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Interfacial Adhesion of Polymer-Metal Composites

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by

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Abstract

The objective of this project was to design and assemble an experimental apparatus to measure the interfacial adhesion between polymer-metal composites using varying surface conditions. The materials used for the polymer-metal composite are 420-grade Stainless Steel (SS) and Acrylonitrile Butadiene Styrene (ABS). A 90-degree peel tester was designed in SolidWorks® as an add-on to an Instron® 5944 Universal Testing Machine. The peel tester was fabricated using both computer numerical controlled machining and manual milling. Sample plates were polished by using several grits of sandpaper, buffing compounds and a sand belt before applying ABS onto their surface. Eight peel tests were performed on untreated ABS-SS samples where force and adhesion energy values were determined.

Acknowledgments

This project would not be possible without the guidance and support of my advisor, Professor Karanjgaokar. Despite the challenges faced throughout the project, Professor Karanjgaokar believed in me and helped me keep on track. Also, even though my partner was unable to complete the project, I owe great gratitude to Jorge Luis Castillo for the initial design idea of the testing apparatus. I would also like to acknowledge the graduate students (Sharada Bhavanam, Hrachyan Kocharyan, and Prajwal Bharadwaj) in the Structures and Materials Lab for teaching me how to use the laboratory equipment. Moreover, I would like to thank Karl Ehlers for spending over 70 hours with me in the machining and assembling of the testing apparatus. Lastly, I would like to thank Andrea Claudio Palacios for her assistance in helping prepare liquid ABS solution for my samples.

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Chapter 1: Introduction

Composites are created by combining two or more materials that result in superior properties than those properties found in the individual materials themselves. While composites date back as far as 4000 B.C. (e.g., Egyptian papyrus paper), new composites involving polymer resin are in high demand in the automotive, aerospace, tooling, medicine, and infrastructure industries. One common method of producing composites is through the use of additive manufacturing (AM). Unlike subtractive manufacturing which creates composites by eliminating material, AM constructs composites in a layer-by-layer fashion; thus, making it low-waste. Among the different types of AM technology, fused deposition modeling (FDM) is the most prominent method for the additive manufacturing of polymers. Recently, the idea of polymer-metal composites is gaining popularity as the use of metal additives in polymers produces improvements in thermal conductivity and radiation shielding. However, the mechanical properties of polymer-metal composites are still limited due to poor adhesion at the interfaces between the metal additive and the polymer matrix.

In order to enhance polymer-metal composite performance, the primary goal of this project is to assess how different surface treatments affect the interfacial adhesion of polymer-metal composites on the macro scale. The metal and polymer which is used in this MQP are 420-grade Stainless Steel (SS) and Acrylonitrile Butadiene Styrene (ABS), respectively. This project is also closely associated with the work done by Professor Lados' MQP team (DL1-1901) which focused on the microscale of adhesion between SS and ABS.

The objectives of this MQP are to design a tensile testing setup and to develop a protocol for quantifying the interfacial adhesion in various polymer-metal composites using metal additives with different composition, morphology, and surface condition. Through running multiple experiments for different surface treatments, the goal is to get insight into the interfacial failure mechanisms in SS and ABS composites by collecting full-field strain measurements and interfacial adhesion measurements. This data is then correlated to the corresponding strength and elongation values in order to enhance the mechanical performance of the composite.

1.1 Project Goals

The goals of this project are to:

1. Design and assemble a tensile tester which will gather full-field strain and interfacial adhesion measurements. The measurements will reveal how each surface treatment affects the mechanical properties of the polymer-metal composite.
2. Develop protocols for testing and preparing SS-ABS composite samples with different surface treatments.
3. Analyze which surface treatments, if any, improve the mechanical performance of SS-ABS composites and recommend ways to continue developing the project.

1.2 Project Design Requirements, Constraints, and Other Considerations

The project design requirements only stated that a tensile tester is created. Thus, much flexibility was given in choosing which type of tensile tester could be made. After reviewing seven widely used tensile testers in research and industry, a peel tester was chosen for its simplicity and many advantages (explained further in Section 2.5.1.1). To save material, money, and time, the design for the peel test was based on creating an add-on for Professor Karanjgaokar's Instron® 5944 tabletop single column tabletop testing system (Figure 1).

Figure 1. Instron® 5944 Tabletop Single Column Testing System [1] © Illinois Tool Works Inc.

In the design of the peel tester, guidelines provided by the American Society of Testing and Materials (ASTM) for 90-degree peel tests [2] were followed. This document posed the following constraints:

1. In the samples, the thickness of the flexible adherend should be at least 0.60 mm (0.025 in) thick and the rigid adherend should be at least 1.60 mm (0.060 in) thick [2]. In this case, the flexible adherend is ABS and the rigid adherend is the SS sample plates.
2. The testing machine should have the capability of maintaining a crosshead speed in the range of 12 mm/min (0.5 in/min) to 250 mm/min (10 in/min), "an adequate pen or computer response to record the force-extension curve," self-aligning grips, a breaking load which falls between 15 to 85 percent of the full scale load range, and "the direction of the applied force needs to be through the centerline of the grip assembly" [2].
3. The unbonded end of the "flexible adherend must be bent perpendicular to the rigid adherend for clamping in the grip of the testing machine" and should be at least 25 mm (1 in) in length [2].
4. At least 76 mm (3 in) of the flexible adherend must be pulled at a constant delamination speed [2].
5. Samples may only be compared when "specimen construction and test conditions are identical" [2].

Aside from the guidelines provided from ASTM, the peel tester was also developed with the consideration that it will be used for the following years by graduate students and other MQP teams. Thus, it was essential that everything is documented in detail.

1.3 Project Management

At first, the project team consisted of two members -- Jorge Luis Castillo and Amanda Toledo Barrios. Unfortunately, one-third into the project, Jorge left the project. Thus, the project was completed by the remaining member. At the time where the team was composed of two members, Jorge took charge of the initial tensile test design (as he knew how to use SolidWorks®) while Amanda documented everything and focused on finding suppliers for the required materials. Once Jorge was no longer part of the project, the SolidWorks® files were irretrievable so Amanda learned how to use SolidWorks and created an updated design. Once the design was finalized, all materials were ordered from McMaster-Carr. Using outside help from a student lab monitor at WPI Washburn Shops, all parts were manufactured using CNC and manual milling machines. As a preliminary presentation to the final MQP presentations in late April, Amanda presented the design of the tensile tester in an AIAA Student conference at the University of Maryland, College Park in early April. The final project was presented on April 19, 2019, where Amanda was awarded an Aerospace MQP Award.

1.4 MQP Objectives, Methods, and Standards

1. Design and assemble a tensile tester
    a. SolidWorks® was used to make a model of the design.
    b. CNC machines and manual milling machines were used to fabricate the parts required for the peel tester. HSM Cam Software, an add-on to SolidWorks®, was used to develop the G-code for the CNC machines.
    c. Used the Instron® 5944 built-in load cell and computer to generate stress-strain results and interfacial adhesion data.
2. Develop protocols for testing and preparing SS-ABS composite samples
    a. Used a grinder to cut the SS into identical-sized sample plates.
    b. Polished the SS plates by hand and then used a sand belt with buffing components to achieve a mirror finish.
    c. Followed ASTM standards for sample specifications (refer to Section 1.2).
    d. Used the same surface treatment methods used by Professor Lados' MQP (DL1-1901).
3. Analyze surface treatment results on SS-ABS composite
    a. Due to time constraints and challenges encountered throughout the project, different surface treatments were not applied to the SS-ABS composite.

Chapter 2: Literature Review

Composites are a growing industry in the applications of automotive, aerospace, tooling, medicine, and infrastructure [3]. New man-made composites are researched and investigated every day because, without new materials, technology cannot advance. In this literature review, I discuss the history and roles of composites and explain how composites have advanced and will continue advancing through additive manufacturing technologies. I then review the concept of adhesion, an important measure of the quality of composites, and provide various ways that adhesion, along with other mechanical properties, can be measured.

2.1 History and Roles of Composites

According to the American Society of Testing and Materials (ASTM), a composite is a "substance consisting of two or more materials, insoluble in one another, which are combined to form a useful engineering material possessing certain properties not possessed by the constituents" [4]. In simpler terms, composites are created by combining two or more materials that result in superior properties than those properties found in the individual materials themselves. Before composites were officially defined, however, they were being utilized by ancient civilizations dating as far back as 4000 B.C. For example, the Egyptians invented papyrus paper by layering strips from the papyrus plant in two layers at 90-degree angles to each other [5]. Furthermore, around 3400 B.C., the Mesopotamian civilization created plywood by gluing wood strips at different angles. Some composites, such as those created by combining mud and straw or wood and clay to make bricks to create structures and buildings, are still used by civilizations today. Despite the early human use of composites, the composite industry did not take off until the early 1900s with the development of polymer resins [3].

A century later, composites have made their way into every market sector including, automotive, aerospace, tooling, medicine, and infrastructure. Composites are manufactured for products characterized into three large categories: (1) consumer, (2) industry, and (3) advanced [3]. Consumer composites are used for products that typically require a cosmetic finish such as boats, recreational vehicles, bathroom fixtures, and sporting goods. Industry composites are used in applications "where corrosion resistance and performance (in adverse environments) are critical" [3]. Examples of industrial composite products include underground storage tanks, scrubbers, piping, fume hoods, water treatment components, and pressure vessels. Lastly, advanced composites are "characterized by the use of high-performance resin systems and high-strength, ultra-stiff fiber reinforcement" [3]. Advanced composites are highly used in the aerospace industry for military and commercial aircraft. The reasons these composites are highly attractive for the aerospace industry is that they save material and weight, they are easier than metals to mold into complex shapes, and they allow for shorter assembly times [4]. Among the most common advanced composites are epoxy resin and carbon fibers [3].

2.2 Additive Manufacturing

One way that composites are formed is through additive manufacturing. As defined from ASTM, additive manufacturing (AM) is "a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" [5]. Other names for AM include additive fabrication, additive processes, additive techniques, additive layer manufacturing, layer manufacturing, and freeform fabrication [5]. Since the 1980s, AM technology has taken off and is widely used in many practical applications in aerospace, automotive, biomedical, energy and other fields [5]. Due to its success, the use of AM by independent service providers has seen a significant increase in revenue between the years of 1994 and 2017 (Figure 2) [6]. In 2017 alone, an estimated $2.955 billion was generated from the sale of parts produced by additive manufacturing systems. This was a 36% increase from the $2.173 billion reported for 2016 [6]. This trend is predicted to keep growing as AM is seen as a revolutionary technology that can change the world.

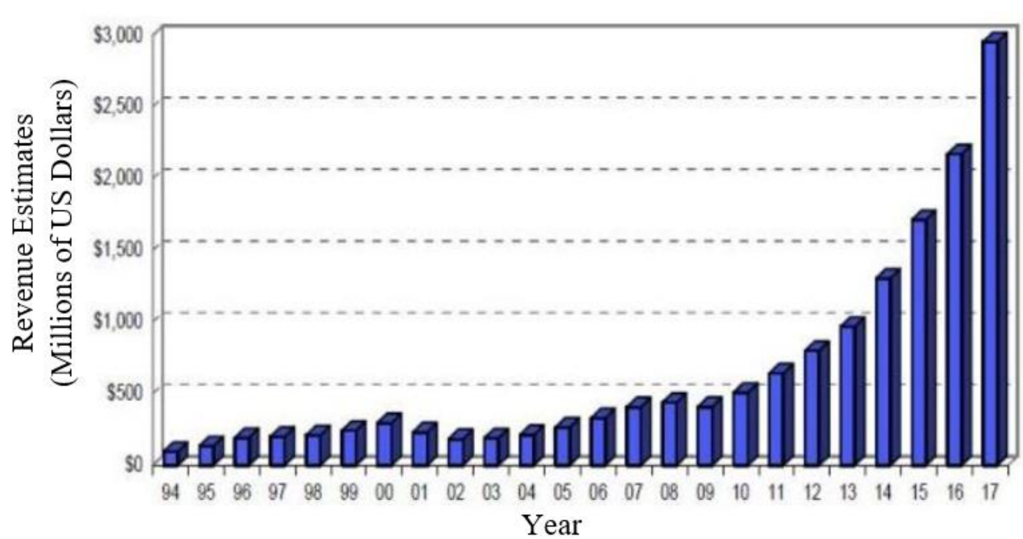

Figure 2. Primary Revenue of AM from 1994 to 2017 (Adapted from [6]) ©2018 Wohlers Associates Inc.

