Metal-Polymer Adhesive Bond Characterization in an Additive Manufacturing Environment

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Madhu S. Madhukar, Major Professor

We have read this thesis and recommend its acceptance:

Brett G. Compton, Stephanie C. TerMaath

Accepted for the Council:

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Metal-Polymer Adhesive Bond Characterization in an Additive Manufacturing Environment

A Thesis Presented for the
Master of Science
Degree
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Daniel Seth Elkins
May 2018
ABSTRACT

Recently, the aerospace industry has turned the focus of its manufacturing efforts towards additive methods. For many aerospace applications, however, hybrid materials are preferred for their ability to combine optimal properties from various material sets, and these materials are not yet compatible with large-scale additive manufacturing. To fix this lack of compatibility, new additive methods must be developed that can print dissimilar hybrid materials on one print bed at a large scale, which will require a reliable dissimilar material joining method.

Among current joining techniques, one of the most promising for this application is adhesive bonding. Typically, adhesive bonding requires optimizing the conditions of bond surfaces by sanding and/or machining. This is inconvenient for gantry-based additive manufacturing systems, as the extra weight of any tools must be accounted for. For this study, the case of adhesively bonding additively manufactured Grade 5 Ti-6Al-4V with carbon fiber-reinforced PPS without any surface modifications is investigated. The flatness of the surface profiles of all the printed PPS samples were measured by a laser profilometer, and a computational model was developed to characterize these surfaces. Small double lap joints of Ti and PPS were bonded using two different commercially available epoxy adhesives. Two different bead orientations and two different bead thicknesses of PPS samples were used. The double lap samples were tested, and the shear strength of each bond was determined.

Due to large variations in the surface flatness of the PPS material, as demonstrated by the laser surface characterization results, the bonded area changed significantly from sample to sample, thus producing a large variation in the measured shear strengths. These bonds, however, were stronger than the ones formed with smooth machined surfaces. It is thus concluded that the poor resolution produced by large-scale extrusion additive manufacturing processes is currently sub-optimal for bonding but shows promise and should be investigated further.
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CHAPTER ONE: INTRODUCTION

Problem Statement

As part of an effort to design a hybrid material additive manufacturing machine, this thesis investigates the largest issue that must be solved before such a machine can be built: dissimilar material joining. The hybrid materials that are of interest in the aerospace industry consist of combinations of metals and polymer composites (this thesis investigates Grade-5 Ti-6Al-4V and PPS reinforced with 40% volume fraction of carbon fibers). Systems of these materials offer increased weight savings and corrosion resistance while still meeting required strength and stiffness constraints. These materials are quite dissimilar, however, and joining them in a convenient manner with desirable properties is a difficult task.

First, a viable joining method for additive manufacturing applications had to be established. Since the work presented in this thesis is part of an initial pre-competitive study, no prior data exists for this specific set of circumstances to provide any guidance or baseline data. Epoxy adhesive bonding was chosen as the bonding method for its availability and established use in both the aerospace industry and the field of dissimilar material joining.

Because of the constraints associated with using a gantry-based additive manufacturing machine, which is necessary for large-scale applications, it is desirable that no part surface modifications are required for joining. Any modifications, such as sanding or machining, would require the heavy equipment be mounted on the gantry, which is extremely limited in the amount of extra weight it can support. Because of this, it was determined that the initial experiments should include composite material with an unfinished surface. This presented a challenge, since the surfaces were uneven due to the low resolution of the parts produced by the large-scale polymer extrusion printing process. To account for this, the evenness of the surface was characterized using a laser profilometer, and the peaks and valleys of every print bead on every surface that was bonded were
measured. Once the surfaces were characterized, double lap joint consisting of titanium between two pieces of PPS/CF composite were created and the evaluated for shear strength properties.

Though it is not the most convenient route, machining the surfaces of the composite material is a feasible option, and samples with a flat bonding surface would theoretically have more consistent bonding properties. To provide baseline data for comparison to demonstrate the effectiveness of one method over the other, double lap joints with machined composite samples were also created and tested.

**Additive Manufacturing**

This thesis mainly concerns additive manufacturing and its applications. Additive manufacturing (AM) is a process that builds new parts one cross-section at a time, forming multiple layers to produce a complete part. AM software reads the geometry data from 3D CAD files and creates directions for the machine to follow. Typically, AM is only recommended for use when complex part geometry is necessary. AM cannot currently match the manufacturing throughput of traditional processes such as casting, molding, and machining for simple objects. One of the major advantages of AM, however, is that it offers the ability to manufacture complete complex objects that would otherwise require either a slow multi-step material joining process, such as welding, or a wasteful subtractive process, such as machining [1].

