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The development of embedded sensors to assess the fatigue response of adhesive joints in marine environments.

Scott McGovern

University of Wollongong

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The Development of Embedded Sensors to Assess the Fatigue Response of Adhesive Joints in Marine Environments

A thesis submitted in fulfilment of the requirements for the award of the degree

Doctor of Philosophy

From

University of Wollongong

By

Scott McGovern
Bachelor of Engineering (Hons)

Department of Materials Engineering

March 2007
DECLARATION

I, Scott T. McGovern, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy in the Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Scott T. McGovern

20 March, 2007
PUBLICATIONS AND CONFERENCE PRESENTATIONS


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LIST OF ABBREVIATIONS

PAn poly aniline
ES emeraldine salt
EB emeraldine base
P(BuA-co-VAc) poly Butyl acrylate-co-vinyl acetate
HCSA Camphor sulfonic acid
PEDT poly 3,4-diethoxythiophene
PVDF poly vinylidene fluoride
Al 5083 Marine grade aluminium alloy 5083
Al₂O₃ Aluminium oxide
AlOOH Boehmite
Al(OH)₃ Bayerite
Gₘₗₙₜ Strain-energy-release-rate
Gₖ Fracture energy
FPL Forest Products Laboratories
FES Ferric sulphate
HCl Hydrochloric acid
ASTM Australian standard test methods
PTFE poly tetrafluoroethylene
NaCl Sodium chloride
DAQ Data acquisition
w/w% Weight percent
S·N Stress vs number of cycles till failure
RH Relative Humidity
NDE Non Destructive Evaluation
ABSTRACT

Historically, the use of adhesives within the marine industry has been limited due to the effects that salt water can have on the adhesive joint in service. Salt water has been shown to have adverse effects on the adhesive bond strength due to corrosion of the adherend surfaces, delamination of the adhesive at the interface and plasticisation of the adhesive material. However, if the progress of such degradation can be properly monitored and better understood then greater confidence may be imparted with the use of adhesives for marine structures, and with adhesive incorporation, the potential benefits of improved weight reduction, speed of manufacture and reduced cost may be realised. The work in this thesis was undertaken to develop miniature sensors that may be embedded within the adhesive bondline so that a continual health monitoring of the adhesive joint in service may be undertaken and a better understanding of the mechanisms of adhesive breakdown in marine environments may be achieved.

Sensor substrates were manufactured from 125 μm polyester insulated platinum wires dip coated with conducting polymer materials. Various conducting polymers were investigated for their ability to sense localised environmental conditions such as the presence of water and pH changes - recognised factors that have been linked to adhesive joint degradation via the instigation of adhesive plasticisation / delamination or the onset of corrosion.

Humidity sensors were manufactured from polyaniline (PAn) based materials due to the high conductivity changes observed with PAn in the presence of water. The best response was obtained from the polymer blend that was manufactured by chemically polymerising aniline monomer using ammonium persulphate in the presence of poly butylacrylate –co-
vinyl acetate (P(BuA-co-VAc)) and camphor sulfonic acid (HCSA) to generate a solid that could be readily dissolved in dichloromethane. A blend of 15 w/w% PAN was developed and a portion of the PAN polymer solid was further de-protonated from the emeraldine salt (ES) to the emeraldine base (EB) form to be applied as a protective barrier layer.

Sensors were constructed by first dip-coating the substrate in 15 w/w% PAN P(BuA-co-VAc) ES polymer followed (after drying) by dip-coating in 15 w/w% PAN P(BuA-co-VAc) EB polymer. The sensors had an exponential response and showed high sensitivities with an 800% resistance change over the entire 95% change in RH. For the largest change in humidity (from 3 to 95% RH) the sensors took approximately 4 to 5 hours to reach 90% of the equilibrium resistance on humidifying and 35 hours was required to reach 90% of the equilibrium resistance upon desiccation.

The best pH sensors were manufactured from a processable polymer blend made from poly 3,4-diethoxythiophene (PEDT) and poly vinylidene fluoride (PVDF). The blend was able to be cast from an acetone solvent and had an approximate PEDT content of 11 w/w%. The sensors showed a linear response to pH changes between 5 and 11 with an approximate 350% increase in resistance when increasing the pH from 1 to 13. However, hysteresis was observed with cycling between high and low pH and significant drift was encountered when cycling over multiple cycles. Further problems were also encountered with the embedding of the sensor in the Araldite 2015 test adhesive, and as such these sensors were abandoned from further study.

To examine the humidity sensor performance in service, Aluminium 5083 Araldite 2015 adhesive joints were constructed in a lap-shear configuration, comparing two different pre-treatments of an Optimised FES (FES) and an acetone solvent wipe (solvent wipe). Joints were exposed to a constant temperature salt water spray and the lap-shear tensile strength
of the adhesive joints was tested after varied time of exposure for joints with and without embedded sensors and for both pre-treatment types. For the same salt water exposure conditions, joints were also exposed to a constant 1 Hz fatigue cycle with a varied load and S-N curves were generated for joints with and without sensors for both pre-treatments.

It was found that the average dry tensile strength of the solvent wipe and FES joints was 10.3 +/- 1.3 MPa and 16.2 +/- 0.3 MPa respectively. The tensile strength of the solvent wiped joints showed a steady decrease with exposure to salt water spray such that after 21 days exposure time, joint strengths had dropped to 50% of the strength of the unexposed samples. In comparison, the FES samples showed no loss in joint strength even after 23 days exposure to salt water spray. The difference in joint performance between the two pre-treatments was attributed to the high degree of surface roughness of the FES treated samples enabling a greater degree of mechanical interlock between the adhesive and substrate.

Solvent wiped joints that were tested in fatigue showed a marked decrease in strength when exposed to marine conditions. It was shown that for the same applied fatigue loads joints that were tested 'dry' lasted approximately 50 times longer than joints that were exposed to a salt water spray. This dramatic change was somewhat uniform across the whole S-N curve even for short exposure times less than 1 day and this accelerated decay of joint strength was attributed to the generation of micro-cracks during the fatigue process that allowed for the faster ingress of water into the joint further accelerating the breakdown seen with static tests.

The greater strength with the FES joints was further highlighted with the fatigue tests. When exposed to marine conditions, the FES joints were seen to last up to 10,000 times longer than solvent wiped joints and no failure was seen with the 'dry' FES joints at all
within the constraints of the testing apparatus. The 10 million cycle fatigue strength of the FES joints exposed to marine conditions was estimated to be approximately 1.3MPa.

It was hoped that the embedded sensors may be used to ascertain a critical water content within each of the adhesive systems that might suggest the onset of adhesive failure, however it was seen that the embedded sensors became unstable between 24 and 48 hours of exposure to salt water. The change in stability of the embedded sensor with static tests was seen after water uptake in the adhesive of 2 w/w%, analogous to an equilibrated environment of approximately 75% relative humidity. It was thought that for each of the tests the sensor breakdown was most likely due to a combination of three main factors:

a) swelling of the adhesive with water ingress, promoting delamination of the sensing polymer from the underlying sensor substrate

b) further deprotonation of the underlying ES sensing material to that of the non-conducting PAn EB

c) the generation of micro cracks and internal strains within the adhesive system (especially within the fatigue tests) that mechanically affected the performance of the embedded sensor response

It was discovered that with full immersion of Araldite 2015 adhesive films in water, the maximum uptake of water that was achievable was approximately 6 w/w% taking over 6 weeks to reach full stability. Due to the short time frame encountered before sensor breakdown in static tests of 24 - 48 hours it could be concluded that a) is not the most likely cause of sensor failure. Likewise c) is less likely due to the absence of any applied external stress during salt water exposure during static tests.

It may be postulated then, that if b) is the likely cause of sensor breakdown, the sudden change in environmental conditions that could initiate a net increase in resistance (and
reduction in the perceived mass uptake of water) by means of deprotonation would be an increase in pH - similar to what is known to occur at the onset of corrosion.

In the current study there were indications that corrosion had been initiated with ingress of water equivalent to 75% RH at the site of the sensor (causing this increase in resistance) and may help explain the significant drop in fatigue strength that was seen with the solvent wiped joints after only 1 day exposure.
Chapter 1

Introduction
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1.1 Aluminium Alloys

Since days gone by the human race has been working with metals. The superior hardness and strength of metals combined with their ability to be easily formed into a variety of shapes has made their use in building commonplace. Advancements in metal alloying has generated materials that are harder, stronger, lighter and much more corrosion resistant than their parent constituents, and in turn has broadened the potential for metals to be used in applications which were previously considered impractical or at least somewhat flawed. One such application is within the marine industry.

Technology has progressed from days where large ocean going frigates were made from wood and powered from the wind. Today’s marine vessels are consistently made from steel and more recently aluminium and its alloys, due to their light weight, high strength and significant corrosion resistance that helps avoid degradation of the metal surfaces in these harsh salty conditions. Aluminium as a bare metal oxidises readily, but upon corrosion, a passive and non-porous oxide layer develops that acts a barrier to oxygen and can help prevent, and in some environments eliminate any further degradation. However, further benefits may be obtained by the alloying aluminium with other elements.

There are various elements that are alloyed with aluminium that are used to either improve the corrosion resistance, hardness or strength of the base metal [1, 2]. For example, copper is the major alloying element of the 2000 series of alloys and is used to impart lattice defects within the crystal structure of the underlying base metal and thus increase its
hardness and strength [2]. In their heat treated forms, the 2000 series can have similar mechanical properties to mild steel but with a greatly reduced weight [2], yet this series does not have the corrosion resistance of various other Al alloy compositions.

Alloys with the best corrosion resistance for marine conditions are that of the 5000 series. These alloys incorporate magnesium as the major alloying element and have moderate to high ultimate tensile strengths of around 290 MPa [2]. A typical composition of common marine grade aluminium Al 5083 may be seen in Table 1.1. Alloys in this series possess good welding characteristics and good corrosion resistance in marine atmospheres [2] and are the likely reasons that these alloys are commonly employed in boat building.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>0.40</td>
</tr>
<tr>
<td>Iron</td>
<td>0.40</td>
</tr>
<tr>
<td>Copper</td>
<td>0.10</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.40 - 0.10</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4.00 - 4.90</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05 - 0.25</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.25</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.15</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

Table 1.1) Typical composition of Al 5083 alloy

1.2 Joining Aluminium

When incorporating these alloys into engineered structures there are a variety of methods employed for joining the materials together. For high load applications, the common method of joining is with welding. High strength welded lap-joints are capable of being
produced with joint strength retentions from 60 to 80% depending upon the alloy and temper [2]. Welded joints also have the advantage over mechanical means of joining (such as riveting) that the joint becomes sealed (both water and air tight) once welded. However, several disadvantages with the welding of aluminium exist that can limit the overall engineering design.

Al 5083 is commonly welded using a gas-shielded arc process. These alloys have a thick dark oxide coating that must be removed prior to welding to ensure consistent weld-metal flow and a low porosity weld [2]. Pre-weld cleaning can be time consuming and normally incorporates washing with detergent solutions to remove excess dirt, wiping with solvent soaked cloths (acetone or similar) to remove grease and oils and scrubbing with wire brushes to remove heavy oxide build-up. Chemical removal of these oxides may also be accomplished by immersion in butyl alcohol – phosphoric acid type solutions, but after the chemical removal the surfaces should be washed thoroughly and dried with hot air.

Even once the weld surface is clean, care must be taken during welding to ensure that the weld does not result in defects such as weld cracking (normally attributed to restrained shrinkage of the weld metal during cooling), porosity and inadequate penetration of the weld metal into the joint. Good quality welds are normally the result of a highly experienced operator that knows how to correctly ‘tweak’ the welding voltage, current and speed to achieve the desired results [2].

Due to the high co-efficient of thermal expansion of aluminium, the design of the joint to be welded should take into account the expectation that dimensional changes when welding aluminium alloys will be about twice that for steels [2]. Also, with the melting point for
aluminium being half of that for steel, the weld speed is an important factor to consider to minimise deformation in the final welded materials. Limitations can exist with the choice of thickness of the materials being joined where commonly metal sheets need to be at least 3mm thick to avoid heat distortion and burn through [2]. This minimum thickness results in aluminium sheets being used that are thicker than may be needed for certain applications and when combined with the mass of the welds themselves can add significant increases to the overall weight of the final structure.

For joining sheets with a larger gauge thickness and when butting sections together it is necessary to weld the joint over multiple passes to build up the required thickness of the weld metal. This too, can be time consuming and result in significantly increased labour costs in the production of the final structure.

1.3 Adhesive Joining

Due to the long construction times, inherent problems with welding and the weight savings that may be generated, several industries have incorporated the use of adhesives in the construction of their engineering structures. The joining with adhesives can be much faster than welding and large cost savings may be realised due to lower labour costs during production. Adhesives have the advantage that they can allow for the joining of dissimilar metals with a reduced risk of cathodic corrosion. Most modern day adhesives that are used within engineering applications are also organic in nature and as such normally have a lower specific gravity to the adherends being joined. This low density can be a major
advantage in applications within the aerospace industry where weight savings are paramount [3, 4].

Figure 1.1 shows the use of adhesives in a Fokker F-100 passenger aircraft and it is clear to see that much of the wing structure, engine housing and fuselage are at least somewhat adhesively bonded. Other areas within the cabin also use adhesives and are commonplace in the construction of the various panels within the airplane structure. For example, Nomex™ honeycomb core is used extensively within the floor panels of airplanes and is adhesively bonded in a sandwich configuration between two fibre glass panel skins [3].

![Figure 1.1) Schematic of a Fokker F-100 passenger aircraft highlighting sections of the aircraft that incorporate the use of adhesives. (Taken from Adhesives and Adhesion Technology [3])](image-url)
The automobile industry also uses adhesives extensively. Figure 1.2 shows a diagram of an automobile body highlighting at least 15 locations where adhesives and sealants are used. Automobile doors commonly incorporate a structure known as the ‘hem-flange’ in which the outer door is adhesively bonded to its inner shell [3, 5]. The outer door is crimped over sections of the inner shell in which adhesives are used to both bond and seal the assembly. Attention should also be noted with the car windshield (considered a load bearing structure) and other windows that are often adhesively bonded in place in newer vehicles. In general, it is the time (and hence cost savings) as well as weight savings that have led to the increased use of adhesives within these structures.

**Figure 1.2** Schematic of an automobile body showing various locations where adhesives may be incorporated within the design of the structure. (Taken from *Adhesives and Adhesion Technology* [3])
1.4 Mechanisms of Adhesion

There are various mechanisms that enable adhesion within an adhesive bond. In general terms each mechanism is due to either mechanical forces or direct chemical bonds with the adherend surface, and adhesive bonds quite often contain a combination of both.

The degree of surface roughness of the material being joined can have a dramatic effect on the resulting joint strength of the adhesive bond. A surface with a high roughness allows the adhesive to penetrate further within the material for an increased surface area of contact between the adhesive and adherend [3-9]. Included with this is a degree of mechanical interlock or ‘keying’ that can occur, allowing the adhesive to properly penetrate into and anchor itself to the adherend surface further increasing the overall joint strength.

Such factors as adhesive viscosity, surface energy and contact angle with the adherend can be important considerations for an engineer who is designing adhesive joints for engineering applications. As can be expected, a low viscosity adhesive will flow better into any surface pores (whether natural or created during any pre-treatment processes) and as such, theories on ‘absorption’ outline the ease that a material is wetted on the surface to be joined and the extent that, upon curing of the adhesive, that an intimate contact occurs between the adhesive and the adherend [3, 5, 10]. If the adhesive does not fully wet the surface then the bottoms of the pores on the surface of the adherend may not be completely filled leading to entrapment of gases or voids [3]. These voids can lead to lowered surface area contact with the adherend and result in points of stress concentration leading to drastically lowered strength in adhesive bonds.
Chemical adhesion processes exist because of molecular contact with the adherend surface and can result in direct primary bonding (such as ionic or covalent bonds) or secondary bonding (acid-base, Van der Waals or dipolar). Dependant upon the choice of material for the adherend, some adhesives are able to interdiffuse into the adherend layer causing molecular entanglement between the adhesive and adherend, which effectively broadens or even eliminates the joint interface. This process is commonplace with adhesively bonded polymers [3, 5, 11]. With these factors in mind and due to their inherent properties of high strength and good wettability, arguably the strongest of all structural engineering adhesive systems are the epoxies.

### 1.5 Epoxy Adhesives

Epoxy adhesive systems contain epoxide resins that are capable of reacting with suitable hardeners to form rigid cross linked matrices of high strength. Their low surface energy gives them great wettability characteristics (as seen in Table 1.2) affording them the ability to bond non-porous substrates. Epoxies have the advantages of excellent chemical resistance, negligible shrinkage and high versatility [4, 5]. Their high cohesive strength in the as-cured state can often exceed the adherend strength and epoxy systems show low creep with better retention of strength under sustained loading than thermoplastic adhesives [4]. This high strength and versatility has generated applications in bonding aluminium to itself (or other metals) as a general substitute for rivets in the aerospace industry. Uses have also been seen within the automotive industry with the attachment of reinforcements to light metals to improve rigidity where welding may cause problems of distortion [4]. Yet
even with these advantages, epoxies also have their limitations. Epoxies are two component systems and must be mixed in the correct ratios to ensure complete curing and maximum strength. They have a limited shelf life and can show poor cure at low temperatures [5].

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface Energy (mJ/m²) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.0</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>43.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>63.4</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>47.7</td>
</tr>
<tr>
<td>n-hexane</td>
<td>18.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>28.9</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>43.9</td>
</tr>
</tbody>
</table>

Table 1.2) Typical surface energies of various familiar liquids

1.6 Optimising Adhesion

The most important role of the adhesive is its ability to transfer loads effectively between the two metals being joined and one of the main problems with the adhesive joining of metals is that the structural joint strength is limited by the strength of the adhesive material being used, (which in most cases is of lower strength to the metal being joined). In accommodating the mechanical properties of the adhesive, the joint design can be of major importance. For example, as high strength epoxy systems are generally hard, joint design should aim to produce forces in tension or compression rather than shear or peel [4, 5].

Alongside this, various oxide layers of the initial parent material populate the surface of all metals. The strength of adhesion of these oxide layers to both the surface of the parent metal and with the adhesive can limit the overall final strength of the adhesive joint [12].
Commonly joint failure will occur at the interface layer that is the weakest, which inherently will become the limiting factor in the overall strength of the adhesive joint [4, 5, 13].

It is seen that joints of low strength will not effectively transfer loads and as such will fail adhesively (or interfacially) within these metal-oxide interfaces. Stronger joints that are able to properly transfer load will fail cohesively through the centre of the adhesive itself. It is thus seen that the oxide interface region is of utmost concern within the design and manufacture of commercial adhesive joints. As such, much research has been undertaken into the modification of these oxides to be more stable and produce high strength joints.

1.7 Adhesive Pre-treatments

There are various adherend surface pre-treatments that can result in dramatically increased strength in the resulting adhesive joint. Simple pre-treatments such as solvent wipes are commonly used that remove surface grease and oils and improve the wettability of the substrate and hence increase forces of adhesion through the adsorption theory. Following this, chemical pre-treatments can be used that change the surface morphology of the adherend to produce oxide layers that not only have a stronger adhesion to the underlying parent material but a higher strength [3-5, 13-15]. These pre-treatments quite often include an acid etch of the surface to increase the surface roughness and result in better mechanical interlock of the adhesive with the adherend. For example the Forest Products Laboratory (FPL) Etch [16, 17] involves the immersion of aluminium in a sodium dichromate and
sulfuric acid solution that converts the oxides to the stronger more stable boehmite form [18] whilst creating micro-pores and pits in the surface that help with mechanical interlock. Yet due to the carcinogenic nature of Chromate VI and the inherent risk to workers, industry is steering away from the use of chromate based pre-treatments, such as FPL.

Another pre-treatment that is used in industry is a ferric sulphate (FES) and sulphuric acid etch as outlined in the ASTM Standard D 2651 – 90 [19] Standard Guide for Preparation of Metal Surfaces. This procedure also involves the immersion of the aluminium to be joined in a bath of the pre-treatment solution at a set temperature for a given time to produce joints with improved strength in adhesive joining. This process has the advantage that it does not involve chromate chemistry in the etching of the adherend surface eliminating the corresponding risks of exposure to carcinogens.

Smeltnieks et al [13] undertook a comprehensive study into the pre-treatment of 5000 and 6000 series aluminium alloys for the adhesive joining in marine environments. A modified or ‘Optimised’ FES pre-treatment was developed that showed remarkable results when compared to other available pre-treatments. The Optimised FES pre-treatment substituted the use of sulfuric acid in the pre-treatment solution for hydrochloric acid and when compared to other pre-treatment methods, (such as FPL), showed extremely high bond strengths for adhesive joints tested in marine conditions in both static tensile strength and under fatigue loading.
1.8 Adhesive Breakdown in Marine Conditions

Even with advances in pre-treatment technology, adhesive joints are well known to breakdown in the presence of water. Water is known to be able to plasticise adhesive systems depressing the $T_g$ making the adhesive itself less strong and more rubbery and in consequence, lowering the strength of any adhesive joint made with these systems [5, 20-22]. Upon plasticisation of the adhesive, disengagement from the micro-rough adherend surface may ensue, resulting in reduced physical bonding and hence reduced joint strength and durability [18].

Water entering a joint can cause swelling of the adhesive which tends to induce stresses, weakening the overall adhesive system. Weitsman has shown that these stresses are manifested at the joint edge, but because the stress concentration decreases with time, he concluded that they do not contribute significantly to long-term structural weakening of the joint [23]. If however, a cyclical fatigue load were to be applied at the joint, the added stresses may have the effect of increasing the likelihood of crack generation and subsequent crack growth.

Water can also lead to corrosion of the metals being joined, affecting oxide layers and converting once stable oxides to a low strength unstable form [5, 13-15, 24, 25]. This corrosion effect is justifiably more pronounced in salt rich marine conditions. The extent of degradation due to water effects on the adhesive joint can be somewhat uncertain and because of this, there is still hesitation into the incorporation of the use of adhesives in the marine industry.
1.9 Marine Corrosion in Adhesive Joints

If it were possible to measure either the extent that water has ingressed into the adhesive joint or the onset of corrosion, then it may be found that it is possible to determine the extent of degradation of the adhesive joint strength in marine conditions and from this, the remaining joint strength at any time may be predicted. With the ability to monitor the health of the adhesive joint at any time, further interest may be generated with the use of adhesives in marine conditions. Such sensors could also be used as a tool to further the understanding of the dynamics of the chemical reactions that occur within the adhesive joint during breakdown in marine service.

The oxidation or corrosion of metals requires two main factors to occur. Firstly, there needs to be a species that drives the reaction by being reduced and accepting electrons (which in many cases is oxygen) and secondly there needs to be an electrolyte to carry ions and allow charge transfer. Most commonly the electrolyte will be water or condensed water vapour though some ‘dry’ corrosion reactions involve charge transfer in solid state electrolytes [26]. During the corrosion of metals an electrochemical cell is created where the oxidation reaction occurs at the anode and the reduction reaction at the cathode. These two reaction sites do not have to be in direct proximity as corrosion can still occur as long as there is a pathway for ions to move (and charge to transfer) and the metal surfaces are wet with electrolyte.
Figure 1.3) Schematic of corrosion that can occur on the surface of iron

For example, upon examination of a garden shovel that has been left outside in moist air with wet dirt adhered to the blade, pitting of the metal surface can occur under the layer of dirt and consequently rust is deposited at the edge of the dirt layer where $O_2$ is more readily available. The schematic in Figure 1.3 shows an example of the corrosion of iron and the ion migration and electron transfer that occurs during this process.

The most common oxidation and reduction reactions for aluminium metal may be seen in Scheme 1. These equations correspond to aluminium being oxidised in the presence of oxygen dissolved in either an acidic electrolyte or water and the standard reduction potentials for each reaction are shown. In these cases aluminium is oxidised to $Al^{3+}$ and oxygen is being reduced to $O^{2-}$, gaining electrons in the process.
Scheme 1) The relevant oxidation / reduction reactions of aluminium metal in the presence of moist air

The rate of reaction and hence the extent that the by products are produced depends upon such factors as temperature, humidity, the concentration of oxygen at the corrosion site and the conductivity of the electrolyte. In a low pH electrolyte, equation 2 will be the predominant reduction reaction and as the pH increases, equation 3 will take over driving the reaction. Notice that if you were to add 4 H⁺ ions to both sides of reaction 3 it can be seen that both equation 2 and 3 are effectively the same reaction. Hence, the corresponding potential is determined by how easily the water molecules dissociate to H⁺ and OH⁻ ions. In either reaction however, it can be seen that pH increases may be expected at the site of reduction with the reaction of H⁺ (at low pH) or the production of OH⁻ ions (at neutral or higher pH), yet there is some speculation as to whether this will be truly translated to within the joint itself especially in the case of pitting where the redox reactions are somewhat separated.
1.10 Health Monitoring of Adhesive Joints

During the corrosion of aluminium metal, Al\(^{3+}\) ions are generated and there is a rise in the pH, and all of this occurs in the presence of an electrolyte that is normally aqueous. In sensing the breakdown of joint strength due to the ingress of water there are a number of directions that the researcher may take. Firstly, and most obviously, the sensor may be constructed to measure the water content itself. This approach can provide important information on the concentration of water in the joint and may be used to determine the level of water at full saturation of the adhesive and, (when correlated against the tensile strength of the joints after different exposure times), a critical water content may be found that over time leads to a loss in joint strength. Such sensors could be used to warn that a critical level of water has been surpassed within the joint that could lead to failure at lower than normal levels.