2.2.1 Potential of Additive Manufacturing

Traditional manufacturing such as casting, forming, molding, and machining are complex processes that involve tooling, machinery, computers, and robots. Furthermore, these processes are subtractive which means that "objects are created through the subtraction of material from a workpiece [7]. Since the final product is dependent on the capability of the tools used, there is a limit on the complexity of the product. On the other hand, AM allows for objects to be constructed from the ground up which makes a huge difference. Not only is AM a green technology since it wastes less material, but it also "allows designers to selectively place material only where it is needed" [7].

With AM technology, the need for assembly lines or supply chains can be diminished or even phased out. Conventional manufacturing typically involves a countless number of parts to be assembled. Most of the parts are typically shipped from outside providers in which their parts could have also been assembled and supplied by other providers [7]. By using AM, an entire final product or even pieces of the final product can be produced in a singular process in a factory rather than relying on the assembly of many smaller parts or shipping parts to other outside providers to complete the product. Eliminating the need to ship parts also greatly reduces the carbon footprint of manufacturing [7]. Furthermore, eliminating the need to ship parts expedites the distribution of designs. With AM files now available as a standardized digital file (.STL), these digital files can now be transferred everywhere via the internet and be printed in 3D by a printer that meets the design parameters (i.e. size, resolution, material) [7].

Having AM files in stock can, in turn, get rid of inventories and inaccuracies from shipped products. With AM printers, products can be printed on demand and in the condition that the designer intended. This means that each manufacturing facility is "capable of printing a huge range of types of products without retooling—and each printing could be customized without additional cost" [7]. Moreover, there is no longer a need to depend on manufacturing platforms such as China. Instead, products can be made in the countries where the product is consumed [7]. Since printing '.STL' files in computer-controlled, operating the printer requires little to no expertise. Thus, printing processes often go unmonitored. This dramatically reduces the time to build products since products can be left to build overnight.

The six major categories in AM are (1) vat photopolymerization, (2) direct energy deposition, (3) material jetting, (4) binder jetting, (5) powder bed fusion, and (6) material extrusion. Although there is a wide range of AM categories, each has its own variations in dimensional accuracy, surface finish and post-processing requirements [8]. As represented in Figure 3, within each category there are several corresponding technologies.

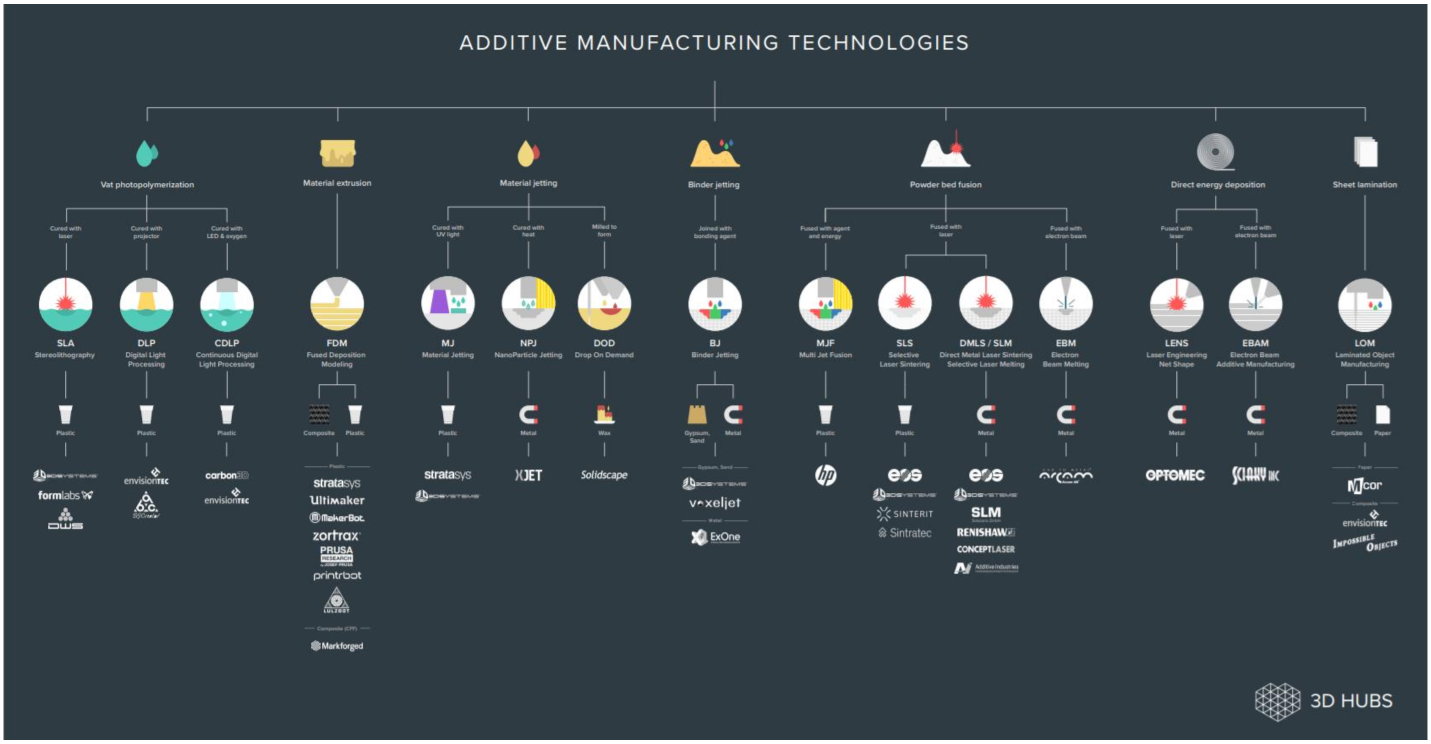

Figure 3. Additive Manufacturing Technologies [8] © 2019 3D Hubs

2.2.2 Main Categories of Additive Manufacturing

Vat photopolymerization uses the chemical reaction of photopolymer resins when exposed to light at a specific wavelength to create a solid [8]. The light is produced from the use of an ultraviolet laser which creates layers by curing and solidifying the photopolymer resin this category, the technologies are stereolithography (SLA), direct light processing (DLP), and continuous DLP (CDLP). SLA works in the same process as described above for vat photopolymerization. DLP is nearly identical to SLA in its method for producing parts but “the main difference is that DLP uses a digital light projector screen to flash a single image of each layer all at once” [8]. From the name, CDLP works exactly as DLP except that it prints in a continuously up motion (z-direction) [8]. Thus, CDLP accelerates the printing process because the printer is not required to stop after each layer is created. Vat polymerization processes are best suited for making small parts with fine details and smooth surfaces such as jewelry. The main disadvantage of vat polymerization processes is that it produces brittle parts [8].

Material jetting is similar to the 2D ink jetting process. However, “instead of jetting drops of ink onto paper, material jetting 3D printers jet layers of liquid photopolymer onto a build tray and cure them instantly using UV light” [9]. The technologies under this category are material jetting, nanoparticle jetting (NP), and drop-on-demand (DOD). Material jetting is the same as mentioned above. NP utilizes a liquid that contains metal nanoparticles. As the liquid undergoes high temperatures, the liquid evaporates and leaves behind metal parts that are jetted [8]. Unlike the previously mentioned technologies, DOD is made up of two print jets where one print jet deposits the build materials while the other dissolves the support material [8]. Material jetting is great for realistic prototypes as it allows for “high detail, multicolor, multi-material prints” [10]. Models can also be made transparent and in bigger sizes than produced from SLA or fused deposition modeling (FDM). Just like vat polymerization, material jetting technologies also produce brittle parts. However, material jetting is more expensive than other AM technologies [10].

Binder jetting uses a binding adhesive agent and powder materials (either ceramic-based or metal) to 3D print. Layers are built one at a time as the binding agent is dispensed onto the power bed. “When a layer is complete, the powder bed moves downwards and a new layer of powder is spread onto the build area” [8]. This process repeats until the product is done. Applications for binder jetting include molds for sand casting and aesthetic models such as architectural models [8]. While binder jetting is more cost-effective than selective laser melting (SLM) and direct metal laser sintering (DMLS), it produces parts with poorer mechanical properties [8].

Powder Bed Fusion (PBF) technologies “produce a solid part using a thermal source that induces fusion (sintering or melting) between the particles of a plastic or metal powder one layer at a time” [8]. PBF includes selective laser sintering (SLS), selective laser melting (SLM), direct metal laser sintering (DMLS), electron beam melting (EBM), and multi-jet fusion (MJF). As in the name, SLS uses a laser to induce fusion that sinters thin layers of powdered material one layer at a time [8]. After a part is completed, it has to be removed from the powder and cleaned. Both SLM and DMLS work in a similar fashion as SLS. The only big difference is that DMLS and SLS are used to produce metal parts. Furthermore, “SLM achieves a full melt of the powder, while

DMLS heats the powder to near melting temperatures until they chemically fuse together" [8]. Unlike the previous three PBF technologies, EBM uses a high energy beam instead of a laser in its process which produces layers at a faster rate and uses less energy [8]. MJF is a combination of SLS and material jetting technologies. A printer carriage similar to that for 2D inkjet printers prints by depositing fusing agent on thin layers of plastic powder. Simultaneously, a detailing agent is ejected near the edge of the part in order to prevent sintering. Then, a high-power infrared energy source passes over the build bed and sinters the areas where the fusing agent was dispensed. This leaves the rest of the powder untouched [8]. The main advantage of PBF technologies is that they do not require structural supports to print a certain design. For example, in Figure 4, to print the letter 'T' requires all of the structural support shown in light grey [9]. Another advantage is that polymer and metal PBF parts have very high strength, stiffness, and other mechanical properties that are comparable than the bulk material [8]. Limitations of PBF include shrinkage or distortion of the parts it produces and the difficulty in disposing of the powder produced.

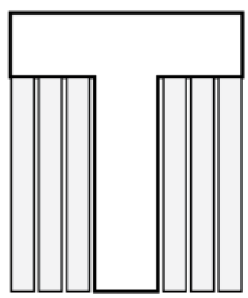

Figure 4. Structural Support Needed to Print the Letter "T" [9]

Direct energy deposition (DED), also known as a metal deposition, melts powder material or wire and deposits the melted material to produce parts [8]. DED is comprised of two technologies called laser engineered net shape (LENS) and electron beam additive manufacture (EBAM). LENS technology is widely used to repair parts. With a deposition head that consists of a laser head, powder dispensing nozzles, and inert gas tubing, it creates a melt pool in the build area and then sprays powder into the pool so that it can solidify [8]. The process for creating parts with EBAM is similar to the process involved in LENS. However, EBAM welds metal powder or wire together by using an electron beam. Compared to the electron beams used in LENS, EBAM electron beams are more efficient and operate under a vacuum. EBAM technology is projected to be used for space applications in the future [8]. Overall, DED is great for making repairs to a part or adding material to existing components. It is not, however, suitable for making parts from scratch [8].

Out of the previously mentioned AM categories, material extrusion is the most widely used 3D printing technology because it is cost-effective and quick. Analogous to the process of squeezing toothpaste out of a tube, "extrusion technologies extrude materials through a nozzle and onto a build plate" [8]. The nozzle then continues to build layer-by-layer as programmed in a '.STL' file. The technology associated with material extrusion is called fused deposition modeling (FDM). Another commonly used term for FDM is fused filament fabrication (FFF) [8]. FDM uses strings of solid thermoplastic material in filament form and pushes it through a heated nozzle. As the material melts, it is placed at precise locations on the printing bed, building layer-by-layer, until the product is completed. FDM is widely used to produce plastic prototypes and functional prototypes from engineering materials such as acrylonitrile butadiene styrene (ABS), nylon, and polycarbonates (PC) [8]. The main disadvantages in FDM technology are that it faces dimensional accuracy problems and it is very anisotropic (i.e. physical properties are different when measured in different directions) [8]. Currently, FDM is being investigated as a technology to make new and advanced polymer-metal composites.

