

**Multi-Material Additive Manufacturing
Through 3D Printing Plastics on
Laser-machined, Chemically Enhanced Metal**

A Thesis Presented for the
Master of Science
Degree
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ABSTRACT

Materials are classified by their chemistry and associated properties. Metals, ceramics, woods, plastics, and all the unmentioned types and subcategories each come with their own qualities which make them suited for specific tasks. To produce parts to fill these roles, a variety of manufacturing disciplines have been created and iterated on such that the best outcomes can be achieved. A more recent form of manufacturing that has gained significant private and public attention and adoption is Additive Manufacturing (AM), where instead of molding matter through the removal of material through cutting and grinding like classical manufacturing, products are created fully formed through the solidification of feed stock.

Hybrid Manufacturing (HM) seeks to bridge the gap between these processes and materials to increase the suitability of the composite as a whole by bolstering advantages or overcoming shortcomings of its melded constituents. The intent of this Thesis is to blend HM and AM processes to create cohesive parts formed from a conventionally manufactured metal plate and additively deposited thermoplastics that perform better than adhering the two disparate materials by conventional means such as commercial glue or epoxy.

Typically in AM, the part is created on a build plate and then removed to then be used in isolation or as a component in a larger machine. This research is focused on replacing the standard build plate with a metallic part such that, when removed from the build area, the final product is one cohesive part with two regions consisting of the properties of either the metal or the plastic. For the extent of this research, this printable surface is replaced with 6061 Aluminum whose surface has been altered to improve adhesion of the interface with the plastic. During the experiments done on a PRUSA 3D printer Polyethylene terephthalate glycol (PETG) and Polyvinyl butyral (PVB) filaments were tested. Key to the alteration of the aluminum is laser-ablating micro-patterns into its surface to physically change its surface energy and provide channels for chemical-altering substances to reside.

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CHAPTER ONE

INTRODUCTION AND GENERAL INFORMATION

1.1 Inspiration

The University of Tennessee Space Institute (UTSI) has a wide array of research areas with interests across many engineering disciplines. The Computational and Experimental Aerospace Research Lab (CEAR) has a division working on the advancement of hybrid manufacturing processes that may one day lead to supporting their initiative to create propulsion systems for cube satellites [1]. Previous experiments by UTSI's CEAR group involved using lasers to engrave embedded manufacturing marks into aluminum (Al) plates [2] [3]. It was suggested that this strategy can be used for the manufacturing process itself rather than solely for making surface-level designs. CEAR's research in laser-ablated channels' interaction between a material and a cutting-tool surface laid the groundwork to extend efforts to the field of additive manufacturing.

Some of these laser applications in hybrid manufacturing research projects had been undertaken in cooperation with UTSI's parent campus, the University of Tennessee, Knoxville. Together they were funded through proposing a new initiative to the United States Army Research Lab (ARL). ARL would proceed to help coordinate efforts between other institutions as well as provide the capital to move the pace of research forward. The leadership of CEAR had a more direct influence on research directives. As efforts continued and problems arose, it was they and their knowledge on a wide breadth of subjects who were consulted on ways to push forward. ARL entrusted the everyday work and experimentation of fulfilling their vision for laser-assisted hybrid manufacturing to the author of this thesis, who intends to continue this project to its conclusion in a doctoral dissertation.

1.2 Standards for Research and Testing

Initially, three objectives were established in pursuit of achieving a strong final hybrid product and a production methodology to recreate its success. Each was an underlying engineering aspect of the hybrid system. The first goal of this project is to research the science behind the adhesion of two dissimilar materials to facilitate hybridization. Once the mechanics underlying their bonding are understood, the project can move toward the next objective of examining manufacturing additives and other strategies that will promote adhesion. This knowledge will then be applied to experimental iterations to optimize the fabrication process of the desired final hybrid part.

During the experimental processes, great care was taken to flesh out intermediary production steps such as print conditions and consistent fabrication of metals in order to achieve these goals. The printability of a variety of plastic compounds was compared to their chemical properties to find the best match for Al. On the other side of the composite, different surface treatments and coatings were examined. Testing of the materials were done according to the applicable American Society for Testing and Materials (ASTM) standards.

1.3 Scope

Six plastic filaments were initially examined but were pared down to the two which, through experimentation, proved the best suited to the task. This mainly involved a series of test prints performed on the PRUSA 3D printer that would be used for all additive manufacturing during this research. Apart from fitness, plastics with differing functional groups were chosen to increase the odds of varying resultant adhesion levels.

Following this, small Al bars would replace the standard build plate as the recipient of the molten plastic. Among them would be different applied surface finishes, minorly changing the metal's interfacial properties. It was hypothesized that to create a strong bond between these two disparate materials, the surface energy would need to be changed such that wetting between their surfaces increased. Initially, it was unknown how greatly roughness would affect wetting, and by extension, adhesion; thus additional testing was required. This was not all that was done to the surface, though. Patterns would then be etched on each of the samples with a green ultrafast laser. After fabricating and experimenting with a sample containing six different pattern variations, it was clear that different pattern geometries would significantly alter the surface properties and adhesion performance. Of those, two patterns were chosen to be paired with the plastics for final pull testing.

Once the idea that the laser channels could act as reservoirs for coating liquid or as anchors for the filament to seep into, additional measures were examined. Silane coatings, which are used in industry such as for binding together dental implants, were the first option examined. According to the supplier, different silanes bond better to different substances. Although four were acquired, only one was used in testing. This silane was reported to be one of the more generally compatible and less toxic of the ones obtained, but stronger options may have been available for specific plastics. While initial testing with the silanes was undertaken, it was suggested to use pre-dissolved plastic to aid in adhesion; thus a second, plastic-solution coating was added to the list of potential experiments. It must also be noted that coatings needed to be cured and dried prior to printing. This distinguishes the process from applying standard glues or epoxies which combine two distinct parts after they are created rather than compounding them during manufacturing.

CHAPTER TWO

LITERATURE REVIEW

The proposal for this research project is that this Thesis would attempt to create hybrid parts through a combination of laser processing and additive manufacturing. Hybrid manufacturing is a wide umbrella term, so how might this unification be classified? An exploration of the constituent manufacturing practices will add insight into how they might be combined in a hybrid fashion. Furthermore, the materials that can be used are restricted by both the requirements of the project's purpose and the capabilities of manufacturing processes. Limiting what polymers, metals, and alloys are available allows the comparison of material properties that can either benefit a hybridized material or enhance the compound's internal bonding. Due to the nature of the interface created by combining these manufacturing disciplines, adhesion science will also need to be understood and then amplified to achieve a truly hybrid part.

2.1 Hybrid Manufacturing

Hybrid manufacturing (HM) has been defined by Gibson et al. as combining two or more processes, within a single workstation, to obtain desired benefits in the end product, like better quality or lower lead time [4]. Put simply by Kozak and Rajurkar, a hybrid process is the resultant from combined processes that is greater than the sum of individual processes [5]. The research goal of combining laser ablation and additive manufacturing (AM) might therefore qualify as HM, given its combination of processes. However, given the divorcing of the laser treatment and the AM portion discussed later in this Thesis, by some definitions this combination would not qualify as true hybrid manufacturing. However, according to CIRP (the International Institution for Production Engineering Research), this is an assisted HM process where a secondary process (the laser) assists the primary process (the printer). This differs from mixed HM, where the processes occur simultaneously [4]. Furthermore, this Thesis presents mainly a proof of concept, so truly mixing the two processes could be done in future work.

Even if the manufacturing processes could be more strongly hybridized, the final product is no doubt a hybrid material. Much like HM, Gibson et al. defines hybrids and their purposes as a combination of two or more materials which have different physical, chemical, and/or mechanical properties [4]. Hybrid materials produce enhanced functional performance in their applications compared to homogeneous materials. For example, a hard, stable, and conductive metal may serve as the base for a light, easily manipulated insulator. The same authors go further to describe some uses for hybrid materials such as high-speed transition shafts. Contact surfaces should have a higher wear resistance, while other parts of the shaft are made from materials with lower weight and better thermal conductivity, which are properties associated with plastics [4] [6].

There is also significant research in using AM with metal-polymer hybrids to create anti-blast, impact- and piercing-resistant shielding [7] [8]. These are formed from metal lattices where the interstitial voids are filled with polymer, so that impact trauma would

have to break through these various different materials that direct energy away from the impact zone. Although a significantly different geometry and manufacturing process, this example does suggest the possibility of using a lighter, lattice-filled outer interfacial layer, which AM plastic could easily create.

2.2 Additive Manufacturing

“AM has exceptional potential to produce parts with hybrid materials such as composites and gradient materials,” according to the authors of *Additive Manufacturing Technologies* [4]. This textbook goes into great detail about additive manufacturing, its history, uses, and branches. Early on it devotes discussion to differentiate AM from traditional manufacturing, such as Computer Numerical Controlled (CNC) machining. CNC is a subtractive manufacturing process where materials are removed by contact with cutting tools, producing chips and debris. It uses Computer Aided Design (CAD) data in a similar but opposite way than AM does. CNC machining requires a block of raw material at least as big as the final part. Meanwhile, in AM powders, filaments, liquids, or other feedstocks are successively combined to create a part that is larger than the feedstock in one or more dimensions [4].

Despite having its roots in Rapid Prototyping, AM, also known as 3D printing, has developed to a point where it often can produce finished products instead of just trialing new ideas. The entire 3D printing process is divided into eight sections, which will need to be kept in mind as this research moves onward [4].

1. Computer Aided Design (CAD) – The process of creating a digital geometric representation through either hand modeling or scanning. During this research, two different CAD programs were used: Solidworks and Onshape [9] [10]. Solidworks is a more professional, traditional design software that is heavily focused on exactness of its parts, as well as a variety of mechanical simulations. More often though, Onshape was used due to its ability to define distinct parts in relation to each other (such as the two halves of a hybrid material), as well as it being an application hosted online such that files could be accessed and edited from an office desktop Windows machine or remotely at the printer on a MacBook laptop. The University of Tennessee provides licenses to both these packages.
2. Conversion to STL format – This is the file type most commonly read by slicing software (software which divides a 3D CAD object into a stack of 2D “slices”) that defines the exterior walls of the model. The modeling software will most likely export the desired geometry in this way if so chosen.
3. Transfer to AM Machine and STL File Manipulation – This step involves slicing the STL file into layers and translating them into machine paths for the printer to follow. This step is done in a slicer that allows orientation and sizing for the part on the printer. The slicer will create a G-code file (which defines the motions, speeds, and paths) that can be transferred to the printer. The slicer used for this project was Ultimaker’s CURA [11].

4. Machine setup – This is done partially in the slicer and partially on the machine itself. It involves build parameters and material selection, along with a host of other options. Some of these will have to be found experimentally, even with recommendations from suppliers, as every machine and print environment is different
5. Build – The printer reads the G-code file and automatically creates the desired part with little supervision just to ensure no errors occur or to manually alter conditions mid-print, if required.
6. Removal – The part must be removed from the build area once temperatures are cooled and all moving parts have ceased. Often, this involves peeling or breaking the part off the build plate; however, the hybrid nature of this project will circumvent this process. The hybrid part will still need to be removed from the build area, but the two will not be intentionally separated except for testing purposes.
7. Post-Processing – Much of the time, AM parts can be rough or weak and require post-processing to clean the surface or strengthen it. Occasionally, support material will also need to be removed in this step.
8. Application – The part is ready to be applied to its intended use, whether this is as a part in a complex machine or a decorative piece on a shelf.

This may seem like a lot of steps; however, when compared to how traditional manufacturing operates, AM can be a relatively quick process. Complexity is practically unconstrained when it comes to modeling for AM. When developing parts that need to be fabricated through traditional subtractive means, heavy consideration must be allotted to how the part will be constructed. Features need to be created in a certain order. Machines can only cut in certain ways or on parts of specific sizes. Material loss is also less of a concern, as subtractive methods often require removal of large amounts of raw material that end up disposed as waste, while AM methods construct parts in a highly localized fashion and much less raw material is usually wasted. Although some thought needs to be directed at printability during additive manufacturing, it is significantly less important in the modeling step, as the printer can create voids and organic surfaces with ease. Details can also be added as the development process goes along and previous versions have proven the object can be made, and perhaps improved. On average it does take AM significantly longer to create the same volume that a CNC machine could remove more quickly [4]. But the geometry of that volume can be significantly more complex. Furthermore, that time can be significantly shorter if time to create molds or specific tools is factored in, although this benefit is diminished if applied to large-scale orders of one specific part.

2.3 Plastic Material Properties

On the campus of UTSI, there are several additive manufacturing machines. For plastics there are both Fused Deposition Modeling (FDM) (also known as Material Extrusion (MEX) printers), as well as Vat Photopolymerization (VPP) resin printers. The FDM printers funnel a plastic filament through a heated nozzle to melt it, while the resin

printer cures a liquid resin with ultraviolet (UV) light to make smaller, more detailed products. A cross section of an FDM nozzle is presented in Figure 2.1. There are many other forms of 3D printing like powder bed fusion, but these two are the only ones readily available to use at UTSI. Yet, only one of the FDM printers will be utilized, for reasons including the ease of adapting its functions to hybrid processes, widespread use outside of research, and the general safety (non-toxicity) of many common polymer filaments.

MEX-type printers work best with polymers that are amorphous (in contrast to crystalline polymers) in nature, similar to commonly used injection molding material. However, prints may exhibit regions of lower strength because of interfacial regions between the layers [4]. The strength of AM plastic will always be weaker in the z-direction due to the nature of the layers being placed discretely one on top of the other, rather than along the planar directions, in which material is laid in a continuous stream. However, this can be partially circumvented with chemical and/or heat-treatment post-processing, as well as fibrous additives that add anchors to which layers can bind. [12] Post-processing can also be done to smooth the outer layers of the product, as, if left alone, the layer lines are easily seen and felt. It must be noted that post-processing would not aid in the production itself and would not be helpful for altering the surface energy for in-fabrication bonding.

Gibson goes on to list several materials that can be extruded with MEX printers including: acrylonitrile butadiene styrene (ABS), polycarbonate (PC), PC/ABS blend, polylactic acid (PLA), polyetherimide (PEI), polymer bound polyamides, polyetheretherketone (PEEK), thermoplastic polyurethane, stainless steel, and even chocolate [4]. Table 2.1 displays some of the material properties of several polymer filaments initially considered for this Thesis. There are also various composites that contain nano-fiber additives such as carbon, nylon, glass, or Kevlar. Other composites can mimic the look and properties of wood and other organic materials. Although metal is typically used in other forms of additive manufacturing, Al, bronze, and other metal filaments are produced for use in FDM. Generally, the materials used in MEX are able to be softened or melted into a malleable state before being placed in a desired location where it re-hardens and/or cools. The material must not get too soft or too brittle during the heating and cooling processes. Thermosets, for example, would be “set” by the extrusion process, making them unsuitable for standard printers. The same goes for materials that require another chemical to cure, like two-part epoxies.