AM can be accomplished through various methods, but this thesis will primarily concern material extrusion and powder bed melting techniques [2]. In material extrusion, solid material is fed into, melted by, and extruded through a nozzle that deposits it directly onto a print bed. As the material is added, it solidifies and the layers fuse together, eventually forming a solid part. The feed material for extrusion is typically in the form of a continuous spool of filament, however in
certain large-scale applications, such as those presented in this thesis, the feed material is in the form of chopped pellets that are fed by a hopper system. To ensure proper melting, material pellets are fed through an extrusion screw in the same way as in traditional injection molding manufacturing processes [5].

In powder bed melting, the print bed is initially covered in a single layer of specially-engineered metallic powder. A heat source, typically a high-energy laser or electron beam, locally deposits enough energy to melt the powder to match the geometry of the part cross-section. Once the first layer is melted, another layer of powder is added and then melted to form the next layer of the part, a process that is continued until the part is complete [6,7].

Manufacturing for Aerospace

In aircraft design, the main constraints are weight, strength, and cost. Aircraft manufacturers now have more aggressive weight targets and tighter windows for building their products than ever before, which will continue to change as the demand for more efficient air travel increases. Improvements to manufacturing methods and processes offer a way to meet these growing demands. The development of novel AM methods, for example, has already demonstrated improvements to the performance and manufacturing efficiency of aircrafts [8].

One way AM has accomplished this is by enabling furthered use of topology optimization in aircraft design. Topology optimization is the process by which structures are geometrically optimized to meet strength and stiffness requirements with as little material as possible. This process is now being implemented in almost every facet of aircraft design, from the structural reinforcement within the wings to the seats in the cabin [9]. Airbus uses powder bed melting to manufacture a topology optimized titanium cabin bracket for its A350 commercial jet that represents a weight reduction of greater than 30% over the traditionally-
manufactured aluminum brackets they had previously used (shown in Figure 1) [8]. Without AM, topology optimized structures are created either by subtractive processes or by welding reinforcing members into the structure. Welding is time-consuming and requires more skilled labor, which is expensive, and subtractive processes waste material.

![Figure 1 A Topology Optimized Titanium Cabin Bracket](image)

Another of the main benefits of AM is that very little material is wasted; almost all the material used to manufacture a part is contained within the final structure. This means that with AM, less material needs to be purchased, which is crucial to expensive industries such as aerospace. If parts are machined, more material must be purchased, and the difference is wasted. In some extreme cases, conventional milling processes can produce up to 95% recyclable waste, none of which is used to build the component that the material was purchased for. Powder melting produces near-final metal parts with only about 5% of the material wasted [8]. Costs are also saved by the elimination of expensive metal casting equipment, since many small powder bed AM parts can be printed on the same bed at once [8].

AM can potentially also aid in rapidizing the certification and qualification process for aircraft parts. With AM, the three sub-phases of the aircraft product development phase are performed concurrently, instead of sequentially like they
are in traditional manufacturing processes. Figure 2 demonstrates the difference between a proposed rapid certification plan that would incorporate this process efficiency and the traditional certification process. This is feasible because AM offers the ability to accurately numerically simulate material processes to predict the strength of parts, which can be tested to evaluate the design for compliance [10]. Adjusting design parameters to meet compliances, should parts fail, is a much simpler process in AM than in traditional manufacturing approaches, and involves making simple numerical adjustments.

![Figure 2 Proposed Rapid Certification Plan for AM Aerospace Parts](image)

**Hybrid Materials**

Hybrid materials are combinations of two-or-more homogenous materials. The goal of hybrid materials engineering is to combine optimal properties of dissimilar materials into one continuous material system that is tailored to meet
specific needs. Examples of hybrid materials include fiber-reinforced composites, particle-reinforced composites, sandwich structures, and cellular structures.

For aerospace materials, low weight, high stiffness, high strength, and resistance to environmental factors are desired. This thesis concerns a metal-polymer composite material system that combines the strength and ductility of metals with the low weight, stiffness, and corrosion resistance of carbon fiber-reinforced polymer [11]. Polymer matrix composites are among the most popular hybrid materials, specifically carbon fiber reinforced polymer, because many polymer matrix composites can be manufactured with the same methods as regular composites (injection molding, compression molding, etc.), with the added advantage of containing reinforcing material for improved properties.

