An Experimental Study of Novel Cold Worked Penetrative Reinforcement of
GFRP/ Aluminium Bonded Joints

By

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Abstract

Stronger, lightweight materials exhibiting fail-safe failure modes are increasingly becoming a necessity amidst concerns of dwindling energy sources, rising pollution levels, and a consumer desire for constantly improving technology. The requirement for stronger and lighter materials has given rise to the implementation of fiber reinforced polymers (FRP). For FRP, metal face sheets are often added to form fiber metal laminates for improved damage tolerance. Bonding of composite materials to metals is challenging. One of the ways to improve the bonding is to use penetrative reinforcements, instead of chemical treatment. Unfortunately, the processes required to produce such modified surfaces is costly, and energy prohibitive for full-scale implementation. The use of a cold working process to form similar penetrative reinforcements provides a more environmentally friendly method.

The investigation of the properties of this technology employed on a single shear lap joint is investigated in this thesis to determine ultimate strength, fatigue performance, impact fatigue, and finally failure modes under different surface configurations. Use of a novel tumbling method to test impact fatigue is developed and test results are reported here. Ultimate tensile strength is found to be comparable to non-reinforced joints, fatigue performance is found, however, to decrease in comparison to non-reinforced joints, and impact fatigue is found to be exceptional compared to non-reinforced joints. Joints with cold-work reinforcements show a substantial increase in failure energy, and damage tolerance. The modified joints show promise for use in a fail-safe design.

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List of Acronyms

CFRP.....	Carbon Fiber Reinforce Polymer
BSE.....	Back Scatter Electron
CMC.....	Ceramic Matrix Composite
EDS.....	Energy Dispersive Spectroscopy
FML.....	Fiber Metal Laminate
FRP.....	Fiber Reinforced Polymer
GFRP.....	Glass Fiber Reinforced Polymer
GLARE.....	Glass Laminate Aluminum Reinforced Epoxy
MEK.....	Methyl Ethyl Ketone
MMC.....	Metal Matrix Composite
PAN.....	Polyacrylonitrile
PEEK.....	Polyether Ether Ketone
PEI.....	Polyetherimide
PMC.....	Polymer Matrix Composite
Pre-Preg.....	Pre- Impregnated
PTFE.....	Polytetrafluoroethylene
SE.....	Secondary Electron
SEM.....	Scanning Electron Microscope

1 Introduction

A wide variety of materials and joining techniques are frequently used in engineering [1]. In the transportation industry as well as many other industries, there has been a desire to use the lightest and strongest materials possible. This has led to extensive research into hybrid materials and joining techniques which combine properties of different materials to create superior and balanced performance [2].

With the presence of environmental pressures from rising atmospheric CO₂ concentrations [3], the economic pressures from the rising costs of energy, and the requirement for safe, fuel-efficient transportation have presented a multifaceted engineering challenge.

A key factor in both fuel efficiency and vehicle safety is material choice; it determines mass, strength, damage tolerance and mode of failure. These factors have led designers to explore engineered materials in hopes of reducing the mass of structures without compromising safety. Many designers have begun implementing composite materials which are stronger and lighter for many applications. Unfortunately, these new materials have proven difficult to join with traditional metallic components. Mechanical fasteners have been explored for joining these items but have added mass and may damage composite materials during installation, in addition to non-uniform load distribution. These shortcomings lead to the use of adhesive bonding to joining these materials, due to the adhesive properties of many composite materials, this lightweight, uniform joining method is the logical solution.

Unfortunately, adhesive joints show a rapid decline in strength after failure initiation or presence of defects, causing catastrophic failure [4]. In addition, the common anodizing treatment employs harmful chemicals. These undesirable properties present the need for more environmentally friendly adhesive joints which exhibit better damage tolerance.

Surface modification, geared towards increasing the microroughness has proven useful for improved bond performance, with anodizing touted as the gold standard of surface preparation of aluminum surfaces [5]. These types of microscopic surface modifications have been well researched, giving an in-depth understanding of the mechanisms which produce increased bond strength; however, macroscopic surface modification has not been studied to the same extent. Recent research into macroscopic surface modification has relied on advanced technologies such as laser modification and additive manufacturing, which have proven promising [6]–[8]. Unfortunately, these technologies require expensive, complex equipment and also consume a large amount of energy[9]–[11]. As such there is a need for a more energy efficient, rapid method to produce effective penetrative reinforcements.

The dilemma presented by the use of a complex technology can be solved through the implementation of a simple solution. The use of a cold working operation to form “protrusions” out of the substrate material lends itself as a simple, energy efficient method to effectively form penetrative reinforcements for use in bonding between metal and composite.

To determine the properties of this type of surface treatment, a broad range of characterizations are needed to understand its performance better. Key mechanical properties, as well as, the failure mode for these loading conditions is carried out in this thesis. More specifically, the use of a plastic deformation process to form penetrative reinforcements is investigated, and testing is conducted to evaluate quasi-static loading, tensile fatigue loading, and impact fatigue loading performance of this new concept. Standard test methods are followed for the evaluation of quasi-static and fatigue performance, and a new simplified impact fatigue test method is developed and employed.

2 Background

2.1 Joining Methods

Many different joining methods have been used to joining materials; these different methods can be grouped into four broad categories: mechanical fastening, welding, adhesive bonding, and hybrid joining.

Mechanical Fastening

The most common method of material joining, mechanical fastening, relies on the use of fasteners to connect two or more members. Shear pin fastening, a type of mechanical fastening, involves the formation of a hole in each member to be joined, and a third member, the pin, is used to transfer the load between each member through shear loading of the pin. Often the pin is designed to cause a clamping force causing friction between the two joining members [12]. Common forms are riveting and bolting.

Riveting requires the plastic deformation of either one or both ends of the rivet to secure the rivet in place. This is done by applying a compressive force axially on the rivet to cause plastic deformation [13]. Depending on the compressive force applied the rivet and joined members will have varying degrees of residual stress introduced [13]. Major concerns with rivets are twofold: firstly, they increase the weight of the structure, and secondly, they present a site for crack initiation by way of fretting between joined members and rivet if vibration exists [13]. Bolted joints use a shear loaded, threaded member to introduce a compressive force by torquing a nut onto the bolt. These fasteners, similar to rivets, increase the weight of a structure and often result in crack initiation sites caused by fretting damage [14].

Welding

Welding is the joining of two materials through the fusion of these materials, generally by way of melting the two materials, and often a filler material is used to aid in joining. There is a multitude of different methods of welding, Generally speaking, the materials are melted by way of arc, combustion, laser energy, or friction [15]. Welding is often a good lightweight, high strength method of material joining; however, it presents issues with dissimilar materials. Welding can cause a localized change in material properties from the heat generated, and it can also cause thermal stresses to form in the material which can promote crack initiation and workpiece distortion [15]. For these reasons, it is impractical for use welding in for many light weight structural applications in aircraft and automotive manufacturing. Specifically, when working with thin aluminum components, there is potential for significant deformation of the workpiece.

Additionally, it cannot be used for joining of advanced materials such PMC (polymer matrix composites) due to their nonmetallic nature.

Adhesive Bonding

An adhesive is a substance which can be applied to two members to bind them together. There is a vast variety of different types of adhesives which can be divided into four main categories: thermosetting adhesives, thermoplastic adhesives, elastomeric adhesives, and alloy adhesives [16]. Thermosetting adhesives rely on chemical cross-linking to cure. Cross-linking makes them resistant to heat and chemical attack, but means they cannot be separated by reheating [16]. Thermoplastic adhesives, on the other hand, do not cross-link, hence lower strength, but can be heated for reshaping. Elastomeric adhesives are made of materials such as rubber, and provide extreme flexibility, but do not bear load well [16]. Adhesive alloys involve the mixture of two different alloys to maximize performance and will perform with a combination of the properties of the adhesives mixed [16]. For use in structural applications, elastomeric adhesives are not suitable, and thermoplastic adhesives do not provide the thermal stability required. Many thermoplastics have issues with dimensional stability, especially at elevated temperatures; although, advances are being made on the development of high-performance thermoplastic adhesives [16], [17]. Adhesive alloys show promise and are used for high strength applications; they, generally use an epoxy base with some form of toughening compound [16]. Specific types of adhesives used as a composite matrix can be found in matrix types.

Hybrid Joining

Hybrid joints combine two (or more) types of joining methods together in order to improve damage tolerance and to add fail-safe redundancy of the joint to avoid catastrophic failure. Hybrid joints are a topic of current research aimed at creating a joint with better performance than either individual joining method. However, results have been mixed. Hybrid joints, by their very nature, vary broadly with different combinations of different bonding methods being combined. Two main hybrid joint types which show promise are hybrid bonded/bolted joints and hybrid penetrative reinforced adhesive joints. Hybrid bonded/ bolted joints have an adhesively bonded joint with drilled holes in the middle where fasteners are inserted. Hybrid penetrative reinforced adhesive bonds, on the other hand, use surface protrusions on the metal component which penetrate the fiber reinforce polymer (FRP) to reinforce the bond. Which has been investigated in this thesis.

2.2 Composite Materials

Composite materials consist of two or more constituents with fundamentally different properties [18]. Composite materials have better properties than either of the individual constituents separately and properties can be modified based on the application [18]. There are many naturally occurring composite materials such as wood and bone [18]. This thesis will only discuss man-made or engineered composite materials.

When looking at man-made composites, the most prolific material which comes to mind is concrete which is made up of aggregate (rock, stones, or sand) and Portland cement.

As material science has progressed, more and more composite materials are being designed to improve strength, reduce weight, and enhance other properties, while reducing production cost and environmental impacts. Due to their high strength and low weight, combined with their damage tolerant nature, continuously reinforced fiber composites have found wide aerospace applications.

Composites can be classified into three main categories, Ceramic Matrix Composites (CMC), Metal Matrix Composites (MMC), and Polymer Matrix Composites (PMC). The goal of composite materials is to integrate a fibrous or particulate reinforcement (e.g., glass fiber, carbon fiber, or aramid fiber) to a matrix to transfer load and provide environmental protection to the fiber or particulate. Fibers tend to be extremely strong in tensile loading; however, when loaded in compression or bending, they have little or no strength, which is why a structural matrix is necessary.

Polymer Matrix Composite

Polymer Matrix Composites (PMC) are a type of composite which consists of fibers set in a polymer matrix [17]. PMC's are often divided into two categories: reinforced plastics and advanced composites [17]. Reinforced plastics tend to be used for relatively low-cost applications, while advanced composites are used for high strength, low weight applications, they are common in the aerospace industry and use epoxy as the matrix with a continuous fiber [17].

Matrix Reinforcement Types

There are four main types of reinforcement geometry for PMC's: whiskers, fibers, fabric, and particulate, as can be seen in [Figure 1](#) ~~Figure 1~~.

Figure 1: Polymer matrix composite reinforcement types A) fibers, B) whiskers, C) particulate, D) fabric [17]

Particulate and whisker type reinforcements are classified as discontinuous reinforcements and are used to increase wear resistance, strength, and stiffness of a material. Whiskers tend to be in the order of 32 times as expensive as particulates [17].

Fiber and fabric reinforcement are continuous reinforcements and are used to increase the toughness and tensile strength of materials.

Fiber Orientation & Weaves

Fiber orientation has a significant effect on load distribution through the structure. Fiber structures are strongest when they are loaded in a 0° orientation to the intended loading direction [19]. Unfortunately for industrial applications, this is not always practical as sometimes it is not possible to have a material loaded in only one direction. Composite materials as an ultimate “design material”, can be tailored to optimize their loading capability by changing the ply orientation of the fibers for better strength in bending, torsion, and in-plane transverse loading [20], [21].

Fiber weaves are frequently used in industry because of their easy of handling [22]; however, it is more difficult to control material properties with fiber weaves. Two of the most common weaves are the plain weave and the 8-harness satin weave, as can be seen in

Figure 2

Figure 2. The plain weave has more fiber bending, while the 8-harness satin weave allows for straighter fibers, giving them a better ability to distribute the load. The 8 harness weave has much better drapability and ability to conform to complex shapes in comparison with the plain weave [23].

Figure 2: 8-Harness satin weave and plain weave [23].

Fiber Types

There are many fiber types; among them are glass fibers, carbon fibers, aramid fibers, silicon carbide fibers and boron fibers. Each has its own unique properties for specific applications, but carbon fiber and glass fiber are the most common for aerospace applications [24].

Glass Fibers

The great advantage of glass fibers is their cost-effectiveness in comparison to other fibers [24]. As can be seen in [Table 1](#), E-Glass costs 1.54 to 3.28 times less than carbon fiber.

When looking at ultimate tensile strength of fibers, glass fiber performs well ([Table 2](#)). Unfortunately, glass fiber tends to have a significantly lower tensile modulus

which leads to failures associated with high strain. Under a 2% yield failure criterion, these materials tend to have a significantly lower allowable tensile design strength. This can be seen in comparison to other selected fibers in [Figure 3](#)~~Figure 3~~. The compressive strength of glass fiber is almost comparable to Boron as can be seen in [Table 2](#)~~Table 2~~. Unfortunately, due to the small fiber diameter, glass fibers are more likely to fail in compression due to buckling.

Despite its shortcomings, glass fiber is the most commonly used type of fiber for the reinforcement of polymer matrix composites due to their low cost and reasonably high strength. Also, they also tend to have good impact energy absorption [24]. Glass fibers are commonly used in the aerospace industry (for example in the fuselage). More specifically they are the backbone of GLARE, a fiber metal laminate (FML) that is currently in service in large portions of the Airbus A380 on its fuselage [25]. Glass fiber is not appropriate for most high strength, high modulus applications due to its low stiffness [24].

Table 1: Fiber Type and related feed stock cost [26].

Fiber (in Epoxy Matrix)	Pre-Preg Feed-stock cost (\$/kg)
E-Glass	65
Aramid	95
High Strength Carbon	100
Intermediate Modulus Carbon	220

Figure 3: Tensile stress vs. tensile strain for selected fibers

Table 2: Fiber properties [27].

Reinforcement Material	Typical Diameter (μm)	Density (g/cm^3)	Tensile Strength (GPa)	Strain to Failure (%)	Tensile Modulus (GPa)	Compressive Strength (GPa)
Glass Fiber						
E-Glass	10 (round)	2.54	3.45	4.8	72.4	4.2
S-Glass	10 (round)	2.49	4.30	5.0	86.9	-
Polyacrylonitrile (PAN) Carbon Fiber						
T-300	7 (round)	1.76	3.65	1.4	231	2.7-3.2
AS-4	7 (round)	1.80	4.07	1.65	248	2.7
T-40	5.1 (round)	1.81	5.65	1.8	290	-
GY-70	8.4 (bilobal)	1.96	1.52	0.38	483	1.06
Mesophase Pitch Carbon Fiber						
P-55	10 (round)	2.0	1.9	0.5	380	-
P-100	10 (round)	2.15	2.41	0.32	758	0.5
Aramid Fiber						
Kevlar 49	11.9 (round)	1.45	3.62	2.8	131	0.35-0.45
Kevlar 149	11.9 (round)	1.47	3.45	1.9	179	-
Others						
SiC Monofilament	140 (round)	3.08	3.44	0.86	400	-
Boron	140 (round)	2.7	3.1	0.79	393	5

Carbon Fibers

The great advantage of carbon fibers is their high tensile modulus which allows them to have a lower failure strain and sustain high loads without significant deformation. As is seen in [Table 1](#), carbon fibers range in cost depending on the application, but they tend to have a high cost in comparison to most other competitors [24].

Polyacrylonitrile (PAN) (high strength) and Mesophase Pitch (high modulus) carbon fibers are the two general distinctions made when discussing carbon fiber, with the major differences being cost and mechanical properties ([Table 1](#)~~Table-1~~, [Table 2](#)~~Table-2~~, [Figure 3](#)~~Figure-3~~). Carbon fiber has a negative coefficient of thermal expansion which means it shrinks when exposed to heat [27]. This gives it interesting applications for high strength at high temperatures where a “pre-stressing” quality occurs at high temperatures.

Due to their high stiffness, failure based on a 2% yield criterion is not relevant, since fiber fracture occurs well in advance of 2% EL. When looking at compressive strength, carbon fiber is vulnerable to compressive load due to buckling. Carbon fiber is used for high strength, low yield applications such as structural members and engine parts in aircraft. Carbon fiber is becoming quite common in the aerospace industry with the Boeing 787 implementing carbon fiber-based structures to make up approximately 50% of its airframe [28]. Similarly, the Bombardier C-Series has implemented carbon fiber for large portions of its airframe as well [29].

Matrix Types

The matrix of PMC's can be divided into two categories: thermosetting resin and thermoplastic resin. Thermosetting resins are often cured at elevated temperatures for a period which causes cross-linking of complex polymer chains and a stable structure to form. Once these links are formed, they are impossible to reverse (only degraded under extreme thermal or chemical environment) which means that thermosetting resins are suitable for high-temperature applications and can withstand exposure to some

solvents. The most common types of thermosetting resins are polyesters, vinyl esters, epoxies, bismaleimides, and polyamides, although most advanced composites are made of epoxies.

In comparison, thermoplastic resins do not cure (rather harden after cooling) but can be molded or deformed at increased temperatures. As such, it is not usually appropriate for high-temperature applications. Since most thermoplastics lack the cross-linked polymer chains, they are vulnerable to solvent attack. However, thermoplastics are more resistant to cracking and impact damage than thermosetting resins and are less costly and faster to produce. There have been recent advances in the thermoplastics for composite applications; for example, the development of polyether-ether ketone (PEEK) highlights the potential for good high-temperature strength and resistance to solvents. The most common types of thermoplastics are polyesters, polyetherimide, polyamide-imide, polyetherimide (PEI), polyphenylene sulfide, and PEEK material properties can be found in Figure 4 and [Table 3](#)~~Table 3~~.

