**The Effects of Surface Pretreatment on the Cyclic-Fatigue
Characteristics of Bonded Aluminium-Alloy Joints**

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Abstract

The present work has used an accelerated test method, based upon cyclic-fatigue testing using a fracture-mechanics approach, to study the durability of organosilane-pretreated joints which were adhesively-bonded using a hot-cured epoxy-film adhesive. The silane primer investigated was γ -glycidoxypyltrimethoxysilane (GPS). The cyclic-fatigue tests were mainly conducted in (a) a 'dry' environment of $25 \pm 2^\circ\text{C}$ with a relative humidity of $55 \pm 5\%$ and (b) a 'wet' environment where the joints were fully immersed in distilled water at $28 \pm 2^\circ\text{C}$. However, tests were also undertaken by varying the relative humidity of the environment. The loci of failure of the joints were identified using various surface specific techniques. The use of the GPS-pretreatment has been shown to be effective in increasing the joint durability, compared with a simple grit-blast and degrease (GBD) treatment and, indeed, gives comparable results to using a chromic-acid etch (CAE) pretreatment.

Keywords: Durability, Environmental Attack, Epoxy Adhesives, Fatigue, Silanes

Running Headline:

Cyclic-Fatigue Characteristics of Bonded Aluminium-Alloy Joints

1. Introduction

The aerospace industry relies on adhesive bonding as a means of joining lightweight aluminium-alloy structures. This is because adhesively-bonded components offer good design flexibility, high strength to weight ratios and excellent fatigue resistance, in comparison to the more traditional, mechanically-fastened, structures. However, a limitation frequently encountered in service with bonded joints is the deleterious effect moisture may have upon joint performance. Hence, one of the greatest challenges in adhesive bonding is to impart good durability to structural adhesive joints when they are exposed to ingressing moisture, especially in the presence of relatively high stresses and cyclic-fatigue loads [1].

It has long been recognised that to attain long service-lives from adhesive joints, which are required to operate in severe, hostile environments, some form of pretreatment is usually required. Currently, most surface pretreatment procedures employed in the bonding of aluminium alloys in the aircraft industry rely on etching and anodising techniques, typically involving aggressive and toxic chemicals. However, chemical compounds based on hexavalent chromium have, in particular, been the cause of considerable concern in recent years, with governmental and environmental bodies applying considerable pressure for their removal from industrial processes. This arises not only from possible hazards to the work force but also as a result of several high profile cases in which Cr(VI) containing waste has not been disposed of correctly and has found its way into the water table supplying domestic drinking water.

Organosilanes are considered as potential environmentally-benign replacements for chromium-based surface pretreatments. Nevertheless, although a considerable amount of research has evaluated the properties of silane-based primers, much uncertainty has remained as to the precise mechanisms associated with the increase in durability that they may impart to an adhesively-bonded joint [1-6]. The current paper considers this issue with particular emphasis on adopting a fracture-mechanics approach to assess the durability when employing organosilane pretreatments, since the use of cyclic-fatigue tests, based upon a fracture mechanics approach, has been shown to provide an excellent accelerated test method for assessing joint durability. The results obtained are discussed in terms of both static (i.e. constant rate of displacement) and dynamic-fatigue loading, together with surface characterisation results from surface specific analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectrometry (ToF-SIMS).

2. Experimental

2.1 Materials

The substrate employed was an aerospace grade aluminium-copper alloy designated '2014-T6'. The composition, in weight %, of this alloy is as follows: Cu: 3.9-5.0, Fe: 0.7, Si: 0.5-1.2, Mn: 0.4-1.2, Mg: 0.2-0.8, Cr: 0.1 with Al: balance. The alloy was obtained in the as-rolled condition in the form of 9.75 mm thick sheets and cut into tapered beams using a computer-controlled milling machine. The adhesive employed was a 120°C curing modified epoxy-film adhesive, which was selected for inclusion in this study due to the absence of silane coupling agents in the formulation. The organosilane investigated was γ -glycidoxypyltrimethoxysilane (GPS).

2.2 Experimental Procedures

All substrate surfaces were initially grit-blasted and degreased (termed a 'GBD' pretreatment) prior to any further surface pretreatment. This involved wiping the surface with acetone, to remove any gross contamination such as oil, then abrading the surface by blasting with 50µm alumina grit. Any residual grit was removed with clean air and the surface again wiped with acetone.

The organosilane primer was applied following the GBD-pretreatment procedure. The GPS silane solution was prepared by diluting 1%v/v GPS in deionised water and adjusting the pH with acetic acid to ensure a pH of 5.0. The resulting solution was then stirred continuously for 60 minutes with a magnetic stirrer. A solution concentration of 1%v/v was chosen, as previous studies [7,8] have indicated that this concentration is optimal for good joint durability. The silane solution was then brush applied to the alloy substrate for 10 minutes, whilst maintaining the surface in a wet condition. The specimens were then tipped vertically and tapped on a paper towel to remove residual silane solution, then immediately inserted into an oven and dried for 60 minutes at 93°C. The specimens were then removed from the oven and allowed to cool below 30°C before bonding immediately.

The above silane-based pretreatment was compared with the conventional chromic-acid etch (CAE) aerospace pretreatment, following the GBD-pretreatment procedure. The CAE pretreatment was performed by immersing samples in a solution containing chromic acid for 20 minutes at 68°C, and then rinsing in distilled water before drying in an oven for 20 minutes at 40°C prior to bonding.