**Metal-Polymer Joining**

It is the goal of this thesis is to investigate the viability of joining metal and polymer in an AM environment. Because metals and polymers are so different from one another, joining them is a difficult task. Traditional arc welding, for instance, is not a viable option because polymers and metals have such different melting temperatures, as shown in Tables 1 and 2 [13-18].

Viable options for metal-polymer joining include adhesive bonding, mechanical fastening, friction stir spot welding, and laser welding [11]. Adhesive bonding, which is discussed in-depth in the next chapter, relies on the polymerization process to form chemical bonds with material surfaces. It is commonly used in many structural applications in the automotive and aerospace industry. Mechanical fastening is the joining of two-or-more materials by way of a foreign connector, such as a bolt, screw, or clamp, in various locations. Mechanical fasteners are convenient because they are easy to attach and remove if necessary. Because of this they are the most popular dissimilar material joining method [11]. The downside to fasteners, however, is that they create stress
concentrations in the joint and in the materials themselves, since holes must be created to facilitate fastening. Friction stir spot welding is a solid-state welding technique that relies on the energy generated by friction to bond two-or-more materials together. Friction stir spot welding works well for localized connections, but the size of the surfaces that can be joined is currently limited. During welding, a high-speed rotating tool is brought into contact with both surfaces that are to be joined. Pressure is applied, and heat is generated from the friction that results. This heat provides enough energy to fuse the two materials together [11].
Table 1 Melting Temperature of Various Metals

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>1604-1660</td>
</tr>
<tr>
<td>Al 1050-H14</td>
<td>646-657</td>
</tr>
<tr>
<td>C 600 Ni Alloy</td>
<td>1350-1413</td>
</tr>
</tbody>
</table>
Table 2 Melting Temperature of Various Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6</td>
<td>216-300</td>
</tr>
<tr>
<td>ABS</td>
<td>180-274</td>
</tr>
<tr>
<td>PPS</td>
<td>280-282</td>
</tr>
</tbody>
</table>
CHAPTER TWO: BACKGROUND

Polymers

Polymers are a class of materials that consist of long chains of organic monomers. Properties of polymers depend on their chemical composition and molecular weight, which, unlike other material classes, can vary greatly between specimens. This is due to the fact that chain lengths within a given polymer are distributed about a mean value [19]. Because of this, an important feature of polymers is that certain desired properties can be attained by adjusting the polymer's molecular weight without changing its chemical composition [19,20]. The molecular weight averages of polymers are controlled by the chemical processes used to synthesize them, and theoretically have no upper limit. Figure 3, taken from a plastic manufacturing textbook, illustrates how polymers with the same organic monomer chains can have vastly different physical structures [19].

![Figure 3 Various Structures of Polymers](image)

Polymer behavior is highly dependent on its microstructure, which is generally classified into two groups: crystalline and amorphous. Crystalline
polymers contain molecular chains that are highly aligned. Amorphous polymers are the opposite and are randomly oriented. Polymers of these two microstructures behave differently from one another, especially in manufacturing applications. Nylon 6, for example, is a thermoplastic polymer that is crystalline. As Nylon 6 is heated, the structure does not begin to undergo change until the glass transition temperature has been reached [21]. Once this occurs, the molecular chain within Nylon 6 are free and the solid material quickly turns into a molten liquid. ABS, on the other hand, is amorphous. As ABS is heated it begins to soften linearly until it is eventually all molten. Understanding this temperature-related behavior is important for engineering new manufacturing applications, since heat is the driving force behind creating the phase changes necessary to shape new geometries.

Polymers can be further divided into two more important categories: thermoset and thermoplastic. Thermoset polymers begin as liquid resins at room temperature and solidify once they are introduced to a curing agent, which initiates the irreversible process of polymerization [22]. During polymerization, the loose molecule chains begin to interlock with one another, resulting in solidification. Thermoset polymers behave this way simply because of their chemical composition, as depicted in Figure 4 [22]. Though many thermoset polymers cure at room temperature, most curing processes are accelerated by the addition of heat, and some even require it. Thermoset polymers are very stiff, strong, and resistant to fatigue, making them ideal for structural applications, particularly as a bonding agent. They also work well as a composite matrix since they can bond to reinforcing materials the same way they can with any surface, resulting in high interfacial strength values and damage tolerance [22,23].

