Environmental Attack on Adhesive Joints*

Part II: Locus of Failure

Panagiotis FRANTZIS

The environmental failure of double-torsion (DT) mild steel adhesive joints was investigated with particular emphasis on the behaviour of the metal oxide/adhesive interface. The joints had previously been subjected to static loading in moist conditions using specifically built apparatus. Modern surface-sensitive analytical techniques, such as scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), were employed to examine the resulting failure surfaces and to assess the effect of the environment.

Key Words: Epoxy Resins, Double-Torsion Adhesive Joints, Long-Term Environmental Attack, Metal Oxide/Epoxy Resin Interface

1. Introduction

An adhesive may be defined as that material whose property is to bond together similar or dissimilar surfaces of materials when applied between them. Adhesion forces are then set up across the interface of the two materials which resist separation. These forces are referred to as "intrinsic" adhesion forces and the establishment of intimate molecular contact at the substrate/adhesive interface is essential for the development of strong and stable adhesive joints.

A great deal of research has been conducted over the years in an attempt to identify the factors which are important in the adhesive bonding of metallic materials and alloys. The main consensus that arises is that some form of pretreatment of the surfaces of the metal prior to bonding is essential if a durable bond is to be achieved. A number of different pretreatments are currently used in the industry^{(1),(2)} and many theories have been proposed to explain the adhesion phenomenon⁽³⁾⁻⁽²⁵⁾. According to these theories adhesive performance depends on a number of important factors, each of which under specific condi-

tions may play a dominant role in establishing the observed performance in practice.

It is very clear from the literature⁽²⁶⁾⁻⁽³²⁾ that adhesive joints may have little resistance to environmental attack. The most severe threat to such joints is water, either in the form of liquid or vapour, and it has been reported that exposure of adhesive joints to water weakens their strength. When metals are bonded together with an adhesive, the metal oxide layer is present between the metal and the adhesive. It has also been reported that the oxide layer is the weakest region in a metal/epoxy resin joint system and studies have therefore concentrated on the nature of the oxide and its behaviour in the presence of different environmental conditions. The suggested mechanisms responsible for the loss in the integrity of the interfacial regions are: (i) the rupture of interfacial bonds and/or any covalent bonds, the latter usually only arise if a silane primer is employed during substrate surface pretreatment, and (ii) chemical or physical changes occurring in the oxide structure as a result of water penetration. In the case of steel/epoxy resin joints, the metal oxide is Fe_2O_3 (ferric oxide), as confirmed by X-ray diffraction studies. In the presence of moisture, the Fe_2O_3 oxide is transformed to Fe_2O_4 which is a weaker oxide.

The literature also reveals that one of the poorest

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** Composites Technology Consultant, 5/25 Sefton Park Road, Liverpool L8 3SL, U.K.

substrate pretreatment is that of grit-blasting. When the above pretreatment is applied to steel substrates prior to bonding, then the forces responsible for adhesion are the "secondary" van der Waal's forces acting along the interface.

The work reported here was carried out at Imperial College, London, and formed part of a large programme of work which was aimed at devising adhesive-assisted repair methods for application to submerged sections of steel offshore structures. New accelerated ageing test equipment have been built to generate the long-term fracture data of structural adhesive joints subjected to static "stress-durability" testing in the presence of distilled water at different temperatures. The test method and specimen geometry used was an extension of the double-torsion (DT) test method⁽³³⁾⁻⁽³⁷⁾ and these results have been reported elsewhere⁽³⁸⁾. The DT specimen configuration was selected in this study because long-term measurements and evaluation of the fracture energy versus crack speed relation cannot be easily made using the existing test methods and specimen geometries (for example single edge-notched, three point bend, compact tension, double cantilever beam) because of the cost and complexity of the specimens and equipment for both applying the loads and monitoring crack growth. A suitable test method without requiring complex test equipment and allowing tests to be easily carried out in hostile environments on both opaque and transparent materials without loss of accuracy was needed, hence the choice of the DT test method. The DT test specimen is easier to fabricate and requires no close tolerances compared to other specimens. To the best of the author's knowledge, no work on DT adhesive joints in hostile environments has been reported in the literature before. Further, there are no investigations reported in the literature on the effect of simultaneously applied static stresses and moisture at different temperatures on the performance of DT adhesive joints. The failure surfaces of the DT adhesive joints have been examined here using high resolution scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The data obtained from this work was then compared with those reported in the literature for the various joint geometries.

