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An in-situ corrosion sensor based on electrochemical impedance spectroscopy (EIS) has been used to detect moisture ingress into aluminum-aluminum and aluminum-composite adhesive bonds. Both wedge tests and tensile button tests (aluminum-aluminum bonds only) were performed. Upon moisture absorption, the impedance spectra change shape with the low-frequency region becoming resistive. The low-frequency impedance decreases by several orders of magnitude, depending on the adhesive and the experimental conditions. For bonds with stable interfaces, such as phosphoric acid anodized (PAA) aluminum, the absorbed moisture causes an initial weakening of the adhesive resulting in reduced strength or small crack propagation. A substantial incubation time prior to substrate hydration and bond degradation allows warning of potential joint deterioration and enables condition-based maintenance. For bonds with smooth interfaces with little or no physical bonding (mechanical interlocking), crack propagation can proceed interfacially with minimal moisture absorption. A comparison of the incubation times for Forest Prodecrts Laboratory (FPL) surfaces both bonded to epoxy adhesives and freely exposed to water or humidity at different temperatures shows that hydration occurs with the same activation energy, independent of whether or not the surface is covered with adhesive. However, the pre-exponential factor in the rate constant is dependent on the concentration of free moisture at the interface so that the hydration rate varies by several orders of magnitude. The results of this study demonstrate that the electrochemical sensor technology can detect the ingress of moisture into an adhesive bond and should be further developed to provide a means to warn of potential dgradation.

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Electrochemical Sensors for Nondestructive Evaluation of Adhesive Bonds

Final Report STTR Contract F49620-98-C-0072

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Executive Summary

An *in-situ* corrosion sensor based on electrochemical impedance spectroscopy (EIS) has been used to detect moisture ingress into aluminum-aluminum and aluminum-composite adhesive bonds. Both wedge tests and tensile button tests (aluminum-aluminum bonds only) were performed. Upon moisture absorption, the impedance spectra change shape with the low-frequency region becoming resistive. The low-frequency impedance decreases by several orders of magnitude, depending on the adhesive and the experimental conditions. For bonds with stable interfaces, such as phosphoric acid anodized (PAA) aluminum, the absorbed moisture causes an initial weakening of the adhesive resulting in reduced strength or small crack propagation. A substantial incubation time prior to substrate hydration and bond degradation allows warning of potential joint deterioration and enables condition-based maintenance. For bonds with smooth interfaces with little or no physical bonding (mechanical interlocking), crack propagation can proceed interfacially with minimal moisture absorption. A comparison of the incubation times for Forest Products Laboratory (FPL) surfaces both bonded to epoxy adhesives and freely exposed to water or humidity at different temperatures shows that hydration occurs with the same activation energy, independent of whether or not the surface is covered with adhesive. However, the pre-exponential factor in the rate constant is dependent on the concentration of free moisture at the interface so that the hydration rate varies by several orders of magnitude. The results of this study demonstrate that the electrochemical sensor technology can detect the ingress of moisture into an adhesive bond and should be further developed to provide a means to warn of potential degradation of adhesive joints and enable condition-based maintenance.

Introduction

Nondestructive inspection and evaluation (NDI, NDE) of adhesive bonds commonly requires separation of an interface or, in limited cases, a kissing unbond that has intimate contact but no interfacial strength. It is currently not possible to nondestructively find weakened bonds or bonds in the process of degradation. Because the principal cause of environmentally induced bond failure is moisture,[1-3] one potential means to monitor such bond degradation is to track the ingress of moisture into the bondline. Depending on the properties of the bonded joint, moisture can promote these types of degradation mechanisms:

- Disruption of secondary interfacial bonds, e.g., van der Waals forces
- Weakening or disruption of primary interfacial bonds, e.g., covalent or ionic bonds
- Plasticization or weakening of the polymeric phase allowing disengagement of mechanical interlocking or physical interfacial bonds or failure within the polymer at stresses less than those required for a freshly cured adhesive
- Hydration or corrosion of a metallic adherend surface, destroying any chemical or physical interfacial bonds and forming corrosion products that add stresses to the bondline.

The details of each of these mechanism types will depend on the materials and surface treatments involved and the environmental conditions to which the system is exposed. For example, epoxy bonds to microscopically smooth aluminum will fail according to the first mechanism very quickly upon exposure to moisture. In contrast, the failure of epoxy bonds to phosphoric acid anodized (PAA) aluminum will fail according to the fourth mechanism, but only after an extended period. The severity of exposure conditions is generally increased by interfacial stresses, temperature extremes and cycles, ionic constituents, and humidity cycling.

Electrochemical impedance spectroscopy (EIS) has been used to study absorption of moisture by coatings and the subsequent corrosion of the substrate under immersion conditions for many years.[4-10] Traditionally, it has required remote counter and reference electrodes with access by the electrolyte to the polymeric surface. As such, it was not suitable for evaluation of adhesive bonds. In the most relevant adhesion study, Simpson and co-workers were able to correlate EIS measurements with paint adhesion by bonding pull stubs to painted surfaces after exposure to aggressive environments.[11,12] Deflorian and Fedrizzi discussed how equivalent circuit elements derived from EIS data were related to moisture uptake and coating deadhesion.[13] Other researchers, as reviewed by Murray,[14] have focused on correlating EIS measurements with different parameters, such as blister area or delamination from a scribe, which may be related to the adhesion of a paint coating, but are not relevant to a structural adhesive bond.

Davis et al. used these conventional EIS measurements on an immersed half-joint specimen (aluminum adherend and epoxy adhesive without a second adherend) to study the adsorption of moisture by the adhesive and the eventual hydration of the aluminum surface.[15,16] They conclusively showed that hydration of a Forest Products Laboratory (FPL) aluminum adherend would occur under an adhesive film and that the hydration products would be capable of inducing bond failure due to their increase in volume.

The application of EIS to coated specimens in ambient conditions has been advanced recently with the development of an *in-situ* corrosion sensor that acts as both the counter and reference electrodes and allows EIS spectra to be obtained in air.[17-20] It has been used to detect moisture absorption and substrate corrosion for coated metals and composite materials (moisture absorption only). Here, we report on the application of this technology to adhesive bonds using both wedge tests and tensile button tests using a pneumatic adhesion tensile testing instrument (PATTI). Moisture ingress was tracked with EIS with bonds exposed mostly to high humidity although immersion was used in a few cases. Because the stability of an aluminum bond once moisture is present is governed by the surface treatment of the adherend surface,[2,3,21] different treatments were evaluated. These treatments ranged from smooth with poor expected performance (polished or sanded) to microscopically rough with excellent expected performance (PAA).

Experimental

Specimen Preparation

Surface preparation of the 2024-T6 aluminum adherends included PAA, the sodium dichromate-sulfuric acid etch or FPL etch, sand or grit blasting, and sanding/polishing.