According to Ebnesajjad, polymers’ surface energy deficit compared to metals causes them to form intrinsically poor bonds without the help of external treatment [13]. The same author suggests maximizing the polar component of the polymer, increasing surface roughness, and removing weak outer material to best improve this adhesion. Many surface treatments of plastics are intended to remove a “weak boundary layer” that is often associated with these types of materials, caused by contamination that is either externally added or even inherent to the plastic itself [13]. It is hoped that printing directly on the bonding interface will circumvent the need to remove much of this interfacial material. Unless the filament feed itself is altered, modification of the polymer side of the bonding

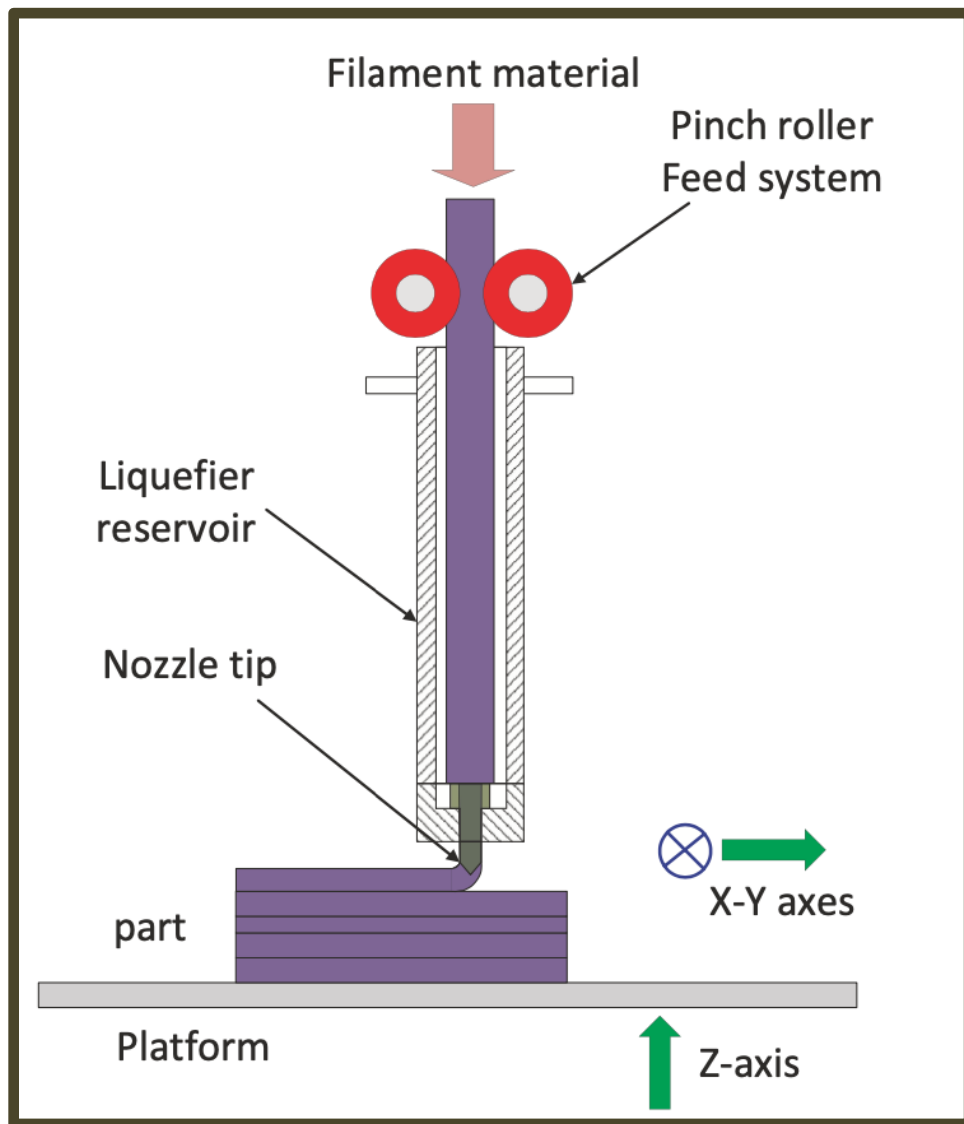


Figure 2.1. Cutaway of an FDM nozzle [4].

Table 2.1. Plastic Material Properties.

	Plastic					
Property	PETG [14]	PVB [15]	PLA [16]	NGEN [17] [18]	CPE [19]	ABS [20]
Typical Melt Mass-Flow Rate [cm ³ /10 min]	N/A	6–7	9–11	N/A	13.2	41
Typical Melt Volume-Flow Rate [cm ³ /10 min]	N/A	5–6	8–10	N/A	N/A	N/A
Density [g/cm ³]	1.27	1.10	1.24	1.20		N/A
Moisture Absorption in 24 hours @ 25 °C and 23% humidity [%]	0.13	0.18	0.13	N/A	N/A	N/A
Moisture Absorption in 7 days	0.19	0.35	0.19	N/A	N/A	N/A
Heat Deflection Temperature (0.45 MPa) [°C]	68.0	63.0	55.0	71.0	70.0	N/A
Heat Deflection Temperature (1.80 MPa) [°C]	74.0	58.0	55.0	63.0	62.0	N/A
Tensile Yield Strength for Filament [MPa]	39.4 ± 0.1	57 ± 1	57 ± 1	50.0	47.0	44.0
Hardness – Shore D (*Rockwell)	79	77	81	105*	72	76
Interlayer Adhesion [MPa]	16.4 ± 1.3	9 ± 1	17 ± 3	N/A	N/A	N/A
Tensile Yield Strength [MPa]	39 ± 2	50 ± 5	51 ± 3	54.0	47.0	41.1
Tensile Modulus [GPa]	1.7 ± 0.1	1.7 ± 0.1	2.3 ± 0.1	1.70	1.54	1.62
Elongation at Yield Point [%]	3.5 ± 0.2	4.6 ± 0.7	2.9 ± 0.3	11.0	N/A	4.70
Flexural Strength [MPa]	60 ± 1	72 ± 1	83 ± 6	67.0	71	79.5
Flexural Modulus [GPa]	1.0 ± 0.1	2.2 ± 0.1	3.1 ± 0.1	1.80	1.86	1.99

Deflection at Flexural Strength [mm]	7.7 ± 0.2	8.4 ± 0.4	7.4 ± 0.2	N/A	N/A	N/A
Impact Strength (Charpy impact test) [kJ/m ²]	23 ± 1	55 ± 7	13 ± 1	3.3	N/A	N/A

interface is impossible. If nothing can be done to the plastic, perhaps something about the underlying metal can be altered such that it will be more accepting of the plastic.

2.4 Aluminum

Of all the various metals used in manufacturing, few are as ubiquitous as Al. Pure Al (Al 99.5) is a material with a relatively low specific weight and other advantages such as corrosion resistance, weldability, and ability to be anodized [21]. Not only is it fairly light and easily manipulated, it reacts with air to naturally create a hard, stable surface layer of aluminum oxide. Pure Al is mainly used in industry in low mechanical stress situations requiring a highly ductile, corrosion-resistant, and good thermal- and electrical-conducting material [21]. One common Al alloy configuration is AL6061-T6, which strengthens the Al with a concoction of other metals and minerals but keeps many of the advantages of its pure counterpart. Al's heavy use in the aerospace industry spurred its use in this research. Low-weight and high-strength materials are in high demand, so creating a hybrid material that can circumvent the need for fasteners would save a few grams of necessary mass. There is significant research in combining Al alloys with titanium alloys in additive manufacturing to achieve topologically optimized, light, and strong airplane parts.

However natural metal oxides are often only weakly bonded to the rest of the material. In fact, of a set of different metals—including Al, stainless steel, cold-rolled steel, copper, and titanium—that were tested with different surface treatments and adhesives, untreated Al had by far the weakest adhesion strength [13]. Therefore, one form of surface treatment of metals includes acid etching to remove the old coating and replace it with a stronger oxide layer. This chemical process isn't the only way to affect the metal's surface energy, though. The easiest and most common way is to use mechanical abrasives on the surface to increase surface roughness. The surface profile of a metal has a lot to do with its intended use. Polishing is often done to smooth out a surface to decrease friction on moving parts or protect the interior metal from contamination. It is also done to increase light reflection, which has applications in thermal control and optics. Buffing and abrasive blasting, meanwhile, are primarily used to remove the outer layer of the material so that other finishes may be applied.

2.5 Laser Manufacturing

There are several branches of additive manufacturing that utilize lasers to cure materials; however, they come into other uses in hybrid AM. Laser have been used to weld layers together or smooth recently deposited material, as seen in Figure 2.2 [4]. However, the use of lasers in this research is different, as the laser machining precedes the material deposition, rather than following it. In this case, the laser will have more much more power over a much shorter time frame. This process will impart enough energy into the sample to remove a miniscule amount of material, altering the metal's surface.

A laser is a coherent stream of high-energy photons that have been directed to primarily flow in one direction [22]. This beam can be steered using mirrors through a microscope's optics such that the beam is focused on a singular point on a surface. For

ultrafast femtosecond laser machining, a material is modified by several picoseconds of energy being applied to the lattice from relaxation of laser-excited electrons [23]. This modification generally happens through nonlinear interactions between the photons and substrate, because focused laser-pulse photons that have wavelengths in the visible or near-infrared spectra often cannot be linearly absorbed if the material's band gap is greater than the photon energy [23]. The band gap is the energy required to excite an electron from the valence band to the conduction band. In some metals and dielectrics, the band gap is often several times larger than the photon energy of visible or infrared wavelengths, and hence, multiple photons must be absorbed simultaneously to excite electrons, which becomes feasible with the extreme irradiances ($>10^{13}$ W/cm²) achieved by focused, ultrafast pulses. [20].

All of this happens nearly instantly (in much less than 1 μ s), leaving a void at the precise location on the surface where the laser was focused. A diagram of this phenomenon for a ns laser pulse is displayed in Figure 2.3 [22]. Note that for shorter fs and ps pulses, heating, melting, and peripheral damage is greatly reduced [20]. The material can then be shifted some distance that would allow another pulse to overlap with the last, over and over again, until a distinct trench is formed. Alternately, the material could be raised or lowered to shift the laser focus relative to the surface, allowing for greater depth control. Depending on the pattern of the laser cut, different outcomes can be reached. According to Philips et al., femtosecond laser-texturing of silicon in SF₆ yields micrometer-sized spikes, which increases the contact angle of a liquid placed on the surface of a material. It was possible for them to control the resulting contact angle and hence the hydrophobic properties of the underlying silicon [24]. Although as a semiconductor silicon is a different material than metals, it could be assumed that applying a pattern across its surface could change the way material from MEX AM would interact with it. A change in overall surface energy and contact area may increase their bonding to one another, even though the size of the plastic emerging from a 3D printing nozzle may be orders of magnitude larger than a laser-created channel.

2.6 Plastic to Metal Linkage

Plastics and metals are two very different materials. Plastics are made up of long, entangled polymer chains, while metals are typically solid blocks made mostly of one element or an alloy. This causes them to have vastly different mechanical and chemical properties, which also dictate that they typically would not like to bond in either of those manners [25]. One would not expect these two inert substances to stick to each other just by touch; therefore, other ways must be examined to bind the two together. Luckily, using MEX AM, the plastic emerges in a molten, semi-solid state. This may hold one of the keys to making this project a success. Related are the very different thermal properties of the two substances. While plastic melts and denatures at printing temperatures, the metal can conduct heat through itself and retain its shape until higher temperatures are reached. This may allow the plastic to melt into the imperfections in a metal's surface. However, increasing temperature has a more prominent effect on a much smaller scale.

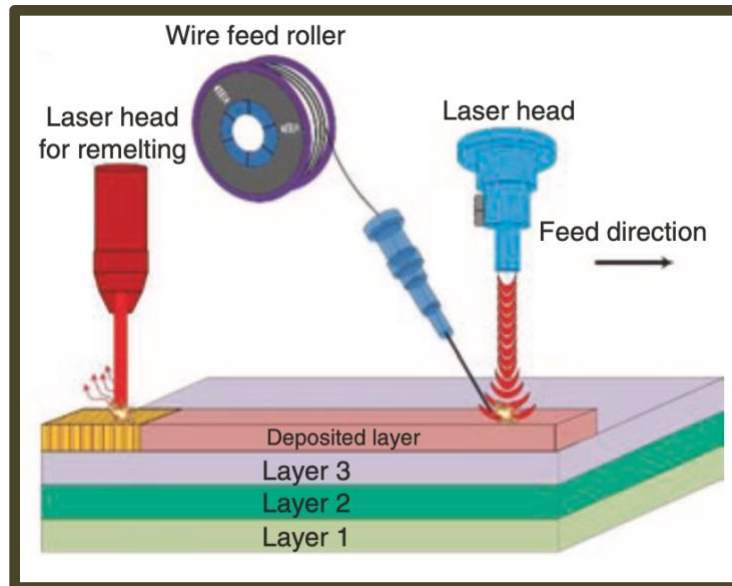


Figure 2.2. Diagram of hybrid laser manufacturing [4].

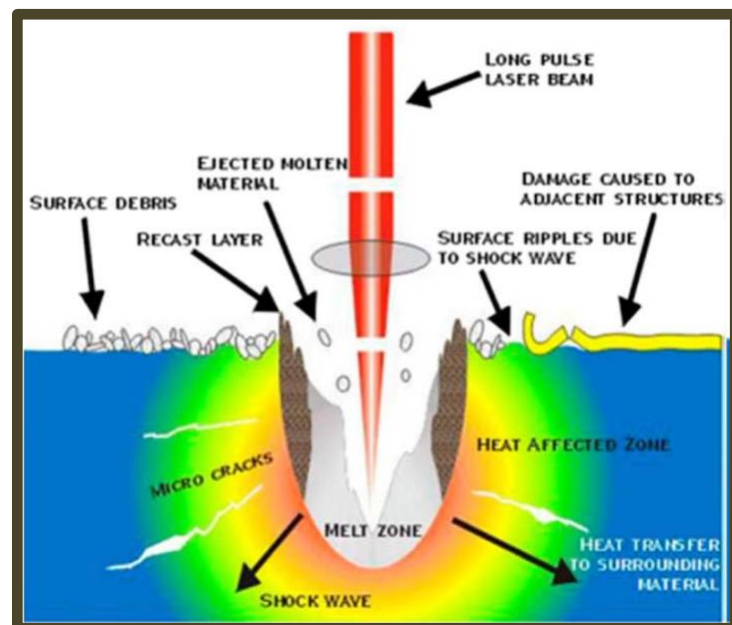


Figure 2.3. Diagram of ns laser ablation [22].

The surface energy of two materials has a significant impact on the ability of two surfaces to stay bound together in an equilibrium state. Often when treating surfaces the morphology and chemical composition are altered such that its energy is elevated sufficiently for adhesion [13]. It can then be assumed that surface energy of a material has significant effect on its ability to adhere to another surface. Adhesion has been defined as the state in which two dissimilar bodies are held together through interfacial contact in a way where mechanical force or work can be transferred across that interface, [13] examples of which arise from van der Waals Forces, chemical bonding, or electrostatic attraction. The mechanical strength of the system is therefore comprised of properties of the two bulk phases, as well as the interfacial zone

Therefore, this project will seek to achieve adhesion through two ways: first by altering the make-up of either side of interface to increase the interfacial forces; second introducing a secondary interface in between the two materials to which they are both more likely to bond. Al is a “high” surface-energy metal with a surface tension of around 200–500 dynes/cm. Polymers, meanwhile, have been classified anywhere from low to high but are significantly lower-energy surfaces than metals [25]. Raising the temperature increases internal energies that can be conducted to a surface, such that the two sides could wet each other more easily. A book on the *Physics of Wetting* by Edward Yu. Bormashenko describes wetting as the ability of a liquid to maintain contact with a solid surface caused by intermolecular interactions [25].

One way to estimate surface energy is by measuring a liquid’s contact angle with the solid surface. The contact angle is a manifestation of that liquid’s surface tension, but also has the correlation to the specific surface Helmholtz free energy [25]. Physically measuring the contact angle between a drop of liquid and a surface does not represent the ideal case, though. Wetting also occurs between two solid surfaces. Unlike liquids, the surface tension of solids is not necessarily equal to the surface free energy. Liquid molecules are highly mobile, able to combine the two phases of an adhesive process in one interaction, breaking up on the surface to immediately rearrange themselves into equilibrium positions. Static molecules of a solid cannot freely enter these equilibrium states [25].