Thermoplastic polymers are solid at room temperature and soften with the addition of heat. Because of this, they are versatile and can be manufactured with many different plastic manufacturing methods. With AM, they are most commonly used in desktop extrusion printers that are for rapid prototyping of small-scale models or small parts that do not require high strength or stiffness. Most commonly in industry, though, thermoplastic parts are manufactured by injection molding,
where molten polymer is extruded by an injection screw into a mold and allowed to cool and solidify [24]. There is typically a high overhead cost associated with traditional thermoplastic manufacturing processes, since the machines and tools are expensive and require a lot of electrical power. These costs are usually made up for, though, with the high-throughput capabilities of traditional manufacturing processes, which are ideal for high-volume manufacturing.

![Crosslinking Process of Thermoset Polymers](image)

Figure 4 The Crosslinking Process of Thermoset Polymers

**Polymer Matrix Composites**

Polymer matrix composites are a class of hybrid materials that include any polymer that is reinforced by another non-polymer. The goal of reinforcing polymeric materials is to create one solid material that possesses the optimal properties of both the polymer matrix and the reinforcement. Polymers are ideal for extrusion, but they are not strong or stiff enough for many structural applications in the aerospace industry. For this reason, very strong and stiff reinforcing material is often added in the form of fibers or particles to create a composite that has the processing capabilities of the polymer matrix with added strength and stiffness from the presence of reinforcement [25].
The mechanics of composite reinforcement are difficult to quantify and predict exactly, but estimations and bounds can be made that predict composite properties by using various models. The Voigt model provides an upper bound for composite properties by assuming ideal conditions [26]. This model is given by (1) and shown plotted in Figure 5.

\[
X_c = X_m V_m + X_r V_r \\
X_c = X \text{ property of the composite} \\
X_m,r = X \text{ property of the matrix/reinforcement} \\
V_m,r = \text{volume fraction of the matrix/reinforcement}
\]

A lower bound for properties of composites can be found by plotting the Reuss model [26]. This model is given by (2) and shown plotted in Figure 5.

\[
X_c = \frac{X_m X_r}{X_m V_r + X_r V_m} \\
X_c = X \text{ property of the composite} \\
X_m,r = X \text{ property of the matrix/reinforcement} \\
V_m,r = \text{volume fraction of the matrix/reinforcement}
\]

The composite material studied in this thesis is polyphenylene sulfide (PPS) reinforced with 40% volume fraction of short carbon fibers. The bounds of the effective elastic modulus of PPS/CF composites are presented in Figure 5, with properties shown in Table 3 [18,27].

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho ) (kg/m(^3))</th>
<th>UTS (MPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS</td>
<td>1370</td>
<td>136</td>
<td>3.73</td>
</tr>
<tr>
<td>CF</td>
<td>1280</td>
<td>121</td>
<td>228</td>
</tr>
</tbody>
</table>

Table 3 Material Properties of PPS and CF
Figure 5 Bounds on Effective Stiffness of PPS/CF
Big Area Additive Manufacturing

Currently, the best method for AM of polymers and polymer composites at a large scale is material extrusion. Material extrusion is ideal for use with thermoplastic material because it can produce parts with serviceable resolution for most applications. Typically, however, with common small desktop thermoplastic extrusion printers, parts are not intended for high-strength or large-scale applications. Desktop thermoplastic printers have small extrusion nozzle diameters, limiting the bead width of the material that is deposited and therefore limiting the amount and type of reinforcing material that can be added to a composite, as well as the manufacturing throughput of the system.

To use thermoplastic extrusion AM to create consistent structures that can meet the high strength and stiffness requirements for aerospace applications, the process had to be scaled up. Big area additive manufacturing (BAAM) is accomplished using a large gantry-based machine with an extrusion screw. A BAAM machine like the one used to print the PPS/CF that was tested in this thesis is shown in Figure 6 [28]. The material is fed into the extruder in the form of chopped pellets from a hopper, as opposed to a coil of filament like smaller desktop printers use.

Figure 6 Cincinnati BAAM Machine
Extrusion screws employ a multi-stage melting process that accomplishes consistent phase change with a combination of heat and shear forces [29]. The melting process is divided into four sections: feed, transition, mixing, and metering (shown in Figure 7) [30]. The feed section receives pellets from the hopper and is responsible for pushing the material through the screw. The transition section compacts the hot pellets together to maximize the amount of shear force they experience, which in turn aids in achieving proper melting. In the mixing section, predominately-molten material is processed with slightly less shear force but with a higher processing rate. This section accounts for the final melting of the material to ensure uniform phase transformation. The metering section is responsible for controlling the rate of the material that is extruded. The rate of the material that is processed and then extruded by the screw is controlled by the temperature and the rotational speed of the screw.