Another sensing approach would be to directly measure the by products that are caused from corrosion of the adherend surface. The changes in pH and the increase in metal ion concentration can both be attributed to corrosion of the adherend, and if the sensor can measure either of these changes then predictions on the condition of the underlying oxides and surface metal of the adherend may be made. Again, if this information is correlated against measured tensile strengths, then in practice the sensor could be used to predict any potential changes in adhesive joint strength, due to the onset of corrosion. Both of these technologies could be further developed into health monitoring devices that predict the structural integrity of adhesive joints during service.
There are various technologies that have been used to measure humidity (or water content) [27-57] and pH [58-71] but very little cross-over has been seen with their application in adhesive joints. Many sensor technologies require direct contact with the compound being sensed, and to obtain reliable information on what is happening within the adhesive there is a need for the direct embedding of the sensor within the adhesive joint. The problem with this approach is that the sensor must be small enough so that it does not threaten the integrity of the joint in any way, either by significantly increasing the joint’s bond-line thickness or by developing areas of stress concentration during the application of loads.

Other less intrusive approaches are to use either ultrasonic analytical techniques [72-74] or dielectric capacitance / electrical impedance methods [54, 55, 75, 76] across the adhesive joint. Here, the response changes with the ingress of water and build-up of oxide layer thickness during corrosion. These methods generate results that are based upon the whole bond area, and results reported are an averaged result across the whole bond. As such, this method has limitations in that it is impossible to pinpoint areas of the joint that are corroding faster than others. Other logistical problems exist in that as the adhesive swells due to water ingress, the capacitance across the joint also changes. Calibrating the curve to account for this ‘swelling’ shift in response is not an easy matter, as measurement of the extent of swelling of the adhesive (with micrometer gauge or other) will no doubt be affected by the build up of oxide layers on the outer surfaces. In essence, the ability to obtain results with a high degree of accuracy with this method is hampered because of the interference between the adhesive swelling and the corrosion of the substrate.

So it can be seen that both of these methods have their inherent limitations.
As depicted in Figure 1.3, corrosion can happen in various areas within the joint and the oxidation and reduction reactions do not necessarily have to be in close proximity. So for research purposes it may be more helpful to understand what is happening at localised areas within the adhesive joint to ascertain the onset and type of corrosion. Embedded sensors can allow us to achieve this aim. This information may then be scaled up to obtain a full picture of adhesive joint breakdown in marine environments. For this procedure to be effective, the sensor must be both small in size and compatible with the adhesive, and the response time must be fast enough to be able to accurately measure changes in the adhesively bonded system.

1.11 Conducting Polymer Sensors

Various sensing materials exist that could be used to produce such embedded sensors, however conducting polymers seem to be among the most promising. Conducting polymers have been widely investigated for sensing changes in humidity [47-51, 77], pH [58-61, 63, 64, 71, 78] and ion concentration [79-81]. A vast range of differing chemistries exist with conducting polymers allowing for better stability in harsh environments, and the various processing methods available provides adaptability during sensor miniaturisation – essential to ensure that the final sensor does not affect the structural integrity of the joint.

The main monomer units that are used to develop the bulk of conducting polymers are aniline, pyrrole and thiophene, and their various derivatives. (Scheme 2 shows the various polymers (I – III) that can be made using these base monomers.) Conducting polymers are able to pass current because of the alternating double bond that exists along the polymer
backbone. In their oxidised and most conducting state, the incorporation of a dopant ion causes the partial delocalisation of the radical cation allowing for electron hopping (and hence current flow) with applied voltages.

![Scheme 2](image)

Scheme 2) (I) Polyaniline (II) Polypyrrole and (III) Polythiophene shown in their 'doped' conducting states

Conducting polymers may be ‘tailored’ such that the dopant ion that is incorporated will react preferentially with another medium. If a molecule is able to interfere with either the conductivity of individual polymer chains (by changing the oxidation state of the polymer or reacting with the dopant), or affect the conductivity between polymer chains (by swelling or other) then the material will be able to ‘sense’ this change by showing a shift in the bulk conductivity of the whole material. As such, these materials are quite commonly used as humidity sensors [47-53] and sometimes pH sensors [58-65].

Conducting polymers are grown from the base monomer unit via electropolymerisation or chemical polymerisation. In the process of electropolymerisation, an electrochemical cell is setup with monomer in a conductive electrolyte. Current is passed through the electrolyte via electrodes that have been inserted into the cell and the monomer is oxidised at the anode. A potentiostat power supply is generally used to control the electrical input (and corresponding reaction) by applying either a constant voltage, constant current or cycled voltage (CV). During each growth cycle the monomer units polymerise to form the
conducting polymer chains and anions in the electrolyte are incorporated into the polymer matrix as a dopant to ensure charge balance. Very thin films may be grown using this method and the polymer may be deposited directly onto the final sensor electrodes however, problems can arise with polymer adhesion to the electrode substrates and uniformity with film morphology.

Chemical polymerisation uses an oxidant (such as ammonium persulphate) to cause polymerisation of the monomer unit. For the highest conductivities the process is normally undertaken in the presence of the dopant ion at low temperatures of 0 – 5°C [78, 82-84] giving results with higher crystallinity, and longer more ordered polymer chains. The polymer usually precipitates, is then collected, washed and can be further purified using dialysis. The chemical polymerisation of aniline is readily achieved and the product can be dissolved in a variety of solvents, enabling the polymer to be cast as thin films. Polymer blends and copolymers may be produced with this method, for example processable polyaniline / polyvinyl chloride (PVC) blends have been made with sulfonic acid dopants [85] which have improved the processability of free standing films by solution casting and melt processing techniques.

This approach can be used to improve the processability [85-94], strength [86, 91, 94, 95] and adhesion [91, 94, 96] of the polyaniline films.
1.12 General Project Aims

The research presented in this thesis aims to obtain a better understanding of the mechanisms of adhesive joint failure in marine conditions. Aluminium 5083 alloy was used with the structural epoxy adhesive Araldite 2015 to construct adhesive joints for testing of tensile strength after exposure in marine salt-spray conditions. These results were compared with ‘dry’ joints exposed to ambient conditions. Two surface pre-treatments were examined consisting of an acetone solvent wipe and the ‘Optimised FES’ pre-treatment (as developed by Smeltnieks et al [13]). Tensile strength was correlated against fatigue strength of the joints for each pre-treatment condition after varied exposure times.

Embedded sensors were developed using conducting polymer blends in the effort to monitor water ingress and pH changes in the joints and the ‘static’ joint strengths and fatigue responses were correlated against the sensor response for each of the joints. The objectives of this work were:

1) To attempt to find a 10 million-cycle fatigue stress in Aluminium 5083/ Araldite 2015 adhesive joints after exposure to a continuous salt-spray environment.

2) To be able to successfully develop and incorporate in-situ sensors into the adhesive joints being tested in fatigue, so that the continual monitoring achieved may provide:
   a) a better understanding of the strength of the joint at any moment in time
   b) a better understanding of the mechanisms of joint failure due to marine exposure
This research was undertaken at the University of Wollongong in conjunction with the support from the ARC Centre of Excellence for Electromaterials Science and Huntsman Specialty Chemicals.
1.13 References


[19] Standard Guide for Preparation of Metal Surfaces,


Chapter 2

Adhesive Testing in Marine Environments
2.1 Introduction

The use of adhesives has been increasingly incorporated into the automotive and aerospace industries, due to the various structural and functional advantages when compared to traditional joining methods. Dissimilar metals may be joined with a reduced risk of cathodic corrosion. Lighter, thinner gauge metal sheets may be employed when joined with adhesives (where traditional welding methods determined the original gauge thickness), and this, along with the elimination of the weight of the welds themselves, can lead to a significant weight reduction in the structure. Adhesive joining methods tend to be faster than traditional welding, leading to cheaper labour costs during construction and repair. Better control of tolerances is achievable with adhesives due to the inherent distortion that can occur from the heat induced in welding processes [1].

Improvements in fatigue strength have been seen with the incorporation of adhesives into the joint design especially with weld-bonded joints (joints that have been made with a combined spot welding and adhesive bonding). Dorn et al [2] found that the combined use of epoxy adhesives with spot welding improved the load bearing capabilities of the joint in shear, impact and especially fatigue when compared to standard spot welding. The improved strength retention was attributed to a more uniform stress distribution caused by additional bonding at the overlap. Likewise, Di Nunzio et al [3] found improved fatigue performance with weld-bonded joints when compared to both the spot welding and CO2 laser welding techniques.

However, even with these advantages, interfacial de-bonding of adhesives is a major concern with their use and has vastly limited their performance.
Degradation of adhesive joints can be linked to the diffusion or ingress of water into the joint promoting desorption of the adhesive from the adherend [4-6], hydration and deterioration of the metal surface oxides [7-15] and the induction of internal stresses [6, 16, 17] which can all consequently lead to a loss in adhesive strength. This effect is justifiably more pronounced in marine environments due to the highly humid and corrosive surroundings and to date there has been little use of adhesives in marine applications.

Within the development of adhesive bonds it is usually favourable to select the adhesive and pre-treatment such that the bonded joint will fail in cohesion when the joint is tested to destruction. This mode of failure regularly attains joints of the highest strengths yet deterioration of the joint due to water ingress can change the mode to adhesive failure due to the mechanisms discussed above.

DeLollis et. al. [5] have published results on experiments conducted upon adhesively bonded aluminium lap-shear specimens that were exposed to high humidities and continuous immersion in water for periods up to two years. The two adhesive systems that were investigated consisted of a nitrile-rubber-phenolic type and nylon-epoxy type adhesives. The water resistant nitrile-rubber-phenolic adhesive specimens showed cohesive failure with each specimen tested over the two year span however the nylon-epoxy bonds progressed from initially cohesive failure to adhesive failure within two months. Consequently the nylon-epoxy adhesive showed a drop in failure stress to 1100 psi after exposure to high humidity and specimens that were completely immersed showed failures stresses as low as 120 psi. This somewhat dramatic loss in bond strength was attributed to water adsorbing preferentially to the metal adherend surface and in turn displacing and desorbing the adhesive from direct contact with the adherend.
This desorption process by water can occur by two mechanisms. The adhesive can adsorb the water, whereupon the water permeates the adhesive to the interface where the desorption phenomenon can take place, or water may wick along the adhesive adherend interface. Laird et al [4] have shown that diffusion of water along the adherend interface of an epoxy resin bonded to E-glass can take place up to 450 times faster than through the epoxy however, the mechanics of the movement of water through an aluminium epoxy adhesive bond can be expected to be somewhat different due to the differences in surface chemistry and the dynamics of hydration of the surface metal oxides. Likewise the choice of adhesive and extent of surface pre-treatment that is undertaken on the adherend can affect the rate that water will diffuse into the bondline and be adsorbed onto the adherend surface.

The ingress of water can result in an attack on the oxides on the bonded surfaces of the adherends, enabling the combined hydration and conversion to less strong and less stable oxide layers. With aluminium based adherends the surface oxide Al₂O₃ formed during the surface pre-treatments can be transformed to the oxyhydroxide AlOOH (boehmite) or trihydroxide Al(OH)₃ (bayerite) forms promoting crack propagation near the hydroxide / metal interface [6, 17] as shown in Figure 2.1. This too can lead to failure at the adherend / adhesive interface resulting in reduced joint strength.

Alongside these effects, water ingress into the adhesive can cause swelling resulting in stress concentrations at the adhesive-adherend interface especially in adhesively bonded metal joints [18]. In this case the metal adherend will not swell with water, resulting in the plane of greatest stress concentration residing at the interface and when combined with loading in fatigue (or other) can result in debonding at the interface leading to adhesive failure.
Figure 2.1) Schematic of hydration caused cracking in an adhesively joined aluminium wedge test specimen (Taken from Handbook of Adhesive Technology [6])

The effects of water have also been shown to dramatically affect the fatigue performance of the adhesive joint in service [19-24]. Much of the literature shows a degradation of the surface oxides of the adherend that leads to crack propagation at far lower values of the strain-energy-release-rate \( (G_{\text{max}}) \) when compared to the adhesive fracture energy \( (G_c) \) [15, 19-21]. In fatigue, this effect has been mainly attributed to the hydration of surface oxides that leads to mechanical weakening of the joint [14, 15, 19-21].

It can be seen that important aspects exist with regard to avoiding bond failure at the adherend / adhesive interface, especially when exposed to highly wet and corrosive environments. Cagle [16] states in the Handbook of Adhesive Bonding that "A first condition in analysing bond failure is the realisation that failure in adhesion of a properly prepared bond is possible, and corrective actions must consider surface modification as a prime requisite in improving the strength and durability of the bonded assembly".
Advancements in the area of surface pre-treatments have enabled the generation of stronger and more chemically resistant oxides for the bonding of aluminium alloys. These processes can produce stable oxide layers that are more resistant to effects of water ingress and corrosion and incorporate a degree of surface roughening that promotes mechanical interlock of the adhesive with the adherend. One standard method used in practice today was developed by Forest Products Laboratories (FPL) and involves the use of sulphuric acid and sodium dichromate to both etch the surface to be bonded and incorporate chromate oxides to help with corrosion resistance [6, 25-28]. Significant increases in joint strength have been found with this method when compared to mechanical etching and degreasing and much of this is attributed to the increase in surface roughness of the adherend without harming the wettability of the substrate [16]. However current practice is for industry to steer away from the use of chromate based methods due to the carcinogenic nature of Chromate VI.

Smeltnieks et al have reported on an adaptation of a non-chromate based pre-treatment system that has been shown to have high strength in the short term when exposed to marine environments. The ‘Optimised FES Pre-treatment’ (FES) was an adaptation of the ASTM Standard D 2651 – 90 [25] Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding [28] and incorporated the use of hydrochloric acid (HCl) instead of sulphuric acid as normally used in the standard. The Optimised FES pre-treatment showed dramatically improved strength retention in fatigue when compared to standard FPL methods, especially when exposed to a marine salt spray environment [28]. Tests were conducted on aluminium K106 epoxy adhesive joints and it was found that the FPL treated joints failed at around
2MPa after 100,000 fatigue cycles. On the other hand, the FES joints remained intact up to 100,000 cycles even with applied fatigue loads of 5 MPa.

The use of this pre-treatment when coupled with a tough water resistant adhesive could give rise to the possibility for stable joints in the long term that, when exposed to marine conditions, have significant strength for practical use.

Here, the mid to long term joint strengths for such an adhesive pre-treatment system are investigated. The tensile strength and fatigue strength of joints have been determined after exposure to marine conditions for varying times. Both tensile strength and fatigue strength were compared with unexposed ‘dry’ joints and joints with a simple solvent wipe pre-treatment. Studies into the effect that salt water has on the adhesive joint strength have been undertaken for the two pre-treatments that were investigated.
2.2 Experimental

The metal adhesive system that was investigated utilised 2.4 mm thick sheets of Al 5083 aluminium alloy joined with Araldite 2015 (Huntsman). 15 mm wide strips were cut from the sheeting and joined in a lap-shear configuration (after surface pre-treatment) with an overlap of 10 – 12 mm.

Two surface pre-treatments were investigated for their ability to aid in overall adhesive joint strength and integrity. The first pre-treatment (Solvent-wipe) consisted of a wiping of the joining surfaces with acetone. A clean section of Kimwipe® lint-free tissue was used for this process to eliminate recontamination of the surface with each subsequent wipe. Each surface was examined visually and cleaned to remove all surface oils and dirt from the joining surfaces to aid in a better bond within the joint.

The second pre-treatment ‘Optimised FES Pre-treatment’ (FES) was the pre-treatment developed by Smeltnieks et al [28] and was an adaptation of the ASTM Standard D 2651 – 90 [25] Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding. This pre-treatment was developed to be non-chromate based and to be more tolerant within marine environments than standard adhesive joining methods that are outlined within the standard.

The solution used for this pre-treatment consists of:

- 50g / L  Ferric Sulphate
- 267g / L  concentrated HCl(aq) (31.0 w/w%)
- 2g / L  Bare Aluminium Filings
- + Distilled Water

The mixing and preparation of the pre-treatment solution was undertaken as follows. The concentrated acid was first added to the distilled water in a large beaker and stirred before
adding the ferric sulphate and aluminium. The solution was stirred overnight before complete integration of all constituents was completed, upon which time the final colour of the solution is a green - yellow. The FES pre-treatment solution was stored in a bottle in ambient conditions for later use.

Before pre-treating of the aluminium surfaces, each sample to be joined was given a surface wipe with acetone to remove excess oils and dirt. The FES solution was poured into a beaker and heated to 45 +/- 1°C at which time the beaker was then immersed in a water bath at 45 +/- 1°C (Figure 2.2). The aluminium strips were held suspended above the warm FES solution and the ends were immersed to a depth of approximately 40 mm for the optimum treatment time of 10 minutes [28]. After this time the strips were removed and washed with distilled water and then hung to dry. The process of adhesive joining was commenced within 24 hours of this pre-treatment process.

![FES Pretreatment Solution](image)

**Figure 2.2** Optimised FES Pre-treatment of Al 5083 strips for adhesive joining

To ensure a constant bond-line thickness between successive tests and to allow room for the embedding of sensors (Chapter 5), the Araldite 2015 adhesive was mixed with a small amount of glass bead filler prior to application to the surfaces to be joined. The glass beads used were graded as 100 – 200μm in size and were sourced from Kisker Biotech. Adhesives
were mixed with a various concentration of glass beads (w/w%) for each pretreatment to obtain the smallest proportion of glass bead component that gave a constant (or near constant) bond-line thickness of 200 µm. This composition of glass beads was used for all later tests.

Equal parts of the Araldite 2015 epoxy were weighed. Glass beads were added to the required amount before complete mixing was undertaken. Adhesive was applied in excess to one of the pre-treated aluminium surfaces that was to be joined. The other joining surface was carefully overlapped and aligned on a sheet of PTFE before application of a 19mm fold-back clip over the exterior of the joint. Joints were allowed to completely cure over 24 hours before removal of the clip. Any excess glue and/or spew fillets were removed with a sharp scalpel prior to commencement of any of the tests.

A span length of 212mm was used for all of the tested samples and was taken as the distance between centres of attachment holes (Figure 2.2). An overlap length of 10-12mm was chosen to ensure a high stress is applied to each joint and that sample failure can occur within the boundaries of the system.

Figure 2.3) A schematic showing the design of a typical adhesive lap shear joint for testing within the Octopus fatigue rig
Adhesive joints were exposed to 'wet' conditions of a constant temperature and pressure salt water spray (5 w/w% NaCl) for varying times and corresponding tensile strengths were compared with control samples that were left 'dry' in ambient conditions. The tensile strength was tested using an Instron 4302 at a constant strain rate of 1mm / minute and the 'static' loss in joint strength was compared for both pre-treatment types for varying times of exposure.

The fatigue strength of joints was also examined for wet and dry conditions for both FES and solvent wipe pre-treatments. The fatigue tests were used to generate S-N curves (Stress vs Number of Cycles to failure) for the adhesive system in wet and dry conditions for each pre-treatment. One main aim for the fatigue tests was to potentially find the 10 million cycle fatigue stress for each of the systems in both wet and dry conditions so that it may later be used as a design criterion when developing joints for practical use.

To facilitate the constant fatigue cycling of the adhesive joints with a salt water spray a machine was designed and developed that was denoted the Octopus.

### 2.3 The Octopus Fatigue Testing Machine

The 'Octopus' is a machine that was designed and built for use in testing the long term fatigue strength of adhesive joints when subject to marine environments and was used extensively in this study (Figure 2.4). It has the capacity to test 8 samples at any one time and interfaces with a Labview program to record the number of cycles that a sample has
withstood up until failure. The machine was originally designed and used by Smeltnieks et al [28] and further adapted by the author to facilitate testing within the bounds of this study.

![A photo of the Octopus fatigue testing rig](image)

**Figure 2.4** A photo of the *Octopus* fatigue testing rig

The *Octopus* has 8 arms that are used to apply a load to the samples to be tested. One end of each arm has the sample attached to it, whilst the other end of the arm has attached a mass of known weight (Figure 2.5). In this way, determination of the applied fatigue force can be estimated by multiplying the length of the moment arm to the pivot point (D) by the applied weight force and dividing the result by the length of the pivot point to the sample (d). This force was accurately verified using a 3.5kN load cell as supplied by Xtran.

The cyclical application of the fatigue force is achieved from the interface of a Crompton Parkinson MA 7244A-K 1440 rpm 3/4hp electric motor with a cam assembly. Each cam is
in continual contact with a lubricated roller on a moment arm (Figure 2.6) and as the cam turns, it pushes down on the moment arm at the sample end, thus supporting the mass and removing the fatigue force experienced by the test sample. The cam continues its rotation, becomes clear of the moment arm and the fatigue force is reapplied to the sample. In this way, as the electric motor turns the cam a sample may be continually fatigued until failure occurs.

**Figure 2.5** A schematic of the operation of one of the arms in the overall Octopus subsystem

The rate of fatigue is set through a gear box and sprocket chain assembly and was not altered throughout the course of testing. The 1440rpm electric motor is hooked up to a Charles and Hunting R5 Reducer 49:1 ratio Speed Reducing Gear Box which is then interfaced with a 45:24 sprocket chain assembly for delivery of power to the camshaft. The resulting fatigue rate is 55.1 rpm or 0.92 Hz which has been chosen to simulate the expected rate of wash that a boat may receive when travelling across the ocean.
Figure 2.6) Photo showing one of the roller/cam interfaces on an Octopus moment arm

Figure 2.7) A schematic of the dampening subsystem for the Octopus
A set of dampeners (or shock absorbers) are used to reduce overall vibration and impact loads in the system. Each moment arm has a Festo DSNU 25-25-P-A 10 Bar air cylinder acting as a dampening subsystem (Figure 2.7) and is separately calibrated for each applied load prior to commencement of testing. The damping cylinders are filled with low viscosity hydraulic oil that is supplied by a reservoir and the extent of dampening is controlled by needle valves at the inlets and outlets of each cylinder.

A series of switches are used to monitor when a sample fails. Upon sample failure the moment arm comes in contact with an idler switch that sends a signal to a computer via a data acquisition (DAQ) card. The switch signals are sent into a control box for digitisation before the signal is then sent along a 50-pin bus cable to the DAQ card in the computer. The software records the date and time of failure from which the number of cycles to failure is calculated from the known speed (0.92Hz). A Labview program monitors the experimental test state and continually backs up data during the test so that when all samples have failed the software stops monitoring the system.

The samples are enclosed within a Perspex bath which allows for the delivery of salt water (via common garden sprinkler heads) to simulate a harsh marine salt-spray environment (Figure 2.8).

A Pondmaster 2800 submersible pump, situated within a holding tank, delivers water to the spray heads and is operated continually throughout each ‘marine’ test. There is an overflow control tap that can be used to control the extent that the water will flow to the sprayers and the resulting pressure. Before the onset of testing this valve was slowly closed until a sufficiently strong mist / spray from the sprinkler heads was achieved. The valve was set at this pressure for the duration of all tests.
The temperature is kept constant through a monitoring system that too, interfaces with the Labview program. A LM335 thermistor measures the temperature of the water that is sprayed onto the samples and this information is passed into the control box for amplification and digitisation before it reaches the computer. The current water temperature is compared to a range of temperatures that the operator sets in the software and the computer either turns a heater (situated in the holding tank) off or on when the water is respectively too hot or too cold.

Two brackets were constructed to hold samples for ‘static’ tests exposed to salt water spray. The brackets were constructed from stainless steel and have a rubber lining to prevent any cathodic corrosion incurred within the aluminium due to contact with the steel (Figure 2.9). Each bracket has the capacity to hold up to 6 samples inside the Perspex bath meaning the Octopus can at any time hold 8 samples for fatigue and 12 samples for static tests in marine conditions.
Capacity was also made for the Octopus electronics to interface later with resistive sensors that were constructed as part of this thesis. Cables were constructed to interface between the embedded sensors and a voltage divider circuit within the control box and the voltage across the sensor was designed to be input into the DAQ card of the computer. From this voltage and the known current the sensor resistance can be determined and monitored over time. 8 sensors may be monitored in this fashion.

