5 Durability of Adhesively Bonded Structures

The long-term durability of adhesively bonded structures is critical in determining their utility in replacing mechanical fastening systems. The achievement of high static shear strengths in bonded joints does not necessarily translate to good performance under load, particularly under dynamic loading conditions and aggressive environments [1, 2]. Water is one of the most aggressive environments in which adhesives can be exposed. Once water has entered a joint there are several ways in which it may cause weakening. The adhesive can be plasticised (which is sometimes a reversible condition) or it can crack, craze or hydrolyse (which are irreversible conditions). Water can also attack the adhesive-substrate interface or cause the adhesive to swell, which creates stresses in the joint.

Several studies have attempted to correlate adhesive strength tests with fatigue life or long-term durability, including finite element analysis [3], wedge testing [4], static loading of joints [5, 6], and variable amplitude fatigue testing [7]. Water is known to be a major factor leading to the degradation of adhesive joints and can affect the bulk adhesive and the adhesive-substrate interface [8]. The durability of galvanised steel to fibreglass joints bonded with polyurethane adhesives and exposed to moisture was shown to be dependent upon the type of fillers used in the adhesive, with polyvinyl chloride/clay fillers giving the most durable bonds [9]. Increasing the loading of fillers in epoxy adhesives leads to enhanced environmental durability [10, 11]. A critical combination of temperature, humidity and load was shown to cause rapid loss of joint strength of steel specimens bonded with epoxies or polyurethanes [12]. Shah and co-workers

[13] showed that fracture in adhesively bonded joints in fibreglass components is mixed mode in nature, involving a combination of tensile and shear-induced failure.

Intensive testing of epoxy aerospace adhesives on aluminium [14] has shown that, from an environmental point of view:

- Adhesives become weak and ductile at high temperatures and brittle at low temperatures.
- The yield stress and modulus of all adhesives decrease with increasing temperature and humidity.
- The plastic behaviour of adhesives at elevated temperatures causes significant shear deformation.
- The mechanical properties of adhesives can be substantially degraded by the absorption of moisture.
- Environmental conditions affect the failure mode as well as mechanical properties.

In terms of fatigue:

- Failure modes indicate that moisture affects adhesive bulk instead of the adhesive-substrate interface.
- One observation was that: lower void in bond line = longer fatigue life.
- Film adhesives show better resistance to moisture (fewer voids?).
- Stress relaxation was increased as the stress level and temperature was increased.
- The load-carrying capabilities of adhesive joints decrease as bond-line thickness increases.

- Increasing bond-line thickness affects the failure mode of bonded joints.
- Accumulation of large plastic strains in thin bond-lines resulted in high substrate interlaminar strains and caused substrate (first-ply) failure.
- Unstable damage development of thick bond-lines (lower plastic strain development) resulted in adhesive cracking in multiple locations with a cohesive-type failure and lower failure strengths.

The durability of epoxy-aluminium joints that used a homopolymerised epoxy resin was studied by researchers based in Spain [15], and the effects of relative humidity, temperature, and salt concentration analysed. The homopolymerised epoxy resin absorbed little water (1.5 wt%) because of its non-polar network structure. Increasing relative humidity and temperature enhanced water uptake, but the joint strength remained constant because of epoxy plasticisation. A saline environment was damaging to the adhesive joints because of metal corrosion, but was not significantly harmful to the epoxy resin because of the lower diffusion coefficient of salt water. The decrease in glass transition temperature of the epoxy adhesive due to water absorption was dependent upon only the amount of absorbed water and was independent of hydrothermal ageing conditions. The durability of epoxy adhesive joints made underwater has been studied [16].

Almost all structural applications of adhesive joints will experience cyclic loading and, in most cases, this is irregular, a form of loading commonly known as ‘variable amplitude fatigue’ (VAF). One article concerned with the VAF of adhesively bonded joints [17] showed that strength wear-out of bonded joints under fatigue is non-linear and that the addition of a small number of overloads to a fatigue spectrum can greatly reduce the fatigue life. It was also found that methods of predicting VAF in bonded joints based on linear damage accumulation are not appropriate and tend to over-predict fatigue life. Improved predictions of fatigue life can be made by application of non-linear strength wear-out methods with cycle mix parameters to account for load interaction effects.

