part of the joint and fracture

may occur by cohesive failure of this layer. Thus, to increase joint durability further attention should be focused on increasing the intrinsic strength of the silane-based primers commonly employed.

The silane primer also appears to be effective on grit-blasted aluminium alloy and Figure 14 shows the adhesive fracture energy G_{Ic} , versus time to fracture for epoxy/silane-primed, aluminium-alloy.⁹ Comparison with the previous results, shown in detail in Figure 11, clearly demonstrates that the presence of a silane at the interface maintains its integrity and forces the fracture to be cohesive in the adhesive and follow the failure behaviour of joints tested in the dry environment.

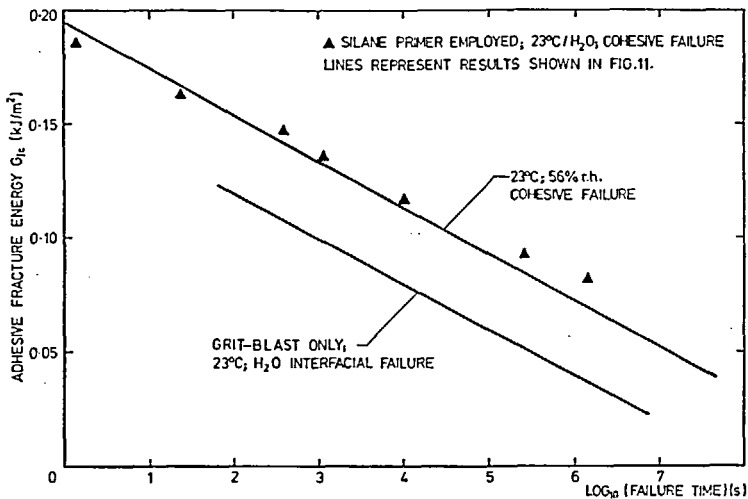


FIGURE 14 Improvement obtained by use of silane-primer on epoxy/aluminium-alloy joints.

It would be of considerable interest if the contribution from interfacial primary, chemical bonds to the intrinsic stability of the interface could be quantified. However, without a detailed knowledge of the type of reactions, and their extent, occurring across the interface, it is at present impossible to calculate their contribution exactly. Nevertheless, an approximate indication may be obtained by taking the interfacial, chemical bond energy as 250 kJ/mol and assuming a coverage of 25 Å²/adsorbed site. This yields an intrinsic work of adhesion of +1650 mJ/m² and from energetic considerations it would be unlikely that water would readily displace such a chemisorbed primer layer. More basic information on the interfacial forces and reaction mechanisms is required before more definitive calculations and predictions can be undertaken.

Finally, the presence of interfacial, covalent bonds may also explain why phenolic-based adhesives generally impart very good durability characteristics.⁴³ The long-term, high-temperature cure conditions used with such resin systems (frequently in the presence of acid catalysts) leads to the evolution of water *via* condensation reactions. The reaction conditions required for this reaction are also precisely those that give the maximum probability of forming ether linkages between oxide surfaces and the resin. However, the existence of such an interface bond has still to be established and such a bond would be susceptible to hydrolysis in water because of its strongly ionic character. Thus the basic mechanisms for explaining the good durability associated with phenolic-based adhesives still remain unresolved.

Reinhart⁴⁴ has examined various primers and techniques for applying primers and, in particular, electro-priming. In this process a conductive tank is filled with a water suspension of the primer-resin system (approximately 10% solids by weight). A precleaned metal substrate is suspended in the tank and made either anodic (positive electrode) or cathodic (negative electrode) depending on the charge contained by the resin particles. The film is initially formed on the part areas of highest current density, by migration of the charged resin particles under the influence of the applied voltage. Using this process Reinhart has studied the interesting possibility of forming the oxide layer on the metal substrate while, at the same time, depositing the polymeric polymer layer. Examination of the interfacial region of such a sample showed that the primer layer did indeed penetrate into the oxide and initial durability trials have been encouraging.