Static fracture and cyclic-fatigue testing were conducted using tapered double-cantilever beam (TDCB) joints [9-12] of the type indicated in Figure 1. Following the surface pretreatment, bonded joints were prepared by initially placing strips of film adhesive across the bonding surface of one half of the tapered beam. A strip of release-agent coated aluminium-foil was then placed on top of the adhesive strip, at the narrow end of the beam. The second half of the beam was then placed on top, such that the bonding surfaces were matched. The beam was then placed into a jig designed to allow both sufficient pressure to be applied to the adhesive layer during cure and the appropriate alignment of the two halves of the joint. Joints were then cured in an oven for 90 minutes at 95°C followed by 45 minutes at 120°C.

The values of the adhesive fracture energy, G_c , were obtained from TDCB joints under monotonic loading (termed ‘static’) conditions in accordance with the linear-elastic fracture-mechanics standard test procedure proposed by Blackman et al. [9,12]. Tests were conducted at a constant crosshead rate of 0.1mm/min, with the crack length being measured using a video camera. Values of the adhesive fracture energy were calculated using equation (1):

$$G_c = \frac{P_c^2}{2b} \frac{dC}{da} \quad (1)$$

where P_c is the load at the onset of crack propagation, b is the specimen width, C is the compliance and a is the crack length.

For the cyclic-fatigue tests, TDCB joints were mounted in a tensile testing machine such that the joints were orthogonal to the direction of the applied load. In each case a sinusoidal loading form was applied at a frequency of 5Hz and a range of maximum displacements δ_{max} employed, such that the displacement ratio $\delta_{max}/\delta_{min}$ was maintained constant at 0.5. Displacement, rather than load, control was selected for these tests, as joints will fail much earlier under load control as compared with displacement control. Fatigue tests were conducted in a range of different environments. Tests were performed in ‘dry’ ambient conditions, i.e. $25 \pm 2^\circ\text{C}$ with a relative humidity of $55 \pm 5\%$. ‘Wet’ tests were also performed by cyclically-loading the TDCB joint whilst they were fully immersed in distilled water at $28 \pm 2^\circ\text{C}$. Also, some GPS-pretreated joints were exposed to various levels of relative humidities, controlled by using appropriate salt solutions. During the cyclic-fatigue tests, the maximum and minimum loads (P_{max} and P_{min}) and the number of cycles, N , were recorded as a function of crack length, as the crack propagated through the tapered beam. Crack lengths were measured along the adhesive layer to an accuracy of $\pm 0.5\text{mm}$, using a travelling microscope. Each fatigue test was run until crack propagation ceased, such that no further crack growth was detected over at least 10^7 fatigue cycles. Fatigue curves were obtained by plotting values of the rate of crack growth per cycle, da/dN , as a function of the maximum strain-energy release-rate, G_{max} , using double logarithmic scales; where G_{max} is given by:

$$G_{max} = \frac{P_{max}^2}{2b} \frac{dC}{da} \quad (2)$$

It should be noted that previous work [13] has shown that the results for da/dN as a function of G_{max} are independent of whether a constant displacement-ratio or constant load-ratio is applied during the cyclic-fatigue tests. In the latter type of testing, a series of different load ratios are needed to acquire the full history of the relationship between da/dN and G_{max} . Clearly, the use of these different test approaches implies somewhat different lengths of exposure of the TDCB specimens to the test environment. However, the previous observations reveal that these somewhat different lengths of exposure time have no significant effect on the results for da/dN as a function of G_{max} . (Since the cyclic-fatigue tests only last a matter of a few weeks, this observation is not unexpected.)

Surface analysis procedures were employed to assess both the control (i.e. unbonded) oxides on the pretreated aluminium-alloy specimens and the fracture surfaces taken from failed joints. For the control oxide studies, aluminium-alloy coupons of approximately 1 cm^2 were employed. GPS films were then applied according to the procedures previously described. For the locus of failure studies, the fracture surfaces were carefully sectioned to approximately $1\text{cm} \times 1\text{cm} \times 0.2\text{cm}$, such that they could be accommodated within the surface analysis instruments. Scanning electron microscopy studies were conducted using a 'JEOL JSM 5300' microscope using an accelerating voltage of 10kV. Prior to examination, surfaces were sputter coated with carbon so as to prevent surface charging effects. Energy dispersive X-ray analysis (EDXA) was also employed to undertake an analysis of the chemical composition of the surfaces. Both X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were employed to characterise

surfaces produced following silane surface pretreatment and joint testing. XPS spectra were recorded using a 'VG Scientific ESCALAB MKII' spectrometer. The analyser was operated at a pass energy of 100 eV for the survey spectra and a pass energy of 50 eV for high resolution spectra. MgK α radiation with a kinetic energy of 1253.6 eV was used. The take-off angle employed was 45° and the analysis area was 5 x 2 mm². In order to assess the distribution of species within the near surface region of the specimen argon ion bombardment was carried out *in-situ*. This was achieved using a VG Scientific AG21 cold cathode ion gun using 6 kV argon ions operated in the partially defocused (focus potential 3 kV) mode. Following short periods of ion etching, XPS analysis was repeated in order to obtain a compositional depth profile. The sputter rate using the conditions described above is approximately 1 nm min⁻¹ on a Ta₂O₅/Ta standard. Imaging XPS was employed to identify the spatial localisation of particular elements over the surface. The instrument employed in this study was a 'VG Scientific ESCALAB 220i XL'. The imaging mode in the current work investigated an area measuring about 5 mm x 4 mm of the specimen surface. The spatial resolution achieved over this area was of the order of 50 μ m. ToF-SIMS analysis was undertaken using a 'VG Scientific Type 23' system with a liquid gallium metal ion source (⁶⁹Ga⁺ at 20 kV) and a two-stage reflectron mass spectrometer. Complementary analyses were also recorded using a Physical Electronics 'Phi 7200' ToF-SIMS spectrometer, which has a higher mass resolution than the V G Scientific instrument. This is a reflection system equipped with a caesium surface ionisation source (¹³³Cs⁺ at 8 kV). In all the ToF-SIMS analyses, care was taken to ensure that the ion dose was within the static limit of 10¹³ ions cm⁻².