Some Al-Al wedge test specimens were prepared as 6.5" x 6" x 0.125" (165mm x 150mm x 3.2mm) panels which were subsequently cut into six 1" x 6" (25mm x 150mm) strips. Others were prepared as individual 1" x 6" (25mm x 150mm) strips. A limited number of Al-graphite/epoxy and Al-glass/epoxy specimens were also individually prepared. Composite panels were autoclave processed prior to bonding to the aluminum substrate. Woven fiberglass prepreg was SP Systems E293 epoxy with 7781 glass fiber, and the carbon fiber woven prepreg was Hexcel AS4 fiber in 8552 epoxy. Both of these prepreg formulations are used as structural laminates in aerospace parts. A standard 350°F-85 PSI process schedule was used to consolidate the panels. The resultant panels were then adhesively bonded to aluminum plates to make the wedge specimens. Both Cytec FM-73 and FM-300 adhesives were used. The FM-73 is a 250°F (121°C)-curing adhesive that exhibits moderate moisture uptake. The FM-300 is a 350°F (177°C)-curing adhesive that absorbs less moisture. For the specimens cut from the plate, one adhesive ply was used; for the individually prepared specimens, two adhesive plies were used. To prevent a metal wedge from shorting out the two adherends, Delrin® acetal resin or polycarbonate wedges were used. After the wedges were driven and the initial cracks allowed to equilibrate, the specimens were placed in humidity chambers operating at 60°C and 95-98%RH. Periodically, they were removed from the chamber and shaken or blown dry with compressed air to remove excess condensed moisture. The crack length was marked and EIS measurements taken (see below).

Tensile button tests were performed on 2" x 2" x 0.125" (50mm x 50mm x 3.2mm) panels prepared as described above. The Al stubs were PAA-treated to force any moisture degradation to the panel interface. The adhesive was 3M DP460 two-part epoxy. Glass beads (45-90 μm in diameter) were used to provide a uniform bond thickness and prevent electrical contact between the stub and the panel. To assure uniform, complete cure prior to any humidity exposure, the specimens were baked at 90°C for 30 minutes prior to testing. Initial bond strengths were determined using the PATTI tester on 2-3 specimens for each surface treatment. The remaining specimens were placed in high humidity (50°C, 95%RH). Periodically, specimens were removed and inspected using the *in-situ* corrosion sensor technology (see below). The bond strengths were measured on selected specimens following different periods of exposure. After approximately three months, the specimens were removed from the humidity and placed in warm (50°C) water in an attempt to accelerate the degradation process while the inspection and testing procedures continued.

EIS Measurements

Temporary *in-situ* corrosion sensors were applied to each adherend of the wedge tests and to the stub and substrate of the PATTI tests when the specimens were removed from the humidity or immersion conditions and monitored. For convenience in these experiments, the sensors were removed following the measurements prior to reinsertion into the exposure environment.

EIS measurements were taken using either a Gamry PC3 Portable Potentiostat/Galvanostat with CMS100/105/300 Corrosion Measurement System or a CH Instruments model 650A electrochemical workstation. The impedance spectra were acquired over the range of approximately 0.1 Hz to 5,000 Hz. The spectra were customarily evaluated in the Bode magnitude plots (impedance magnitude vs frequency). Bode phase angle plots (phase angle vs frequency) were used to confirm interpretation of the magnitude plots.

Results

Tensile Button Tests

A typical series of impedance spectra for the tensile button tests is given in Figure 1. Initially, the spectra are capacitive in nature (slope of −1 on the log impedance vs log frequency graph) with high impedance at low frequencies. This behavior is similar to that of a good protective coating and reflects a polymer with no pathways of low resistance. As the adhesive absorbs moisture, the low-frequency spectrum decreases in impedance and becomes resistive or independent of frequency. This behavior reflects moisture ingress into the pores of a polymer and formation of pathways of relatively low resistance. It is typical of a protective coating in the process of degradation. The decrease of the low-frequency impedance for this specimen is shown in Figure 2 and reflects the absorption of moisture. This specimen exhibited a fairly steady impedance decrease (aside from one measurement which might be an artifact). Other specimens exhibited smaller decreases or a plateau, depending on microdifferences in the humidity chamber or small differences in the specimens. For these measurements, the data are dominated by the region of the specimen with the lowest impedance. In this case, the data represent the impedance of the near-edge region of the bondline where moisture saturation first occurs.

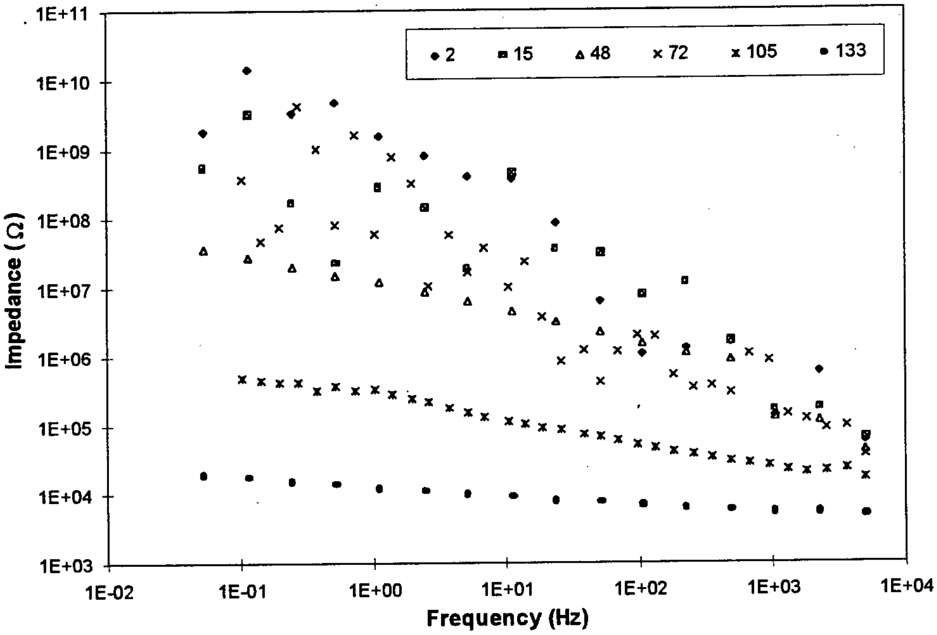

Figure 1. Impedance spectra for a PAA tensile specimen with one of the largest uptakes of moisture. The number of days is given in the legend.

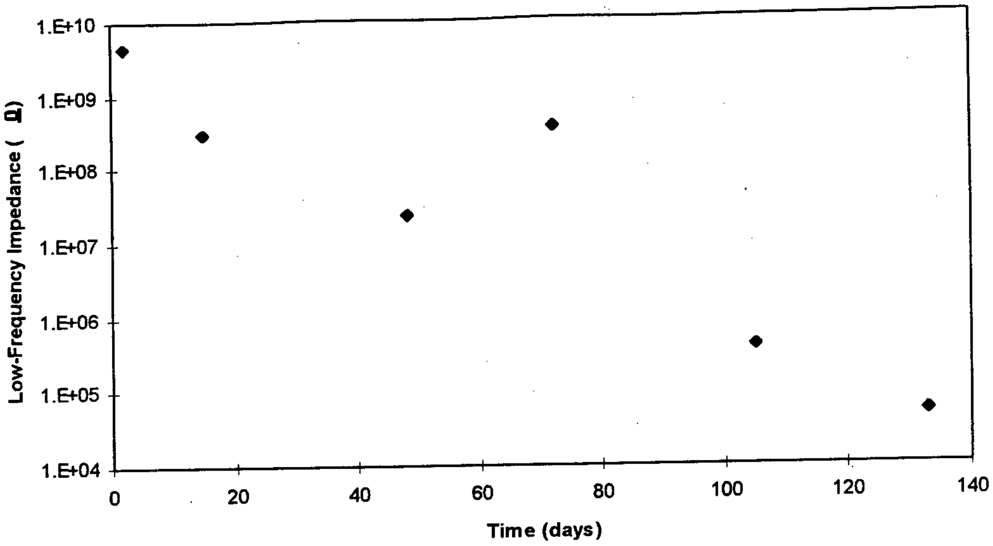

Figure 2. Geometric mean of the low frequency impedance as a function of exposure time for the PAA-treated button pull specimen of Figure 1.