This solid-to-solid wetting is of more interest, since even though the plastic is a molten semi-solid when it is being deposited, it quickly cools and hardens. Yet it is impossible to directly measure a solid’s surface energy in the same way as a liquid [25]. Therefore, this Thesis will be estimating the relative surface energy of solids by observing their interactions with water’s surface tension. By measuring the water’s surface energy, we can ascribe certain amounts of hydrophobicity and hydrophilicity to materials and therefore ascertain an approximant relative surface energy for the material.

CHAPTER THREE TESTING METHODOLOGY

Having explored several types of manufacturing and how they play into making strong, cohesive products, Chapter Three seeks to document the road to creating hybrid parts through additive manufacturing. Yet, establishing a new manufacturing process is not as simple as dictating an experimental procedure. To get to that point many iterations and tests must be undertaken. With knowledge of what particular properties lead to the strongest bonds, Section 3.1 delves into the printable thermoplastics. Keeping their chemical makeup in mind from Section 2.3, this section takes a variety of commercially available plastics and compares their physical properties covering quantifiable qualities like print surface roughness and other aspects like printability.

Section 3.2 examines the options for the pseudo-print bed. It was already decided that a sturdier, metallic material was to be used as the second half of the hybrid material. This section explores what can be done to Al to enhance its adhesion to the plastic that is to be deposited on top of it. The Al's surface was altered in various ways from physically abrading the surface to adding coatings that would bridge the gap between the disparate materials. All the while, an eye was kept on the properties that indicated advantageous wettability. Finally, Section 3.3 culminates in describing the testing of all these combined methods through adhesion-pull experimentation.

3.1 Plastic Testing

Due to time and financial constraints, not every available filament can be tested. From all the possible printable materials, two would be selected that pair well with Al. There are hundreds of commercially available filaments ranging from widely adopted polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) to lesser known NGEN and co-polyester (CPE). Furthermore, all of these have marginally different properties depending on the manufacturer. However, commercial printers are assembled to best process the most common types of thermoplastics with nozzles that cannot process the more exotic filaments.

To align this study with the common commercial equipment and materials, only simple plastics with no additives were used. UTSI is equipped with a PRUSA Mark 2 FDM 3D printer furnished with a 0.4 mm nozzle that is displayed in Figure 3.1 [26]. The PRUSA Research company provides a list of officially compatible filaments. Samples of six of these potential candidates were acquired, three common plastics and three uncommon. Hobbyist will often print in PLA, polyethylene terephthalate glycol (PETG), or ABS while polyvinyl butyral (PVB), CPE, and NGEN are more niche. Spools of all these obtained can be viewed in Figure 3.2.

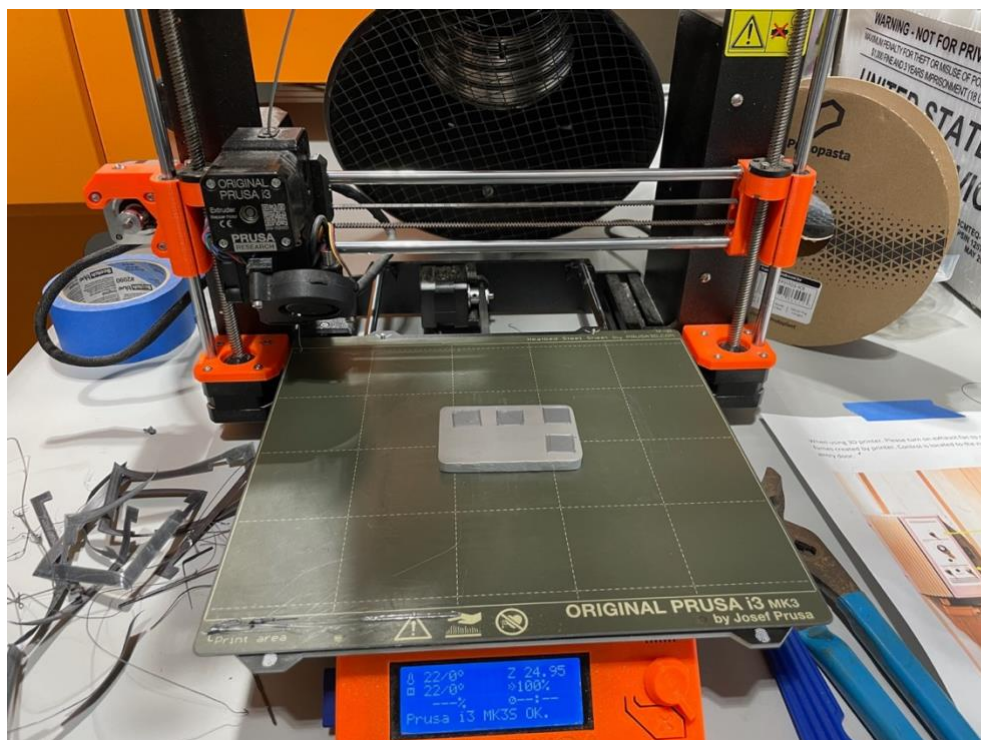


Figure 3.1. PRUSA i3 MK3 3D printer.



Figure 3.2. Filament spools. From left to right: PLA, PETG, PVB, NGEN, ABS, CPE.

Different colors were chosen for each to aid their identification during experimentation. It must be noted that the pigmentation additives do have an appreciable effect on the print quality. According to Valerga et al, both intense coloration and transparency tends to decrease print accuracy when printed with the same settings as a neutral, opaque filament [27]. However, their effects will be minimized by optimizing the print settings for each filament individually. The materials that were considered are the following: clear PLA from Proto-Pasta, gray PETG from Overature, black ABS from 3DxTech, red CPE from Fillamentum, orange PVB from PRUSA, and green NGEN from Matterhackers.

3.1.1 Printing the Plastics

Three sets of experiments were done to pare down the material selection. A substantial amount of time was devoted to firstly dialing in optimal print conditions for each plastic. Each has recommended nozzle and bed temperature ranges provided by its manufacturer. Ideal print conditions still had to be derived through repeated testing in this specific lab space, as the ambient lab conditions may differ from that of the manufacturer's ideal space. Also, to print ABS safely, a vent was placed next to the printer to remove potential toxic fumes. It is common to use test prints when getting accustomed to a new printer or filament so that the operator can gauge how the set-up performs various actions with specific settings. A file that has often used in these sorts of tests designed by Marián Trpkoš was sourced online to be printed in each of the aforementioned filaments [28]. The object would task the printer settings with bridging gaps, encircling vacancies, forging spires, bending overhangs, and other geometries. How accurate the test print is compared to the STL file reveals the advantages or shortcomings of the selected filament. Figure 3.3 compares these prints to each other.

Once the STL was downloaded it was imported into a specialized application which “slices” the 3D object into machining path G-code for the printer to follow. The slicer provides a simple front end for the manipulation of the complex set of commands and values in the background. Although PRUSA has its own licensed slicer, UltiMaker's Cura slicer was used instead due to its more gradual learning curve and generous amount of online support [11]. This first set of tests were done to observe the ease of printing and specific feature qualities for each plastic, as well as using this slicer and printer combination. Given the struggle to get a completed print from some of the filaments, it was clear some tuning still needed to be done. After these initial prints were completed at the recommended temperature, additional test prints were done at varying nozzle temperatures ranging up to ± 20 °C around the recommended value in 5 °C intervals. Bed temperature, meanwhile was kept static at the manufacturer's suggested value. Similar to the first test file, a set of files were acquired on Thingiverse (an online 3D file sharing website) that could be stacked and printed at these increasing temperatures [29]. Ultimaker's online guide to complete these thermal tests was consulted when slicing the file [30].

3.1.2 Hot Press Adhesion Examination

To gauge potential adhesion to Al, small amounts of plastic were sandwiched between

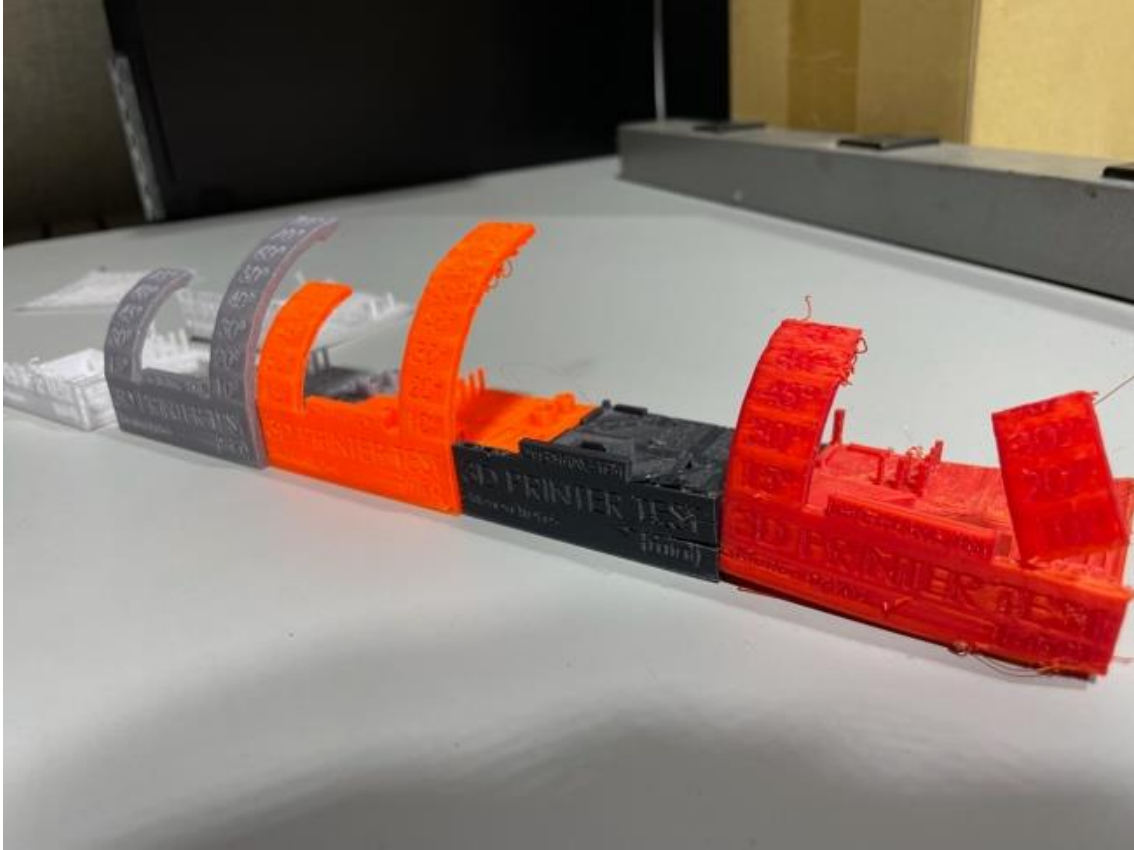


Figure 3.3. Test prints.

pieces of Al foil and put inside of a Simpliment® 1000 automatic mounting press. The hot press consists of a heated chamber that is compressed by a cylindrical piston from below. The combination of heat and pressure should be enough to simulate the properties of the plastic coming out of the printing nozzle. The machine shown in Figure 3.4 was unsealed so that a circular cut of Al foil was gently set into the test chamber. The commercial Al foil was cut via scissors, tracing around a cylindrical blank that was the same diameter as the hot press. Then about 0.2 g of plastic was placed in the center before a second sheet of Al was added. The piston lowered the sample into the chamber before it was sealed. The chamber was heated to 180 °C at 1200 psi for 30 s and then was let cool for 5 minutes. The plastics were measured out in a weigh boat on a digital scale by cutting off a few millimeters of the filament into small pieces. Commercial Al foil tended to have surface roughness and energy values within the ranges of the larger Al blanks that will be used later; therefore, it should represent an analogous amount of adhesion [31].

Once they were all cooled and removed from the machine, the Al foil layers were slowly pulled apart by hand while observations were recorded on their resistance to removal. To guarantee the filament version of the plastics were not dissimilar to more-commonly used configurations, other forms of some plastics that were in the lab space were also used in the hot press experiment. For example, powdered PVB, as well as sheets of ABS and PLA, had been used in other laboratory experiments, and therefore they were easy to use as additional samples. This wasn't done for every plastic, but the results were similar enough in the materials that were tested to dissuade concerns about potential abnormalities.

3.1.3 Printed Plastic Surface Qualities

The final experiments to characterize the aptitude of the thermoplastics were centered on their surface qualities. A small rectangle of each filament was produced on the PRUSA printer. A picture of the set of them can be viewed in Figure 3.5. Each was placed under a Leica DVM6 digital microscope to be analyzed. Stacked-focus images were taken in three random areas on both the build plate and nozzle sides for each type of plastic. The images were imported into Leica MAPS so that a surface roughness measurement could be taken. MAPS takes the data from a stacked image and parses it as a color map where hot (red) areas are the peaks and cool (blue) areas are the valleys. Sections of this data can be selected to be processed through a variety of ways into a roughness value. An example of some of these stacked images can be seen in Figure 3.6.

After the roughness scans, the blocks were moved to a KRUSS EASYDROP Drop Shape Analysis System (2005 version as seen in Figure 3.7) which could be used to measure contact angle. A small droplet of 0.5 ml deionized water was pushed out the tip of a pipet by the machine-operated plunger while the plastic was moved up to collide with the water. Once the droplet contacted the plastic, the stage was retracted slowly so that the water would transfer from the pipet to the block. A picture was taken after the droplet had settled and the contact angle between the drop and the plastic surface was logged. These same

two surface tests were done on the Al samples and will be explored in greater detail in the next section. Because the surface of the plastic parts cannot be altered during the printing process and it is too late to boost adhesion post-print, the surface qualities of the Al are the real independent variable here.

3.2 Metal Testing

The surface conditions of the Al are equally, if not more, important than the make-up of the plastic. No matter the type, the plastic is still coming out of the printing nozzle in a malleable state. Ensuring the print surface is able to retain its new plastic interface through its physical and chemical makeup is necessary to produce a successful part. Although some conditions can be altered during the print process, like the plastic temperature and print speed, the make-up of the filament itself cannot be changed. Therefore, it is more reasonable to alter the surface being printed on than attempting to change the composition of the plastic. This can be done in a multitude of ways such as altering its temperature or surface profile.

During research of the topic outlined in Section 2.6, several methods of enhancing adhesion were discovered. It was the intention of this research to apply these strategies to additive manufacturing while using laser-ablated channels to increase their efficacy. Two avenues for modification were pursued. The first was modifying the surface of the Al through mechanical means. A second, compounding method was adding a coating that would help bridge the gap between the two disparate materials.

Of the additives observed, two showed promises through former research discussed in Section 2.4. Silanes have two functional groups, one that adheres to metallic surfaces and the other that bonds to plastics. For this Thesis 3-glycidoxypentyl trimethoxysilane specifically was chosen, as its epoxy group is likely to help the most across the widest range of materials. This silane will henceforth be referred to by the manufacturer's identification, KMB-403. Another less-complex route can be found by adding a thin layer of dissolved plastic that matches the material that is to be printed. Dichloromethane is able to dissolve all of the thermoplastics listed in Section 3.1. A small amount of solution can be poured onto the Al surface to give the extruded filament a similar compound to adhere to.