3. Results and Discussion

3.1 Static tests

In order to gain an estimate of the crack propagation resistance of the adhesive system selected for study, static tests were undertaken using TDCB joints. Thus, the critical adhesive fracture energy, G_c , required to achieve ultimate failure of the joints could be determined. The results are shown in Table 1 and are the average values taken from at least five replicates per pretreatment. As expected, the lowest value of G_c was obtained for the GBD joints. The values G_c for the CAE- and GPS-pretreated joints are not significantly different. These observations were not unexpected, since the loci of joint failure for the CAE- and GPS-pretreated joints were via cohesive failure through the adhesive layer, whilst the GBD-pretreated joints revealed evidence of interfacial failure.

3.2 ‘Dry’ cyclic-fatigue tests

Cyclic-fatigue tests were carried out in the ‘dry’ environment of $25 \pm 2^\circ\text{C}$ with a relative humidity of $55 \pm 5\%$. They were replicated in duplicate or triplicate and the results showed good agreement, thus confirming the validity of the data obtained. Values of the threshold fracture energy, G_{th} , (i.e. the value of G_{max} below which no fatigue crack growth was found to occur) were ascertained and were found to be far lower than the adhesive fracture energy, G_c , obtained under static-loading conditions. Table 2 records the results obtained from cyclic-fatigue experiments conducted in a ‘dry’ ambient environment. Thus, such fatigue tests clearly reveal the damaging effect of the cyclic-loading conditions, compared with static loading. This is consistent with work reported by others [14,15] and reveals, of course, the particularly damaging

effects of subjecting materials, including polymeric adhesives, to cyclic-fatigue loading.

Figure 2 shows a comparison of the fatigue curves obtained for each pretreatment. The values of the threshold fracture energy, G_{th} , are derived from the plot of $\log_{10} da/dN$ against $\log_{10} G_{max}$ where the fatigue curve tends to a straight line, i.e. where a constant (lower-bound) value of G_{max} is obtained. As can be seen, data for the GPS- and CAE-pretreated joints lie, within experimental error, on the same line. This clearly demonstrates that the GPS-pretreated joints, when tested in the ‘dry’ environment, have a similar threshold fracture energy, G_{th} , value to those joints which were prepared using the CAE pretreatment. Furthermore, both of these pretreatments are seen to result in higher threshold fracture energies than recorded when simply using the GBD pretreatment alone. These results are summarised in Table 2. Indeed, the complete fatigue curve for the GBD-pretreated joint lies to the left of that for the GPS- and CAE-pretreated joints. For example, for a given value of G_{max} (when $G_{max} > G_{th}$), the rate of crack growth, da/dN , per cycle is significantly higher by a factor of approximately one hundred for the GBD-pretreated joints compared with the GPS- and CAE-pretreated joints. Failures were cohesive in the adhesive layer for both the GPS- and CAE-pretreated joints, but visually interfacial for the GBD-pretreated joints.

It is particularly interesting to compare ratios of G_{th}/G_c as a means of ranking the effect of pretreatment on joint performance, see Table 2. These values also demonstrate that the application of a chemical pretreatment to the grit-blasted surface can help counter the deleterious effects of cyclic-fatigue loading. For example, the threshold fracture energy, G_{th} , of the GBD-pretreated joints after cyclic-fatigue

loading is about 13% of the corresponding adhesive fracture energy, G_c , obtained under static loading; and this value decreases to only 5% if based upon the value of G_c for a cohesive failure of the adhesive, i.e. a G_c value of about 1500 Jm^{-2} . However, the ratio of the threshold value to the adhesive fracture energy, G_{th}/G_c for the CAE-pretreated joints is significantly higher at 15%, and this is approximately equivalent to that for the GPS-pretreated joints at 17%. This, of course, emphasises the importance of employing a chemical pretreatment for attaining an enhanced joint performance, even in a relatively ‘dry’ environment where environmental attack is unlikely to be significant.

3.3 ‘Wet’ cyclic-fatigue tests

As noted previously, one of the most hostile environments that adhesive joints can encounter is one comprising water in its various forms, especially if elevated temperatures and cyclic-fatigue loads are also present. Indeed, if cyclic-fatigue tests are conducted in a ‘wet’ environment it is well established [1,10,11,14,15] that the performance of adhesively-bonded joints may rapidly deteriorate.

Indeed, the present ‘wet’ fatigue tests clearly reveal the detrimental effect an aggressive environment may have upon the toughness of adhesive joints, and highlights the important influence of employing a chemical surface pretreatment on joint durability. As shown in Tables 2 and 3, for all the adhesive joints the effect of water immersion was found to reduce the threshold value, G_{th} , from the value of approximately 250 Jm^{-2} , corresponding to a ‘dry’ environment test when failure occurs cohesively through the adhesive layer. The greatest reduction in the value of G_{th} corresponding to a ‘wet’ environment, see Table 3, was recorded for the GBD-pretreated joints, which have a G_{th}/G_c ratio of only 2%. Reductions in the threshold

energies were also recorded for both the GPS- and CAE-pretreated joints, although to a somewhat lesser extent; with G_{th}/G_c values of approximately 6 to 7% being recorded. Thus, significant improvements in durability were demonstrated by the GPS-pretreated joints, compared to the GBD pretreatment and from Table 3, the value of the threshold energy, G_{th} , in the ‘wet’ environment for the GPS-pretreated joints was 100 Jm^{-2} , compared with only 15 Jm^{-2} for the GBD-pretreated joints.