Figure 4: Fracture vs. strength [30]

Table 3: Cured resin properties

Material	Young's Modulus (GPa)	Ultimate Tensile Strength(MPa)	Percent Elongation (%)	Glass Transition Temperature (°C)
Epoxy	2.9 – 4.1 [24]	50-130 [31]	1.5-8.4 [24]	107-218 [24]
PEEK	3.6 [24]	90-100 [31]	30 [24]	145 [24]
PEI	4.0 [24]	105 [31]	60 [24]	215 [24]
Al-2024-T3	73.1 [32]	485 [33]	18 [32]	-
AL-7075-T6	71.7 [34]	570 [33]	11 [34]	-
High Strength Graphite/ Epoxy	145 [35]	1240 [35]	0.9 [35]	-
E-Glass/ Epoxy	45 [35]	1020 [35]	2.3 [35]	-

2.3 Manufacturing Methods

For the application of aerospace materials, fiber reinforced epoxy matrix composites are the most commonly used. The manufacturing process of these materials is complicated and relatively expensive compared to other composite materials due to the autoclave curing cycle of thermoset epoxy. For bonding to metals to form adhesive joints with these composites, co-curing is done. Co-curing allows for the curing of the epoxy matrix onto the metal which forms an adhesive bond. A general overview of fiber reinforced, epoxy matrix composites production can be summarized in [Figure 5](#).

Figure 5: Polymer matrix composite manufacturing process flow diagram [36], [37]

Pre-Preg

Pre-impregnated fibers (pre-preg) is the most commonly used method for manufacturing fiber metal laminates in the aerospace industry due to its ability to have consistent results. There are other methods of layup such as liquid resin molding, but they tend to be used in the non-aerospace industry [24].

Pre-preg lay-up consists of thermosetting plastics such as epoxy being coated or impregnated onto the fibers with a hardening agent which is activated upon sufficient heat and pressure. The combined epoxy and fiber is partially hardened into a pliable,

sticky sheet in a continuous process, this type of material is called a B-staged epoxy resin [24], [38], [39]. There are different processes for producing pre-preg, but the most common one is the solution dip process [39].

Lay-Up

There are many methods for curing composite materials. For the aerospace industry, the most common method is through a bag-molding process [38]. Other methods involve liquid molding set up and compression molding. Lay-up is the setup and placement of fibers and epoxy in the position in which it is meant to be cured. The metal components may be incorporated at this point if co-curing is desired to bond a PMC to a metal.

Figure 6: Vacuum bagging lay-up [39][40]

Compression molding can also be used with a pre-preg layup procedure, although it is normally used with a “wet lay-up” procedure where liquid resin is pumped into a sealed

mold immediately before curing. In compression molding with pre-preg, a sheet of pre-preg is placed on the bottom die, and a matching top die is forced down to produce the pressure required for curing. Compression molding is commonly referred to as hot pressing. Issues with this are that it is difficult to achieve uniform pressure distributed across the whole part, particularly for curved parts. A standard lay-up using pre-preg can be seen for compression molding in [Figure 7](#)~~Figure-7~~.

Figure 7: Pre-preg compression molding lay-up [41]

Curing Cycles

Curing cycles for pre-preg usually involve a two-stage process [38]. It starts with a temperature ramp up to a specified dwell temperature known as a soak temperature. The temperature is then held for a period, and a positive pressure is introduced. At the dwell temperature, the viscosity of the resin decreases to a minimum allowing the resin to flow. The soak stage is an important part of the cure cycle as the resin flow ensures that all volatile gases are forced out of the resin, reducing the void content. Voids present in the epoxy after curing are a major cause of decreased strength in PMC as can be seen in [Figure 8](#)~~Figure-8~~.

Figure 8: Effect of void volume fraction on interlaminar shear strength [38]

The next stage of the cure is the actual curing portion of the cycle. A second temperature ramp-up is experienced while maintaining constant pressure. This temperature ramp-up stops when it achieves the secondary dwelling temperature. At this temperature, the resin begins to rapidly increase in viscosity as cross-linking of the epoxy begins, and the resin begins to cure. This temperature is held for a set period allowing the epoxy to cure sufficiently. After the curing, the temperature is slowly ramped back down, and the pressure is reduced. [Figure 9](#) shows a characteristic two-stage cure cycle.

Figure 9: Characteristic resin cure cycle [38]

There are many types of curing methods, but the one most commonly used in the aerospace industry involves the use of an autoclave. An autoclave is a pressure vessel which can maintain a fixed pressure while being heated. Often the vessel is purged several times with nitrogen to remove oxygen and other undesirable gases. Vacuum lines are often also installed to maintain a vacuum in the bag which is used in combination with an autoclave curing cycle.

Autoclave

An autoclave is a vessel capable of controlling temperature and pressure, and is run in connection with a controller unit which allows for specified cooling and heating rates, as well as, pressure increase rates and decrease rates. The vessel is also purged with nitrogen to ensure no reactivity.

Figure 10: Autoclave for composite curing

Out of Autoclave Curing

Although the use of an autoclave is the standard practice in the aerospace industry, there are many other options. Oven curing is an alternative to autoclave curing.

Temperature is controlled through the use of heating and cooling elements, but there is no pressurization (some ovens have active vacuum lines for the vacuum bag). The lack of pressurization often results in poor (higher) void content in comparison to autoclaves due to a lack of pressure application. Methods of pressure application in oven curing have been developed over the years, including shrink wrap tape, inflatable bladders, and weighted rubberized mats. Although these options provide some improvement, they have limitations in achieving the same results offered by an autoclave [42].

Liquid resin transfer systems are another method for curing in which a preformed mold is used in combination with hot resin injected into the mold. Similarly, Resin Transfer Molding (RTM) provides resin pressurization to ensure resin infiltration into a bed of dry fibers which are in the mold [24].

VARTM

Vacuum Assisted Resin Transfer Molding (VARTM) uses a tool plate to provide a mold.

Dry fiber is placed in the mold, a bag is used to seal the system, and a hot resin port is attached to one side of the mold. A vacuum is drawn from the other side of the bag, and resin is pulled through into the mold by the vacuum and gravity as the resin flows from a reservoir into the mold. An oven is used to heat the resin which creates a temperatures at which the part will cure. The negative pressure from the vacuum creates the only applied pressure to the mold. [Figure 11](#) shows a schematic diagram of VARTM setup.

Figure 11: Vacuum assisted resin transfer molding schematic [43]

2.4 Joining Mechanisms

There are many different joining mechanisms for adhesives. Many of which only apply to certain types of adhesives. For this investigation joining mechanisms for the bonding of aluminum to epoxy will be explored. A combination of many different mechanisms causes adhesion.

Physical Adsorption

One mechanism for the bonding between adhesive and metal surface is physical adsorption through intermolecular Van der Waals forces [44]. There are three types of Van der Waals forces: dipole to dipole attraction (Keesom Forces) [45], dipole to non-polar molecule attraction (Debye Forces) [46], and non-polar to non-polar molecule attraction (London Dispersion Forces) [47]. These forces are small and have a very short distance of effect, often only affecting 1 or 2 layers of molecules on an interface. As with many other mechanisms, the greater the surface area of the bonding, the stronger the bond. An effective way to increase bond area without varying the dimensions is by altering the roughness. As can be seen in [Figure 12](#)~~Figure 12~~, the greater the roughness, the more surface area it has. Surface area is particularly relevant in this research as several different configurations of surface topography are examined for bonding strength improvement.

Figure 12: Surface roughness vs. surface area

Mechanical Interlocking

In addition to Van der Waals forces, another adhesion mechanism is mechanical interlocking. A rough surface allows for adhesives, both thermosetting epoxies and thermoplastics, to penetrate into and cure within the concavities, providing mechanical resistance to movement. For this reason, aerospace aluminum surfaces are often anodized or etched before bonding to form a porous or fibril oxide layers, which in turn increases the bond strength through the effect of mechanical interlocking [44], [48].

Interlock bonding also prevents crack propagation through the bond line by way of crack deflection. Crack deflection transfers the mode of failure from an interfacial failure to a possible cohesive failure [49]. Much investigation has been dedicated to examining the effects of mechanical interlocking. Kim et al. (2010)[49] found that by inducing “micro trenches” in a surface with different spacing ratios (width of trench: width between trenches), the adhesion strength was altered significantly [49]. As the ratio increased from 1:1 to 8:1 it was seen that the peak load to failure was significantly higher. [Figure](#)

[13](#) shows the micro-patterning done by Kim et al. (2010). When the surface

roughness is induced randomly, the increase in surface roughness increases the adhesion strength of the bond [50]. However, as the surface roughness continues to increase, the adhesion strength begins to decrease. A decrease in adhesion strength is caused by poor wetting, void formation and stress concentration [50].

Figure 13: Micropatterning from Kim et al. (2010) experiment[49]

Chemical Adsorption

In certain cases, an adhesive promoting coating such as Sol-Gel [51], [52] is used; this allows a formation of covalent bonds between both the aluminum substrate and the epoxy adhesive. The specific bond which is exploited is a covalent bond formed between silane and organic compounds such as epoxy [44].

2.5 Surface Preparation

Surface preparation is vital to ensure bonding between Al and matrix when bonding a polymer matrix composite to a metal surface. Research has shown that failure to increase surface energy and eliminate contamination has led to premature failure [5].

Ultrasonic Cleaning

Ultra-sonic cleaning uses vibrations in the range of 20 to 60 kHz to create cavitation in a fluid such as soapy water or a solvent [53]. The cavitation dislodges most debris on the surface being cleaned.

Degreasing

This process is used to remove grease and other organic matter from the surface.

Sometimes it is coupled with deoxidizing or alkaline cleaning [5]. Chemicals such as alcohol, and acetone are often used for this purpose, but Methyl Ethyl Ketone (MEK) is considered a better degreasing agent which dries fast and leaves no residue and is a highly volatile, toxic substance [54], [55]. Parts are degreased by submerging it in a container of the fluid, with agitation, followed by drying, or through a wiping procedure of the surface.

Mechanical Roughening

This process involves creating a coarse finish on the part to promote adhesive bonding. The issue with mechanical roughening is that it can cause an alteration to the material microstructure and introduce residual stresses, affecting the formability and the service life of the parts. Mechanical roughening can be achieved by several means, manual

abrasion, grit blasting [56], chemical patterning, and more recently, laser ablation. Manual abrasion is done by scouring the surface with an abrasive material. Grit blasting uses pressure to propel grit at a surface, and oil-free propellant must be used to prevent contamination [5]. Increase in propellant pressure will increase the adhesion of the surface [57], and a rougher surface produces greater bonding strength [58]. Chemical etching in a pattern can be done to alter surface roughness predictably. Work by Kim et al. [49] showed a nitric acid solution could be used to etch micro-trenches into steel ([Figure 13](#)~~Figure 13~~). Lasers can also be used to modify the surface through laser ablation; this is done by making microscopic patterns on the surface to promote adhesion through mechanical interlocking. Kromer et al. [59] showed that the angle and separation of these modifications made using lasers made a difference in adhesion strength ([Figure 14](#)~~Figure 14~~). Results for laser ablation experiments were similar to those of chemical patterning, finding that the closer trenches are, the better the adhesion [49], [59].

Figure 14: Micro-patterning by Kromer et al. (2015) [59]

Acid Etching & Conversion Coatings

Bonded Al panels used for aerospace applications commonly go through acid etching to clean the surface and increase bonding potential. The standard for acid etching is the

optimized Forest Products Laboratory (FPL) etch, although due to concerns over its use of chromate, a P_2 etch has become more common, these procedures both create a network of aluminum oxide fibrils which promote bonding [5], [60], [61].

Conversion coatings are group of coatings which similarly form a layer of porous aluminum oxide reinforced with either chromium or zirconium, this coating promotes bonding and is convenient as it can be applied in the field [5], [62], [63]

Anodizing

Anodizing is accomplished by putting an aluminum part in an electrolyte solution (usually an acid) and passing current through the solution with the part as the anode (hence, anodizing). This process causes an accumulation of oxygen at the anode surface, and the oxidization of the aluminum occurs, creating a hard aluminum oxide surface. The presence of the acid also partially dissolves the aluminum oxide and slows the oxide formation rate to allow micropores to be created. There are three frequently used types of anodizing: sulfuric acid anodizing (SAA), phosphoric acid anodizing (PAA), and chromic acid anodizing (CAA). For most applications direct current is used; however, there are applications where alternating current can be used. SAA is considered to be inferior to both CAA and PAA [1], [5], [64]. CAA and PAA offer comparable bonding, CAA is used by European aircraft manufacturers, while PAA is used by the Boeing Aircraft [5], [65].

Sol-Gel

Sol-Gel AC130 is a type of surface coating developed by Boeing which creates a film layer promoting organic-inorganic bonding. This coating is a water-based silicon-zirconium sol-

gel and is sprayed on a surface and allowed to cure naturally. Under certain conditions, Sol-Gel AC-130 is considered comparable to several anodizing processes and is used for repairs of previously anodized surfaces where re-anodizing is not practical [66]–[68]. Sol-Gel AC-130 is significantly less toxic and environmentally harmful when compared to many of the other processes discussed [68].

2.6 Recent Advancements in Hybrid Joint Reinforcement

It should be noted that for the rest of this thesis reinforcement will refer to a secondary joining technique used to enhance bonding of a joint, this include bolts, and protrusions which penetrates the fiber/epoxy matrix. Fiber will not be referred to as a reinforcement, but rather as an integral part to a FRP.

Hybrid Bonded/ Bolted Joints for Composite/ Metal Bonding

Hybrid bonded/ bolted joints have been used as a fail-safe method of joining for some time. Recently much investigation has gone into their failure modes in an attempt to increase the ultimate strength of the joints [69]–[71]. The barrier to an increased strength of a bonded/ bolted joint has been attributed to a failure of the hybrid joint to appropriately share the applied load in parallel, with a load path forming through the adhesive and the adhesive failing before significant loading of the bolt can occur. Lopez [69] and Kelly [71] found that this behavior was owing to the large differences in stiffness of the adhesive and the bolt, the tolerance fitting of the bolt and bolt hole, and the adhesive and adherend thicknesses. These studies showed a detectable failure of the adhesive bond before loading of the bolts which led to a F vs. D behavior resembling

a bolted joint with no adhesive bond. To improve the load sharing capabilities Matsuzaki et al. studied the co-curing of a bolt and a CFRP (carbon fiber reinforced polymer) adherend [70]. Results showed a modest increase in load bearing before failure of the adhesive bond, at which point the joint exhibited similar properties to a bolted joint. Lopez [69] tested a condition where adhesive bond strength outperformed bolt strength, in this situation a modest increase in peak strength was detected followed by adhesive failure, after failure, the joint reverted to a Force vs. Displacement behavior similar to a bolted joint. Interestingly, both Matsuzaki et al. [70] and Lopez [69] found that the strength of the joint after initial adhesive failure performed slightly better than bolted joints. The improved performance is hypothesized to be caused by frictional contributions of the failed adhesive surface. Figure 15~~Figure 15~~ shows characteristic Force vs. Displacement plots representing the work of Matsuzaki et al. [70] (Figure 15~~Figure 15~~ (A)), and Lopez [69] (Figure 15~~Figure 15~~ (B)).

(A)

(B)

Figure 15: Force vs displacement obtained by Lopez and Matsuzaki et al. [69], [70]

Penetrative Reinforcement for Composite/ Metal Bonding

Research into the use of penetrative surface treatment can be divided into three major groups: Surfi-Sculpt formed protrusions, additively manufactured pins, and welded pins [6], [72]–[74].

Surfi-Sculpt relies on the use of a “power beam” generated from an electron beam, laser beam or the like to melt a substrate material. The liquid material is then manipulated, by taking advantage of surface tension and the thermal gradient of the liquid metal to progressively form a protrusion (~~Figure 16~~Figure 16 (A) & (B)) [73]. These protrusions are formed in arrays, and they penetrate into the adherend which is being bonded. The presence of Surfi-Sculpt improved the strength of certain bond configurations [8], [73], [75]. Application of this technology has been used to create a joint referred to as a Comeld joint which uses Surfi-Sculpt to produce surface protrusions and a DLS (double lap shear) joint co-cured together to optimize the reinforcement strength. Variation of these types of bonds is based on hooked material and matrix/ fiber material. Use of Ti-6Al-4V and Carbon Fiber Reinforced Polymer (CFRP) shows no increase in ultimate tensile strength compared to an adhesively bonded joint with no protrusions, this joint also demonstrated the same joint stiffness (~~Figure 17~~Figure 17) [73]. What is different is the joint shows a significant increase in elongation under peak tensile strength, indicating a substantial increase in failure energy which improves the fail-safe nature of the joint. In comparison, the application of a Comeld joint with 316 stainless steel and a polyester matrix GFRP (glass fiber reinforced polymer), an appreciable increase in both tensile strength and elongation is seen when compared to an adhesively bonded joint,

all while maintaining the same stiffness ([Figure 17](#)~~Figure 17~~) [73].