![Figure 7 Extrusion Screw Features](image)

The build platform of BAAM can accommodate parts as big as 6 m in length, 2.4 m in width, and 1.8 m in height, approximately 10x what is capable with the biggest desktop printers [31]. During printing, the platform is heated to 95°C to preventing warping and encourage adhesion. The extruder moves along the plane of the platform and deposits material in the normal direction one layer at a time.

Because of the large print bead diameter (2.5-7.6 mm) produced by BAAM, a higher concentration of reinforcing material, usually carbon fiber, can be extruded than in desktop printers. An issue with this increase in diameter, however, is that the fibers are less aligned than they would be from a smaller nozzle. A nozzle with
a smaller diameter exerts a higher shear rate on the material as it extrudes, causing the fibers to orient in a consistent direction [32]. With large-diameter nozzles, this effect only occurs on the outer ~1 mm of the material, with the rest of the fibers randomly oriented [31]. This is important because the highly anisotropic nature of fiber properties. If fibers are oriented more uniformly, the composite will exhibit properties closer to those that are predicted by the Voigt model. A modified version of this model (3) was developed by Fu and Lauke to account for this phenomenon in short-fiber reinforced composites [25].

\[
X_c = X_m V_m + \chi_1 \chi_2 V_r
\]

\( X_c = X \) property of the composite

\( X_{m,r} = X \) property of the matrix/reinforcement

\( V_{m,r} = \) volume fraction of the matrix/reinforcement

\( \chi_1 \chi_2 = \) fiber orientation \((\chi_1)\) and fiber length \((\chi_2)\) factors

It is important to note that though parts produced by BAAM are relatively accurate for their length-scale, the bead size of the material cause ridges in the surface that prevent them from printing smaller features. This is important in the context of this thesis, as the composite samples that were cut from BAAM parts were only about 20 mm tall, 30 mm wide, and 10 mm thick. The ridges along the surface of the samples, an example of which is shown in Figure 8, were inconsistent between samples and often highly uneven.

Figure 8 Surface Profile of BAAM Composite Material
**Powder Bed Electron Beam Melting**

One of the most popular methods for AM of metals is powder bed electron beam melting (EBM). As opposed to laser melting, EBM employs a preheating process that provides an in-situ heat treatment which can nearly eliminate intrinsic thermal stress (values of 5-10% of the UTS have been observed) and prevent cracks [7,33]. Electron beams also have a higher power density than lasers, leading to higher-quality builds [34]. They can be viewed as essentially being a higher-powered version of a scanning electron microscope, and require a filament, magnetic coils to deflect the beam spatially, and an electron beam column [33].

During manufacturing, the powder is fed onto the bed where it is distributed by a metal rake. Before distribution, however, the electron beam will sinter some of the powder surrounding the build plate to provide stability and prevent the plate from becoming dislodged by the rake [33]. The build plate in EBM is made from stainless steel and provides a thermal path to dissipate heat. The structural stability of the build plate is crucial to the geometry of the part and must be maintained at all times during the manufacturing process. Once the build is complete, the unused powder is passed through a powder recovery system that filters the sintered material from the rest of the powder [33].

Additively manufactured Ti-6Al-4V has a columnar microstructure because of the EBM process. This results in some anisotropy of the mechanical properties of Ti-6Al-4V [34]. A solidification map has been developed by Kobryn and Semiatin that relates the process parameters of EBM welding to the thermal gradient, solidification rate, and final microstructure [35]. This model has potential for crossover into predicting the anisotropy of AM EBM parts.

**Adhesive Bonding**

Adhesive bonding is a solid-state joining technique that relies on the formation of chemical bonds. Thermoset polymer is used for bonding because of
its stiffness and resistance to fatigue and heat. For structural applications, if strong enough bonds can be formed, adhesive bonding is preferred over mechanical fastening for its larger joint surface area and lack of need for material removal, which both result in stress concentrations [36]. Adhesives also influence mass reduction strategies by enabling the use of multi-piece assemblies. The main downside, however, is that bonding typically requires extensive surface preparation in the form of cleaning and physical alteration, such as machining and sanding, and is an irreversible process, making it difficult to remove bonded joints.