3.2.1 Fabrication of Samples

Many steps need to be undertaken before the Al can be prepped for printing. First off, commercial bars of $\frac{1}{4}'' \times 2'' \times 48''$ 6061 Al from McMaster-Carr needed to be cut down to manageable $\frac{1}{4}'' \times 2'' \times 3''$ blanks. For this specific set of experiments two bars of stock were purchased and were cut on a band saw into 30 usable blocks, with the rest of the material as excess or lost in processing. From here they were separated into four batches of seven, leaving aside the other two to keep as control samples. Each batch was then stacked together and brought to a sander to ensure parity between the dimensions for all of the samples in the batch. The edges were also deburred to both protect the handler from



Figure 3.4. Hot press machine.



Figure 3.5. Surface quality samples. From left to right: PLA, PETG, PVB, CPE, NGEN, ABS.

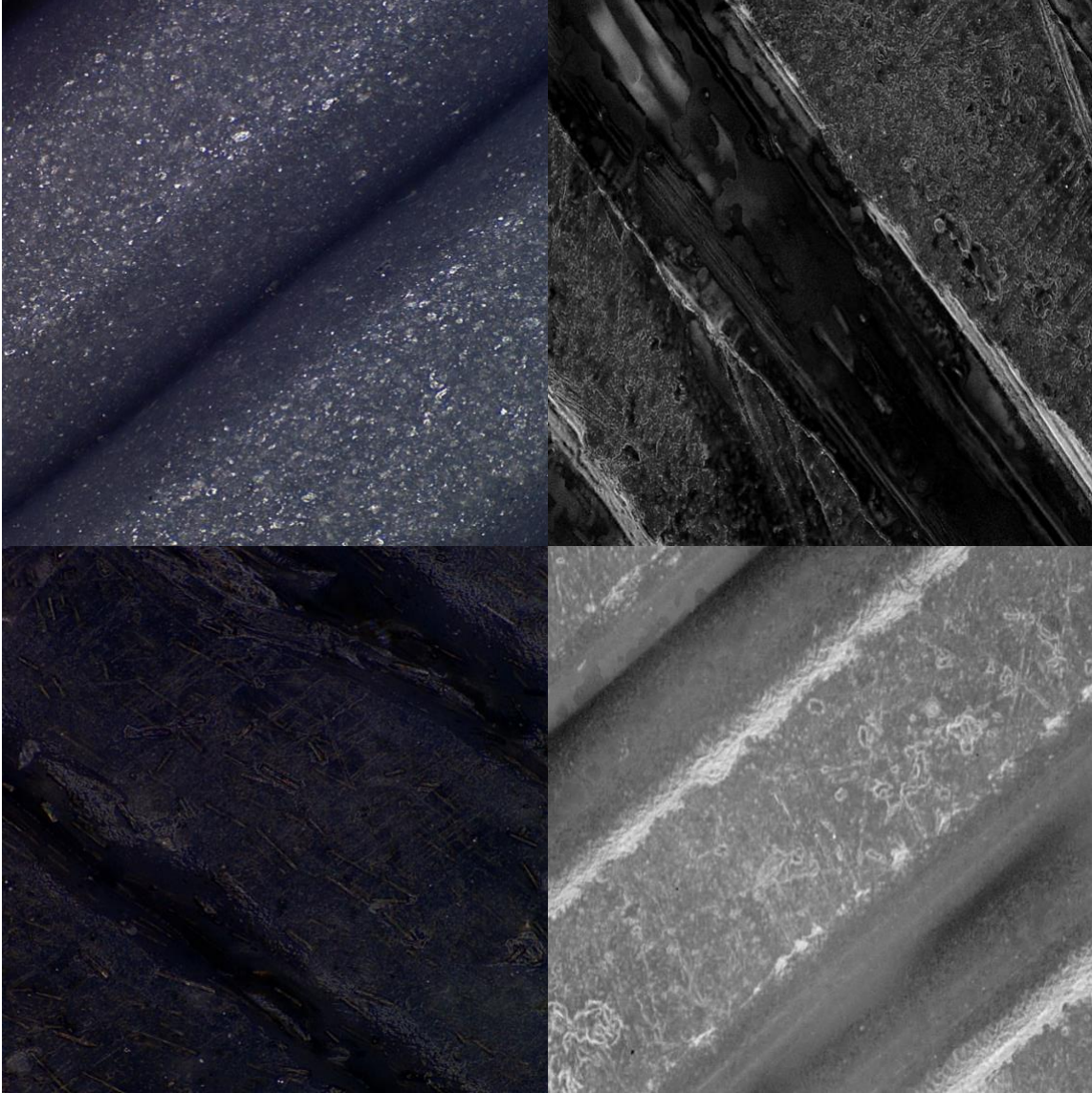


Figure 3.6. Stacked optical micrographs of plastic prints. Top left: PLA with shiny particulates; top right: CPE; bottom left: ABS; bottom right: NGEN.



Figure 3.7. Contact angle machine.

cuts, as well as to maintain completely flat surfaces. They then all had to be degreased by washing with soap and water for several minutes.

One batch was handed off to a machinist to have their face surfaces altered on a buffing wheel. This process left the samples with visible horizontal striations in which material was removed. Another batch was moved to a sand-blasting enclosure. Once the machine was sealed and powered on, sand was mixed into pressurized air and sent out a hose directed toward a sample, which was turned by glove-protected hands until no surface was left unaltered. There was an attempt to maintain uniform sanding by keeping the nozzle at a constant distance while passing it over the sample, never staying in a spot too long. The same was done on each of the seven samples in the batch, while an identical process was done to a separate batch except for the particles that were used. These samples were introduced to a finer silica-glass abrasive, as opposed to the sand-blasted samples. A final batch of samples were brought to a set of polishing wheels to attempt to get the smoothest surfaces of the bunch.

On one wheel the Al bar would be applied to a series of spinning sandpaper disks, while on another it would be finished with suspended alumina mixtures added to a microfiber fabric. Beginning with coarse 160 grit, the disk was locked in place and spun up to 200 rpm with a constant but minimal stream of water added via faucet. A raw blank of Al was held in place on the wheel without touching the edges nor center to attempt to capture a consistent material removal rate across the metal. Light, even pressure downward on the Al was applied by hand, with occasional removal to check progress. The process was continued until the entire worked face exhibited scrape lines in the same direction as the wheel rotation. This was done to ensure the surface was ground past where the previous abrasive treatment had reached, eliminating most places where the surface plunged into unreachable valleys. Occasionally, especially with the higher grit ratings, one piece of sandpaper would not be enough to fully grind down the surface, so it would be replaced before the sanding continued. This process was repeated for sand papers with grits: 240, 320, 400, 600, 1200, and 2400. After the sanding, a second, fabric-covered polishing wheel, also spinning at 200 rpm, would be coated with a 1 μm alumina suspension. Similarly, the sample was held there until the previous grind-lines were removed. This was checked periodically by rinsing the now alumina-coated sample with water before being returned to the wheel. The same process was repeated for 0.3 μm and 0.05 μm suspensions. Ideally this would leave a mirror shine on the samples; however, most of the samples were left with some scratches or a cloudy appearance, likely due to uneven pressure caused by human error in the sanding process, or inadequate polishing time.

3.2.3 Laser Ablation

Some of these samples needed to be taken under the laser to be engraved with patterns for the hot plastic to cover. Before decisions were made about the pattern geometry and embedded on all of the test samples, one polished sample was brought into the clean room that houses the laser. Discussions of options with those who knew the laser well gave an idea what its capabilities were. Some patterns were faster and easier to

machine than others. At this first testing juncture, it wouldn't be worth creating complex patterns, e.g., a honeycomb pattern, so it was decided to investigate basic patterns only involving straight lines and arcs.

The polished sample surface was split into 6 sectors, each to house a different laser-patterned configuration. 3 sectors would use a pulse length of 0.3 ps and the other 3 would use longer pulses at 8 ps. This would give two depth options. The first pattern applied would be a set of horizontal lines that filled a square 10 mm by 10 mm. The second was filled with concentric circles ending at diameter 10 mm. A third option was given with a cross-hatch pattern where a second, vertical set of lines were passed over the top of a copy of the first pattern. As for spacing between successive laser paths within a pattern, it was decided to leave 15 μm . This polished sample was the test case for many early assumptions about the role surface roughness alterations and surface energy would play in this research. It was scanned with the DVM6 just like the plastics before and would later be printed on and observed.

After extensive testing with the original sample had concluded, two additional samples for each surface treatment group were brought into the clean room after fabrication to be ablated with the laser. One would have a 25 mm diameter circle of horizontal lines cut in the center, while the other would have the same area filled with concentric rings. Figure 3.8 displays these samples after they had been through hybrid testing. They both used the same pulse length and pattern distance, so the only contributing factor to printability would be the geometry of the pattern itself (linear or arc). These patterns were also reproduced on each side of the Al plate so that when printing was done later, one side could exclusively hold PETG while the other would accept PVB. This was done so that there would be no cross-contamination of material if the acid cleaning described in the next section failed to completely remove any residual material.

3.2.2 Acid Cleaning

To remove any debris from manufacturing, treatment, and the environment, the sample must be cleaned. The ASTM standards for adhesion testing heavily recommend acid cleaning [32]. Luckily, they also have a standard for the cleaning process for a variety of metals including Al, also used in the dollies for the adhesion tester discussed in Section 3.3 [33]. In accordance with this standard, 300 g (163 ml) of sulfuric acid, 65 g of sodium dichromate and 836 ml of deionized (DI) water were combined to create one liter of ~16% acid solution in a sealable plastic container. This mixture, as well as every experiment done with the acid, was conducted in a fume hood with proper personal protective equipment, primarily gloves to avoid splashes. Before the Al can be placed in the bath, it must be heated to 70 °C on a hot plate. Once the temperature is reached the Al bars can be gently lowered into the bath with as much of its surface area exposed as possible. This process was often done with between 4 and 10 bars at a time. The bars were left to rest in the bath for 15 minutes before being removed. Each would then be rinsed with alternating isopropyl alcohol and DI water baths before being patted dry with Kimtech wipes. The samples must then be used or coated within 72 hours. When not in use the acid bath

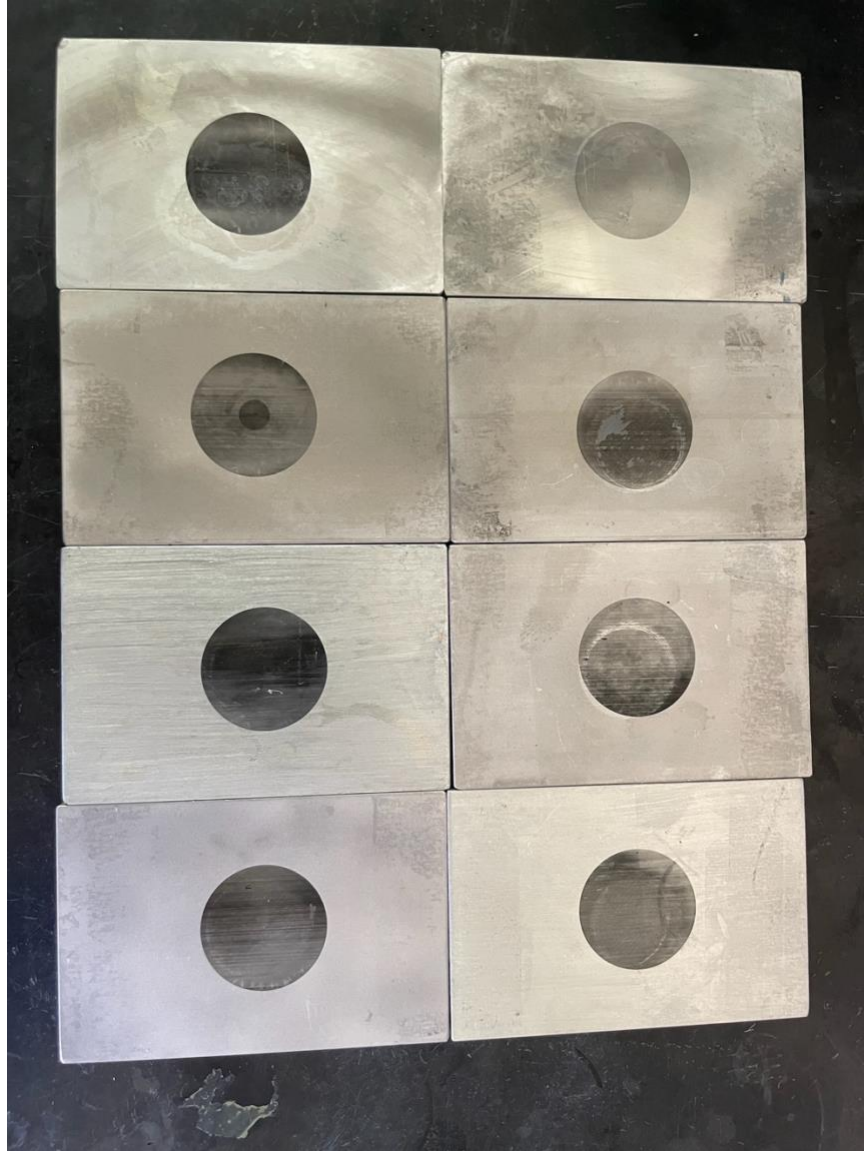


Figure 3.7. Used laser-patterned samples.
Left: concentric circles. Right: lines. Top to bottom: polished, sand-blasted, buffed, glass-blasted.

container is placed inside a bigger secondary plastic container to prevent spills. Samples would be treated in this acid bath directly after fabrication and after use with the adhesion tester so that they would be clean for the next print. In between cleaning and application, the Al would be individually wrapped in Kimtech wipes and enclosed in resealable plastic bags for ease of transport and to reduce excess exposure to atmosphere.

3.2.3 Coating Application

As mentioned previously, there are two coatings that show promise at boosting adhesion: silanes, which are typically used in traditional manufacturing, and plastic welding through dissolved plastic. Having ensured that the samples are clean, coatings can be applied. In preparation for this step, four types of silanes were purchased based on their potential compatibility with the polymers and Al used. Several had specific types of plastic to which their functional groups were more likely to bind. For the purpose of trialing the general usability of silanes, one of the more generally adaptable chemicals was chosen.

2.5 ml of trimethoxy(propyl)silane (KBM-503) was combined with isopropyl alcohol to produce a 5% concentration solution inside a fume hood, as silanes can be very toxic. One Al bar from each batch was also moved to the fume hood and held in a 3D printed rack container with slots for the Al bars to rest in while being treated. Al foil was first placed in its cavities so that silane solution did not leak through the porous plastic. A small amount of silane solution was deposited onto each Al sample with a disposable plastic pipette, such that there was just enough liquid to cover the top surface. The beaker was also covered with Al foil and stored in the fume hood for later use. The samples were then left for the solution to evaporate in the fume hood for several days. Once they had completed drying, they were turned over so that the other side could be coated. An image of the completed, coated samples in their drying rack is present in Figure 3.9. The rest of the silane solution was then disposed of in a marked glass chemical hazard jug to prevent possible incidents.

The same purpose-built container (after be thoroughly cleaned) was also used for the second type of coating applied to a separate set of Al bars. This time, about 0.25 g of plastic filament was added to a vial holding 10 ml of dichloromethane. A cap was placed on the vial, and it was then shaken before resting for a couple hours. In that time, the plastic dissolved into the dichloromethane leaving a 10% plastic solution. Two of these coating vials were made, one utilizing PETG and the other PVB. This was done so that the coating would match the printing filament. Some of this solution was extracted via a plastic disposable dropper and distributed across an entire face of the Al much like the silane treatment. It must be noted that with extended exposure the plastic dropper would also be dissolved by the solution, but given the short time the two were in contact, the effect was considered negligible. It was then let sit overnight in the fume hood for the solution to evaporate, leaving a thin film of plastic coating. The resultant coat for PVB can be found in Figure 3.10. The other side was also coated in the same way before any excess plastic solution was disposed of in a different glass bottle to eliminate possible unforeseen reactions from cross-contamination of the two coatings or other laboratory waste.