Figure 16: Penetrative reinforcement concepts: A) Surfi-Sculpt protrusion concept, B) electron beam formed protrusions (Aluminium) [76] , C) hybrid penetrative reinforcement pins, D) additively manufactured pins (Ti-6Al-4V) [6]

Figure 17: Comeld F vs. D curves for GFRP/ 316 SS and CFRP/Ti-6Al-4V [73]

Additively manufactured and welded pins performed the same as Surfi-Sculpt protrusions with an array of pins penetrating into an adherend to increase bonding. These pins usually have shaped heads to improve form closing at the end of the pins, anchoring them in place ([Figure 16](#) ~~Figure 16~~ (C) & (D)). These reinforcements showed an improvement in tensile strength in certain studies and a substantial increase in failure energy in all cases [6], [72], [74].

Development of pin reinforcements has shown varying success. Ucsnik et al. [74] used an arc-welding process, CMT (cold metal transfer), to apply 304 stainless steel pins (3 mm) to a surface, these pins were penetrated into carbon fibers before being co-curing

in an epoxy matrix, forming a DLS (Double Lap Shear) joint. Both cylindrical, and ball head shaped pins were created. Ucsnik et al. showed that the bonded structure had an approximately 50% increase in ultimate strength from the ball head shaped pins with extensive deformation before failure [74], while the cylindrical pins showed only an approximately 10% increase in ultimate strength. The failure mode was different, the cylindrical pins deformed and pulling out with a slow, steady decrease in load bearing, while the ball head pins exhibited a rapid failure due to pin fracture. The Force vs. Strain (~~Figure 18~~~~Figure 18~~) shows the loading profile of the joints comparatively, the failure point of the adhesive can be identified by the significant change in stiffness of the joint. Although the increases in ultimate tensile strength are important, of equal importance is the significant increase in failure energy which is seen with these joints.

Joesbury [72] conducted a similar study in which the experiment conducted in Ucsnik et al.[74] was replicated using pre-preg and an autoclave instead of RTM. When inspecting the F vs. ϵ (~~Figure 18~~~~Figure 18~~) plot, the pike shaped pins follow the same stiffness as the adhesively bonded control sample, then a sharp drop can be observed, indicative of adhesive failure. This drop is followed by a modest increase in load and then a steady decrease. Final failure of the pike shaped pins is through significant deformation and finally a fracture at the base. Compared to the work by Ucsnik et al.[74], the failure energy measured by Joesbury is much lower.

Figure 18: F vs. ϵ for research done by Joesbury & Ucsnik et al. [72], [74]

Parkes et al. [4] used Ti-6Al-4V pins which were additively manufactured onto a substrate, the pins were penetrated into CFRP pre-preg and co-cured into an SLS (single lap shear) joint in an autoclave. An optimize arrowhead pinhead was used, and two pin array types were tested. Reviewing the F vs. D plot ([Figure 19](#)), no loss in joint stiffness or load bearing upon adhesive failure is observed and an ultimate tensile strength of 6.5 times that of the control adhesive bond is seen; failure occurs through fracture at the base of the pins. As a reference, a (polytetra fluoroethylene) PTFE coated sample was tested to determine pin strength separate from the adhesive bond. This test showed a substantial increase in ultimate strength over the control adhesive bond indicating the substantial contribution of mechanical interlocking effects demonstrated by these pins.

Figure 19: F vs. D plot of Parkes et al. research [4]

Surface modifications of aluminum alloys present challenges. Research into the use of electron beams or laser beams to implement Surfi-Sculpt protrusions on aluminum has resulted in protrusions with porosities and poor shear strength when compared to microsurface modifications by laser ablation [77], [78]. No studies into additive manufacturing or welding of aluminum pins were found, but these processes are known to present manufacturing issues such as large heat affected zones and large weld pools due to high thermal properties of aluminum [79] and the oxidation propensity of Al alloys during thermal processing. These issues make aluminum surface modifications challenging.

2.7 Failure Modes of Adhesive Joints and Prevention Methods

There are many failure modes of adhesively bonded joints, when dealing with hybrid joints, different modes may occur one after the other. Hybrid joints demonstrate primary and secondary failure due to the existence of different load paths. A primary failure is usually a failure of the adhesive bond, while a secondary failure is the failure of the reinforcement [6].

Adhesive Failure

Adhesive failure is the failure of a bond at the adhesive substrate interface ([Figure 20](#)~~Figure 20~~ b). These failures occur when the adhesive bonding is weaker than the bulk adhesive; it commonly occurs due to poor surface preparation [5]. To prevent adhesive failure, surface preparation such as anodizing, grit blasting, acid etching, laser ablation, and/or coating the surface with an adhesion promoting agent have been used [5].

Cohesive Failure

Cohesive failure occurs when the strength of the bonding surface exceeds the bulk strength of the adhesive ([Figure 20](#)~~Figure 20~~ a). A decrease in adhesive thickness to minimize stresses in the adhesive and decreasing void content through refinement of manufacturing processes can help to mitigate cohesive failure [38].

Figure 20: A) Cohesive vs. B) adhesive failure

Substrate Failure

Substrate failure occurs when the material properties of the substrate are inadequate in comparison to the adhesive. Stress concentrators are usually present in the substrate causing vulnerability to fatigue cracking, or the adhesive bond acts as a stress concentrator (adhesive fillets) [80]. Substrate failure can be prevented by optimizing the joint to avoid stress concentrators and using a substrate material having a sufficient strength.

Fiber/Matrix Delamination

When fibers are present in a joint, they provide opportunities for fiber/matrix interface delamination. Fiber/matrix delamination can be prevented by conditioning fibers to provide appropriate interfacial bonding between the matrix and the fiber. The addition of a penetrative reinforcement perpendicular to the fiber pack plane acts to bridge the fiber plies, and also helps to prevent fiber/ matrix delamination. The presence of these reinforcements acts to distribute the load between fiber plies, minimizing the shear stress at the interfaces; these reinforcements also act as crack arrestors slowing the propagation of delamination [27], [81].

Penetrative Reinforcement Pull Out

Pull out of reinforcements is commonly seen along with reinforcement deformation, this failure mode is characterized by a reinforcement being pulled out of the bonded matrix.

Pull out can be prevented by the increase in the surface area of reinforcements inside the matrix with balls and arrowheads to increase bonding surface, and through mechanical interlocking and form closure [74].

Reinforcement Failure

This failure mode occurs when the reinforcement hooks fracture and fail while still embedded in the fiber matrix. To avoid this increase in reinforcement size should be used [6].

2.8 Survey of Test Methods

ASTM standards can classify most test methods. [Table 4](#) gives a list of test methods and their corresponding ASTM standards.

Table 4: Test methods and corresponding ASTM standards

Test Method	ASTM Standard(s)
Lap Joint Tensile Testing	D4896-01, D3166-99, D1002-10
Torsional Fatigue	STP 546
Three Point Bend	E855-08, D7264/D7264M – 15
Four Point Bend	E855-08, D7264/D7264M – 15
Double Cantilever Beam Testing	D5528-13

Lap Joint Tensile Testing

There are many types of lap joint testing; some are summarized in [Figure 21](#)~~Figure 21~~.

These tests are used to evaluate the shear strength of bonded joints as well as the interlaminar shear strength of laminar composites.

Figure 21: Lap joint testing types [82].

Single lap shear joint tensile testing is often carried out for many types of materials and bonding configurations. The most important thing is to ensure that loading is along the center of the bond line with the loading vector being parallel to the adhesive bond line, this can be done by many methods; the first method uses alignment tabs to ensure that the sample is clamped in a way so that the load vector is through the center of the bond line creating a pure shear condition ([Figure 22](#)~~Figure 22~~). Potential issues with this method are slipping of the alignment tabs and the possibility of repeatability issues depending on how precisely the alignment tabs are placed.

Figure 22: Single lap joint testing with alignment tabs [82]

Another method is to cut out sections in a larger piece such that there is no requirement for alignment. This method is shown in [Figure 23](#)~~Figure 23~~, for testing the adhesive properties of a co-curing adhesive [96]. This method may present issues for testing of interlaminar shear strength due to the resin flow during curing. In particular, the resin may become bonded to the axial portion of the cutout, causing increased bond strength and deviating the pure shear stress condition.

Figure 23: Single lap joint testing with cut out sections [83]

Another method used is the double notching method where notches are cut out of a fully bonded piece around a central test zone to isolate the bond strength assessment in a small region, as in [Figure 24](#)~~Figure 24~~. The downside of this method is that compression

and deformation of the matrix may result in loading non-parallel to the bond line thus altering the pure shear condition[84].

Figure 24: Single lap joint testing using the double notch method [84]

Another method used for single lap joint testing is pinning, instead of clamping. The ASTM standard D3165-07 [85] suggests this as the recommended method of sample loading. In this method, the double notch is used. The major concern with this method is the existence of stress concentrators produced around the pinhole and as such a certain distance must be maintained between the loading holes and the testing zone, labeled in

[Figure 25](#)~~Figure 25.~~

Figure 25: Single lap joint testing ASTM proposed form[85]

Finally, use of self-aligning grips is also an option ([Figure 26](#)). Use of self-aligning grips is the recommended loading method for metal-metal bonded samples based on ASTM D3166-99 [86].

Figure 26: Single lap joint testing self-aligning grips [86]

Double Cantilever Beam Testing

Double cantilever beam testing is used to measure the fracture toughness of an adhesive by inducing mode I loading at a bond line. Mode I loading is accomplished by loading at the locations of two pin holes causing separation and bending of the adhesive and the adherend, as is shown in [Figure 27](#).

Figure 27: Double cantilever beam schematic [87]

Three-point and Four Point Bend Testing

Three or four-point bend testing induces flexure in the sample to study interlaminar shear properties of materials. Four-point bend tests tend to be better for non-homogenous materials such as composite because composite materials tend to be more vulnerable to premature failure due to discontinuities in the material. Four-point bending distributes the load out evenly.

[Figure 28](#)

[Figure 28](#) shows a schematic of both these tests.

Figure 28: Three-point and four-point bend testing [88]

Single Cantilever Bending Test

A hybrid of the double cantilever bending test and the single leg bending test has been designed to test the adhesion between plies of a laminate. It relies on the stiffness of the metal ply in comparison to the bond strength. [Figure 29](#) shows a schematic of the setup.

Figure 29: Single cantilever beam bending test [89]

Impact fatigue

Impact fatigue is the repetitive loading of a sample at high strain rates. Many different methods can be used to load samples in high strain rate, but few are capable of efficiently loading samples repeatedly. A drop tower can be used for repeated impact tests but is

inefficient. The experimental set-up for this type of test can be seen in [Figure 30](#)~~Figure 30~~.

Figure 30: Drop tower for use in impact testing [90].

Another method for impact fatigue testing is through repeated impact by way of an impact hammer which is actuated by some method, one common method seen is a rotating disk with a catch which releases the hammer every rotation at a specific height. A schematic diagram of this test set up can be seen in [Figure 31](#)~~Figure 31~~. Results of testing of this type are relatively sparse, but show a way to test fatigue of materials at moderately high strain rates (1000 min^{-1}), producing results in the form of a standard S-N curve [91].

Figure 31: Impact hammer fatigue testing machine diagram [91]

Another method for loading samples at high strain rates is the Split-Hopkinson Pressure Bar test. This test uses the production of a shock through two bars clamped on either end of a sample; the shock wave is then reflected back through the sample inducing a high strain rate loading of the sample. Figure 32 shows a diagram of this experimental setup.

Figure 32: Split Hopkinson pressure bar test [92]

3 Summary and Objectives of the Thesis

Based on the literature reviewed there remains a need for a low cost, high-performance method for joining FRP (fiber reinforced polymers) to metal surfaces for use in both the aerospace and automotive industry. Adhesive bonding on its own has good performance, but the lack of damage tolerance presents a source of concern. Traditional mechanically fastened joints require drilling of holes into to composite materials and increase the component weight. Hybrid joints show improved damage tolerance, compared to their individual constituents, but similar maximum load.

The advent of penetrative reinforcement of FRP/metal bonded joints has shown promise with significant increases in joint strength before failure and increased failure energy before failure. However, the production of these penetrative reinforcements uses costly, complex processes, prohibiting it from being used for mass production in industries. For that reason, there is a need for an inexpensive, rapid method to

successfully reinforce adhesive bonds, increase strength, and provide a damage tolerant design.

The need for a new metal/FRP bonding technology gives rise to the concept of GRIP-Metal manufactured by Nucap [93] this has shown great performance in the automotive industry as a brake pad adhesion mechanism. The major concern with this product is the potential stress concentration effects of the surface modification on fatigue behavior of bonded structure. With common fatigue testing practices being long and tedious, a new type of testing method for batch ranking needs to be employed to test realistic fatigue loading properties of this new process. In addition, a traditional fatigue property characterization (uniaxial loading and unloading of a lap joint with MTS system) is needed so that the results can be applicable to design of bonded structure.

This research combines the assessment of a new penetrative reinforcement method with the evaluation of a new testing methodology used to assess bond fatigue performance under two test conditions (impact and lap shear). The research objectives of this thesis are:

- To establish the load carrying capacity of these hybrid cold worked penetrative reinforcement joints in both quasi-static and fatigue loading conditions.
- To evaluate the failure mode of these reinforcements and to better understand load bearing and the root cause of failure.
- To verify the use of impact fatigue testing via tumbler testing in ranking fatigue properties.

- To determine the applicability of cold worked protrusions for use in a hybrid penetrative reinforced adhesive bond for joining of FRP to metal.

During this research, seven different surface preparation variants for tumbler impact fatigue testing and three different surface preparation variants for tensile fatigue testing and quasi-static testing were employed. These consisted of the application of a protruded metal surface treatment with two different protrusion geometries (rolled and straight), as well as, a standard flat surface used as a control. Three different chemical surface treatments were used on these modified surfaces: MEK degreasing, Sol-Gel AC-130, and Loctite Frekote. Three test methods were used to evaluate:

- 1) single lap shear joint cyclic tensile testing through the use of an MTS hydraulic test frame machine
- 2) single lap shear joint quasi-static testing through the use of an MTS hydraulic test frame machine
- 3) impact test by elevation and dropping samples in a tumbler.

The samples were prepared by co-curing GFRP (glass fiber reinforced polymer) to a mechanically modified aluminum surface. Evaluation of fatigue and quasi static behaviour through traditional tensile fatigue, increase strain rate fatigue, as well as, quasi-static loading will be completed. Results for traditional fatigue and fatigue through tumbling will be compared to determine agreeability. The failure modes of these samples will be inspected through the use of SEM (scanning electron microscope) to identify failure causing damage. Finally, the results of these investigations will be

assessed to decide if cold worked protrusions have promise to enhance the FRP/ metal adhesive joining.

4 Material selection and Experimental Procedures

4.1 Material Selection

Sheet Metal

2024-T3 aluminum was chosen as the substrate metal as it is a commonly used metal for manufacturing of aerospace components. Most penetrative reinforcement research has been done on titanium and steel, but little research has been done into the use with aluminum surfaces. Residual stress issues induced by non-uniform cold working during GRIP-Metal process led to the selection of 1/16" thick aluminum to prevent distortion.

Table 5: Aluminum Specifications

Thickness	1/16" (1.5875 mm)
Grade	Al-2024-T3
Supplier	McKinnon Metals Inc.

Pre-Preg Selection

For the fiber and matrix, glass fiber in an epoxy matrix was chosen for use in a pre-preg format. The reason for choosing glass fiber was twofold; first glass fiber is not as hazardous when preparing compared to carbon fiber, and second contact between carbon fiber and aluminum results in galvanic corrosion which presents serious issues with long-term application. A fiber weave was chosen instead of unidirectional fiber

layup, in hopes that a weave would interact better with the reinforcement and transfer load more readily, all specifications of the pre-preg used are stated in [Table 6](#)~~Table 6~~.

Table 6: Pre-Preg Specifications

Pre-Preg Supplier	ACP Composites
Pre-Preg Resin	TCR UF3325 Thermosetting Epoxy
Pre-Preg Fiber Weave	8-Harness Satin Weave
Fiber Type	E-Glass
Fiber Thickness	0.008"

Grit-Blasting & Sol-Gel AC-130

Grit blasting was used to induce surface roughness and remove the exterior oxide layer on all bonding surfaces which were then coated with sol-gel. Sol-gel creates a covalent bond between alkoxyzirconium and aluminum, alkoxyzirconium and glycidoxysilane, and glycidoxysilane and epoxy [51], [52], effectively forming a bridge between metal and epoxy to ensure stronger bonding. For sol-gel to work effectively, it requires a freshly grit blasted surface.

GRIP-Metal

GRIP-Metal is a macro-surface modification technique which uses a “plowing” cold work deformation process to form hook protrusions out of a metal substrate. These hooks can be seen in [Figure 33](#)~~Figure 33~~. They have two different types of orientations, straight and rolled. Rolled are initially straight hooks which are rolled forward further after being produced. These hooks can be produced with a multitude of heights. The profile of these hooks can be seen in rows of opposite direction, to balance the residual stresses and subsequent distortion.

Figure 33: GRIP-Metal Concept [93]

GRIP-Metal with mini hooks may potentially find use in composite materials as penetrative bonding reinforcement. It is known that penetrative reinforcement of FRP's improves joint properties and as such the application of GRIP-Metal should have similar results [6], [7], [73], [74].

Figure 34: a) GRIP-Metal composite concept b) GRIP-Metal up close [93]

For this test GRIP-Metal micro-sized hooks were chosen. The parameters of these hooks are stated in Table 7.