2.4 Operation of the Octopus

2.4.1 Calibration of the applied force

For fatigue tests, the force that is to be applied to each test station was chosen, monitored and calibrated with the load cell prior to the commencement of any test to ensure an
accurate calculation of the peak load. Impact loads were removed by adjusting the length of
the attachment arm with a turn buckle (length ‘L’ of Figure 2.5) and any further vibration
was minimised by adjusting the dampening of the cylinders via the needle valves. Once the
fatigue cycle was calibrated for each load, the load cell was removed and replaced with the
sample to be tested. A typical load cell output and subsequent calibration of the fatigue
cycle may be seen in Figure 2.10).

![Correctly damped load](image)

**Figure 2.10** Calibration of a typical fatigue cycle for the Octopus subsystem

### 2.4.2 Lubrication of the system

To prevent excessive wear the cam shaft operates with a continual flow of oil dripping onto
each of the cams (Figure 2.11) and excess oil is collected in the sump below the camshaft.
Fresh oil is delivered from a reservoir and is controlled via two valves to ensure adequate
delivery of oil throughout the lifetime of a test. This reservoir is continually topped up to ensure that fresh oil is delivered to the cams. An overflow pipe allows excess oil from the sump to flow to a basin at the base of the system which is emptied periodically.

![Figure 2.11) Photo of a lubrication pipe for delivery of oil to rotating cams](image)

The Octopus system continuously fatigues a sample at a rate of 0.92Hz with a known applied force set by the operator. The load on the sample is chosen and verified with the load cell and any vibration is calibrated and removed prior to initiation of the test. The computer system monitors the number of fatigue cycles that a specimen has endured and the time and no. of cycles to failure. The set-up simulates a constant temperature and pressure water-sprayed environment (salt water spray for marine simulations) throughout the lifetime of the tests and has the capacity to monitor embedded sensor readings at specified intervals that are set by the operator (utilised in later chapters).
2.5 Results and Discussion

2.5.1 Determination of correct weight % component of glass bead filler in Al 5083 / Araldite 2015 adhesive joints

Figure 2.12) Variation in bond-line thickness of Al 5083 / Araldite 2015 adhesive joints with different weight component of glass bead filler. The error bars shown are one standard deviation away from the mean.

Figure 2.12 shows the variation in bond-line thickness of the adhesive joints for different weight components of 100 – 200 µm glass bead filler material. It was found that for each w/w% component of glass beads added to the adhesive, the aluminium strips that had a solvent wipe pre-treatment had an overall bond-line thickness that was higher than that of
the FES pre-treatment. This was attributed to the higher surface roughness of the FES pre-treatment allowing for the beads to settle into the ‘valleys’ of the etched surface.

Figure 2.13) Variation in tensile strength of Al 5083 / Araldite 2015 adhesive joints with different weight components of glass bead filler. The error bars shown are one standard deviation away from the mean.

Figure 2.13 shows the variation in tensile strength with different weight components of glass bead filler material. With the adhesive / adherend interface being the main limiting factor to joint strength, it can be expected that there will be a certain bond-line thickness which enables full transfer of stresses to the adhesive itself resulting in maximum joint strengths. This is what was seen with a slight increase in joint strength (approximately 10 –
15%) with the addition of small amounts of filler material (1 - 2 w/w%) and directly corresponds to the large initial increase in bond-line thickness observed in Figure 2.12).

For each of the tests it was seen that approximately 2 w/w% glass beads was the common minimum component of filler that would give the most uniform bond-line thickness and least variability with tensile strength for both of the pre-treatments investigated. This was thus chosen as an appropriate level of filler component to add to the adhesive mixture to ensure the least variability within all following tests.

2.5.2 Determination of the tensile strength of Al 5083 / Araldite 2015 joints before and after exposure to marine conditions

With 2 w/w% glass beads it was found that the average tensile strength of the dry samples for solvent wipe pre-treatment was 10.3 +/- 1.3 MPa whereas for the FES pre-treatment the average tensile strength was 16.2 +/- 0.3 MPa (Figure 2.14). Two distinct advantages could be seen with the use of the FES pre-treatment in that significant increases in joint strength were obtained as well as a less variable and more uniform distribution with joint strength.

Increases in strength were attributed to the higher degree of surface roughness that increases the surface area of contact for the adhesive system enhancing the mechanical interlock of the adhesive with the aluminium surface. The mode of failure, adhesive or cohesive was determined by visual examination after testing to help test this hypothesis. The results were
clear cut with no mixed failure and it was seen that each and every one of the FES samples failed cohesively in comparison to the solvent wiped samples that all failed adhesively.

Without the etching process the solvent wipe pre-treatment has inherent variability with the resulting joint strengths and with minimal surface roughness the main process of adhesion is due to the chemical interactions of the epoxy material with the adherend surface. Any slight changes in the surface chemistry (whether oxide or contaminant) or variability in the surface morphology could result in a marked change in the surface area of contact of the adhesive with the metal surface (albeit localised) and will result in changes in the related joint strength.

![Figure 2.14](image) Deterioration in joint strength with different lengths of exposure to marine conditions

To ensure that the salt water spray environment is similar to full immersion of the joints in salt water, samples were constructed for both pre-treatment types and exposed (unloaded) to environments of constant temperature salt water spray and constant temperature salt water
immersion. The tensile strength of each of the samples was tested after exposure (Figure 2.14) and no significant change in strength can be seen between the two different environments, for each pre-treatment type. This ensures that data obtained may significantly relate to joints that were used in marine service located either below or above the water line.

The variability in adhesion strength for each pre-treatment is more strongly highlighted with examination of results for samples that have been exposed to the marine salt water spray (Figure 2.14). Samples that were pre-treated using the Optimised FES process sustained their initial joint strength over 28 days exposure to salt water spray, and showed little variability with strengths over time. In comparison, solvent wiped samples show a clear deterioration in joint strength even after 10 days exposure and after 21 days joint strengths were 50% of the strength of unexposed samples.

The scatter in data obtained for the solvent wiped samples is quite wide as evidenced by the range of adhesive strengths obtained from multiple samples tested after 10 days immersion. The deterioration in joint strength was attributed to the penetration of water between the metal surface and adhesive layer, helping the initiation of a crack along the interface. It appears that degradation occurs due to a combination of swelling of the adhesive at the joint edge which forces apart the metal surfaces initiating a crack [18], and water ingress into the joint edge that enables a desorption of the adhesive from the adherend surface. The poor interfacial strength is further highlighted by the fact that all of the solvent wiped samples failed adhesively along the interface while the FES samples failed cohesively through the centre of the adhesive layer.
2.5.3 Determination of fatigue strength of Al 5083 / Araldite 2015 adhesive joints before and after exposure to marine conditions

Solvent wiped joints were subjected to cyclical fatigue loads of varying magnitudes at a rate of 0.92Hz and the number of cycles to failure was plotted against the peak stress on the joint. ‘Dry’ joints were compared with joints that were exposed to salt water spray (Figure 2.15).

**Figure 2.15** S-N curve for solvent wipe pre-treated Al 5083 / Araldite 2015 adhesive joints.
Initially joint failure occurred at much lower loads in fatigue than was seen for the static tests (Figure 2.14). Although an expected result, this observation reinforces the importance of studying the cyclical application of loads when evaluating an adhesive system’s suitability for engineering designs.

The most interesting factor with the results is the extent of degradation in joint strength that occurred with the fatigue of adhesive joints exposed to salt water spray. A significant loss in fatigue strength was seen for the solvent wiped samples upon exposure to the wet salt spray conditions, to the extent that dry joints (i.e. those that did not experience the salt spray) survived up to 50 times longer than the wet joints under the same fatigue loads. For example, it was seen that for the application of a cyclical load of 3MPa, the solvent wipe joints lasted less than 5 minutes when exposed to salt water spray, whereas in dry conditions and for the same load, similarly constructed joints lasted several hours. This effect cannot be explained simply by the exposure to salt water alone, as joint strengths were seen to be relatively unchanged for static samples for up to 7 days exposure to salt water spray (Figure 2.14). It is the combination of fatigue loads in salt water spray that leads to rapid attack.

Upon the fatigue loading of adhesive joints there is a generation of micro cracks within the adhesive matrix [29, 30]. These cracks likely allow for the accelerated ingress of water into the adhesive joint further accentuating the crack growth and oxide breakdown that was seen with the static tests. Under this mechanism, salt water was able to more readily penetrate directly between the adhesive and aluminium metal, resulting in further oxide attack and premature adhesive failure at the relatively weak interface in all test cases.

The FES treated samples were found to be much stronger in fatigue. Dry tests were conducted on FES samples with applied loads up to 4.3 MPa and no failure was seen even
after 3.45 million cycles. The samples were removed from the Octopus and static tensile tests were conducted at this point to try to ascertain the extent of strength loss that the samples had received from the fatigue process. These results may be seen in Figure 2.16). No significant loss in the adhesive joint strength was seen for the application of fatigue stresses up to 3.5MPa. The single point that showed a clear drop in tensile strength was for an applied stress of 4.3MPa, and corresponded to an approximate 13% strength loss when compared to the tensile stress of non-fatigued samples.

Figure 2.16) Tensile strength of samples after being fatigued for 3.45 million cycles at different fatigue stresses.

For similar sized loads on solvent wipe samples in dry conditions, adhesive failure occurred within the joint even before as little as 1000 cycles (Figure 2.15) and highlights the vast
improvements in fatigue strength that may be achieved with the use of appropriate etching pre-treatments.

The FES joints also fared much better than the solvent wiped joints after exposure to marine conditions. So much so, that for the application of low stresses of 3 MPa or less with salt water spray, failure actually occurred through the metal strip at 500,000 or more cycles. This was also seen for the application of several higher loads, for example with an applied lap-shear stress to the joint of 6.1MPa the Al 5083 strip failed at 53,000 cycles and may have been due to an internal weakness within the aluminium adherend substrate.

![Figure 2.17) S-N Fatigue curve of FES pre-treated Al 5083 / Araldite 2015 adhesive joints](image)
In fact it was difficult (within the boundaries which the Octopus works) to achieve a failure through the FES pre-treated samples at all. Even so, from the results obtained it was seen that the FES pre-treated samples survived up to 4 orders of magnitude longer than the solvent wipe joints after exposure to salt water spray. For example, with an applied cyclical load of 3MPa the solvent wipe pre-treated joints failed at around 200 cycles (Figure 2.15), however FES pre-treated joints failed at around 2 million cycles (Figure 2.17). Each of the FES pre-treated samples that did fail broke cohesively through the adhesive bondline, and again the enhanced strength of the FES joints was attributed to an improved degree of mechanical interlock between the adhesive and the adherend surface.

In determining the 10 million cycle fatigue strength of the adhesive joints it was found that the solvent wipe joints failed well before this time frame was reached, such that the 10 million cycle fatigue strength would be of such a small load, that it would be of limited practical use for engineering design. The dry FES joints could not be stressed to a high enough degree to instigate failure (within the boundaries of the Octopus system) however it was found that there was no significant strength loss in the joint after an application of approximately 3.5MPa for 3.45 million cycles. Obtaining this value for the wet FES samples was also seen to be problematic, seeing that many of the aluminium samples failed through the metal itself. However, by extrapolating the S-N curve (Figure 2.17) the 10 million cycle fatigue stress for the wet FES joints may be estimated to be approximately 1.3MPa.
2.6 Conclusions

Static tensile testing and tensile fatigue testing of Al 5083 Araldite 2015 adhesive joints was undertaken with two different adhesive pre-treatments with and without exposure to marine environments.

It was found that solvent-wiped joints had considerably lower joint strengths to Optimised FES joints in both static tensile testing and fatigue. As well as this, solvent wiped joints showed a much higher variability within recorded joint strengths when compared to FES treated samples. These results were attributed to the enhancement of the adherend / adhesive interface during the FES pre-treatment process where the acid etching increases the surface roughness (and resulting surface area) and hence improves the mechanical interlock of the adhesive with the adherend.

Solvent wiped joints had an average dry tensile strength of 10.3 +/- 1.3 MPa whereas FES pre-treated joints showed strengths in the order of 16.2 +/- 0.3 MPa. The tensile strength of solvent wiped joints showed a steady decrease with exposure to salt water spray to the extent that after 21 days exposure, joint strengths had dropped by 50% to the unexposed samples. The effect of this was attributed to the ingress of water into the adhesive resulting in both a swelling of the adhesive layer generating a crack at the joint edge and water ingress into the joint edge that enables a desorption of the adhesive from the adherend surface.

In comparison, the FES samples showed no loss in joint strength up to 28 days exposure to salt water spray. The difference in joint performance between the two pre-treatments was again attributed to the degree of surface roughness of the FES samples enabling a greater
degree of mechanical interlock between the adhesive and substrate, as well as limiting the extent that water can wick between the adhesive and adherend surfaces.

Solvent wiped joints that were tested in fatigue showed a marked decrease in strength when exposed to marine conditions. It was shown that for the same applied fatigue loads, joints that were tested ‘dry’ lasted approximately 50 times longer than joints that were exposed to a salt water spray. This dramatic change was somewhat uniform across the whole S-N curve (even for short exposure times less than 1 day) and this accelerated decay of joint strength was attributed to the generation of micro-cracks, and subsequent crack growth at the adhesive and adherend surfaces that can occur during the fatigue process [29, 30]. Such crack generation could lead to a faster ingress of water into the joint along the adhesive/adherend interface, further accelerating the breakdown mechanisms seen with the static tests, resulting in adhesive failure for all tested samples.

FES pre-treated joints were found to be considerably stronger than the solvent wiped joints, so much so that no failure was seen after exposure to an applied stress of 4.3MPa for 3.45 million fatigue cycles when tested in ‘dry’ conditions. When tested wet, many of the samples failed through the Aluminium 5083 adherend and samples that failed at the adhesive lasted greater than 10,000 times longer than samples that were solvent wipe pre-treated. The Optimised FES samples all failed cohesively and the improved joint strength of the these samples was attributed to a combination of improved mechanical interlock between the adhesive and adherend surfaces as well as stronger and more corrosion resistant oxides developed on the adherend surface during the pre-treatment process [28].

The 10 million cycle fatigue strength was estimated to be approximately 1.3 MPa for the wet FES samples.
2.7 Appendix

Specifications and Design

Mechanics

Electric Motor: Crompton Parkinson MA 7244A-K 1440 rpm 3/4hp electric motor

Gear Box: Charles and Hunting R5 Reducer 49:1 ratio Speed Reducing Gear Box interfacing

Sprocket/Chain Ratio of 45 : 24 teeth

Camshaft: Standard 8 cam petrol engine camshaft.

Dampeners: 8 x Festo DSNU 25-25-P-A 10 Bar air cylinders that have been primed with thin hydraulic oil

Electrics

Heater: Large submersible coil heater (1200 W)

Temperature sensor: LM335
Load Cell

Make and Model: Xtran S1 (sealed/ splash proof)
Rated Capacity: 3.5kN (max) in compression and tension
Excitation: Recommended 10V, Maximum 20V
Rated Output (nominal): 3mV / V_{excitation}
Safe Overload: 150%

The load cell has an internal Wheatstone Bridge electrical design, and as such has a linear and stable response up to 150% of the rated capacity. If the excitation is at 10V, then the output will be in the range of +/- 30mV, which relates to a load of +/- 3.5kN respectively. Connector ends were constructed to fit into the existing test specimen sites of the Octopus. They utilized a screw thread and lock nut to ensure a good grip on the load cell body and consistent results between tests.

DAQ card

The DAQ card that was used to interface with the Octopus was a National Instruments Lab PC card. It has 8 analog input channels and 24 (3 x 8) bidirectional digital input/output channels, Ports PA, PB and PC. Because of the wide variety of components within the system the design of the data lines had to be chosen quite carefully. The data lines were allocated in the following manner:
• The first eight analog inputs were for embedded sensors. These analog channels can be used in either Referenced Single Ended mode (RSE), Non-Referenced Single Ended mode (NRSE) or Differential mode which is chosen as a pin default allocated on the board and then selected in the NiDAQ setup program.

• The first set of 8 digital lines (Port PA) was being used to take in the state of the switches that monitor when a sample has failed.

• The second set of 8 digital lines (Port PB) was being used to control the operation of the heater. A signal was sent to turn the heater on when the temperature of the water dropped too low. When the water temperature got too high, the heater was turned off through the same data line.

• The third set of 8 digital lines (Port PC) was being used to send the water temperature into the computer.

The pin assignments for the Lab PC card may be seen on the following page.
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<thead>
<tr>
<th>Pin</th>
<th>Signal Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-8</td>
<td>ACH0 through ACH7</td>
<td>Analog input Channels 0 through 7 (single-ended).</td>
</tr>
<tr>
<td>9</td>
<td>AISENSE/AIGND</td>
<td>Analog input ground in RSE mode, AISENSE in NRSE mode. Bi-directional.</td>
</tr>
<tr>
<td>10</td>
<td>DAC0 OUT</td>
<td>Voltage output signal for analog output Channel 0.</td>
</tr>
<tr>
<td>11</td>
<td>AGND</td>
<td>Analog ground. Analog output ground for analog output mode. Analog input ground for DEF or NRSE mode. Bi-directional.</td>
</tr>
<tr>
<td>12</td>
<td>DAC1 OUT</td>
<td>Voltage output signal for analog output Channel 1.</td>
</tr>
<tr>
<td>13</td>
<td>DGND</td>
<td>Digital ground. Output.</td>
</tr>
<tr>
<td>14-21</td>
<td>PA0 through PA7</td>
<td>Bidirectional data lines for Port A. PA7 is the MSB, PA0 the LSB.</td>
</tr>
<tr>
<td>22-29</td>
<td>PB0 through PB7</td>
<td>Bidirectional data lines for Port B. PB7 is the MSB, PB0 the LSB.</td>
</tr>
<tr>
<td>30-37</td>
<td>PC0 through PC7</td>
<td>Bidirectional data lines for Port C. PC7 is the MSB, PC0 the LSB.</td>
</tr>
<tr>
<td>38</td>
<td>EXTTRIG</td>
<td>External control signal to start a timed conversion sequence. Input.</td>
</tr>
<tr>
<td>39</td>
<td>EXUPDATE*</td>
<td>External control signal to update DAC outputs. Input.</td>
</tr>
<tr>
<td>40</td>
<td>EXTCONV*</td>
<td>External control signal to trigger A/D conversions. Bi-directional.</td>
</tr>
<tr>
<td>41</td>
<td>OUTB0</td>
<td>Counter B0 output.</td>
</tr>
<tr>
<td>42</td>
<td>GATB0</td>
<td>Counter B0 gate. Input.</td>
</tr>
<tr>
<td>43</td>
<td>OUTB1</td>
<td>Counter B1 output or pulled high (selectable).</td>
</tr>
<tr>
<td>44</td>
<td>GATB1</td>
<td>Counter B1 gate. Input.</td>
</tr>
<tr>
<td>45</td>
<td>CCLKB1</td>
<td>Counter B1 clock (selectable). Input.</td>
</tr>
<tr>
<td>46</td>
<td>OUTB2</td>
<td>Counter B2 output.</td>
</tr>
<tr>
<td>47</td>
<td>GATB2</td>
<td>Counter B2 gate. Input.</td>
</tr>
<tr>
<td>48</td>
<td>CLKB2</td>
<td>Counter B2 clock. Input.</td>
</tr>
<tr>
<td>49</td>
<td>+5V</td>
<td>+5 V out, 1 A maximum. Output.</td>
</tr>
<tr>
<td>50</td>
<td>DGND</td>
<td>Digital ground. Output.</td>
</tr>
</tbody>
</table>

*Indicates that the signal is active low.
2.8 References


Chapter 3

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3.1 Introduction

Various studies have been conducted on the fatigue life of araldite epoxies used as adhesives in aluminium joints. Information into adhesive failure is usually obtained after the test has been completed using surface analysis techniques that can identify the surface roughness, what type of failure has occurred (interfacial or cohesive) and what type of oxides are present at the time of failure [1-9]. As such, little is known of the processes of joint degradation contributing to fatigue failure, especially when the joint has been subjected to harsh marine conditions.

When subjected to fatigue cycling, small micro cracks begin to appear within the joint which grow and ultimately lead to failure [10-20]. One effect of these cracks is they tend to allow more water to pass into the joint through capillary action which can reduce the joint strength by not only plasticising the epoxy (hence reducing the epoxy strength) but also altering the oxide at the adhesive interface to a weaker and less mechanically stable oxide layer. As can be expected, these processes can be accelerated within the humid and salty conditions that may be experienced in marine environments.

Normally the rate of water ingress into a joint (J) can be predicted using the following standard diffusion equation,

\[ J = \frac{D(C^m_1 - C^m_2)}{l} \]

where:

\[ C^m_1, C^m_2 = \text{the concentration of water at different depths within the adhesive,} \]
\[ l = \text{the linear distance between these two points and,} \]
\[ D, \text{the time dependant diffusion co-efficient can be determined experimentally.} \]
However, during fatigue, cracks tend to grow from internal defects such as voids and the crack's length and position within the joint at any point in time can be somewhat random and almost impossible to predict. Alongside this, the extent of water ingress into the joint through capillary action can be further accelerated as the crack grows, so the simple diffusion equation above cannot be used to accurately predict the ingress of water into a joint under fatigue cycling.

One of the key modes of adhesive joint breakdown is due to the conversion of adherend oxides to less strong and more unstable forms. It has been shown that upon hydration of the surface oxide (Al₂O₃) on aluminium adherends a conversion to the lower strength boehmite (AlOOH) and then trihydroxide (Al(OH)₃) forms occurs [6, 21, 22] leading to a dramatically reduced joint strength. Davis et al has shown that there may be a critical relative humidity (at 65%) that leads to joint degradation through these processes [23]. Abel et al [14] confirmed this phenomenon and their work implied the existence of a critical humidity somewhere between 55 and 80%. If this value can be confirmed (and determined accurately), then significant advancement may be made into the incorporation and designing of adhesive joints for marine environments. The effect of different surface pre-treatments and the incorporation of water inhibitors into the adhesive matrix after marine exposure may be better understood, and adhesive systems may be better tailored to produce stronger and more stable joints to withstand the aggressive nature of marine environments.

One solution to measuring the water content in adhesive joints is to embed humidity sensors within the joint to obtain some form of continual feedback on its condition during fatigue service. Such sensors could be used to obtain useful information on the ingress of
water into the joint during service, allowing the prediction of a %water content that could initiate catastrophic failure. The same sensors would give a better understanding of the failure of adhesive joints in fatigue and could even potentially act as an early warning system for impending failure.

There are certain design criteria that are necessary for the sensor to behave effectively within an adhesive joint. Apart from reliably sensing moisture content, the sensor must not harm the joint’s strength in any way. As such, the sensor needs to be small enough so that when embedded, the joint thickness is not increased nor the integrity of the joint’s strength altered.

Various studies have been conducted into novel materials that can be used to detect humidity. Some studies have concentrated upon ceramic materials where the change in dielectric properties of the system were used to detect the ingress of water [24-28]. Other systems incorporate humidity sensing polymers [29-34] where either dielectric, capacitive or resistance based parameters have been found to change with water ingress. Each system in its own right measures the change in humidity (with consideration taken to hysteresis, linearity and reproducibility) but problems with overall size and processability of the sensing material can restrict applications within adhesive joints.

Ceramic humidity sensors based on ZnO, TiO$_2$ and SiO$_2$ films have been developed that show highly sensitive, reversible and linear responses [24-26]. Processability of such designs however can be somewhat tedious requiring high temperatures and a multi layered construction to the sensor substrate. The use of sol-gels has improved this processability.
but most designs still require a glass or quartz crystal substrate which can restrict the degree of miniaturisation.

Much work has also been undertaken into the humidity sensing properties of conducting polymers. It is known that water increases the electrical conductivity of polyaniline through an increase in the interchain electron transfers [39-42] and / or by increasing the mobility of dopant ions [43]. Conductivity increases of several orders in magnitude in the presence of water have been recorded with linear and reversible responses [42-44]. Ogura et.al. [43] have shown that polyaniline/polyvinyl alcohol (PAn/PVA) polymer blends can act as a suitable sensing material for humidity. The advantage of this blend in particular is the ease that it may be processed into a liquid that may be cast as a thin film [45].

Jain et al [42] have also reported linear responses of PAn and styrene butyl acrylate (SBA) copolymer blends over the range 10 – 95% RH. Presumably, the linear response was due solely to the PAn since the SBA matrix has a low affinity for water. The film resistances were in the tens of MΩ range and could be an attractive alternative to the PAn / PVA blends. A similar conducting polymer blend Poly aniline / Poly (butyl acrylate -co- vinyl acetate) (PAn/P(BuA-co-VAc)) has been found to have high strength and high conductivity [46] and can also be cast as thin films.

Polymer based thin film humidity sensors have the advantage that the high processability of the material allows for a much simpler and hence smaller sensor design. The ease of processing gives a low cost sensor, whilst the small size and good mechanical properties give a robust flexible sensor that is able to be used in applications where dynamic stresses and strains are encountered. With these advantages in mind, the aim of this section of work was to design, fabricate and evaluate small humidity sensors using processable polyaniline blends as the sensing medium.
3.2 Experimental

3.2.1 Polymer Blends

A processable PAn/PVA blend prepared as described previously [45] was made to facilitate our sensor substrate. In this work, aniline was chemically polymerised in the presence of PVA ($M_w = 89000-98000$) and HCl (to be used as the dopant) with ammonium persulphate as an oxidant. Various blends were prepared with PAn concentrations of approximately 5, 10, 20, 30, 40, 50 and 60% by weight. The polymer structures are shown in Scheme 1.

