ABSTRACT
With the increase in use of composite materials on primary and secondary structures of commercial and military aircrafts, acceptable long term performance of adhesively bonded composite joints (ABCJs) has become an increasingly important factor when determining the airworthiness of an aircraft. Though significant amount of research has been conducted on the initial bond strength characterization of ABCJs, improvements in procedures for evaluating bond strength durability of these materials could significantly aid in predicting long term structural integrity. This study is aimed to develop a durability test procedure that can be used for evaluating the long term strength durability of ABCJs. It includes the investigation of undesirable bonding conditions by characterizing the initial performance of the bonds at various contamination levels and then characterizing the durability performance with similar surface conditions. An extensive literature review on existing testing procedures for bond strength durability was conducted and conclusions of the advantages and shortcomings of the tests were reached as to their applicability to ABCJs. A detailed testing procedure including specimen configuration and fixtures to be used is presented. Two different peel plies (nylon and polyester) are used in the manufacture of the coupons to determine their effects on long term durability. The test includes two stages. First, a set of specimens are rapidly aged inside an environmental...
chamber while submitted to a fully reversed fatigue load. The specimens are then tested for bond strength using a double cantilever beam test configuration. Results are compared with baseline specimens that have not been mechanically fatigued or environmentally aged. Preliminary results of durability are presented and include fracture toughness and mode of failure of the bonds. Additionally, surface characterization using a solid-state electrochemical sensor is conducted and results are presented.

1. INTRODUCTION

Composite materials offer advantages over conventional materials used in aerospace structures due to their high strength-to-weight ratio. However, joining of composite materials often requires the use of adhesive bonding and classical bonding techniques (riveting and bolting). The requirement of having a dual mechanism to ensure joint reliability reduces the benefits of using composites on aircraft structures.

The level of safety as governed by the strength and durability of bonded structures is of paramount importance to the manufacturers and consumers. Bond durability can be characterized by a bond’s ability to retain its initial strength after being subjected to loading and/or other external conditions over time. For adhesive bonds in aircraft structures, the external conditions are primarily elevated temperatures and humidity. While significant gains have been made in understanding of the science of adhesively bonded composite materials, a better understanding of this phenomenon including the identification of key processing parameters, important material characteristics and their effect on long-term durability of bonded composite structures requires further investigation. Significant research efforts in industry and academia have focused on
characterizing the initial bond strength of these materials. Lap shear and double cantilever beam (DCB) tests are typical test methods used to quantify the strength of the initial bond. Criteria and acceptance, however, for long-term durability has yet to be established.

The primary focus of this work is to develop a method to test the long-term durability of adhesively bonded composite joints. The technical approach and layout of this document is as follows:

- Overview of existing methodologies and strategies used for testing short and long-term durability of bonded joints
- Specimen preparation
- Surface characterization methods
- Accelerated bond degradation
- Experimental testing (DCB) and surface characterization results

1.1 Literature Review

The literature review presented in this section provides a brief overview of research conducted on the durability of adhesive bonds and is intended to provide rationale for the suggested testing approach discussed in later sections. For a complete review, see Reference [1]. The review includes short and long-term durability tests and any modifications performed to enable the study of adhesively bonded composite joints. The tests typically have focused on DCB, wedge and lap-shear tests.

The DCB test is a standardized experimental method that was established to determine the interlaminar fracture toughness and delamination growth onset resulting from a Mode I loading
condition (ASTM D5528, D6115, D3433). This test provides data for the energy release rate, crack growth length, and also provides the dominant mode of failure. Generally, conditioning of adhesively bonded DCB specimens prior to fracture testing involves exposure of the specimens to a harsh environment. A few of these studies that address durability for adhesively bonded composites are briefly described in this section.