The bond strength and durability of adhesively bonded titanium joints were investigated under different environmental conditions using an epoxy resin as structural adhesive and a sol-gel as adhesion promoter [18]. Tests were carried out on two groups of double-lap shear samples. One group was tested directly after sample preparation under different conditions (room temperature/dry (baseline), hot/dry (at 60 °C and 0% relative humidity) and low/dry (at –40 °C and 0% relative humidity). The second group was conditioned in water for 14 days at 71 °C and tested under conditions of hot/wet (at 71 °C and 90% relative humidity) and wet (at room temperature and 90% relative humidity). Samples exhibited different failure modes depending on the surface treatment of titanium, moisture conditioning and test conditions. Researchers based in the UK compared the Boeing wedge test (BWT), the forced wedge test (FWT), and the double cantilever beam (DCB) test to assess adhesive bonds under an assortment of environmental conditions. They showed that the FWT is not to be recommended whereas the BWT and the DCB test expose the joints to quite different environments [19].

5.1 Surface Treatments for Metals

The ability to clean and prime metals with environmentally-compliant and environmentally-friendly chemicals is being studied in all industries to maximise adhesive strength and enhance long-term durability.

Corrosion has been the major factor causing joint failure in the aerospace industry and this is still an issue facing potential industrial and automotive users, particularly if metals such as steel or copper are used [20]. Researchers based in Japan [21] showed that acid treatment of steel does not improve the fracture toughness of bonds with toughened epoxies, but it does increase the fatigue growth crack resistance by changing the locus of crack initiation from the adhesive-metal interface to the bulk adhesive itself. Work in China has demonstrated the utility of anti-corrosive polymer coatings on steel as improvements over phosphating if bonding with epoxy adhesives [22]. Plasma spraying of Ni-Cr and Ni-Cr-Zn onto steel has been shown to produce environmentally-durable bonds with epoxy adhesives [23]. Researchers based in China treated copper with aminosilanes before bonding with epoxies and showed a large increase in resistance to salt solutions. This was attributed to a reinforcement of the metal/adhesive interface due to coordination between the copper and the amino groups in the silane [24].

In the aerospace industry, aluminium and alloys are used widely and there are essentially two steps used to prepare these surfaces for bonding, i.e., an etching or anodisation process (to maximise adhesive strength) and a priming process (to prevent corrosion of assembled joints).

For aluminium alloys, there are three common surface-preparation techniques utilised for aerospace applications:

- The Forest Products Laboratory etching procedure utilising chromic-sulphuric acid.
- The Phosphoric Acid Anodisation process utilising phosphoric acid solutions. This was originally developed by the Boeing Company and is the treatment of choice for critical applications in the USA.
- Chromic Acid Anodisation is widely used to improve the corrosion protection of bare aluminium surfaces such as in window frames and other architectural applications. It is also the commonest pre-treatment process used for aerospace bonding in Europe.

Primers are also used and are typically organic solvent-based solutions of epoxies or phenolic adhesives. They provide several major functions:

(1) Protecting a chemically prepared surface during storage and handling

(2) Providing protection against corrosion inside and outside of bond lines

(3) Providing a surface that is readily bonded by adhesive films

(4) Providing protection against chemicals and being able to transfer loads from the aluminium substrate to the adhesive

Water-borne primers have been evaluated [25]. Davies and co-workers [26] described the improvement in adhesive bonding of aluminium alloys by anodising before bonding. This work showed that the morphology of the oxide and penetration of the adhesive into the porous oxide strongly influences bond performance.

Brewis and Critchlow [27] investigated the locus of failure of aluminium joints bonded with epoxies and polyurethanes and measured peel strengths after water immersion. Significant differences were found between different surface-treatment techniques, which included phosphoric anodisation, chromic-acid treatment, and epoxy primers.