The EIS spectra can be modeled with an RC circuit, such as the typical coated metal circuit of Figure 3, where R_{po} and C_c represent coating properties, R_{cor} and C_{DL} represent interfacial properties, and R_{sol} represents the solution resistance (not relevant in this case). The dry specimen would have a very high R_{po} value so that C_c dominates the spectrum. As moisture is absorbed, the R_{po} value would decrease by several orders of magnitude and begin to dominate at low frequencies when the impedance associated with C_c is very high. The C_c value would also increase (the impedance associated with the capacitor would decrease), but on a much smaller scale, because of the larger dielectric constant of water compared to the adhesive. Initially, the interfacial parameters would remain unchanged. These parameters would reflect adherend hydration or other interfacial reactions once they occur.

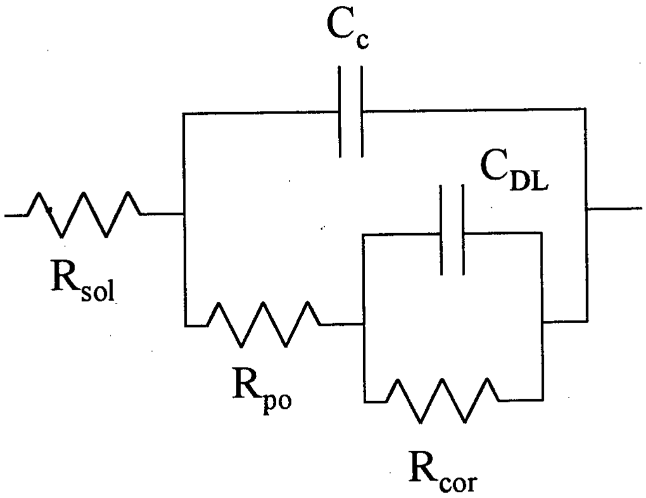

Figure 3. Typical equivalent circuit for a coated metal.

The effect of this moisture absorption on the tensile pull strength strongly depends on the surface treatment. This dependence is illustrated in Figure 4. The initial decrease in pull strengths from approximately 38 MPa to 27 MPa corresponds to a decrease in the cohesive strength of the adhesive as moisture is absorbed. For PAA specimens, the length of time available for this experiment (approximately five months) under these conditions (humidity, followed by immersion) was insufficient to induce hydration. Accordingly, the microcomposite interphase formed by the porous PAA oxide[22] and the adhesive remained stable and stronger than the cohesive strength of the adhesive so that failure was almost entirely within the adhesive (Figure 5). Similar behavior was also observed for grit blasted and FPL-etched specimens (Figure 6), with the exception of an FPL surface at the end of the experiment where the strength decreased by approximately 50% and partial interfacial failure occurred. XPS analysis of the interfacial region of this specimen showed that, where failure was interfacial, hydration had occurred under the adhesive. In contrast, because the sanded surfaces exhibit no evolved microroughness, their bonds to the epoxy adhesive rely more on secondary bonds, such as van der Waals forces, which are readily disrupted by moisture. The locus of failure gradually shifts to increasingly more interfacial with the interfacial region beginning along one segment of the edge and growing along the circumference and toward the center. Although the interface is weakened considerably by the moisture, it still retains some strength as indicated by Figure 7 where the extrapolated pull strength at 0% cohesive failure (100% interfacial failure) is approximately 15 MPa. By comparison, the dry interfacial strength must be at least 40 MPa or else the interface would be the weakest link of the bond.

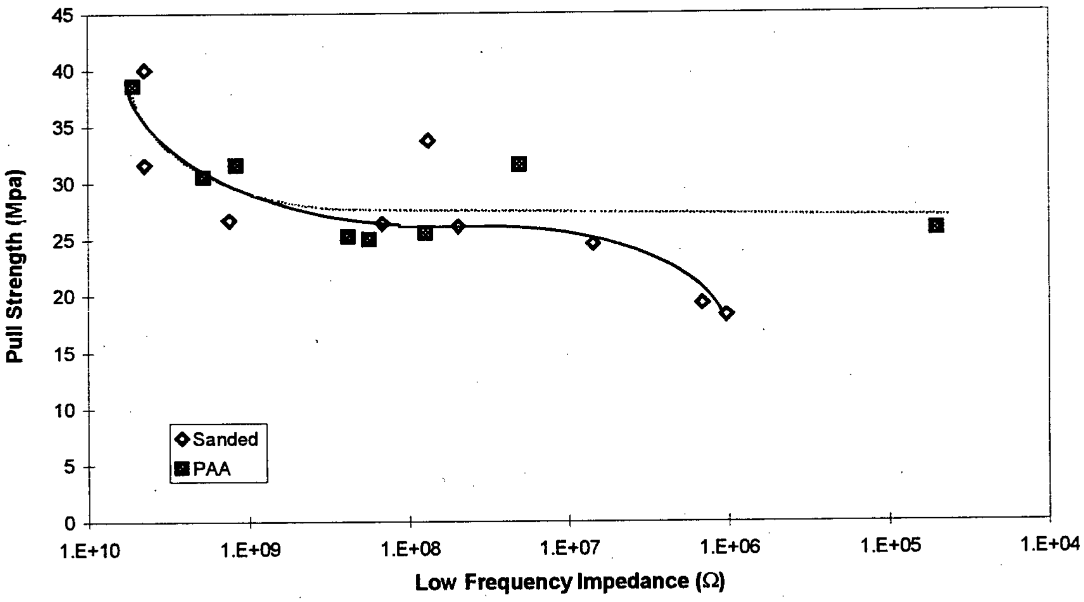

Figure 4. Tensile pull strengths as a function of low-frequency impedance for PAA and sanded aluminum surfaces.

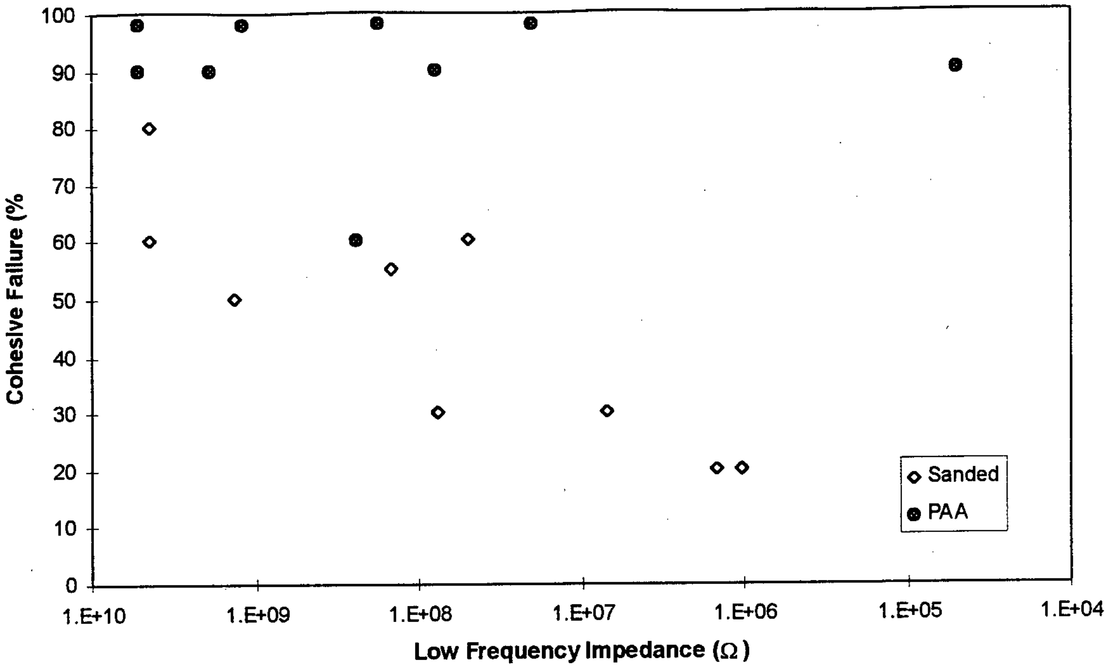

Figure 5. Percentage of cohesive failure in the adhesive as a function of low-frequency impedance for PAA and sanded aluminum surfaces.