2. Theories of Adhesion : a Review

2.1 Adsorption theory

The existence and importance of the van der Waal's forces have been demonstrated and shown to arise from electrostatic dipoles between atoms and molecules⁽³⁾. The van der Waal's forces between atoms and non-polar molecules, that is molecules

without permanent multiple moments, are attractive. For small separations van der Waal's are weaker than chemical binding forces, and for large separations they are weak compared with electrostatic forces. However, in absence of chemical and electrostatic forces they are the main attractive forces between atoms and molecules. Other investigators have shown that⁽⁴⁾, van der Waal's attractive forces are present and responsible for the adhesion between elastic bodies even when contact is made under the influence of different solutions. The primary mechanism of adhesion in adhesive joints made from a cross-linked amorphous rubber and rigid polymeric substrates has been reported to be due to the formation of interfacial van der Waal's forces⁽⁵⁾. The importance of primary chemical bonds is also reported in the literature, especially with silane-based primers to improve joint durability⁽⁶⁾⁻⁽⁸⁾.

2.2 Electronic theory

Experiments to investigate the adhesion of films on solid substrates during peeling testing have been reported⁽⁹⁾⁻⁽¹¹⁾. The tests were performed in the dark and was observed that flashes of light and a cracking noise accompanied the peeling process. These observations have led to generate the electrical theory of film adhesion. However, it may generally be concluded from the literature that⁽¹²⁾⁻⁽¹⁴⁾, for most substrate/adhesive interfaces, any electrical double layer which is generated does not contribute significantly to the intrinsic adhesion. Indeed, any electrical phenomena observed, for example during the peel test, arise from the failure process rather than causing the adhesion between the materials.

2.3 Mechanical theory

It has been reported that⁽¹⁵⁾, when the surfaces of metallic substrates prior to adhesive bonding were mechanically roughened an increase in the measured joint strength was recorded. The explanation was that the roughening treatment might have resulted in a surface topography with cavities suitable for mechanical interlocking between the adhesive and the surface irregularities of the metallic substrate, thus generating the mechanical theory of adhesion. However, it has been observed that^{(16),(17)}, chemically roughened metallic substrates in peeling tests, where a very rough microfibrinous oxide surface was produced, showed higher strengths. The effect of chemically roughening the substrate surfaces has also been shown to result in higher strengths compared to the mechanical roughening⁽¹⁸⁾, and it was therefore concluded that the effect of increasing surface roughness was not so much to give true mechanical interlocking but more to form a "micro-composite" interface and so to increase the degree of plastic deformation that the

adhesive undergoes. It has also been suggested that⁽¹⁹⁾, the increase in joint strength might not have occurred due to mechanical interlocking but from other sources. Indeed, mechanical interlocking may not occur at all and its contribution to the stability of the interface between the substrate and the adhesive may be of no importance.

2.4 Diffusion theory

This theory has been proposed after investigations into the adhesion between high polymers^{(20)–(24)}. Polyisoprene and polyisobutylene sheets were brought into contact and the variation in adhesion strength obtained from peeling tests showed a parabolic law. This phenomenon was explained as a result of diffusion of species across the interface of the two polymers. It was also emphasized that diffusion can only take place between mutually soluble polymers and that the strength of the bond may be proportional to the number of molecules diffusing at the interface and to the depth of their penetration. Diffusion of one species into another or into itself, is a function of the solubilities in each other. In the case of the adhesion of polymers to metals, the molecules of metals are immobile and their mutual solubilities are negligible. If it was assumed that diffusion is the major cause of adhesion between the polymer and the metal, it would then be expected that zero bond strength should be achieved at the interface.