Table 7: GRIP-Metal Specifications

Hook Type	GRIP-Metal Mini
Hook Height	0.04 in (1 mm)
Hook Density	84 hooks/in ² (13 hooks/cm ²)

4.2 Sample Design & Test Design

Impact Samples

Impact samples were designed based on the concept of single lap joint. 12 layers of pre-preg were used, laminated by a sheet of 1/16" Al-2024-T3 on either side. Due to the nature of GRIP-Metal, hooks were not able to be applied to a width as small as 0.4 in. As such hooks were generated to a 0.675" width and some of the hooks were milled off in the unneeded region (Figure 35 (C)). A circular sample was used to reduce stress concentrators. Samples were designed to have a diameter of 1.2 in, with a bond overlap of 0.4 in. Similar to the ASTM D3166-99 recommended bond dimensions of 0.375 in and 1 in width. Bond thickness was decided to be 2.6 mm (0.102 in) to ensure that hooks could penetrate the composite layers without contacting the surface of the plate on the other side (Figure 36). These samples were cured in an autoclave using the vacuum bagging method.

When cured the epoxy in samples expanded more than expected leaving the contact width of each face to be 0.54 in with a fillet formed (Figure 35 (B)). Water jet cutting was used to cut the circular samples out of the cured plates. The samples were weighed after

curing and cutting and the average mass was found to be 6.54 g. The final dimension of the impact sample is shown in Figure 35 (A) and an as-manufactured image can be seen in Figure 35 (B). The edges of the samples were inspected under optical microscope to ensure no delamination or crack formation caused by water jet cutting.

For reference, unhooked samples had an average sample thickness of 0.206 ± 0.002 in, while hooked samples had an average sample thickness of 0.226 ± 0.02 in. The variation in height is caused by the presence of hooks which increase the thickness of the bondline due to incomplete hook penetration.

Figure 35: Impact tumbler fatigue sample: A) as-designed, B) as-manufactured, C)

unbonded surface

Figure 36: Bond line schematic

Fatigue & Tensile Samples

Fatigue and tensile samples were fabricated with similar bonding regions as impact samples. These samples were cured in an autoclave using a vacuum bagging method as well.

Once cured in the autoclave, spacers measured 1.2 in x 2 in x 0.16 in were attached to the upper clamping zones on both sides of the samples using quick set epoxy (Figure 37 (C)). This was done to ensure pure shear during fatigue testing using MTS machine. For these samples, the hooked samples showed an average bond thickness of 0.222 ± 0.001 in and the unhooked samples had an average bond thickness of 0.210 ± 0.002 in. When cured the epoxy in the samples expanded more than expected leaving a 0.54 in contact width and a fillet visible in both Figure 37 (A) & (C). These samples were then cut with diamond blade saw and end milling using a carbide tipped cutter was used to finish samples to precise dimensions, as shown in Figure 37 (B). Due to the nature of GRIP-Metal, hooks were not able to be applied to a width as small as 0.4 in. As such hooks were applied to a 0.675 in wide region and the hooks were milled off in the unneeded region.

Figure 37: A) as-cured tensile fatigue sample, B) As-designed tensile fatigue sample, C) as-built tensile fatigue sample

Tumbler Design

A tumbler was designed to load coin shaped samples to achieve impact by repeatedly elevating then dropping the samples. A 201-series portable drum roller from Morse Drum

(Syracuse, NY) was purchased along with a 16 gal. drum from Uline (Pleasant Prairie, WI) as the tumbling container (Figure 39 (A) and (B)). The peak rotational speed for a 55 Gal. was converted to 16 gal. drum. The calculated RPM was confirmed by testing to be 35 RPM for a 16 gal. Drum. To elevate the samples, “fins” were mounted to the drum using 1/8” blind rivets at three locations in the drum running the length of the drum in three segments. These fins were manufactured from 1/16” mild steel and were bent to an angle of 55° leaving a section of 2 in to elevate the samples. Between each compartment of the drum a 1/8” thick poly-carbonate ring was force fitted into each rib in the drum. This was to prevent lateral movement of the drum. After approximately 500,000 cycles the rivets holding some of the fins failed and a decision was made to instead use fins the length of the drum and remove the polycarbonate rings (Figure 38). It was found that the drum “walked” forward or backward and so a hemispherical roller was mounted on either side of the roller unit to prevent the drum from moving off the roller unit. Figure 39 (C) shows a diagram of how samples interact with the drum and Figure 39 (D) shows how samples sit in the drum on the fins. Table 8 shows the specifications of the tumbling unit.

Figure 38: Drum interior after polycarbonate ring removal and fin replacement

Table 8: Tumbler Specification

Roller Unit	
Roller Type	Portable Drum Roller 201 Series
Roller Manufacturer	Morse Drum
Max Rotation Speed (55 Gal. Drum)	20
Motor Specifications	½ HP, 60 Hz, 115 V, 1800 RPM, Single Phase
Drum	
Drum Type	Steel
Drum Manufacturer	Uline
Drum Wall Thickness	0.9 mm
Drum Diameter (Internal)	14 in
Drum Height (Internal)	25.6 in

Figure 39: A) Tumbler unit, B) & D) drum images, C) tumbler with samples inside.

4.3 Bonding Procedure

Degreasing Procedure

Sunlight dish soap and water was used as a degreasing agent for the ultrasonic cleaning. Ultrasonic cleaning was conducted for a minimum of 15 minutes, a ratio of 1-part dish soap to 340 parts water was used to minimize soap residue on samples. A copper wire rack (Figure 40 (A)) was used to separate samples to prevent bonding surface damage. Once this was completed samples were rinsed with water to remove any soap residue and a wiping procedure was used in which a lint-free disposable wipe was wetted with Methyl Ethyl Ketone (MEK) and the surface was wiped down until the wipe was free of contamination by visual inspection. Due to the nature of the hooked surface, a secondary degreasing procedure was employed. This procedure consisted of placing each sample in a graduated cylinder filled with MEK (Fisher Scientific) and agitating, by hand, the sample for 30 seconds (Figure 40 (B)). Then the sample was placed in a second graduated cylinder filled with MEK; the sample was again agitated for 30 seconds to ensure any remaining grease was removed. Cleanliness was verified by use of a water break test. A surface free of contaminants was verified based on the uniform water distribution on the surface (Figure 40 (C), (D), (E)).

Figure 40: Degreasing Procedure: A) ultrasonic cleaning, B) MEK degreasing, C) water break testing, D) water break surface, E) water break surface guide [94]

Grit Blasting & Sol-Gel Procedure

A grit pressure was determined based on observation of hooks after grit blasting to ensure there was no apparent hook damage. Operating parameters and specifications can be found in Table 9. For grit blasting samples were attached to a metal plate using tacky tape. The samples were then placed in the grit blaster cabinet where samples maintained approximately the same distance and angle (Figure 41 (A)). Once this was finished pressurized nitrogen was used to clear the surface of any grit remnants (Figure 41 (B)).

Table 9: Grit Blast Specifications

Grit	220 grit (alumina)
Grit Manufacturer	Treibacher-Schleifmittel
Grit Blast Type	Suction Blast System
Grit Blast Pressure	60 psi
Grit Blast Angle	$\approx 70^\circ$
Grit Blast Distance	≈ 120 mm
Purging Gas	Nitrogen
Grit Blaster Manufacturer	Empire Abrasive Equipment

Once the surface was grit blasted, sol-gel (Table 10) was applied using a spray bottle to mist the surface with sol-gel, ensuring that the surface remained wet for 2 minutes (Figure 41 (C)). After this, the excess sol-gel was drained for 10 minutes. Next, the samples were placed in an oven for 60 minutes at 140°F to aid gel drying, at this point samples were ready to be cured.

Table 10: Sol-gel AC-130 specifications

Bonding Agent	Sol-gel AC-130
Supplier	3M

Figure 41: A) grit blasting samples, B) cleaning off grit, and C) applying sol-gel

Lay-Up & Curing Procedure

Once samples have been degreased and all surface treatments have been conducted, lay-up for curing can begin.

A clean work surface was prepared in a clean room with positive pressure, and the work surface was cleaned using isopropyl alcohol. The pre-preg was cut into rectangles around five times the size of the required bonding area using a razor blade and rulers.

Next, the pre-preg was laid up to 3 plies thick using a roller (Figure 42 (A)) to flatten the layers and force any trapped air bubbles out. This 3-ply laminate was then debulked (Figure 42 (B)) in a debulking table at -29.8 in (Hg) vacuum for a minimum of 30 minutes.

These 3-ply laminates were then cut into required sizes and layered onto each other, compacted using a roller each time, to form a 12-layer laminate of the correct dimension. This laminate was then de-bulked at -29.8 in (Hg) vacuum for a minimum of 1 hour.

Figure 42: A) Rolling pre-preg and B) debulking table

Next a sheet of Teflon was cut to just smaller than size of a tool plate and taped to a tool plate using flash tape to protect the tool plate from epoxy. Samples were then placed on the Teflon sheet in a single lap joint set up with the debulked 12-layer thick pre-preg sections sandwiched between two pieces of 2024 aluminum. One side of the lap joint was elevated being supported by a stack of two Al shims of 0.0625 in (1.588 mm) and 0.079 in (2 mm) (Figure 43 (A)) to maintain uniform thickness. These samples were then taped down using flash tape to ensure no sample movement, and all samples were labeled with a Sharpie Marker (Figure 43 (B)). Thermocouples were taped to both the part to be cured as well as the tool plate and lines were run past the edge of the tool plate. These samples were arranged to leave enough room for the placement of pressure taps on opposite sides of the tool plate.

Next, a sheet of perforated Teflon and a sheet of breather was cut to just smaller than the size of the tool plate. The perforated Teflon was placed over the samples followed by the breather material. Then a sheet of bagging film was cut, and two holes were cut in the place where space had been left for the pressure taps. Tacky Tape was then placed around the perimeter of the tool plate over the thermocouple lines, pressure taps were mounted to the bagging film, and the bagging film was applied to the Tacky Tape and sealed.

Vacuum was drawn from one of the pressure taps, and a pressure gauge was attached to the other tap. Once vacuum was drawn the edges were inspected for leaks, and which

were found were sealed. Next, the bag was left sealed under vacuum disconnected from the vacuum pump for 15 minutes to ensure there was no pressure change (Figure 43 (C)).

Next, the tool plate was placed in the autoclave, vacuum lines were connected to the pressure taps, and thermocouple lines were connected to the autoclave (Figure 43 (D)).

Finally, the autoclave was turned on, and the curing cycle began. The curing parameters can be found in Table 11.

Figure 43: A) Sample lay-up shims, B) sample lay-up, C) vacuum bagged tool plate, and D) tool plate in autoclave

Table 11: Autoclave curing parameters

Autoclave Pressure	55 psi (3.8 Bar)
Vacuum Vent Pressure	20 psi (1.38 Bar)
Autoclave Temperature	305°F (152°C)
Ramp- Up Temperature Rate	5°F/min (2.78°C)
Ramp-Down Temperature Rate	5°F/min (2.78°C)
Soak Time	360 min

Impact Fatigue Testing Procedure

All circular samples were placed in the tumbler drum, and the samples were distributed evenly along the length drum. A drum cap was secured to the top of the drum, and the drum was placed on the top of a rolling unit. The hemispherical rollers were secured in place to restrict movement of the drum. An RPM of 35 was set before the test was started. The time was recorded. After a period set time, the drum was shut off and the time recorded. The exact intervals are detailed in the Appendix Once the drum was shut off all samples were visually inspected for signs of delamination. The delaminated samples were removed from the drum, and the failure locations of these samples were recorded.

Tensile Fatigue Testing Procedure

Tensile samples were placed in the MTS 810 Material Test System Figure 44 (A). The sample was lined up vertically with the aid of a 90° angle gauge. Then the bottom wedge clamp was engaged at low clamping pressure around 100 psi until the full length of the clamp contacted the sample. Then the collet was disengaged, and the upper clamp was lowered such that the top part of the sample was fully inside the wedge clamp mouth. Once this was accomplished the collet was re-engaged, and the top clamp was engaged.

The clamping pressure was then increased to 1000 psi. Sample positioning in the MTS can be seen in Figure 44 (B).

Figure 44: A) MTS machine, B) MTS sample placement

Initially, a quasi-static test was run for a flat sol-gel sample to determine the fatigue loading condition. It was found that the ultimate tensile load was 2.376 kN. Thus 50% of this value was taken to be the maximum cyclic load for the test.

Next, the force and displacement gauges were zeroed, and the testing program was run, testing parameters are outlined in Table 12.

Table 12: Tensile Fatigue Testing Parameters

Cycle Type	Sinusoidal
Cycle Frequency	5 Hz
R-Value	0
Maximum Load	1.186 kN (50% of UTS)
Data Acquisition Method	Peak & Valley

It should be noted that the selection of a loading regime was deviated from ASTM standard D3166-99. This was based on the need to streamline test condition and reduce the number of test conditions.

Quasi-Static Testing Procedure

Tensile samples were placed in an MTS 810 Material Test System, using the same procedure as is detailed for the fatigue samples. Position control was used for this test, and the feed rate was set to 0.1 in/ min.

Polishing Procedure

Samples were polished before SEM investigation; first samples were cut using a diamond blade saw, or a band saw, no difference in bond line damage was seen between the two cutting methods. Once samples were cut the samples were either hot or cold mount. The hot mounting process used a Buehler (Switzerland) Simplimet II (Figure 45 (A)) and phenolic powder to cure samples inside pucks. Samples were heated with a pressure of 5 ksi for 20 minutes to cure. Also, cold mounting was conducted; this employed the use of Presi (France) MA2+ epoxy resin and catalyst. The resin and catalyst were mixed with a 2:1 ratio and poured over the samples placed in the mounting molds.

Once the samples were mounted, the polishing began. The hot mounted samples were large enough to put in a Buehler Automet 300 (Figure 45 (B)) where they were polished

with the following: 180 grit wet sandpaper, 240 grit wet sandpaper, 9 μm diamond suspension on an ultra-pad, 3 μm diamond suspension on a trident pad, and finally 0.03 μm alumina suspension on a fine polishing cloth. For the cold mounted samples, they were polished by hand (Figure 45 (C)) using 180 grit wet sandpaper, 240 grit wet sandpaper, 360 grit wet sandpaper, 420 grit wet sandpaper, and finally 600 grit wet sandpaper.

Figure 45: A) Buehler Simplimet II, B) Buehler Automet 300, C) hand polishing station

Once samples were polished, they were taken to an SEM (Tescan Vega II-XMU) where they were examined using SEM. Both SE (Secondary Electron) and BSE (Back Scatter Electron) mode imaging and EDS (energy-dispersive spectroscopy) composition analysis were carried out.

Figure 46: TESCAN VEGA II-XMU SEM

5 Results

Results presented in this thesis have been organized into impact/impact fatigue, quasi-static/uniaxial quasi-static tensile test and tensile/uniaxial fatigue. The naming convention for samples processed using different surface preparation methods is dictated below in Figure 48.

Surface Preparation	-	Hook Type	-	Test Type	-	Number
F- Frekote		S- Straight		T- Tensile Fatigue		
M- MEK Degrease		R- Rolled		I- Impact Fatigue		
S- Sol-Gel & Grit Blast		F- Flat		Q-Quasi-Static Tensile		

Figure 47: Sample naming convention diagram

Frekote is used on the samples to prevent bonding of the epoxy to the underlying surface. This was used to isolate the effects of GRIP-Metal on bonding strength. MEK was used to examine the effects of a completely clean surface on bonding with and without GRIP-Metal. Sol-Gel coupled with grit blasting was used to study the effects of surface activation on GRIP-Metal bonding performance and to compare samples processed under different conditions

The number of samples tested in each test was divided up into three different categories, Frekote treated, MEK treated, and sol-gel treated samples. Each category was further divided up based on the mechanical modifications made to each surface different treatments applied to. The three mechanical modifications are flat, straight hooked, and rolled. To reduce the number of test samples, the types of samples tested were hybridized

and as such not every combination was tested for each test. A summary of the different categories tested can be seen in [Figure 48](#).

Figure 48: Test matrix

5.1 SEM Investigation of As-Manufactured Samples

Samples were dissected, and the cross-section of samples was inspected using SEM to give a baseline for further inspection and to see the interaction of hooks and fibers. Figure 49 shows the surface inspected by SEM. It should be noted that the samples inspected are untested samples, manufactured and dissected the same way as all tested samples.

Figure 49: As-manufactured samples

Cross-Sectional SEM Investigation of Manufactured Sol-Gel Straight Hook Sample

The as-manufactured Sol-Gel Straight hook sample (S-S) cross section can be seen in Figure 50. Voids around the base of hooks can be seen, also the hooks do not properly penetrate the fiber weaves, but rather the fibers bend around the hooks, it appears that the hooks are embedded into a few plies of the fiber weave, it is unclear if they are displacing or cutting the fibers. High magnification inspection of the bond line shows the fine layer of sol-gel on the substrate surface, and there is no matrix or bond line damage seen in this sample.

Figure 50: SEM cross-sectional investigation of sol-gel straight hook as-manufactured sample

Cross-Sectional SEM Investigation of Manufactured Frekote Straight Hook Sample

The as-manufactured Frekote Straight hook sample (F-S) cross section can be seen in Figure 51. Voids around the base of hooks can be seen, but it is dispersed within Frekote coating. The hooks do not properly penetrate the fiber weaves, but rather the fibers bend around the hooks, like the (S-S) samples. High magnification inspection shows a fine layer

of Frekote going up the sides of the surface as well as on the base substrate. Frekote coating is seen on the bond line and no matrix damage is visible.