![Scheme 1](image)

- **Scheme 1**
  - (I) poly vinyl alcohol
  - (II) poly(butyl acrylate -co- vinyl acetate)
  - (III) polyaniline (emeraldine salt)
Another processable polymer was also made by the chemical polymerisation of aniline monomer with ammonium persulphate in an emulsion of poly (butyl acrylate-co-vinyl acetate) P(BuA-co-VAc) copolymer (40 w/w%) [47]. The P(BuA-co-VAc) copolymer (Scheme 1) was synthesised according to previously reported methods [48, 49] and the polymerisation took place with camphor sulphonic acid (HCSA) being used as the dopant. The product was purified with a de-ionised water wash prior to centrifuging and the resulting solid was dried to a powder. Two PAn/ P(BuA-co-VAc) blends were developed and the PAn percentages were determined from elemental analysis to be 15 and 30 w/w%. The resulting solid was redissolved in CH₂Cl₂ solvent at 1-2% by weight to create a dark green liquid which could be readily stored in an easily processable form.

### 3.2.2 Selection of the best humidity sensing polymer

Films of each of the polymer blends were separately cast or spin coated across printed electrodes to examine the humidity sensing performance of the polymer in an attempt to eliminate variables such as polymer film thickness. This process was used to cast a film of uniform thickness across the electrode for selection of the best conducting polymer blend for sensing humidity, that would be later incorporated into the final miniaturised design.

Two electrode types were investigated each consisting of either silver or carbon printed electrode patterns on PET (Polyethylene terephthalate) (Figure 3.1). A 30μL drop of each polymer was spin coated onto the silver patterned electrodes at a speed of 2500 rpm and an acceleration of 20,000 rpm/s for 30 seconds.

For the carbon printed electrodes, two different masks were used to generate a rectangular well (7mm x 4mm wide) where a 30μL drop of polymer may be placed to bridge the
conducting electrodes before for air drying. Each mask was 45 and 250µm thickness respectively and was removed once the polymer was completely dry.

Figure 3.1) Photograph of printed PET electrodes before coating with conducting polymer.

3.2.3 Testing and Calibration of the Sensors

An Agilent 34401A Multimeter was used to measure resistances across the sensors when placed in chambers of varying humidities. For extremely high resistances, a voltage divider circuit was used to measure values, albeit with increased error. The relative humidities (RH) in each chamber were created using saturated salt solutions of LiCl, MgCl₂, Ca(NO₃)₂, NaN₃, and Distilled water which correspond to relative humidities of 11, 33, 54, 76 and 95%, respectively[50]. A chamber containing silica gel was also used and was found to give a 3% RH after checking with a commercial humidity sensor. These data have been represented in Table 3.1. The sensor resistance for each humidity level was measured after equilibration in each of the humidity chambers to produce an overall bulk resistance calibration curve for each sensor.
Saturated Salt Solution | Relative Humidity (RH)
-------------------------|------------------
Silica Gel               | 3% RH            
LiCl                     | 11% RH           
MgCl\(_2\)              | 33% RH           
Ca(NO\(_3\))\(_2\)       | 51% RH           
NaNO\(_3\)              | 74% RH           
Distilled H\(_2\)O       | 95% RH           

Table 3.1) Contents of various conical flasks and the related relative humidities (RH) associated with each chamber

The resistance reading at either 74 or 95%RH for each sensor was set as a baseline and the % change in resistance was then calculated for each RH and second calibration curve produced. In particular, the sensor response was assessed for linearity, sensitivity, bulk resistance, stability, lifetime and response time.

3.2.4 Sensor substrate construction

The final sensor substrate design incorporated fine insulated platinum wires that were dipped in the polymer blend being tested. Platinum was used because of its corrosion resistance (necessary when in contact with the acidic conducting form of PAn) and the insulation is necessary to eliminate the risk of short circuits with the aluminium metal when placed within the adhesive joint. It was hoped that a better adhesion with the conducting
electrodes may be achieved if they were totally encapsulated within the sensing polymer.

The process for sensor substrate construction can be seen in Figure 3.2.

The sensor electrodes were made from 125μm platinum wire that was insulated with a 14μm polyester coating, as supplied from Goodfellow (UK). A 7cm section of wire was cut, then folded in half and its ends were twitched together to create two parallel wire electrodes connected at one end by a loop of bare platinum. The insulation coating from both ends and the loop section was removed by scorching with a hot Bunsen burner flame. The parallel wire sections were glued together in a flat orientation with cross-linked polyvinyl alcohol (PVA) and left to dry before the platinum wire loop was cut. The final substrate was checked to ensure that its thickness was no more than 150μm and the spacing...
between electrode ends was less than 500μm. A typical finished sensor substrate can be seen in Figure 3.3.

![Figure 3.3](image)

**Figure 3.3** Finished sensor substrate ready for coating (a), and as seen at higher magnification (b) showing bared insulation and gap of approx. 250μm. Scale bar shown is 1 mm in length.

The substrate was then dip-coated with the conducting polymer that was to be used as the sensing material and allowed to dry completely within a desiccator. With this design the width of the conducting electrodes was the main limiting factor to the overall size. This was kept to a minimum by aligning the electrodes under a microscope ensuring that no short circuits were present when tested with a standard multimeter. The width was thus kept to around 500μm or less before the process of polymer dip-coating to ensure that the sensor was small enough not to harm the joint strength in any way. The polymer coating thickness was examined under a microscope and was estimated to be 25μm or less for each of the sensors produced. This enabled the thickness directly between wire electrodes (bridging thickness) to be from 50 – 80 μm.
To ensure reliable connections for monitoring the resistance across the platinum wire substrates, the Pt wires were soldered into the female ends of a 2-pin IC socket to act as a form of electrical 'plug'. A photo of the completed sensor may be seen in Figure 3.5.

Another separate 8-pin IC socket was soldered to a series of wires that passed snugly through a rubber stopper and could be easily connected to a multi-meter device for sensor monitoring. The sensors were 'plugged' into the 8-pin connector and the stopper placed in
a conical flask in such a way that 4 sensors could have their resistances monitored whilst being exposed to the enclosed environment within the conical flask chamber (Figure 3.6).

![Diagram of testing chamber setup showing multiple sensors in place ready for testing](image)

**Figure 3.6** Schematic of testing chamber setup showing multiple sensors in place ready for testing

### 3.2.5 Humidity Stability within Araldite 2015 environment

Once the sensors have been able to be calibrated and a working sensor was produced in air it was necessary to confirm that the sensor would be stable within the embedded epoxy. Sensor stability was examined once embedded within Araldite 2015 to ensure that the epoxy would not irrevocably harm the performance of the sensor in any way. Calibrated sensors were embedded within Araldite 2015 and the response to RH was re-examined to confirm any change to the overall response.
3.2.6 Sensor Conversion from Relative Humidity Determination to Mass Uptake of Water

As the sensors were planned to be used embedded within an Araldite 2015 epoxy it was necessary to convert the Resistance vs Relative Humidity calibration curves to a more meaningful measurement for an embedded system of Resistance vs Weight % Water. As such, films were cast of both the PAN sensing material used in the final sensor design as well as Araldite 2015 used for the construction of adhesive joints. These films were allowed to cure and placed within chambers of the same saturated salt solutions of Table 3.1 (being held over the air gap above the salt water) to take up moisture. The films were quickly removed from the chambers and weighed using an accurate balance (accurate to +/- 10μg) before being returned to the humidity chambers. Before weighing, care was taken to remove any water that had condensed on the outside surface of the films by patting dry with a Kimwipes® tissue. Masses were registered for each relative humidity over time until an equilibrium mass was reached for each film. A conversion curve was generated for both the sensing material and the Araldite 2015 adhesive of Relative Humidity vs Weight % water so that an accurate assessment may be made of the Weight % of water in the adhesive joints for each resistive sensor reading.
3.3 Results and Discussion

3.3.1 Selection of the best humidity sensing polymer

Initially humidity sensitive polymer films were cast across flat PET polymer sheets that had been printed with either carbon black or silver electrodes (Figure 3.1). It was hoped that a standard response for each of the investigated processable PAN based polymers may be easily found, allowing the best polymer for sensing humidity to be incorporated in the final sensor design.

![Figure 3.7](image.png)

*Figure 3.7* a) Typical photos of polymer coated carbon printed electrodes, b) Close up of 10 w/w% PAN PVA coating on PET printed electrode. Note the peeling of the polymer from the PET surface.
Both spin coating (at various speeds) and drop casting of polymer films was investigated but the results showed a huge degree of variance and error both within the same sensor at different times and different sensors cast from the same polymer blend. This variance was attributed to a lack of adhesion of the PAN polymers to the PET surface resulting in a peeling of the polymer film from the surface of the PET thus affecting the contact with electrodes and overall sensor resistance. The poor adhesion was verified by close examination of the polymer films with a microscope. A typical film may be seen in Figure 3.7 b.

It was deemed necessary to test the PAN sensor materials utilising the final sensor substrate design for embedding within the joints. This was achieved for two reasons:

a) To ensure that any resistive response measured was solely due to chemical polymer interactions with water (or other species) and not due to a failure of the substrate itself

b) To ensure that the verification and subsequent calibration used to choose the polymer blend will not change when ‘wired’ to a different substrate

3.3.2 PAN PVA Sensors

An approximately linear logarithmic calibration curve was obtained for PAN/PVA blends having low PAN content (< 10%) and showed a very high sensitivity to RH between 30% and 95% (Figure 3.8). The sensor showed little response below 30% RH. As with many previous reports [39-41, 51-53], the resistance of the blend decreased as the humidity level increased (above 30% RH). Similarly, the basis of this response has been attributed to a combination of two factors: easier interchain electron hopping along water molecules
between chains with increasing levels of water ingress [39-41], as well as a delocalisation of the dopant ions with water ingress [43], allowing for easier intra-chain electron transfers. Unfortunately, the bulk resistances of these sensors were found to be very high (10 - 10,000 MΩ) so that they were virtually unusable for practical applications.

![Graph](image)

**Figure 3.8** Typical calibration curve of bulk resistances for 5% PAn/PVA polymer blend

As expected, for blends having higher PAn content (10% or greater) bulk resistances were found to be considerably lower. Unfortunately, the sensitivity of the sensor was significantly compromised (Figure 3.9 and 3.10), showing little response to changes in humidity below 75% RH.
Figure 3.9) Typical calibration curve of bulk resistances for 10% PAn/PVA polymer blends

Figure 3.10) Typical calibration curve of bulk resistances for 20% PAn/PVA polymer blends
At 20 (or greater) w/w% PAn the shape of the calibration curve was also reversed with resistances increasing at high humidity (Figure 3.10). These observations suggest some cross-over in dominance of two competing responses between each of the two blend constituents: PAn decreasing overall resistance at higher humidities, and PVA increasing resistance at higher humidities. The curve seen for 10 w/w% PAn is attributed to roughly equal combination of these two competing responses, and although the resistances are much lower, the sensitivities were still compromised.

One possible explanation is that at high concentrations of PAn in the blend, the conducting polymer tends to form aggregates of PAn in a PVA matrix. The PVA in the blend would swell in the presence of water separating these conducting domains and causing a resistance increase. This effect outweighed the drop in resistance that can be expected from PAn alone.

To examine this theory, the blend was cast as a thin film and optical micrographs were produced. The presence of aggregates is observed at PAn% concentrations above 20% by weight (Figure 3.11) which coincides with the change in shape of the calibration curves.

**Figure 3.11** Optical microscope images of (a) 5 w/w% PAn/PVA and (b) 20 w/w% PAn/PVA thin films cast on glass slide. Scale bar shown is 100μm in length.
UV-visible spectrum were also examined at both low and high humidities and the thin films showed little or no conformational or doping change with water ingress (Figure 3.12).

In summary, the humidity response of the PAN/PVA blends can be separated into two types. In the ‘miscible’ blends (at least with PAN phases < 1µm) the behaviour is dominated by the PAN response so that the resistance decreases rapidly with increasing humidity. However, at higher PAN contents (> 20 %) the blends become immiscible and the resistance change with increasing humidity is much smaller. For the immiscible blends, an increase in humidity causes swelling of the PVA matrix and a resultant decrease in conductivity between the separated PAN domains. This process causes an increase in the overall resistance that negates the lower resistance within the individual PAN domains.

The very high resistances of the low w/w% PAN blends at low RH mean that they are of limited practical use. Blends with higher w/w% PAN had little response over much of the RH range and as such, other sensing media were investigated.
Figure 3.12) UV-visible spectrums of (a) 5 and (b) 20 w/w% PAn/PVA films after equilibration in a desiccator and at 95% relative humidity
3.3.3 PAn/ P(BuA-co-VAc) sensors

To analyse the ability of the PAn P(BuA-co-VAc) blends as possible humidity sensing materials, eight sensors were constructed from each blend and the resistance of each was measured over time with step exposure from dry (3%RH) to ‘wet’ conditions (11 to 95% RH) and back for each RH environment.

Bulk Resistance

The final spacing of the conducting electrodes was found to be the main determining factor in the resulting sensor resistance, having a major impact on the bridging thickness (the width of the conducting pathway) seen in Figure 3.4. With electrodes that were less than 1mm apart, each blend gave sensors that showed bulk resistance measurements (at 3% RH) less than 10 kΩ, making it an easily measurable response.

Linearity/ Sensitivity

A standard calibration curve for the 30 w/w% polymer was found to be approximately linear and showed high sensitivity with over a 100% resistance change. In contrast, the 15 w/w% polymer blend had an exponential response and showed even higher sensitivities with an 800% resistance change over the entire 95% change in RH. This blend was especially sensitive for low RH changes. The % change in resistance calibration curves were repeated multiple times for each blend and the average values can be seen in Figure 3.13.
Figure 3.13) % Change in Resistance calibration curves for (a) 15 w/w% (b) and 30 w/w% PAN/P(BuA-co-VAc) sensors
**Response Time**

The rate of water ingress into or out of the polymer was seen to be dependant on the differential between the current concentration of water in the sensor and the concentration of water in the surrounding atmosphere. As could be expected, the larger this differential, the longer the time needed to reach equilibrium in the sensor and the times required to reach equilibrium for humidifying stages were much faster than that for desiccating stages. It was seen for the largest differential (from 3 to 95% RH) it took approximately 2 to 3 hours to reach 90% of the equilibrium resistance on humidifying, whereas 24 hours was required to reach 90% of the equilibrium resistance on desiccating. Typical sensor response curves may be seen in Figure 3.14 for a step changes in RH.

a) **Resistances measured over time for 3% RH to 11% RH and back**
b) Resistance Change with transfer from 3% RH to 33% RH and back

![Graph showing resistance change over time for 3% RH to 33% RH and back.](image)

- **Bulk Resistance (Ohms)**
- **Time (hrs)**

- 3% RH
- 33% RH

c) Resistance Change over Time for 3% RH to 51% RH and back

![Graph showing resistance change over time for 3% RH to 51% RH and back.](image)

- **Bulk Resistance (Ohms)**
- **Time (hrs)**

- 3% RH
- 51% RH
Figure 3.14) Typical PAn P(BuA-co-VAc) sensor response curves for changes in RH between 3% and a) 11%RH b) 33% RH c) 51% RH d) 74% RH and e) 95% RH
In general, the sensors required several hours to equilibrate after a step change in RH. The response time could be reduced by producing thinner coatings over a substrate with a smaller gap between platinum wire electrodes, however these response times were deemed fast enough for the application of interest.

**Reversibility**

The sensors showed clearly defined reversible responses without hysteresis as seen in Figure 3.14. Time was needed to ensure that the equilibrium response was reached for each sensor during the desiccation stage however sensor responses reached their stable equilibrium resistance for each RH after cycling.

**Temperature Response**

The sensors have been found to be slightly responsive to temperature as shown by the calibration curve from temperature changes of 5 to 60°C in Figure 3.15. Similar resistance decreases have been reported for PAN with increases in temperature [54-56] and likewise have been attributed to an increased mobility and movement of conducting electrons or dopant ions.
Figure 3.15) Typical temperature calibration curves for four different 15 w/w% PAn/P(BuA-co-VAc) sensors

**Stability**

The response to RH was seen to be highly reversible without hysteresis though a continuous increase in resistance or 'drift' was seen for a constant RH over long periods of time. The drift was thought to be mainly due to an over-oxidation of the sensing polymer in air. This effect was examined by comparing the response of one sensor in the standard silica gel chamber with that of another in a modified silica gel chamber that allows the atmosphere to be purged with nitrogen gas. Sensors were allowed to equilibrate over multiple days prior to initiation of the test. Mid-term responses of over more than 11 days were determined (Figure 3.16) with a substantial decrease in the drift seen for the 'nitrogen
purged' sensor. The dip in the response seen at around 120 hrs was attributed to an increase in the ambient temperature during the recording of these measurements and was clearly shown with both sensors. It is expected that this drift may be eliminated with a suitable coating that could allow for the transport of water while blocking direct air contact to the polymer surface. Still, only a 20% change in the overall response was seen after 10 days with the sensor in air.

![Figure 3.16](image)

**Figure 3.16** Comparison of resistance changes (or 'drift') over time between two sensors in constant 3% RH seen in air and nitrogen purged atmospheres. The dashed lines have been provided to help guide the eye.

**Lifetime**

Sensors were tested over extended periods and were found to produce reliable and predictable responses to known humidities. The drift was still evident within these responses, but the magnitude of resistance change from one humidity level to the next was consistent. A typical long term- curve can be seen in Figure 3.17) where RHs were
oscillated between 3 and 11% RH, allowing for equilibration in response between each stage.

![Graph showing % change in resistance over time for 3% and 11% RH](image)

**Figure 3.17** Typical long term response of 30 w/w% PAN/P(BuA-co-VAc) sensors whilst oscillating relative humidity from 3 to 11%.

### 3.3.4 Sensor response inside Araldite 2015

PAN P(BuA-co-VAc) sensors were embedded inside the epoxy polymer Araldite 2015 (Huntsman) to ascertain the stability of the performance for use in measuring water content in epoxy composites and adhesives. Initially, it was discovered that a sudden, unrecoverable increase in resistance was recorded with the embedding of the PAN P(BuA-co-VAc) ES sensors (Figure 3.18). The pH of the two components of the Araldite 2015 adhesive was examined and it was found that the resin component had a pH at approximately 7 but the hardener component had a pH around 10 or 11. The increase in
resistance was thus attributed to a de-doping of the conducting polymer PAN emeraldine salt (ES), to the non conducting emeraldine base (EB) form in the presence of the alkaline, amine rich hardener component of the epoxy blend.

Figure 3.18) Typical response of a PAN P(BuA-co-VAc) sensor after embedding in Araldite 2015

To properly verify this de-doping process, further sensors were constructed and embedded inside Araldite 2015 and the surface was ground down after curing and dry polished to view a clear cross-section of the sensor substrate. An optical image of this cross-section was obtained (Figure 3.19).
Figure 3.19) Typical image of a PAn P(BuA-co-VAc) ES sensor quarter section after embedding in Araldite 2015

Figure 3.20) Schematic of the cross-section of a PAn P(BuA-co-VAc) ES sensor a) before and b) after embedding in Araldite 2015

From these images it was found that the outside surface in direct contact with the Araldite 2015 showed a clear colour change and had indeed been converted to the blue, fully deprotonated EB form of PAn up to a depth of approximately 15μm, which was further
verified by examination and comparison of a map of Raman spectra across the surface (Figure 3.21).

Raman bands observed at 1166 cm\(^{-1}\) were attributed to the bending of the C-H bonds in the benzoid ring of the PAN structure [57] and bands at 1340 cm\(^{-1}\) and 1513 cm\(^{-1}\) were attributed to C-N\(^+\) stretching and N-H bending of the bipolaron structure, respectively [57, 58]. Thus, the spectra seen in Figure 3.21b) relate to the doped and conducting form of PAN ES.

When the sensor is in direct contact with the Araldite 2015 a shift in the peak at 1166 cm\(^{-1}\) to 1160 cm\(^{-1}\) was observed and this can be attributed to C-H bending of the quinoid ring of the EB structure [57]. This shift, combined with the peak at 1466 cm\(^{-1}\) (attributed to C=N stretching of the quinoid ring [57, 58] ) and the decrease in intensity at 1340 cm\(^{-1}\) and 1513 cm\(^{-1}\) confirms the presence of PAN EB along the edge of the sensor.

![Figure 3.21)](image-url) Typical Raman spectra seen across the sensor cross-section at a) the outside surface of the sensor in direct contact with Araldite 2015, and b) inner surfaces not in direct contact with Araldite 2015
A typical spectrum of the Araldite 2015 epoxy may also be seen in Figure 3.22, and from this it may be seen that the epoxy shows a high degree of fluorescence with very little peak definition. As such, it can be concluded that the spectra seen in Figure 3.21 has not been affected by percolation of the Araldite 2015 embedding media into the PAN based sensing material.

With the outside ES coating thicknesses greater than 40 μm, the polymer thickness directly between the conducting electrodes (or bridging thickness) tended to be around 80 μm or greater. Once embedded in Araldite 2015, it was seen that the outside layer was fully deprotonated to a depth of 15μm, which still left a 40 - 50 μm internal pathway of (at least
somewhat) conducting PAN ES material (Figure 3.20b). In essence, it was seen that these sensors showed a clear and definitive response to water, albeit of a much higher resistance.

Taking the depth of deprotonation into consideration it could be expected that the resistance of the system would be double after embedding within the Araldite 2015. With further examination of Figure 3.18, it can be seen that the resistance increases seen are to an even larger extent than this and take place over many days. It is believed that after the initial deprotonation that occurs during cure of the Araldite 2015 adhesive, an equilibrium between EB and ES polymer at the interface is being generated and that some of the ES polymer within the internal conducting pathway is being partially deprotonated causing an even greater increase in resistance. Even so, a seven-fold increase in resistance was seen after 10 days causing significant practical issues with interpretation of the sensor response.

There is a fundamental problem with the possibility of using these sensors in this capacity, in that any resistance change due to de-protonation will alter the calibration curve that is measured prior to embedding. Once the sensor has been embedded within the epoxy system and resides within an adhesive joint, it is impossible to find the new calibration curve for the system – especially if the sensor is to be placed in service on ocean-going vessels. Thus it was deemed necessary to find an appropriate protective coating for the sensors that would ensure that the overall calibration curve was not altered during the process of embedding within the adhesive joints.
3.3.4.1 Identification of a suitable protective barrier coating for the PAn sensors for use in the embedded epoxy Araldite 2015

Various polymer coatings were examined for their ability to provide protection to the PAn sensor after embedding within Araldite 2015. Poly Acrylic Acid (PAA), Cross-linked PAA, Silicone and Cross-linked PVA were investigated with varying success. Each of these polymers were chosen for their ability to be cast as thin films.

PAn P(BuA–co-VAc) sensors were made and a protective coating of each of the above materials was applied to the surface. The sensors were placed in a constant 3% RH environment and the resistance was allowed to equilibrate over 4 days, after which time, one of each of the sensors was embedded within the Araldite 2015. The % change in resistance results may be seen below in Figure 3.23. It was hoped that a suitable sensor coating would be found that could ensure a stable response after embedding within the epoxy.

Each of the coatings affected the sensor response in different ways. The PAA coatings showed an increase in resistance during desiccation which was presumably a PAn response to water. However, a wide variance with sensor response became evident with embedding in Araldite and as such PAA (either cross-linked or not) was deemed unsuitable as a possible barrier coating.

The PVA coated sensors actually showed a decrease in resistance with desiccation, which could possibly be explained with a similar argument to the high w/w% PAn PVA sensors that were developed within section 3.3.1. If, upon coating with PVA, a transition layer was formed at the barrier between the PAn and PVA consisting of a high w/w% PAn, then
removal of water from the sensing material would reduce swelling in the PVA bringing the concentrated conducting PAN particles together hence lowering the resistance. As such, with the PVA material causing a competing response with the PAN sensing material the sensitivity of the overall sensor system was compromised and as such cross-linked PVA was also deemed unsuitable as a barrier coating for the sensors.

![Graph showing stability of PAN P(BuA-co-VAc) sensors with various barrier coatings with and without embedding in Araldite.](image)

**Figure 3.23**) Stability of PAN P(BuA-co-VAc) sensors with various barrier coatings with and without embedding in Araldite.