2.3 Polymer-Metal Composites

Although not many applications for polymer-metal composites exist yet, their future is promising. Most studies done so far on these composites focus on the improvement of thermal conductivity and radiation shielding [11]. Perfecting these properties can lead to certain futuristic applications such as making aircraft undetectable in RADAR and even magnetic seals or locks. For example, if a fire is detected in an aircraft, a polymer-metal seal can automatically clasp together, preventing the fire to spread. Moreover, thermal conductivity is always a good property to have. In the leading edge of airfoils where skin friction is prominent, airfoils experience higher temperatures which are damaging. By increasing the thermal conductivity of the airfoil, the temperature can be better distributed.

Despite the potential for polymer-metal composites, progress is slow in coming up with the perfect mixture of both materials; this is due to the fact that polymers and metals do not like to bond together. In general, there are four types of bonds: (1) ionic, (2) covalent, (3) metallic, and (4) Van der Waals. "Ionic bonding is associated with ceramics, covalent bonding is associated with polymers, metallic bonding is associated with metals, and van der Waals bonding is associated with molecular solids" [12]. Since covalent bonds are between nonmetals, metals cannot participate in covalent bonding. Thus, making polymers-metal composites is difficult.

2.4 Adhesion

To improve the bonding between the polymer and metal interfaces, it is critical to understand how they stick together through adhesion.

2.4.1 Importance of Adhesion

Adhesion plays a critical role in understanding failure mechanisms at the interface. In fact, adhesion is one of the critical damage mechanisms that occur in composites for two main reasons:

1. in many composites, the adhesion strength between matrix and fiber dictates the resulting mechanical properties, and
2. a large area is occupied by interfaces; hence damage is initially generated through interface fracture.

Thus, it is important to establish the relationship between adhesion and the resulting material properties through mechanical tests.

2.4.2 Definition of Adhesion

Adhesion is "the state in which two surfaces are held together by interphase forces" [13]. When studying adhesion between materials, however, there are two types that can be measured: (1) basic adhesion and (2) practical adhesion.

Basic adhesion relies solely on interfacial properties to signify the interfacial bond strength. To calculate it, you sum all the intermolecular or interatomic interactions together [7]. An example of a basic adhesion calculation involves observing the wetting behavior of the adherate in liquid form (Figure 5).

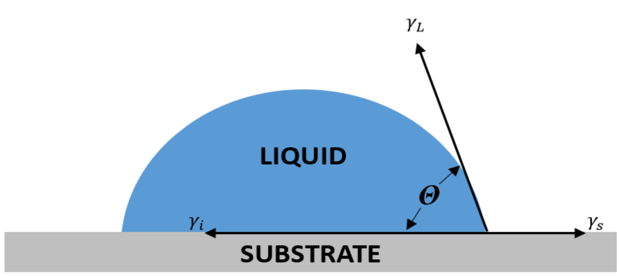

Figure 5. Contact Angle Between a Substrate and Liquid Adherate (Adapted from [14])

By applying Young's equation (2.1)

$$\gamma_s = \gamma_i + \gamma_L cos\theta \quad (2.1)$$

where γ_s is the substrate/liquid interfacial free energy, $\gamma_i$is the substrate surface free energy, $\gamma_L$is the liquid surface free energy, and θ is the contact angle between γ_L and γ_i, one can calculate the interfacial energy between the substrate and the adherate in liquid form [14].

Practical adhesion is calculated experimentally and is measured "in terms of forces and work of detachment or separation of the adhering phases" [15]. It is expressed in terms of tensile strength, peel strength, or shear strength. Peel strength is measured in terms of the force divided by the width required to maintain the continuous detachment of a strip of adherate from an adherend at a specified detachment rate. Tensile strength is defined as the force over area required to remove a specific area of the adherate when the entire area of the adherate is pulled in a direction perpendicular to the adherend surface. Shear strength is similar to tensile strength except that it is measured when the adherate is pulled in a direction parallel to the adherend surface [15].

2.5 Surface Treatment of Metals

Whether adhesion is determined via practical or basic adhesion, one way to improve adhesion at the interface of two materials is through the application of surface treatments. Surface treatments have been found to increase mechanical properties such as tensile strength and ductility (MQP DL1-1901). Surface treatments of metals are done by either physically altering the interface or by chemically increasing the chemical bonds between a metal and polymer matrix.

Physical treatments are used frequently on metals to roughen their surfaces. This can improve adhesion, according to a common mechanical interfacing theory, as it provides more surface area for adhesion to take force [16]. A common method that increases the surface area for adhesion is mechanical abrasion. Mechanical abrasion can be done both quickly and inexpensively, through sandblasting, wire brushing, or with sandpaper [17]. However, surfaces cannot typically be consistently and accurately controlled on the microscale level, due to the imprecise nature of abrasion; therefore, it is inappropriate for some metal surface modification, such as with powders.

Chemical treatments are also utilized to alter the surface geometry of some metals. In general, chemical treatments of metals can be categorized into two groups: etching treatments and additional treatments. Etching treatments are processes in which a metal's surface is exposed to an acidic environment in order to modify its contours. Acid etching can be further broken down into other categories: pickling, passivation, chelating, and electropolishing [18]. Pickling, which is done with both weak and strong acids, such as hydrofluoric acid, eliminates impurities from the surface by removing a small portion of the surface material of the metal. Passivation, which is done with acids such as nitric acid, oxidizes the surface of the metal, thus removing impurities and increasing the oxide layer thickness. Chelating, often done with carboxylic acids, removes light surface contaminants. Finally, electropolishing, done with acids like sulfuric acid, both removes surface impurities and smooths the surface [18]. Variations in acid selections can be made depending on the desired surface effect and extent of material alteration.

Addition treatments, which change the surface characteristics of metal by adding compounds or elements to its surface, have the same goal as other surface treatments; they seek to modify and improve properties such as wear resistance, corrosion resistance, hardness, wetting, adhesion, friction or appearance [19]. Addition treatments, or surface coatings, can include paints, synthetic coatings, adhesive films, pigments, oxide layers, and much other metals and chemical coatings. Adhesion promoters, or coupling agents, act at the interface of an organic polymer and inorganic surface to enhance the adhesion between the two materials [20]. Silane coupling agents are very commonly used in surface modification of microparticles to alter wetting and adhesion characteristics of the substrate.

2.6 Adhesion Measurement Methods

Measurement methods to measure practical adhesion are categorized as destructive or nondestructive. Destructive methods involve applying a load to a coating in a manner that the resulting damage can be analyzed. Nondestructive methods "typically apply a pulse of energy to the coating/substrate system and then try to identify a specific portion of the energy that can be assigned to losses occurring because of mechanisms operating only at the interface" [21]. The majority of adhesion measurements fall into the destructive category.

2.6.1 Most Common Destructive Tests

Since substrate coatings range from being either soft and flexible to hard and brittle, different destructive tests apply for each situation. For example, a peel test produces the best result for a soft and flexible coating. Oppositely, a scratch test is limited to hard and brittle coatings. Tests that work well for a range of coatings are pull tests, indentation debonding tests, and beam-bending tests.

2.6.1.1 Peel Tests

The most common configurations of the peel tests are the 90-degree peel test, the 180-degree peel test, the climbing drum peel test, and the T peel test as shown in Figure 6.

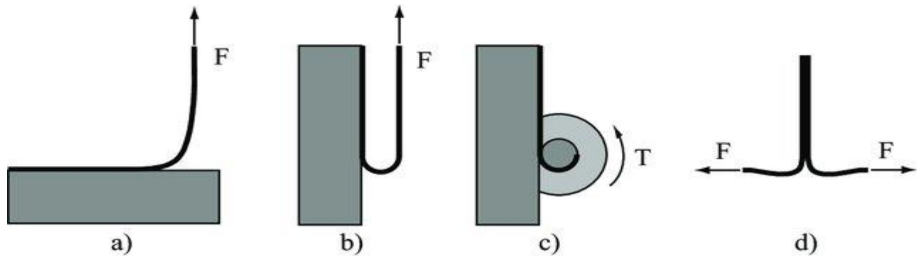

Figure 6. Common configurations for peel tests: (a) 90-degree peel test, (b) 180-degree peel test, (c) climbing drum peel test, and (d) the T peel test (Adapted from [21])

The 90-degree peel test (Figure 6a) is by far the most prevalent and studied test as "it is a favored test for flexible coatings on rigid substrates" [21]. When space is constrained, however, it is advantageous to use the 180-degree peel test (Figure 6b) instead. Ideally, a peel test can be set up at any angle between 0 and 180 degrees but, maintaining either a 90-degree or 180-degree angle reveals more information on how interfacial adhesion varies between both modes I (tensile loads) and mode II (shear loads), respectively.

Climbing drum peel tests (Figure 6c) are predominantly used in the tire industry to test the adhesion of rubbers. Due to the fact that they maintain a constant radius of curvature, climbing drum peel tests simplify the numerical analysis of the data collected [21]. Finally, if you are finding the adhesion energy between two flexible adherends, a T peel test (Figure 6d) is the most suitable test.

Overall, peel tests have many advantages. One huge advantage is that sample preparation for peel tests is easy. In particular, samples can be treated with multiple surface treatments and then be ranked for the coating adhesion to the substrate. Another advantage is that peel tests allow for the direct study of the rate dependence of adhesion strength on the rate of delamination. This is due to the fact that the rate of delamination can be controlled by the testing equipment. Lastly, the peel test can be used in a multitude of controlled temperatures and environments [21].

On the other hand, one of the challenges that peel tests face is that they do not accurately predict how a coating performs in actual usage. This is due to the fact that peel tests place high strain levels at the peel-bend of the coating which in turn skew the results of delamination of the substrate. Another disadvantage is that peel tests can only be used to test tough and flexible substrates. Lastly, it is difficult to initiate the peel strip if the substrate has strong adhesion [21].

2.6.1.2 Pull Tests

A pull test setup (Figure 7) requires two additional materials aside from the coating and the substrate being tested. These materials are a test stud or test dolly and an adhesive. The test dolly is typically made from stiff (high-modulus) metal or ceramic material. An adhesive (e.g. epoxy) is then used to stick the test dolly to the coating. A tensile test apparatus then pulls the dolly upwards.

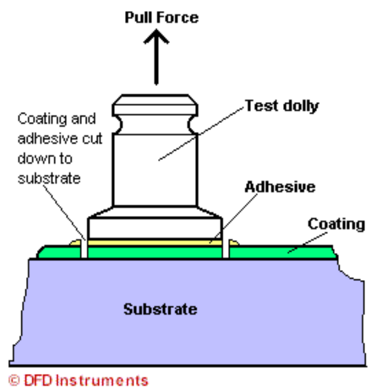

Figure 7. Pull Test Setup [22]. © DFD Instruments

Pull tests can be used to examine a wide variety of coatings including “relatively soft flexible polymer coatings to hard brittle coatings” [21]. Qualitatively, pull tests allow for easy visualization of the pull-off fracture surface to determine whether the failure was cohesive or interfacial between the coating and the substrate. Quantitatively, pull tests produce stress fields that make it easy to observe the most vulnerable flaw. Moreover, sample preparation for pull tests is relatively easy [21].

Although a simple concept, a pull test has many flaws. The main flaw of this technique is that data analysis is very difficult as there is a large variation in the test data. This is due to the fact that there are rapid uncontrollable failure modes. For example, if the load is not applied properly to the test dolly, there will be an off-axis component of force which will “induce a bending moment to the sample in addition to the tensile load” [21]. Even if the sample is experiencing full tensile loading, any bonding weaknesses or defects will be accentuated. Since all samples are not perfect, the aforementioned will occur every time and failure will propagate until complete separation. Failure can also occur in multiple failure modes. Thus, to deal with these complexities, the pull test has to be run multiple times concurrently with statistical analysis in order to obtain reliable data.

2.6.1.3 Indentation Debonding Tests

The indentation debonding test works by using an indenter to compress the coating directly onto the indenter tip. Figure 8 demonstrates the stages of this test. At first, the indenter makes contact with the coating (Figure 8a). As the force F is increased, the indenter penetrates the surface of the coating (Figure 8b) which causes plastic deformation from the substrate to pile up around the indenter tip. When the tensile stress exceeds the strength of the bonds, delamination of the substrate occurs. This results in the debonded area as shown in Figure 8c. By taking measurements of the maximum and minimum dimensions of the debonded area, a peeling parameter can be found that relates “the limit of adhesion between a specific combination of substrate and bonded polymer layer” [23].