Reinhart has also studied the use of water soluble polymers such as phenol-formaldehyde, resorcinol-formaldehyde, urea-formaldehyde and their physical blends and copolymers, as well as the speciality types of water soluble epoxy resins, as potential candidates for improved primer formulations. The advantages of using water as the solvent in the formulation include its low cost, non-flammability, non-toxicity and non-polluting characteristics. The formulations evaluated have encompassed compositions including single-stage resoles as well as two-stage novolacs and cure of these latter primers was achieved by the addition of formalin, paraformaldehyde or polymeric curing agents. Various other additives were also required such as flow control, levelling and wetting agents, stabilisers, film tougheners and corrosion inhibiting materials. The water-based primers were applied directly to the pretreated metal substrates by dipping, spraying or brushing and the solids contents were adjusted by dilution with water to achieve the desired primer film thickness. The primers were normally dried and cured at room or elevated temperatures prior to adhesive application and bonding. Initial results from accelerated environmental trials are shown in Table IV and, as may be seen, while the preliminary results from the water-soluble

primers are not quite as good as those from a commercially available primer (non-water based), the durability achieved is definitely promising. Reinhart considered that a somewhat thinner and tougher primer film was required to perform satisfactorily in the lap-shear test.

TABLE IV
Durability trials on water-based primers

Primer formulation	Boeing wedge test; crack growth (mm)		Lap-shear stress (MPa)			
	After 1 hour	After 24 hours	Unexposed 23°C	82°C	30 days/95% RH/49°C 23°C	82°C
Commercial control	2.5	2.5	31.0	20.7	28.3	10.3
Resorcinol-formaldehyde based	2.5	5.1	26.4	13.0	8.5	2.6
Phenol-formaldehyde (Novolac) based	3.8	6.4	20.7	14.5	7.2	4.8
Phenol-formaldehyde (Resole) based	2.5	5.1	25.1	9.0	17.8	4.8

Notes: (a) Aluminium-alloy, chromic-sulphuric acid etched; modified-epoxy adhesive.
(b) Standard Boeing wedge-test (see Figure 13), exposed to 95% RH; 49°C.

Oxide structure

Workers at Boeing^{45,46} have developed a new surface treatment for aluminium-alloys based upon a phosphoric-acid anodizing method. This technique results in a much thicker, and more porous, oxide layer on the aluminium alloy, compared to a chromic-sulphuric acid etch and this may be seen from the diagrammatic representations in Figure 15. Further, X-ray photoelectron spectroscopy evidence, cited by Noland,²⁰ shows that the oxide produced by this new method is more stable in the presence of hot/wet environments. The increases in joint durability which have been reported from using the phosphoric-acid anodizing technique are illustrated in Figure 16.

Bascom⁴⁷ has recently drawn attention to the point that penetration of adhesive resin molecules into these complex, porous microstructures would result in a resin/metal oxide composite interphase that may contribute significantly to joint durability, since failure through the oxide would involve plastic and viscoelastic deformations of ligaments of adhesive. Also in such a process mechanical interlocking may contribute significantly to the intrinsic adhesion⁴⁷⁻⁵⁰ and thus invalidate the thermodynamic work of adhesion as a sole criteria for interphase stability. Hence it appears that in certain instances the oxide must possess both a resistance to attack by water and the "correct" microstructure for maximum joint durability.

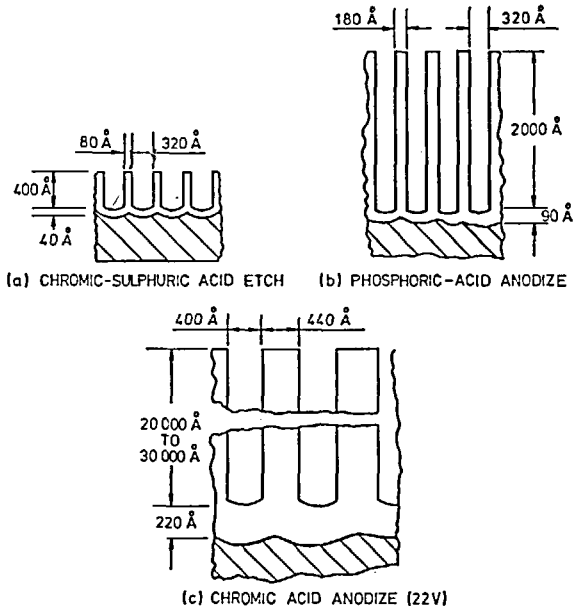


FIGURE 15 Oxide morphology on aluminium-alloy after pretreatment.

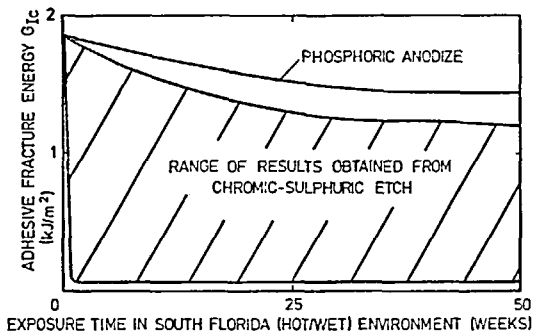


FIGURE 16 Effect of substrate surface pretreatment on the durability of epoxy/aluminium-alloy joints.