Figure 51: SEM cross-sectional investigation of Frekote straight hook as-manufactured sample

Cross-Sectional SEM Investigation of Manufactured Sol-Gel Flat Sample

The as-manufactured Sol-Gel Flat sample (S-F) cross section can be seen in Figure 52. It demonstrates excellent bonding, and upon high magnification inspection, a thin coating of sol-gel can be seen. Unlike the hooked samples, the fiber weaves run parallel to the aluminum surface as is expected since there are no hooks to cause fiber bending.

Inspection of the bond line and bulk epoxy matrix showed no evidence of damage or delamination.

Figure 52: SEM cross-sectional investigation of sol-gel flat as-manufactured sample

5.2 Impact Fatigue Testing

One of the objectives of this research is to determine the fatigue properties of cold worked penetrative reinforcements for use bonding FRP to aluminum. To achieve this, a novel impact fatigue testing method was designed and used to rank the fatigue performance of different bonds qualitatively. The metric used to classify material performance was based on the number of cycles survived and full delamination detected through visual observation classified failure.

The methodology behind this method is that all samples are repeatedly elevated to the same height and fell, inducing the same amount of energy into all samples. The loading condition of samples is not controlled, as the nature of free falling samples and the interaction of these samples is very difficult to quantify, but the assumption is that the net effect on the samples over many cycles is the same for all samples. The manufacturing of samples in a lap joint configuration presents a specific case scenario where impact will cause more damage in axial impact than in other directions with impact on sample edges loading the bond line in a multi-mode loading condition, dependent on impact angle a combination of mode I and mode II will occur depending on the angle of the random impact.

Impact fatigue testing was ceased at approximately 1,500,000 (1,451,684) cycles; this was determined to be an “endurance limit” and an understanding that a failure trend had been captured. Figure 54 depicts the average life of all impact samples. It is clear that GRIP-Metal improves the resistance to impact fatigue based a “total joint failure” criterion.

Both S-S-I and S-R-I class samples showed no total joint failures, indicating that they performed best among all samples, for this reason the abbreviation RO (run out) was used to indicate that tests were terminated prior to final sample failure. The next best performing sample type was M-S-I with an average life of 936,000 (936,115) cycles, showing improvement over the M-R-I class samples which had an average life of 839,000 (838,781) cycles. The F-S-I class samples had an average life of 806,000 (806,009) cycles, outperforming the S-F-I class samples which had an average life of 565,000 (565,532)

cycles. The M-F-I class samples had an average life of 3,500 (3,517), this was significantly impacted by the number of samples which failed upon manufacturing.

The S-F-I class samples had an average failure life below the average life of all GRIP-Metal samples, including the F-S-I class samples. This is unexpected as the Frekote acts to prevent the epoxy from bonding to the bonding surface, suggesting that the main active bonding mechanism is the mechanical interlocking of hooks for this mode of loading. It is believed that this is a result of combined loading mechanism and criterion to define failure. Impact loads have different effects on materials when compared to lower strain rate loading cases.

During impact fatigue, the properties of base materials change through repeated impact. Research conducted by Johnson et al. [95] suggests that for steels, impact loading increase material properties such as yield strength and ultimate tensile strength due to cold work. This leads to the important point that steels loaded through impact fatigue have longer lives than steels loaded through traditional tensile cyclic fatigue. However, in a bonded joint, the base material property has limited impact on the joint integrity. Silberschmidt et al. [96] suggest that for adhesively bonded joints impact fatigue life is less than that of traditional tensile cyclic fatigue life.

In the current setup, as the failure is based on gross bond line separation, it is believed that the deep penetration of the hooks into the fiber-reinforced epoxy adhesive allows for better load distribution across the multiple layers of fibers and also delayed total bond

line separation. This prevents the cohesive failure seen in the non-GRIP-Metal samples and the fiber breakage of single weave planes.

Impact Fatigue Statistical Analysis

Two tailed t-tests were conducted on all data from the impact fatigue testing to determine if the null hypothesis could be rejected and to verify that each data set showed a difference. A significance level (α) of 0.05 was used and the calculations were conducted using the excel t-test function.

Based on the t-tests, [Table 13](#) shows if the null hypothesis can be rejected for different data combinations. [Table 17](#) in the appendix summarizes the calculated t-statistics and t-statistic critical value for all combinations.

Table 13: Rejection of the null hypothesis based on the impact fatigue data set

	<i>S-S</i>	<i>S-R</i>	<i>M-F</i>	<i>F-S</i>	<i>S-F</i>	<i>M-R</i>	<i>M-S</i>
F-S	Yes	Yes	Yes	-	Yes	No	No
M-R	Yes	Yes	Yes	No	Yes	-	Yes
M-S	Yes	Yes	Yes	No	Yes	Yes	-
S-S	-	-	Yes	Yes	Yes	Yes	Yes
S-R	-	-	Yes	Yes	Yes	Yes	Yes
M-F	Yes	Yes	-	Yes	Yes	Yes	Yes
S-F	Yes	Yes	Yes	Yes	-	Yes	Yes

[Table 13](#) shows that the null hypothesis cannot be rejected for the combinations F-S-I & M-R-I and F-S-I & M-S-I. For the F-S-I & M-S-I combination the t-statistic was 2.01 while the critical t-statistic was 2.09. Based on this a small change of the significance level would allow for rejection of the null hypothesis. F-S-I & M-R-I had a t-statistic of 0.49 and

a critical t-statistic of 2.10, indicating that further testing needs to be conducted to better characterize the relationship. It has been demonstrated that the null hypothesis can be rejected for all other data sets.

Impact Fatigue SEM Investigation

Samples were dissected, to examine the damage sustained; cuts were made across the bond as depicted in Figure 53. Once dissected the internal face of the sample is mounted, and polished in preparation for SEM cross-sectional investigation. For failure analysis the side with which the least adhesive was present was inspected, Figure 55 identifies this surface for both a flat and hooked sample surface.

Figure 53: SEM cross-sectional sample dissection and inspection face, impact samples

Figure 54: Impact fatigue test cycles to failure graph

Figure 55: Failure surface inspection zones, impact samples (A) hooked and (B) flat

MEK Surface Treated Impact Flat and Hooked Samples

M-F-I (MEK-Flat-Impact) samples were not inspected as most samples failed before testing (indicative of insufficient bonding preparation). The samples which reached testing survived for the first inspection period (4,500 cycles) except for one which survived to 11,000 cycles. It is suspected that most of these samples failed well before 4,500 cycles, but due to the nature of testing, this cannot be confirmed. All samples exhibited clear interfacial delamination with no epoxy or fiber remnants on the surface.

The hooked samples performed much better; Figure 56 shows the cross-section of M-R-I (MEK-Rolled-Impact) and M-S-I (MEK-Straight-Impact) class samples after 850,000 cycles. Figure 56 (A) & (B) shows a matrix cracking (indicated by the arrow) and interfacial delamination of an M-S-I class sample, indicative of adhesive failure. Figure 56 (C) shows matrix cracking and interfacial

delamination of an M-R-I sample. Both M-R-I and M-S-I class samples exhibited similar behavior during this investigation.

Figure 56: SEM cross-sectional investigation after 850,000 cycles: A) MEK-Straight Hook-Impact (M-S-I-12) matrix cracking and delamination, B) MEK-Straight Hook-Impact (M-S-I-12) matrix cracking and delamination (high magnification), C) MEK Rolled Hook-Impact (M-R-I-5) matrix cracking and delamination

By inspecting the failure surface of M-S-I and M-R-I class samples the failure mode can be better understood. [Figure 57](#) depicts the failure surface of an M-S-I class sample; epoxy can be seen at the base of the hooks. The pattern observed in the epoxy is from the fibers originally bonded and is indicative of fiber pull out. Within these patterned channels, there are also some fibers which broke instead of pulling out. The presence of aluminum oxide was also identified, as dark spots on the aluminum ([Figure 57](#)). Aluminum oxide can hinder bond performance, its presence is expected as mechanical roughening or acid is

required to remove it [5]. Finally, sheared hooks can also be seen in [Figure 57](#) ~~Figure 57~~ which indicates load transfer from the sheet metal to the hooks and that some of the hooks failed before net hook pull out occurred. [Figure 58](#) ~~Figure 58~~ shows the failure surface of an M-R-I class sample. The sample surface looks very similar, sheared hooks, fiber pull out, and fiber fragments are present.

Figure 57: SEM failure surface investigation MEK-Straight Hooked- Impact (M-S-I-9)

Figure 58: SEM failure surface investigation MEK-Rolled Hooked- Impact (M-R-I-6)

MEK hooked samples appear to provide intermediate bonding; the hooks add strength to the bond as a MEK degreased surface is unable to maintain a bond with epoxy without hooks. This is emphasized by the failure of all flat MEK samples within the first inspection cycle with many of these failing before testing.

Sol-Gel Surface Treated Hooked Impact Samples

Figure 59 shows the cross-section of S-R-I (Sol Gel-Rolled Hook-Impact) and S-S-I (Sol Gel-Straight-Impact) samples after 850,000 cycles. Figure 59 (A) shows a small crack in a hook on the S-S-I sample, suggesting load transfer to the hook. Additionally, a small amount of voiding can be seen at the base of the hook. Figure 59 (C) similarly shows a hook on the S-R-I sample, the presence of a large void at the base of the hook is evident, in addition to a crack in the hook tip. It is unclear if a rolling operation induced this crack or if impact loading induced it. When looking at the bond line, the S-S-I sample proves to be resilient to bond line damage showing an intact bond line in

Figure 59 (B). Figure 59 (D) exhibits matrix cracking and interfacial delamination of an S-R-I sample.

Figure 59: SEM cross-sectional investigation after 850,000 cycles, Sol-Gel- Straight Hooked-Impact and Sol-Gel Rolled Hooked-Impact: A) S-S-I-6 hook, B) S-S-I-6 perfect bonding, C) S-R-I-2 hook, D) S-R-I-2 matrix cracking and delamination

Figure 60 shows the cross-section of an S-R-I class sample after 1,500,000 cycles. Further cracking and delamination can be seen. Matrix cracking can be seen between fiber bundles in Figure 60 (A), pointed by the arrow), suggesting a cohesive failure in these samples although interfacial delamination is also seen in Figure 60 (C). Finally, cracks can be seen in Figure 60 (B)

which indicates load transfer to the hooks. A void can once again be observed around the base of the hook as indicated in Figure 60 (B).

Figure 60: SEM cross-sectional investigation after 1,500,000 cycles, Sol-Gel-Rolled Hooked

Impact: A) S-R-I-11 matrix cracking, B) S-R-I-11 hook, C) S-R-I-11 interfacial delamination

Figure 61 shows the cross-section of an S-S-I class sample after 1,500,000 cycles. Figure 61 (A) displays cracks in a hook and voids at the base of a hook, while Figure 61 (B) shows matrix cracking between fiber bundles close to the interface suggesting shear-induced between plies. Figure 61 (C) shows micro cracks in the aluminum substrate, suggesting the interfacial bond is strong enough that the adherend began to develop cracks. Figure 61 (A) shows serration on one edge of the hook; this appears to be the result of cross sectioning of the plastic deformation ridges.

Figure 61: SEM cross-sectional investigation after 1,500,000 cycles, Sol-Gel-Straight Hooked-

Impact, A) S-S-I-16 hook, B) S-S-I-16 matrix crack, C) substrate cracking

No failure surfaces were available for investigation for S-S-I or S-R-I class samples as no samples failed during testing, but it is believed that a combination of cohesive and adhesive failure would be observed with some sheared hooks present, fiber pull out, and fiber breakage. The cross-sectional analysis gives strong evidence to support this theory with the presence of the combination of matrix cracking along fiber plies and interfacial delamination, as well as cracks present in hooks. The major difference apparent between straight and rolled hooks for these samples appears to be the void size. Additionally, it is thought the profile of the hook may have a small effect on the bonding strength, with rolled hooks exhibiting bond damage before straight hooks.

Sol-Gel Surface Treated Flat Impact Samples

Figure 62~~Figure 62~~ shows the failure surface of an S-F-I (Sol Gel-Flat-Impact) sample. Due to the coverage of non-conductive material (epoxy) on this surface excessive electron accumulation occurred, to remedy this, the nitrogen pressure was increased. Increased nitrogen pressure causes a higher impedance for electrons, leading to a fuzzy SEM image. For this reason, an optical image was used to represent the overall failure surface. This type of sample delaminated between fiber plies with no interfacial delamination. Delamination of plies tended to occur relatively close to the bonding surface, with a couple of plies of fiber still bonded to the surface. Upon closer inspection in SEM, a consistent layer of bare fibers can be observed indicating that delamination occurred at the fiber epoxy interface. The presence of broken fibers in certain locations indicates that although fiber/epoxy delamination was the dominant mode of failure, some fiber breakage occurred. Finally, aluminum particles were detected on the failure surface; this indicates the surface contamination occurred, this is unavoidable by the nature of the test,

but is important to note as the tumbling may have caused further damage to the failure surface after failure.

Figure 62: SEM failure surface investigation Sol-Gel-Flat -Impact (S-F-I-10) (left - optical, right – SEM)

Frekote Surface Treated Impact Samples

Figure 63 shows the cross-section of an F-S-I (Frekote-Straight-Impact) sample after 850,000 cycles. Figure 63 (A) depicts the clear separation of the matrix from the hook in the sample, demonstrating the effect of Frekote on bonding, and its effectiveness both on the flat bonding surface, as well as, the hook surface. Figure 63 (B) shows a 27 µm thick zone where significant cracking in the matrix has occurred, perhaps due to the lack of reinforcing fiber in this region.

Figure 63: SEM cross-sectional investigation after 850,000 cycles, Frekote-Straight Hooked-Impact: A) F-S-I-13, B) F-S-I-13 matrix cracking and delamination

Figure 64 shows the failure surface of an F-S-I class sample. The surface of this sample shows no epoxy residue on the surface; additionally, there are many sheared hooks, and the remaining hooks stumps are indicated by the arrows. Also, the hook stumps are also rounded, suggesting exposure to damage after surface failure. Due to the nature of testing, it is impossible to know if there was fiber still bonded to the ends of hooks after failure. Regardless, this surface indicates that the hooks carried substantial load in this sample based on the number of sheared hooks.

Figure 64: SEM failure surface investigation Frekote-Straight Hooked-Impact (F-S-I-16)

5.3 Quasi-Static Tensile Testing

Quasi-static tensile testing was carried out to determine the tensile properties of adhesive bonding, mechanical reinforcement, and combined adhesive bonding and mechanical reinforcement. Using a combination of GRIP-Metal, Frekote, and Sol-Gel, different types of bonds can be studied. A Force vs. Displacement graph can be seen in [Figure 66](#), where curves are depicted for each sample tested. The red curves representing the S-F-Q (Sol Gel-Flat-Quasi Static) samples, these samples can be seen to experience brittle failure, which is typical of a bonded joint. The elastic zone of these samples has the steepest slope suggesting the highest Young's modulus. The green curves represent the S-S-Q (Sol Gel-Straight-Quasi static) samples. S-S-Q samples exhibited mixed failure mode, where fiber damage near the hooks are observed. These samples showed two distinct points where load suddenly drop, indicative of progressive

failure. The first drop of load occurs at the same displacement as the max value of the bonded specimens S-S-Q, suggesting this drop in load is caused by the adhesive bond. The S-S-Q samples once passed the initial load reductions, went on to experience the highest load before final fracture. This further load carrying capability of S-S-Q is attributed to the presence of penetrative reinforcement. S-S-Q samples exhibited ductile fracture surface as the final mode of failure. S-S-Q samples elastic region showed a shallower slope than S-F-Q samples, suggesting an intermediate Young's modulus. The blue curves represent F-S-Q (Frekote-Straight-Quasi-static) samples, exhibiting a shallow increase in force with displacement followed by low peak loading before final failure. Finally, F-S-Q samples displayed a slow and steady unloading behavior. F-S-Q samples had the lowest elastic region suggesting the lowest Young's modulus of the samples tested.

Quasi-Static Tensile Sample SEM Investigation

A SEM was used to better understand the failure mode of F-S-Q, S-S-Q, and S-F-Q samples. [Figure 65](#) shows the examined region of the three different types of samples investigated in this section.

Figure 65: Quasi-static SEM failure surface investigation surfaces

Figure 66: Quasi-static tensile testing force vs. displacement graph

Sol-Gel Flat Quasi-Static (S-F-Q) Samples

Inspection of the failure surface of an S-F-Q class sample shows cohesive failure, the desired failure mode, as seen in Figure 67. A layer of epoxy residue can be seen on the surface, fiber/ epoxy delamination is evident in some regions based on the smooth channels left (where fibers were located) in the epoxy, and some bare fibers are remaining on the surface, some of which are coated in epoxy. Additionally, there are intermittent spots where bulk substrate aluminum coated with Sol-Gel can be seen, and in other regions, there is a very thin layer of epoxy on the surface. Delamination occurred near the surface of the S-F-Q class samples, alternating between the adhesive and near interface cohesive failure.