The silicone used for the coating of the sensors was a high viscosity Silastic rubber sealant. The sensors that were coated with silicone showed very similar responses to the sensors embedded in epoxy and the control sensor coated and left dry in the desiccator. However, due to its high viscosity it was extremely hard to produce a uniform thin coating over the
sensor, and the use of this coating increased the sensor dimensions to an unacceptable level.
The lack of processability of the silicon coating was thus deemed problematic for its potential use as a coating material such that it would be hard to ensure both uniformity in size from one sensor to the next and it could not be ensured that the sensors may be small enough that later embedding within an adhesive joint would not harm the overall joint performance. It was thought that if the processability of the Silastic rubber could be improved then uniform thin films may be generated that would still allow water vapour to penetrate into the PAn sensing material. The problem with each of these approaches is that the membrane coating thickness is critical. It must be thick enough to fully restrict the deprotonating nature of the curing epoxy, however no so thick that the sensitivity and size are significantly affected. As such, another different media was investigated.

It was thought that if we were able to produce a processable PAn emeraldine base (EB) blend, then this could not be deprotonated any further when it came into contact with the Araldite 2015 and may be found useful as a protective barrier coating for the underlying PAn ES sensing blend during cure of the adhesive.

3.3.4.2 Development of a processable PAn/ P(BuA-co-VAc) EB polymer blend

The 15w/w% PAn processable PAn/ P(BuA-co-VAc) blend sensing material was used in the development of a protective coating for the humidity sensors as it was expected that a better compatibility between the ES and EB layers would result ensuring a more uniform ingress of water into the sensing material. In the initial production of the PAn P(BuA-co-VAc) blend a portion of the solid polymer was set aside before dissolving in
dichloromethane. This portion was taken to deprotonate the PAN component of the blend to
the emeraldine base (EB) form. The solid was added to concentrated ammonia solution
(approx 1M) and stirred vigorously for approximately 1 hour to de-dope the PAN to EB
(Scheme 1). The solid residue was then filtered from the ammonia and washed with
distilled water until a neutral pH was realised with the waste water, upon which time it was
then dried to a powder in an oven at 80°C. The EB polymer was then separately redissolved
in CH₂Cl₂ solvent at 1-2% by weight to create a dark blue liquid which could be readily
stored in an easily processable form.

3.3.4.3 Testing of the PAN EB coated PAN P(BuA-co-VAc) sensors

The sensor substrate as developed previously was dip-coated with the PAN ES blend and
allowed to dry completely in a desiccator. After drying, a second layer of PAN EB was
applied to the surface by dip coating, for protection of the underlying PAN ES. This layer
was applied to stabilise the ES sensing material and protect it from the possibility of de-
doping to the non-conductive EB form, which would lead to a change in the humidity
response. In this fashion the sensor response could be verified and a calibration curve
produced in the as-protected state (using the method described in section 3.2.3) so that the
sensor may be stored ready for later use in the adhesive system.

With this overall design the width of the conducting electrodes was again the main limiting
factor to the overall size. The EB polymer coating thickness was examined under a
microscope and was estimated to be around 25μm for the protective PAN P(BuA-co-VAc)
EB) polymer coatings on the produced sensors.
**Bulk Resistance**

Again it was seen that the main factor determining the bulk resistance in the final sensor was the spacing of the platinum electrodes in the manufacture of the substrate. With the application of the EB coating the underlying base resistance of the sensor was not increased. It was seen for an electrode spacing of less than 1mm, each sensor showed a bulk resistance measurement (at 3% RH) less than 10 kΩ.

**Linearity / Sensitivity**

The % change in resistance calibration curves were repeated many times for sensors with and without the protective coating and the average values can be seen in Figure 3.24 along with the standard deviation at each RH level. Calibration curves for the 15 w/w% PAN ES blend with EB protective coating responses were found to be exponential and from 11 – 74%RH and showed that both the overall response and sensor sensitivities were almost identical when compared to the unprotected sensors. Similarly to the unprotected sensors, a high sensitivity was recorded with over a 300% resistance change from 11 – 74%RH.

EB coated sensors were compared with unprotected PAN P(BuA-co-VAc) ES sensors to examine any shift in response that may have occurred due to the addition of the protective coating. It was found that the EB coated sensors were still especially sensitive for low RH changes and no significant shift in response was recorded between the barrier coated and uncoated samples.
Figure 3.24 | Comparison of the change in resistance calibration curve for PAn P(BuA-co-VAc) ES sensors with and without EB protective coating

Response Time

As previously, the rate of water ingress into or out of the polymer was seen to be dependant on the differential between the current concentration of water in the sensor and the concentration of water in the surrounding atmosphere - the larger this differential, the longer the time needed to reach equilibrium in the sensor. The times required to reach equilibrium for humidifying stages were much faster than that for desiccating stages and for each RH step tested, the sensor response had a similar shaped curve to that of the unprotected PAn P(BuA-co-VAc) sensors. Figure 3.25 shows a typical sensor response
curve for PAn P(BuA-co-VAc) EB coated sensors that were tested over time between relative humidities of 11 and 74%.

As water had to pass through the EB coating before it could reach the ES sensing material the EB coated sensors took longer for each of the humidifying and dessicating steps than the unprotected sensors. It was seen for the largest differential (from 3 to 95% RH) the EB coated sensors took approximately 4 to 5 hours to reach 90% of the equilibrium resistance on humidifying and 35 hours was required to reach 90% of the equilibrium resistance on desiccating (as compared to 2 to 3 hours and 24 hours respectively for the unprotected sensors).

Figure 3.25) Two typical PAn P(BuA-co-VAc) EB coated sensor response curves showing changes in RH between 11% and 74%
In general, the sensors required several hours to equilibrate after a step change in RH. Again, it is expected that producing thinner coatings over a substrate with a smaller gap between platinum wire electrodes could further reduce the sensor response time.

**Temperature Response**

With the EB coating, the sensors were still found to be slightly responsive to temperature and the calibration curves for temperature changes from 5 to 60°C in constant 3% RH, were typically identical to that of the unprotected sensors.

**Araldite 2015 stability**

The two sensor types PAn ES (unprotected) and PAn EB coated were placed in a desiccating chamber, allowed to stabilise, and then coated with Araldite 2015 to examine the extent of protection that could occur from the EB coating. The sensor response was monitored over time and in this case a % change in resistance was defined as a change from the minimum resistance that was reached just after coating with Araldite 2015 (Figure 3.26).

When embedded at constant RH, each of the sensors showed an initial drop in resistance (from water in the uncured epoxy) and started to reach stability after complete curing of the epoxy (24 hrs). With the standard PAn ES sensors, even though partial de-doping of the polymer surface occurred, the resistance of the sensor stayed within a measurable range. Therefore a clear response was still recorded. Within this response it was noted that the PAn ES (unprotected) sensors showed a large variation that was attributed to the differing extent of deprotonation into the ES core due to slight variations in initial coating thickness and electrode spacing. It is almost impossible to accurately calibrate the unprotected
sensors for such a variation in response and further highlights the need for a protective coating.

Figure 3.26 Sensor response of EB coated and uncoated sensors once embedded in Araldite 2015 at constant 3% RH

The EB coated sensors on the other hand, showed responses that almost overlapped albeit with a slightly slower response. From these initial results it was concluded that the EB coating was acting as a successful barrier to the de-protonating nature of the Araldite 2015 epoxy, and ensured a more consistent response from one sensor to the next.

To ensure accuracy of the sensor response after being embedded in Araldite 2015 multiple EB protected sensors were calibrated and then coated with Araldite 2015. These sensors were equilibrated over time in various RH environments (Figure 3.27).
In each of the humidity chambers water ingress into the sensors via the adhesive was slow and took several days to reach equilibrium. Sensor responses at high humidities closely matched the calibration curve and show that sensors with an EB protective coating are suitable for measuring the water content within Araldite 2015 epoxy.

Figure 3.27) Response of PAn P(BuA-co-VAc) EB coated sensors that have been embedded in Araldite 2015 and exposed to varied RH environments. The solid line represents the standard calibration curve without Araldite 2015 exposure.

 Resistances for low humidities failed to accurately match the original standard calibration curve for the protected sensors showing a variance from the expected response by about 20%. This may have been because the true equilibrium water content in the sensor / epoxy system at these low RHs had not been achieved before exposure to the next RH
environment. An alternative explanation would suggest that the drift in the response (as was seen in Figure 3.16) had not been completely removed by the addition of each of the coatings (EB and Araldite 2015) and as such the increased resistance for these humidities was due to drift that may have occurred over the time taken to achieve these results. Even so good accuracy was seen with the sensors at humidities higher than 11\%RH.

3.3.5 Conversion of RH sensor readings to mass uptake of water

To be able to use the sensors to determine the water content in the adhesive joints it was necessary to undertake a conversion of the relative humidity response to a mass uptake of water in the Araldite 2015 adhesive.

Films of PAN P(BuA-co-VAc) ES were cast and the mass uptake of water in the film was weighed after exposure to various RH environments (Figure 3.28). The time taken for each of the films to equilibrate in mass for each step change in RH was seen to be a maximum of 5 days for a change from 74 to 95\% RH. This was several times longer that that taken for a sensor to reach equilibrium in the same environment but was attributed to the larger mass of polymer used in each of the films as compared to the mass of polymer required for each sensor.

Larger errors were seen with the measurements taken at 95 \% RH which was attributed to the inherent drying of the film that occurred between removal from the humidity chamber and subsequent weighing. The water uptake in the PAN sensing material was seen to be approximately linear up to 70\% RH at which time a steep exponential increase was seen to full saturation. The straight-line portion of the graph showed a steady increase to around 5 w/w\% water where a sharp uptake was seen to full saturation of about 23 w/w\% water.
In comparison with the PAn P(BuA-co-VAc) response, the water uptake in the Araldite 2015 epoxy was much smaller (Figure 3.29) and took longer to reach equilibrium (Figure 3.30). The water uptake was seen to be exponential for varying RH with the maximum uptake of water in the Araldite 2015 seen at approximately 5.5% for complete saturation.

![Conversion curve for the equilibrium mass uptake of water in PAn P(BuA-co-VAc) ES films in various RH environments.](image)

The time required to reach an equilibrium uptake of the water in the Araldite 2015 was found to be dependant on the RH environment. For example, to reach 90% of the equilibrium mass it took approximately 10 days for a step change from 33 to 51%RH, 20 days for a change from 51 to 74%RH and 30 days for a change from 74 to 95%RH. The longer equilibrium times taken for each step change in RH can be explained by the larger mass of water entering the polymer. This slow rate of water uptake in the Araldite 2015
shows its low affinity with water when compared to the PAN P(BuA-co-VAc) sensing material. With the PAN sensing material showing greater water affinity, it is expected that (once sensors were embedded in adhesive joints), the very small mass of PAN polymer used within the sensor with respect to the mass of adhesive (approximately 0.1 w/w%) would not significantly increase the total mass of water taken up by the Araldite 2015 adhesive joints.

**Figure 3.29** Conversion curve for the equilibrium mass uptake of water in Araldite 2015 films in various RH environments.
Importantly it can be seen that the sensor response (and weight % water in the PAN) equilibrates much faster than that of the water ingressing into the Araldite 2015, and as such the sensor will be able to give an accurate determination (without time lag) of the current water content in the surrounding Araldite for later tests. A calibration curve was obtained for sensors embedded in the Araldite 2015 with a baseline resistance at 74%RH (Figure 3.31).

Figure 3.30) Typical mass uptake in Araldite 2015 films over time for increasing RH step changes
Figure 3.31) Calibration curve for PAN P(BuA-co-VAc) EB coated humidity sensors embedded in Araldite 2015 adhesive.

In this figure, the corresponding data points for each ‘RH’ value have been shown for ease in comparison with the original humidity calibration curve. It can be seen that these sensors can be used to very accurately determine water content in Araldite 2015 up to 2% by weight water.
3.4 Conclusions

Micro humidity sensors were constructed from polyester insulated platinum wire substrates to have a thickness of no more than 150μm. Two processable polyaniline blends were developed with polyvinyl alcohol (PVA) or butyl acrylate / vinyl acetate copolymer (P(BuA/VAc)). These blends were investigated for their ability to sense atmospheric humidity.

Polyaniline blends containing PVA had a response to humidity that was directly related to the mix ratios of PAn:PVA. Low w/w% levels of PAn (<10%) showed high sensitivities to humidity, but bulk resistances were too high for most practical uses. At increased levels of PAn (10 w/w% or greater) bulk resistances were found to be considerably lower, but the sensitivity to humidity was drastically reduced. A change in the nature of the response was also seen for blends with a PAn content of 20w/w% or higher where a resistance increase was detected for increasing humidity and this was attributed to an aggregation of PAn colloidal particles at the higher PAn levels. At high humidity levels the PVA most likely swells causing a separation of the conducting PAn domains and resulting in an increase in the resistance.

Polyaniline blends containing P(BuA-co-VAc) showed much more consistent and measurable responses. 30 w/w% PAn blends were found to show linear responses with over a 100% resistance change over the entire 95% change in RH. 15 w/w% polymer blends had an exponential response and showed even higher sensitivities with an 800% resistance change over the entire 95% change in RH.
Sensors were found to have consistent results over a long-term testing of over 6 weeks though it was found that the responses showed a slow but consistent drift (or increase in resistance) which was attributed to an over oxidation of the PAN in air.

Sensors were also shown to exhibit an unacceptably high degree of drift once embedded within Araldite 2015 which may be attributed to the de-doping of the PAN sensing material to the EB non-conducting form. This de-doping was seen to occur into the PAN ES surface up to depths of approximately 15-20µm and as such changed the shape of the calibration curve that was calculated prior to embedding.

To counteract this drift, a PAN P(BuA-co-VAc) coating was made with PAN in its emeraldine base form. This was used as a protective barrier coating over the PAN ES sensing material to ensure a stable response with the sensor after embedding in Araldite 2015. No significant change in the nature of the calibration curve was seen with the incorporation of this coating though sensor response times were slowed. For the largest change in humidity (from 3 to 95% RH) the EB coated sensors took approximately 4 to 5 hours to reach 90% of the equilibrium resistance on humidifying and 35 hours was required to reach 90% of the equilibrium resistance on desiccating (as compared to 2 to 3 hours and 24 hours respectively for the unprotected sensors).

EB protected sensors were examined for their ability to accurately measure water content in Araldite 2015 for various relative humidity environments and showed a good correlation to the calibration curve for humidities higher than 11%.

Water uptake in PAN P(BuA-co-VAc) ES films was compared to the water uptake in Araldite 2015 for varied relative humidity environments. The maximum uptake of water by mass in the PAN films was approximately 23% as compared to only 5.5% in the Araldite 2015 films. It was found that the PAN sensing material had a much faster uptake of water
than the Araldite 2015 and due to this it can be expected that sensor readings obtained after embedding would be equilibrated without a time lag enabling accurate and instantaneous monitoring of water content at all times.
3.5 References


Chapter 4

pH Sensor Development
4.1 Introduction

One of the main factors leading to adhesive joint degradation is the onset of corrosion in the metals being joined. Corrosion can lead to the formation of unstable oxides which have detrimental effects on the adhesive joint strength in two main ways. Firstly these oxides can have a much lower adhesion to either the underlying base metal or the adhesive film itself, resulting in interfacial or adhesive failure at much lower loads than for non-corroded joints [1-4]. Secondly, the formation of these oxides can lead to the generation of cracks between the interface of the metal and adhesive, which can allow more water to penetrate within the joint leading to further corrosion and, if the cracks are allowed to grow to their critical length, can cause catastrophic failure of the joint [1, 5].

The ability to be able to sense the reactions that are involved with the onset of corrosion would be a useful tool to help further the understanding of adhesive joint degradation and could be used in an early warning or health monitoring regime for the adhesive joint in service.

(1) \( \text{Al}_{(s)} \rightleftharpoons \text{Al}^{3+} + 3 \text{e}^- \)  
Oxidation \( E^{\circ}_{\text{ox}} = 1.66 \text{V} \)

(2) \( \text{O}_2_{(g)} + 4 \text{H}^+ + 4 \text{e}^- \rightleftharpoons 2 \text{H}_2\text{O} \)  
Reduction \( E^{\circ}_{\text{red}} = 1.23 \text{V} \)

(3) \( \text{O}_2_{(g)} + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightleftharpoons 4 \text{OH}^- \)  
Reduction \( E^{\circ}_{\text{red}} = 0.40 \text{V} \)

Scheme 4.1) Typical oxidation and reduction reactions that occur during the corrosion of aluminium metal

(Reproduced from Chapter 1)
The corrosion in aluminium metal is known to occur with the reactions in Scheme 4.1 (reproduced from Chapter 1). So, in the result of the reduction reactions 2 and 3 occurring, we should expect the pH to increase at the reduction site (by either using up free H+ ions or producing OH- ions), if only at a localised level. As such, the embedding of a stable and sensitive pH sensor within the adhesive joint may be a useful tool to determine the onset and extent of corrosion.

Upon the onset of corrosion, the pH levels at different locations within adhesive joints can vary quite widely depending upon the species being corroded and the type of corrosion that is occurring. For example, in the presence of an electrolyte such as salt water, the site of reduction and consequent corrosion of the metal do not necessarily need to be in close proximity. Corrosion can occur at sites where oxygen is not necessarily in high supply, and in these cases it is typical for electrons to be transferred along the metal to the site of reduction (where the oxygen is in higher concentrations) as long as the electrolyte is in contact with both redox sites and the corresponding metal ions can move. In this case it can be expected that crevice corrosion or pitting of the metal occurs at the oxidation site, and ion migration through the electrolyte will result in the deposition of metal oxides at the oxygen rich site of reduction. During this process, the pH will increase at the reduction site where the oxides are deposited, but the effect on the pH at the site of oxidation is relatively unknown. If such pH changes could be quantified, then a suitable pH sensor may be used to predict the onset and location of the oxidation reaction and subsequent corrosion.

Research has been undertaken into the effect of pH changes on the structural strength of adhesively bonded aluminium. These studies were undertaken by immersing joints in
different pH solutions and studying the effects of pH on both the adhesive [6, 7] and the adherend [7-9] and the degradation mechanisms that can occur due to such conditions. It was found that the adhesive joints had a sensitivity to pH conditions at both low [8, 9] and high pH [7-9] values. The mechanisms of degradation due to pH were eluded by Brockmann et al [8] who stated that degradation can be caused by (1) an alkaline course of destruction caused by the influence of moisture on the Al₂O₃ in epoxy resin systems and (2) an acidic degradation which can occur alongside electrochemical corrosion of the underlying adherend metal.

In contrast to these results, Nakanishi [6] examined the effect of acidic water, salt water and distilled water on carbon fibre re-inforced plastics that had been adhesively bonded with epoxy adhesives. His work found that for the same adhesive, the degree of deterioration of the shear strength of the bonded joints was not affected by the pH of the water that the joints were immersed in. Thus it could be assumed that a high degree of the strength loss in adhesively bonded aluminium that has been exposed to low pH conditions is due to acidic degradation of the aluminium substrate, and not the epoxy adhesive.

Thus, if a pH change is able to be measured during the service of the adhesive joint (whether it is an increase or a decrease) then further information may be obtained upon the instigation and type of corrosion that may be occurring within the joint. In doing so this would provide valuable information to determining the possible processes of corrosion and the build up of certain oxide layers within the adhesive joint in service (especially if measured at a localised area). It may also be found that the onset of corrosion itself, generates a pH change at the adherend surface (whether it is an increase or a decrease) leading to further pH degradation as discussed above.
This information could be used as a health monitoring tool to warn the engineer that pH values have reached critical levels or that corrosion may be occurring on the surface of the adherend metal or hidden within the joint itself. If experiments were conducted so that the pH results were correlated against adhesive joint strength, then these sensors could be used to perform a prediction on the adhesive joint strength during later service.

There are various methods for determining the pH of solutions.Traditionally these consist of chemical or electrochemical methods. In electrochemical methods, the voltage across a reference cell is monitored (after placing in the solution of interest) to determine the underlying pH of the solution. Commonly with the chemical methods, certain dyes or indicators change colour on exposure to set range of pH environments and may be used to determine when the pH of a solution has been raised or lowered past the pH that is critical to the colour change. For instances where the pH change causes the oxidation or reduction of the indicator species, the chemical indicator may be incorporated into transistor devices or ChemFETs. Here, the induced voltage due to the change in oxidation state of the indicator may be used to adjust the gate voltage at the transistor and the response to pH is recorded as a flow in current through the transistor. Real-time monitoring may be undertaken with the data being stored in a computer or other such device.

pH sensors have also been constructed for use in biological and engineering applications that utilise changes in the material characteristics as either a mechanical, optical or electrical response. Gerlach et al have constructed hydrogel based sensors that utilise the swelling characteristics of the material in different pH environments [10] to apply a mechanical force to a bending plate that is connected to mechano-electrical transducers. In
this setup, the stress state change in the membrane changes the resistivity of the transducers, and a voltage change is recorded that corresponds to a change in the pH. The design of such a device requires a spatial orientation that allows for mechanical movement of both the bending plate and the hydrogel, and as such, minaturisation of such a device for embedding within adhesive joints is unfeasible.

Some of the more promising designs for pH sensors that have the potential for miniatuirisation incorporate fibre optic cables. These sensors utilise pH sensitive dyes as the sensing medium and fluorescent spectral analysis techniques are undertaken to determine the pH at any time [11-16]. Sol-gel materials [11, 12] have also been used in these devices to help encapsulate and immobilise the pH sensitive dye. A linear operating range from 3–10 pH has been obtained with short response times of < 45s [15]. However, the problem with these designs is that the analysis of the optical signal can require bulky and expensive apparatus.

Conducting polymers (ICP) have advantages over each of these methods in that the signal generated can be an electrical resistance or voltage that may be measured with a hand-held multimeter, as with conventional glass electrodes and ChemFets. Advantages with the processability of ICP’s enable improvements in fabrication. Many conducting polymers may be grown or cast to produce thin flexible films, which improves the chances of producing a reliable design that may be scaled-down to fit within the boundaries of the adhesive joint. The vast range of chemistries can also enable better compatibility with the adhesive used within the joint and it is also possible to extend the range of pH monitoring over a wide range of pH values.
Various conducting polymers have been shown to possess a pH response and as such have been developed into reproducible thin film sensors [17-26]. Both polyaniline (PAn) [17-26] and polypyrrole (PPy) [17-21, 26] have been shown many times to have sensitive responses with several orders of magnitude change in resistance with pH.

The conducting polymer polyaniline is conductive in its doped and protonated emeraldine salt form. As the pH rises to above 4 it becomes deprotonated to its non-conducting emeraldine base form. It has been reported that with pH cycling between pH 0 and 7, PAn can be expected to show conductivity changes up to 2 orders of magnitude [18]. It could therefore be a possible material that can be used as an indicator that the pH has changed. It is thought that the humidity sensors developed in Chapter 3 may be able to achieve a secondary response to pH, such that upon pH increases the response is represented as an increase in resistance when the PAn is converted from ES to EB.

Polypyrrole has also been found to have great potential for measuring pH. The conductivity changes with PPy were tested over a larger range of pH and were shown to have conductivity changes close to 3 orders of magnitude from pH 0 to 14. However, processability of PPy is limited in that highly conductive, consistent films are most readily obtainable from electrochemical polymerisation.

Another conducting polymer that has been recently shown to have a pH response is poly 3,4-diethoxythiophene (PEDT) [27]. PEDT films may be produced electrochemically, chemically, or via vapour phase deposition with a high conductivity and when grown chemically it may be blended with other polymers to improve its processability. The sulfonated form of PEDT can be dissolved in water and good dispersions may be generated, however films cast with these dispersions can have poor adhesion when placed
in moist environments. By blending the PEDT with other organic polymers it is possible to produce films that are soluble in organic solvents and when cast have a hydrophobic character and hence better adhesion in moist environments.

Winther-Jensen [27] has shown that PEDT has a reversible pH response that shows significant decreases in conductivity with increases in pH with an almost flat-line section in the middle of the curve between pH’s of about 5 and 9 (Figure 4.1). The general theory behind this conductivity change is that the polymer oxidises at low pH and reduces at high pH. This has been attributed to the fact that oxygen is a stronger oxidant in acidic media and relies on the same reduction half equations that are seen with the oxidation of aluminium (Scheme 4.1).

Thus at low pH’s the equilibrium in the PEDT polymer shifts from the reduced state to the oxidised state. Why the reverse of this happens at high pH and in the absence of H⁺ is still unexplained. It may be suggested that the equilibrium of reaction 2 becomes reversed to balance the increased pH to that of neutral, and in doing so the water oxidises to O₂ and H⁺ and the PEDT polymer becomes reduced. The response is real and could be useful in the
production of sensors as PEDT may be developed easily into processable solutions, especially when polymerised in the presence of other polymers to form blends.