DCB tests can be used to evaluate a number of adhesive bonding process parameters including surface preparation methods, precure moisture in peel ply [4] and contamination effects [5]. Adams, et al.[6], Xu, et al.[7], and Datla, et al.[8], all studied the effects of temperature and humidity of metal or conductive laminates on strain energy release rates obtained using DCB tests or slight variations of DCB testing. Johnson, et al.[9], used DCB specimens to evaluate bond durability for composite/metal joints by exposing specimens to hot/wet environments prior to fatigue testing. Kinloch, et al. [10], used aluminum substrates in tapered DCB specimens to evaluate simultaneous mechanically loading and environmental aging. Smith and Pothakamuri [11] created a frame that allowed for similar testing conditions and evaluated the durability of adhesively bonded composite substrates.

The wedge test consists of an adhesively bonded metal specimen that is loaded by forcing a wedge into one end of the laminate which results in a tensile stress in the region near the crack tip (Mode I). The initial crack arrests when the tensile stresses are just below tensile ultimate for the adhesive. That leaves the interface under extreme stresses so any degradation of the interface, such as by hydration, will result in interfacial failure [12]. The wedge test is used to evaluate durability by subjecting the wedged specimens to an accelerated aging environment. A
significant advantage is the fact that multiple specimens can be easily fabricated and subsequently subjected to a variety of environmental conditions. Because of its potential to evaluate durability of adhesive bonds, previous studies have adapted the wedge test to evaluate bond strength durability in composite joints. Hart-Smith [3] recommends that wedge-crack specimens be made from unidirectional (0°) tape plies oriented in the longitudinal direction of the specimen to prevent diversion of the delamination due to the weak interlaminar tension in other fiber orientations. Adams, et al. [6], used metal adherend specimens in high temperature water to evaluate various durability test methods including DCB tests and variations of the wedge test (forced wedge test). Bardis and Kedward [2] conducted static wedge tests with partially wedged composite samples in water, sulfuric acid/water solution and sodium hydroxide solution.

One of the most utilized shear tests for assessing initial adhesive bonds strength is the lap shear test (ASTM D1002). For a single lap, the tension force results in a shear (Mode II) and peel (Mode I) load between the substrates and the adhesive. The use of lap shear test for evaluating bond quality has generated controversy among authors. Davis and Tomblin [13] conducted a survey of 20 organizations that indicated 77 percent of designers use lap-shear test results to establish design allowables. However, the authors indicate that its use is not considered best practice. Furthermore, Bardis and Kedward [2] found that “lap shear tests provided limited verification of bonded assembly reliability, especially when considering prolonged loading and environmental conditions”.

The effect of test temperature and prebond moisture on carbon fiber reinforced polyester composites was investigated by Parker [14,15,16] using single lap joints. Cyclic environmental ageing was studied by Xu, et al. [7], using metal to composite adherends in lap shear tests. Other researchers have extended the preconditioning to include mechanical loading in addition to exposure to harsh environments. Briskham and Smith [17] evaluated both metal to metal adherends and metal to composite adherends using lap joints with cyclic mechanical loads in a hot water environment. Smith and Pothakamuri [11] studied the effects of creep loading in a hot wet environment using various peel ply and moisture conditions. It should be noted that their tests were conducted using thick wide lap shear coupons.

1.2 Proposed Methodology

The general approach for achieving a better understanding of durability performance starts with developing a testing protocol that can reliably evaluate the durability of adhesively bonded composite joints. Based on information obtained in the literature review, bond durability assessment would optimally utilize testing with specimens that have been preconditioned with a harsh environmental while simultaneously exposing the specimen to mechanical loading. The preconditioning of specimens prior to fracture tests, emulates the conditioning of bonded components in service. The application of this type of conditioning presents challenges in establishing an appropriate experimental setup.

The proposed methodology focuses on using DCB coupons that are mechanically fatigued while exposed to harsh environmental conditions. Fracture toughness will be determined for specimens that have been preconditioned with both the mechanical loading and exposure to the harsh environment. Comparisons will also be made with the fracture toughness of baseline
specimens and specimens that are exposed to just the mechanical loading or to the environment. Correlations between each aspect of the preconditioning can then be established. This type of approach also allows for various surface preparation methods to be investigated as well as the effect of bonding with undesirable conditions (i.e. contamination) on long-term durability.