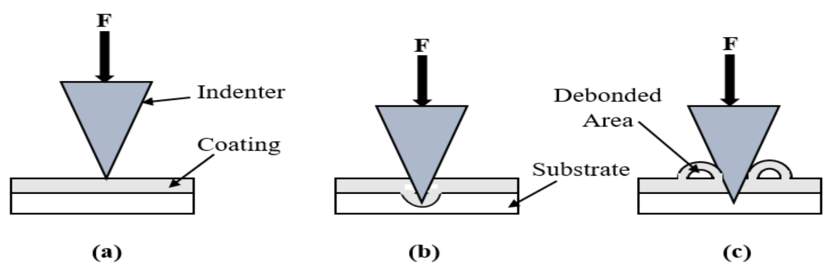

Figure 8. Stages of an Indentation Debonding Test: (a) Beginning Indentation, (b) Indentation before Debonding, (c) Debonding (Adapted from [23])

The indentation debonding test has many advantages. Among the top advantages are that it is applicable to a wide variety of coating and substrate systems (e.g. soft flexible or hard brittle), it does not require a lot of work to prepare samples, and it is readily available as commercial equipment. In fact, the equipment is available off-the-shelf in the form of “indentation test equipment and powerful microscopes with digital interferometers for evaluating both substrate damage and deformation” [21]. This ensures that the experiment will have quality control. This test also offers quantitative (e.g. a limit of adhesion) and qualitative (e.g. estimation of coating durability) results.

On the other hand, a major disadvantage of the indentation debonding test is that it experiences complex modes of loading which involve "high compressive stress and high shear strains" [21]. These complex modes of loading produce erroneous results for coating substrate systems that are subjected to large temperature gradients as they experience different load conditions and delamination on the edges. Furthermore, if dealing with a hard coating, the indentation debonding test generates large hoop stress which causes radial cracking in both the coating and the substrate. Thus, having multiple modes of loading also leads to the complication of interpreting the data collected and also understanding how the coating is delaminating. To produce more accurate results, indentation debonding tests should be applied only to coatings that will "endure abrasive conditions and contact with potentially penetrating surfaces" [21].

2.6.1.4 Scratch Tests

The scratch test is similar to the indentation debonding test in the way that it uses an indenter, or stylus, to apply pressure to the coating-substrate system except now the indenter is translated along the surface. This test is performed by either applying a progressive (linearly increasing) load or a constant load until delamination occurs [21]. A visualization of the scratch test is represented in Figure 9.

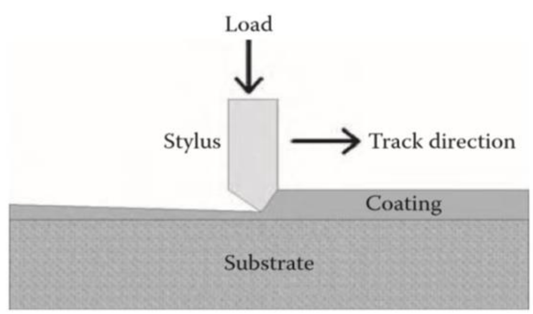

Figure 9. Schematic of Scratch Test [21]

Scratch tests are highly popular in industry and academia due to its versatility for evaluating a wide range of coating-substrate systems. The indenter itself serves as a tool for finding coating hardness and other elastic properties. By using an additional instrument, such as acoustic spectroscopy, more information can be discovered on "surface topography, mechanical properties, and modes of deformation and delamination" [21]. Moreover, there is ease in sample preparation for the scratch test.

Unfortunately, the scratch test is limited to hard brittle coatings. This is due to the fact that soft metals and polymers tend to deform around the indenter. As a result, the coating only piles up around the edges of the scratch track and in front of the indenter. Furthermore, acoustic spectroscopy is not useful since soft coatings will not produce a signal where the failure occurs. Some coatings are also impossible to achieve complete removal which is required for proper adhesion strength analysis [21].

Another limitation about the scratch test is that it is mechanically complex. The pushing down of the indenter on the coating and substrate induces a lot of high stresses and deformations to the coating-substrate system. This causes a lot of highly nonlinear viscoplastic material behaviors and failure modes which have not been studied in depth [21]. Thus, simply applying elastic mechanical equations to the data collected does not take care of this problem.

2.6.1.5 Beam-Bending Tests

While the indenter test is mechanically complex, beam-bending tests are more simple to use and provide qualitative results that are easier to understand. Since there exist extensive studies on the mechanics of bending beams, it is easy to find solutions for nearly any beam configuration. The load-displacement curve data can be converted into fracture toughness or surface fracture results that can be directly attributed to fracture mechanics models [21]. Amongst the most commonly used beam-bending tests are the three-point bend test, the standard double-cantilever beam test, and the wedge test (Figure 10).

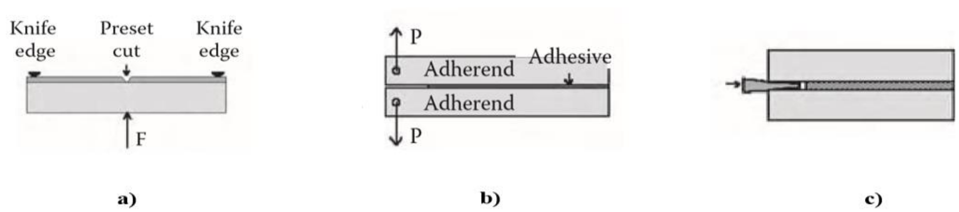

Figure 10. Common Beam-Bending Tests: (a) Three-point bend test, (b) Standard double cantilever beam test, (c) wedge test (Adapted from [21])

The three-point bend test is used to evaluate elastic modulus in bending, stress-strain behavior, fracture toughness, and failure limits in bending [24]. As shown in the three-point bend test setup (Figure 10a), the convex side of the sample is placed in tension while the outer fibers are subjected to maximum stress and strain. Failure occurs when the strain or elongation exceeds the material’s limits [24]. Moreover, this test is perfect “for investigating the effect of different surface preparation procedures and adhesive formulations on the adherend/substrate adhesion strength” [21].

The double cantilever beam test, also known as the DCB test, works by pulling apart a sandwich of adherents and adhesive by applying equal and opposite loads at an edge. The setup, as shown in Figure 10b, involves gluing two identical beams of a substrate with a thin layer of adhesive. To ensure that the adhesive has a controlled thickness, some sort of spacer such as Teflon is inserted between the beams [21]. This technique is primarily used to study the strength and reliability of structural adhesives required to bond lightweight and high-performance composite materials [21].

Unlike the double cantilevered test which requires two beams to be pulled apart, the wedge test forces a wedge into the adhesive sandwiched by the substrates (Figure 10c). This inserted wedge then creates a constant load at a level right before crack propagation initiates. The sample can then be tested in different environmental conditions (e.g. high temperatures and humidity) to track the progress of any pre-existing crack [21]. Depending on how a crack propagates identifies whether the bond between the adhesive and substrate is good or bad. For example, if a short crack occurs and it remains in the adhesive layer, then the bond is good. In contrast, a bad bond is when the crack is relatively long and propagates along the adhesive-substrate interface [21]. Due to the ease and cheap cost of fabricating samples, this test is widely used in the aircraft industry to “evaluate the durability of sandwich layers of thin aluminum sheets bonded with an adhesive” [21].

As stated in the introduction of this section, the main advantage of beam-bending tests is that they produce results that can easily be analyzed qualitatively due to the extensive research and findings from fracture mechanics. Since fracture mechanics is one of the most studied topics in applied mechanics, it is highly likely that stress and strain solutions already exist for a given beam configuration; if none exists, it can be found through more analysis. Another advantage of beam-bending tests is that sample preparation is easy. Thus, a large number of samples can be fabricated at a time and tested under a wide variety of conditions [21].

2.6.2 Most Common Nondestructive Tests

Unlike destructive tests which measure the force required to pull apart stuck together materials, nondestructive tests focus on measuring “some quantity that depends on how well two materials are joined at their common interface” [21]. In particular, the concept behind nondestructive adhesion tests focuses on determining the ability to transmit strain/deformation across an interface and to transmit vibrations along an interface [21]. Two types of nondestructive tests are the dynamic modulus test and the surface acoustic waves test.

2.6.2.1 Dynamic Modulus Test

The dynamic modulus test uses theory from the atomic relaxation phenomena in thin films. The apparatus, as depicted in Figure 11, can be used “to measure the internal friction and dynamic modulus of thin, reed-like specimens” [21]. A harmonic driving force is applied to the tip of the reed and then removed. After removing the force, the resulting damped vibration is measured by another set of electrodes near the base of the sample [21]. Provided that the length, thickness, and density of the reed are known, the modulus (E) of the reed can be found through equation 2.2 [21]:

$$\mathcal{F}_n = \frac{\alpha_n^2 d}{l^2\sqrt{3\pi}}\sqrt{\frac{E}{\rho}}, n = 1,2,3, \ldots \infty \tag{2.2}$$

where

$\mathcal{F}_n$ = Frequency of the *n*th normal mode of vibration
α_n = Mode number associated with the *n*th normal mode of vibration
E = Young’s modulus of reed
ρ = Reed density
d = Reed thickness
l = Reed length

‘

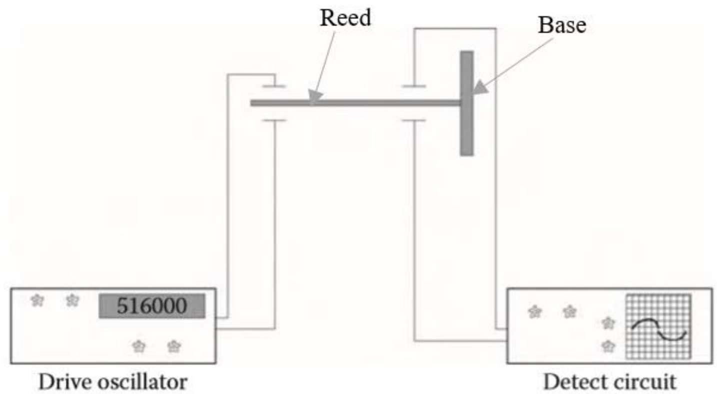

Figure 11. Typical Dynamic Modulus Test Setup (Adapted from [21])

The dynamic modulus test is most useful in “the research-and-development laboratory for specialized applications of the adhesion of thin films to microelectronic substrate materials such as silicon and vitreous silica” [21]. The main advantages of this test are that it is nondestructive and it is capable of evaluating both adhesion strength and the thermal-mechanical properties of thin films by measuring internal friction. Internal friction is important because it can identify “defect structures and impurity migration along grain boundaries in metal films and is also a sensitive way to detect the glass transition and secondary relaxation processes in polymer coatings” [21].

Since the reeds have to be constructed exactly the same, any inaccuracies yield inaccurate data. Thus, a disadvantage of the dynamic modulus test is that sample preparation is difficult. Furthermore, the samples are limited to a specific configuration. Also, the nondestructive nature of the dynamic modulus test makes it difficult to relate it to any of the other standard tests mentioned in Section 2.5.1.

2.6.2.2 Surface Acoustic Waves Test

Surface acoustic waves (SAWs) are a special class of waves that propagate only on the surface of a material. By using piezoelectric coupling or another controllable method, the SAWs test monitors high-frequency waves as they propagate throughout a structure [21]. Figure 12 represents the typical SAWs test setup. The transducer on one side generates the SAWs and propagates them to the other transducer on the other side. As the waves travel through the interface between the coating and the substrate, velocity and amplitude effects are monitored. A shift in velocity represents "dispersion effects that are detectable when several different frequencies are present" [21]; thus, revealing loss mechanisms such as poor coupling between the coating and substrate.