Figure 3 shows the actual fatigue curve obtained for the GBD- and GPS-pretreated joints in tested in the ‘wet’ and ‘dry’ environments. The major effects of water attack are to lower G_{th} , the threshold value, and to shift the curve to the left. In the ‘wet’ environment, the value of G_{th} for the GBD-pretreated joints is found to be approximately six times lower than that for the GPS-pretreated joints. Water, therefore, clearly has a greater effect on the GBD-pretreated joints, and this is in accord with the observation that environmental attack increases the degree of interfacial failure in GBD-pretreated joints to the extent that the adhesive partially debonded from both substrate surfaces during the fatigue test.

Visual examination of the fracture surfaces of the GBD-pretreated joints revealed that the crack path was predominantly along the adhesive/substrate interfaces. It was also noted that the ‘metal’ side of the fractured joint did not appear light and shiny, as was observed for interfacial failure in ‘dry’ failure conditions. In contrast, the ‘metal’ side of the fractured ‘wet’ tested joint had a dark, dull appearance. This darkening of the apparently bare aluminium oxide surface could be due to hydration of the aluminium oxide, forming aluminium hydroxide. Hardwick *et al.* [16] have observed that, for adhesive joints tested in water, the dull regions of the

failure surface corresponded to a hydrated surface whilst the shiny regions corresponded to an oxide coated with a thin adhesive layer.

Thus, the effect of water attack has a significantly less detrimental effect on the value of G_{th} for the GPS-pretreated joints than for the GBD-pretreated joints. However, the reduction in the cyclic-fatigue properties for the GPS-pretreated joints may still be accounted for by the transition in the mode of failure from cohesive in the adhesive layer to interfacial, indicated by the dashed line in Figure 3. As may be seen from Figure 4, the crack path is initially within the adhesive, as adhesive is seen on both sides of the fracture surface. However, the crack path changes to being visually along the adhesive/substrate interface at longer crack lengths, as the threshold region is approached. Also, visual examination of the fracture surfaces indicates that the crack path was not confined exclusively to one adhesive/oxide interface, but jumped from one interface to the other. A similar result has been observed by Gettings and Kinloch [4].

Finally, the results, see for example Table 3, demonstrate that the application of the environmentally-friendly GPS pretreatment is as effective as the conventional aerospace CAE pretreatment, in terms of the joint durability that is observed.

3.4 Analysis of Failure Surfaces

3.4.1 Initial investigations

As highlighted above, water immersion during the fatigue test caused the locus of failure of the joints to essentially change from cohesive within the adhesive layer to visually interfacial. The GBD-pretreated joints exhibited 100% interfacial behaviour with no cohesive areas, whereas the CAE- and GPS-pretreated joints appeared to

resist water attack for a greater number of cycles before the locus of failure became visually interfacial, as the fatigue threshold region was approached. However, it was not possible to determine visually whether this apparent interfacial failure had actually occurred at the adhesive/silane or silane/metal interfaces, or possibly through the metal oxide or the silane-primer layer. To assess the precise nature of the failure processes, various surface analysis techniques were employed.

Scanning electron microscopy was used to examine the fracture surfaces obtained near the fatigue threshold limit of the GBD- and GPS-pretreated joints which had been cyclically tested in the ‘wet’ environment. The fracture surfaces of the ‘metal’ side of the joints were found to be far more similar in topography to the original grit-blasted surface, than to the topography of the joints which had failed cohesively through the adhesive layer. Hence, these results suggest that both GBD and GPS joints tested in water failed at, or very close to, the metal oxide interface, thus, tentatively at least, confirming the visual observations. However, to identify the precise nature of the failure processes, further work using XPS and SIMS was undertaken.

3.4.2 XPS studies

In the ‘dry’ ambient conditions, the locus of failure of the joints tested via both the static and cyclic-fatigue loading was observed to be cohesive in the adhesive for the GPS-pretreated joints, but visually interfacial for the GBD-pretreated joints. Hence, XPS was used to analyse the GBD fracture surface to investigate whether the failure was truly interfacial. XPS analysis of the fractured surfaces near the threshold region of the GBD-pretreated joints that had been cyclically loaded in the ‘dry’ ambient conditions revealed that failure was indeed truly interfacial, since only a negligibly

small concentration of aluminium was detected on the ‘adhesive’ side of the failed joint, and no adhesive material was detected as having been transferred to the ‘metal’ side.

When tested in the ‘wet’ environment, both the GBD- and GPS-pretreated joints appeared to fail interfacially. Visual and scanning electron microscopy observation of the fracture surfaces of these joints indicated a ‘metal’ side where adhesive was absent, and an ‘adhesive’ side where no metallic areas were visible. The quantitative surface analyses by XPS for the interfacial metal and polymer failure surfaces of GBD- and GPS-treated joints are tabulated in Table 4. The XPS survey spectrum is shown in Figure 5 of the ‘adhesive’ side of a failed GBD-pretreated joint which had been tested under cyclic fatigue loading in a ‘wet’ environment. Only a very small amount of aluminium was detected, seen in the spectrum of Figure 5 as very minor contributions from the Al2p (ca. 74 eV) and Al2s (ca. 124 eV) electrons, which suggests that failure mainly occurred through the adhesive/metal interface; since a much higher aluminium concentration would have been expected for failure through the aluminium-oxide layer. This very small concentration of aluminium that was detected might have been due to the crack growing through the oxide asperities, as the crack travelled along the adhesive/substrate interface. Alternatively, such a small amount of aluminium may have resulted from surface contamination, such as metal debris as a result of machining the sample, rather than any retained aluminium oxide on top of the adhesive layer. (It should be noted that a clean, unbonded, GBD surface will have a surface concentration of aluminium of ~ 25 at. %.) In Figure 5, the nitrogen 1s signal at 400 eV, equivalent to a concentration of ca. 3 at. %, is characteristic of the amine curing-agent employed in the adhesive. The assignment of an interfacial failure locus is reinforced by the data of Table 4. For the GBD-

pretreated specimen the level of carbon observed on the interfacial adhesive failure surface is relatively high at 71 at. %, and this is consistent with the surface analysis of an epoxy adhesive. On the metal side, however, this is reduced dramatically to 45%, a value which is on the upper bounds of what one would expect from a clean oxidised metal surface prepared employing a mechanical abrasion pretreatment.