Figure 3.8. Dry silane coatings.



Figure 3.9. Dissolved PVB coating.

3.2.4 Surface Qualities

The Al bars were tested both before and after applying the coating to see if the extra layer of chemicals changed the roughness or energy in the active surface. One can make qualitative observations of the surface quality via the use of eyesight and touch, but neither of those methods can quantitatively measure or compare the magnitude of roughness. When the samples were first manufactured, they were taken to an optical microscope just to gauge their appearance optically on a microscopic level. It was important to note early on the different particular aspects of each sample to tell which one was which at a glance when going back through the data; for instance, the parallel ridges of the buffed samples versus the more sporadic scratches on the less-polished samples, or the color differences between the glass- and sand-blasted samples.

Exactly like the prior plastic samples, the next step was done initially on the Leica microscope. Having both sets of surface roughness measurements done on the same machine with identical zoom and optics ensures parity between the sample types. However, unlike the plastic, the Al caused some problems for the DVM6's optical sensor. Many more overall scans needed to be taken to get proper average roughness and the scan settings needed to be slightly altered. The initially polished samples were nearly a mirror surface, so the reflected light of the optical microscope completely overexposed the image. Brightness, exposure, and gamma were altered to give the best odds of acquiring images, but sometimes the image stack would pick up no surface roughness at all. The various pits on the sand and glass blasted samples also caused lighting issues, as it was difficult finding a middle ground between the bright heights and the dark pits. Because the depth of any point on the surface was measured via differences in light intensity, any discrepancy dramatically altered the results.

Although the DVM6 data was kept, when new samples were made, they were scanned using a newly purchased device that would hopefully have fewer issues. A Keyence VK-X 3000 confocal laser profilometer gave better readings for the differences in metal surfaces. While it could acquire optical scans like the DVM6, it could also shine a laser to more accurately gauge depth using similar mechanics [34]. Each Al surface-alteration type was scanned multiple times to achieve an average roughness, in addition to a raw (untouched) blank of the Al and the laser-machined samples. The profilometer would then import its scans into a separate Keyence program that could analyze the scans it took. An example scan for each of the four Al surfaces can be found in Figure 3.11.

In the analysis program the scans could be corrected for levelness and compared. Various forms of roughness could be measured from here. It had several options for both surface roughness and line roughness. There was also an option for the program to identify which roughness measurement would be the most impactful to compare. In the end a couple readings were saved that would give a slightly more nuanced view of how rough a surface was both qualitatively and quantitatively. However, average surface roughness (Sa) was the most often used metric of comparison. In an aside, the profilometer also had to be used for rescans as the DVM6 suffered software and mechanical operational issues.

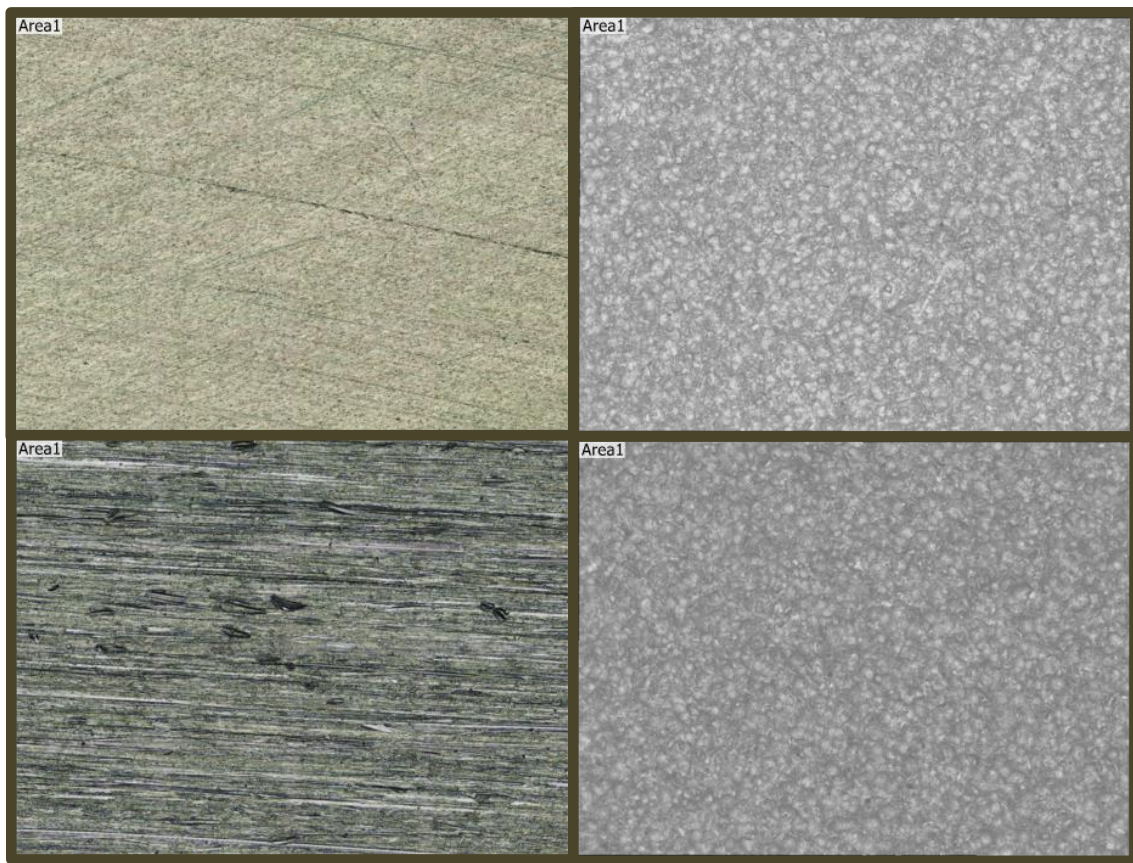


Figure 3.10. Clockwise from upper left: Polished, glass-blasted, sand-blasted, and buffed surfaces, respectively.

3.3 Hybridization

3.3.1 Testing Iteration

It took many iterations to perfect the printing process to create the hybrid materials. The PRUSA, like all commercial 3D printers, was designed to print a removable part on top of the build plate. This test would require circumventing the intended application to add ¼" of extra material (the Al samples) on top of the build plate. This would require physically securing the Al to the build plate so it wouldn't slide around, as the plate and nozzle both move to create the print. The print settings that were so tirelessly investigated earlier now had to be recalibrated. The developed G-code itself also had to be altered so that the nozzle didn't crash into the metal.

Finding a securement method was the first step to pursuing a hybrid system. The first (and coincidentally final) attempt was to use painter's tape to hold the edges of the bar to the plate while also leaving a large bare section in the center to receive the print. This was thought of because not only would the painter's tape stand up well to the heat of the build plate, but it also is occasionally used by hobbyists to increase bed adhesion in the case of consistent print failure. It also came with some downsides, such as the nuisance of having to constantly replace it, and the extreme difficulty in maintaining each bar's position in the dead center of the build plate. Luckily, this became less of an issue when final testing procedures were fleshed out, as they required far less print surface as some other prints.

However, despite the painter's tape method working, a more consistent, robust mounting method was desired. One of 3D printing's other monikers gave a potential solution: rapid prototyping. In the online Computer Aided Design (CAD) application Onshape a bracket was designed that consisted of two arms which would secure a central ring housing the Al to the near and far edges of the build plate. This would eliminate lateral rotation as well as translation, so long as the tolerances were tight enough. Vertical give would be prevented by the nozzle. The initial design was printed in PLA but was then reprinted in PETG once the PLA version became completely unusable due to warping from the required heat of the build plate. The PETG, despite having a better heating tolerance, also warped under the pressure of the bracket and pushed the Al bar into the nozzle, instantly causing failure. The design was slightly altered and handed to a machinist to cut out of Al. This worked far better than the trial plastic version, with some massive caveats that forced an abandonment of the idea. First, the metal bracket was mirrored in error so that one of its arms overlapped with where the nozzle was cleaned before every print, which required special G-code modification. The tolerancing on the arms also wasn't perfect, causing there to be too much give, requiring the use of tape to keep it in place anyway. It also meant that some minor, near invisible variations in the Al bar caused a few of the fresh samples to not fit in the cavity. Instead of spending time and money having the manufacturing error corrected and tolerances tightened for the purposes of researching the feasibility of this method, it was decided to abandon the full metal bracket for expediency.

The Al bars were remeasured with calipers to ensure the surface alterations didn't remove a significant amount of the ¼" (6.35 mm) metal. An extension was added into the slicing software Cura to enable the ability to add an initial vertical offset of the entire print. Adding the 6.35 mm offset to a test print proved that the nozzle was significantly too high to create a successful print. This was a combination of both the unusual closeness to the nozzle these samples required to succeed, and an extra offset the Cura extension added to prevent collisions. At this point extra edits to the G-code were made so that the Al bars could be mounted to the PRUSA. First, a stop command (M0) was added after the auto-leveling program ended but before the nozzle cleaning could be done. During this time the bar would be added. If the bar was added at the start of the file, then the nozzle would have collided with the bar during the auto-level phase and if the pause was added after the cleaning step, the nozzle would leak molten plastic that built up as it cooled. Second, a quick move up 10 mm (G1 Z10) was added after the clean step so that the nozzle would descend diagonally to the center of the surface rather than rise and potentially hit the lip.

Several test prints were done on this surface once files could be sliced. From the get-go, there were discussions of how the tensile testing would be done, so the first test prints were 20 mm wide disks. Noticing how sometimes the circular nature of the print path occasionally gave issues, 5 two-layer thick lines were next printed to observe the nozzle's ability to follow nearly the exact same path forward and back. Then bigger rectangles were printed in attempt to simulate more useful parts. Adding complexity produced two different prints, one that was visually appealing and another which would allow the hand to grip and attempt to pull off a sample. These two prints can be seen in Figures 3.12 and 3.13, respectively. These gave many insights on small changes that needed to be done to the slicing process, which resulted in the final printing parameters.

3.3.2 Pull Testing

Now that the hybrid printing methodology was consistently producing complete samples, the strength of their bonds could be tested. An Elcometer 510 Model S Automatic Adhesion Tester (as seen in Figure 3.14) was acquired to abide by the ASTM pull adhesion test standards. It was briefly considered utilizing a standard tensile tester, which is primarily used to verify the stress and strain properties of dog-bone shaped materials. This idea was ultimately discarded for a host of reasons. Although 3D modeling software is capable of creating almost any size and shape of object, the restrictions of printing on the Al bars produced samples that were not fitting to be placed in the jaws of the tensile machine. There was also no guarantee that the sample would be in the dead center of the Al, meaning there could be unpredicted rotational moments on the part, creating an unwanted bending moment while the tester is pulling. Furthermore, the pull strength of the tensile tester is likely much greater than the strength of the hybrid parts. Assuming that the force provided by the load cell does break the sample in a range readable by the sensors, it is likely to be in a range where noise caused by the moving of the machine would throw off the data.

Standard number D4541-22 was used to guide the experimental procedure of the final batch testing of the hybrid samples on the handheld adhesion tester [32]. The pull



Figure 3.11. Complex hybrid test print.



Figure 3.12. Set of PETG, PVB, and PLA hand-pull tests.



Figure 3.13. Elcometer 510 Model S Automatic Adhesion Tester [35].

tester's hydraulic load cell is attached to an Al 20 mm diameter dolly, which is designed to be bonded to the sample with epoxy. However, due to time constraints and concerns about the speedy reusability of the dollies, the standard practice was circumvented. Instead of printing a small disk to be glued to the Al dolly, a full plastic replica was printed instead. The dolly replacement was modeled in Onshape by using calipers to hand-measure the principal dimensions of the metal version, before being extended by 2 mm to account for the height of the original adhesion disk print. The model of the new dolly can be found in Figure 3.15 [5]. Although this strategy more than triples the print time from the 8–10 min disk to 30 min for the whole dolly (including heating and setup time), it avoids the 24 hr recommended cure time for the epoxy and the limitation of only having 10 standardized metal dollies on hand from the manufacturer.

Once a batch was printed and let cool, the samples could be tested on the 510 Adhesion Tester. The tester would grab the dolly and push off the metal portion of the sample using a skirt that enshrouds the dolly. A cutout of this interaction can be viewed in Figure 3.16. As the dolly is being pulled, the screen of the adhesion tester would show the pressure being applied to the system. It would pull until either the hybrid interface tore or the maximum pull load was reached. After the run was complete, the data for the run would be saved to the tester to later be transferred to a computer for processing and analysis. However, it must be noted that if the minimum verifiable pull load was not met by the sample, the data would not save, as the machine cannot reach an acceptably low margin of error. The adhesion sample would have to withstand about 150 lbs of force (667 N) to be verifiable by the 510 Adhesion Tester [36]. It was decided the maximum strength reported by the machine while it was running would be manually written down by an observer instead of relying on digital data. Because of this reliance on data for which the 510 Adhesion Tester was not calibrated, a series of verification tests were done as well. The Al dollies it shipped with were attached to the Al bars with a variety of common commercial adhesives. This ranged from various tapes, glues, epoxies, and silicone.

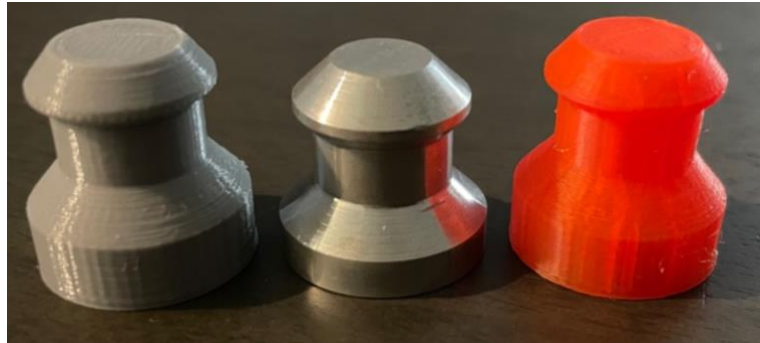


Figure 3.14. Standard metal dolly between a PETG dolly (left) and a PVB dolly (right).

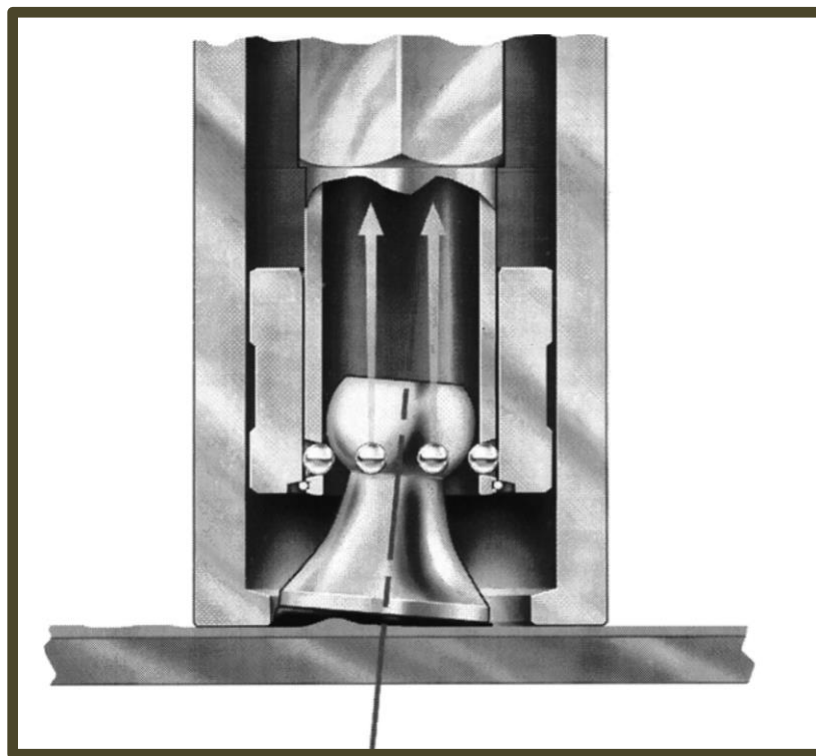


Figure 3.16. Adhesion tester cutout [32].