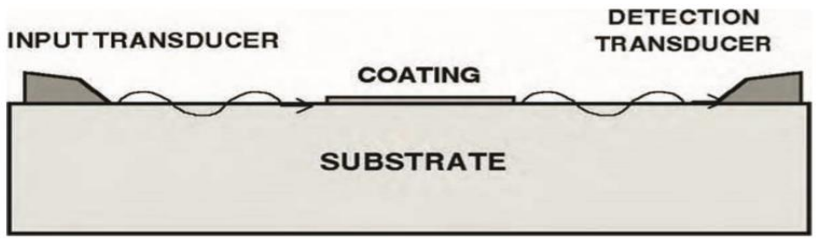

Figure 12. Surface Acoustic Waves Test Setup [21]

One advantage of the SAWs test is that it is a nondestructive test. Thus, it can be used in real-time as a quality control tool. Instead of using a transducer to initiate waves, a laser pulse along with interferometry (techniques for superimposing waves) as a detector can also be used [21]. This allows for fast coating inspections without damaging them. Another advantage is the SAWs test "can be calibrated against standard destructive adhesion measurement experiments to provide quantitative results related to surface fracture energies" [21].

Despite its many advantages, the SAWs test does not yield direct adhesion strength data. In addition, the setup of the apparatus and sample preparation is very tedious and non-trivial. For instance, the SAWs test has to be calibrated against a more standard test in order to properly compare results [21]. Also, since most materials do not have natural piezoelectric behavior (i.e. quartz substrates), coupling the input and output transducers to the substrate is a challenge [21]. At times, other methods of coupling the electric signal (i.e. coupling fluid) to the substrate must be used. This just further complicates the experiment [21].

Chapter 3: Methodology

After comparing the different adhesion measurement methods as described in Chapter 2, a peel test was selected as the basis for the design of the testing apparatus due to its ease of use and the simplicity involved in sample preparation. Once the peel test was assembled, the project moved onto its next stage: specimen fabrication. This process involved a lot of trial and error until a working method was finally established.

3.1 Testing Apparatus Design

Under the peel test section (Section 2.6.1.1), the tests which were examined were the 90-degree peel test, the 180-degree peel test, the climbing drum peel test, and the T peel test. The peel test which was selected for the final design was a variation of the 90-degree peel test. The inspiration for a custom made 90-degree peel test originated from Srdjan Kisin's Ph.D. dissertation from Technische Universiteit Eindhoven [25]. In his thesis, Kisin studied the interfacial adhesion between copper and ABS. He designed a 90-degree peel tester, as shown in Figure 13, where a motor moves a load cell along rails at 45 degrees, thus maintaining the peel arm at a constant 90-degree angle.

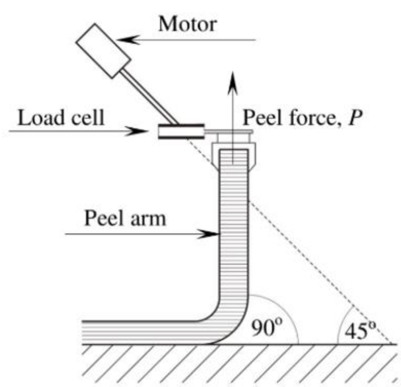

Figure 13. Srdjan Kisin's Peel Test Design [25]. © 2006 Srdjan Kisin

3.1.1 Design Summary and Terminology

Taking a similar approach, an adaptor for the Instron® 5944 crosshead was created to maintain the load cell at a 45-degree angle. The load cell then attaches to a clamp where the tip of the peel arm attaches. To ensure that the peel arm of the sample was maintained at a 90-degree angle, a triangular mount was created at an incline of 45 degrees. The mount attaches to a breadboard which screws down to the base beam of the Instron® 5944. A plate is then mounted on top of the mount which contains slots for the sample plates of SS and ABS to screw into. As the crosshead moves upward along the column, the ABS is peeled off at a constant 90-degree angle. The terminology for the Instron® 5944 is demonstrated below in Figure 14.

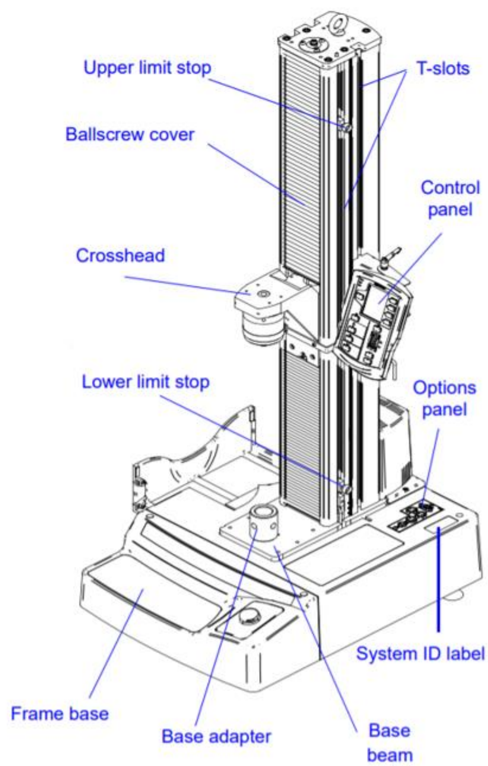

Figure 14. Instron® 5944 Components [26]. © Illinois Tool Works Inc.

Thus the main components which were fabricated for this design are the: (1) adapter, (2) clamp, (3) mount support, (4) mounting plate, and (5) sample plate. Parts (1) through (4) were made from Aluminum 6061 as it is a very soft and lightweight metal that is easy to machine. These parts were fabricated from a combination of CNC machining and manual milling. For those parts made in the CNC machine, HSMWorks CAM software, a plugin for SolidWorks®, was used to develop the G-code. The sample plates were cut out from a larger piece of SS via a grinder. Each component is shown in the final setup (Figure 15) and is explained in detail in the following sections.

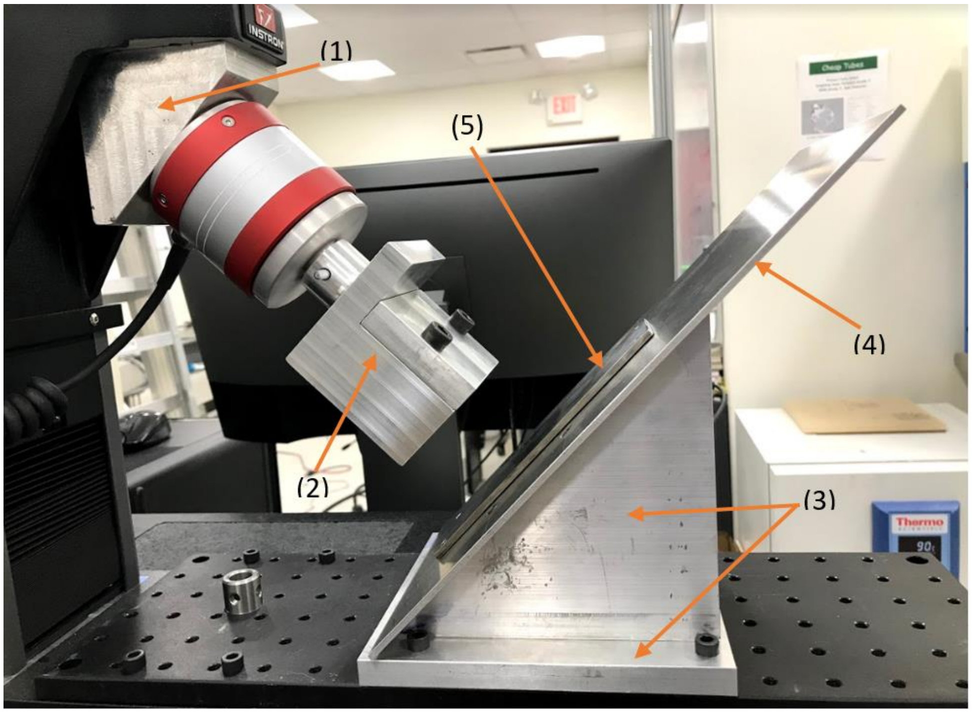

Figure 15. Fabricated Components of Peel Test Design

3.1.2 Adapter

As shown in Figure 16, the adapter was created such that one face would be at 45 degrees while the other face would be parallel to the crosshead surface. The 45-degree face is attached to the load cell by a cap-head screw while the parallel face attaches to the crosshead by a hex-bolt screw. Both faces have holes for dowel pins. The purpose of the dowel pins is to maintain alignment such that the adapter and load cell do not rotate during operation. The load cell and the crosshead have built-in places for the dowel pins (Figure 17 and 18) which were mirrored in the adapter. The adapter was created from a manual milling machine. Since the size of the adapter was underestimated, extra aluminum was welded onto the adapter in order to fit the dowel holes.

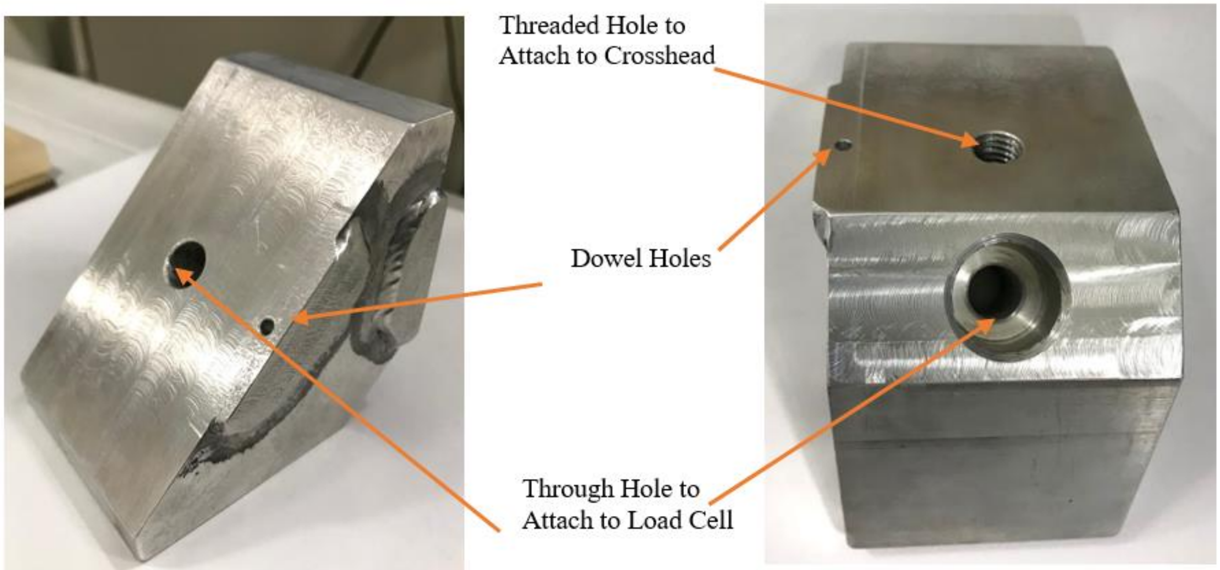

Figure 16. Machined Adapter

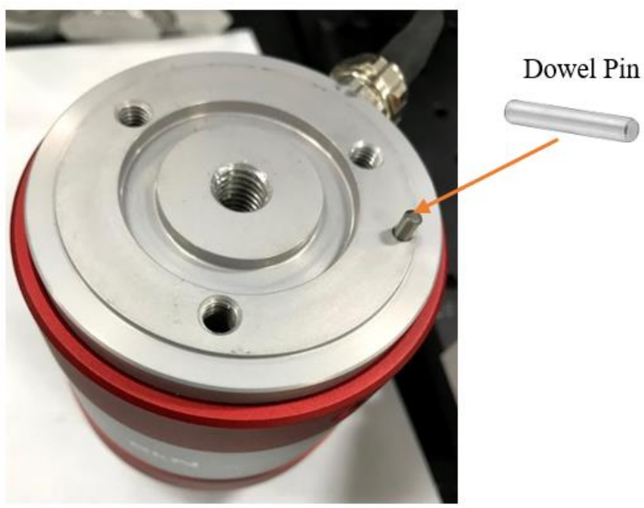

Figure 17. Load Cell with Dowel Pin © 2012 McMaster-Carr Supply Company

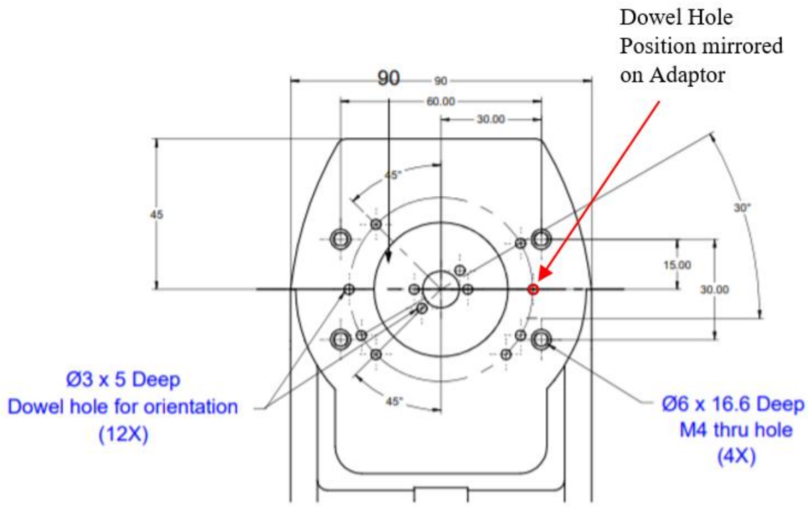

Figure 18. Crosshead Mounting Dimensions [26] © Illinois Tool Works Inc.