2.5 Kinetics of wetting

Experiments have been carried out to investigate the dependence of adhesion on the rheological properties of the substrate surfaces⁽²⁵⁾. When bonded structures are formed by applying a fluid adhesive between rigid substrates, good adhesion may be achieved if the adhesive can flow around asperities and into the substrate surface irregularities. This process is known as the wetting process. Indeed, a relatively large fraction of practical problems involving poor adhesive performance may be a result of incomplete wetting at the interface. The kinetics of wetting may therefore play a decisive role in adhesion. To support this theory, mild steel substrates were used to measure the peeling force required to separate poly (n-butyl methacrylate) from these substrates⁽²⁵⁾. The steel substrates were baked for an hour at different temperatures. The results showed that at temperatures above 72°C cohesive failure was observed and below this temperature failure was interfacial. Wetting was not completed in the sample baked at 100°C. In this sample, large and numerous unbonded interfacial areas were found at low values of peel force. Any remaining non-wetted areas in the sample baked at 150°C were sufficient small so that fracture occurred at higher loads.

2.6 Summary

To summarise, the nature of adhesion between two surfaces in contact has been of major interest to many workers. Different investigators have attempted to identify the main factors that determine the strength of adhesive joints. As a result of these investigations, various theories have been proposed to account for the phenomena observed in practice. The main theory is the adsorption theory which regards adhesion as a purely surface process and explains the formation of a strong bond as a result of the action of molecular forces at the interface: molecular van der Waal's forces and/or chemical bonds. Thus, the formation of primary, that is the chemical bonds, and secondary, that is the van der Waal's bonds, attraction forces at the interface of two substrates in intimate contact, due to the reaction of molecules or atoms and/or chemical groups, may be sufficient in most cases to explain the phenomenon of adhesion. In the case of metal substrate/epoxy resin joint systems, the formation of primary and secondary bonds are certainly adequate to explain the good adhesion observed in practice.

3. Effect of Surface Treatment

Experiments to investigate the durability of single-lap adhesive joints exposed to adverse environments⁽¹⁾, have clearly demonstrated the strong effect of the water on the joints and the importance of the surface preparation prior to bonding. An epoxy-polyamide adhesive was used (American Cyanamid FM 1000) to bond aluminium panels of 2 mm thickness. The different pretreatments were as follows:

- (a) Vapour degrease alone or followed by one of the following,
- (b) Solvent.
- (c) Chromic-sulphuric acid etch.
- (d) Alkaline etch.
- (e) Phosphoric acid etch.

The results showed that chromic-sulphuric acid etching was a superior surface pretreatment for improving bond durability. In addition, it was observed that the mode of fracture of the adhesive joints changed progressively from cohesive-in-adhesive to predominantly interfacial. These observations led to the conclusion that the primary role of water in joint degradation was to displace the adhesive from the metal substrate and not to induce cohesive failure of the adhesive.

Similar investigations on the behaviour of single-lap joints exposed to moist air have also been reported⁽²⁷⁾. Aluminium alloy substrates were used which were pretreated by one of various methods. The adhesive was an epoxy resin (Epitoke 828). The

joints were first placed in an environmental chamber at 50°C and 97–100% relative humidity for predetermined periods. The results showed that joint strength increased in the order chromic acid anodize > chromic acid etch > sandblast > degrease. Except for the anodized joints, all joints tested displayed a typical decay in joint strength. The strength of the anodized joints increased and this behaviour was explained as being due to the absorbed water relieving the internal stresses in the joints.

In the present work, the substrate surface pretreatment chosen was grit-blasting followed by degreasing in a solvent in order to assist in constructing new environmental test equipment⁽³⁸⁾.