Recently there has been a shift away from chemical-intensive and toxic processes. Several air forces have developed abrasion processes that include the application of silane coupling agents to prepare non-ferrous surfaces for adhesive bonding. These processes [27, 28], which are directed mainly at field-level repair, offer many advantages such as low-toxicity materials and fairly simple procedures. Boeing Corporation [29] and Dexter [30] described the testing of low-volatile organic compounds primers. Novel anodising techniques have been shown to be useful for the replacement of the chromic acid anodising process in structural bonding applications [31]. Recent trends in surface-treatment technologies for airframe adhesive bonding processing have been reviewed [32].

Silanes have become widely accepted as primers in several adhesive systems to prevent degradation of bonded joints due to the ingress of water. These molecules contain hydrophilic and hydrophobic moieties, and act as a coupling system between organic adhesives and metal or glass surfaces. In addition to enhancing adhesion, they provide resistance to hydrolytic degradation of adhesive bonds. The rate of hydrolysis of the primers on metal surfaces and catalysis by tin salts has been studied [33, 34].

However, silanes must be chosen carefully for each adhesive system. For example, in a study on the effectiveness of silanes as primers for the bonding of aluminium alloys with epoxies [35], it was found that bis(triethoxysilyl)ethane increased the durability of bonds exposed to acidified salt-spray by decreasing the hydrolysis and/or corrosion at the metal-adhesive interface, whereas gamma-aminopropyltriethoxysilane increased the strength of the bond but increased the corrosion rate, leading to bond failure. Other authors have shown that gamma-glycidilyaminopropyltrimethoxysilan e increased the fracture energy of epoxy bonds after exposure to water [36]. Authors based in Spain [37] showed that silanisation parameters such as solution concentration and drying temperature had a great influence on the durability of aluminium joints bonded with reactive acrylic adhesives. However, pH had only a slight influence. Preparation of the substrate surface before silanisation was found to be a significant factor.

It has been shown that a bilayer silanisation film layer on aluminium alloy prepared from two kinds of silanes, bis(3-(triethoxysilyl)-propyl)tetrasulfide and γ-glycidoxypropyltrimethoxysilane (epoxy functional silane), gave corrosion resistance and bond durability that is superior to those of epoxy functional silanisation used alone [38]. Alcoa researchers [39] investigated the bonding of aluminium alloys to steel for potential use in automobile body panels. In this study, lap-shear and peel specimens were prepared and treated under processing conditions currently used for steel designs. Aluminium substrates were prepared by vapour degreasing and alkali cleaning. The steel substrates were cleaned by wiping with methyl ethyl ketone solvent. Following the cleaning steps, a water-based forming lubricant was applied to the aluminium and the same lubricant or an anti-corrosion oil applied to the steel. Stiffeners were attached to the specimens to eliminate bowing caused by the difference in thermal expansion coefficients between the two metals. Following assembly with adhesive and curing, the assembled panels were zinc-phosphated and electrocoated, which are established procedures for steel surfaces to provide corrosion resistance and improve paint adhesion, respectively. The adhesives studied were a wide range of epoxy, toughened epoxy, epoxy urethane, and tough acrylics. Joint strengths of specimens were measured at room temperature and at 100 °C after immersion in common salt solutions and after exposure to 100% relative humidity conditions for periods up to 60 days. Long-term outdoor exposure was also carried out. Many adhesives give lap shear strengths of >14 Mpa if tested at room temperature and peel values of 70-175 N/cm. However, testing at 100 °C began to show dramatic differences between adhesives. At this temperature, we expect to see the effects of softening of the adhesive itself and the results of internal stresses set up by the differences in thermal expansion coefficients of the metals. All of the adhesives showed significant decreases in shear strength, with only four retaining strengths >10.5 Mpa. Humidity was by far the harshest environment for the specimens. Many of the adhesives do not survive the duration of the test, and peel strength decreases significantly in the humidity and immersion testing. Only two adhesives, a toughened epoxy and an epoxy-urethane, retained strength with all three alloys and under all environmental conditions.