The mechanical loading will utilize a composite bonded specimen geometrically similar to those found in ASTM D790 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials). The specimens will be placed in a fixture that supplies support at the ends and is cyclically loaded at the center using a pneumatic cylinder to control the force/displacement imposed. This will allow for the use of different test frequencies and amplitudes. The magnitude of the shear load distribution of the specimen will remain constant along the specimen and the tension or compression loads at the bondline approaches zero. This configuration challenges the interlaminar shear strength at the centroid of the specimen and can be adapted to fit within an environmental chamber.

2. EXPERIMENTATION

2.1 Specimen Preparation and Experimental Testing

For this study, DCB specimens were fabricated and tested. The specimens were designed to resemble those specified in ASTM D5528 (Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites) with the use of adhesively bonded laminates. This modification allows for the calculation of Mode I fracture toughness of the adhesive bond. The material used to manufacture specimens was a unidirectional carbon epoxy prepreg system, DA 411U 150, obtained from Adhesive Prepregs for Composite Manufactures. The adhesive used in the bonding process was a film adhesive.
AF163-2U from 3M. The curing process for fabrication and bonding was conducted in accordance with the manufacturer’s specifications. The composite laminates were bonded using secondary curing.

Effects of surface preparation were studied by evaluating laminates manufactured with 3 types of peel ply: a nylon and a polyester peel ply from Fibreglast Developments, and the 60001 polyester peel ply from Precision Fabrics. Half of the specimens fabricated were surface treated prior to secondary bonding using a 60 grit Al$_2$O$_3$ sandpaper [18]. Composite panels were manufactured by bonding two 12 ply laminates with all 0° ply orientation. Two unsupported adhesive films were used as the adhesive. The laminates were cured at 350°F and the secondary bonding was performed at 250°F. The laminates measured approximately 1 ft in length by 1 ft width.

After the bonding process was completed, each of the panels was cut to define 8 specimens per panel, each specimen measuring 9 inches in length by 1 inch in width. With the aforementioned dimensions, remaining material from each panel was utilized in the surface characterization study. Specimens manufactured with each peel ply were separated into two groups: baseline specimens that were not preconditioned and specimens that were exposed to a harsh environment. Future work will include additional preconditioning with the use of the fatigue fixture.

The specimens were environmentally aged by placing them inside a chamber for 21 days having controlled temperature and humidity conditions (50°C and 95% RH). The environmental chamber used was a Thermotron 2800. For all specimens, two 1.5 inch wide steel hinges were glued at
one end to provide grips necessary for DCB testing on a universal testing machine (UTM). The UTM utilized was an 858 Table Top System manufactured by MTS. The DCB testing were conducted using a loading rate of 2.5 to 5.0 mm/min. Changes in loading rates on this range did not provide any effect in fracture toughness results. The crack length was measured with a traveling microscope and the specimens were marked for measuring the crack growth according to the ASTM 5528. Figure 1 illustrates a typical DCB test conducted in this study.

Figure 1. DCB testing of bonded composite laminates.

In addition to DCB testing, the bondline thicknesses of the specimens were inspected to determine the variability. As mentioned previously, two unsupported adhesive films were used in the manufacturing of the specimens. All specimens were manufactured using two high finish plates for tooling. Figure 2 shows optical measurements taken at three different locations of the bondline: 2.5 cm, 3.0cm, and 3.5cm from the pre-crack. Figure 3 shows the bondline distribution for all specimens. Generally, all specimen groups had larger bondline thicknesses near the center of the panel and lower thicknesses toward the edge. However, a significant amount of variability in bondline thickness was observed.
2.2 Fatigue Apparatus