For the case of bonding metals and polymers, epoxy adhesive is preferred for its high stiffness and ability to fill small cracks [37]. They have been available for longer than any other engineering adhesive and are the most widely used for structural applications. Epoxy adhesives are two-part resin-hardener system. Once the two components are mixed together, the polymerization process begins, and the polymer begins to harden. Epoxies also have very little shrinkage occur after bonding compared to other adhesives, which is important for reducing stress concentrations. Table 4 shows ranges for shear strength values of common thermoplastic adhesives [38-41]. Of these, epoxy exhibits the highest upper limit by a large margin.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Shear Strength Range (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>1.00-172</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>1.00-32.0</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>0.352-19.7</td>
</tr>
<tr>
<td>Silicone</td>
<td>0.0827-3.45</td>
</tr>
</tbody>
</table>

Though the adhesive material has a high stress tolerance, the bonds do not resist stress as well. This is evident when comparing the shear strength
distributions of the bonds to the peel and cleavage distributions. The stress in the shear loading scenario is distributed at both ends, shown in Figure 9, and does bear much load in the center [37]. The viability of the bond then becomes dependent on the mechanical properties of the adhesive. The cleavage and peel scenarios shown in Figure 10, however, bear the load almost entirely in the interface of the adherend and the adhesive at the location of the applied load [37]. Once cracking occurs, cleavage and peel stress quickly propagates through the bond causing failure. Failure of the interfacial bonds between the adherend and the adhesive is referred to as adhesive failure, while failure of the adhesive material is referred to as cohesive failure.
Figure 9 Shear Stress Concentrations
Figure 10 Cleavage and Peel Stress Concentrations
CHAPTER THREE: METHODOLOGY

Sample Preparation

The PPS/CF material used to create the samples in this study was not specially printed for this purpose. They were cut from samples that were previously printed on the Cincinnati BAAM machine at Oak Ridge National Laboratory’s (ORNL) Manufacturing Demonstration Facility (MDF) in Knoxville, TN but weren’t needed by ORNL so they were donated to this project. The cutting process involved using a water-cooled tile saw with a diamond-coated blade. The samples were approximately 20 mm tall x 30 mm wide x 10 mm thick. To investigate the existence of anisotropy in the bonds, samples were cut with two different bead sizes oriented 0, 45, and 90-degrees from the vertical direction. Once each sample was cut and labeled, its exact dimensions were measured using precise calipers. For the samples with flat surfaces, this process was almost the same, the only difference being that the print beads were cut off.

The Ti-6AL-4V samples, however, were printed by Boeing at MDF specifically for this project. 64 of these samples were printed in an Arcam Q10+ EBM machine, each one measuring 25.4 mm tall x 30 mm wide x 3 mm thick (shown below in Figure 11). These samples were taken from the print bed with their support structures still attached, which were later removed by hand with a pair of pliers. An image of the surface of one of the Ti-6Al-4V samples was taken by a Keyence VHX-5000 optical microscope and is shown in Figure 12.

Figure 11 Ti-6Al-4V Coupons Printed at ORNL
Figure 12 Additively Manufactured Ti-6Al-4V Surface
Surface Characterization

The surface properties of the two materials play an important role in forming an effective bond. The surfaces of the titanium pieces are highly consistent from sample to sample, so their effects are normalized. The surfaces of the PPS/CF samples, however, are inconsistent from sample to sample and often highly uneven. To address this issue, a composite surface characterization method was developed. In this method, a laser profilometer was used to measure the surface profile of each composite sample. The data collection screen of the profilometer is shown below in Figure 15. In the window on the right side of the screen, the profile of the composite is displayed. From this window, the distance of each peak and valley in the profile from the bottom of the table was measured. The experimental setup for this process is shown in Figure 16.

This data was used to generate an approximation for the gap area that exists between the PPS/CF and the Ti-6Al-4V when they are pressed together. An example of this gap is shown in Figure 13. In MATLAB, peak and valley values were used to create a series of trapezoids that approximated each set of print beads, depicted in Figure 14. The area of this system of trapezoids was then compared to an “ideal rectangle,” which is a rectangle with dimensions ranging from the lowest valley value to the highest peak value. The area of the trapezoid system was subtracted from the area of the ideal rectangle for each sample to produce a value for the so-called gap area.

![Gap in bonded sample](image)

Figure 13 The Gap Between PPS/CF and Ti-6Al-4V Samples
Figure 14 Surface Characterization Method
Figure 15 The Results Screen of the Laser Profilometer
Figure 16 Experimental Setup for Laser Profilometer Measurements
**Bonding**

Determining an effective method of bonding the joints while maintaining a flat profile along the bottom of the samples was a difficult task. Eventually, the method that was selected involved the use of screw clamps to apply pressure, shown in Figure 17. The two adhesives that were chosen for comparison were 3M Scotch-Weld 1838L Translucent Epoxy Adhesive and Devcon 2Ton Epoxy. Both are readily available and have been recommended by their manufacturers for metal-polymer bonding applications. The only major difference between these two adhesives is their work life: the 3M adhesive had a work life of approximately 60 minutes while the Devcon adhesive had a work life of approximately 10 minutes.