Figure 67: Sol-gel flat quasi-static (S-F-Q-2) tensile sample failure surface SEM investigation

Sol-Gel Straight Quasi-Static Tensile Samples

When looking at the interaction of the hooks with the epoxy and fiber matrix, the failure surface of an S-S-Q sample gives good insight (Figure 68). A large portion of epoxy/ fiber can be seen in the top right-hand corner where large bundles of delaminated, broken

fibers remain. Moving to the left, there is exposed aluminum with patches of epoxy and fiber. Focused on the hooks, the presence of sheared hooks is observed, epoxy can be seen filling in the hook grooves and fiber can be seen attached via epoxy to the hook surfaces. Upon closer inspection of the hooks, epoxy channels were fibers delaminated can be seen, additionally bare fibers and broke fibers can also be seen. This suggests that the hooks bonded well with the epoxy and provided load transfer from Al to the fibers. However, there is still delamination between fiber plies and epoxies due to the fiber/epoxy interface bonding strength. Compared to the S-F-Q samples these samples showed a greater presence of fibers on the fracture surface.

Figure 68: sol-gel straight quasi-static tensile (S-S-Q-4) sample failure surface SEM investigation

Frekote Straight Quasi-Static Tensile Samples

The application of Frekote allows for the investigation of hook performance without adhesion. This sample relies solely on the mechanical interlocking effects caused by the embedding of the hooks. The F-S-Q sample failure surface can be seen in Figure 69. No

fiber or epoxy can be seen on the surface, and only Frekote is detected. Interestingly for this sample, there was no hook shearing observed. This indicates that the hooks pull out of the epoxy before final failure.

Figure 69: Frekote straight quasi-static tensile (F-S-Q-3) sample failure surface SEM investigation

5.4 Tensile Fatigue Testing

Tensile fatigue testing was carried out to determine the fatigue properties of different bonded joints using mechanical reinforcement and adhesive bonding. This was aimed to identify the differences and similarities of these materials fatigue properties and to determine the effect of mechanical reinforcement on bonded joints, as well as, its interaction with adhesives. Tensile fatigue testing results can also be compared to impact fatigue testing results to compare the effects of strain rate on bond life. Tensile fatigue

testing was conducted by use of an MTS machine inducing mode II loading of a single lap joint bond.

Figure 70 shows the average life to failure of 3 types of samples S-S-T (Sol Gel-Straight-Tensile), S-F-T (Sol Gel-Flat-Tensile), and F-S-T (Frekote-Straight-Tensile). Failure of the S-S-T sample appeared to be bi-modal with a combination of mixed-mode delamination failure and substrate failure by fatigue crack propagation. F-S-T class samples showed very low life with the failure mode being strictly adhesive delamination, while S-F-T class samples had the longest lifetime with a predominantly mix mode failure of adhesive and cohesive failure.

TENSILE FATIGUE SAMPLE SEM INVESTIGATION

Due to the failure of both bonds and substrates in these tests multiple different types of failure surfaces were inspected. Figure 71 shows the regions in which SEM was used to inspect the failure surface. For the S-S-T samples, the substrate failure surface was inspected to determine the site of crack initiation and confirm fatigue crack propagation. Further to this, cross-sectional inspection of the non-delaminated part of the sample was done to understand the damage led to failure. Figure 72 shows how the sample was dissected and the cross-sectional region inspected.

Figure 70: Tensile fatigue mean cycle life

Figure 71: Failure surface inspection tensile fatigue

Figure 72: Cross-sectional inspection tensile fatigue

Sol-Gel Surface Treated Hooked Samples

Sol-gel straight hooked samples failed mainly through substrate failure. An SEM investigation was done to determine the location of crack initiation and propagation.

Figure 73 depicts a full analysis of the fracture surface of S-S-T-1, the failure mode is deemed to be crack initiation at the root region of hooks followed by fatigue crack propagation through Al and finally ductile failure of the remaining connected material. Analysis of both sides of the fracture surface indicates two sites of crack initiation both originating from the base of a hook or the edge of a hook groove. One of the crack initiation sites was obscured, by a plastically deformed piece of aluminum which was connected only by a small section of Al. Once SEM was completed this piece was removed to reveal the crack initiation site to be the base of the hook. The second crack initiation site was found to be at a narrow point between two hook grooves, close to the root of the hooks. Finally, ductile failure of the sample is detected in one region of the face, characterized by microvoid coalescence appearing as dimples. Although most S-S-T class samples failed through substrate failure, there were two samples (with much lower fatigue cycles to failure) which failed through delamination. The delamination occurred in a mixed mode, with both adhesive and cohesive manner. Since epoxy has a lower fracture toughness when compared to aluminum, delamination propagation in epoxy happens faster than that in Al once initiated [30]. Figure 74 shows the failure surface of S-S-T-6, both bare aluminum and epoxy/ fiber can be seen on the surface, with a concentration in the hook grooves. Inspection of hooks shows bare fibers still attached to the hook face. The hook root shows numerous cracks. In other regions, there is evidence of hook shearing with cavernous cracking which suggests fatigue cracking of the hooks.

Figure 73: Sol-gel straight hooked tensile (S-S-T-2) sample failure surface and crack propagation

Figure 74: SEM failure surface sol-gel-straight hook-tensile (S-S-T-6)

Cross-sectional evaluation of an S-S-T class sample (Figure 75 (A)) shows matrix damage close to the bonding interface; interestingly these cracks tend to follow the epoxy/ fiber interface, suggesting that the weak point of these bonds is the fiber matrix bonding. Figure 75 (B) shows a region where hook pull out occurred in the same sample, around the region of hook pull out at the tip of where the hook was attached; fiber breakage can be seen suggesting load transfer to the fibers at that point.

Figure 75: SEM cross-section investigation sol-gel-straight hook-tensile (S-S-T-1), A) matrix cracking, B) hook pull out and fiber breakage

Sol-Gel Surface Treated Flat Samples

S-F-T samples had two different characteristic failure modes; one consisted of near interface cohesive failure while the other consisted of near interface cohesive failure with ply jumping, i.e., having damage spreads through fiber plies (S-F-T-1 in Figure 76). This is due to delamination following the path of least resistance through the material. S-F-T-2 demonstrated near interface, cohesive failure (Figure 77). Evidence of a thin coating of epoxy can be seen on this surface with smooth epoxy channels indicating delamination between epoxy and fiber. Some broken fibers can be seen on the surface, as well as, small patches of bare aluminum where the delamination followed along the aluminum substrate.

Figure 76: Sol-gel-flat-tensile (S-F-T-1) failure surface

Figure 77: SEM failure surface sol-gel-straight hook-tensile (S-F-T-2)

Cross-sectional analysis of the failed samples was also conducted to understand the damage along the cross section. A cross section of the remaining bonded portion after failure was examined. The results of this investigation are presented in Figure 78. Figure

78 (A) shows the presence of a quite large crack in the substrate; this crack is located near the tip of the fillet formed by the epoxy. A different cross-section of the same sample was evaluated to see the extent of the crack (Figure 78 (B)), and it was found that the crack likely propagated from the fillet region towards Al outer surface. Further to this, it was seen that the crack was linked to matrix cracking. It is unclear as to which came first, the matrix crack or the substrate crack, but based on the fracture toughness of the two materials ($\sim 32 \text{ MPa}\sqrt{m}$ for aluminum [32] and $\sim 2 \text{ MPa}\sqrt{m}$ for epoxy [97]) it is likely the crack initiated in the substrate. No substrate cracks were discovered in any other S-F-T samples, perhaps there was a single crack that led to the fracture of the samples. This particular sample had the longest life among all samples of this type, tested with a life of 2,350,000 (2,343,557) cycles. It is likely that the bond fillet acted as a stress concentrator and initiated fatigue cracking. In addition to matrix cracking associated with the crack in the substrate there was also significant matrix cracking found. Figure 78 (C) shows near interface matrix cracking which diverts towards fibers causing fiber/ epoxy delamination.

Figure 78: SEM cross-section investigation sol-gel-flat-tensile (S-F-T-3), A) cross-section #1, B) cross-section #2, C) matrix cracking

Frekote Surface Treated Samples

Figure 79 shows the failure surface of an F-S-T type sample. The sample shows that most hooks appear to be intact, with little evidence of epoxy or fiber is present on the bulk of the surface. Small portions of fibers can be seen around the hooks; it appears the hooks embedded themselves in the fibers pulling those fibers out upon fracture. Another possibility is that the Frekote did not coat the hooks as well as it did to the substrate surface allowing some bonding to occur with the epoxy coated fibers.

Figure 79: SEM failure surface Frekote-straight hook-tensile (F-S-T-3)

Figure 80 ~~Figure 80~~ shows the non-delaminated cross-section of sample F-S-T-3. Figure 80 ~~Figure 80~~ (A) depicts an intact Frekote coating free of cracking, while Figure 80 ~~Figure 80~~ (B) shows a fully fractured hook, suggesting that little to no strength is being contributed by adhesive bonding and the hooks are taking the full load, resulting in fatigue failure of the hook roots.

Figure 80: SEM cross-section investigation F-S-T-3, A) Frekote coating intact, B) fractured hook

6 Discussion

6.1 Impact Fatigue

The results of this research discovered many findings and allowed for a better understanding of the effects of cold worked reinforcements on composite bonding strength under different conditions. Additionally, it gave insight into the effectiveness of impact fatigue testing based on tumbling. It was initially envisioned that the bonds would perform similarly as that in a standard fatigue test, but this was not the case.

Impact fatigue is a field which has been given little attention in comparison to its counterpart, standard fatigue [98]. Among the few experiments which have investigated this type of failure mode used the dropping of an elevated hammer on to a sample repeatedly. Upon impact the sample is exposed to a rapid tensile load induced by the hammer hitting a surface clamped on all sides. The drop hammer method is very lengthy and only one sample can be tested. To expedite this process the tumbling process

developed in this thesis has been employed to understand the impact fatigue properties of a bond better. This method does not restrict the loading mode, but rather relies on the sample shape to control the mode of damage. The basis of this test method is that the load induced by the impact on the contact location, where repeated high peak stresses are experienced. The net force will then be transferred to the bonded region. The intention is for the sample to be loaded primarily in mode II loading, the most damaging mode of loading based on sample geometry.

This testing has been conducted on the premise that not every impact will have the same load profile, but over millions of cycles, each sample will see approximately the same load profile. The data collected and depicted in [Figure 54](#) confirms this assumption based on a consistent range in which different types of samples all fail. Although this data cannot be used quantitatively, it can be used qualitatively to understand the properties of bonded joints better when exposed to impact fatigue loading and to understand the failure mode seen for such scenarios.

Results show that impact fatigue and standard fatigue are not comparable when evaluating fatigue performance of jointed samples. Strain rate sensitivity of bonding materials and loading condition have significant effects on the bonding performance. Work carried out by Silberschmidt et al.[96] showed that the damage sustained during impact fatigue of toughened adhesively bonded joints is quite detrimental to the structure, inducing matrix cracking and interfacial delamination. Both impact energy, and peak force affected the ultimate properties. Quasi-static or low strain rate loading enables a large amount of energy absorbed through sample deformation, while high strain rate

loading of adhesives leads to an increase in yield stress. This phenomenon results in energy concentration at the crack tip and a reduction in the plastic zone known to retard crack propagation [99]. Interestingly there is such evidence based on the research of Ray et al. [100] in which it shows that effects of impact on fatigue damage is reduced when an adhesive bond has high defect concentration; this is due to the decrease in stiffness associated with higher defect density which acts to dampen the impact. Similarly, this research found the greater lifetime of the mechanically reinforced samples can be attributed to their ability to sustain primary adhesive damage and remain joined. Even as the matrix sustains damage (often deeper into the sample and not at the bonding interface), the samples remain intact. It is believed that this is due to a decrease in stiffness of the bond as damage is sustained. This would suggest that the bond exhibits a defense mechanism to impact damage reducing the effect of impact damage as more and more impacts occur.

Research by Graham et al. [101] looked into the performance of penetrative reinforced bonds and found a significant improvement in high strain rate loading of these joints with a two-fold increase of maximum ultimate tensile strength when compared to quasi-static results. The reason for this performance is a combination of the resistance to impact with decreasing stiffness and a bridging mechanism which allows for stress to be effectively bridged across the cracks and delamination's through the hooks.

Results in Figure 54 show error for failed samples, this error is likely caused by the variability in hook dimensions.

6.2 Load Paths in Quasi-Static Tested Samples

Load paths in hybrid joints have presented an issue, with bonded/ bolted joints showing little capability to share load between adhesives and bolts due to the higher stiffness of the adhesive [69]–[71]. Fortunately, hybrid penetrative reinforced adhesive joints show promise, with optimized methods, substantial increases in joint strength above standard adhesive strength can be achieved, while maintaining similar stiffness to that of a non-reinforced joint [4], [73]. Unfortunately, this load sharing did not seem to occur in the samples tested in this study. A slight reduction in joint stiffness was observed for the sol-gel straight hooked quasi-static samples, a product of reduced bonding area. Primary failure of the joint occurred at a strength marginally below the failure of the non-reinforced joint. It occurred in two stages with the adhesive bond on each side of the joint beginning to fail separately. This was characterized by an indicative drop in load bearing, like that seen in bonded/ bolted joints upon adhesive failure, followed by a recovery of the joint strength as the hooks fully distributed the load among themselves. With the load distributed to the hooks, the stiffness of the bond can be seen to drop. Continued loading of the hooks can be seen until hooks begin to shear. Hook shear was apparent at the edge of the bonding zone. Similar to the failure mode portrayed in Parke et al. [4] in which failure was caused by increased loading of the hooks at the edge of the bond line due to the slight rotation characteristic of the single lap shear joints upon loading and the stress concentration created by the bonding fillet. Once the tips of these hooks have sheared the joint continues to induce an axial component on the remaining hook portions. The interfacial stress is lower at the end of the hook compared to the root allowing for a bond

to remain intact at the end of the hook. This is corroborated by the presence of epoxy bonded to the end of many hooks with fiber pull out in the direction which load was applied. This bond resists pull out causing a delay before hook pull out. This pull out is characterized by a steep decrease in load bearing capability as the hooks pull out of the composite and the joint fails.

To increase load transfer for this style of joint, an increase in fiber penetration is required by way of layer by layer lay-up onto the hooks. Additionally, an alteration of the hook profile to allow for better penetration into the fiber weaves are required; a looser fiber weave may improve penetration; however, it may compromise the properties of FRP. To prevent hook, pull out, a pull out resistant hook profile and surface treatment are required.

When evaluating the failure mode of Frekote coated samples failure mode, the Force vs. Displacement plot shown in Figure 66 shows a lower stiffness compared to the other two joints and a lower peak in ultimate strength proceeded by a long, slow decline in load bearing capability caused by hook pull out. Due to the use of Frekote, the hooks rely completely on mechanical interlocking, which is insufficient.

The presence of a rapid drop in load after an adhesive failure occurs in this study for both the sol-gel flat samples and the sol-gel straight hook samples, but not the Frekote straight hook samples. Results for other penetrative reinforcements, did not show this drop. The only other study which could be found where this happens was that of Joesbury [72]. Graham et al. [101] discussed the concept of shear strength ratio between pins and

adhesives, claiming that if the shear strength is not high enough compared to the adhesive strength a shift in failure mode can be seen. It is believed that this can be used to explain the absence of load drops upon adhesive failure in the majority of the published studies where the reinforcement geometry has been optimized. Upon brittle failure of the adhesive bond, all load is transferred to the reinforcements effectively until final failure.

6.3 Fatigue

Under standard, low strain rate fatigue loading, flat sol-gel samples performed best. with the average number of cycles to failure being approximately 1,565,000 cycles, the standard deviation of this data was around +/- 617,000 cycles which is indicative of the variability of fatigue in adhesively bonded joints. Bonded joints with no defects exhibit excellent fatigue properties, resisting crack initiation, but once a fatigue crack initiates, fatigue propagation is relatively fast due to the low fracture toughness exhibited by epoxy ($2 \text{ MPa}\sqrt{m}$ for epoxy[97]). In comparison penetrative reinforced joints have been shown to have fast crack initiation times, with long periods of stable crack growth, this was shown by both Graham et al. [101] and Parkes et al. [7]. Stable crack growth was found to be due to the crack arresting by the reinforcement hooks. Graham et al. [101] showed fatigue performance of penetrative reinforced joints exceeding that of co-cured samples, using a loading condition of $\sigma_{max} = 0.5\sigma_{UTS}$ of the specific test sample and an $R=0.1$.

When visiting results of this research, the same trend was not found. The straight hooked sol-gel samples being outperformed substantially by the flat sol-gel samples. The straight hooked sol-gel samples showed a bi-modal failure mode with delamination of the bond line (Figure 74 & Figure 75) much earlier (30% of the duration), while two-thirds failed due to substrate fracture caused by fatigue (Figure 73). Frekote coated samples (with no metal and polymer bonding mechanism) showed even lower fatigue life, as the hooks pulled out of the fiber/epoxy matrix. A failure investigation was conducted to determine the source of the fatigue cracks in the aluminum substrate of the straight hook sol-gel samples. It showed that crack initiation in the substrate occurred at the base of a reinforcing hook in the row of hooks closest to the edge of the bond. One flat sol-gel sample also exhibited evidence of substrate cracking although the sample subsequently failed from delamination; the crack was present close to the edge of the bond near the fillet in the same place as the reinforced samples due to stress concentration.

Failure of the hook reinforced samples through delamination and the comparatively low lifetime compared to the adhesively bonded joints can be explained by investigating testing parameters. $\sigma_{max} = 0.5\sigma_{UTS}$ was used in this study to test all three types of samples, similar to that used in other studies, but the value of σ_{UTS} was determined for a flat sol-gel sample (no hooks). In addition, further quasi-static testing after the completion of fatigue testing was conducted for the flat sol gel samples, this testing showed a large range of σ_{UTS} with a much higher average value of 3.41 kN per unit area and a standard deviation of 0.55 kN per unit area. Perhaps if a higher $0.5\sigma_{max}$ was used in the fatigue test, the hook reinforced samples would have performed comparatively better to the flat

sol-gel samples. For proper evaluation of these bonds at different load regimes it is necessary to evaluate the performance of both sample types under a high cycle and low cycle fatigue regime.