The proposed experimental specimens consist of DCB coupons manufactured with two rectangular carbon fiber laminates of equal dimensions bonded to form a similar specimen described in the ASTM D5528-0. The specimen will be placed inside an environmental chamber where it will be subjected to a cyclic 3-point bending load. Once the number of desired loading cycles is reached, the specimen will be placed on a UTM and tested for bond fracture strength (Figure 4).
The material used to fabricate the initial specimens is a unidirectional carbon epoxy prepreg system - DA 4518U (350 F cure), bonded with a Scotch Weld Structural Adhesive Film - AF 163-2 (250 F cure). The laminate layup was defined based on the mechanical properties of the adhesive. Table 1 shows the fatigue properties of AF 163-2 provided by 3M. Maximum loads at the surfaces and required forces to cause the desired shear stress at the bond line were calculated and are also provided in Table 1.

### Table 1. Mechanical Fatigue Properties of AF 163-2

<table>
<thead>
<tr>
<th>Max Stress (psi)</th>
<th>Avg. Life (Cycles)</th>
<th>Force Req. for a 30 Ply 9 inch long specimen (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4500</td>
<td>1.58 x 10^4</td>
<td>-</td>
</tr>
<tr>
<td>4000</td>
<td>5.28 x 10^4</td>
<td>-</td>
</tr>
<tr>
<td>3500</td>
<td>4.75 x 10^5</td>
<td>420</td>
</tr>
<tr>
<td><strong>3000</strong></td>
<td><strong>2.67 x 10^6</strong></td>
<td><strong>360</strong></td>
</tr>
<tr>
<td>2200</td>
<td>1.03 x 10^7 + (No failure)</td>
<td>264</td>
</tr>
</tbody>
</table>

Table 2 provides the displacement and force requirements as a function of number of plies. These parameters were obtained by requiring that a 3000 psi shear load was achieved at the bondline. Based on this table, the specimen design resulted in 24 plies of a unidirectional
laminated (0.14 in thick) with a reasonable force load of 288 lbs and a displacement of 0.9 inches.

Table 2. Displacement and Force Requirements vs Number of Plies

<table>
<thead>
<tr>
<th># Plies</th>
<th>Stress at surface (psi)</th>
<th>Force require by piston (lb)</th>
<th>Displacement (in)</th>
<th>70% displacement (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>136.36</td>
<td>264</td>
<td>1.53</td>
<td>1.07</td>
</tr>
<tr>
<td>24</td>
<td>125.00</td>
<td>288</td>
<td>1.28</td>
<td>0.90</td>
</tr>
<tr>
<td>26</td>
<td>115.38</td>
<td>312</td>
<td>1.09</td>
<td>0.76</td>
</tr>
<tr>
<td>28</td>
<td>107.14</td>
<td>336</td>
<td>0.94</td>
<td>0.66</td>
</tr>
<tr>
<td>30</td>
<td>100.00</td>
<td>360</td>
<td>0.82</td>
<td>0.57</td>
</tr>
</tbody>
</table>

The fatigue fixture that was developed and will be used in future conditioning of the DCB specimens is shown in Figure 5. The fixture, which can be placed into an environmental chamber (Figure 6), was designed to mechanically load DCB specimens with a fully reversible thee point bending type load. By orchestrating the design of the DCB specimen in conjunction with the design of the fixture, it was possible to determine the specimen dimensions and fixture displacement/load parameters that will provide a close-to-even shear load along the bondline without exceeding the specimens’ tensile and bending yield parameters. The bending of the specimens is caused by a hydraulic powered piston driven by computer controlled rapid acting valves. This allows the use of different loading frequencies, pressures and pressure profiles. The fixture can cyclically load up to four specimens and has a footprint that measures 4 ft x 2 ft. The fatigue fixture was designed to provide a 1 inch maximum deflection at half the length of each specimen. Using finite element analysis, it was determined that this configuration provides a
relatively uniform shear load at the bondline of approximately 3000 psi, requiring 288 lb of force per specimen.