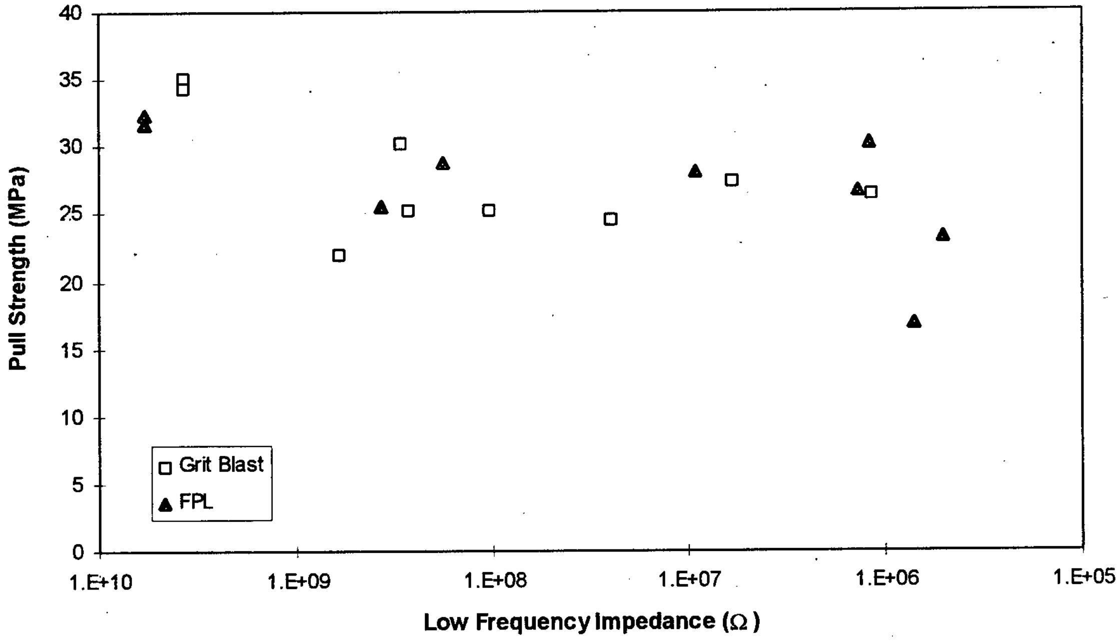

Figure 6. Tensile pull strength as a function of low-frequency impedance for grit blasted and FPL-etched aluminum surfaces.

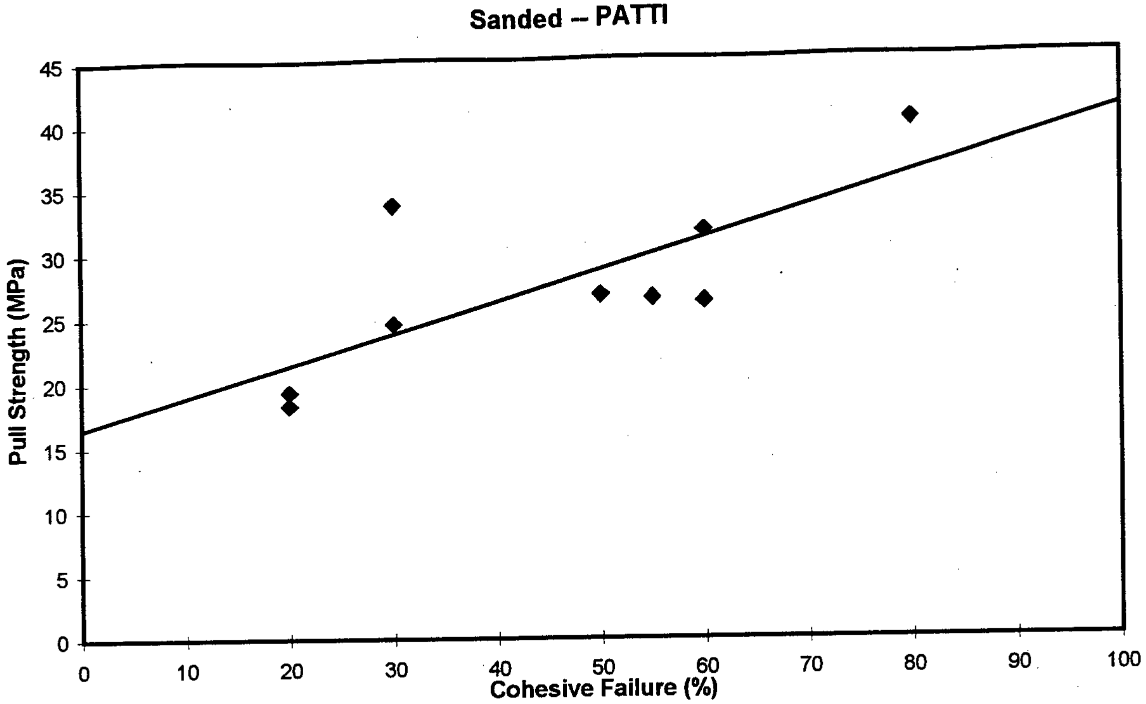

Figure 7. Tensile pull strength as a function of percentage of cohesive failure for sanded aluminum surfaces.

Wedge Tests

Joints tested in the wedge test configuration exhibit similar behavior to the PATTI specimens as indicated in Figure 8. Initially, the adhesive shows completely capacitive behavior. As moisture is absorbed, the low-frequency region of the spectra becomes resistive in nature with the extent of the resistive region generally increasing in frequency extent as more moisture is absorbed. The geometric mean of the low frequency impedance is given in Figure 9. Although there is considerable scatter, the data show a two-decade decrease in the low-frequency impedance between 100 and 200 hours as the adhesive absorbs moisture. Because the moisture uptake is governed by the adhesive, there is little or no dependence on surface preparation. The PAA specimens consistently exhibit slightly lower impedance than the other two treatments. This may be reflective of the lower crack length of the PAA specimens. At small crack lengths, the adhesive at the crack tip is subject to tensile stresses that increase the free volume of the polymer and allow more moisture absorption. An even greater dependence of the impedance (moisture absorption) on crack length was previously observed.[16]