In contrast, Figure 6 shows the survey spectrum of the ‘adhesive’ side of a failed GPS-pretreated joint which was obtained near the fatigue threshold limit. In this case, relatively high levels of aluminium were detected, similar on both sides of the ‘wet’ GPS-pretreated joints: 16 at. % for the metal side and 14 at. % for the adhesive failure surface (see Table 4). This suggests that failure had occurred within the aluminium-oxide layer. Indeed, examination of the Al 2p spectra for the ‘adhesive’ side for such ‘wet’ tested GPS-pretreated joints revealed a single intense aluminium peak at a binding energy of approximately 74 eV. This corresponds to aluminium in the oxidised form, thus confirming that the aluminium present on the ‘adhesive’ side is aluminium oxide resulting from joint failure through the oxide layer or at the metal/oxide interface. It is important to note the absence of silicon in this spectrum (Si2p ~ 100 eV, Si2s ~ 150 eV). This indicates that the locus of failure is not associated with the silane layer or any Al/Si oxide layer that has grown during the drying process at 93°C.

Only a single, symmetrical, Al 2p peak, corresponding to the oxide form, was detected on the ‘metal’ sides of both the GBD- and GPS-pretreated joints that had been tested in the ‘wet’ environment. However, two Al 2p peaks were recorded on the ‘metal’ side of the GBD-pretreated joints which were tested in the ‘dry’ environment. These two components at ca. 72 and 74 eV from the ‘dry’ tests are assigned to

metallic aluminium (Al^0) and oxidised aluminium (Al^{3+}), respectively, and the fact that the underlying metal can be observed in the spectrum indicates that the oxide is thinner than the analysis depth of XPS, about 6nm for the $\text{Al}2\text{p}$ electrons. Thus, these observations demonstrate that the oxide present on the fracture surfaces of the ‘metal’ side of both types of ‘wet’ tested joints is thicker than that present on the ‘metal’ side of the ‘dry’ tested GBD-pretreated joint. It was also observed that, for the ‘wet’ tested GPS-pretreated joints, only one component, corresponding to aluminium in the oxide form (i.e. $\text{Al}2\text{p}$ at ~ 74 eV), was detected on the ‘adhesive’ side; and no Al^0 component was observed from the underlying base metal. This indicates that the thickness of the retained oxide layer on the ‘adhesive’ side of the ‘wet’ tested GPS-pretreated joints exceeds the depth of XPS analysis of about 6 nm. These observations are not unexpected, since the oxide present on the alloy surface is known to increase in thickness due to hydration in ‘wet’ environments, especially once the joint has fractured and fresh oxide surface is exposed to the ‘wet’ environment. This aspect is discussed in more detail below, when the results from the ToF-SIMS studies are presented. (It should be noted that the oxide layer may also grow somewhat in thickness, with the incorporation of some silicon from the GPS, during the initial curing process prior to joint fabrication [17].)

Gettings and Kinloch [4] have obtained results different to these for steel joints pretreated with GPS. They found that failure of GPS-pretreated joints which had been exposed for a month in distilled water at 60°C occurred through the silane layer. Similar results were obtained for aluminium joints by Rider and Arnott [18]. However, the absence of silicon from the ‘adhesive’ side of the GPS-pretreated joints tested in the present work suggests that failure occurred in the oxide layer, and not within the silane layer. Although trace amounts of silicon were detected on the ‘metal’

side of the fractured GPS-pretreated joint, it is most likely this could have come from silicon within the alloy or the alumina grit, or from silicone contamination (such as poly(dimethyl siloxane) from the release film or other unidentified sources). Indeed, the cohesive fracture surfaces from ‘dry’ tested GPS-pretreated joints revealed similar levels of silicon present on the ‘adhesive’ surface. In addition, a bare aluminium surface was also shown to have silicon present, at a level of 1 at. % on an unbonded GBD surface, as illustrated by XPS results from the GBD-pretreated aluminium.

To gain a greater understanding of the nature of the failure processes occurring in the GPS-pretreated joints, XPS depth-profiling experiments were performed through the ‘adhesive’ side of a GPS joint that had been subjected to cyclic-fatigue failure near the threshold regions in a ‘wet’ environment. The results are shown in Figure 7 and reveal the extent to which the concentrations of the main elements present in the failure zone varied as a function of depth down through the failure surface. Using argon ions to etch down to a depth of approximately 35 nm (i.e. equivalent to 2000 s on the abscissa of Figure 7), then for the first 3 nm a sharp decrease in carbon concentration was observed, which can be attributed to the removal of atmospheric contamination from the sample surface. Sharp increases in both aluminium and oxygen concentration were also observed, which provides confirmation of a layer of aluminium oxide present beneath a thin layer of carbonaceous contamination. Interestingly, it was also noted that the atomic concentrations of aluminium and oxygen levelled off after the first few nanometres, and remained fairly constant thereafter. This, of course, suggests that the layer of aluminium oxide covering the adhesive is relatively thick, at least greater than 35 nm in thickness. This oxide thickness is known to be much thicker than the original oxide on a fresh GBD-pretreated surface, which is [19] approximately 4 nm, that is slightly

thicker than the expected Mott thickness but a not unreasonable value. The carbon level within the depth profile stays fairly constant following the initial reduction and the reason for this is not clear, but it is anticipated that it is a combination of the result of ion beam shadowing during the etching of the rough, grit blasted, surface and the incorporation of a small amount of carbon, from the GPS primer, during the oxide growth occurring as the silane is cured. Another possibility is that of a mixed mode failure with small islands of oxide remaining on the underside of the adhesive. The depth profile then merely reflects the removal of the hydrocarbon from these small fragments of oxide and thereafter shows no change. (It should be noted that it is unlikely that such an observation results from the removal of residual abrasive particle from the grit-blasting process, as scanning electron microscopy presented no evidence of alumina particles imbedded in the metal surface.)