3.1.3 Clamp

The bottom of the load cell has two sets of through holes where other accessories made by Instron® such as grips and fixtures can attach and be held together by a clevis pin (Figure 19). Thus, a similar cylindrical piece with a through hole was made in the clamp so that it could attach to the load cell (Figure 20). The front of the clamp has 90-degree faces where the tip of the peel arm attaches to the longest face (Figure 21). The peel is arm is then clamped down by a rectangular piece with two screws (Figure 22). As can be seen in Figure 23, the angle made between the peel arm and the plate where the sample is mounted is maintained at 90 degrees.

The clamp was made via CNC machinining and manual milling machining. The rectangular piece which completes the clamp was made by using a horizontal band saw to cut a block of aluminum 6061 and then using a manual milling machine to drill holes.

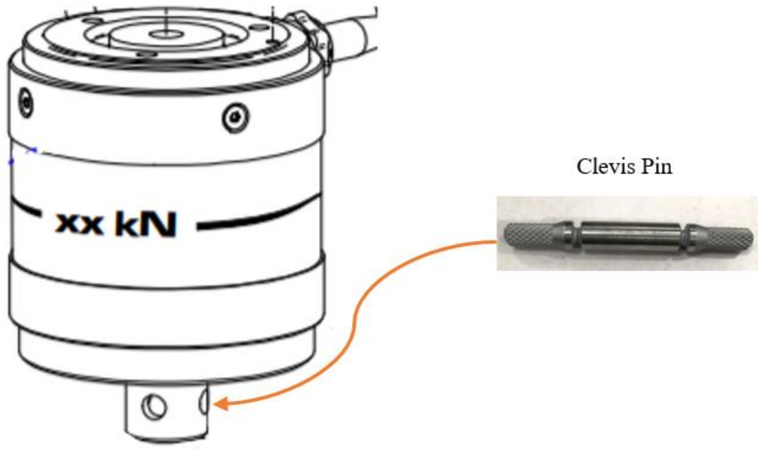

Figure 19. Load Cell and Clevis Pin Diagram [27] © Illinois Tool Works Inc.

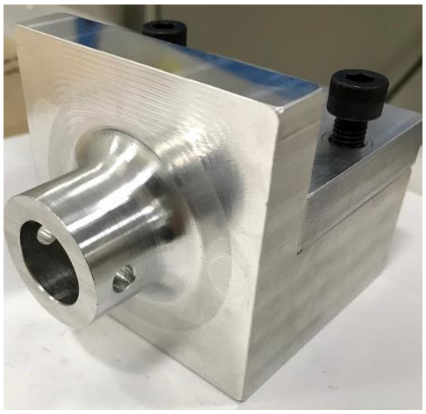

Figure 20. Machined Clamp (Back View)

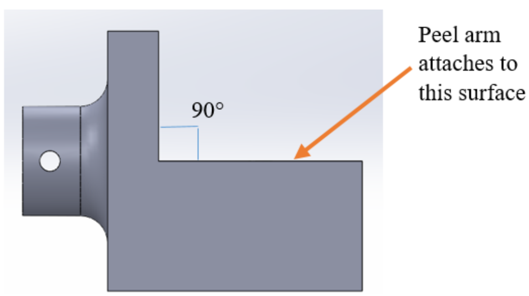

Figure 21. Clamp CAD Model (Side View)

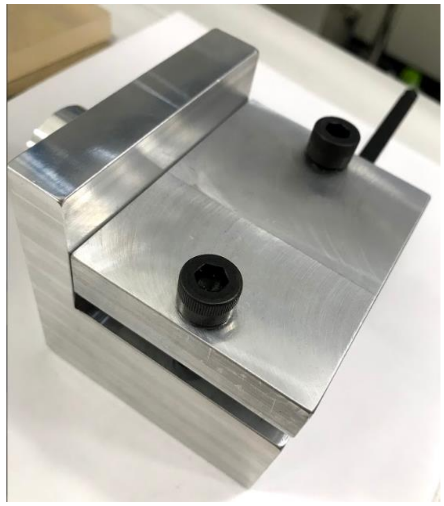

Figure 22. Machined Clamp (Front View)

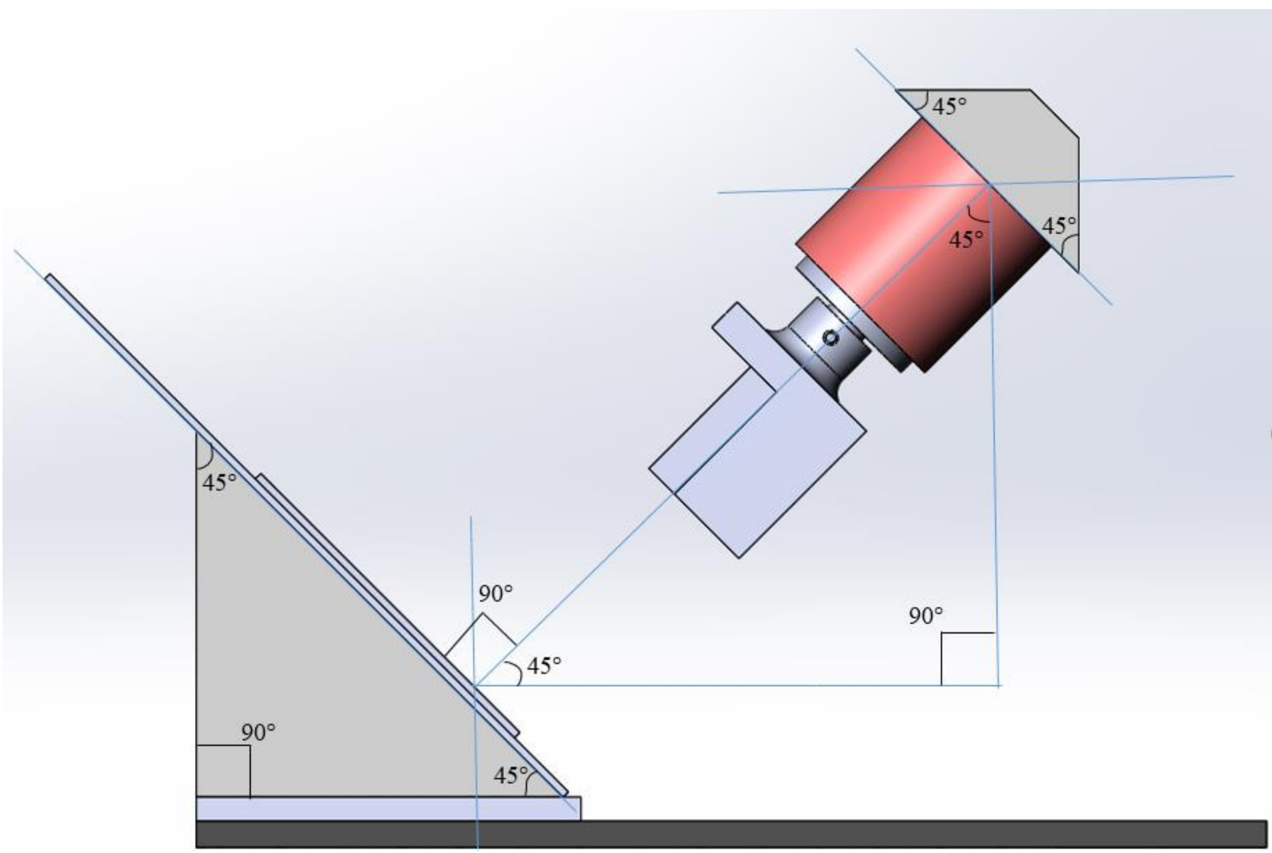

Figure 23. Angle Configuration of Testing Setup

3.1.4 Mount Support

The mounting support (Figure 24) is made up of three main parts: (1) the elevator base, (2) the breadboard, and (3) the triangular wedges. The elevator base (Figure 25) allows for the triangular wedges to be screwed on from the bottom up in a countersink fashion so that the screw heads do not stick out. This is necessary since the breadboard threads are made in only one direction (top to bottom) and thus the bottom of the triangular wedges cannot directly screw onto the breadboard. The elevator base then attaches to the breadboard by placing screws from the top of the breadboard surface to the bottom. Since the breadboard has many rows of threaded holes, the elevator base is free to move along the length of the breadboard as needed. The breadboard then attaches to the base of the Instron® by four screws (Figure 26).

It is important to note that as shown in Figure 23 of Section 3.1.3, the triangular wedges are 45-45-90 degree triangles. Having a 45-degree incline is vital for measurement accuracy to maintain the peel arm of the sample at 90-degrees during the peel. This can only happen if the incline on the triangle and the inclined face of the adapter are parallel to each other. Also shown in Figure 24, the inclined faces of the triangular wedges have four holes where the plate which holds the samples attaches.

The elevator base and triangular wedges were made using a horizontal band saw and a manual milling machine. The breadboard was already available in Professor Karanjgaokar's lab. The only adjustments made to the breadboard were the holes needed in order to mount it to the bottom of the Instron®. These holes were also made by a manual milling machine.

