INTRODUCTION

Several factors have held back the more widespread use of adhesives. These principally are the detrimental effect of moisture on bond strength and also the lack of a suitable non-destructive testing technique for detecting strength loss due to environmental attack. It is the latter problem that this work attempts to answer. The focus of this work has been to look at the bonding of aluminium to aluminium using epoxy based adhesives, as would be used in the aerospace industry. Bonding of aluminium has been performed in the aerospace industry for many years, and there has been much work done to improve the durability of this type of joint. It has been seen that the improvement in corrosion resistance that can be achieved by treating aluminium prior to bonding has a significant effect on the durability of the bond produced. This is not surprising when it is often seen that a joint which has been exposed to a hot-wet environment will fail along the interface between the aluminium and epoxy, as opposed to through the adhesive when the joint has remained dry [1]. Therefore it is this interface region that is to be examined when searching for environmental attack. The most common form of pretreatment that is used when environmental attack is a concern is anodisation of the surface to be bonded. Anodising produces a thin oxide layer on the aluminium surface, typically 1-3 μm thick. Joints that have been anodised are considerably more durable than joints that are not anodised, but they will still exhibit interfacial failure after exposure to hot-wet environments [1]. The problem for NDT techniques is that the oxide layer which we need to inspect is orders of magnitude smaller than the bounding layers; the aluminium being 1-5mm, and the adhesive being 0.1-0.5mm thick, as shown in Figure 1. Ultrasonics has appeared to be the most promising technique for inspecting for degradation of adhesive joints, and it is this technique on which we have concentrated our efforts [2-4].

SPECIMENS

A range of specimens has been used for this work. They have covered a range of common pretreatments used in the preparation of aluminium joints from the least durable, grit blasted, through chromic acid etch (similar to Forest Products Laboratory etch, FPL) to the most durable which are Phosphoric and Chromic Acid Anodising (PAA and CAA). There have been two main types of specimen employing these pretreatments, one a two-
layer design using just a single 4mm aluminium plate and a 2mm thick layer of epoxy adhesive, and the other a three-layer specimen with two aluminium plates and a 0.3mm epoxy bondline. The two-layer specimen was chosen for several reasons. Firstly, the epoxy used is an unmodified, clear resin, which allows a visual inspection of the interface to be performed. Secondly, the thicker epoxy layer allows a large separation between reflections of ultrasonic waves from the different layers. Thirdly, the possibility of changes occurring due to water uptake in the epoxy could be investigated without the epoxy saturating too rapidly, taking around 3 months to saturate the adhesive next to the interface. This saturation would also occur in a uniform manner. The three-layer specimens are designed to be more representative of a genuine adhesive joint. Previous work had indicated that environmental attack was more likely to advance interfacially, as opposed to through water uptake in the epoxy [5]. To allow the very edge of the epoxy layer to be interrogated ultrasonically through the aluminium, it is necessary for the aluminium to extend beyond the edge of the epoxy. Figure 2 shows the geometry used. One of each of the recessed and flush edges were sealed so that the difference between open and sealed interfaces could be seen. The three-layer specimens have a similar geometry, the only difference being the presence of the second adherend, and the reduction of the epoxy thickness from 2mm to 0.3mm. The presence of the second adherend makes a large difference both to the overall stiffness of the specimen and to the rate at which water can enter the joint via diffusion through the epoxy.

ULTRASONICS

Two main techniques have been used in this work, and although the results discussed will be obtained solely from one, they are both significant. The first is normal incidence, high frequency, pulse-echo ultrasonics. This has been undertaken using a 50MHz focused immersion probe, with the focal length optimised to give the shortest possible water path length, while keeping the reflection from the first aluminium-epoxy interface in focus. This is done so that the highest possible frequency is incident on the interface, which produces the smallest possible spot size. In these experiments this has resulted in a centre frequency of the reflected pulse of 55MHz, with useful bandwidth up to 85MHz. This frequency has allowed the signals from the bondline to be gated (either interface for the three-layer specimens), which allows for directing monitoring of the reflection from the interface of interest. The scanning system used allows for scanning at a resolution of 10 µm. The other technique that has been used extensively is oblique incidence scanning [5]. This has involved using a pair of probes at oblique incidence to generate shear waves in the aluminium at around 37 degrees, by mode conversion at the water-aluminium interface. This approach has also been used by other research groups investigating interfacial properties [6]. This angle was chosen as response modelling of the interlayer had indicated that this should be the most sensitive to variations in the properties of the interlayer. This also has the benefit of being beyond the longitudinal critical angle in aluminium. However there are several drawbacks to this technique. With two probes, alignment is more difficult, and each probe must have a clear path to the interface meaning that the signal is more easily lost near edges. Also, because the waves produced are at an oblique angle, they must propagate through more material, which limits the maximum frequency usable. Scattering
and attenuation in the aluminium limits the useful frequency to around 20MHz when the adherends are 4mm aluminium. This then also limits the maximum attainable resolution.