However, further confirmation of failure through the oxide layer was obtained from elemental mapping using XPS and EDXA. Such XPS studies indicated that the oxide layer retained on the ‘adhesive’ side of the failed GPS-pretreated joints was relatively uniformly distributed over the fracture surface, with no obvious areas of relatively high aluminium concentration. Similarly, EDXA studies also revealed a uniform concentration of aluminium across the ‘adhesive’ failure surface.

3.4.3 ToF-SIMS studies

The fracture surfaces of GBD- and GPS-pretreated joints tested under cyclic-fatigue loading in the ‘wet’ environment were also examined using time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis. Figure 8 shows a positive ToF-SIMS spectrum in the mass range of $m/z = 400$ to 1000 Da. for the ‘adhesive’ side of the fracture surface taken from the apparently interfacial failure region, near the fatigue

threshold, for the GBD- and GPS-pretreated joints. Characteristic clusters of peaks associated with the various forms of aluminium oxide and hydroxide were detected at high masses on both fracture surfaces of the GPS-pretreated joints and in both positive and negative ToF-SIMS. Although only a small portion of the positive SIMS spectrum is shown in Figure 8b, the complete set of assignments in both positive and negative SIMS for aluminium oxide/hydroxide fragments is give in Table 5. However, these diagnostic inorganic peaks were absent from the ‘adhesive’ side of the fracture surface of ‘wet’ tested GBD-pretreated joints, see Figure 8a. This confirms the XPS results discussed above, which suggested that in the ‘wet’ environment the GBD-pretreated joints failed mainly at the aluminium oxide/adhesive interface, whereas the GPS-pretreated joints failed mainly within the oxide layer.

The ToF-SIMS spectrum from the GBD-pretreated failure surface, Figure 8a, shows peaks which are typical of an epoxy-based structural adhesive. Although it is not possible to assign all fragments at this stage those at $m/z = 429$ and 549 Da. are produced by fragmentation of the epoxy/curing agent structure to yield the ions shown in the schemes below:

ToF-SIMS depth profiling was used to examine the ‘adhesive’ side of a fractured GPS-pretreated joint which had been tested under cyclic-fatigue loading in a ‘wet’ environment and had failed near the fatigue threshold region. Using this technique, with controlled ion etching via the incident beam, enabled SIMS analyses to be taken at successive depths into the oxide layer, which had already been shown by XPS analysis to exist on the ‘adhesive’ side. This allowed changes in the chemical nature of the oxide throughout its depth to be observed. The results revealed that the intensity of the oxide (O^-) peak increased with etching time on the ‘metal’ side of the failed joint, with the oxide peak from the ‘adhesive’ side being less intense and decreasing a little with etching time, as may be seen in Figure 9. The intensity of the hydroxide ion (OH^-) was found to decrease with etching time (and thus depth) for both the ‘metal’ and ‘adhesive’ sides of the joint. Hence, the ratio of OH^-/O^- for both the

‘metal’ and ‘adhesive’ sides decreased during etching, as shown in Figure 9, although the reduction is far more pronounced for the ‘metal’ side of the failed joint. This indicates that the phenomenon is not merely a result of the hydration of a pre-existing oxide layer, occurring post-failure of the joint. Thus, the available evidence suggests that failure occurred within a predominantly hydroxide layer, which is known to be weaker than the initial oxide [20,21]. Therefore, oxide weakening arising from hydration of the oxide *in-situ* by the ingressing moisture appears to have initiated joint failure, as has previously [11] been demonstrated to occur via transmission electron microscopy studies.

3.5 Effect of varying the relative humidity

Numerous studies have revealed that adhesive joints can often withstand exposure to relatively low humidities for long periods of time without any obvious signs of degradation. Such observations have led several authors, most notably Gledhill et al. [22] and Brewis et al. [23], to propose the idea that there must be a critical water concentration, C_c , in the adhesive layer, below which environmental attack does not occur.

Therefore, it was of interest to investigate the effect of humidity on joint durability by performing cyclic-fatigue tests via subjecting TDCB joints to different levels of relative humidities. GPS-pretreated joints were chosen for this study since they had shown a clear transition from cohesive failure in ambient, ‘dry’, conditions, to interfacial failure when tested immersed in water near the fatigue threshold. Fatigue tests on the silane-pretreated joints were conducted in an enclosed chamber, with the humidity controlled using various saturated salt solutions.

The results obtained are highlighted in Figure 10. As can be seen, an apparent discontinuity exists in the value of the threshold value, G_{th} , at approximately 55 to 80% RH; the value of G_{th} being virtually invariant with humidity below about 55% RH, but substantially dependent upon RH beyond this value. This result implies the existence of a critical humidity, somewhere between 55 to 80% RH, below which there is no significant loss of fatigue resistance as the RH is varied. This is, of course, a particularly significant result in that it demonstrates the possibility that such adhesive joints could be exposed to relatively dry environments with humidities below 55% RH for prolonged periods without any significant loss in joint performance.