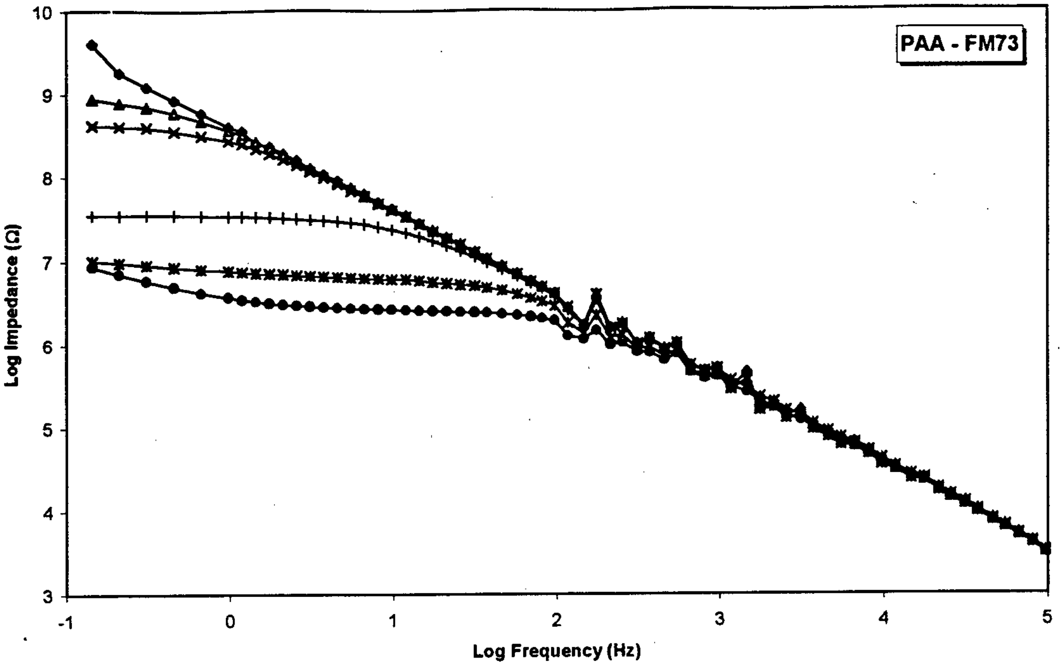

Figure 8. EIS spectra of a PAA wedge test using FM-73 adhesive. The humidity exposure ranged from 0 to 430 hours.

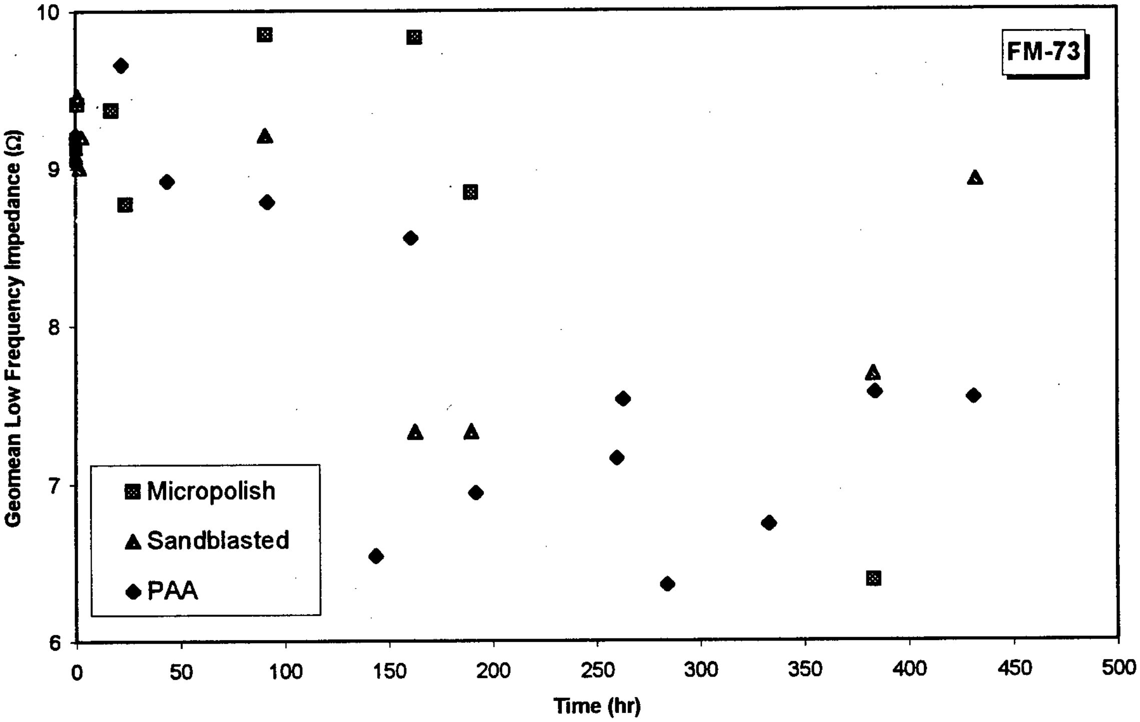

Figure 9. Geometric mean of the impedance over the lowest frequency decade for micropolished, sandblasted, and PAA aluminum wedge specimens using FM-73

Crack length measurements are given in Figure 10. Two distinct behaviors are noted, depending on surface preparation. All start cohesively between the two FM-73 plies. The crack in the PAA specimens remains between the two adhesive films and only slowly propagates. Its interface remains stable under these conditions, as expected. The cracks for the other two treatments very quickly shift to the interface. The smooth interface of the micropolished adherends can withstand very little stress and the crack propagates almost to the end of the specimen upon exposure to humidity as the moisture disrupts the secondary interfacial forces. The sandblasted specimens are able to support some interfacial stress as a result of low-quality roughness and the crack rapidly advances to the point where the limiting stress is reached.

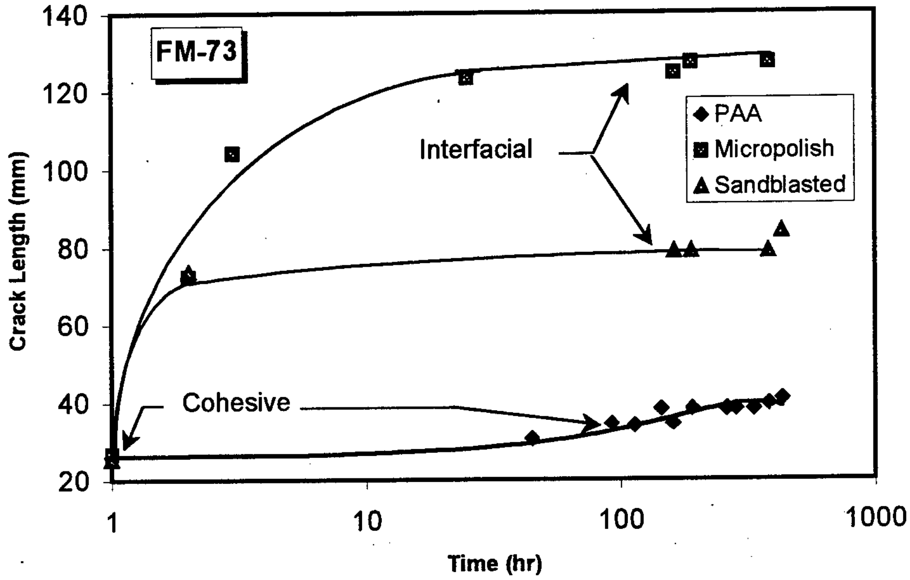

Figure 10. Crack length vs time for FM-73 wedge test specimens. The data represent two individual specimens.