**MECHANICAL TESTING**

Mechanical tests have been carried out on samples after extended periods in hot water at 50°C. Identical tests have also been done on samples which were manufactured at the same time, and have been stored in a desiccator at room temperature. In order to test the two-layer specimens, and gain some information about the spatial distribution of interfacial strength, the following procedure was followed. First, the specimen to be tested was cut into strips. These strips should be narrow so as to optimise the spatial resolution, but the amount of material lost in sectioning prevents them being too small; 10mm wide strips were used. These strips are then bonded to a stiff steel plate, epoxy side down, as shown in Figure 3. Bonding to a stiff plate tends to force the failure path along the interface between the aluminium and the epoxy, which allows a direct comparison between the wet and dry samples, the failure path being interfacial in both cases. The aluminium is then peeled from the epoxy, with constant rate displacement applied to one end of the specimen, and the load is measured. To obtain the interfacial fracture energy the crack length must also be measured. This is done by video-recording the test and measuring the crack length. To obtain accurate spatial values of the interfacial fracture energy, \( G_c \), the crack must propagate smoothly. To do this requires a crack velocity above 20mm/min. However the crack velocity is not constant as the distance to the point of applied load varies, as can be seen from Figure 3, and so a test rate has been chosen to give uniform peeling across the majority of the specimen.

A similar procedure was followed for the three-layer specimens. However in this case the specimens are symmetrical, with the load being applied to end blocks bonded to the top and bottom adherends. In a specimen with good interfacial toughness the crack will tend to run through the centre of the epoxy. When the interface is less tough than the epoxy, the failure moves from the epoxy to the interface. A similar procedure to that followed for the two-layer specimens can be employed for a three-layer specimen, where the specimen is bonded to a stiff base, in this case the failure tends toward the uppermost interface. This was done to obtain an interfacial toughness value for a three-layer specimen before degradation had occurred.

The results for these mechanical tests are presented in a similar manner to a C-scan. Each strip from a specimen yields a fracture toughness for a given crack length. The fracture toughness is then shown as a grey square, with the shade of grey being relative to the toughness value. Each line of data from the specimen is then placed in the correct
Figure 4. Comparison of visual and ultrasonic scan for 2 layer gritblast specimen.

position relative to the other strips, producing a map of the toughness. A gap in the data along a strip indicates that the crack front jumped, and in some cases there are missing strips.

RESULTS

2-layer specimens

The benefits of using a clear adhesive quickly became apparent with the two-layer specimens. Visual inspection, particularly of the two-layer grit blast specimen, readily showed changes occurring, apparently at the interface. This can be seen from Figure 4, taken from the specimen after 265 days in water. Large disbonds starting from the edges of the specimen were visible both by eye and ultrasonically. However there are also many
Figure 5. Photograph and C-scan from 2-layer CAA specimen after 465 days in water. More defects visible on the specimen by eye, but not necessarily from the ultrasonics, such as lines and spots. What does become detectable very quickly by the ultrasonics are the small spot disbonds, but there is still a resolution limit which determines the detectability of these; they must be of the order of 0.5 mm in diameter before detection is assured. This is approximately the focal spot size of the probe. The lines also become detectable once their width is of a similar size. The lines appear to be acting as a water path to most of the small spot disbonds, which are probably corrosion sites. Our preliminary conclusion is that all the lines and spots seen visually would be detectable ultrasonically if a high enough frequency, giving a sufficiently small spot size, could be employed.