Inspection of the failure surface of the straight hooked sol-gel samples showed sheared hooks in the middle of the bonding region, with cavernous cracking (characteristic of fatigue cracking) occurring on these hooks, and other hooks showing cracks, as well (Figure 74). The matrix around hooks are seen to have cracked fibers being pull out. This suggests that after adhesive failure, load was carried by the hooks, until a combination of hook fatigue and hook pull out occurred.

Connecting all this a sequence of events can be summarized as shown in [Figure 81](#)~~Figure 81~~, different modes for different fatigue samples.

I. Delamination initiation

II. Hook shearing at the edge of the sample

III. Cohesive/adhesive delamination propagation often following fibers

IV. Hook fatigue occurs at the base, and substrate fatigue cracking begins.

Va. Hook pull-out occurs, and sample separates (disbond failure)

Vb. Substrate forms fatigue crack, and substrate fails (substrate failure)

6.4 Improvement of Joint Design

Through this study great insight was gained into the performance and failure mode of cold-worked penetrative reinforcements, the knowledge gained through this investigation gives an idea of what an optimal joint design might look like.

To begin with, the hook geometry needs to be optimized to improve penetration, the fiber weave needs to be altered to allow for better hook penetration, and the layup procedure should be altered to ensure penetration occurs. An optimized hook geometry would demonstrate a hook which penetrates deeper into the GFRP, portraying a thick hook root to increase shear strength, but a thin upper portion to allow for better penetration and interaction with fiber bundles.

A looser fiber weave is required to improve hook penetration. The high density of fibers in the pre-preg prevents the penetration of the GRIP-metal appropriately, reducing the potential improved bond strength enabled by utilizing penetrative reinforcement. Alternatively, the use of unidirectional fiber plies may prove more beneficial for the modified metal surface. A proposed ply lay-up would be repeating combinations of a 45/-45/0/90 up to the thickness required. Application of plies should be made one at a time with each ply being debulked separately if a pre-preg is used. Alternatives to a pre-preg would be the use of resin and an RTM process. This would allow for placement of bare fibers on hooks and ensure better intimate contact between fibers and hooks. Dependent on the method chosen, the use of an ultrasonic horn similar to that used in Parkes et al. [4] is recommended to help work hooks into the pre-preg. Once most of the layers have

been engaged with the hooks it is recommended that the top 1 mm of the hook be rolled down to better hook on to the fibers. If a dry layup is chosen, use of pre-rolled hooks may prove possible. This hook profiled reinforcement will reduce likely hook of hook pull out and crease the mechanical interlocking effect between fibers and hooks. Grit blasting of the substrate surface as a surface preparation should allow or extra focus on the roots of the hooks in hopes of rounding the stress concentrators of the hook bases.

Figure 81: Fatigue Failure Modes

7 Conclusions

This study assessed the performance of cold worked 2024-T3 aluminum penetrative hooks in the bonding between an aluminum substrate and a co-cured GFRP. Quasi-static, fatigue and impact fatigue behavior was evaluated, including the use of a novel impact fatigue testing method through tumbling was employed. The following conclusions were drawn from this research.

- Use of cold worked hooks to reinforce an adhesive bond between aluminum and GFRP shows great promise, optimization of hook geometry is critical for further advancement of this technology.
- Impact fatigue life of all hooked sol-gel samples (both straight and rolled hook) exceeded the test length with the test stopping at 1,450,000 cycles, in contrast the flat sol-gel samples had an average life of 565,000 cycles. This shows that the use of sol-gel as a surface preparation and the application of penetrative reinforcing hooks improves the impact fatigue performance substantially.
- Use of tumbling to test the impact fatigue properties of bonds proved beneficial for ranking of large sample size. Processing of data showed reasonable trends in sample performance, supporting the assumption that all samples would have approximately the same load profile after a large number of cycles.
- Increased strain rate loading (during tumbling) was found to result in different joint fatigue behavior as compared to that from standard fatigue test procedure detailed in ASTM D1002-10.

- The maximum ultimate strength of the sol-gel straight hook samples showed an average maximum tensile load of 3.7 kN, similar to the flat sol-gel samples which had an average maximum tensile load of 3.4 kN as well, while the frekote hooked samples had an average maximum tensile load of 1.8 kN.
- The load carrying capability of penetrative reinforcing hooks was found to be reliant on the interaction with the GFRP matrix and fibers. Improved load carrying ability was achieved through deeper penetration into the fiber reinforcements for improved mechanical interlocking, preventing hook pull out.
- Under quasi-static condition, a significant increase in failure energy was observed in joints employing penetrative reinforcing hooks (sol-gel straight hooked and Frekote straight hooked samples), when compared to non-reinforced joints (sol-gel flat).
- Fatigue failure saw a mix of adhesive and cohesive delamination of the adhesive bond followed by a combination of hook fatigue and hook pull out. Fatigue testing also identified a stress concentrating effect which was caused by the sharp corner of the hooks; this combined with a region of increased stress led to failure of many of the samples through substrate fatigue cracking.
- Average fatigue life of the sol-gel straight hooked samples which failed through delamination was 230,000 cycles, while the sol-gel straight hooked samples which failed through substrate fracture demonstrated a fatigue life of 745,000 cycles. The sol-gel flat samples without hooks had a fatigue life of 1,565,000.

8 Future Work

Cold worked penetrative reinforcing hooks have shown a great promise for use in improving the damage tolerance of bonds between GFRP and 2024-T3 aluminum. For this reason, it is recommended that research into this concept continue. Optimization of hook geometry to maximize fiber penetration and mechanical interlocking is paramount. The variations of hook geometry should be addressed and manufacturing procedures be improved. Alteration of the joint type by use of a GFRP adherend co-cured to aluminum adherends in a double lap joint shear configuration may provide better performance, providing a more effective method of loading these reinforcements. A modified layup procedure to accommodate the necessity of hook penetration by way of dry fiber layup and an RMT process may prove beneficial. Implementation of non-destructive testing to identify delamination and failure before final joint failure will also allow for a better understanding of the interaction between the adhesive/fiber and the cold worked penetrative reinforcements. It is critical that the stress concentration effect of the hooks be minimized during cold work process to prevent substrate fatigue failure. Additionally, due to the low impact energy it is possible that the onset of failure of some samples occurred but, the hooks may have allowed for samples to stay bonded. To study the progression of failure in these samples, tensile testing should be conducted over several intervals of tumbling cycles. Evaluation of the GRIP metal hooks should be conducted to characterize the consistency of the geometry and spacing. Use of other metals such as titanium should be investigated in the future to overcome the galvanic corrosion issues.

associated with the use of aluminum and carbon fibers. Finally, tumbling method should be conducted using simpler joints, e.g., butt joint, to validate the concept.

9 References

- [1] R. Adams, A. Öchsner, and L. F. M. Silva, *Handbook of adhesion technology*. Berlin;London; Springer, 2011.
- [2] J.-M. Bertholet, "Composite materials: mechanical behavior and structural analysis ." Springer , New York , 1999.
- [3] NASA, "Climate change: How do we know?" [Online]. Available: <https://climate.nasa.gov/evidence/>. [Accessed: 13-Jul-2016].
- [4] P. N. Parkes, R. Butler, J. Meyer, and A. de Oliveira, "Static strength of metal-composite joints with penetrative reinforcement," *Compos. Struct.*, vol. 118, no. 1, pp. 250–256, 2014.
- [5] G. W. Critchlow and D. M. Brewis, "Review of surface pretreatments for aluminium alloys," *Int. J. Adhes. Adhes.*, vol. 16, no. 4, pp. 255–274, 1996.
- [6] P. N. Parkes, R. Butler, J. Meyer, and A. de Oliveira, "Static strength of metal-composite joints with penetrative reinforcement," *Compos. Struct.*, vol. 118, no. 1, pp. 250–256, 2014.
- [7] D. P. A. Philip N. Parkes, Richard Butler, "Fatigue of metal-composite joints with penetrative reinforcement," *Proc. 54th AIAA/ASME/ASCE/AHS/ASC Struct. Struct. Dyn. Mater. Conf.*, pp. 1–8, 2013.
- [8] Z. Zhang, J. Shan, X. Tan, and J. Zhang, "Improvement of the laser joining of CFRP and aluminum via laser pre-treatment," *Int. J. Adv. Manuf. Technol.*, vol. 90, no. 9–12, pp. 3465–3472, 2017.
- [9] H. S. Yoon *et al.*, "A comparison of energy consumption in bulk forming, subtractive, and additive processes: Review and case study," *Int. J. Precis. Eng. Manuf. - Green Technol.*, vol. 1, no. 3, pp. 261–279, 2014.
- [10] T. G. Gutowski, M. S. Branham, J. B. Dahmus, a. J. Jones, a. Thiriez, and D. P. Sekulic, "Thermodynamic Analysis of Processes," *Environ. Sci. Technol.*, vol. 43, no. 5, pp. 1584–1590, 2009.
- [11] M. Baumers, P. Dickens, C. Tuck, and R. Hague, "The cost of additive manufacturing: Machine productivity, economies of scale and technology-push," *Technol. Forecast. Soc. Change*, vol. 102, pp. 193–201, 2016.
- [12] K. L. Richards and C. R. C. Press, *Design engineer's handbook*, 1st ed. Boca Raton, Fla: CRC Press.
- [13] C. Rans, "The Role of Rivet Installation on the Fatigue Performance of Riveted Lap Joints," Carleton University, 2007.

- [14] and Y. Z. S. Yazhou Xu, Zhen Sun, “Experimental and Numerical Investigations of Fretting Fatigue Behavior for Steel Q235 Single-Lap Bolted Joints,” *Adv. Mater. Sci. Eng.*, vol. 2016, p. 10, 2016.
- [15] G. Mathers, *Welding of Aluminium and Its Alloys*. Woodhead Publishing, 2002.
- [16] S. Ebnesajjad and A. H. Landrock, “Adhesives Technology Handbook (3rd Edition).” Elsevier.
- [17] US Congress, “Advanced Materials by Design,” 1988.
- [18] Royal Society of Chemistry [RSC], “Composite Materials,” *R. Soc. Chem.*, pp. 3–5, 2015.
- [19] S. E. Moussavi-Torshizi, S. Dariushi, M. Sadighi, and P. Safarpour, “A study on tensile properties of a novel fiber/metal laminates,” *Mater. Sci. Eng. A*, vol. 527, no. 18–19, pp. 4920–4925, 2010.
- [20] M. Sadighi and S. Dariushi, “An experimental study of the fibre orientation and laminate sequencing effects on mechanical properties of Glare,” *Proc. Inst. Mech. Eng. Part G J. Aerosp. Eng.*, vol. 222, no. 7, pp. 1015–1024, 2008.
- [21] G. Hassan, M. Fahmy, and I. Goda, “The Effect of Fiber Orientation and Laminate Stacking Sequences on the Torsional Natural Frequencies of Laminated Composite Beams,” *J. Mech. Des. ...*, vol. 1, no. 1, pp. 20–26, 2014.
- [22] B. Salgin, Ö. Özkanat, J. M. C. Mol, H. Terry, and M. Rohwerder, “Role of surface oxide properties on the aluminum/epoxy interfacial bonding,” *J. Phys. Chem. C*, vol. 117, no. 9, pp. 4480–4487, 2013.
- [23] Aviation Safety Bureau, “Advanced Composite Materials.” [Online]. Available: <http://content.aviation-safety-bureau.com/allmembers/faa-h-8083-31-amt-airframe-vol-1/sections/chapter7.php>. [Accessed: 29-Apr-2017].
- [24] A. Baker, S. Dutton, and D. Kelly, Eds., *Composite Materials for Aircraft Structures*, 2nd ed. Reston: American Institute of Aeronautics and Astronautics, 2004.
- [25] AirBus, “A380 Family.” [Online]. Available: <http://www.airbus.com/aircraftfamilies/passengeraircraft/a380family/innovation/>. [Accessed: 27-Apr-2017].
- [26] M. G. Bader, “Selection of composite materials and manufacturing routes for cost-effective performance,” *Compos. Part A Appl. Sci. Manuf.*, vol. 33, pp. 913–934, 2002.
- [27] P. . Mallick, “Materials,” in *Fiber-Reinforced Composites*, CRC Press, 2007.

- [28] Boeing, "787 Advanced Composite Use," *Boeing*. [Online]. Available: <http://www.boeing.com/commercial/787/by-design#/advanced-composite-use>. [Accessed: 27-Oct-2017].
- [29] Bombardier, "Bombardier C Series Technology," *Bombardier*. [Online]. Available: <http://commercialaircraft.bombardier.com/en/cseries/Technology.html>. [Accessed: 27-Oct-2017].
- [30] Cambridge University Engineering Department, *Materials data book*. 2003.
- [31] T. . Peters, Ed., *Handbook of Composites*, 2nd ed. London: Chapman-Hall.
- [32] ASM Aerospace Specification Metals Inc., "ASM Material Data Sheet-2024-T3." [Online]. Available: <http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=MA2024T3>. [Accessed: 14-Jun-2017].
- [33] E. J. F. Shackelford and W. Alexander, "Mechanical Properties of Materials," in *Materials Science and Engineering Handbook*, 2001.
- [34] ASM Aerospace Specification Metals Inc., "ASM Material Data Sheet - 7075-T6." [Online]. Available: <http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=MA7075T6>. [Accessed: 14-Jun-2017].
- [35] P. K. Mallick, *Composites engineering handbook*. New York: Dekker, 1997.
- [36] Composites World, "Fiber-metal laminates in the spotlight : CompositesWorld." [Online]. Available: <https://www.compositesworld.com/articles/fiber-metal-laminates-in-the-spotlight>. [Accessed: 23-Nov-2017].
- [37] Composites and Polymer Engineering Laboratory, "Processing Equipment." [Online]. Available: <https://www.sdsmt.edu/Research/Research-Laboratories/CAPE/Facilities-and-Equipment/Processing-Equipment/>. [Accessed: 23-Nov-2017].
- [38] P. . Mallick, "Manufacturing," in *Fiber-Reinforced Composites*, CRC Press, 2007.
- [39] J. C. Seferis, R. W. Hillermeier, and F. U. Buehler, "2.20 - Prepregging and Autoclaving of Thermoset Composites," in *Comprehensive Composite Materials*, 2000, pp. 701–736.
- [40] eBay, "Vacuum Bagging Kit Bag & Vacuum Sealant Tape & Polyester Peel & Breather Ply | eBay." [Online]. Available: https://www.ebay.com.au/p/Vacuum-Bagging-Kit-Bag-Vacuum-Sealant-Tape-Polyester-Peel-Breather-Ply/1031523402?_trksid=p2047675.m4097.l9055. [Accessed: 23-Nov-2017].

- [41] "Canadian researchers employ recycled carbon-fiber mats to produce thermoset composites - SAE International." [Online]. Available: <http://articles.sae.org/12559/>. [Accessed: 25-May-2017].
- [42] J. Ramaswamy Setty, A. R. Upadhyay, G. N. Dayananda, G. M. Kamalakannan, and J. Christopher Daniel, "Autoclaves for aerospace applications: Issues and challenges," *Int. J. Aerosp. Eng.*, vol. 2011, 2011.
- [43] S. Prabhakaran, V. Krishnaraj, K. Senthil Kumar, and R. Zitoune, *Sound and Vibration Damping Properties of Flax Fiber Reinforced Composites*, vol. 97. 2014.
- [44] R. D. Adams, *Adhesive bonding : science, technology and applications*. CRC Press, 2005.
- [45] W. H. Keesom, "The second virial coefficient for rigid spherical molecules, whose mutual attraction is equivalent to that of a quadruplet placed at their centre," in *KNAW Proceedings*, 1915, vol. 181, no. September, pp. 636–646.
- [46] P. Debye, *Polar Molecules*. New York: The Chemical Catalogue Company Inc, 1929.
- [47] Purdue University, "London Dispersion Forces." [Online]. Available: <https://www.chem.purdue.edu/gchelp/liquids/disperse.html>. [Accessed: 01-May-2017].
- [48] H. Kollek, "Some aspects of chemistry in adhesion on anodized aluminium," *Int. J. Adhes. Adhes.*, vol. 5, no. 2, pp. 75–80, 1985.
- [49] W. S. Kim, I. H. Yun, J. J. Lee, and H. T. Jung, "Evaluation of mechanical interlock effect on adhesion strength of polymer metal interfaces using micro-patterned surface topography," *Int. J. Adhes. Adhes.*, vol. 30, no. 6, pp. 408–417, 2010.
- [50] S. G. Prolongo, G. Rosario, and A. Ureña, "Study of the effect of substrate roughness on adhesive joints by SEM image analysis," *J. Adhes. Sci. Technol.*, vol. 20, no. 5, pp. 457–470, 2006.
- [51] K. Blohowiak, J. Osborne, and K. Krienke, "US . Patent: 5869140," 5,869,140, 1999.
- [52] K. Blohowiak, "US Patent: 6037060," 6037060, 2000.
- [53] D. Ensminger and F. Stulen, *Ultrasonics: Data, Equations and Their Practical Uses*. Boca Raton: CRC Press, 2008.
- [54] Recochem Inc., "Methyl Ethyl Ketone (MEK) - Anti-freeze, windshield wash, solvents, Global supplier of automotive liquids & household chemicals - Recochem Inc." [Online]. Available: http://www.recochem.com/products/paint_thinners_solvents/mek. [Accessed: 07-Apr-2017].