Figure 5. Fatigue fixture for DCB specimens.

Figure 6. Fatigue fixture in environmental chamber.

2.3 Laminate Surface Characterization Using a Solid-state Electrochemical Sensor

Since this study considers various surface preparation methods, effort also focuses on trying to understand and quantify differences in the preparation methods.
A solid-state electrochemical sensor (ECS) has been developed at the University of Miami and Florida International University to measure changes in electrochemical activity across composite surfaces [19,20]. Differences in the measurements reflect levels of electrochemical activity or lack of activity due to contamination. Measurements can be obtained by conducting cyclic voltammetry (CV) or electrochemical impedance spectroscopy (EIS) tests.

The ECS has undergone a variety of evaluations and improvements over the past few years. Recently, modifications to the design of the sensor have been implemented and a schematic of the new sensor is illustrated in Figure 7. With this design, the internal resistance of the ECS is significantly reduced and both CV and EIS tests can be conducted using the same sensor. This was not the case in the previous designs.

![Figure 7. Schematic of the solid-state electrochemical sensor.](image)

3. RESULTS

3.1 Double Cantilever Beam Tests

Various sets of coupons were manufactured with each peel ply – some were preconditioned in an environmental chamber for three weeks at 50 C and 95% relative humidity and others were
tested without exposure. A subset of each surface ply type was sanded with 60 grit Al$_2$O$_3$ sanding paper to provide additional information on surface treatment. Figure 8(a) shows strain energy release rates for baseline specimens (not environmentally aged) and Figure 8(b) shows results that were subjected to the environmental aging.

![Figure 8](image)

Figure 8. $G_{IC}$ values for (a) baseline specimens and (b) environmentally aged specimens.

Figure 8(a) shows that for the as tooled specimens, the 60001 polyester peel ply provided the largest $G_{IC}$ values. Sanded specimens had an improved response; however it is not clear why the nylon sanded specimens increase was so dramatic. Figure 8(b) shows the same trend for the environmentally aged specimens. It should be noted that for the environmental conditions imposed, there was not a significant reduction in fracture toughness. It is likely that the amount of time of exposure should be increased to see a significant change.

The majority of specimens what were bonded “as tooled” resulted in adhesion failure. A few of those manufactured with the polyester PF60001 peel ply showed a mix mode failure (adhesion/interlaminar) with the adhesion failure being the dominant mode. All specimens that
were sanded with 60 grit sandpaper resulted in 100% interlaminar or a mix of interlaminar/adhesion failures with interlaminar failure being the dominant mode. Figure 9(a) shows an “as tooled” specimen prepared with the nylon peel ply. Figure 9(b) shows a specimen manufactured with the nylon peel ply and sanded prior to bonding.

![Figure 9](image.png)

Figure 9. Fracture surfaces of DCB coupons with no environmental aging and prepared with nylon peel ply: (a) as tooled (b) sanded.

Figure 10 shows environmentally aged specimens prepared with polyester 60001 peel ply. Figure 10(a) show the fracture surface as tooled and Figure 10(b) shows the fracture surface of a specimen sanded prior to bonding. Similar to the specimens that were not environmentally aged, the specimens that were bonded “as tooled” demonstrated dominant adhesion failure. The specimens that were sanded prior to bonding exhibited dominant interlaminar failure with adhesion failure toward the center of the width of the specimens. This can be an indicator of the degradation in the interlaminar fracture toughness resulting from the hydrothermal effects introduced by the harsh environment. It should be noted that no cohesion failures were obtained for the combination of materials used. This is likely due to low interlaminar fracture toughness of the DA 411U 150 prepreg from APCM.
3.2 Electrochemical Sensor Tests