Scans from the two-layer CAA specimen show far less sign of change than has been seen on the grit blast specimen, and this would be expected due to its considerable improvement in corrosion protection. This can be seen from Figure 5, which shows the only...
Figure 7. Mechanical test results for 2 layer grit blast specimen.

area of the specimen where any change has been observed. There are several points to be
seen from this figure. First, the absence of any change except the obvious disbonding, with
no lines or disbonds visible away from the edge. Secondly, it can be seen that the areas of
recent disbonding show as a black area, which indicates that there is a reflection increase
from these areas and that there is a clean disbond. Areas that have been disbonded for some
time quickly become corroded, with a corresponding increase in surface roughness, and
hence signal loss. Thirdly, it can be seen that there are cracks in the adhesive around the
disbond, indicating that there is more strength in the interface than the epoxy, even in areas
immediately adjacent to disbonding. This is confirmed by the scan which shows a clean
dge between heavily corroded areas and apparently untouched epoxy. (It should also be
noted that the exposure time of this specimen is 465 days compared to 265 days for the grit
blast specimen, with the total disbonded area of the CAA specimen being less than half that
of the grit blast specimen.)

Mechanical test results from the 2-layer CAA specimen discussed above can be seen
in Figure 6, compared to results from the dry specimen. It can be seen from that there is no
significant toughness decrease across much of the wet specimen, and in fact across the
majority of the specimen there has been an increase in toughness. This can be explained by
the plasticisation of the epoxy by the water. It can be seen that there is some reduction in
toughness towards one of the unsealed edges. This cannot necessarily be attributed to water
as a similar variability can be seen in the dry specimen.

Figure 7 shows the results from both wet and dry grit blast specimens. Although
only a limited number of strips have been tested from these specimens there is a clear
distinction in the toughness values obtained from these two specimens. The reduction in
toughness in the wet specimen is distributed across the whole of the specimen and does not
appear as localised changes. This is in contrast to the ultrasonics results already discussed
for this specimen. The ultrasonic results showed a distribution of small defects at the
bondline. These could be seen to be more numerous in certain areas of the specimen than
others, but this is not reflected in the mechanical results. However, comparing the results
from both the CAA and grit blast specimens it can be seen that this significant drop in the
toughness of the wet sample is accompanied by the appearance of very small bondline
defects, distributed throughout the specimen.

Table 1 shows a summary of the results obtained for the whole range of
pretreatments used on the 2-layer specimens. This shows that the rate at which disbonding
advances is controlled by the corrosion protection of the pre-treatment, with the anodisation
treatments performing better than the others. It can also be seen that the appearance of
micro-defects is related to a loss in toughness of the remaining bond. However the degree
Table 1. Summary of 2-layer specimen results

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Exposure time (days)</th>
<th>Disbond Area (mm²)</th>
<th>Rate (mm²/day)</th>
<th>Micro defects</th>
<th>G_c wet Jm⁻²</th>
<th>G_c dry Jm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grit Blast</td>
<td>223</td>
<td>1464</td>
<td>6.6</td>
<td>V. many</td>
<td>42</td>
<td>55</td>
</tr>
<tr>
<td>CAE</td>
<td>194</td>
<td>1958</td>
<td>10.1</td>
<td>Many</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PAA</td>
<td>393</td>
<td>1274</td>
<td>3.2</td>
<td>Few</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>CAA</td>
<td>465</td>
<td>1013</td>
<td>2.2</td>
<td>None</td>
<td>93</td>
<td>78</td>
</tr>
<tr>
<td>CAE repeat</td>
<td>185</td>
<td>685</td>
<td>3.7</td>
<td>V. few</td>
<td>99</td>
<td>103</td>
</tr>
</tbody>
</table>

The toughness loss does not appear to be directly related to the extent of the micro-defects. The CAE repeat results were produced to fill in gaps in the data. However the results are noticeably different. This may be explained by a considerable difference in the exposure pattern for this sample. Whereas the other specimens were removed from the hot water periodically for examination, this repeat sample was left in water for a single long period, and resulted in a specimen which showed considerably fewer micro-defects than the previous samples with the same pretreatment but more cyclic exposure. The repeat of the dry sample is also considerably higher than the other dry samples, which is to be explained.