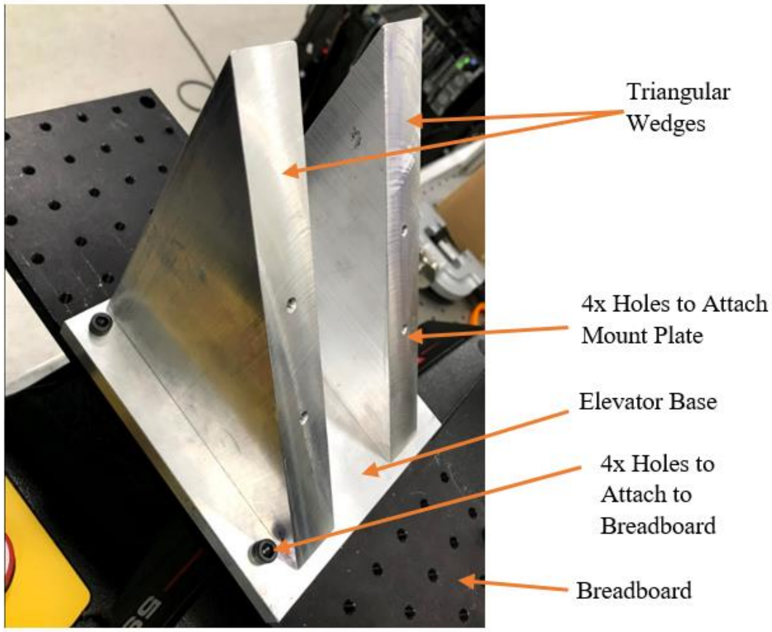

Figure 24. Machined Mount Support

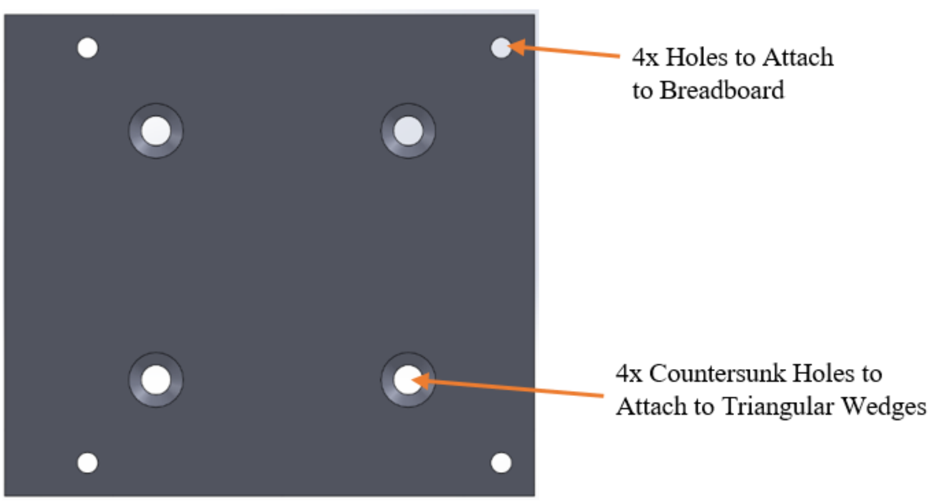

Figure 25. Elevator Base CAD Model

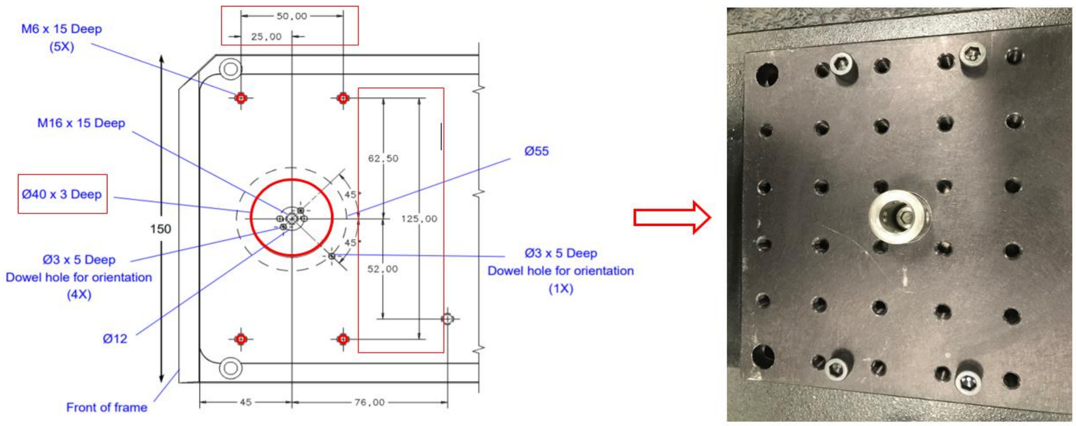

Figure 26. Breadboard Adjustment [27] © Illinois Tool Works Inc.

3.1.5 Mount Plate

The mounting plate (Figure 27) attaches to the triangular wedges by four countersunk screws on the hypotenuse surface of the wedges. Thus, the mounting plate makes a 45-degree angle to the breadboard and the surface of the adapter (Figure 23). The mounting plate also includes four through holes where screws can hold a sample plate by using hex nuts. All holes were made using a drill press. To countersink the holes required, a countersink drill bit was used.

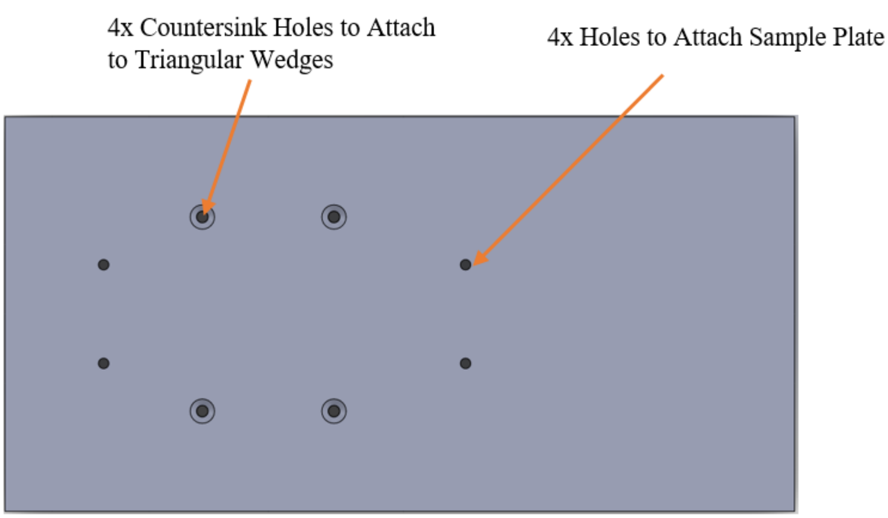

Figure 27. Mount Plate CAD Model

3.1.6 Sample Plates

A total of eight sample plates were cut out from two 420-grade hardened stainless steel plates via a grinder. Following the constraints put in place by ASTM (Section 1.2), the sample plates (Figure 28) were designed so that the peel arm met the minimum length of 1 inch and that at least 3 inches of the ABS could be peeled off.

The sample plate surfaces were also smoothed out and polished (in preparation for surface treatments) by the following protocols:

1. Applied 120, 220, 320, 400, and 600 grit sandpaper (silicon carbide paper) simultaneously with WD-40 oil in the stated order to smooth out the sample plate surface and to remove any scratches or pits.
2. Utilized three buffing compounds (Figure 29) in the belt-sander to achieve a mirror-finish on the sample plate surface. The buffing compounds were applied in the order of least abrasive to most abrasive: White Rouge, Red Rouge, and Emery Cake (Black).

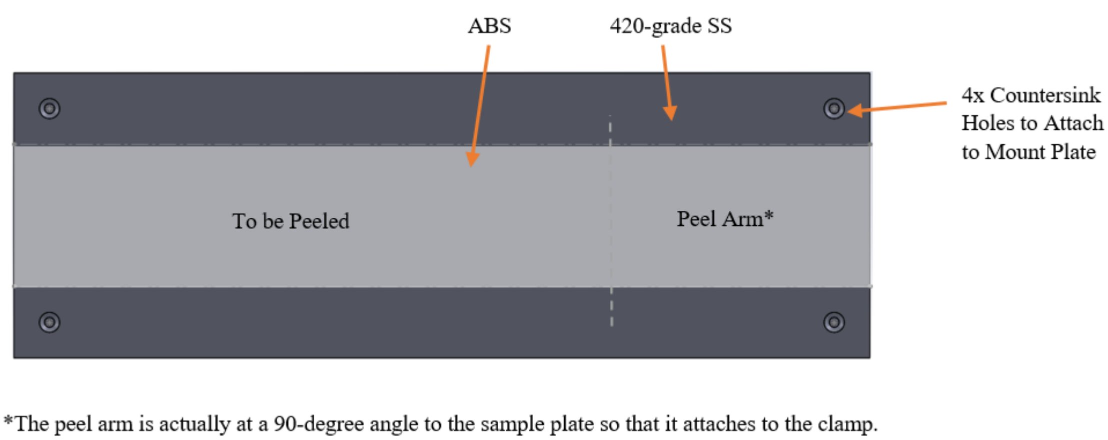

Figure 28. Sample Plate CAD Model

Figure 29. Buffing Compound Set for Polishing SS Plates © 2019 Formax Manufacturing

3.2 Specimen Fabrication

With the SS plates ready, the next step was to prepare the samples. In a process of trial and error, four different experimental methods were tried to achieve good adhesion between the metal and polymer interface. The first two methods involved using the liquid form of ABS. The last two methods involved using ABS strips or a combination of ABS strips with liquid ABS. The fourth method was eventually selected as the protocol for making the ABS-SS composites.

3.2.1 Experimental Methods

The first method involved using the following steps:

1. Pour liquid ABS into a 3D-printed mold over the SS plate
2. Place the sample on a spin-coater and run two times to achieve a uniform thickness
3. Wait 30 minutes until the ABS properly adheres to the SS plate
4. Use a blade to scrape 1.5 inches of the ABS to create a peel arm

This method created non-uniform samples with varying widths and a lot of porosity. Since the liquid ABS was made by dissolving acetone with ABS pellets, the evaporating acetone created a lot of pores.

The second method was similar to the first method except that the sample was degassed in a vacuum degassing chamber between steps 2 and 3. This was done with an attempt to get rid of the trapped gases in the ABS. Another idea was to degas the liquid ABS itself before pouring it into the mold but liquid ABS solidifies really quickly. Thus, this was not achievable. Both degassing techniques had no success.

The third method involved using a roll of ABS strip purchased from McMaster-Carr®. The following steps used in this method were:

1. Heat up the SS plate in an oven to 150°C for 20 minutes
2. Immediately apply ABS strip to hot SS plate
3. Use another SS plate (at room temp.) to sandwich the ABS strip with the hot SS plate
4. Use a blade to scrape 1.5 inches of the ABS to create a peel arm

The temperature of 150°C was determined as the temperature required to melt a small piece of ABS strip on a SS plate while heated on a hot plate. This method was very hard to achieve. Once the SS plate was taken out of the oven, the ABS strip needed to be placed on the SS plate immediately and accurately. Furthermore, the ABS tended to adhere only in the middle of the SS plate rather than on the sides.

The fourth method was based on the concept that polymers like to stick better to polymers rather than metals. Thus, by using the liquid ABS as a "glue" to stick the ABS strip onto the SS plate, a successful method was found. This process is described below:

1. Sandwich ABS strip between two SS plates & place on a hot plate of 220°C for 5 minutes
2. Apply liquid ABS to one side of the ABS strip and place on the SS plate
3. Use a roller to evenly spread out the strip on the SS surface (roll 20 times up and down)
4. Place in an oven heated to 50°C for 20 minutes
5. Use a blade to scrape 1.5 inches of the ABS to create a peel arm

Figure 30. Flattening the ABS Strip

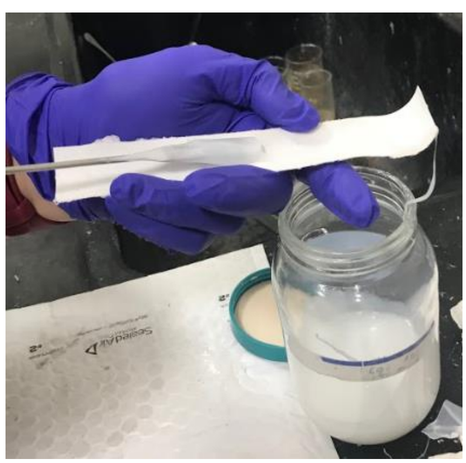

Figure 31. Applying Liquid ABS to the ABS Strip

Figure 32. Finished ABS-SS Sample (Untreated)

3.2.2 Surface Treatments

To observe how surface treatments affect the adhesion of ABS-SS composites, two different surface treatments were chosen to modify the surface of the SS plates both physically and chemically. These treatments are acetic acid etching (30 vol% solution) and silane coupling. These treatments were selected from the best results achieved from Professor Lados' MQP (DL1-1901) since acetic acid etching was found to increase tensile strength while the silane coupling increased ductility. The procedures shown in the following sections for each treatment are also based on the same procedures developed from Professor Lados' MQP (DL1-1901) which involved SS powders instead of plates.

3.2.2.1 Acetic Acid Etching (30 Vol% Solution)

The procedure for acetic acid etching entailed three main steps:

1. Measure out 40 mL of acetic acid for a 200 mL beaker. Dilute acetic acid from stock room with deionized (DI) water, as necessary, to achieve 20vol% acetic acid.

2. Heat up the beaker with the acetic acid on a hot plate to 55ºC, measuring with a digital thermometer.

3. Submerge the SS plate in the beaker for 120 minutes.

After etching the surface, the same procedures described by method four is used to attach the ABS to the SS surface.

3.2.2.2 Silane Coupling

Silane coupling is done with a solution of 1vol% APDS (3-aminopropylmethyldiethoxysilane), 4vol% DI water, and 95vol% ethanol. The procedure is:

1. Pour 190 mL of ethanol and 8 mL of DI water into a 250 mL beaker.
2. Using a pipette, measure out 2 mL of APDS (3-aminopropylmethyldiethoxysilane) into a graduated cylinder and add to the beaker containing ethanol and water.

3. Allow the 1%(volume/volume) silane solution sit in the beaker for 20 minutes, stirring the mixture briefly with a glass rod at 5-minute intervals to allow for hydrolysis and silanol formation. Immediately use solution with SS plate.