All solid-state electrochemical sensors were fabricated using a Ag|AgNO_3 electrode as the working electrode, a Ag|AgCl electrode as the reference electrode, a platinum sheet as the counter electrode, and a piece of Nafion 117 film as the polymer electrolyte/seperator. The counter and reference electrodes were placed on the same side and the working electrode was placed on the opposite side of the Nafion film. The assembly of the electrode chemical sensor was placed on top of the surface of composite laminate specimens. The working electrode was replaced after each successive test. CV measurements were conducted with a scanning rate of 10 mV/s and are provided in Figure 11 through Figure 13. For all as tooled specimens, only a few small negative current peaks were observed. The negative peaks can correspond to an active surface or contamination. The active surface consists of dense dangling bonds (unsatisfied bonds) that tend to form a stronger interface between adherend and adhesive. Dangling bonds that are caused by surface activation including polishing and laser treatment have the propensity to receive electrons. Under a specific negative potential, the electron flow for filling the dangling
bond can be revealed in the CV measurements as a negative electrical current peak. However, there are numerous substances that are electron acceptors such as nitrates, sulfates, and species containing iron (III) and manganese (IV). It is clear that if contaminates consist of these species, negative current peaks will appear in the CV measurements.

It was observed that the magnitude of the negative current peaks was less than 0.005 A. However, after sanding and nitrogen blowing, there was a significant increase in the number of negative peaks. The magnitude of current peaks were as high as 0.09 A. Since the sanding and nitrogen blowing process results in a cleaner surface, it is likely that the peaks indicate a more active surface. In a comparison among the as tooled specimens, the Fiberglast polyester peel ply specimens had the smallest negative peaks. Based on these observations, the Fiberglast polyester specimens were either less contaminated or less active relative to the Precision Fabric 60001 and the Fiberglast nylon specimens.

![Graphs showing CV measurements for Precision Fabric 60001 polyester peel ply specimens.](image)

(a) as tooled  
(b) sanded

Figure 11. CV for Precision Fabric 60001 polyester peel ply specimens.
An approach for testing the durability of adhesively bonded composite joints is proposed after reviewing relevant literature available and applying lessons learned from the review. This includes the conditioning of DCB specimens in an environmental chamber while simultaneously fatiguing the adhesive bond. A fatigue fixture has been designed and assembled for this use. Initial data is presented that includes the conditioning of specimens in an environmental chamber.
Six sets of specimens were generated for DCB testing. This included specimens manufactured with Fiberglast polyester and nylon peel ply and Precision Fabric 60001 polyester peel ply. Half of each peel ply set was abraded with sandpaper prior to bonding. Additionally, a portion of each resulting sets was conditioned in an environmental chamber. DCB fracture toughness tests were conducted on all specimens. Results demonstrate that the specimens manufactured with PF60001 yielded the largest fracture toughness for the as tooled specimens that were not environmentally aged. All the sanded specimens resulted in higher $G_{IC}$’s than theirs as tooled counterparts including those that were environmentally aged. In general, the environmental aging did not yield a significant degradation of the $G_{IC}$’s for the time of exposure utilized. This suggests that significantly longer exposure time will be needed in future testing. It is interesting to note that after sanding, specimens prepared with the nylon peel ply showed significant improvement in its fracture toughness.

The modes of failure were either adhesion or adhesion/interlaminar. Results indicate that a stronger matrix needs to be utilized to obtain cohesion failures. All specimens that were tested as tooled, had adhesion failures. For specimens that were environmentally exposed, changes in failure mode indicated areas of hydration in the bond line.

Surface characterization of laminate surfaces was conducted prior to bonding using a solid-state electrochemical sensor to obtain CV measurements. The CV analysis demonstrated that for all as tooled specimens, only a few small negative current peaks were observed. The negative peaks can correspond to either an active surface or contamination. After sanding and nitrogen blowing,
there was a significant increase in the number of negative peaks. The magnitude of the current peaks were as high as 0.09 A, suggesting an improved bonding surface.

5. REFERENCES