Figure 4.1) Resistive response of PEDT films after equilibration a) in different pH environments and b) with oscillation between acid and base solutions of pH 1 and pH13 (Taken from Towards Micro-patterning of Conducting Polymers [27])

Such a blend could be a useful sensing material as PEDT shows a stable response around neutral conditions of pH 7 (salt water) and any conductivity change that is seen during initial exposure will most likely due to salt water ingress into the adhesive surrounding the sensor and not changes in pH. Likewise, after an equilibrium water content has been reached, any later change in sensor resistance will be most likely due to a significant change in pH either higher than pH 9 or lower than pH 5. Such a sensor has the capacity to not only show a response to water but also to detect changes in pH. This chapter outlines the attempts made to produce sensors that can measure pH with high sensitivity and reproducibility.
4.2 Experimental

4.2.1 Polymer Blends

4.2.1.1 PAn P(BuA-co-VAc) polymer blends

The 15 w/w% PAn P(BuA-co-VAc) humidity sensors of Chapter 3 were examined for any secondary response to pH. The response to humidity was examined and a humidity response calibration curve was examined on multiple sensors. From this point the sensors were placed in different pH solutions and monitored on 30 min intervals to examine any shift in response due to changes in the polymer doping level.

4.2.1.2 PEDT polymer blends

A processable PEDT polymer blend was developed as a composite of poly vinylidene fluoride (PVDF) and PEDT to be able to be cast from an acetone solvent. The blend was developed to incorporate PVDF because of its high chemical and electrical stability and its low affinity with water. The main aim was to generate a composite blend that contained a dispersion of conducting PEDT particles in a matrix of processable polymer that could be cast into clean flat films.

The polymer blend was made by reacting two solutions together. One solution contained dissolved PVDF polymer and unreacted thiophene monomer and the other solution contained the chemical oxidant, which when mixed reacted to oxidise the thiophene based monomer to the conducting polymer PEDT. The full process to construct the PEDT / PVDF blend is as follows:
1) 6.4g of PVDF pellets were dissolved in 80 mL of N-N dimethyl formamide (DMF) under low heat and vigorous stirring.

2) Upon complete dissolution of the PVDF pellets the solution was cooled to room temperature and 14.2g of 3,4 - diethoxythiophene (EDT) monomer was added to the solution.

3) Acetonitrile was added to make the solution up to 350 mL and this first monomer solution was stirred vigorously and sonicated for approximately 5 minutes to allow complete mixing of the constituents.

4) A second solution containing oxidant was made by dissolving 16.2g FeCl₃ in 100mL of acetonitrile.

5) The whole of the second solution was added to the first solution dropwise with vigorous stirring to oxidise the monomer. After mixing the final solution was stirred for 24 hrs to allow the reaction to complete and then dried to a slurry in a cool oven at 80°C.

6) Water was added to the slurry and stirred to allow removal of excess FeCl₃ oxidant. This was then filtered and the filtrate was continually washed until the waste water turned clear.

7) The filtrate was next washed with methanol to remove excess EDT monomer, and this process was again continued until the waste methanol turned clear.

8) The filtrate was then dried again in a cool oven at 80°C and weighed to ascertain an approximate PEDT:PVDF ratio.
The final mass of the dried polymer was 7.2g and (assuming no loss of PVDF and complete washing of unreacted oxidant and monomer) gave an approximate PEDT content of 11w/w%. The dried polymer was then redissolved in acetone under low heat and vigorous stirring to develop a processable solution that may be cast over our sensor substrates. A schematic of the chemical structure of PEDT and PVDF may be seen in Scheme 4.3.

![Chemical structures of PEDT and PVDF](image)

**Scheme 4.3** Schematic of the chemical structure of both a) PEDT and b) PVDF

### 4.2.2 Sensor substrates

The PAN and PEDT sensing polymers were cast over the surface of the platinum wire substrates that were developed in Chapter 3. These substrates were used to ensure a minimal thickness to the final sensor so that the small sensor size would not harm the integrity of the joint in any way. Substrates were dip-coated in each of the processable polymer solutions to have an inner bridging thickness of approximately 50 – 80 μm for both the PAN / PVA and PEDT / PVDF sensors. The PAN P(BuA-co-VAc) sensors were tested using the refined design from Chapter 3 with the protective coating of EB polymer.
4.2.3 Testing and Calibration

For calibration of the sensor response to pH, various buffer solutions were utilised as sourced from *Fixanal® Riedel-de Haën®* and *BDH Laboratory Supplies®*. Table 4.1 shows the salts contained in each different pH buffer solution.

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KCl / HCl</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₈O₇ / NaCl</td>
</tr>
<tr>
<td>3-6</td>
<td>C₆H₈O₇ / NaOH</td>
</tr>
<tr>
<td>7</td>
<td>KH₂PO₄ / Na₂HPO₄</td>
</tr>
<tr>
<td>8-9</td>
<td>Na₂B₄O₇ / HCl</td>
</tr>
<tr>
<td>10</td>
<td>BDH Laboratory Supplies</td>
</tr>
<tr>
<td>11</td>
<td>H₃BO₃ / NaOH / KCl</td>
</tr>
<tr>
<td>12</td>
<td>Na₂HPO₄ / NaOH</td>
</tr>
<tr>
<td>13</td>
<td>NH₂CH₂COOH / NaCl / NaOH</td>
</tr>
</tbody>
</table>

Table 4.1) Table of the buffer solutions used for pH experiments and the corresponding salts in each solution

Sensors constructed with each of the sensing polymers were immersed in the buffer solutions and the change in resistance was monitored over time to obtain the equilibrium resistance for each pH environment. Sensors were initially immersed in a buffer solution of...
pH 7 to show the fully saturated response and then swapped to higher and lower pH solutions to see the response to both acid and base solutions. Tests were performed on linearity, sensitivity, reversibility, sensor stability and lifetime.

4.3 Results and Discussion

4.3.1 PAn P(BuA-co-VAc) sensors

The pH response of the PAn P(BuA-co-VAc) sensors was examined to see if a secondary response to pH may be generated within the sensor after equilibration at high humidities. It was also necessary to undertake these tests to see any possible interference effects that may occur due to pH changes within the adhesive joints, once the mechanisms of adhesive breakdown and corrosion have begun. The humidity spectra were first analysed for each of the sensors tested to enable the generation of a calibration curve for humidity. Sensors were exposed to 11 and then 74%RH until stability was reached to enable fitting of these responses to the standard calibration curve from Chapter 3. Following this, one of each of the sensors were placed into buffer solutions of pH 2, 4, 6, 8, 10 and 12 respectively. The response to this step change in pH was examined over time.

The test was conducted over 11 days and it was seen that within an hour of full immersion in the buffer solution there was an initial drop in resistance for each of the sensors that was presumably a moisture response (Figure 4.2).
Figure 4.2) Initial response of PAN P(BuAco-VAc) sensors that were exposed to changes in humidity before immersion in different pH buffer solutions

From this point, significant increases in resistance were seen with each of the sensors, which is quite contrary to what was expected. Polyaniline is known to be conductive and stable (in its ES state) in acidic conditions. If the pH rises to above pH 4, deprotonation of the ES to the non-conducting EB form occurs [28]. As such, it was expected that immersion in low pH buffers would lead to improved conductivity. The reverse of this was seen where the sensor placed in the pH 2 buffer solution showed an increase of an almost 3000% change in resistance from the lowest resistance baseline within half a day of exposure (Figure 4.3).
In fact no clear trend with pH was encountered with much of these results and the only real conclusion that can be made is that for each pH examined there was a general increase in resistance with time. There also appears to be a stronger response to temperature which was observed after 4 days of the test with the cycling of resistance with time which would correspond to temperature changes between day and night (Figure 4.4).
There are two likely mechanisms that could be in place to instigate a change in resistance. One mechanism is through a change in the protonation level of the underlying sensing polymer, and the other is through a change in the adhesion of the sensing polymer to the underlying substrate. If the first of these mechanisms alone was seen, then it is likely that sensors exposed to low pH buffer solutions (of pH 2 and 4) would be expected to show resistance decreases rather than increases and the rate of the resistance increase in each of the other sensors should be graded by pH. This is not the case. Sensors that were exposed to low pH solutions (pH 2 and 4) had a final resistance that was higher than those exposed
to higher pH solutions (pH 6, 8 and 10). For this reason, it is believed that another mechanism such as a change in polymer adhesion to the substrate (resulting in an increased contact resistance) is also occurring.

The sensor that was exposed to the pH 12 buffer solution however, did show a significantly higher increase in resistance (at least double the increase to each of the other sensors) when compared to the other sensor responses. Here it is likely that the deprotonation effects of the buffer solution may be seen to be dominant in the resistance response where the pH is high enough to draw protons from the ES sensing material through the EB outer layer and into solution.

Since the PAN P(BuA-co-VAc) system showed no significantly clear trend with pH, this polymer was also deemed unsuitable for our designs of measuring pH and further characterisation of the performance was abandoned.

4.3.2 PEDT / PVDF Sensors

Multiple sensors were constructed by dip-coating the sensor substrates in the PEDT / PVDF polymer blend and allowing the polymer coating to dry in a desiccator for at least 24 hours prior to testing. The resistive response to pH was examined over time for various tests. The sensors were assessed for linearity and sensitivity, bulk resistance, response time, temperature and humidity responses, stability and reversibility, lifetime and stability within Araldite 2015.
Linearity/ Sensitivity

Figure 4.5 shows a typical pH response curve for a PEDT / PVDF sensor that was tested over multiple days in buffer solutions of pH 1 to pH 13. The colour coding represents the pH of the solution throughout the test (from purple at pH 13 to red at pH 1) and shows a clear and stable response with an approximately 350% change in resistance (from a baseline at pH 1) over the entire pH range tested.

![Decreasing pH](image)

**Figure 4.5** Resistance response of PEDT/PVDF sensors that were exposed to different pH buffer solutions over time
Calibration curves were generated for the PEDT / PVDF sensors over a one-pass drop in pH from basic to acidic conditions. A baseline was set for resistances at a pH 7 and the % change in resistance after equilibrium was plotted against the pH of the test solution (Figure 4.6). The response is almost linear between pH of 5 and 11, outside which range the sensing properties of the polymer are somewhat compromised. A large variance in response is seen with high pH (greater than pH 11) and low sensitivity is seen with a pH of 4 or less.

**Figure 4.6** Average results for sensors that were tested in one pass for decreasing pH from basic to acidic conditions
**Bulk resistance**

Like the PAn P(BuA-coVAc) sensors the PEDT / PVDF sensor resistance was mainly controlled by the final spacing of the conducting electrodes. With electrode spacing less than 1mm the sensors showed as cast and dry (3% RH) bulk resistances that were less than 15kΩ giving a wide response for measurement purposes and allowing the response to be easily measured with a standard multimeter.

**Response time**

The response time (Figure 4.7) was shown to be faster in changes from low to high pH (reduction of PEDT) than changes from high to low pH environments (oxidation of PEDT). In the oxidation sensing phases (lowered pH) the response time for pH shifts of pH 12 to pH 7 and pH 7 to pH 2 took approximately 2 to 3 days for each step change to reach a stable reading that was within 90% of the equilibrium resistance. It was seen for changes in pH from 2 to pH 7 the response took approximately 24 hours and likewise, for pH shifts from pH 7 to pH 12 the response time was faster still, taking approximately 12 hours to reach 90% of the equilibrium resistance.

In general, the sensor response is quite slow and required multiple hours to equilibrate after a step change in RH. It is believed that the response time could be improved by both producing polymer blends with a higher PEDT loading and casting thinner coatings over a substrate with a smaller gap between platinum wire electrodes. The development of a polymer coating that was more porous would also improve the response time. It was envisaged however, that these slow response times would not be too detrimental for
determining pH changes within marine exposed adhesive joints, as the corrosion reactions that were predicted to occur to the underlying adherend surface would be slowed by the hindered ion migration through the low permeability epoxy adhesive.

Figure 4.7) Typical response time curve for PEDT / PVDF sensors showing step pH changes between pH 2, 7 and 12

Temperature and Humidity Response

The sensors were seen to be slightly responsive to both temperature and humidity (Figure 4.8 and Figure 4.9). In a solution of pH 7, the sensors had an approximate 35% change in resistance when shifting temperature from 5 to 65°C. This relates to a 0.5% shift in resistance per degree Celsius. The response was linear and showed a drop in resistance with increases in temperature over this range. The drop in resistance is attributed to an increase
in the movement and mobility of conducting electrons and free anion dopants within the polymer [29-31].

Figure 4.8) Temperature response of PEDT / PVDF sensors between temperatures of 3 and 65°C in a solution of pH 7

As for experiments conducted within Chapter 3, to examine any response to humidity, sensors were held in the air gap of enclosed chambers holding different saturated salt solutions and the sensor resistance was monitored over time (Figure 4.9). After equilibration at 3% relative humidity (RH), sensors were exposed to step increases to 11%, 33%, 51%, 74% and 95% RH before being returned to a desiccator of 3% RH.
Upon exposure to low levels of water (less than or equal to 51% RH) the resistive response of the PEDT / PVDF sensors was quite stable and showed little response. At higher humidities however, (74% RH or greater) there was a sudden significant drop in resistance which was followed by a later increase in resistance (tending to indicate a competing resistive response within the sensor). It is known that PVDF is somewhat hydrophobic and any water ingress into the sensor due to a change in humidity will be slowed due to the incompatibility of water with the sensor matrix material. Thus at low humidities, any response seen would be primarily due to surface effects and does not significantly affect the underlying resistance of the sensor. At higher humidities, the equilibrium depth at which the water can penetrate the polymer is increased (when compared to that of the completely dry sensor) and in these environments a resistive response is seen when the water has ingressed to a depth to interact with the bulk of the sensing material.
With the PVDF matrix having a low affinity for water, the initial drop in resistance (for a step increase in humidity from 51 to 74%) was attributed to a more rapid ingress of water into the conducting PEDT material which, (like the PAn sensors) allowed for the delocalisation of dopant ions on the polymer chains and subsequent improvement of intra-chain electron transfers [32].

After several hours the resistance began to show a marked increase which plateaued after several days. A similar increase in resistance with water content was seen by Winther-Jensen [27] who attributed the response to a change in the localised pH of the polymer film. In his study, PEDT was polymerised in a low pH environment to produce a film in the fully oxidised and conducting state, so that when the film was placed in water of pH 6 or 7 the equilibrium of the oxidation state of the PEDT polymer was shifted to that of partially reduced.

In our system, however, it is believed that the resistance increase with water content is due to other factors. If the oxidation state of the PEDT sensing material was being shifted to that of partially reduced, there should have been an unrecoverable increase in resistance observed upon final desiccation of the sensor. This was not seen. As such, here the increase in resistance was attributed to the slow swelling of the PVDF matrix causing a separation of highly conducting domains (similar to what was seen with the PAn / PVA blends). This mechanism is further confirmed with desiccation of the sensor from 95 to 3 % RH (Figure 4.9) where the hydrophobic PVDF matrix initially allows a fast release of the water resulting in a subsequent shrinking and resistance decrease, and the later resistance increase is due to the slower response of the water leaving the conducting PEDT material reducing the movement of dopant ions.
The somewhat erratic response seen at 95% RH has been attributed to changes in temperature, however the general shape shows an initial drop followed by a slow increase in resistance like was seen with the step change to 74% RH.

**Stability / Reversibility**

Sensors were constructed and cycled multiple times in pH environments from neutral to acidic to neutral to basic conditions using pH buffers of 2, 7 and 12. The response of this cycling can be seen in Figure 4.10 where the time left in each buffer solution was increased for each cycle.

![Figure 4.10](image.png)

**Figure 4.10** Response of PEDT / PVDF sensors to a continuously cycled pH from neutral to acidic to neutral to basic using pH values of 2, 7 and 12
This particular cyclic sequence was undertaken to obtain an accurate determination of both response time and the presence of hysteresis. The final equilibrium values before each step change in pH were recorded and may be seen in Figure 4.11. This graph shows a clear hysteresis response and a drift to the more oxidised and conductive state of PEDT over time.

![Graph showing hysteresis in PEDT/PVDF sensors response to pH cycling](image)

**Figure 4.11** Hysteresis present in the response of PEDT / PVDF sensors to a continuously cycled pH from neutral to acidic to neutral to basic

An explanation of this drift could be that the PEDT polymer is only being partially reduced at pH 12 (Figure 4.1) and hence by the end of each pH cycle (from the basic to acidic conditions) the polymer is more oxidised than in each previous cycle. It is thought that
penetration of the buffer into the sensing polymer is not complete due to the hydrophobic nature of PVDF, and as such, the central portion of the polymer is not being directly affected by ingress of the solution (either pH 2 or 12), but more from a migration of H\(^+\) ions through the polymer thickness during the oxidation cycle, resulting in a drift to the more oxidised form of PEDT.

**Lifetime**

Sensors were continuously cycled from increasing to decreasing pH from step changes through buffer solutions of pH 2, 7 and 12 over almost 4 months (Figure 4.12). Like the stability response, the sensors equilibrium resistance for each step change showed a consistent drop over time and is likely due to the PEDT polymer being more oxidised with each full pH cycle. It can be seen that the drift in response upon oxidation of the polymer (at pH 2) is eliminated after 4 cycles, and a return to the equilibrium resistance may be achieved with each subsequent cycle thereafter. Similar results (albeit with slight error) were observed with step changes to pH 7, however, the equilibrium resistance for pH 12 shows a steady decline over the life of the experiment. It is expected that with further cycling, the drift in the equilibrium resistance for sensors exposed to pH 12 buffer solutions may also be eliminated, however, by this point the sensitivity of the sensor will be significantly compromised.
Figure 4.12) Long term response of PEDT / PVDF sensors to a continuously cycled pH from neutral to acidic to neutral to basic using pH values of 2, 7 and 12

Sensor Response in Araldite 2015

Sensors were allowed to equilibrate in 3%RH before being coated in Araldite 2015 and the sensors ability to measure pH was confirmed with the Araldite coating. Upon complete cure of the epoxy the sensors were placed in pH solutions of 7, 2, 12 and then back to pH 7 and the resistive response was measured with a multiplexer (Figure 4.13).
Upon coating with Araldite 2015 the sensors showed a significant increase in resistance which was attributed to the high pH of the amine hardeners reducing the PEDT polymer to the non conducting form. Upon equilibration and after immersion in buffer solution of pH 7 an initial drop in resistance was recorded followed by a slow increase that was similar to the humidity response of Figure 4.9. The initial drop in resistance occurred over 3 hours and was attributed to a combination of a partial oxidation of the PEDT polymer to its conducting form as well as a delocalisation of the dopant ion as seen in the humidity response.

The sensors were then placed in pH 2 buffer solution to see if it was possible to measure any further drop in the localised pH. There was no further drop in resistance recorded upon immersion however a slow increase in resistance or drift was seen which was most likely...
due to swelling of the polymer coating around the sensor, leading to a reduced contact with the platinum wire electrodes and an increased resistance.

Upon an increase in pH (pH 12) each sensor showed a quick (albeit sometimes small) increase in resistance, however the dynamics of the response were still overshadowed by the consistent increasing resistance drift over the entire system and a true equilibrium response was not achieved after 36 hours exposure to pH 12. A final decrease in pH, (back to pH 7) was not registered with the resistive response at all, and it was believed that any response that should have been seen from this pH change was again being overshadowed by a swelling of the polymer around the sensor coating.

It was seen that there were two main problems with the use of these sensors once embedded within Araldite 2015 epoxy. After only a short cycling of the pH environment the embedded sensor became insensitive to pH changes. Also, a constant drift in the resistance over time was encountered making it impossible to reach an equilibrium resistance value for later conversion to pH. Large sensor inaccuracies were evident which were attributed to a combination of both the swelling / drift response and the inherent hysteresis. This combined with the limited reversibility of the sensor meant that the PEDT / PVDF sensors were unsuitable for embedding within Araldite 2015 / Al 5083 adhesive joints for the purpose of measuring pH. It is thought that this sensor system may still find use within other less harsh environments where for example a miniature sensor is needed to measure changes in the pH of vapours, and any resistive changes due to polymer swelling would be minimal.
4.4 Conclusions

It is understood that the ability to measure pH within the adhesive joint, especially upon exposure to marine conditions, may give great insight into the health of the joint in service. Micro sensors were constructed from polyester insulated platinum wire substrates to have a thickness of no more than 150µm. The polyaniline blend from Chapter 3 (poly butyl acrylate / vinyl acetate copolymer (P(BuA-co-VAc)) was investigated for the ability to sense changes in pH. Another poly 3,4-dioethoxythiophene blend with poly vinylidene fluoride (PVDF) was developed and was also examined for its ability to sense changes in pH.

When exposed to different pH buffer solutions the PAN P(BuA-co-VAc) sensors showed a significant increase in resistance for each of the buffers examined however there was no clear trend seen with the resistive response of the sensors to enable the determination of pH. These sensors were deemed unsuitable for use as pH sensors.

Sensors that were constructed from the PEDT / PVDF blend showed a much more stable response to pH. The sensor response showed an approximate 350% increase in resistance when increasing the pH from 1 to 13 and was approximately linear between pH of 5 and 11. However, the sensitivity of the response was compromised when determining low pH (pH 4 or less) and accuracy of the response was compromised for high pH (greater than pH 11).

The sensors showed a slight response to temperature with an approximate change in resistance of 0.5% per °C change in temperature. Sensors were approximately stable in relative humidity environments less than or equal to 51%RH but at higher humidities showed an initial drop in resistance that was attributed to a delocalisation of dopant ions on
the polymer chains and subsequent improvement of intra-chain electron transfers. Directly following this, an increase in resistance was seen that was attributed to a swelling of the sensing material that separated the conducting PEDT domains.

With cycling of pH, the sensors showed both hysteresis with each cycle and a slow drift to the more conducting and oxidised form of the PEDT sensing material over multiple cycles. The drift reached stability when measuring low pH (pH2) after 4 or more cycles, and as such this was attributed to the PEDT polymer oxidation state shifting to be more oxidised with each full pH cycle. Such a drift may be further investigated by attempting to ‘artificially’ shift the oxidation state of the PEDT polymer prior to manufacture. This may be achieved by bubbling the processable solution with either ozone or ammonia gas to respectively shift the oxidation state to that of more oxidised or reduced. In such a system, the drift would be expected to be eliminated for a shift to a more oxidised state or enhanced for a shift to that of a more reduced state, however, due to the problems encountered with a lack of stability in the Araldite 2015 environment, this experiment was not undertaken.

The sensor response once embedded within Araldite 2015 was severely compromised. After initial embedding it was possible to observe a drop in the resistance when exposed to lowered pH environments (neutral pH 7) however further drops in pH were not registered from the sensors. The response to subsequent increases in pH was also seen to be masked by the slow increasing resistance drift which was attributed to a swelling of the Araldite 2015 and PEDT / PVDF coating and the response was eliminated after short cycling of the pH. The PEDT / PVDF sensors were thus deemed unsuitable for use in the application of interest, i.e. in the embedding within Araldite 2015 / Al 5083 adhesive joints for continual monitoring of pH. These sensors may find use in other applications where environmental conditions are less harsh.
4.5 References


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Chapter 5

Embedded Sensor Response in Marine Environments
5.1 Introduction

In previous chapters the several structural and economical advantages that may be gained from the use of adhesives have been discussed. Faster production, lower weight and (in certain designs) better performance has been shown with the incorporation of adhesives, however significant strength losses in adhesive systems can be seen with exposure to wet and humid conditions. As such a general reluctance has been seen to take up this technology in the marine industry.

In chapters 1 and 2 it was seen that water can have multiple detrimental effects on the strength of the adhesive joint in service by:

a) Lowering the $T_g$ of the adhesive, and hence lowering the strength of the adhesive material

b) Swelling the joint, enabling the generation of cracks at the adhesive interface which when loaded can cause failure at lower than normal loads.

c) Attacking the oxide layers at the adherend surface, hydrating and converting them to less strong and more unstable forms, leading to failure at the interface at much lower loads than would normally be seen.

If the engineer was able to monitor the performance of the adhesive joint within the moist environment and obtain sufficient data on the structural integrity of the joint at any time during service, then greater confidence may be generated with the use of adhesives in marine structures and a general upsurge in the use of these technologies may result. The health monitoring tool that would be needed for such a system would comprise an array of sensors along the length of the joint that could relay information
back to the operator concerning water content within the adhesive and other such factors as the onset of corrosion or concentrations of stress.

To date there has been very little integration of non-destructive evaluation (NDE) sensing technologies within marine structures for the monitoring of the structural integrity of adhesive joints. The limited technology that has been used incorporates either intrusive techniques (by embedding the sensor within the joint) or non-intrusive techniques where sensor systems are external to the adhesive bond. For intrusive techniques to be successful, the sensor must be small enough so that it does not harm the joint strength in any way, yet it must still be stable and accurate. Due to these limitations, the majority of NDE technology for marine structures utilises the non-intrusive techniques of ultrasonic [1-6] or dielectric impedance [7-12] to determine either the concentration of water in the joint or the generation and growth of cracks. These systems provide data to make predictions on joint strength from the measured breakdown of the adhesive system.

With ultrasonic detection, acoustic waves are generated through the adhesive bond from a piezo-electric transducer or other source, and the reflection of the waves as they pass through the joint is examined over small time intervals. This can be a useful tool in the determination of porosity within the adhesive and the generation of cracks under load [2, 5, 6]. With a suitable sensor array, the advancement of a crack front may too be monitored as the crack grows under load [5]. However, there are inherent limitations with such a system.