The influence of humidity on the locus of failure of the above discussed joints was to drive the locus of failure from cohesive within the adhesive layer in ‘dry’ conditions to increasingly visually interfacial at the later stages of crack growth (i.e. near the threshold region) in the more humid environments. Continuing on this theme, Table 6 shows that the locus of failure becomes visually interfacial at humidities approaching approximately 60% RH and above. However, the results of the XPS analysis revealed that, what appeared visually to be interfacial failure, is in fact either joint failure within the GPS layer or within the oxide layer. Interestingly, the results suggest that the effect of increasing humidity, and hence the moisture content of the adhesive layer, is to progressively lead to the locus of failure being through the silane layer, then ultimately through the aluminium oxide layer at the highest humidities.

Davis et al. [24] have suggested that an incubation time is required for hydration of the aluminium surface to occur and that this time period is dependent on such factors as amount of water present at the interface, temperature and pH of the aqueous

environment. The fact that the XPS analyses reveal failure within the oxide layer for both fully immersed joints and those subjected to 100% RH indicates that the presence of an apparent critical humidity is dictated by the attainment of a critical concentration of water required to hydrate the oxide layer, such that mechanical weakening, followed by failure of the oxide layer (and hence the joint), occurs. Interestingly, this is in accord with an earlier suggestion from Brewis et al. [23].

It is, however, uncertain why the silane layer should be susceptible to hydrolytic attack at intermediate humidities. However, since an apparent critical concentration of water may be necessary to facilitate hydration of the oxide layer, it is perhaps logical to assume that at intermediate humidities the water concentration within the adhesive layer may be sufficient to cause damage to the silane layer. Thus, at intermediate humidities, with the extent of oxide hydration at a minimal level, joint failure initiates and occurs within the silane layer. This, therefore, emphasises the important nature of the silane layer in terms of its ability to withstand degradation by aqueous environments. This requirement being in addition to the requirements (a) to protect the aluminium oxide layer from hydration, and (b) to enhance the environmental stability of the intrinsic adhesion at the adhesive/substrate interface.

Thus, in terms of even further enhancing the durability of silane-pretreated joints, three aspects would seem to be of prime importance. Firstly, one might consider the use of a crosslinking agent to improve the cohesive properties of the silane layer [e.g. 25]. Secondly, the possible use of hydration inhibitors to impart hydration resistance to the oxide layer is worthy of further study [e.g. 24,26]. Thirdly, one must ensure that the intrinsic adhesion at the adhesive/substrate is enhanced by

the presence of the silane, for example by the creation of covalent bonds as opposed to the formation of only van der Waals interface bonds [4,5,27] .

4. Conclusions

The present work has used an accelerated test method, based upon cyclic-fatigue testing using a fracture-mechanics approach, to study the durability of organosilane-pretreated joints which were adhesively-bonded using a hot-cured epoxy-film adhesive. The silane primer investigated was γ -glycidoxypyrtrimethoxysilane (GPS). The cyclic-fatigue tests were mainly conducted in (a) a ‘dry’ environment of $25 \pm 2^\circ\text{C}$ with a relative humidity of $55 \pm 5\%$ and (b) a ‘wet’ environment where the joints were fully immersed in distilled water at $28 \pm 2^\circ\text{C}$. However, tests were also conducted, using the GPS-pretreated joints, by varying the relative humidity of the environment. The loci of failure of the joints were identified using various surface specific techniques.

The main conclusions were:

- From the cyclic-fatigue tests conducted in the ‘dry’ environment, values of the threshold fracture energy, G_{th} , (i.e. the value of G_{max} below which no fatigue crack growth was found to occur under cyclic loading) were ascertained and were found to be far lower in value than the adhesive fracture energy, G_c , obtained under static-loading conditions.
- Furthermore, in the case of the grit-blasted and degreased (GBD) pretreated joints, the value of G_{th} decreased dramatically in the presence of water when the joints were tested in the ‘wet’ environment.

- Significant improvements in durability were demonstrated by the GPS-pretreated joints. The value of the threshold energy, G_{th} , in the ‘wet’ environment for the GPS-pretreated joints was 100 Jm^{-2} , compared with only 15 Jm^{-2} for the GBD-pretreated joints.
- This value of G_{th} in the ‘wet’ environment for the GPS-pretreated joints of 100 Jm^{-2} was comparable with the value of G_{th} for joints pretreated using a chromic-acid etch (CAE) pretreatment.
- The values of G_{th} for the GPS-pretreated joints as a function of the relative humidity of the environment implies the existence of a critical humidity, somewhere between 55 to 80% RH, below which there is no significant effect of moisture upon the joint. This is, of course, a particularly significant result in that it demonstrates the possibility that such adhesive joints could be exposed to relatively dry environments with humidities below about 55% RH for prolonged periods without any significant loss in joint performance.
- The loci of failure studies revealed that upon testing in a ‘dry’ and ‘wet’ environment that the GBD-pretreated joints exhibited failure along the adhesive/aluminium-oxide interface.
- However, the presence of the GPS primer clearly increased the intrinsic adhesion such that failure along the adhesive/aluminium-oxide interface of the GPS-pretreated joints did not occur in either the ‘dry’ or ‘wet’ environmental fatigue tests. Instead, in the former environment the joints failed cohesively through the adhesive layer, whilst in the latter environment they eventually failed through the aluminium-oxide layer. Furthermore, at intermediate concentrations of water

between 55%RH and 100%RH (or liquid water), failure through the GPS primer layer was recorded.

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Table 1. Summary of data from constant displacement rate (i.e. static) tests performed in the ‘dry’ environment, i.e. 55% RH at 25°C.

Pretreatment	Adhesive fracture energy $G_c (\pm 100 \text{ Jm}^{-2})$	Visual locus of failure
GBD	680	Interfacial
CAE	1690	Cohesive
GPS	1465	Cohesive

Table 2. Summary of data from the static and the cyclic-fatigue tests performed in the ‘dry’ environment.