4. Experimental Procedure

4.1 Test equipment

A detailed description of the environmental test equipment and experimental procedure of the fracture tests can be found elsewhere⁽³⁸⁾. Mild steel substrates of about 26 mm width, 100 mm length and 3 mm thickness (and hence the thickness of the adhesive layer used in this study was 3 mm) were bonded together to give a total width of a DT joint of about 53.4 mm, that is the adhesive layer had a width of about 1.4 mm. Dry tests were performed using a tensile-testing machine to provide a base line for comparisons⁽³⁸⁾. In order to identify the locus of joint failure, a Cambridge Stereoscan model 250 MK 2 scanning electron microscope (SEM) and an X-ray photoelectron spectrometer (XPS), or as it sometimes called electron spectroscopy for chemical analysis (ESCA), were used. The fracture surfaces of the DT adhesive joints have been examined here in order to be able to assess in more detail the combined effect of static stress and distilled water at 25°C, 40°C and 55°C on crack initiation and subsequent failure from a crack propagating along the adhesive layer of these joints⁽³⁸⁾. Small samples for the SEM work were cut from the joints and were coated with a thin film of gold (100 Å – 300 Å) using a Polaron specimen coating unit E 5000. Micrographs were taken of the pretreated steel surface prior to bonding and joint sections after exposure to distilled water and stress using either Ilford Ortho film (50 ASA) or Polaroid type 55 land film (50 ASA). X-ray photoelectron spectroscopy is a technique which allows quantitative elemental analysis of a sample's surface. The technique involves irradiating the sample in vacuum with soft X-rays, typically AlK α , detecting the omitted core-level photoelectrons and then analysing them according to their energies. The technique is extremely sensitive as the omitted photoelectrons must reach the detector without losing any energy and so, in general, useful information can

only be obtained from the outermost 100 Å of a surface.

4.2 Materials

The epoxy resin employed was a diglycidyl ether of bisphenol-A (DGEBA-MY 750 supplied by Ciba Geigy plc). The curing agent was piperidine used at a concentration of 5 parts per hundred of resin by weight (phr) and the cure schedule 16 hours at 120°C. Small particles of rubber-epoxy copolymer were also formed in the unmodified matrix of the epoxide. The rubber was a carboxyl-terminated random copolymer of butadiene and acrylonitrile, CTBN (carboxyl content, 2.37 wt %; acrylonitrile content, 18 wt %; molar mass, 2 500 g mol⁻¹), used at a concentration of 15 phr. Mild steel substrates were bonded together to give the DT joint design. Details about preparation of the DT joints and adhesives used can be found elsewhere⁽³⁸⁾.

5. Results and Discussion

5.1 Crack initiation : visual examination

Cohesive starter cracks were initially inserted in the joints. However, visual examination of the failure surfaces revealed that artificial starter cracks did not propagate, but instead a new crack was formed very near the steel/adhesive interface. Final assessment of the fracture process, as revealed by the analytical methods employed here, showed that this new interfacial crack was responsible for the failure of the DT adhesive joints.

5.2 Crack propagation : visual examination

Figure 1 shows a schematic representation of one side of a DT fracture surface and is representative of both joints tested dry and those which have been tested in water. On the upper region ("Region A") of the surface there was clearly a strip of cohesive-in-adhesive failure completely along the joint. This was where compressive stresses had acted upon the DT joint whilst it was being tested. These turned from

Fig. 1 Schematic representation of a typical DT fracture surface ("Region A" and "Region B" are also shown)

Fig. 2 SEM photographs of the substrate surface prior to bonding at magnifications $\times 150$ (a) and $\times 1000$ (b) respectively

compressive to tensile as the crack grew, as the neutral axis moved upwards as the crack propagated^{(36),(37)}. Along the lower region ("Region B") there appeared to be interfacial failure. The lower region was subjected to tensile stresses during testing.

5.3 Scanning Electron Microscopy (SEM)

5.3.1 Metal surfaces, dry testing Figure 2 shows the mild steel substrate prior to bonding. The angular features of the grit-blasted surface are clearly visible.

Figure 3 shows micrographs of an unmodified DT joint tested dry. Figures 3(a) and 3(b) show "Region A", where the cohesive-in-adhesive failure in the upper part of the joint may be clearly seen, and "Region B". In the more important lower part ("Region B"), where the tensile forces had acted, it appears that interfacial failure at the metal oxide/adhesive interface had occurred but with isolated areas of cohesive-in-adhesive failure leaving behind patches of retained adhesive. Figure 4 shows "Region B" at a higher magnification and appears identical to Fig. 2(b). This confirms that interfacial failure occurred in much of "Region B".