CHAPTER FOUR

RESULTS

4.1 Preliminary Test Prints and Hot Press

4.1.1 Test Prints

It took many iterative prints both on and off of the Al bar to get every filament's ideal print temperature solidified. PETG and PVB showed the most promise as stable prints with similar print conditions. PLA occasionally had issues, but as a very common filament it was used for the majority of trial prints on the Al. NGEN, despite being a relatively niche plastic, was surprisingly smooth to print. In the overhang test, it proved to hold its shape the best, most likely due to some decreased viscosity of its molten state. As previously seen in Figure 3.3, some materials had a much more difficult time being printed. ABS, even though it is the most commonly used plastic out there, had the hardest time printing. It had adhesion issues with both the Al and the PRUSA build plate. Additionally, after a couple layers of printing, the model would often fail either from a new layer not adhering or a previous layer shifting. However, this may have been the cause of older, improperly stored filament that could have gathered dust and moisture. CPE had similar issues to the ABS but doesn't have the quality excuse, as it was much more carefully stored. All of the final print settings used appear in Table 4.1.

The test prints on the Al with PLA granted many insights into how the adhesion tester dollies would have to be eventually printed. A trio of these test prints that will be discussed can be viewed in Figure 4.1. The initial thin disks exhibited the nozzle struggling to connect to itself as it would graze previous lines as it went around if there was any adhesion issue. This pushed the decision to print much closer to the print bed than usual, causing a decrease in nozzle distance by about 0.150 mm. The straight-line tests reinforced this idea, as well as the need to print the initial layers much slower than typical print speeds. However, this reduced speed did not necessarily extend to the rest of the print. This was tested on some of the taller print samples that could have a variety of geometries without greatly affecting the bottom surface. Yet, one geometric feature did seem to help adhesion.

Tapering the edges of the model such that there would be a gentle lead-up to the desired part shape altered the direction of some forces, causing a stronger adhesion to the surface. Larger samples also suggested understandably that having a substantial interface area leads to stronger bonds, where they usually had to be physically removed rather than falling off on their own, which was sometimes observed with the thinner prints. Yet, larger prints proved difficult in other ways. Having larger initial print layers so close to the surface was more likely to cause clogs in the nozzle. Large samples also emphasized the difficulty of placing the prints in the center of the Al bar. If the nozzle passed over the lip of the Al, it was unlikely that the print would continue successfully.

This host of early adhesion experiments also led to a few qualitative observations that would later need to be corroborated with the adhesion tester. The rougher Al samples

Table 4.1. Print settings and notes.

Filament	Print Temp (°C)	Bed Temp (°C)	Altered Bed Temp (°C)	Bed Adhesion	Other Notes	Universal Print Settings
PLA	208	60	70	Good	Despite being commonly used elsewhere, it struggled with detailing.	Nozzle: 0.4 mm Layer Height: 0.15 mm Infill: 20% Triangle pattern Wall Thickness: 0.8 mm Number of Top/Bottom Layers: 6 Print Speed: 80 mm/s
PETG	238	80	90	Great	Best bed adhesion and model accuracy.	
PVB	215	70	80	Great	Able to complete all tests with some stringing.	
ABS	250	90	90	Bad	Required Ventilation. Often failed after a few layers.	
CPE	235	80	90	Bad	Had significant trouble adhering to the bed.	
NGEN	230	80	90	Good	Felt like a much sturdier print. Little stringing and great overhang.	



Figure 4.1. Test prints on Al.

Top left: thin disk on glass-blasted Al; top right: straight line test with positioning failure; bottom: laser pattern test.

like the sand- and glass-blasted samples were easier to print on, but were more likely to pop off on their own as they cooled. This could be due to the microscopic contracting of the peaks on the surface moving further than the plastic, physically pushing it away. Meanwhile, polished samples cause a lot more problems for initial print adhesion, as the molten plastic would just be dragged along the surface, not finding purchase. If successful, these prints were likely to hold up to prodding; however, it felt more like the ambient air pressure was providing the supporting adhesion rather than a true bond that would maintain against significant force. Test prints on the first set of laser patterns showed a significant preference toward circular and cross-hatch patterns rather than straight lines, but it may not have been specifically because of the laser cuts. The circular patterns had cut off edges compared to the square-cut lines that gave the plastic untouched surfaces to hold on to. Meanwhile the lines were the first patterns to be printed so if there were any initial issues with the print, they would be the first to suffer.

4.1.2 Hot Press

The goal of using the hot press was to simulate the base strength of each of the sample filaments with Al foil as a stand in for the interface between the Al bar and 3D printed plastic. First, it must be noted, any time non-filament-based plastic was used (polypropylene (PP), ABS sheets, PVB powder, and PLA powder) the result had better or worse adhesion than the filaments. However, it was more consistent in its qualities. It was noted that the process of cutting the filament left jagged edges that tended to pierce into the foil, which, while occasionally increasing adhesion would more likely cause the experiment to fail, as plastic would leak out the hole rather than spread across the Al surface.

The adhesion observed at the hot press was generally analogous to that seen on the standard PRUSA PEI bed. PLA showed some adhesion but was generally poor at it. ABS (and PP, although there was no filament version) showed little to no adhesion. The NGEN was good but was more notable because of how little spread there was and how ridged it remained. CPE actually showed better adhesion properties here, but given how much trouble it was to print with, it was not strong enough to stir further pursuit. PVB and PETG continued to shine and adhered the best. This solidified that PETG and PVB would be the final two plastics that would be utilized for further tests. An example of the PETG press sample can be viewed in Figure 4.2.

4.2 Surface Scan and Contact Angle Acquisition

4.2.1 Discussion of measurements

Roughness was measured through both the average height (S_a) of the surface as well as the root mean square height (S_q), also known as the standard deviation. The equation the profilometer and optical microscope used to find S_q is given in Equation 1. This is a slight modification of the S_a found in Equation 2, which weights the maximum

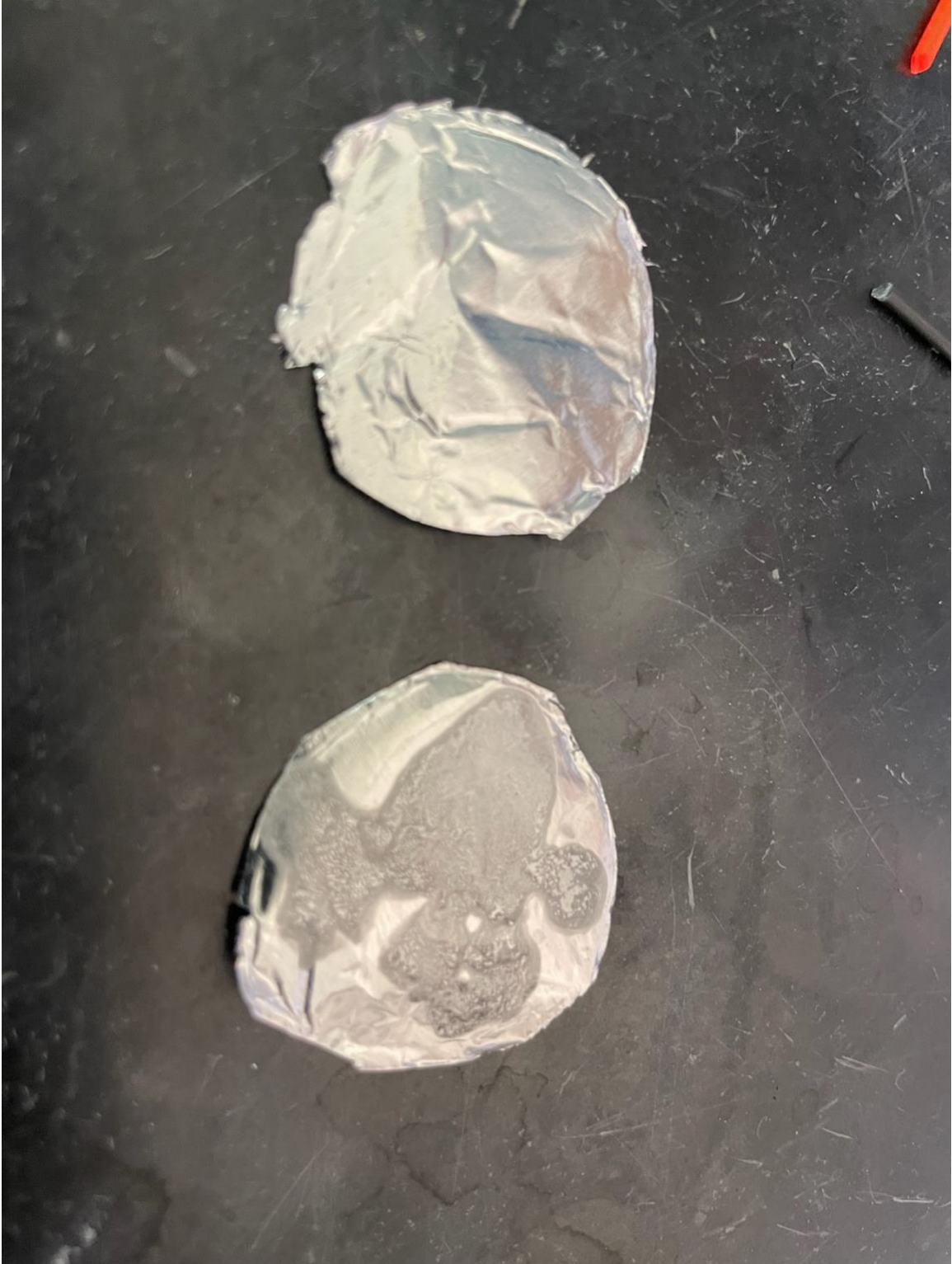


Figure 4.2. Hot pressed PETG.

peaks and valleys more. Both of these surface measurements are better quantifiers of the unevenness of the surface, while other measurements such as the skewness (SSK) or kurtosis (SKU) are more suited to evaluating height distribution.

$$Sq = \sqrt{\frac{1}{A} \iint_A Z^2(x, y) dx dy} \quad (1)$$

$$Sa = \frac{1}{A} \iint_A |Z(x, y)| dx dy \quad (2)$$

A is the total area of the sample and Z is the height of the sample at coordinates (x, y) [34].

The surface roughness measurements are meant to be a representation of the physical attributes of the surface. To attain a general understanding of its impact, surface roughness discussed in this Chapter will henceforth refer to the average roughness Sa , unless otherwise specified. According to the literature rougher surfaces should be better for long term adhesion given that they allow for more surface area, and by extension, surface energy. However, the previous test prints also showed there was some boon for having relatively flat surfaces. There is likely some intermediary roughness that gives the best result.

Adhesion should also be chemically linked to the surface energy. As discussed previously this will be represented by a contact angle measurement. The primary way this is done by measuring the angle between the target surface and the tangents of the round edges of a water droplet before finally averaging the left and right sides. These tests were done in multiple locations across the surface and measured with a variety of other methods to converge upon an average for that material. Even with gaining an average for both surface roughness and contact angle, there was likely a fair amount of error among both methods. For contact angle, the average range of measurements were typically within a 10° range, but it was not unheard of to find a location on the surface that had a major deviation in droplet shape, causing fluctuations in excess of 30° . The roughness for each material showed a similar range of small deviations across its surfaces, but also would occasionally have outliers with upwards of 30% divergence. Averaging out the readings should still give a fairly good estimate, given the number of points scanned.

4.2.2 Plastics

Despite the fact that all the plastic bars scanned followed the same model design, the roughness scans showed that the surfaces were not as equal. Furthermore, there was a large difference between the top of the print surface, which was last to be created, and the bottom, which remained in contact with the heated bed for the entirety of the print. The bottom faces all were contained in the 10 to 100 μm range. ABS and CPE were the smoothest, then moving to equally distributed NGEN, PLA, PVB, and the PETG. The top faces, while still different, had a tighter grouping between average surface roughness values between 10 and 30 μm . The continuous additional heat most likely contributed to the divergence, causing the plastic to spread out slightly onto the bed. When looked at under a microscope, there were wider gaps between the polymer paths on top through

which the layer underneath could be seen. That gap had been melted closed on the bottom cases.

In contrast, the contact angles on the surfaces were consistent for each plastic. The top and bottom surfaces had similar interactions with the water. When plotted against surface roughness, the top sides gathered together on the smooth side of the graph while a near linear relation could be drawn between the bottom samples. This plot can be viewed in Figure 4.3. All polymers showed hydrophilic tendencies, which oddly enough was not expected. As discussed earlier, polymers should have low surface energy and therefore hydrophobic features. It is possible that this is partially due to surface geometry and roughness rather than the plastic itself. The pictures that the contact angles were measured from were taken only seconds after the sessile drop touched the surface. After a very short time, the water diffused into the porous block of plastic. If the contact angle was purely a function of surface energy rather than a combination of factors, it would be expected that the top and bottom faces of the plastic print would be equal. Yet, due to being exposed to the heated bed during the duration of the print, the two surfaces maintain differing structural geometries and therefore incongruous contact angles.

4.2.3 Al

As expected, polishing decreased surface roughness while sand blasting roughened the surface. Glass-blasted surface treatment was closely associated with its sand counterpart, only being slightly smoother, leaving the buffed sample between those and the polished sample. There was a correlation between rougher surface and lower contact angle. This was the relation expected, as described in the literature. Yet there was a deviation when it came to the hydrophobic/philic nature of Al. Given metal's natural "high energy" surface, each sample should have been hydrophilic, except that the polished samples showed a high amount of hydrophobicity, even for the buffed sample. This could be a natural result from the surface alteration process, or it could be an anomaly occurring from letting the samples sit too long between the time they were cleaned and when they were measured. The highly reactive surface may have already gathered dust and oils, which propped up the water droplet.

Compared to the plastics, the Al bars covered a larger relative range, most likely due to the intentionally smoothing and roughing processes. However, it must be noted that the entire range is held within 2 μm , with the polished sample not exceeding 0.1 μm . These values were gathered from the original proof-of-concept Al samples scanned using the DVM6. The graph of their roughness compared to the contact angle can be found in Figure 4.4, including the preliminary laser-ablated polished sample and initial coating trials, which will be discussed in the next Subsection. Once a greater number of Al samples were made, they were rescanned on the profilometer and compiled in Figure 4.5, which compares the two scan values. Despite lacking the laser tracking of the profilometer, the DVM6 scans are close enough to be validated by this new data, which shows the same trends.