After applying the silane couple surface treatment to the SS plate, the same procedures described by method four is used to attach the ABS to the SS surface.

Chapter 4: Results and Analysis

A total of eight samples were prepared of untreated ABS-SS composites. Each sample was mounted to the testing apparatus and run with a delamination rate (i.e., rate of peeling) of 20 mm/min. Due to time constraints, the surface treatments were not implemented. The data collected by the Instron® will be displayed and analyzed in this section.

4.1 Data Collection

Each sample was mounted such that the peel arm was maintained at a 90-degree angle with respect to the surface of the sample surface (Figure 33). Using Bluehill® Universal Software, the software compatible with the Instron®, the correct values were input about the specimen such as the length of the peel arm and the width of the specimen. To obtain a value of average peel force to use in the adhesion energy formula, peel force and displacement were chosen as parameters for the software to record. Before starting a test, two buttons for balancing the forces and zeroing the displacement were pressed.

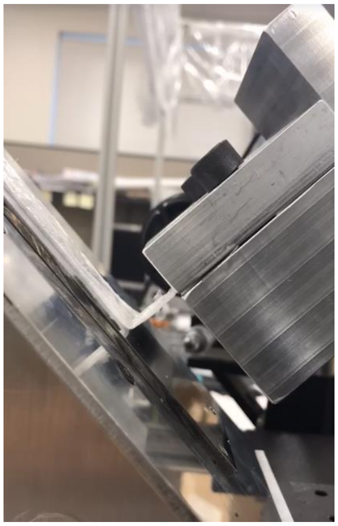

Figure 33. Peel Arm Mounted at 90-Degree Angle

Concurrently with the peeling of a sample, the Bluehill® Universal software produced a plot of peel force in kiloNewtons versus the displacement of the ABS peeled in millimeters. A sample of this graph is shown in Figure 34. As can be seen, there is a region where the peel force is relatively stable. These are the values of interest which need to be averaged to determine the average peel force value.

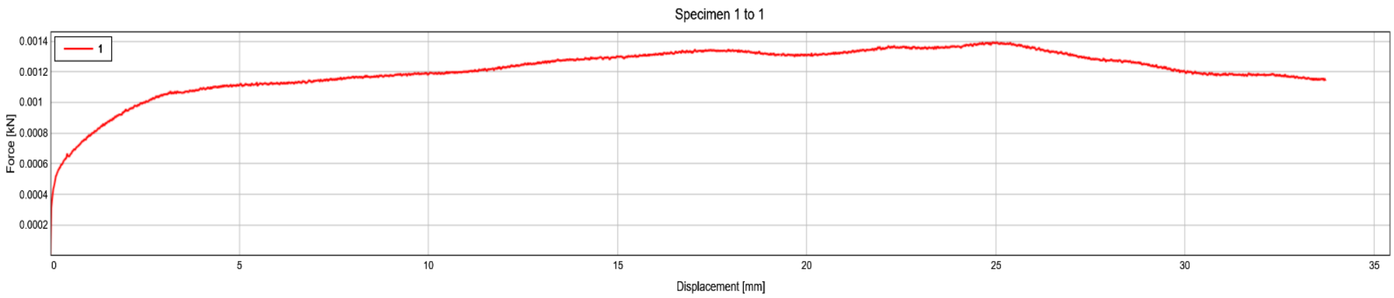

Figure 34. Instron® Force [kN] vs. Displacement [mm] Graph

The values recorded for force and displacement were then exported into a Microsoft® Excel file (Figure 35) where the AVERAGE() command was used on the steady peel force values to determine the average peel force value.

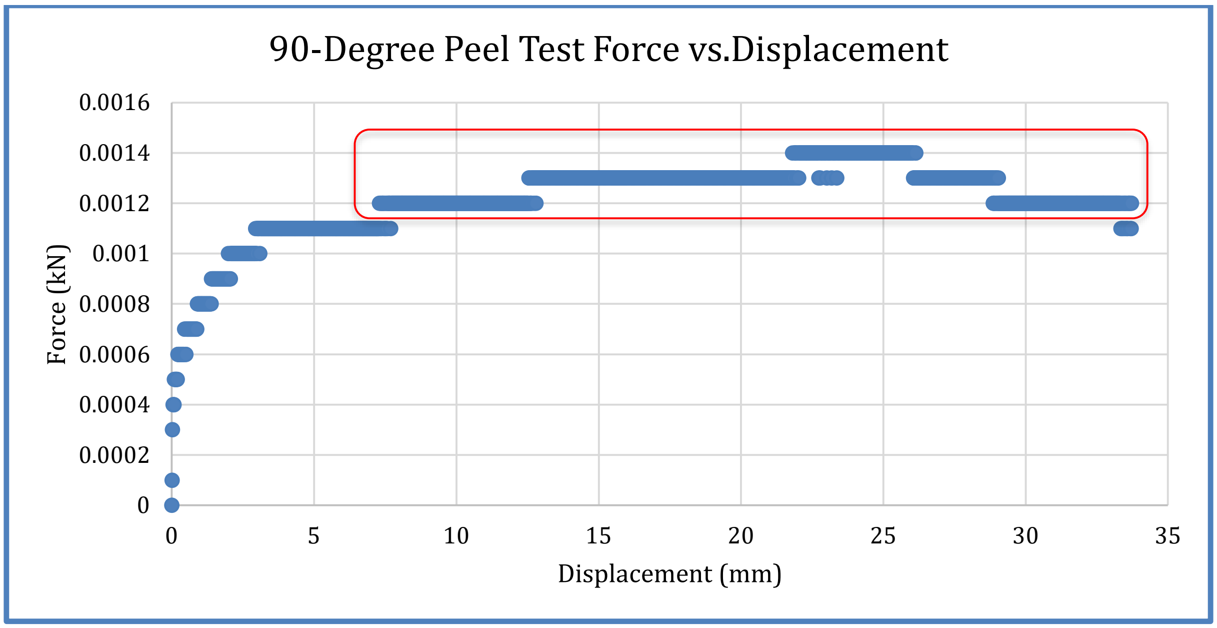

Figure 35. Steady-State Peeling Section of Force [kN] vs. Displacement [mm] Graph

For the data shown in Figures 34 and 35, the average peel force was found to be approximately 1.278 Newtons. Using a peel width of 1 inch (25.4 millimeters) and the peel force value, those values were then substituted into the adhesion energy formula (Equation 2.1) where the adhesion energy resulted as 0.0503 Newtons per millimeter. This process was repeated for all samples. The results are shown in the following section.

4.2 Results & Analysis

The data collected for eight ABS-SS samples are shown in Table 1. As can be seen, the data for sample 3 did not record at all. Other samples, such as sample 5 and sample 8, produced very skewed data. Thus, sample 3, 5, and 8 were outliers and not considered for the final value of the peel force and adhesion energy.

The potential causes for such drastic readings in samples 3, 5, and 8 can be caused by inconsistent peel arm lengths or by varying times in letting the ABS dry on the SS plate before testing the samples. Another cause can be the accuracy that the load cell can measure. According to a load cell specification sheet from Instron®, "accuracy has been found to be equal to or better than 0.025% of the load cell rated output or 0.25% of the indicated load" [28].

Table 1. Data for Untreated ABS-SS Samples (With Outliers)

Sample	Avg. Peel Force (N)	Adhesion Energy (N/mm)
1	1.277050223	0.050277568
2	2.227272727	0.087687903
3	-	-
4	3.88	0.152755906
5	11.7125	0.461122047
6	2.985714286	0.117547807
7	3.124137931	0.087687903
8	0.287545126	0.011320674

After removing the outliers (Table 2), the final peel force value and adhesion energy value was found to be approximately 2.7 Newtons and 0.01 Newtons per millimeter, respectively. For reference, the peel force required to pull Scotch® tape (same dimensions and delamination rate) is 0.7 Newtons. This value was confirmed both by my testing apparatus and through literature [29].

Table 2. Final Data for Untreated ABS-SS Samples (Without Outliers)

Sample	Peel Force (N)	Adhesion Energy (N/mm)
1	1.277050223	0.050277568
2	2.227272727	0.087687903
3	3.88	0.152755906
4	2.985714286	0.117547807
5	3.124137931	0.087687903
Average Values:	**2.698835033**	**0.099191417**

As mentioned previously, results for the acetic acid etched and silane coupling surface treatments were not obtained due to time constraints. These treatments will instead be implemented in future work.

Chapter 5: Summary, Conclusions, Recommendations, Broader Impacts

5.1 Summary

In a time where polymer-metal composites are gaining popularity in the automotive, aerospace, tooling, medicine, and infrastructure industries due to improved thermal conductivity and radiation shielding properties, they are still limited due to poor adhesion at the interfaces between the metal additive and the polymer matrix. To enhance polymer-metal composite performance, different surface treatments must be assessed to understand how each affects the interfacial adhesion. The first step required before running experiments is to design an experimental apparatus that is capable of measuring interfacial adhesion energy.

After evaluating seven different categories of adhesion measurement methods, the peel test was selected as the basis for the design due to its many advantages. One of these advantages includes the fact that add-on parts could be made to an Instron® 5944, a tabletop column testing system that was already available in the Structures and Material Lab on campus. Thus, this saved both time and money.

A total of five parts were manufactured for the peel test apparatus by using a combination of methods such as CNC, manual milling machining, drill press, grinder, and sand belt. Most parts were made from Aluminum 6061 as it is a very lightweight and soft metal. The sample plates were made from 420-grade SS and follow the guidelines put in place by ASTM® International.

To adhere the ABS to the SS plates, a lot of trial and error was involved before a final working method was selected. Once this method was solidified, a total of eight untreated ABS-SS specimens were prepared and tested with a delamination rate of 20 millimeters per minute. Ignoring the outliers, an average peel force of approximately 2.7 Newtons was determined to pull ABS of SS. Associated with this peel force value and a sample width of one inch, the adhesion energy value was calculated to be 0.01 Newtons per millimeter. Due to a shortage of time in the project, acetic acid etching and silane coupling surface treatments were not applied to the SS plates.

5.2 Conclusions

A testing apparatus was successfully designed and manufactured to measure the interfacial adhesion for polymer metal composites. Initial results were obtained for peel tests of untreated ABS-SS composites for 90-degree peel angles. Through this series of experiments, I gained experience in computer-aided design software (SolidWorks, HSM CAM) and machining (CNC, Manual). Challenges encountered in this research project were primarily in the fabrication of the ABS-SS test specimens. Several iterations of fabricating the samples were necessary before I developed a sustainable methodology.

5.3 Future Work

To continue developing this work, I will be conducting three more terms of directed research the following year as an extension of this project. During my research, I aim to:

1. Apply two surface treatments to the SS-ABS composite. The two different surface treatments that will be applied to the SS plates are (based of MQP team DL1-1901): (1) acetic acid etched (30 vol% solution), and (2) silane coupling. The data collected can then be compared to the results from the other MQP team.
2. Utilize a profilometer to measure the surface roughness of the samples before and after surface treatments. This will provide a better understanding of how the interfaces are being affected.
3. Dive deeper into the data by relating semi-empirical analytical models that quantify adhesion energy. By studying these models, the cohesive law can be generalized for predicting modulus or strength.

5.4 Broader Impacts

Polymer-metal composites are gaining popularity due to their economic benefits and global and societal potential. Compared to carbon-fiber nanotubes, which are also polymers with metal additives, polymer-metal composites are a low-cost alternative because of their simple production through the use of additive manufacturing (AM) technology. Thus, they can be more widely used in all sectors of industry.

Polymer-metal composites also have radiation shielding capabilities which are a big investment in the defense sector. For example, by using polymer-metal composites in tanks, submarines, and aircraft, each can be made undetectable under RADAR. In addition, polymer-metal composites can promote safety. One concept that is currently in development is that of magnetic seals or locks. For instance, if a short-circuit were to occur on an aircraft, departments within the aircraft can utilize magnetic seals to automatically close off and prevent the spread of fire.

Aside from polymer-metal composites, the testing apparatus developed in this project can be used to test other composite systems such as biological systems. For example, the interfacial adhesion can be examined to understand the mechanics of soft cellular materials. Research like this is currently being investigated over cell adhesion [30].

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