Pretreatment	Adhesive fracture energy, G_c $G_c (\pm 100 \text{ Jm}^{-2})$	Threshold fatigue fracture energy, G_{th} $G_{th} (\pm 10 \text{ Jm}^{-2})$	G_{th}/G_c	Visual locus of failure (cyclic tests)
GBD	680	85	0.13	Interfacial
CAE	1690	250	0.15	Cohesive
GPS	1465	250	0.17	Cohesive

Table 3. Summary of cyclic-fatigue data from tests performed in the ‘wet’ environment, i.e. fully immersed in water at 28°C.

Pretreatment	Threshold fatigue fracture energy $G_{th} (\pm 5 \text{ Jm}^{-2})$	G_{th}/G_c (Jm^{-2})	Visual locus of failure (at threshold)
GBD	15	0.02	Interfacial
CAE	95	0.06	Interfacial
GPS	100	0.07	Interfacial

Table 4. Surface chemical analyses of the interfacial fracture surfaces of GBD- and GPS-pretreated joints tested under cyclic-fatigue loading in the ‘wet’ environment.

Pretreatment	Failure Surface	Surface Composition/atomic %				
		C	O	Al	Si	N
GBD	Metal	45	40	13	2	0
GBD	Adhesive	71	23	2	1	3
GPS	Metal	37	45	16	1	2
GPS	Adhesive	43	42	14	0	1

Table 5. Nominal masses of positive and negative ions in the SIMS spectra of oxidised aluminium.

Positive SIMS		Negative SIMS	
Nominal Mass	Assignment	Nominal Mass	Assignment
	$(\text{Al}_2\text{O}_3)_n\text{H}^+$		$(\text{Al}_2\text{O}_3)_n\text{OH}^-$
103	n = 1	17	n = 0
205	n = 2	119	n = 1
307	n = 3	221	n = 2
408	n = 4	323	n = 3
511	n = 5	425	n = 4
613	n = 6	527	n = 5
	$(\text{Al}_2\text{O}_3)_n\text{AlO}^+$		$(\text{Al}_2\text{O}_3)_n\text{AlO}_2^-$
247	n = 2	59	n = 0
349	n = 3	161	n = 1
451	n = 4	263	n = 2
553	n = 5	365	n = 3
655	n = 6	467	n = 4
757	n = 7	569	n = 5
223	$\text{Al}_4\text{O}_7\text{H}_3^+$		$(\text{Al}_2\text{O}_3)_n\text{AlO}(\text{OH})_2^-$
265	$\text{Al}_5\text{O}_8\text{H}_3^+$	77	n = 0
325	$\text{Al}_6\text{O}_{10}\text{H}_3^+$	179	n = 1
		281	n = 2
		383	n = 3
		485	n = 4
		587	n = 5

Table 6. The loci of failure of silane (GPS)-pretreated joints tested under cyclic-fatigue loading (near the fatigue threshold) at various humidities and in liquid water.

RH (%)	Visual assessment	XPS analysis
15	cohesive	-
30	cohesive	-
32	cohesive	-
42	cohesive	-
55 ('dry')	cohesive	-
60	interfacial	in silane layer
77	interfacial	in silane layer
100	interfacial	in oxide layer
liquid water ('wet')	interfacial	in oxide layer

Figure Captions

- Figure 1 Sketch of the tapered double-cantilever beam (TDCB) adhesive joint.
- Figure 2 Logarithmic crack growth rate per cycle, da/dN , versus logarithmic G_{max} for the TDCB joints employing different pretreatments tested in the 'dry' environment of 25°C and 55 % relative humidity. Pretreatments are: diamonds: GBD; squares: GPS; and circles: CAE. Values of G_{th} are in Jm^{-2} .
- Figure 3 Logarithmic crack growth rate per cycle, da/dN , versus logarithmic G_{max} for the TDCB joints employing the GBD and GPS pretreatments tested in the 'dry' environment of 25°C and 55 % relative humidity and 'wet' environment of water immersion at 28°C. Pretreatments are: open diamonds: GBD 'wet'; closed diamonds: GBD 'dry'; open squares: GPS 'wet'; closed squares: GPS 'dry'.
- Figure 4 Fracture surfaces of GPS-pretreated joint cyclically tested in the 'wet' environment. The photograph shows cohesive failure in the adhesive layer early in the cyclic-test regime changing to visually interfacial at longer crack lengths, as the threshold region is approached. (The final cohesive failure region occurs via fast fracture when the test is stopped and is therefore an artefact.)
- Figure 5 XPS spectrum of the 'adhesive' side from a GBD-pretreated joint cyclically tested in the 'wet' environment and which failed near the threshold region.
- Figure 6 XPS spectrum of the 'adhesive' side from a GPS-pretreated joint cyclically tested in the 'wet' environment and which failed near the threshold region.
- Figure 7 XPS depth profile of the 'adhesive, side from a GPS-pretreated joint cyclically tested in the 'wet' environment.
- Figure 8 Positive ToF SIMS spectra of the 'adhesive' side from (a) a GBD-pretreated joint and (b) a GPS-pretreated joint tested cyclically tested in the 'wet' environment and which failed near the threshold region.
- Figure 9 The negative ToF-SIMS intensities for OH^- and O^- ions and the OH^-/O^- ratios from ToF-SIMS depth profiles from the 'metal' and 'adhesive' sides of a GPS-pretreated joint cyclically tested in the 'wet' environment.

Figure 10   The threshold, G_{th} , value from cyclically-loaded fatigue tests as a function of the relative humidity of the test environment for GPS-pretreated joints. (The data point from the ‘wet’ test environment of immersion in water is also shown.)

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