Workers at Fokker^{51,52} have also examined the influence of various chemical pretreatments on the surface morphology and peel-strength of aluminium-alloys. They concluded that surfaces should be acid etched and then anodized, and for the highest peel strengths a chromic-sulphuric acid etch followed by anodizing in chromic acid gave the optimum results; etching in sulphuric acid alone gave inferior peel strengths. Transmission

and scanning electron micrographs showed a relation between surface morphology and bondability and a fine etchpit structure within coarser etchpits gave the most desirable structure. They considered that low strengths were associated with either a weak oxide layer or a weakened aluminium surface.

These models of a resin/oxide inter phase at the adhesive/substrate boundary become even more complicated when a primer is also applied prior to bonding. The primer should wet and penetrate the porous oxide, inhibit any chemical changes in the oxide and exhibit energy dissipative mechanisms upon failure of the primer/oxide interphase region.⁴⁷ Optimization of oxide type and microstructure and primer composition is therefore an extremely complex procedure.

Indeed it is not, at present, really understood exactly which surface chemical and physical parameters are important for producing an oxide layer which will impart good environmental resistance to an adhesive joint. While the adhesion scientist may talk generally about requiring a contamination free, strong, stable, receptive surface with the right morphology, the detailed parameters involved, their required values and how to logically obtain them are virtually unknown. Nevertheless it is to be hoped that by employing the new surface analytical techniques that are now available surfaces will be fully characterized and this information related to the subsequent environmental resistance of adhesive joints. Only by this type of approach will new improved adhesives, primers and surface pretreatments be rapidly developed.

MECHANICS OF ENVIRONMENTAL FAILURE

Having considered the various parameters involved in the environmental failure of structural adhesive joints the overall mechanics of the process may be identified.

The first stage is the accumulation of a critical concentration of water in the interfacial regions which must be exceeded for environmental attack to occur. The rate of attaining this critical concentration appears to be governed by the rate of water diffusion through the adhesive and this is obviously accelerated by temperature and, possibly, by stress. Also of interest is the fact that the new generation of rubber-modified epoxy adhesives achieve their high toughness partially through the formation of crazes.⁵³ Obviously the presence of crazes would considerably increase the rate of diffusion. With some simple adhesive/substrate combinations the kinetics of the environmental failure mechanism are governed by the rate of water diffusion.

The second stage involves a loss in the integrity of the interfacial regions due to, depending upon the particular adhesive/substrate combination:

- i) The rupture of interfacial secondary bonds.
- ii) Subtle changes occurring in the oxide structure, *e.g.*, hydration, which causes a mechanical weakening of the oxide layer.
- iii) Gross corrosion and delamination of a clad-layer on the metal substrate.
- iv) Cohesive failure in a primer layer. The primer layer may have increased the intrinsic strength of the original adhesive/substrate interface, and hence joint durability, but may itself now be the weakest link in the chain, *e.g.*, hydrolysis of a polysiloxane primer layer.

The rate of loss of strength of the interfacial regions will be faster if a stress is present, albeit an externally applied stress or internal stresses induced by adhesive shrinkage, incurred during cure, or by adhesive swelling due to water uptake. However, the presence of stress as a necessary requirement for environmental attack to occur has yet to be conclusively established but a primary or secondary bond will obviously be more susceptible to attack if stressed.

The third stage concerns the ultimate failure of the adhesive joint. However, for the joint to fracture or lose an appreciable amount of its original strength upon subsequent testing it is not usually necessary for the weakening of the interfacial regions to have proceeded completely through the joint. From basic fracture mechanical considerations only a relatively small environmental crack is required to have developed before a substantially decreased failure time, under a constant-load test, or a diminished joint strength is observed. From the Griffith equation the fracture stress is proportional to $1/\sqrt{(\text{crack length})}$ and thus a small increase in crack length has a considerable effect on fracture stress. Indeed with many joint geometries subjected to an imposed load and moisture, catastrophic failure will occur when the environmental crack, which is growing by the mechanisms outlined above, attains a critical length. This is analogous to a critical Griffith crack size in homogeneous materials. However, on the positive side, plasticization of the adhesive by water may diminish stresses by stress-relaxation and crack blunting mechanisms.