Comparing the EIS measurements with crack lengths shows two different types of correlations, depending on the locus of crack propagation (Figure 11). For sandblasted and micropolished specimens, for which the crack propagates interfacially, the initial, rapid crack growth occurs with minimal change in the low-frequency impedance. For these weak interfaces, the crack propagates as soon as moisture reaches the interface – before it has a chance to absorb into the bulk adhesive and change the impedance. Over time, this absorption occurs and the impedance decreases, but the crack has arrested or is growing very slowly as it reaches the point of sustainable stress. For the PAA specimens, the limiting factor governing crack propagation under these conditions and time is not the interface, but rather, it is the weakening of the adhesive due to moisture absorption. In this case, there is a distinct relationship between the low-frequency impedance (absorbed moisture) and crack growth until the crack arrests after approximately one centimeter of propagation. At that point, the adhesive continues to absorb moisture, but without additional crack growth.

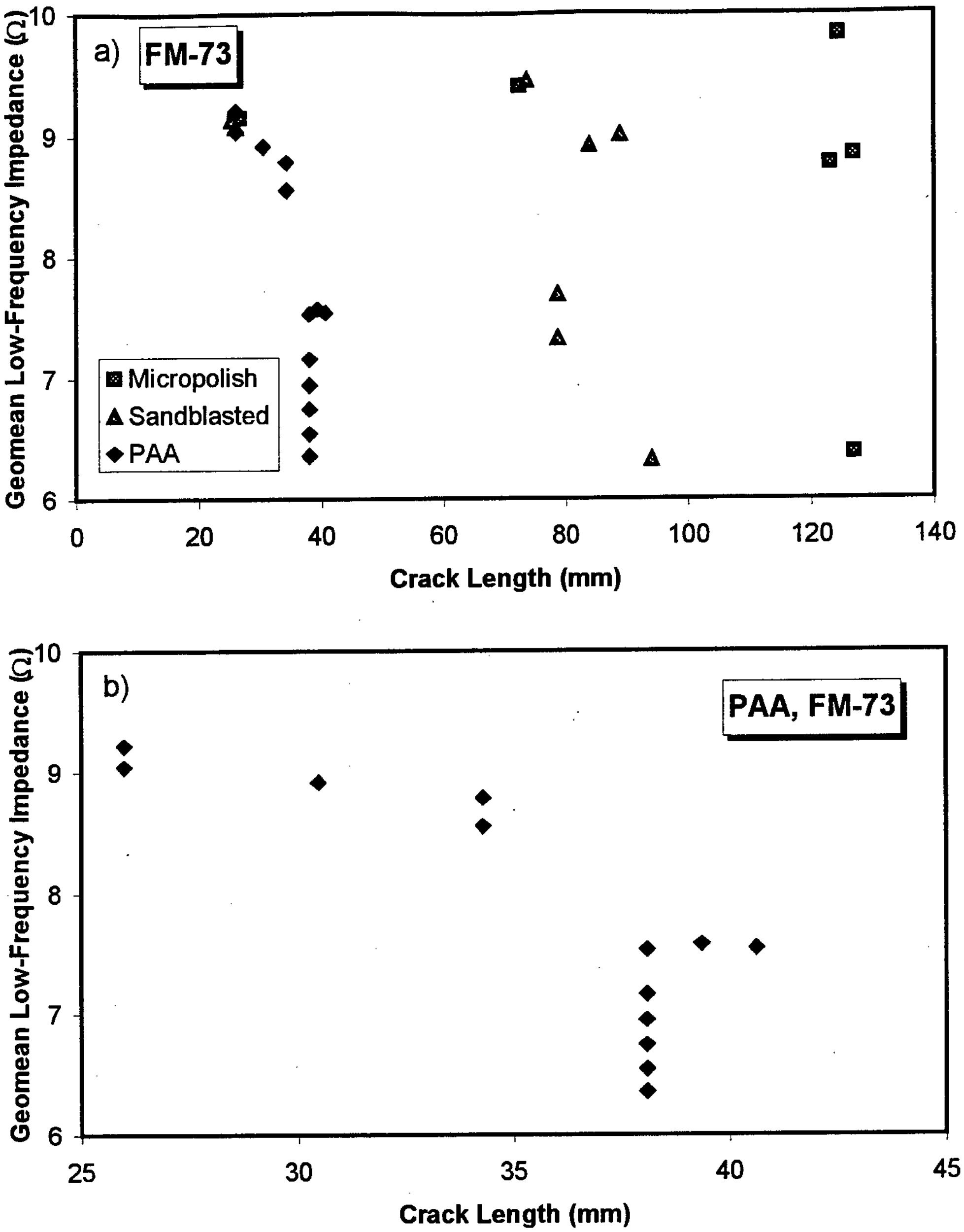

Figure 11. Geometric mean of the low frequency impedance as a function of crack length for FM-73 adhesive. a) all three surface treatments; b) increased scale for PAA only.

Similar results were obtained with wedge tests using FM-300 adhesive except that these specimens exhibit less moisture absorption by the adhesive and, hence, a smaller decrease in the low-frequency impedance of the EIS spectra. Again, the interfacial crack propagation of the sandblasted and micropolished specimens allowed crack growth before there was significant absorption of moisture by the adhesive. On the other hand, moisture absorption appeared to be a prime factor in crack propagation within the adhesive for the PAA specimens as reflected by the correlation in Figure 12.

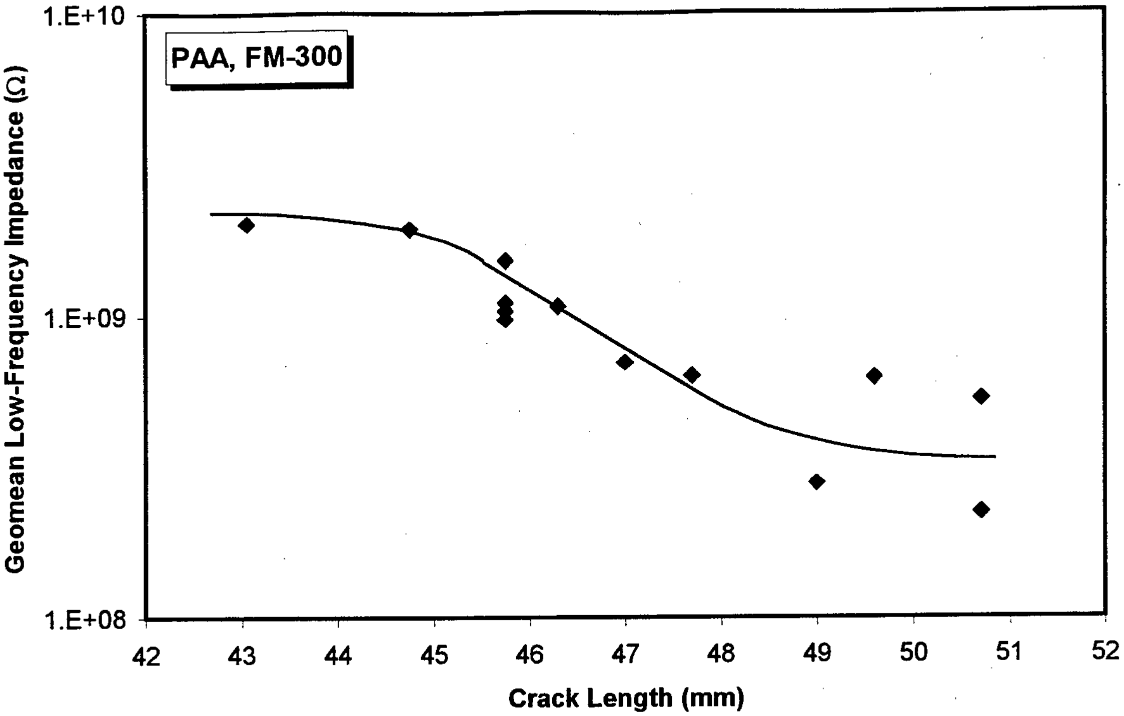

Figure 12. Geometric mean of the low frequency impedance as a function of crack length for PAA specimens with FM-300 adhesive.