3-layer specimens

Ultrasonic results from the 3-layer specimens have generally shown very little sign of change. This is true for both normal and oblique incidence scans. The only change that has been seen is the very slow encroaching of corrosion from the unsealed edges, and this has been much slower than on the 2-layer specimens. There has also been an almost total absence of the appearance of any micro-defects, with a single minor exception. Table 2 shows a summary of the results obtained from the 3-layer specimens. The most important result that can be seen from this table is that there is a difference in the failure type of two of the wet specimens, those being the PAA and grit blast samples. For all the dry samples and the wet samples of the other treatments, the failure was cohesive. It is extremely unlikely that water could have entered the centre of these specimens via diffusion through the epoxy, as a Fickian diffusion calculation for a joint of this geometry shows very little water in the epoxy more than 10mm into the joint. It can also been seen from the table that there is also a noticeable reduction in the toughness of the wet specimens that failed cohesively. It was thought that this could easily be due to the effects of heat alone. To confirm this a specimen was made which was a given a 6 week postcure. This resulted in a fracture toughness of 61 Jm⁻², considerably lower than that obtained when the specimen is kept at room temperature. There was also a concern that if a crack was initiated at the interface for some reason then it might run for the length of the specimen along the interface, and that this might results in a much lower G_c without there being significant interfacial toughness loss. To confirm this a 3-layer PAA specimen was made and tested in a similar manner to the 2-layer specimens. This sample failed along the interface, and yielded a fracture toughness of 185 Jm⁻², considerably higher than when the failure is

Table 2. Summary of 3-layer specimen results.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Exposure time (days)</th>
<th>Disbond Area (mm²)</th>
<th>Primary Failure</th>
<th>G_c Wet Jm⁻²</th>
<th>G_c Dry Jm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grit Blast</td>
<td>251</td>
<td>25</td>
<td>Interfacial</td>
<td>48</td>
<td>tbc</td>
</tr>
<tr>
<td>CAE</td>
<td>411</td>
<td>300</td>
<td>Cohesive</td>
<td>84</td>
<td>127</td>
</tr>
<tr>
<td>PAA</td>
<td>566</td>
<td>~0</td>
<td>Interfacial</td>
<td>55</td>
<td>120</td>
</tr>
<tr>
<td>CAA</td>
<td>566</td>
<td>~0</td>
<td>Cohesive</td>
<td>95</td>
<td>130</td>
</tr>
</tbody>
</table>
Examination of the failure surface for the 3-layer PAA specimen that failed along the interface revealed a similar pattern of lines that has already been seen on some 2-layer specimens; this is shown in figure 8. This suggests that there may be a similar mechanism for strength loss in the 3-layer specimens as is occurring in the 2-layer specimens. However these defects have not been detectable ultrasonically. A possible reason for this could be that when a line of weakness occurs on a 2-layer specimen and the epoxy tries to move away from the interface there is only the epoxy layer constraining it, and so a gap can open up. This produces a significant change in the reflection coefficient and so detection is possible. However in a 3-layer specimen this is not the case as the second aluminium sheet prevents the epoxy from lifting away, and so the epoxy is kept in intimate contact with the lower substrate, which results in little change in reflection coefficient. This will also help to decrease the rate at which these defects can expand.

CONCLUSIONS

There are several important conclusions that can be drawn from this work. We have seen what appears to be two mechanisms of environmental attack occurring in these specimens. Firstly there is the undercutting corrosion which has been advancing primarily from unsealed edges, and this has been readily detected, if it advances sufficiently far from the edge of the joint. The second mechanism has been a weakening of the interface, distributed throughout the area of the joint. This has been accompanied in the 2-layer specimens by the appearance of micro-defects, although the number and extent of these micro-defects has not been seen to correlate exactly with the degree of toughness loss. Some of the 3-layer specimens appear to have suffered from a similar loss of toughness across the whole specimen, with lines along the interface similar to those seen on the 2-layer specimens. However these lines have not been detected ultrasonically, possibly due to the stiffness of the 3-layer sandwich.

REFERENCES