First, the samples were wiped down to remove any large particles that were on the bonding surfaces. The adhesive was then applied to each bonding surface, with special care taken to ensure that all parts of the surfaces were covered in adhesive. Once the surfaces were covered, the samples were turned vertically and pressed together by hand. While carefully make sure that the bottom of the joint was flat against the table, the screw-tightening clamps were used to apply pressure to the joint until curing was finished several hours later. Depictions of the three different types of joints are shown in Figure 18.

![Figure 17 Sample Bonding Setup](image)
Figure 18 3D CAD Rendering of Different Double Lap Joints
Testing

To determine the strength of the bonded joints, shear compression tests were performed as depicted in Figure 19. An aluminum testing block with a slit cut out in the middle was machined that allowed only for the Ti samples to be pushed through. This fixture was placed between two platens on an MTS electric testing machine, and the joints were placed on top of it, with special care taken to correctly align the Ti with the slit in the aluminum fixture. A small piece of bronze was placed on top of the Ti sample to prevent scratching of the metal platen that was pushing down. To prevent dynamic loading conditions, a test rate of 0.02 mm/s was used. The maximum load to cause bond separation was recorded for each sample.
Figure 19 Depiction of Double Lap Shear Compression Test
CHAPTER FOUR: RESULTS AND DISCUSSION

Surface Characterization Results

The data shown in Figures 20 and 21 are the results of the surface characterization measurements. These figures demonstrate the large range in values of the gap area between the Ti and PPS/CF surfaces. Because of this, the repeatability of these results is not very high. To avoid this issue, either the BAAM methods have to be improved or machining or other surface post-processing methods will have to be considered. It should be noted, however, that larger PPS/CF samples should give more consistent results.

These results are reflected in the large variation in bonding area that was observed by examination of surface of the broken samples following testing. An example of one of these samples is shown in Figure 22. Before the adhesive could fully cure, some of it flowed through the relatively large channels that were created by the presence of the gap area and settled on one side of the sample. Only small parts of the Ti and PPS surfaces were bonded.

![Figure 20 Laser Measurement Results for Small Bead Samples](image-url)
Figure 21 Laser Measurement Results for Large Bead Samples
Figure 22 A Broken Double Lap Joint Following Testing
Mechanical Test Results

The results of the mechanical tests for the unprocessed samples, shown as box plots in Figures 23, 24, and 25, demonstrate how large the range of values for the shear strength of the samples was. It is important to note that the results shown below were calculated using a bonding area value equal to the width of the Ti multiplied by the height of the PPS/CF for both sides, which is an overestimation for every sample. This means that actual shear stress values are higher than what is shown. There exist no noticeable trends in median stress values between bead orientations or epoxy type. The large variation in the range of these values, however, indicates that outliers are preventing trends from forming. Figures 34 and 35 in the appendix section show the raw data generated by the testing machine for each sample, plotted as force as a function of displacement.

Notable outliers exist in these figures, such as Test 99, for example. Test 99 was performed on a sample that was bonded with the 3M epoxy and had a 0-degree bead orientation and large beads (shown in Figure 26). This sample failed at approximately 11.2 N/mm², which is more than double the median value. Test 95 (shown in Figure 27), which is of the same bead orientation and bead size, however, failed at approximately 3.04 N/mm², which is well below the median. The raw data from the compression tests that were performed are plotted in Figure 28.

A likely explanation for the discrepancy in the results is the visible difference in bonded area, which is caused by a difference in the gap area formed between the PPS/CF surface and the titanium surface. The variation in the bonded area can be observed in the Appendix, where photographs of every sample that was tested are shown. It can also be observed that the variation in bonded area is larger for the samples with 3M epoxy than it is for the samples with Devcon epoxy. The long work life of 3M meant that it was in a fully liquid state for six-times longer than Devcon, giving it a much larger window of opportunity to flow through the gap between the PPS/CF and the Ti.
The results of the tests of the joints that were bonded using flat PPS/CF samples are shown in Figures 29 and 30 and provide results that can be expected if machined surfaces are desired. Interestingly, the joints with flat surfaces were not as strong as those without modification. The range of the data for the flat surfaces, however, was much smaller, so there is a greater chance that these results can be expected. It is also important to note that the surface area of the bonds with the flat samples was much larger and more consistent, as shown in the photographs in the Appendix. As previously mentioned, the results for joints with unprocessed PPS/CF samples were an underestimation of their actual shear stress value, meaning that the actual difference in shear stress between the two cases is even greater than what is shown in the figures.