A limited number of experiments were performed using PAA aluminum adherends bonded to either glass fiber-reinforced (epoxy) composites (GFC) or carbon fiber-reinforced (epoxy) composites (CFC). Crack propagation for these specimens was within the composite near the adhesive interface. The interface with the adhesive was not the limiting factor for these specimens under these conditions.

The EIS measurements reflect both the adhesive and the composite. The greater impedance of the GFC data (Figure 13) compared to that of the CFC data and that of the aluminum/aluminum data (Figure 9) indicate that the impedance of the glass composite is dominating over that of the adhesive. By comparison, the lower impedance (greater conductivity) of the graphite epoxy is evident. There is a small, but distinct trend for the impedance of the GFC specimens to decrease over time. We attribute this to absorption of moisture by the composite itself. Detection of moisture absorption in both GDC and CFC monolithic material has been previously reported using the *in-situ* sensors.[23] Based on the previous data, the amount of moisture absorbed by the GFC under these conditions is small, less than 1%. No indications of moisture absorption in the CFC is seen, but moisture detection in these materials has required equivalent circuit analysis which was not done in this case.

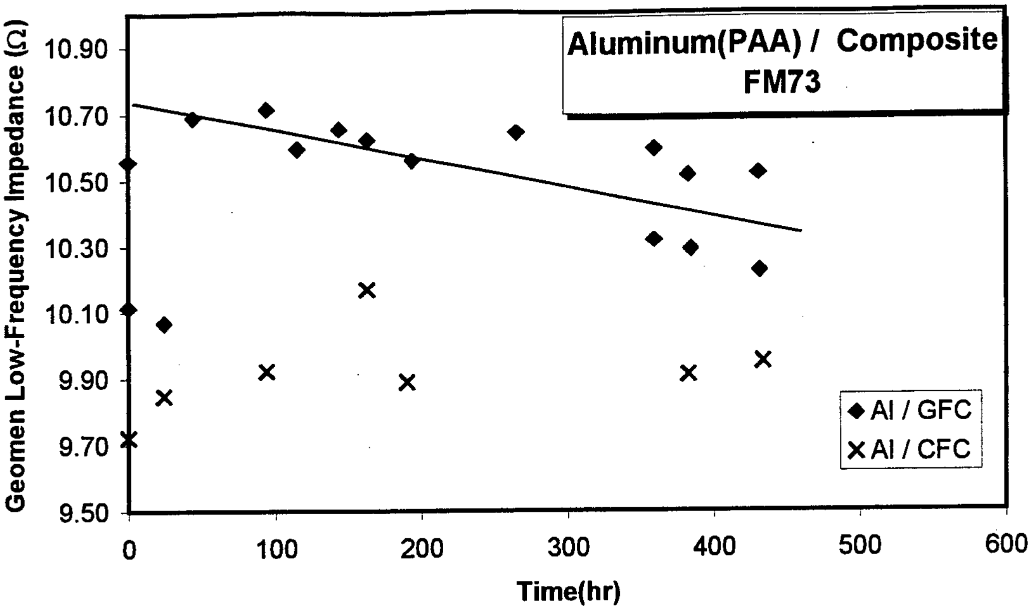

Figure 13. Geometric mean of the low-frequency impedance as a function of time for aluminum / glass fiber-reinforced composites and aluminum / carbon fiber-reinforced composites.

Discussion

The utility of tracking moisture adsorption in a bondline as a means of health monitoring an adhesive joint is dependent on the surface preparation of the adherends and the resulting failure mechanism. The use of EIS or other moisture-sensitive probes is best suited for situations where relatively long exposure to moisture results in joint failure from plasticization or other weakening of the adhesive or from hydration or other corrosion of the adherend surface. PAA adherends are one example in which these conditions are met. For these joints, the impedance spectrum significantly changes in shape and the low-frequency impedance decreases by one to three orders of magnitude (depending on the adhesive) well before hydration of the oxide and joint failure. Thus there is ample time to warn of impeding bond degradation and preventative action can be taken.

This ability to warn is in contrast to the situation with polished or sandblasted adherends where crack propagation occurs interfacially with the very first ingress of moisture to the interface. The smooth adherends, without a high density of physical bonds, fail as soon as a small amount of moisture reaches the interface. There is no need for the adhesive to absorb moisture and for the moisture to be in contact with the interface for an extended period of time. Fortunately, these types of surface preparations and the resulting bonds are not used where strong, durable joints are required. Structures for which these bonds are acceptable would not be candidates for bondline health monitoring.

It is interesting to compare the time scales required for degradation in these experiments and similar experiments. The tensile button tests lasted up to 183 days or approximately 6 months in high humidity and subsequent water immersion. During that time, the sanded specimens showed definite degradation; the PAA specimens showed minimal adhesion strength decrease and no signs of interfacial degradation; and one FPL specimen showed partial interfacial failure toward the end. For these specimens, moisture has to diffuse into the adhesive from the edges without scrim cloth or other medium that might aid moisture ingress. The first effect of the moisture is to weaken the adhesive and this was observed for all surface treatments (Figure 4 and Figure 6).

Subsequent degradation occurs as the moisture reaches the interface and begins to react with the interfacial bonds and the aluminum oxide. The rate at which interfacial degradation occurs depends on the quality and quantity of physical bonds (mechanical interlocking) between the oxide and polymer and the stability of the oxide against hydration. For interfaces with minimal physical bonds, such as the sanded specimens, bond failure occurs relatively rapidly, but still requires sufficient moisture to reach the interface. In the other extreme, PAA interfaces have very evolved physical bonds which are disrupted only after the oxide slowly hydrates.[21-24,] This combination serves to provide excellent durability under service conditions and requires even accelerated tests like this one to take a long time for degradation to occur. Intermediate between these two extremes is the FPL surface. It has less evolved physical bonds and only fair resistance to hydration.[21,22,25]

A comparison can be made for the times for hydration to occur, t_i, for FPL surfaces under different conditions. In this experiment where moisture had to diffuse from the edge of an adhesive, one specimen showed hydration beginning after 140 days; others showed no hydration after 120 and 135 days. The 140-day period represents a minimum value of the incubation time at 50°C under these conditions. For specimens covered with an epoxy adhesive, but with a free epoxy surface exposed to water at 58°C so that moisture only had to absorb through the thickness of the adhesive, Davis et al. found hydration beginning after approximately 110 days.[15] At 75°C, the incubation time decreased to approximately 229 hours.[26] For bare specimens, the incubation time is much shorter. McNamara and Agoff found incubation times to range from 3 minutes at 70°C to 85 minutes at 40°C for immersion; for humidity, the times ranged from 5 hours at 45°C to 27 hours at 35°C.[27] These data are compiled on the Arrhenius plot of Figure 14 for the equation

$$1/t_i \propto k = Ae^{-E_a/RT}.$$

Based on the immersed, bare substrates, the activation energy, E_a, which is proportional to the slope, is calculated to be 82 kJ/mole. This value compares well to that determined by Alwitt of 78 kJ/mole for hydration of the amorphous oxide on pure Al.[28] Within the accuracy of the limited data, the activation energy for hydration is the same for each condition, as expected for similar surfaces. Although not available from the data reported here, the activation energy for hydration of a PAA surface would be much higher so that the incubation time would be much longer for identical conditions. Previous experiments indicate that the incubation time for PAA surfaces is approximately two orders of magnitude longer that that for FPL surfaces.[29] Accordingly, it is not surprising that we did not detect any hydration of the PAA tensile-button specimens during our testing.