One of these limitations is that this type of sensor can only be used to monitor and determine the extent of damage that has already occurred within the joint. This system can be useful to monitor the need for repairs, but cannot provide information that may
be used to avoid such damage before it occurs. Likewise, the system cannot be used to accurately measure the presence of harmful chemical species that may lead to the adhesive breakdown, such as the ingress of water, and as such may only find limited use in the marine industry where water ingress is of the utmost concern.

Adhesive joint monitoring may also be undertaken with the use of impedance techniques. Here the impedance response across the adhesive joint will change with the ingress of water and from this it may be possible to generate a profile of the concentration of water throughout the adhesive joint [7, 8, 10, 12]. The formation of stress concentrations due to water exposure can be predicted from such data, however significant errors can exist with the procedure due to swelling of the adhesive with water ingress or oxide build-up during corrosion, both of which have the capacity to expand the bond line thickness and affect the impedance response. Significant calibration regimes are necessary to interpret the data, and even with these regimes, accuracy with the final sensor response is compromised. Alongside this, impedance techniques typically give results that are an average along the whole bond-length, making it difficult to pin-point areas of the greatest structural concern.

Due to these issues, interest has grown with the use of intrusive techniques for NDE of adhesive joints. By embedding the sensor within the joint it is possible to accurately determine the localised joint conditions directly around the sensor, both for chemical and mechanical sensing, without the need to calibrate for such issues as swelling. The integration of an array of multiple sensors has the possibility to generate a virtual map of the water ingress (or other factors such as strain) within the joint at any time, and with these methods, a localisation of potential hazard points can be achieved.
Optical fibres have been incorporated into fibre-reinforced composite systems for the monitoring of such factors as strain and moisture ingress, however such systems can be costly in both sensor manufacture and interrogation [13].

Truong et.al. [14] have undertaken investigations into an adhesive bond degradation sensor utilising conducting polymers as the moisture sensitive element. The system utilises flat discs of compressed polypyrrole (PPy) powder embedded within an epoxy adhesive joining two aluminium substrates. A large increase (> 20 times increase) in DC resistance was seen with water ingress into the compressed PPy powder system and has been attributed to a swelling of the humidity sensitive material where the water molecules may block electronic pathways in the conductive substrate. It was found that this system had good thermal stability and joints that were tested ‘dry’ had no significant loss in adhesive bond strength when compared to joints without sensors. However, after immersion in 0.001M NaCl solution for ~ 800hrs samples fell apart under zero load making such a system unsuitable for long-term use within marine conditions.

Girshovich et. al. [15] have developed an invention that uses a polypyrrole conducting polymer coated fabric as a moisture sensitive element that is incorporated within the bondline of adhesive joints for the aircraft industry. The dielectric response of the system is monitored over time where the increase in resistance has been found to be proportional to the increase in water content within the adhesive bondline. The system has been designed for the aircraft industry and has not been tested within the marine industry where it can be expected that changes in bondline water content may occur to larger degrees. Other problems with this system exist in that the response has not been shown to be reversible and the extent of miniaturisation of the invention is greatly
reduced by the fact that the sensing element is a coated fabric that is held in place with a frame, and as such may limit the potential applications that may incorporate such a device.

Wilson et. al. [16-18] have developed a system that embeds a small silicon chip device into the adhesive bondline of aircraft structures for the monitoring of corrosion of the adherend surfaces. This multi-layered device utilises a series of sensor 'studs' to measure the electrochemical voltage characteristics within the adhesive joint under open circuit or constant applied current, the output of which has been seen to relate to the extent of corrosion of the underlying aluminium substrate. The device incorporates CMOS circuitry and has been manufactured to be under 100µm in thickness, giving the capability to be embedded within the adhesive bondline, however the design of such a chip requires a variety of washing and etching techniques followed by photoresist patterning, sputtering and electroplating of circuit connections upon each layer of the device, resulting in a labour intensive and potentially costly manufacture.

In chapter 3 and 4 work was undertaken to develop miniature humidity and pH sensors that could be incorporated within the adhesive joint during construction. A simple, small sensor system was investigated that had the capacity for further miniaturisation. Certain developmental problems were seen with the humidity sensors in that the high pH of the curing adhesive system was seen to irrevocably harm the underlying sensing material. The pH sensors were seen to show a consistent drift, and the response to pH was significantly affected after embedding in Araldite 2015. These problems were overcome in the case of the humidity sensors, and in this chapter adhesive joints were constructed with the embedded humidity sensors of the final design from Chapter 3.
Testing of the lap-shear strength of the joints with the embedded humidity sensors was undertaken in marine conditions for both static and fatigue test regimes, to ascertain the significance of salt water exposure to the strength of the adhesive joint. The water uptake sensor response was correlated against tensile strength over varying salt water exposure times in fatigue and static testing and the results have been discussed.

5.2 Experimental

Sensors were constructed using the design developed in Chapter 3 (Section 3.3.3.2). After dip-coating, each sensor was dried for 24 hrs at ambient temperature in a desiccating chamber that contained silica gel. Sensors were placed inside humidity chambers of 11 and 74% RH and the resistances monitored until a stable resistance was reached for low and high RH values. These values were used for two reasons:

1) to ensure that the sensors followed the standard calibration curve from Chapter 3.

2) to calculate a suitable baseline resistance for each sensor for determination of the % Change in resistance from this baseline.

During sensor calibration, the measured sensor resistance was first fitted to a set of known relative humidity environments that were later converted to Weight % water in the adhesive (Araldite 2015). During calibration the unknown variable was the sensor resistance, but during service the unknown variable will be the Weight % water in Araldite 2015. As such, a reinterpretation of the standard calibration curve was
necessary to correctly interpret the sensor resistive response to a mass uptake of water in the adhesive.

A mathematical expression of the sensor response was fitted to the shape of the known calibration curve of % change in resistance vs mass uptake of water in Araldite 2015. The curve was fitted to ensure that it passed within one standard deviation of the mean for all of the weight % water points measured experimentally. When curves were fitted to this response it was found that the mathematical expression that gave the best fit followed an inverse shape and had the following formula:

\[
y = \frac{67}{x + 0.139} + 160
\]

where:

- \( y \) = Change in Sensor Resistance from the baseline, and
- \( x \) = Weight % water in Araldite 2015

This formula was rearranged to show an expression for \( x \), such that any resistive response that was read from the embedded sensor during service could be directly converted to a mass uptake of water in the Araldite 2015 adhesive bond.

\[
x = \frac{89.24 - 0.139y}{y - 160}
\]

Araldite 2015 Aluminium 5083 adhesive joints were constructed using the procedure described in Chapter 2, however in this case humidity sensors were embedded within the adhesive bondline for monitoring of the water ingress into the adhesive joint during service. Sensors were placed along the centre of the bondline to reduce the effect that the embedded sensor may have on any peel stresses that may be present under loading. One of the adherend surfaces was clamped using an in-house made holding jig, and the
sensor was aligned within the prospective joint. Araldite 2015 adhesive was applied to the other adherend surface, and the two adherends were brought together sandwiching the sensor within the joint in the process.

The male ‘plug’ connector on each sensor was glued onto the outside of one of the adherend surfaces to anchor it sufficiently and to eliminate excessive forces being applied to the thin wires protruding from the joint. A 50 mm section of rubber tubing was cut lengthways and glued with 5 minute Araldite as a protective sheath over the connector plug to eliminate corrosion at the plug interface and the top opening to the tubing was sealed with the use of 5 minute Araldite. In this way, adhesive joints with embedded sensors were constructed for testing that, once cured, could be easily placed within the Octopus test apparatus. Once positioned within the machine, insulated wires with a female plug were connected to the sensor for continual monitoring of the sensor response and adhesive performance.

To measure the sensor resistance, a voltage divider circuit was utilised (Figure 5.1) so that the sensor was placed in series with a variable buffer resistor of a known set resistance. A 5V DC power source ($V_s$) was applied across the sensor and buffer resistor to ground, and the voltage between the sensor and buffer resistor was monitored over time. The current through the circuit was determined from the voltage $V_{in}$ and the known resistance of the buffer resistor, and this was used along with the voltage drop across the sensor to calculate the sensor resistance at any time during the test. Sensor resistances were recorded at 30 minute intervals to a file on the Octopus computer. This data was later compared to the baseline resistance determined during calibration and fitted to the mathematical expression generated previously to produce plots of mass uptake of water ($x$) vs time for the duration of all tests.
\[ \text{Sensor Resistance} = \frac{R_{\text{var}} \cdot (V_S - V_{\text{in}})}{V_{\text{in}}} \]

**Figure 5.1** Voltage divider circuit utilised for interrogation of the sensor resistance

Similarly to the experiments of Chapter 2, the adhesive joints with the embedded sensors were exposed to a salt water spray under static and fatigue conditions and the sensor response was correlated against the fatigue response and strength losses due to static salt water exposure.

## 5.3 Results and Discussion

### 5.3.1 Equipment optimisation

Initial problems were encountered for joints with embedded sensors where it was found that excessive corrosion occurred within the joint after several days exposure to saltwater conditions. It was found that with a constant applied voltage of approximately 2V or less across the sensor, pitting corrosion occurred both around the sensor and at
the edge of the lap shear joint at areas of high oxygen concentrations. Excessive corrosion may also be seen at the bottom of the aluminium strip where water concentrations were highest due to pooling of the sprayed water at the holding bolt. Photographic images of a typical joint may be seen in Figure 5.2. This excessive corrosion was attributed to an electrochemical cell being setup between the sensor and the adherend surface that had accelerated the onset of corrosion and was thought to be due to direct electrical contacts between the adherend and either exposed platinum wires or the conducting polymer.

![Image of sensor joint with excessive corrosion]

**Figure 5.2** Excessive corrosion of the salt water exposed embedded sensor joints

Interrogation of the sensor was thus changed so that a constant update of the sensor status was undertaken on a 15 minute basis where the voltage was applied for less than 1 second and the corresponding resistance reading was obtained before the voltage to the sensor was removed.

As a further precaution, the sensors were also coated with a poly vinylidene fluoride (PVDF) polymer as a physical electrical barrier to contact with the adherend surface. PVDF was chosen due to a low reactivity and ability to produce extremely thin porous films from standard drop cast methods. This electrical barrier coating was created from PVDF pellets (MW: 530,000) as supplied by SigmaAldrich (347078-250G). The pellets
were dissolved in lightly boiling acetone with rapid stirring. The acetone was replenished during the dissolution of the PVDF to keep the volume constant and the approximate final concentration of the PVDF in solution was 0.5g:10g acetone or 5 w/w%. When applied to a surface and dried in ambient conditions the pore size of the dried film had two main domain sizes. The larger pores were found to be a maximum of 250μm where the finer pores were approximately 1μm in diameter (Figure 5.3). Sensors with the design of Chapter 3 were dipped in the PVDF solution and allowed to dry. Several coatings were applied until the sensor tips were a continuous white colour (Figure 5.3).

Figure 5.3) Photographic images of as cast PVDF films on a) glass slide at 40X magnification (scale bar shown is 200μm in size), b) glass slide at 400X magnification (scale bar shown is 20μm in size), c) constructed humidity sensor, and d) close up of the constructed humidity sensor (scale bar shown is 250μm in size).
Calibration curves of the PVDF coated sensors were determined and it was found that the magnitude of the response seen for exposure to each relative humidity environment was unchanged compared to sensors without the PVDF coating (Figure 5.4). The measured calibration curve of the PVDF coated sensors may be seen to fit the mathematical curve fit as described in section 5.2. Even with this extra barrier coating around the sensor, the response time was only slightly slowed by approximately 30mins in the humidifying stage for the largest range tested (11 – 95% RH). The minimal change in sensor response time was attributed to the large pore size of the PVDF polymer coating.

![Calibration curves of PVDF coated humidity sensors](image)

**Figure 5.4** Calibration curves of PVDF coated humidity sensors

These sensors were placed within adhesive joints and it was found that these new design measures along with the changed sensor interrogation rate, eliminated all visual evidence of accelerated corrosion within the salt water exposed adhesive joints.
5.3.2 Examination of possible strength losses within the adhesive joints due to sensor incorporation

Adhesive joints were constructed with embedded sensors for both solvent wipe and Optimised FES pre-treatments and exposed to salt water spray for a varied length of time. Sensor data was obtained during the marine exposure and the strength of the joints was examined under zero load (static) and during fatigue cycling. The strength data of these tests may be seen in Figure 5.5 and Figure 5.6 and has been combined with data from Chapter 2 for comparison with joints without sensors.

In the salt water exposed static tests, no clear drop in tensile strength was found for the joints with embedded sensors, regardless of the pre-treatment type. These results indicate that the sensors are small enough as to not significantly affect the overall joint strength.

![Figure 5.5](image)

**Figure 5.5** Tensile strength of Aluminium 5083 Araldite 2015 adhesive joints with and without embedded sensors for solvent wipe and Optimised FES pre-treatments after exposure to salt water spray marine conditions
It was also seen that no significant loss in fatigue strength for the FES joints was seen with the incorporation of the sensor within the joint (Figure 5.6). However, the fatigue performance of the solvent wipe joints did appear to be sensitive to the sensors as several of the joints that were tested in fatigue showed a drop in fatigue strength when compared to joints without sensors. This reduced fatigue resistance is most likely due to a stress concentration at the site of the sensor that helps initiate crack growth within the relatively weak adhesive joint at the adhesive / adherend interface. This phenomenon was not seen with the FES joints due to the significantly higher fatigue strength experienced with this pre-treatment. Even so, several of the solvent wipe samples were seen to fail along the standard S-N curve and data obtained from these samples can be expected to show a reliable representation of the joint conditions during the test.

**Figure 5.6** S-N curves of Aluminium 5083 Araldite 2015 adhesive joints with and without embedded sensors for solvent wipe and Optimised FES pre-treatments for a constant exposure to salt water spray marine conditions
5.3.3 Aluminium 5083 Araldite 2015 embedded sensor response to static tests

5.3.3.1 Solvent wipe pre-treatment

Sensors that were embedded within adhesive joints that had been treated with the solvent-wipe pre-treatment of Chapter 2 were monitored for a constant exposure to salt water spray marine conditions under zero load. The standard bulk resistance curves of several sensors may be seen in Figure 5.7. As can be expected, a consistent drop in resistance was experienced for each sensor with water ingress into the adhesive joint that appeared to plateau after 24 hrs exposure. The bulk resistance was converted to a mass uptake of water within the adhesive for each sensor, and the conversion of the results of Figure 5.7 may be seen in Figure 5.8.

![Figure 5.7](image)

Figure 5.7) Bulk resistance sensor response of humidity sensors embedded in solvent wipe pre-treated Al5083 Araldite 2015 adhesive joints with exposure to constant salt water spray marine conditions.
Figure 5.8) Conversion to mass uptake of water in the adhesive for several embedded sensor solvent wipe pre-treated Al 5083 Araldite 2015 adhesive joints exposed to salt water spray marine conditions under zero load. a) Response seen over 1 week exposure, and b) Response seen over the first two days of exposure.
Initially, the mass uptake of water within the adhesive may be seen to increase with time corresponding to the drop in resistance seen in Figure 5.7. After 24 hrs exposure and at approximately 2 w/w% water in the adhesive it can be noticed that the sensor records a drop in water uptake in the adhesive joint. This response is counterintuitive to what would be expected for adhesive joints that were under a constant exposure to salt water spray, especially considering that it was found in Chapter 3 that the maximum uptake of water within Araldite 2015 was approximately 6 w/w%.

It is believed that there is another factor involved with the sensor response that is competing with the resistance drop that can be seen with water ingress. There are two possible factors that could be forcing an increase in resistance in the sensor system.

a) Swelling of the adhesive can possibly occur with water ingress that promotes delamination of the sensing polymer from the underlying sensor substrate.

b) Deprotonation of the underlying ES sensing material to that of the nonconductive PAn EB.

It is believed that the extent of swelling that would occur within the adhesive at such short time frames would be minimal, and as such the phenomenon was thought to be mainly attributed to a deprotonation that could occur with the PAn sensing material upon exposure to increases in pH, such as what can be experienced with the onset of corrosion. It is thought that after 24hrs exposure, the deprotonation that occurs with any possible corrosion related pH increases overwhelms any resistance decreases that may be due to water ingress, and the overall sensor response shows an increase in resistance and a perceived drop in water content.

After 2 or more days exposure, the response in many of the sensors for the solvent-wipe pre-treated joints becomes erratic at best. Sudden large increases in mass uptake of water that were recorded are a direct result of small changes in sensor resistance and are.
most likely due to a poor electrical connection that is shorting against the underlying adherend surface. This could again be caused by localised corrosion that has resulted in a decomposition of either the polyester coating on the platinum wires or the PAN sensing material. Due to the breakdown of the sensor response, much of the data that was acquired after 2 days exposure for solvent wipe pre-treated joints is unreliable. Even so, interesting data was obtained for exposure of shorter times and further tests were undertaken with the Optimised FES pre-treatment in an effort to further investigate the breakdown mechanisms that may be occurring within the salt water exposed adhesive joints.

5.3.3.2 FES pre-treatment

Several Optimised FES pre-treated adhesive joints were constructed with embedded sensors and were exposed to salt water spray marine conditions under zero load (Figure 5.9). With the FES pre-treated joints, a similar competing response to water ingress was observed. The sensor response indicated a drop in water concentration within the adhesive, this time after approximately 3 days salt water exposure. This change occurred at a similar water level to the solvent wipe pre-treated samples. The greater time required to reach this level is attributed to the greater surface roughness created with the FES pre-treatment that possibly hinders the water ingress directly between the adhesive and adherend surfaces.
Figure 5.9) A typical converted mass uptake of water sensor response for an embedded sensor FES pre-treated Al 5083 Araldite 2015 adhesive joint exposed to salt water spray marine conditions under zero load. a) Response seen over 3 weeks exposure, and b) Response seen over the first week of exposure.
Similar to the solvent wipe pre-treatments, the sensors showed a breakdown in response after this perceived drop in mass uptake of water and where the signal is shown to be somewhat erratic, it can be noted however, that these changes were no where near as severe as could be seen in Figure 5.8 with the solvent wipe pre-treated joints. As such, if these changes are due to corrosion related pH changes then it can be assumed that the extent of corrosion in the Optimised FES joints is to a lower extent to that of the solvent wipe pre-treated joints.

5.3.4 Aluminium 5083 Araldite 2015 embedded sensor response to fatigue tests

5.3.4.1 Solvent Wipe pre-treatment

From the static embedded sensor tests it was seen that there appears to be a critical water level within the adhesive joint that leads to significant decomposition of the sensor response. This water level is approximately 2 w/w% water within the Araldite 2015 adhesive and for solvent wipe pre-treated joints occurs at or after 2 days exposure to experimental marine conditions (or after approximately 160,000 fatigue cycles at 0.92Hz). It was hard to achieve this length of time of exposure for solvent wipe pre-treated samples due to the low applied forces necessary to achieve failure after this time frame (Figure 2.15). Many of the samples were found to fail before 2000 fatigue cycles, even for small loads, and when the interrogation of the sensor response was undertaken at a rate of one data sample every 15 minutes (or once every 828 cycles) very little reliable sensor data was obtained from the solvent wipe joints tested in fatigue.

Of the samples that did survive longer time frames, a typical embedded sensor response indicates that water enters the joint at a fast and consistent rate and reaches approximately 1.2 w/w% after 120 minutes (Figure 5.10). The maximum water level
indicated by the sensor was 1.8 w/w% at 400 minutes, after which the sensor response shows a similar perceived drop in water level to static tests, until failure at 600 mins. Throughout the course of the tests the salt water spray is held at a continuous and consistent pressure and temperature, so again it is believed that this unlikely drop in water content read by the sensor is more likely due to other factors affecting the PAN sensing material that may cause a resistance increase, such as the onset of corrosion or possibly, mechanical deformation of the miniature sensor.

![Graph](attachment:graph.png)

**Figure 5.10** Typical embedded sensor response of low load solvent wipe fatigue samples in marine conditions.

What can be seen from this response is that there is a slight degree of noise that is generated within the sensor signal at approximately 120 mins. It is believed that this is the point where sensor breakdown initiates within the joint, and as such could be the
point where corrosion actually starts adversely affecting the sensor response. At the 400 minute mark the competing response is seen to dominate and the net resistance increases, resulting in a perceived drop in water content by the embedded sensor.

What is also interesting to note is that the water ingress into the joint for the solvent wipe fatigue tests occurs at a much faster rate to the unloaded static tests. For example, within the fatigue results of Figure 5.10 it took approximately 3hrs to reach a water level of 1.5w/w% as compared to 12hrs for the static tests (Figure 5.8). This could be attributed to crack growth within the fatigue tested adhesive samples allowing for a faster ingress of water through to the embedded sensor.

**5.3.4.2 Optimised FES pre-treatment**

Several joints were pre-treated with the Optimised FES pre-treatment and were assembled with embedded sensors to examine the sensor response during fatigue testing (Figure 5.11). Like the static results, the response shows an increase in water uptake within the adhesive until about 2 w/w% water where upon the sensor response shows a drop in water content or perceived desiccation of the joint. This point occurred after fatigue cycling for between 1 and 2 days and happened faster for higher loads.

When compared to the solvent wiped samples, the water ingress into the FES fatigue samples was seen to be at a slower rate, no matter whether the solvent wiped samples were tested statically or in fatigue. This effect may be due to an easier wicking of water along the adhesive / adherend interface in the solvent wipe joints, where a low level of surface roughness and mechanical interlock adhesion was generated in the absence of any etching processes within the surface pre-treatment.
Figure 5.11) Typical embedded sensor responses of Optimised FES pre-treated adhesive joints tested in fatigue and exposed to marine conditions, a) response seen after 18 days exposure, b) response over the first 7 days of exposure.
In addition, there was an expected increase in the rate of water uptake for the fatigue loaded FES joints over the statically tested FES joints (1 to 2 days to reach the peak water level for the fatigue samples as compared to 2 to 3 days for the static samples). It is believed that the faster ingress of water for the fatigue loaded FES samples was due to crack generation within the adhesive (which may occur during cyclical loading) that allows a faster ingress of water to the underlying sensor.

Again it is believed that corrosion may be the cause for the changes in sensor response seen this time at around 1 - 2 days exposure. It can be noticed however, that throughout this change in the sensor response, and up to 9 days exposure the response encountered was much more stable than that of the long exposure times seen with the static solvent wipe pre-treated joints. It is believed that the considerable noise in the response that was manifested after this point was due to a combination of either a breakdown of the PAn sensor coating or the polyester insulation on the platinum wires, similar to the response seen after 2 days exposure in the static solvent wipe pre-treated tests.

5.3.5 Sensor Autopsy

From the static and fatigue tests with embedded sensors it was believed that the increase in sensor resistance that was seen after around 2 days exposure to salt water spray was possibly due to deprotonation of the polyaniline sensor material from emeraldine salt form to emeraldine base form. This resistance drop was not seen with sensor testing when the sensors were embedded in epoxy and immersed in salt water (Chapter 3), suggesting that it is the aluminium substrate that may be causing this change. The deprotonation process occurs with an increase in pH, which may be generated within the adhesive from the onset of corrosion of the Al substrate. To help corroborate this
theory an ‘autopsy’ was undertaken of an embedded sensor after completion of the salt water exposed static test.

Upon exposure to marine conditions and subsequent testing of the tensile strength of the joint, the embedded sensor was left attached to one of the aluminium adherend surfaces, albeit encapsulated in Araldite 2015 (Figure 5.12a). Joints that were prepared with the Optimised FES pre-treatment failed cohesively, and as such the embedded sensors within these joints were destroyed upon failure. Solvent wipe pre-treated joints failed adhesively, and the embedded sensors within these joints were found to be relatively intact upon failure.

An embedded sensor from an adhesive sample that was solvent wipe pre-treated and exposed to marine conditions was cut from the aluminium adherend after tensile testing and a cross section was taken for analysis under a Raman microscope to determine the extent of deprotonation after exposure to marine conditions (Figure 5.12 b) Details of the Raman experiment may be seen in Table 5.1.

Table 5.1) Raman experimental conditions used for mapping of sensor cross-section

<table>
<thead>
<tr>
<th>Machine:</th>
<th>Jobin Yvon Horiba HR 800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser:</td>
<td>632.8nm</td>
</tr>
<tr>
<td>Grating:</td>
<td>300</td>
</tr>
<tr>
<td>Lens:</td>
<td>10X with auto z focus</td>
</tr>
<tr>
<td>Filter:</td>
<td>0.6</td>
</tr>
<tr>
<td>Hole:</td>
<td>1100um</td>
</tr>
<tr>
<td>Slit:</td>
<td>200um</td>
</tr>
<tr>
<td>Time:</td>
<td>5 scans at 7.5s per data point</td>
</tr>
</tbody>
</table>

The image of the sensor cross-section was focussed with a 10X objective lens and a map of the Raman response across the surface was undertaken with 7.5 x 7.5µm step size (Figure 5.13).
To ensure that the laser was focussed across the cross-section of the sensor during the lifetime of the test, an auto z focus tool was used. This tool enables a re-focusing of the laser before spectral sampling to ensure the maximum signal is obtained for each position on the 7.5μm grid, and helps eliminate relative changes in intensity that may be due to surface roughness.