A similar picture emerges for the rubber-modified DT joints tested dry. Figure 5 shows that in "Region

Fig. 3 SEM photographs of the fracture surface of an unmodified DT joint tested dry at magnifications $\times 150$ (a) and $\times 200$ (b) respectively (photograph (a) shows "Region A" (left) and "Region B" and photograph (b) shows mainly "Region A")

Fig. 4 SEM photograph of the fracture surface of an unmodified DT joint at magnification $\times 1000$ ("Region B") tested dry

A" cohesive-in-adhesive failure occurred but in "Region B" it was a mixture of interfacial and cohesive-in-adhesive fracture, see Fig. 5(a). In Fig. 5(b) an area of cohesive-in-adhesive fracture from "Region B" is shown at higher magnification and the

Fig. 5 SEM photographs of the fracture surface of a rubber-modified DT joint tested dry at magnifications $\times 100$ (a) and $\times 1000$ (b) respectively (photograph (a) shows "Region A" (left) and "Region B" and photograph (b) shows "Region B")

Fig. 6 SEM photograph of the fracture surface of a rubber-modified DT joint after exposure to water at 55°C at magnification $\times 150$ ("Region A" (top) and "Region B" are shown)

rubber particles may be clearly seen in the fracture surface of the rubber-modified adhesive.

5.3.2 Metal surfaces after environmental attack

Figure 6 shows a typical fracture surface of a rubber-modified DT joint after exposure to water at 55°C. In

Fig. 7 SEM photographs of the fracture surface of a rubber-modified DT joint after exposure to water at 40°C (a) and 55°C (b) at magnification $\times 1000$ ("Region B")

the lower part of the joint ("Region B") a mixture of interfacial failure and isolated patches of cohesive-in-adhesive failure are clearly visible. It is difficult to make a quantitative judgement as to the amount of interfacial failure that occurred, but by comparing Figs. 5(a) and 6 it does seem that exposure to water had increased the amount of interfacial failure. Higher-magnifications micrographs of "Region B" in these joints are given in Fig. 7. The areas of metal oxide, where interfacial failure occurred, and patches of adhesive, where cohesive-in-adhesive failure occurred, are both clearly visible. The latter, of course, having the distinctive rubber particles present. Thus, the micrographs in Fig. 7 confirm that interfacial failure had mainly occurred, with a few isolated patches of cohesive-in-adhesive fracture. The other joints tested using unmodified adhesive, at different loads and temperatures, all showed the same locus of failure as described above.

5.4 X-ray Photoelectron Spectroscopy (XPS)

5.4.1 Surfaces prior to bonding XPS results using a metal surface prior to bonding are shown in Fig. 8 as a plot of the electron binding energy against counts per second (electrons detected per second).

Fig. 8 XPS results from mild steel substrate surface prior to bonding

Fig. 9 XPS results from bulk unmodified adhesive sample

Fig. 10 XPS results from bulk rubber-modified adhesive sample

Peaks at about 710 eV, 540 eV, and 285 eV were detected indicating the existence of iron (Fe), oxygen (O), and carbon (C) respectively. The oxygen peak was formed due to the metal oxide, or hydroxide, or carbon-oxygen (C-O) species. The carbon peak was strong indicating the presence of a high level of contamination. The rise in the background in the Fe peak indicates a continuous layer of oxide, that is no pin-holes.

XPS results using the bulk unmodified adhesive and rubber-modified adhesive samples are shown in Figs. 9 and 10 respectively. The samples were cut from plates of the adhesives so that fresh adhesive

Fig. 11 XPS spectra of unmodified DT adhesive joint after exposure to water at 40°C and failure. The spectra was obtained from the surface where failure was cohesive-in-adhesive ("Region A")

Fig. 12 XPS spectra of unmodified DT adhesive joint after exposure to water at 40°C and failure. The spectra was obtained from the surface where failure was mainly interfacial ("Region B")

surfaces were examined. The bulk adhesive spectra showed that strong peaks at about 285 eV and 540 eV were detected in both the unmodified and rubber-modified adhesives which are characteristic of carbon and oxygen respectively. Weaker peaks at 400 eV, 850 eV, 210 eV, and 485 eV were also detected, but these peaks were much weaker compared to the carbon and oxygen peaks. However, a difference between the two spectra in Figs. 9 and 10 was the detection of silicon, Si, in the rubber-modified adhesive, at about 100 eV and 150 eV. The silicon was therefore associated with the rubber, that is as an additive used in the preparation of the rubber.