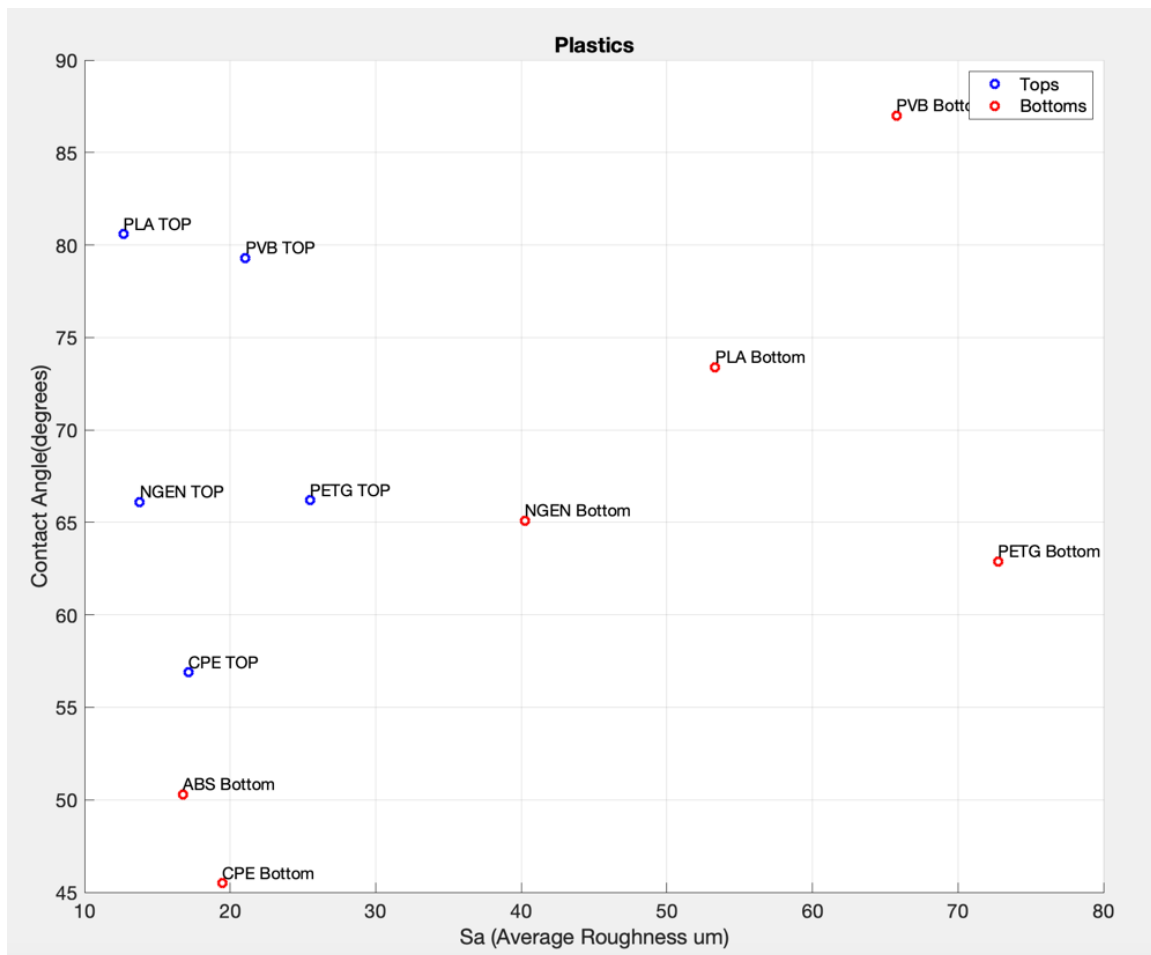


Figure 4.3. Plastic surface roughness versus contact angle.

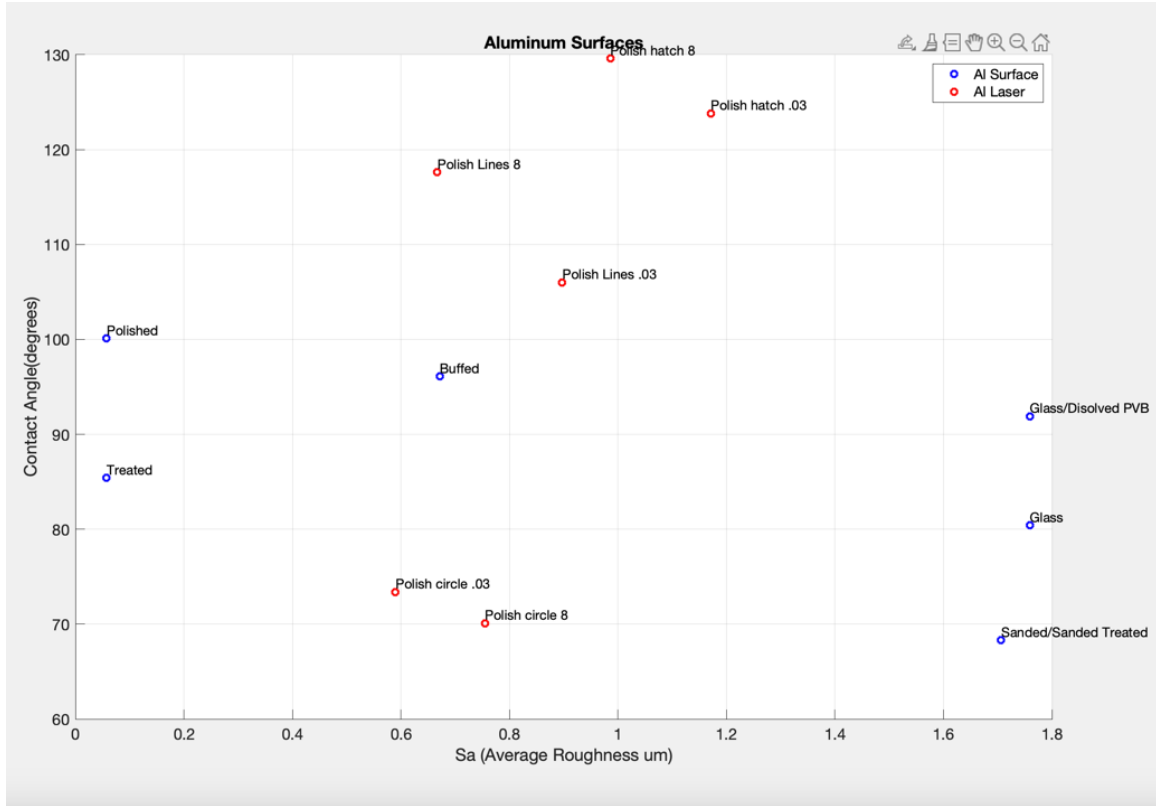


Figure 4.4. Metal surface roughness versus contact angle.

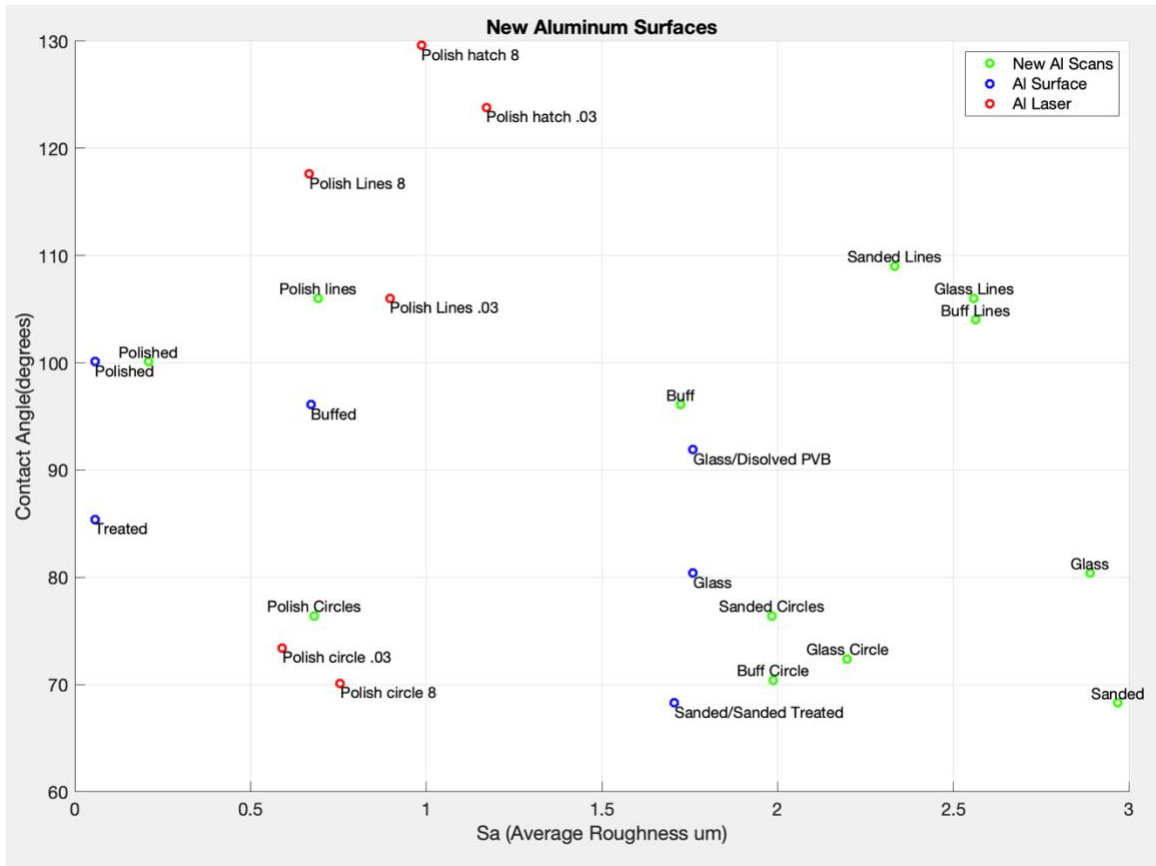


Figure 4.5. Metal surface roughness versus contact angle updated.

4.2.3 Laser and Coating effects

Figure 4.3 provides a significant amount of information regarding the effects of laser machining on both the surface roughness and the contact angle. The most dramatic difference is that the circular pattern significantly decreased the contact angle, while the lines and hatch increased it from the base polished surface. The two overlapping laser channels that created the hatch clearly led to sharp peaks upon which a full drop of water could sit. The two passes also created an increased roughness. This was partially caused by an excess of recast debris left by the ablative process on top of the extra cuts. The other two patterns had similar roughness, since they had much more similar channel densities. It can be inferred that the significant deviation in contact angle would then be caused by the laser pattern itself. Something about the curvature of the circle pattern must have broken the droplet's surface tension and directed the water around its grooves. The pulse length of the laser also had a predictable impact on the contact angle, with longer laser exposure amplifying the pattern's effects.

Figure 4.4 retains the trends seen in 4.3. Although the profilometer did reveal that the samples were rougher than the optical microscope measured, they are still within a range very close to the original readings and are all generally shifted right by a similar amount. Adding laser-engraved lines also increased roughness for the buffed samples but decreased it for the sand- and glass-blasted samples. This enforced the idea that the laser interacted with the surfaces in different ways depending on its composition. The pock-marked blast-abraded samples likely had pits that sunk further beneath the surface than the laser was focused to remove. The high peaks may have also led to places in the path scanned for shorter times than needed to reach the desired depth. The profile of the buffed sample consisted of uniform ridges which still slightly emerged in the laser machining, leading to the best of both worlds where the initial roughness promoted the extra machining. The line and circle patterns continued to have similar effects on the contact angle.

Figure 4.4 also has three marks for the original attempts at applying coatings to Al samples. A polished and a sanded sample were both coated in a very thin layer of silane while a glass-blasted sample had a thin layer of PVB that was dissolved in acetone applied to it. These three coatings were made before either the coating's concentration or their application methods had been clarified. Given how thin these two coatings were, the surface roughness was barely changed; however, their surface energy properties were significantly altered. Both silane samples decreased contact angle, while the dissolved PVB increased it.

However, when it came time to test these on the printer, other changes were noted. It was initially unclear if the silane samples did much at first, given that these prints were done before adhesion testing was fully underway. Yet, once the samples were physically separated from their treated Al base plates, the bottom layer of plastic felt completely different. It was smoother to the touch. Repeat experiments on the same piece of Al demonstrated that this wasn't the coating being peeled away either, as subsequent plastic

would still have this altered face. Meanwhile, printing PVB on the PVB coating led to the strongest bond experienced so far, as it wasn't able to be removed by hand. This led to a brief tangent experimenting with applying different concentrations of dissolved plastics with alternate solvents at different moments in the process. For instance, similar adhesion properties could be achieved by placing a pre-printed part on the Al bar with the plastic coating while it was still drying. The fact that a dry coat being printed was able to mimic the properties of a drying wet adhesive gave credence to this coating as well. The parts in question can be seen in Figure 4.6.

Figure 4.7 includes a more comprehensive graph of the final silane and plastic coatings utilized for the adhesion pull testing. These coatings were significantly thicker. Given the thicknesses of the coatings, the surface roughness more drastically changed, increasing Sa by an order of magnitude. The silane concentration was decreased but it was poured over the top of the Al and let completely evaporate rather than with the initial sample, which was dunked in silane before drying. The plastic coatings were done in dichloromethane rather than acetone, which more completely dissolves the plastics other than PVB. Interestingly, these changes inverted how the contact angle was affected. This time, the silanes nearly made each sample hydrophobic. Although this may be in disagreement with the initial silane treatment, it is more in line with what the literature asserts a silane coating would do. Despite making the sample more hydrophobic, preliminary prints showed promising amounts of adhesion. The same goes for both the PVB coating and the new PETG coating. These didn't decrease contact angle to the extent of the full plastic blocks, but they did maintain hydrophilic properties. There was a caveat, though. The thicker coating may have stuck very well to the plastic prints on top of them, but failure of the part usually meant the entire plastic coating would peel off with it. It was able to spread out the force of a pull but was unable to hold as well as the thin coat did. A full graph of all of the samples surface roughness and contact angle can be found in Figure 4.8.