The pre-exponential factor, A, is a function, among other factors, of the concentration of water available for reacting with the surface. As a result, the rate constant, k, varies dramatically with experiment conditions. The most water is available in immersion and the rate constant is correspondingly highest (incubation time is shortest). Even though a thin film of condensed moisture may have been present on the humidity exposed specimens all or part of the time, the amount of water available for reaction is less and this reduction is reflected in the smaller rate constant (longer incubation time). The lowest amount of water available is when the surface is covered with epoxy. A typical epoxy can absorb 1-2.5% moisture, but not all of this moisture is available to react with the surface – much of it will be bound to the polymer via hydrogen bonding. Consequently the reduction of approximately three orders of magnitude in incubation times for bare surfaces exposed to humidity and epoxy-covered surfaces is reasonable.

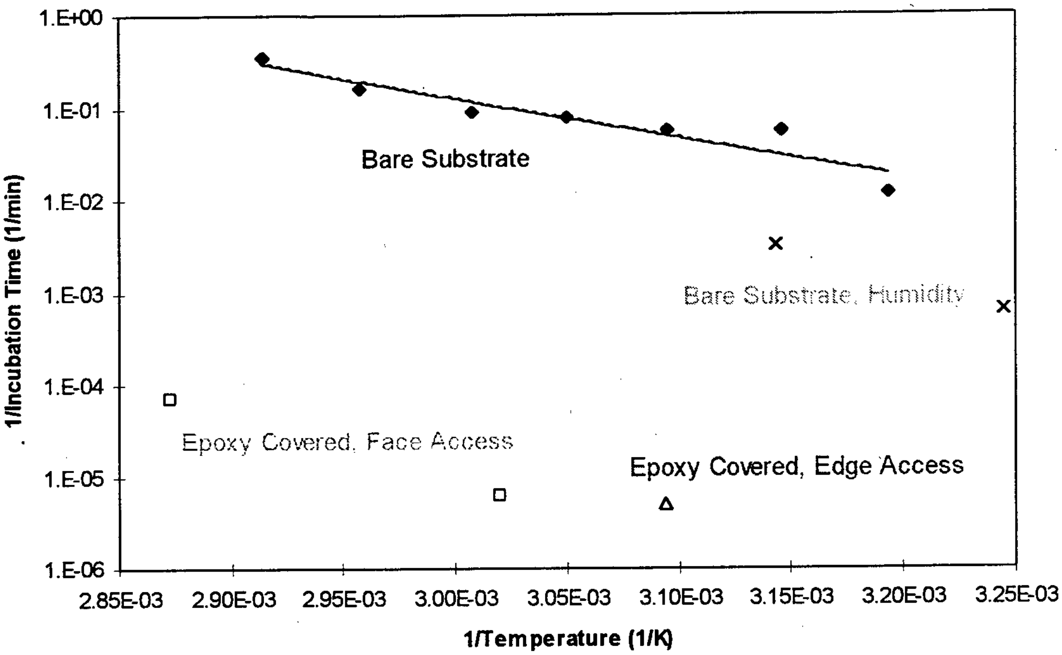

Figure 14. Arrhenius plot of incubation times prior to hydration of FPL aluminum under various conditions. The bare substrate data are from Ref. 27; the epoxy covered, face access data are from Refs. 15 and 26; the epoxy covered, edge access datum is from the current work.

The small rate constant for hydration of epoxy-coated specimens and the slow rate of bond degradation for the tensile button specimens demonstrate the limitations of using short-term lap shear, tensile button, or similar joint configurations to test the durability of surface preparations. Failure of poorly prepared surfaces, as denoted by interfacial failure of the sanded specimens, was detected in our experiments after one to two months. Failure of FPL-etched surfaces, which exhibit the poorest durability of any commonly used, high-performance surface treatment of structural aluminum joints, began to occur only toward the end of the five-month exposure. No failure was observed for the PAA specimens that should show the best durability. Based on differences in the incubation times, we would expect the PAA specimens to begin to fail only after approximately five years. The addition of primers and other common procedures would further delay hydration and bond failure and is reflected in the long-term success of the PAA treatment for aircraft and other structures.

Discrimination of surface treatments based on wedge tests is much more rapid, as is widely practiced. For example, FPL adherends typically show interfacial failure after a few hours in wedge tests as opposed to 140 days for the tensile buttons. A one-week wedge test allows ready distinction between different surface treatments, and often the differences are apparent after only 24 hours. The tensile button tests were just beginning to show a distinction after five months.

Summary and Conclusions

Electrochemical impedance spectroscopy (EIS) measurements using an *in-situ* corrosion sensor were able to detect the absorption of moisture in adhesive joints in the wedge test and tensile button configurations. For high-performance surface treatments, such as phosphoric acid anodization (PAA), where there is a high density of physical bonds and the oxide is resistant to hydration, the low-frequency impedance values correlate with bond performance and give substantial warning before hydration and joint failure ultimately occurs. This warning would enable condition-based maintenance where remedial action or repair can be scheduled before irreversible, environmentally induced bond degradation becomes serious. For smooth surfaces with little or no opportunity for mechanical interlocking, bond failure can begin as soon as moisture reaches the interface, especially in cases of opening stresses, such as a wedge test. In these cases, little warning is available from the EIS measurements. However, these treatments are not used in critical bondlines where durability in moist conditions is required. Such structures would not be candidates for health monitoring.

In the case of composite/aluminum bonds, the EIS measurements are reflective of both the adhesive and the composite. For glass fiber-reinforced composites (GFC), the composite dominates the signal and moisture ingress into the GFC can be detected. For carbon fiber-reinforced composites, the conductive nature of the graphite fibers complicates the signal and more sophisticated data analysis is needed.

An analysis of the failure modes and incubation times for hydration of FPL surfaces within a bond and freely exposed to moisture under a variety of conditions reconfirms that hydration of the aluminum surface occurs in a joint and is the primary cause of moisture-induced interfacial failure. The data show that the activation energy for hydration of an FPL surface is the same whether or not the surface is covered with adhesive. In contrast, the rate constant, which also depends on the concentration of water at the interface, among other factors, is very different for bare surfaces and surfaces within a joint. The reaction rate will be three to four orders of magnitude slower within a joint that has no opening stresses. These kinetics must be taken into account in the design of experiments to test surface preparations.

Recommendations for Future Work

The results of this program clearly show that electrochemical impedance spectroscopy (EIS) is able to detect the ingress of moisture into an adhesive bond. It is applicable for both laboratory investigations and field inspection. In the latter case, it can be used to detect moisture and the potential for environmental degradation of the bondline well before irreversible damage occurs in PAA or FPL bonds, the only ones currently in use for critical aerospace structures. Establishment of the behavior of sensor measurements for a variety of adhesives, primers, and adherends and the warning provided before serious damage would be needed before it could be implemented in the field. Also needed would be refined data acquisition and analysis protocols and development of robust, user-friendly software. Sensor placement on aircraft and other large structures has not yet been addressed. Several different models of instrumentation to interrogate the sensor and analyze the measurements are currently available or are being developed by the instrument manufacturers. Determination of the best instrument for field inspection would also be needed.

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