5. 4. 2 Metal surfaces after environmental attack

The XPS spectra of all double-torsion joints examined were found to be similar and typical results are shown in Figs. 11 and 12. Figure 11 shows the spectra obtained from the substrate surface where failure was cohesive-in-the-adhesive ("Region A"). Carbon and oxygen peaks were visible on the adhesive surface. Silicon peaks were also detectable at about 100 eV and 150 eV. Figure 12 shows the spectra obtained from the substrate surface where failure was

mainly interfacial ("Region B"). Carbon, oxygen, iron and silicon peaks were detected.

From Figs. 8 and 12 it appeared that the mainly interfacial region of the fracture surface of the DT joint had a strong concentration of iron, arising from the oxide layer. However, the iron peak was weaker than for the substrate surface prior to bonding (Fig. 8) and this, together with the relatively strong carbon and oxygen signals, confirmed the locus of failure concluded from the scanning electron microscopy results. This was that fracture of the joint in this region ("Region B") occurred by interfacial failure at the metal oxide/adhesive interface but with isolated patches of cohesive-in-adhesive fracture leading to areas of retained adhesive.

Considering other possibilities, then there was no evidence of iron retained on the opposite fracture surface ("Region B"). It was therefore unlikely to have been fracture in the oxide layer itself. Another possibility is that a thin layer of adhesive of a few nanometers at most had covered the iron oxide surface. However, this is considered unlikely bearing in mind the relatively strong iron signal (Fig. 12). Finally, from the above discussion, the presence of silicon on all the failure surfaces of the unmodified joints was surprising. One possible explanation was that silicon containing compounds have been leached from the silicone-based sealant used to seal the water baths, resulting in silicon contamination of the surfaces after failure.

The XPS technique has been used to investigate the locus of failure of single-lap joints tested either in dry conditions or after exposure to water at 60°C using a tensile-testing machine⁽³⁹⁾, and these results are discussed here to illustrate the use of such surface analytical technique and compare with the present work. Steel substrates were first pretreated by immersing in dilute aqueous solutions of Γ -amino-propyltriethoxy silane (Γ -APS) at pH 10.4 or 8.0 and then bonded together using an epoxy resin. Strong bands characteristic of the adhesive and the oxide were obtained near 532.9 eV and 529.6 eV in the adherent O (oxygen) spectra of the joints which were prepared from adherents primed with Γ -APS at pH 10.4 and tested under dry conditions. Only a weak band related to the primer was obtained near 102.0 eV in the Si (silane) spectra indicating that failure was mostly near the primer/oxide interface but with islands of adhesive left on the surface. The O and Si spectra obtained from the analysis of the adhesive failure surface showed strong bands characteristic of the primer near 532.3 eV and 102.1 eV supporting the conclusion of failure near the primer/oxide interface. The O spectra obtained from the adherend surfaces of

joints primed with Γ -APS at pH 10.4 and fractured after immersion in water at 60°C for 7 days showed a strong band near 529.6 eV that were characteristic of the oxide and the Si spectra were very weak. The Si spectra from the adhesive failure surfaces were strong and the O spectra were observed near 532.0 eV and were typical of the silane primer indicating that failure after immersion in water was very near the oxide/primer interface. Similar spectra were obtained for joints pretreated with Γ -APS at pH 8.0 and tested under dry conditions and after immersion in water at 60°C for seven days. The O spectra from the substrate failure surfaces showed strong bands typical of surface oxides and hydroxides while the Si spectra were very weak. The O spectra of the adhesive failure surfaces were near 532.0 eV and the Si spectra were very strong. It was therefore concluded that the joints prepared from adherends primed with Γ -APS at pH 8.0 always failed very near the primer/oxide interface with very little adhesive left on the adherent failure surface.