- [55] ScienceLab.com, "Material Safety Data Sheet Methyl Ethyl Ketone." [Online]. Available: <http://www.sciencelab.com/msds.php?msdsId=9927358>. [Accessed: 07-Apr-2017].
- [56] Parker Chomerics, "RECOMMENDED SURFACE PREPARATION FOR EPOXIES, ACRYLICS AND SILICONES," 2013. [Online]. Available: [https://www.parker.com/literature/Chomerics/Parker Chomerics Surface Preparation.pdf](https://www.parker.com/literature/Chomerics/Parker%20Chomerics%20Surface%20Preparation.pdf). [Accessed: 07-Apr-2017].
- [57] M. H. Staia *et al.*, "Effect of substrate roughness induced by grit blasting upon adhesion of WC-17% Co thermal sprayed coatings," *Thin Solid Films*, vol. 377–378, pp. 657–664, 2000.
- [58] M. Shahid and S. A. Hashim, "Effect of surface roughness on the strength of cleavage joints," *Int. J. Adhes. Adhes.*, vol. 22, no. 3, pp. 235–244, 2002.
- [59] R. Kromer *et al.*, "Laser surface patterning to enhance adhesion of plasma sprayed coatings," *Surf. Coatings Technol.*, vol. 278, no. 2015, pp. 171–182, 2015.
- [60] S. Ebnesajjad and C. Ebnesajjad, *Surface Treatment of Materials for Adhesive Bonding*, vol. 2; 2nd; Saint Louis: William Andrew, 2013.
- [61] W. Russel and E. Garnis, "Chromate-Free Method of Preparing Aluminium Surfaces for Adhesive Bonding, an Etchant Composition of Low Toxicity," Dover, New Jersey, 1978.
- [62] A. Makhoul and S. Hamdy, *Handbook of smart coatings for materials protection*. London: Woodhead Publishing, 2014.
- [63] H. R. Asemani, P. Ahmadi, A. A. Sarabi, and H. Eivaz Mohammadloo, "Effect of zirconium conversion coating: Adhesion and anti-corrosion properties of epoxy organic coating containing zinc aluminum polyphosphate (ZAPP) pigment on carbon mild steel," *Prog. Org. Coatings*, vol. 94, pp. 18–27, 2016.
- [64] A. Vaillancourt and T. Abele, "Adhesive Technology: Surface Preparation Techniques on Aluminum," Worcester.
- [65] G. Boisier, N. Pébère, C. Druez, M. Villatte, and S. Suel, "FESEM and EIS Study of Sealed AA2024 T3 Anodized in Sulfuric Acid Electrolytes: Influence of Tartaric Acid," *J. Electrochem. Soc.*, vol. 155, no. 11, p. C521, 2008.
- [66] K. Blohowiak, "Improvements in Surface Preparation Methods for Adhesive Bonding." Boeing, 2008.
- [67] K. Blohowiak and T. Boeing, "Structural Technology and Analysis Program (STAP). Delivery Order 0010 : Sol-Gel Technology for Surface Preparation of Metal ... AFRL-ML-WP-TR-2003-4169," no. March 2001, 2015.

- [68] S. P. Pp-, J. J. Mazza, W. A. F. Base, and U. S. N. Navair, "Sol-gel technology for low-voc, nonchromated adhesive bonding applications," no. September 2002, 2004.
- [69] P. Lopez-Cruz, "Experimental and Numerical Study on Bolted / Bonded Composite Joints for Aircraft by Affairs in partial fulfillment of the requirements for the degree of," 2016.
- [70] R. Matsuzaki, M. Shibata, and A. Todoroki, "Improving performance of GFRP/aluminum single lap joints using bolted/co-cured hybrid method," *Compos. Part A Appl. Sci. Manuf.*, vol. 39, no. 2, pp. 154–163, 2008.
- [71] G. Kelly, "Load transfer in hybrid (bonded/bolted) composite single-lap joints," *Compos. Struct.*, vol. 69, no. 1, pp. 35–43, 2005.
- [72] A. Joesbury, "NEW APPROACHES TO COMPOSITE METAL JOINING," Cranfield University.
- [73] F. Smith, "COMELD™: An innovation in composite to metal joining," *Mater. Technol.*, vol. 20, no. 2, pp. 91–96, 2005.
- [74] S. Ucsnik, M. Scheerer, S. Zaremba, and D. H. Pahr, "Experimental investigation of a novel hybrid metal-composite joining technology," *Compos. Part A Appl. Sci. Manuf.*, vol. 41, no. 3, pp. 369–374, 2010.
- [75] W. Tu, P. H. Wen, P. J. Hogg, and F. J. Guild, "Optimisation of the protrusion geometry in Comeld™ joints," *Compos. Sci. Technol.*, vol. 71, no. 6, pp. 868–876, 2011.
- [76] J. Taendl and N.ENZINGER, "Electron beam surface structuring of AA6016 aluminum alloy," *Weld. World*, vol. 58, no. 6, pp. 795–803, 2014.
- [77] A. N. Fuchs, F. X. Wirth, P. Rinck, and M. F. Zaeh, "Laser-generated macroscopic and microscopic surface structures for the joining of aluminum and thermoplastics using friction press joining," *Phys. Procedia*, vol. 56, no. C, pp. 801–810, 2014.
- [78] A. Heckert and M. F. Zaeh, "Laser surface pre-treatment of aluminium for hybrid joints with glass fibre reinforced thermoplastics," *Phys. Procedia*, vol. 56, no. C, pp. 1171–1181, 2014.
- [79] Y. Li and D. Gu, "Parametric analysis of thermal behavior during selective laser melting additive manufacturing of aluminum alloy powder," *Mater. Des.*, vol. 63, pp. 856–867, 2014.
- [80] J. A. Pascoe, R. C. Alderliesten, and R. Benedictus, "Methods for the prediction of fatigue delamination growth in composites and adhesive bonds – A critical review," *Eng. Fract. Mech.*, vol. 112, pp. 72–96, 2013.
- [81] A. P. Mouritz, "Review of z-pinned composite laminates," *Compos. Part A Appl. Sci. Manuf.*, vol. 38, no. 12, pp. 2383–2397, 2007.

- [82] "ADMET - How to Perform an Adhesive Lap Joint Shear Strength Test - ASTM D1002." [Online]. Available: <http://www.admet.com/how-to-perform-an-adhesive-lap-joint-shear-strength-test-astm-d1002/>. [Accessed: 19-May-2017].
- [83] K. C. Shin, J. J. Lee, and D. G. Lee, "Study on the lap shear strength of a co-cured single lap joint," *J. Adhes. Sci. Technol.*, vol. 14, no. 1, pp. 123–139, 2000.
- [84] G. Li, S. S. Pang, E. Woldesenbet, M. A. Stubblefield, P. F. Mensah, and S. I. Ibekwe, "Investigation of prepreg bonded composite single lap joint," *Compos. Part B Engineering*, vol. 32, no. 8, pp. 651–658, 2001.
- [85] ASTM, "Strength Properties of Adhesives in Shear by Tension Loading of Single-Lap-Joint Laminated Assemblies," vol. D 3156. 2014.
- [86] ASTM, "Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal / Metal) 1," *ASTM*, vol. D3166-99. 2012.
- [87] M. M. Abou-Hamda, M. M. Megahed, and M. M. I. Hammouda, "Fatigue crack growth in double cantilever beam specimen with an adhesive layer," *Eng. Fract. Mech.*, vol. 60, no. 5–6, pp. 605–614, 1998.
- [88] ASTM, "Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials." pp. 1–10, 2017.
- [89] T. Sinmazçelik, E. Avcu, M. Ö. Bora, and O. Çoban, "A review: Fibre metal laminates, background, bonding types and applied test methods," *Mater. Des.*, vol. 32, no. 7, pp. 3671–3685, 2011.
- [90] ASTM, "Standard Test Method for Measuring the Damage Resistance of a Fiber-Reinforced Polymer Matrix Composite to a Drop-Weight Impact Event," *ASTM*. pp. 1–16, 2005.
- [91] R. E. Schramm, R. L. Durcholz, and R. P. Reed, "Apparatus for impact-fatigue testing," *J. Res. Natl. Bur. Stand. Eng. Instrum.*, vol. 75, no. 2, pp. 95–98, 1971.
- [92] R. B. Berke and J. Lambros, "Ultraviolet digital image correlation (UV-DIC) for high temperature applications," *Rev. Sci. Instrum.*, vol. 85, no. 4, p. 45121, Apr. 2014.
- [93] "GRIP Metal | Grip Metal." [Online]. Available: <http://www.gripmetal.com/products/gripmetal/>. [Accessed: 01-Jun-2017].
- [94] TechNotes, "water break test." [Online]. Available: <http://technotes.alconox.com/detergents/what-is-the-water-break-test/>. [Accessed: 01-Dec-2017].
- [95] A. A. Johnson and R. J. Storey, "The impact fatigue properties of iron and steel," *J. Sound Vib.*, vol. 308, no. 3–5, pp. 458–466, 2007.

- [96] V. V Silberschmidt, J. P. Casas-Rodriguez, and I. A. Ashcroft, "Impact fatigue in adhesive joints," *J. Mech. Eng. Sci.*, vol. 222, no. 10, pp. 1981–1994, 2008.
- [97] W. Araki, K. Nemoto, T. Adachi, and A. Yamaji, "Fracture toughness for mixed mode I/II of epoxy resin," *Acta Mater.*, vol. 53, no. 3, pp. 869–875, 2005.
- [98] J. P. Casas-Rodriguez, I. A. Ashcroft, and V. V. Silberschmidt, "Damage in adhesively bonded CFRP joints: Sinusoidal and impact-fatigue," *Compos. Sci. Technol.*, vol. 68, no. 13, pp. 2663–2670, 2008.
- [99] L. . Slepyan, *Models and phenomena in fracture mechanics*. Berlin: Springer, 2002.
- [100] D. Ray, B. K. Sarkar, and N. R. Bose, "Impact fatigue behaviour of vinylester resin matrix composites reinforced with alkali treated jute fibres," *Compos. - Part A Appl. Sci. Manuf.*, vol. 33, no. 2, pp. 233–241, 2002.
- [101] D. P. Graham, A. Rezai, D. Baker, P. A. Smith, and J. F. Watts, "The development and scalability of a high strength, damage tolerant, hybrid joining scheme for composite-metal structures," *Compos. Part A Appl. Sci. Manuf.*, vol. 64, pp. 11–24, 2014.

10 Appendix

Table 14: Impact Fatigue Test Log

Start Date	Cycle Time Running		Cycles	Total Cycles	Broken Samples
	Hours	Minutes			
August 29th, 2016			0	0	M-F-1, M-F-2, M-F-4, M-F-9
August 30th, 2016			4445	4445	M-F-3, M-F-5, M-F-6, M-F-7, M-F-10, M-F-11, M-F-12
August 31st, 2016			11095	15540	M-F-8
September 7th, 2016	2	3	4305	19845	NONE
September 26th, 2016			9999	29844	NONE
October 7th, 2016	4	30	9450	39294	NONE
October 11th, 2016	5	15	11025	50319	NONE
October 12th, 2016	5	14	10990	61309	NONE
October 13th, 2016	5	25	11375	72684	NONE
October 14th, 2016	6	35	13825	86509	NONE
October 17th, 2016	6	31	13685	100194	NONE
October 18th, 2016	6	42	14070	114264	NONE
October 19th, 2016	6	0	12600	126864	NONE
October 20th, 2016	7	11	15085	141949	NONE
October 21st, 2016	7	0	14700	156649	NONE
October 24th, 2016	7	0	14700	171349	NONE
October 25th, 2016	7	21	15435	186784	NONE
October 26th, 2016	24	30	51450	238234	NONE
October 27th, 2016	24	25	51275	289509	NONE
November 2nd, 2016	24	40	51800	341309	NONE
November 3rd, 2016	24	0	50400	391709	S-F-3
November 8th, 2016	23	45	49875	441584	S-F-10
November 9th, 2016	25	0	52500	494084	S-F-1
November 10th, 2016	5	12	10920	505004	No inspection
November 14th, 2016	27	6	56910	561914	F-S-17, S-F-11, S-F-6, S-F-4
November 15th, 2016	44	43	93905	655819	F-S-14, F-S-16, S-F-5
April 13th, 2017	24	0	50400	706219	M-R-3, F-S-1, F-S-12, F-S-11, F-S-10, F-S-7
April 20th, 2017	47	0	98700	804919	M-S-1, M-S-6, M-S-18, M-R-2, M-S-5, F-S-18

April 21st, 2017	24	0	50400	855319	S-F-9, M-S-14, M-R-8, M-R-7, M-R-10
June 7th, 2017	24	0	50400	905719	M-S-7, M-S-13, F-S-5, M-S-15, F-S-3, F-S-4, F- S-9
June 8th, 2017	23	45	49875	955594	M-S-2, M-R-6, M-S-11
June 9th, 2017	47	23	99505	1055099	M-S-16, M-S-1, M-S-17
June 11th, 2017	24	8	50680	1105779	M-S-9
June 12th, 2017	23	50	50050	1155829	NONE
June 13th, 2017	23	20	49000	1204829	NONE
June 14th, 2017	24	0	50400	1255229	NONE
June 15th, 2017	24	7	50645	1305874	NONE
June 16th, 2017	69	26	145810	1451684	NONE

Table 15: Fatigue Test Log

Testing Start Date	Sample Number	Load Frequency	Maximum Load	Minimum Load	Sampling Mode	Cycles at Failure	Grip Strength	Failure Type
		Hz	kN	kN			psi	
15-Jul-17	S-S-T-1	5	1.186	0	Peak and Valley	1,059,900	1000	Substrate
21-Jul-17	F-S-T-1	5	1.186	0	Peak and Valley	4,532	1000	Delamination
21-Jul-17	S-F-T-1	5	1.186	0	Peak and Valley	834,824	1000	Delamination
26-Jul-17	F-S-T-2	5	1.186	0	Peak and Valley	4,683	1000	Delamination
26-Jul-17	F-S-T-3	5	1.186	0	Peak and Valley	3,638	1000	Delamination
04-Aug-17	S-F-T-2	5	1.186	0	Peak and Valley	1,517,696	1000	Delamination
08-Aug-17	S-S-T-2	5	1.186	0	Peak and Valley	511,181	1000	Substrate
10-Aug-17	S-S-T-3	5	1.186	0	Peak and Valley	162,095	1000	Delamination
23-Nov-17	S-F-T-3	5	1.186	0	Peak and Valley	2,343,557	1000	Delamination
07-Dec-17	F-S-T-4	5	1.186	0	Peak and Valley	4,621	1000	Delamination
07-Dec-17	S-S-T-4	5	1.186	0	Peak and Valley	644,947	1000	Substrate
12-Dec-17	S-S-T-5	5	1.186	0	Peak and Valley	757,813	1000	Substrate
15-Dec-17	S-S-T-6	5	1.186	0	Peak and Valley	299,304	1000	Delamination

Table 16: Quasi-Static Test Log

Sample	UTS	Average	Standard Deviation
F-S-Q-1	1.876452		
F-S-Q-2	2.123687		
F-S-Q-3	1.673885	F-S-Q AVG	F-S-Q STD
F-S-Q-4	1.368613	1.760659	0.276779292
S-F-Q-1	2.564394		
S-F-Q-2	3.51186		
S-F-Q-3	4.091143	S-F-Q AVG	S-F-Q STD
S-F-Q-4	3.486637	3.413509	0.54662717
S-S-Q-1	4.030177		
S-S-Q-2	3.713958		
S-S-Q-3	3.569136	S-S-Q AVG	S-S-Q STD
S-S-Q-4	3.619058	3.733082	0.179241989

Table 17: t-test matrix

	<i>(S-F) t-stat</i>		<i>(M-R) t-stat</i>		<i>(M-S) t-stat</i>	
	t Stat	t Critical two-tail	t Stat	t Critical two-tail	t Stat	t Critical two-tail
F-S	-3.13	2.09	-0.49	2.10	-2.01	2.09
M-R	-4.52	2.20	-	-	-2.20	2.16
M-S	-6.35	2.18	-2.20	2.16	-	-
S-S	-17.55	2.36	-18.43	2.57	-17.66	2.18
S-R	-17.55	2.36	-18.43	2.57	-17.66	2.18
M-F	11.13	2.36	25.13	2.57	31.93	2.18
S-F	-	-	-4.52	2.20	-6.35	2.18

	<i>(S-S) t-stat</i>		<i>(S-R) t-stat</i>		<i>(M-F) t-stat</i>		<i>(F-S) t-stat</i>	
	t Stat	t Critical two-tail	t Stat	t Critical two-tail	t Stat	t Critical two-tail	t Stat	t Critical two-tail
F-S	-11.14	2.16	-11.14	2.16	13.85	2.16	-	-
M-R	-18.43	2.57	-18.43	2.57	25.13	2.57	0.49	2.10
M-S	-17.66	2.18	-17.66	2.18	31.93	2.18	2.01	2.09
S-S	-	-	-	-	1565.6	2.20	11.1	2.16
S-R	-	-	-	-	1565.6	2.20	11.1	2.16
M-F	1565.6	2.20	1565.6	2.20	-	-	13.8	2.16
S-F	-17.55	2.36	-17.55	2.36	11.13	2.36	3.13	2.09