**Figure 5.12** a) Photos of an embedded sensor encapsulated within the Araldite 2015 adhesive after completion of static marine exposed adhesive joint testing, b) Cross-section of sensor cut from the same
The spectra seen across the mapped surface showed two typical shapes that were attributed to the presence of PAn ES and PAn EB (Figure 5.14). In Figure 5.14 b), the peaks at 1334 cm\(^{-1}\) and 1503 cm\(^{-1}\) may be attributed to C-N\(^{+}\) stretching and N-H bending of the bipolaron structure, respectively \([19, 20]\) confirming the presence of PAn ES in these regions. The absence of these peaks in Figure 5.14 a) suggests a low level of doping and conductivity in these regions signifying the presence of PAn EB. The most notable feature of each spectrum however, is the peak at wave number 1477 cm\(^{-1}\) (or absence of) that can be attributed to C=N stretching of the quinoid ring \([19, 20]\) typically encountered in polyaniline in the emeraldine base form. This peak combined with the shift of the peak from 1165 to 1162 (which can be attributed to a change from C-H bending of the benzoid ring to C-H bending of the quinoid ring \([19]\)), supports the claim that regions that have the spectrum of Figure 5.14 a) contain PAn in the EB form and those of Figure 5.14 b) contain PAn in the ES form.

**Figure 5.13** a) Image of sensor cross-section using the 10X objective lens on the Raman microscope, b) with Raman grid map overlay
Figure 5.14) a) Typical PAN EB Spectrum and b) Typical PAN ES Spectrum
Examination across the sensor surface of the relative intensity of the main peak at 1477 cm⁻¹ (peak area between wave numbers of 1400 and 1530 cm⁻¹) allows the generation of a colour map that clearly highlights the PAn ES and EB regions (Figure 5.15). It can be noted that the outlying PAn EB protective layer has stayed intact, however it can be seen that several areas within the original inner PAn ES region of the sensor have become fully de-protonated to the EB form (circled in red Figure 5.15a).

Such changes in protonation state of the sensor material can only be due to an increase in the localised pH at or within the sensor, suggesting that during service, i.e. once embedded within the adhesive joint and after exposure to marine conditions, an increase in pH was encountered.

Tanabe et. al. [21] report that pH increases can be encountered during the pitting corrosion of nitrogen rich stainless steel. Measurements were undertaken with a microelectrode tip operated in situ with scanning electrochemical microscopy (SECM). Initially, at pit formation a decrease in pH is seen, however during pit growth the formation of ammonium ions at the site of corrosion leads to an increase in the localised pH.

Park et al. [22, 23] have also seen a similar pH response within aluminium alloys that have Fe inclusions in the metal surface. In this system, the Fe rich sites cause a localised pH increase upon the initiation of pitting where a stable pH of approximately 8.5 was reached after 3 hrs of exposure to a corrosive environment. It was estimated that pH 11 was possible at these inclusions sites and measurements as high as pH of 9.5 were recorded within the course of the experiment, which were attributed to the reduction of oxygen at the pitting site.
Figure 5.15) a) Raman map of sensor cross-section, showing intensity of peak areas between wave numbers of 1400 and 1530 cm\(^{-1}\). (Highlighted areas show patches of significant deprotonation of the PAn emeraldine salt to PAn emeraldine base). b) Raman Map overlaid over original optical image. Dark blue overlay shows areas of maximum intensity of wave numbers between 1400 and 1530 cm\(^{-1}\).
This system is similar to what could be observed with the Optimised FES pre-treated samples. The acid etch solution used in this pre-treatment contains the ferric sulphate salt, which is designed to bind to the aluminium metal and cause localised areas of passivation. Such pre-treated areas can have the capacity to lower the degree of corrosion, however any localised pH increases that are instigated within the passivation process could convert PAn – ES to PAn – EB. This reaction would reduce the conductivity of the PAn based embedded sensor, and signal an apparent drop in moisture content.

For the solvent wipe samples and with the absence of the FES pre-treatment, it is unclear to whether the embedded sensor itself is acting as a site for the reduction of oxygen. However, it should be noted that the Al 5083 alloy contains several additive metals (including Fe) that could also have the capacity to reduce oxygen in the same way as described by Park et. al.

For both pre-treatment types, increases in resistance of the sensor response were seen after approximately 1.5 – 2 days exposure to marine conditions. A Raman map across a sensor cross-section showed a clear de-protonation of the polyaniline emeraldine salt sensor material to the emeraldine base form within regions of the embedded sensors from solvent wipe pre-treated samples. These changes could justify the resistance increases encountered, affecting the calibration of the humidity response calculated prior to testing of the sensor in service.

Due to the long term stability of the sensor response in Araldite 2015 with exposure to different RH environments (Figure 3.27) and with no significant shift in the calibration curve, examination of the Raman response on fresh EB coated samples in the epoxy adhesive was not undertaken. As such, these observations in relation to deprotonation of the ES material can only truly be qualified, as we cannot be absolutely sure that some of
the deprotonation effects did not occur during embedding within the adhesive joints. However, it is highly unlikely that any other mechanism is occurring to raise the resistance to the level seen in the tests – especially considering that during the sensor development the resistances were stable for sensors exposed to the Araldite 2015 adhesive, and that in the images of Figure 5.15 there are several island areas of clear deprotonation to the EB form, deep within the sensor cross section.

5.3.6 Comparison of sensor responses with strength data

In Chapter 2, the solvent wipe pre-treatment was seen to generate a great deal of variability in the strength of the as-constructed adhesive joint. For this pre-treatment, a wide degree of scatter was evident with the strength of the salt water exposed adhesive joints that were not mechanically loaded, highlighting the need for other pre-treatments. With such scatter in these strength results (Figure 5.5), correlation of time based sensor data for the unloaded solvent wipe samples back to the final as-tested strength of the joints is fraught with error. It can be noted however, that the sensors do show a breakdown in response at or before 24 hours exposure to salt water spray (Figure 5.8), which is believed to be corrosion related and may help explain the poor reproducibility of tensile strength data of the solvent wiped samples exposed to these conditions.

In contrast, the Optimised FES joints showed no clear drop in strength over the 4 weeks of testing (Figure 5.5). Similarly, correlation of the sensor data to these samples generates the simple conclusion that whatever is happening within the joint with exposure to marine conditions (corrosion or otherwise) does not adversely affect the tensile strength of the unloaded FES samples.
Interestingly, when a fatigue cycle is applied to these joints under the same environmental conditions a dramatic shift in joint strength may be seen. For the solvent wipe pre-treated joints and with a fatigue cycle of an applied 0.95MPa, an increase in noise of the sensor response was observed at approximately 120 mins exposure to the salt water spray (Figure 5.10) or after about 6500 fatigue cycles. The mass uptake of water at this point was seen to be about 1.2 w/w% in the Araldite 2015 adhesive, which equates to the same concentration of water that can be observed within the adhesive at equilibrium in a relative humidity environment of 70% (Figure 3.28).

Abel et. al. [24] found that there exists a critical relative humidity somewhere between 55 and 80\% RH (for grit blasted and degreased aluminium alloy epoxy adhesive joints) above which moisture ingress on the joint begins to show a loss in fracture toughness. These joints would have a higher degree of surface roughness than the standard solvent wipe pre-treated joints, but without chemical modification of the underlying oxides on the adherend surface, the mechanisms of joint failure would be similar.

For the solvent wipe pre-treated joints tested in fatigue there are two main mechanisms that most likely lead to adhesive joint failure:

a) Development of micro cracks through the adhesive layer that are allowed to grow and combine till a critical crack length has been achieved and catastrophic failure ensues

b) The onset of corrosion within the joint (aided by water ingress through the micro cracks) that affects the strength of the underlying oxides resulting in failure at the oxide surface.

It is believed that the water content within the joint needs to be at a critical level before corrosion reactions can occur that can adversely affect the strength of the underlying oxide layers. If, for the solvent wipe adhesive joints, corrosion has been instigated at a
water content of approximately 1.2 w/w%, any exposure to fatigue merely hastens this process through the accelerated water ingress through micro cracks generated within the adhesive.

The Optimised FES pre-treated joints were seen to be significantly stronger in fatigue than the solvent wipe joints (Figure 5.6) and each of the joints shown in Figure 5.11 failed after 1.5 - 2 million fatigue cycles. It was hoped that a clear sensor response at joint failure may be recorded for both of the examined pre-treatments, however this was not found for the FES joints due to their high fatigue strength. As such, correlation of the sensor data with a strength loss was hard to obtain as sensor breakdown was instigated before any of the samples failed. When compared to the solvent wipe joints, the increase in noise of the response occurred much later in the FES joints (after approximately 10 days exposure or 800,000 fatigue cycles) and this later time frame may be due to the conversion of the adherend oxides generated within the pre-treatment process to that of a more corrosion resistant structure. This breakdown occurred significantly later than the recorded drop in water content from the sensor (approximately 8 – 9 days later) and any corrosion that has been generated during these times was not significant enough to alter the inherently high strength of these joints.

The observable breakdown in sensor response at 10 days was seen at a point before adhesive failure, and with further calibration may be used as an indicator that excessive corrosion within the joint, or increased adhesive strains may have been generated that could lead to a loss in joint strength below some critical value.
5.4 Conclusions

Embedded moisture sensors were used to monitor the health of Al – epoxy joints exposed to a marine environment.

It was hoped that an observable increase in water content may be seen within the adhesive joint using the PAn moisture sensors embedded in the adhesive. The sensor response was found to be more complicated: initially showing an increase in water content and then a perceived drop in water content for samples of both pre-treatments, whether they were tested in fatigue or unloaded during marine exposure. This second response could be due to mechanical strains affecting the sensor response, but was also seen to be prevalent in unloaded samples, and as such were mainly attributed to a change in the localised pH conditions around the sensor. The pH changes could be due to an onset of corrosion in the joint raising the localised pH and deprotonating the PAn sensing material to the non-conducting PAn EB.

The competing response between water ingress and possible pH related resistance changes was consistent for all samples tested, and the increase in resistance was seen to dominate at a point between 1.5 and 2 w/w% water for each of the tested samples, analogous to the equilibrium water content that could be reached for this adhesive under exposure to 70 -75% RH. It may be seen then, that the onset of corrosion within these joints occurs at (or before) this water level is reached. This observation supports the findings in literature of an observable critical relative humidity that occurs somewhere between 55 and 80% RH (for grit blasted and degreased aluminium alloy epoxy adhesive joints) whereupon a loss in fracture toughness and fatigue resistance is observed [24, 25]. It is once this water level has been surpassed that hydration of the underlying oxide inures, degrading the oxide strength and enabling failure to occur within the oxide layer itself at the adhesive/adherend interface [24, 26].
This critical water level was reached in a shorter time frame for solvent wipe samples when compared to the Optimised FES pre-treated samples and was attributed to the greater surface roughness of the FES samples hindering the water ingress directly between the adhesive and adherend surfaces. Secondly, the unloaded FES pre-treated samples retained their bond strength even after a measured moisture ingress and pH change. Despite the differing rates of moisture ingress and corrosion, the embedded sensor responses suggest that both the solvent wipe and FES treated samples appeared to react similarly to exposure to the salt spray. However, the FES treated samples showed little change in bond strength while the solvent wiped samples showed considerable loss of strength. These observations suggest that the FES treatment produces an adhesive-adherend interface that is significantly more resistant to moisture and/or pH changes than solvent wiped samples.

The data obtained from these sensors could be a useful indicator that harmful localised environmental conditions have been generated within the adhesive joint in service that could be of concern to the underlying joint strength. With further work it may be found that it is possible that the breakdown of the sensors could be used as an indication point that excessive corrosion may have occurred within the joint and that joint failure is imminent within a certain time frame from the record of such a response.

To properly achieve and calibrate this phenomenon it would be necessary to test joints with a pre-treatment that gave an intermediate joint strength for unloaded joints, and showed a stable strength loss upon marine exposure such that a reliable correlation of strength loss for different marine exposure times could be generated. With this system, more solid conclusions could be made between the sensor response and modes of degradation within the adhesive joint.
5.5 References


Chapter 6

Conclusions
Historically, the use of adhesives within the marine industry has been limited due to the effects that salt water can have on the adhesive joint strength. If the progress of marine degradation can be properly monitored and better understood then greater confidence may be imparted with the use of adhesives for marine structures, and with adhesive incorporation, the potential benefits of improved weight reduction, speed of manufacture and reduced cost may be realised. The work in this thesis was undertaken to develop miniature sensors that may be embedded within the adhesive bondline so that a continual health monitoring of the adhesive joint in service may be undertaken and a better understanding of the mechanisms of adhesive breakdown in marine environments may be achieved.

For such an approach to be successful it was necessary to ensure that the final sensors were of small enough dimensions to not hinder the performance of the adhesive joint. As such, sensor substrates were manufactured from 125 μm polyester insulated platinum wires for dip coating of thin films of chemically polymerised conducting polymer sensing materials. Various conducting polymers were investigated for their ability to sense localised environmental conditions such as the presence of water and pH changes - recognised factors that have been linked to adhesive joint degradation via the instigation of adhesive plasticisation, delamination and the onset of corrosion.

Humidity sensors were manufactured from polyaniline (PAn) based materials due to the high conductivity changes that can be seen with PAn in the presence of water. Two PAn composite blends were investigated of varied w/w% PAn concentrations for their ability to produce a reproducible resistive response to the presence of water. PAn PVA polymer blends containing PAn concentrations of 5, 10, 20, 30, 40, 50 and 60 w/w% were
developed that could be easily cast from 1M HCl and PAn (P(BuA-co-VAc)) blends with PAn concentrations of 15 and 30 w/w% were also developed that could be readily cast from dichloromethane.

With increases in humidity, PAn / PVA sensors showed a competing response between the resistance drop due to water ingress into the PAn rich domains and resistance increases from swelling of the PVA rich domains. The 5 w/w% PAn blend showed a large change in resistance with changes in humidity however resistances were extremely high severely limiting any practical use. Due to the competing response, blends of 10 w/w% or higher showed little change in resistance over much of the humidity range and as such the PAn PVA sensors were deemed unsuitable for use as sensing media for determination of water concentration.

The best response was obtained from the 15 w/w% PAn (P(BuA-co-VAc)) polymer blend. Sensors were constructed by first dip-coating the substrate in PAn P(BuA-co-VAc) ES polymer followed (after drying) by dip-coating in PAn P(BuA-co-VAc) EB polymer. The sensors had an exponential response and showed high sensitivities with an 800% resistance change over the entire 95% change in RH. For the largest change in humidity (from 3 to 95% RH) the sensors took approximately 4 to 5 hours to reach 90% of the equilibrium resistance on humidifying and 35 hours was required to reach 90% of the equilibrium resistance on desiccating.

The best pH sensors were manufactured from a processable polymer blend made from poly 3,4 -diethoxythiophene (PEDT) and poly vinylidene fluoride (PVDF). The blend was able to be cast from an acetone solvent and had an approximate PEDT content of 11 w/w%. The sensors showed an almost linear resistive response between pH 5 and pH
11 with an approximate 350% change in resistance when increasing the pH from 1 to 13. However, hysteresis was observed with cycling between acidic and basic conditions and significant drift was encountered over long term cycling. Further problems were also encountered with the embedding of the sensor in the Araldite 2015 test adhesive, and as such these sensors were abandoned from further study.

To examine the humidity sensor performance in service, Aluminium 5083 Araldite 2015 adhesive joints were constructed in a lap-shear configuration with two different pre-treatments of an Optimised FES and Acetone solvent wipe. Joints were exposed to a constant temperature salt water spray and the lap-shear tensile strength of the adhesive joints was tested after varied time of exposure for joints with and without embedded sensors and for both pre-treatment types. For the same salt water exposure conditions, joints were also exposed to a 0.92 Hz fatigue cycle with different applied loads and S-N curves were generated for joints with and without sensors for both pre-treatments.

It was found that the average dry tensile strength of the solvent wipe and FES joints was 10.3 +/- 1.3 MPa and 16.2 +/- 0.3 MPa respectively. The tensile strength of the solvent wiped joints showed a steady decrease with exposure to salt water spray such that after 21 days exposure time, joint strengths had dropped to 50% of the strength of the unexposed samples. In comparison, the FES samples showed no loss in joint strength even after 23 days exposure to salt water spray. The difference in joint performance between the two pre-treatments was attributed to the degree of surface roughness of the FES samples enabling a greater degree of mechanical interlock between the adhesive and substrate.
Solvent wiped joints that were tested in fatigue showed a marked decrease in strength when exposed to marine conditions. It was shown that for the same applied fatigue loads joints that were tested ‘dry’ lasted approximately 50 times longer than joints that were exposed to a salt water spray. This dramatic change was somewhat uniform across the whole S-N curve even for short exposure times less than 1 day and this accelerated decay of joint strength was attributed to the generation of micro-cracks during the fatigue process that allowed for the faster ingress of water into the joint further accelerating the breakdown seen with static tests.

The greater strength with the FES joints was further highlighted with the fatigue tests. When exposed to marine conditions, the FES joints were seen to last up to 4 orders of magnitude longer than solvent wiped joints and no failure was seen with the ‘dry’ FES joints at all within the constraints of the testing apparatus.

The solvent wipe joints were too weak to be able to measure the 10 million cycle fatigue strength in both wet and dry conditions. For this pre-treatment the highest recorded fatigue lifetime was seen in dry conditions, and was less than 200,000 cycles for an applied load of approximately 1.5 MPa. The 10 million cycle fatigue strength of the marine exposed FES joints was hard to find due to consistent failure of the aluminium adherend at or before 1 million cycles, and not the adhesive joint. However, through extrapolation of the S-N curve, the 10 million cycle fatigue strength of the FES joints tested in marine conditions was estimated to be approximately 1.3MPa.

It was hoped that the embedded sensors may be used to ascertain a critical water content within each of the adhesive systems that might suggest the onset of adhesive failure, however it was seen that the embedded sensors became unstable after approximately 24
hours salt water exposure. The change in stability of the embedded sensor with static tests was seen after water uptake in the adhesive of 2 w/w%, analogous to an equilibrated environment of approximately 75% relative humidity. It was thought that for each of the tests the sensor breakdown was most likely due to a combination of three main factors:

a) swelling of the adhesive with water ingress, promoting delamination of the sensing polymer from the underlying sensor substrate

b) further deprotonation of the underlying ES sensing material to that of the non-conducting PAn EB

c) the generation of micro cracks and internal strains within the adhesive system (especially within the fatigue tests) that mechanically affected the performance of the embedded sensor response

It was discovered that with full immersion of Araldite 2015 adhesive films in water, the maximum uptake of water that was achievable was approximately 6 w/w% which took multiple weeks to reach stability. Due to the short time frame encountered before sensor breakdown in static tests of less than 24 hours it could be concluded that a) is not the most likely cause of sensor failure. Likewise c) is less likely to occur due to the absence of any applied external stress during salt water exposure during static tests.

It may be postulated then, that if b) is the likely cause of sensor breakdown, the sudden change in environmental conditions that could initiate a net increase in resistance (and reduction in the perceived mass uptake of water) by means of deprotonation would be an increase in pH. This is similar to what is known to occur at the onset of corrosion. This deprotonation was confirmed by examination of the cross-section of an embedded sensor
after exposure to marine conditions using a Raman microscope. It was found that a significant proportion of the PAN sensor material had been converted to the EB form.

Abel et. al. [1] found that there exists a critical relative humidity somewhere between 55 and 80% RH (for grit blasted and degreased aluminium alloy epoxy adhesive joints) above which moisture ingress on the joint begins to show a loss in fracture toughness. The current study shows indications that corrosion had possibly been initiated by 70 - 75% RH at the site of the sensor which would support the claims of Abel et. al. and may help explain the significant drop in fatigue strength that was seen with the solvent wiped joints after only 1 day exposure.

The unloaded solvent wipe pre-treated joints were seen to show a high variation in the strength for exposure to marine environments. With such scatter in these strength results, correlation of any time based sensor data to the joint strength is hard to quantify. The sensors show a breakdown in response at or before 24 hours exposure to salt water spray, which was attributed to corrosion, and could be an indicator that significant deterioration of the joint strength has resulted.

Over 4 weeks of testing for the Optimised FES pre-treated joints no clear drop in joint strength was seen after exposure to marine conditions. The same perceived drop in water content within the adhesive was found for these samples and it was concluded that whatever is happening with the FES joint with exposure to marine conditions (corrosion or otherwise) does not adversely affect the tensile strength of unloaded samples. The main reason for this was attributed to the higher degree of surface roughness generated
within the FES pre-treatment that improved adhesion through mechanical interlock between the adhesive and adherend.

The Optimised FES pre-treated joints were seen to be significantly stronger in fatigue than the solvent wipe joints and in comparison, it can be seen that the increase in noise of the sensor response occurred much later in the FES joints (approximately 8 – 9 days later) than those with the solvent wipe pre-treatment. This was thought to be due to the conversion of the adherend oxides generated within the pre-treatment to that of a more corrosion resistant structure. The critical water content within the adhesive (when the dominance of the sensor response shifted from humidification to possible pH changes) occurs at a similar level of 1.5 – 2 w/w% water, and was not determined by pre-treatment type. As such, there is a time frame in the FES samples of approximately 7 days where if corrosion had occurred, no significant drop in joint strength was seen. It was believed that any corrosion that could have been generated during these times was not significant enough to alter the underlying joint strength that is dominated by the high degree of surface roughness and improved strength through mechanical interlock adhesion.

There is no easy way to know exactly what is happening with the breakdown of adhesive joints during exposure to marine conditions. This study has attempted to highlight correlations with adhesive breakdown in Araldite 2015 Aluminium 5083 adhesive joints upon exposure to marine conditions, through the use of developed PAN based humidity sensors that were embedded within the adhesive bondline. The findings show that there is a critical water content within the adhesive joint of around 1.5 - 2 w/w% water that suggest the possible onset of corrosion at the adherend surface. It would have been
advantageous if various other sensors that were available commercially could have been incorporated into the bondline to obtain further information that may help support the findings of the research, however due to the small spatial constraints encountered within the adhesive bondline (< 200 μm), this was not possible. Significant further work incorporating surface analysis and various impedance techniques could be utilised to prove that the sensor response seen is truly due to pH changes linked with the onset of corrosion, however this is outside the scope of the present study.

The great benefit with the developed sensors is the capacity to be able to tell whether the adhesive joint has reached this critical water level and that corrosion has been instigated. Such sensors may be useful as a health monitoring tool highlighting a possible loss in joint strength, however these sensor tools are limited in that they cannot determine the extent that corrosion has occurred nor can they be used to determine exactly what corrosion reactions are taking place.

Further work is needed with these sensors to show that the development of a multi-sensor array can prove the concept that the humidity sensors developed may be used to pinpoint areas of high water concentration and possibly the onset of corrosion within specific test areas in large adhesive joints of different geometries. Fatigue testing undertaken on the adhesive joints exposed to environments with a controlled relative humidity level could be utilised to more accurately predict critical environments that promote adhesive failure. Such experiments could also be utilised to find a relationship between the time of exposure to a critical water level and the degradation in adhesive joint strength. This data would then enable these small sensors to be used to make a prediction of the joint strength at any time, based on the water level history of the adhesive joint in service.
There is a growing trend in the need for technologies that incorporate miniature sensors. In this work, minimising the size of the sensor created the capacity to fit the sensor within small spatial constraints, such as within the bondline of adhesive joints. However, other advantages may be obtained from sensor miniaturisation that include reduced material costs, smaller power consumption and the capacity to fit multiple sensors into the same spatial area. These factors are required within applications such as Remote Autonomous Monitoring [2-4] (small, cheap, low power devices for wireless monitoring), and Lab-on-a-chip devices [5] (small, autonomous analytical sensing systems).

This project utilised the thin film processability of various conducting polymer blends to enable significant miniaturisation of the sensor for embedding within an adhesive joint. The use of such technology for sensors has been alluded to for a number of years but there is very little reported evidence of such sensors being designed, constructed and used in service. Through this work it was seen that miniature sensors may be developed with the use of conducting polymer blends, and reliable sensor responses may be achieved that can provide a meaningful signal, even when tested within harsh environmental conditions. The work covered critical aspects essential to reliable sensor design such as the testing and tailoring of the polymeric material's sensor response to the application, as well as the design and construction of reliable electrical connections and interrogation of the sensor response. This project has demonstrated methods for incorporation of conducting polymer based materials into extremely small sensing technologies and may help lay the platform for the use of these materials in other leading edge applications requiring sensor miniaturisation, such as within Remote Autonomous Monitoring and Lab-on-a-chip devices.
6.1 References