These ideas have been applied³⁹ to the relatively simple mild-steel/epoxy system where the butt joint strength as a function of time of immersion in water at different temperatures has been previously reported.⁸ Firstly, from diffusion data for the adhesive, plots such as that shown in Figure 4 may be calculated at each temperature. Secondly, by assigning a constant, critical water concentration for debonding them from such plots the interfacial, environmental crack-length as a function of time in environment may be deduced. Thirdly, this crack-length may be combined with the independently measured values of fracture-energy and modulus of the adhesive³⁴ to yield the expected fracture stress as a function of time in environment. The

predictions for the butt joints so calculated are compared to the experimentally determined values in Figure 17 and the results are in good agreement. However, this analysis will obviously be more complex where, for example, interfacial chemical bonding is present and the kinetics of the failure process are probably no longer governed by the rate of water diffusion.

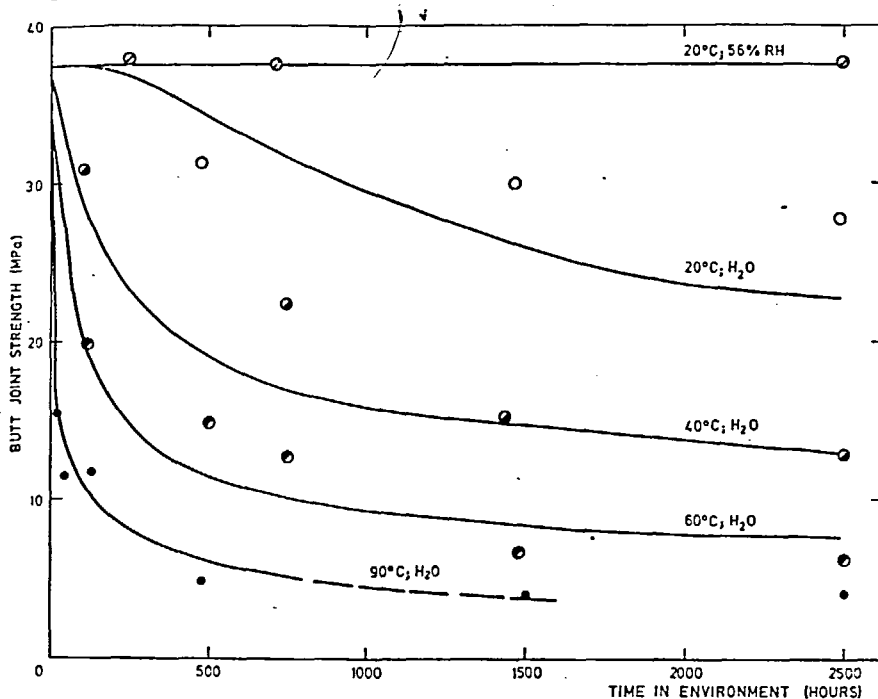


FIGURE 17 Comparison of measured and predicted durability for mild-steel/epoxy joints. ($G_{Ic} = 0.4 \text{ kJ/m}^2$; $E = 2.8 \text{ GPa}$; Critical water concn. = 1.35%; points expt., solid lines theoretical.)

CONCLUSIONS

The main conclusions to be drawn are:

- 1) Water is a particularly aggressive environment for adhesive joints and especially when the bonded component is also subjected to conditions of relatively high stress and temperature.
- 2) Environmental failure usually occurs at, or close to, the adhesive/substrate interface.
- 3) From studies of the interfacial fracture mechanical aspects, the following failure mechanisms have been identified:
 - a) Displacement of adhesive on the metal oxide by water and this can be

predicted from thermodynamic considerations. The kinetics of this mechanism may be governed by the rate of diffusion of water through the adhesive to the interface.

b) Loss of strength and failure of the oxide on the metal substrate due to subtle changes in the nature of the oxide.

c) In special circumstances only, for example with clad aluminium-alloys or in a sea-water environment, is gross corrosion of the substrate a failure mechanism.

4) By combining thermodynamic, water diffusion and oxide structure information with a continuum fracture mechanical approach a general model for environmental failure can be postulated and may yield quantitative predictions as to expected service-lifetimes.

5) To increase environmental resistance either:

a) Water must be prevented from reaching the interface in sufficient concentration, or

b) Stable, receptive oxides must be formed and stronger interfacial forces must be forged which are resistant to rupture by water. It is argued that this approach has been the more successful to date and is more likely to yield the most significant improvements in the future.

Acknowledgements

This paper was presented at the conferences on *Bonding Joints and Preparation for Bonding* held as NATO-AGARD Lecture Series No. 102 in April, 1979 at Oslo and The Hague.

The author would like to thank Dr. W. D. Bascom (ONR), Mr. M. Bergh (PERME), Dr. J. Comyn (Leicester Polytechnic) and Dr. W. C. Wake for helpful discussions and comments.

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