More recent investigations have reported that the initial interfacial starter cracks in symmetrical bimaterial joints (which were prepared by bonding the epoxy adhesive directly to the aluminium alloy substrate) post-cured at 20°C did not continue to propagate along the aluminium/epoxy interface but immediately diverted into the adhesive layer⁽⁴⁰⁾. For joints post-cured at 45, 80, 120 and 150°C, then the original interfacial starter crack did initially propagate along the interface for some distance before it suddenly diverted into the adhesive layer. Thus, the final locus of joint failure was via cohesive failure in the adhesive. The method of substrate pretreatment was similar to the one employed here and the tests were performed in air at room temperature using a tensile-testing machine.

Other investigators have shown that the locus of failure (examined with the SEM and XPS techniques) of copper/epoxy joints using peel and blister tests in various solutions at room temperature was partially in the metal oxide/epoxy interface and partially in the oxide itself⁽³²⁾. Copper oxides were formed on the substrates using various oxide formation techniques.

Failure in aluminium/epoxy shear joints (examined with the SEM technique) tested using a tensile-testing machine in air at room temperature has been reported to have occurred near the interface with the substrate surface fully covered by the adhesive, that is cohesive failure⁽³¹⁾. The substrates were chemically treated prior to bonding using trichloroethylene, a solvent and sodium dichromate sulphuric acid/distilled water.

Failure in single lap aluminium/epoxy resin joints

(also examined with the SEM technique) subjected to combined shear creep stresses and torsional oscillations applied simultaneously using specifically built apparatus, has also been reported to have occurred near the interface with a cohesive-in-adhesive manner⁽⁴¹⁾. The aluminium substrates were cleaned with trichloroethylene and isopropylalcohol prior to bonding.

Finally, the locus of joint failure examined in this work was found to be similar at all temperatures and loads considered. This observation has led to the suggestion that the locus of joint failure was determined by the properties of the materials forming the bond, the detailed substrate pretreatment and the presence of the hostile environment. Thus, the application of external stresses and an increase in the temperature of the water might have changed the rate of the environmental failure process but not the locus of joint failure.

A detailed investigation into the mechanisms and mechanics of environmental attack can be found elsewhere⁽⁴²⁾.

6. Conclusions

From the studies on the locus of failure of DT adhesive joints, using new accelerated ageing test equipment designed to generate the long-term fracture data of these adhesive joints subjected to static "stress-durability" testing in the presence of distilled water at different temperatures, the following conclusions may be reached:

(1) Crack initiation which resulted to a crack propagating along the interface of the DT joints occurred at the interface and not at the originally inserted cohesive sharp cracks. This phenomenon indicated that the interface was indeed the weakest region of the DT adhesive joints and therefore better pretreatment methods were needed, and that a new interfacial crack was formed because of the presence of the water and the applied static stresses.

(2) The mechanisms of stress-assisted environmental attack appeared to be via water entering the interfacial region of the DT adhesive joints by rupturing the secondary bonds acting across the metal oxide/epoxy resin interface.

(3) In the upper region of the DT joints, where compressive stresses acted during testing, the locus of failure was always by cohesive-in-the adhesive fracture.

(4) In the more important lower region, where tensile stresses acted, the locus of failure before environmental attack appeared to be via failure largely at the metal oxide/adhesive interface with patches of cohesive-in-adhesive fracture.

(5) In the lower region of the DT joints after environmental attack the locus of failure was very similar to that described above but it appeared that there was more metal oxide/adhesive failure and less cohesive-in-adhesive failure, although it was difficult to quantify this statement.

(6) The locus of joint failure was determined by the properties of the materials forming the bond, the detailed substrate pretreatment and the presence of the hostile environment.

(7) The type of adhesive, load or test temperature had no effect on the locus of failure in the presence of water. Thus, these factors appeared not to affect the mechanisms of water attack but merely to change the rate of environmental attack.

(8) The feature that in the DT joints the upper region failed by cohesive-in-adhesive fracture, even after long exposure to water at 55°C, suggested that compressive stresses inhibited the mechanisms of environmental attack or the rate at which such attack occurred.

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