A significant finding from this work was that there was no evidence of galvanic corrosion in the specimens in the accelerated testing or in the long-term exposures after one year. It is encouraging that bonds involving aluminium substrates appear to be less susceptible to environmental damage than those with steel because this is a factor that has limited the use of structural adhesives on steel. Pocius and co-workers [41] showed that in comparing the bond durability of steel and aluminium, dry lap-shear strengths can be similar but stressed lap-shear joints of steel substrates that are exposed to a humid environment fail in <30 days whereas the aluminium joints last for >3000 days.

Researchers in Sweden [42] investigated relatively simple surface treatments for aluminium with the goal of discovering what level of treatment is necessary to survive various environments. They found that the more corrosion-resistant low-strength alloys can often be treated by degreasing or brushing when exposed to non-severe environments such as indoor applications but, in severe climates or for water immersion, primers or anodisation are critical, particularly with high-strength, less corrosion-resistant alloys. Elbing and co-workers studied the surface pre-treatment of aluminium components by dry ice-blasting as well as a process optimisation for the enhancement of the adhesive strength of industrial epoxy and polyurethane adhesives on aluminium surfaces [43]. They found increases of adhesive strength by up to 99% for epoxy and 27% for polyurethane compared with untreated surfaces. Other environmentally-friendly pre-treatment methods include treatment of aluminium with excimer laser [44], CO_2-laser [45], electric arc treatment [46] and cryoblasting [47]. The subject of surface treatment and long-term durability of adhesively bonded aluminium has been reviewed [48-50]. Plasma spraying of inorganic powders onto aluminium and titanium surfaces has been shown to be equivalent to chemical treatments in enhancing the durability of adhesive bonds [51, 52].

5.2 Testing and Inspection of Adhesive Bonds

The most commonly used methods for evaluation of adhesive bonds are mechanical tests such as tensile shear and peel tests that determine the weakest link in a bonded assembly. Although these tests are useful in the development and quality control of adhesives, they are destructive and cannot offer failure prediction for in-service components. Ultrasonic inspection is the most commonly used non-destructive test method and can accurately assess debonding in single adhesive bonds, providing that the sensor is perpendicular to the defect plane. However, ultrasound has some limitations in multi-layered specimens and if the sensor cannot be aligned easily. Guide-wave technology has been described for evaluation of bonds in curved aircraft surfaces [53]. Jagasivamani and Smith [54] measured the acoustic properties of adhesive bonds under stress and could detect poor and good bonds by the influence of their stress sensitive properties on the acoustic wave time-of-flight and by temperature changes within the adhesive. One promising ultrasonic technique, angle-beam reflection, has been used to study the environmental degradation of adhesive joints [55]. It was found that this technique allowed distinction between degradation of the bulk adhesive and failures at the adhesive-substrate interface. Laser-induced ultrasound has been shown to be able to detect defects in bonded joints [56]. Authors based in France [57] have used ultrasonic measurements to measure the durability of pre-treated aluminium joints before and after exposure to a hot atmosphere (70 °C) for several cycles, each of 67 hours. The Australian Defence Force Academy has used holographic interferometry [58] to detect weakly bonded joints due to bond line-surface or adhesive degradation. Other researchers used dielectric spectroscopy to investigate the rate of ingress of water or solvent into composites or metals bonded with epoxies and correlated this with the loss of strength of the bonds [59-67]. Neutron radiography has been shown to be able to detect defects in steel substrates bonded with epoxies [68]. Direct current-resistance measurements have been used to determine the stages of degradation in steel joints bonded with epoxies [69]. Small-spot X-ray photoelectron spectroscopy can detect bond defects and verify the mechanism of delamination [70].

Automotive companies have used a four-poster road simulator rig with environmental conditioning to establish correlations with conventional adhesive testing methods [71].

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