Another important observation is that the failure method of the joints with unprocessed material varied from sample to sample, demonstrating that some of the bonds were strong enough to last until the epoxy failed (cohesive failure). An example of this is shown in Figure 31. The flat-surface samples however, all had the same failure method: the bonds disadhered from the PPS/CF surfaces. The bond's interface was the weak point of every sample.

It was also observed that the machining process weakened the adhesion between the beads in the PPS/CF. Figures 32 and 33 demonstrate how the bond between the adhesive and the PPS/CF material was sometime stronger than the print bead adhesion. This phenomenon was not observed for any of the unprocessed PPS/CF samples. These results are concerning for structural applications, further reinforcing the idea that machining should be avoided if possible.
Figure 23 Test Results for 0-degree Orientation
Figure 24: Test Results for 45-degree Orientation
Figure 25 Test Results for 90-degree Orientation
Figure 27 Test 95
Figure 28 Raw Compression Test Data Comparison
Figure 29 Test Results for Flat PPS/CF with 0-degree Orientation
Figure 30 Test Results for Flat PPS/CF with 90-degree Orientation.
Figure 31 Cohesive Failure
Figure 32 Lack of Adhesion Between Beads Example 1
Figure 33 Lack of Adhesion Between Beads Example 2
CHAPTER FIVE: CONCLUSIONS AND FUTURE WORK

From these results, it can be concluded that the unprocessed PPS/CF material formed better bonded joints than the PPS/CF that was machined flat while also avoiding surface damage from the machining process. Though these results show promise for this technique moving forward, it cannot be ignored that the evenness of the surfaces is uncontrollable and unpredictable and can cause variations in shear strength properties. Further study of these bonding interfaces is recommended.

Future work should include an analysis of these phenomena on multiple length scales. It is likely that the resolution of the BAAM parts does not cause a significant gap area for larger parts. This relationship will need to be studied in-depth with various adhesives that are approved for use in the aerospace industry. It is also likely that the weakness of the bonds with flat PPS/CF material can be attributed to the smoothness of the surface. Methods to develop PPS/CF samples with flat-but-rough surface profiles should be investigated. This will give more information about what caused the unprocessed surfaces to form better bonds. The varying failure methods of the bonds in the samples with unprocessed surfaces should also be investigated. It is likely that the variation in bonding area plays a large role in this. Cutting-edge image analysis methods may offer a solution for accurately calculating the area of the adhesive that formed bonds in the joints.

These results give hope for a solution for joining dissimilar additively manufactured parts. There is still much more work needs to be done. Because of the work presented in this thesis, however, the path forward is clearer.


[27] http://www.matweb.com/search/DataSheet.aspx?MatGUID=e64a41d1b5de4440b253699429dfde3b


[38] http://www.matweb.com/search/DataSheet.aspx?MatGUID=c1ec1ad603c74f628578663aaf44f261


[40] http://www.matweb.com/search/DataSheet.aspx?MatGUID=8e7443671b9f4760bf1f3b5d11a222d

APPENDIX
3M Adhesive Photographs
Devcon Adhesive Photographs
3M Adhesive Flat-surface Photographs
Devcon Adhesive Flat-surface Photographs
Figure 34 Raw Compression Test Data for the 3M Adhesive
Figure 35 Raw Compression Test Data for the Devcon Adhesive
VITA

Daniel Elkins was born in Richlands, VA, and is the younger child of Kevin and Connie Elkins, his only sibling being his sister Bethany Elkins. He graduated from Richlands High School in Richlands, VA, before attending The University of Tennessee in Knoxville, TN. In Knoxville, Daniel studied Nuclear Engineering, earning his Bachelor of Science degree in 2016. That same year, he acquired a position as an undergraduate researcher in Dr. Brett Compton’s research group studying fiber reinforced composite materials. From this experience, he decided that his interests are better suited for the field of Mechanical Engineering. Since January 2017 he has been a graduate research assistant in the Mechanical, Aerospace, and Biomedical Engineering Department at The University of Tennessee, working towards his Master of Science degree on a project funded by the National Science Foundation. Following graduation, he will continue his education as a Doctor of Philosophy student in Mechanical Engineering at Virginia Polytechnic Institute and State University in Blacksburg, VA.