4.3 Adhesion Dolly Pull Tests

A trial run was done in which an uncoated, sanded sample was able to withstand about 0.43 MPa of pressure before breaking. Over a 20 mm radius circle that equates to 135 N or 30.3 lbs of force. This may be fairly substantial for a 20 mm diameter disk, but it was far below the minimum strength of 2 MPa (628 N or 141 lbs over the interface) the adhesion tester required to be able to validate the data. It was also much weaker than the epoxy that held the disk to the dolly. Before more adhesion data can be reported the failure rate of these tests must be discussed. Of all the samples printed only about 50% of them were able to be read by the adhesion tester. These failures come in many varieties. Some failed during the printing process, mostly due to user error. Many simply slid off the Al in the short transport from the printer to where the adhesion tester was stored, as all adhesion was lost after cooling had completed. There were others which retained marginal adhesion up until it was time for the dolly to be attached to the tester, during which the interface broke apart. These errors were more likely to occur with PETG; however, this was more

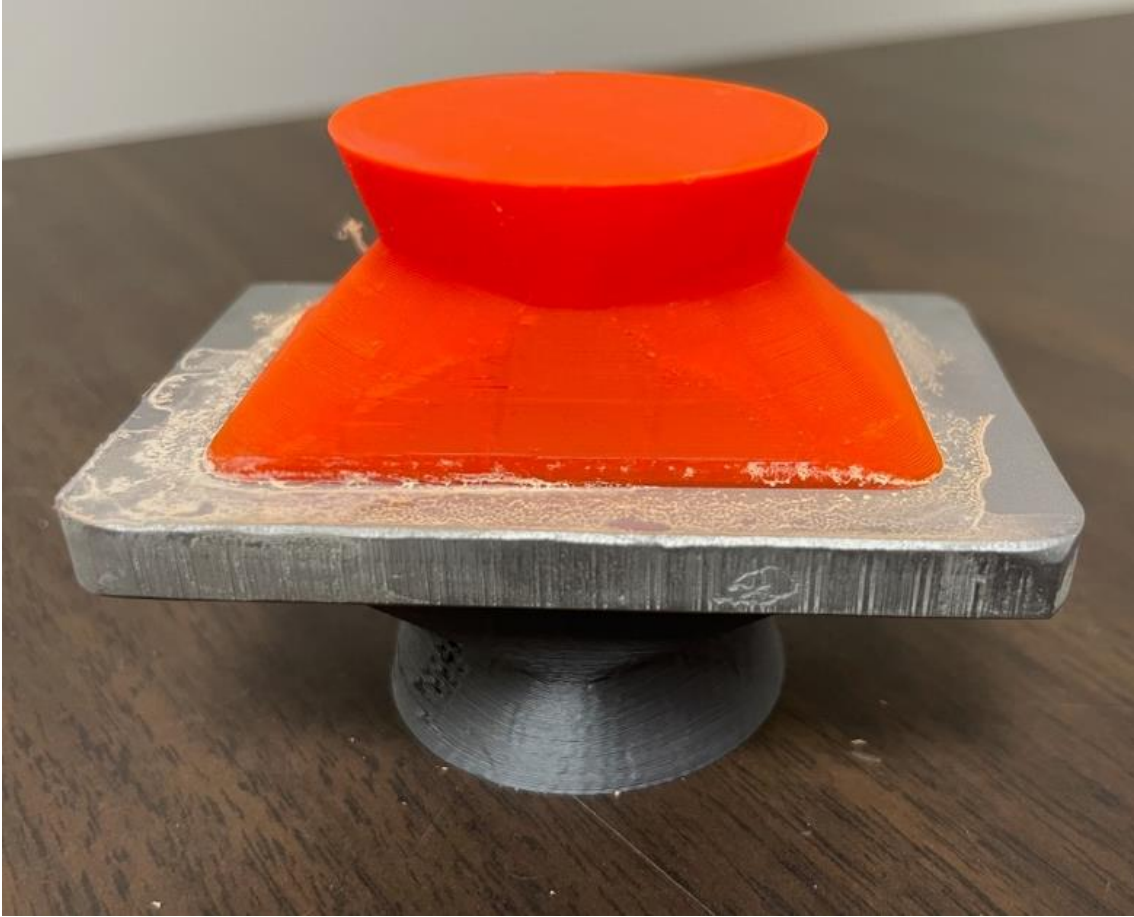


Figure 4.6. Thin PVB coating with test print.

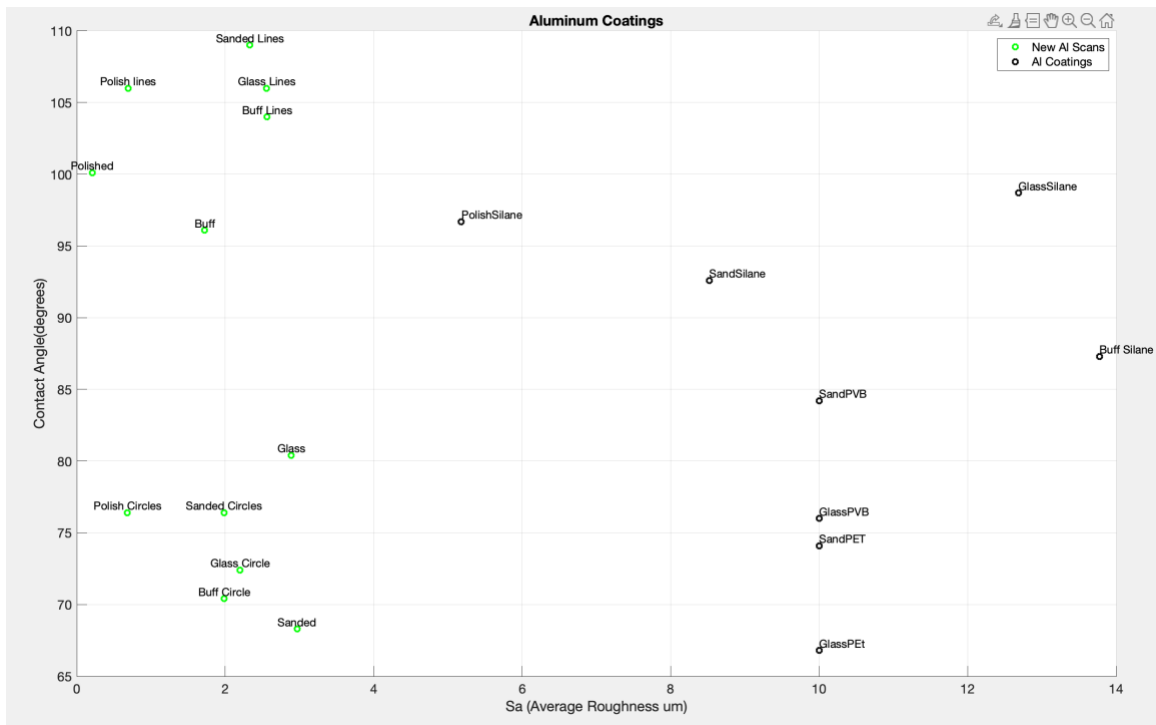


Figure 4.7. Al surfaces vs. different coatings.

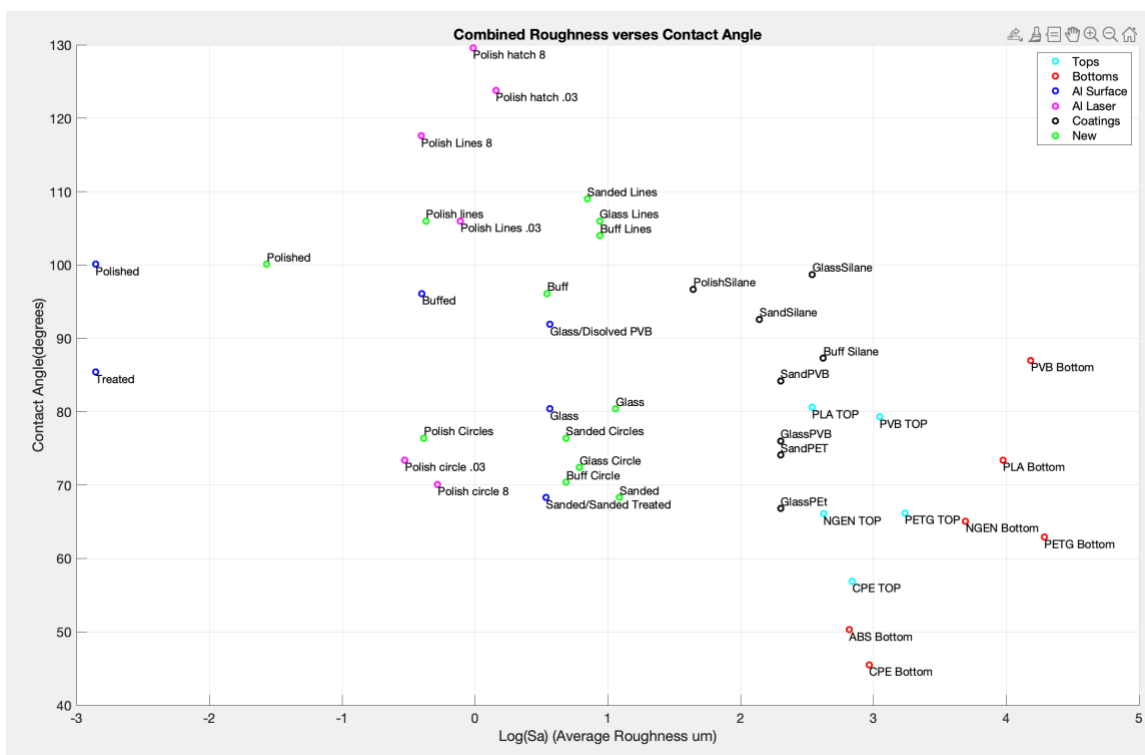


Figure 4.8. Roughness vs. contact angle for all samples.

likely due to a larger sampling size and being the first material to be tested while the processes were still new.

21 of a total 43 printed PETG dollies have a recorded pull strength. These 21 values are spread out over the various combinations of Al surface finish, laser pattern, and coatings. There were 20 permutations, so naturally several had no values attributed whatsoever. However, the lack of data for these points also gives insight into which combinations were typically the worst. For instance, the PETG plastic coating, despite having a promising roughness and contact angle, would either show very weak adhesion averaging around 0.44 MPa, or would have the entire center of the coating peel off, leaving only the edges. The coating therefore successfully bound to the print but not the Al. The completely untouched samples had a consistent chance to pop off before pulling could begin, like was observed in early testing. Successful pulls only averaged about 0.39 MPa across all bare surface varieties. Silanes by far did the best, consistently averaging around 0.60 MPa. The laser-ablated samples had the most variety to them. Circles typically had better adhesion than the lines, which had a high chance for failure. However, the line pattern currently holds the record for strongest combination without an assisting coating on the sanded sample. Furthermore, despite circles consistently reaching 0.60 MPa, those only represented about half of their sampling set with the other half rarely surpassing 0.40 MPa, with no indication why.

PVB dolly samples show a much better failure rate, having 22 successes over 29 runs. However, this higher success rate is mostly due to the majority of prints undertaken with PVB were focused on confirming the strength of the plastic coatings. There were a few dolly prints that succeeded but had their pull data erased before it could be noted down. The silanes were among that group. Silanes retained strong bonds, but they still did not exceed PETG. The PVB coating met expectations set by the test prints. Although some coating samples barely cracked 0.30 MPa, this seemed to be for the same reason they failed with PETG. The coating was applied too thick and therefore could not provide a strong link between the Al and plastic. A coated, sanded sample posted 0.91 MPa which was the highest seen yet and sparked retests of the PVB coatings. The coated polished, buffed, glassed, and sanded samples averaged 0.62, 0.98, 0.82, and 0.94 MPa, respectively with the maximum strength recorded for a polished sample that hit 1.24 MPa. The line laser pattern did oddly better overall than the circles for PVB, mainly sticking to the 0.50–0.60 MPa range, while the circles mostly failed before making it very far beyond the minimum 0.30 MPa line. Attempting to print directly onto Al generally failed without producing significant data. It must be reiterated that these are very small sample sizes and any trends identified will need further testing.

After having tested all the dollies, the adhesion tester needed to be evaluated to see if it was accurate for strengths less than its intended calibration. For this, an adhesive with a known strength between 0.75 and 1.75 MPa was needed. Different commercial glues were either too weak (craft glues) or too strong (super glues). Epoxies also fell above this range. Although lower than the desired range, double-sided Intertape paper tape advertised

as having 0.02 MPa of adhesion on stainless steel was tested [37]. Worryingly, the adhesion tester reported an average pull strength of 0.47 MPa. It is possible the tape is much stronger than advertised, but what is more likely is that pressures far below the tester's minimum calibration level are highly inaccurate. However, RDI (Red Devil Industrial) RTV (Room-Temperature Vulcanizing) silicone sealant that was rated at 1.50 MPa was also tested [38]. This time, the tester read a more reasonable 1.04 MPa, averaged over four samples. This lends credence to the data accuracy getting more accurate as the intend range is approached.

CHAPTER FIVE

CONCLUSIONS AND DISCUSSION

Over the course of this Thesis, there was a goal to fabricate a composite, hybrid material by combining laser and additive manufacturing. To do so, the forces that contribute to the binding of two materials together had to be understood. The primary driver of adhesion, surface energy, can be affected by altering the surface's physical profile or its chemical makeup by use of coatings. Because the materials being combined (Al and a plastic) have such disparate properties, surface alteration is required. The effects that different modifications such as laser machining and post-production finishes had on the surface energy of the Al were investigated. A 3D printer was used to assemble a dolly that could be pulled by an adhesion tester to gauge the strength of each permutation. Coatings shined at increasing the adhesion between Al and plastic, with the most successful being those made of the same plastic itself. Although the laser machining did seem to increase adhesion, it will likely be more useful for creating reservoirs for retaining coatings.

5.1 Surface Conditions

There was a correlation observed between roughness and contact angle. For the Al surface finishes tested, the contact angle generally decreased with increased roughness. It could be assumed that the rougher the surface was, the more hydrophilic it was, and therefore it had greater surface energy. However, the opposite was true with the plastics. This aspect was more likely because of the geometry of the 3D printed blocks than because of the mechanical properties of the plastic. These trends can be circumvented in myriad ways. Altering the Al's surface with a laser slightly increased the roughness, unless the surface was already significantly roughened, while heavily altering the contact angle. Linear patterns served to increase the contact angle, as the water droplet floated on the peaks between the laser cuts, while circular patterns decreased the contact angle through guiding the similarly round drop through its channels. The coatings also change the contact angle, as the new material intercepted the droplet before it could spread on the Al surface.

5.2 Pull Test Successes and Failures

Although many of the tests did fail, the strategies to increase adhesion did in fact work. A definitive set of approaches came out on top, yet there are still benefits to the other combinations. Coatings were by far the best way to improve the adhesion over the untouched samples. Silanes did fare well, but dissolved plastic coatings were the strongest contender, so long as they were thin enough to not peel off. Silanes had a much better ability to be used again for testing purposes when compared to the plastic coats, which would often need to be stripped and reapplied. Although the laser patterns only had middling success, their potential in relation to increasing the reliability of the coatings maintains interest in their future use. Many of the failures were tied to combinations that did not have significant surface energy for adhesion in the first place. More still occurred before pulling even began, where numerical data could still have been salvaged. Given there are some prints completed in preliminary testing that could not be easily removed

gives credence to the idea that there could still be strong bonds to be found here with more testing.

Any additional coating needs to be thick enough to make a new layer in which it takes up most of the interface but not so thick that the print does not interact with the Al at all. The decisive contact angle differences guided an inference that the difference between the two would be much more dramatic. It was likely that the channels were just way too small for the printer to deposit into them. They would likely work better at containing anchorages for the coating that could then better grip the polymers.

5.3 Final Thoughts

Through all the research and experimentation, it would have been great to have a final product. It must be said it is unclear if this is the best solution to creating hybrid materials through additive manufacturing. After all, using commercial adhesives to bind the two materials may create a much stronger bond. This would circumvent the point of creating the product in a hybrid manner in the first place but may still benefit from the various manufacturing strategies. A few preliminary tests were done soon after acquiring the portable adhesion tester but before adapting the dolly setup to be fully printable. The epoxy holding the print to the tester was stronger than the bond to any of the Al samples, regardless of laser pattern or coating. Although this was done before the capabilities of the adhesion tester were fully grasped, it did in fact illustrate that conventional adhesive would likely be far stronger than those bonds forged in these experiments.

The epoxy shipped with the adhesion tester and dollies was Araldite standard two-part epoxy. This and similar epoxies were reported to have strengths (~30 MPa) two orders of magnitude greater than those measured between the plastic and the metal [39] [40] [41]. These were mostly found via lap shear tensile tests which would produce slightly different forces than the pull tests done for this Thesis, yet the difference in strengths could not be ignored. However, all is not lost. Of the epoxy datasheets retrieved, one also showed a massive discrepancy between its effectiveness on metals and plastics, with various plastics hovering around 5 MPa [41]. If the goal was to find a niche where this style of manufacturing would be advantageous, this may be the benchmark to clear but would require a further examination of different epoxies and adhesives on various surfaces. It is also worth noting that using adhesives between the parts still requires there to be two distinct parts in the first place, removing the benefits from manufacturing them together. Either way, further testing is required.

5.4 Application and Future Work

As this is a novel manufacturing process, it is unclear exactly which direction this work will go. That is why a significant portion of the future work in this field will be putting it to good use. There is promise in making hybrid armors that have a strong metal base with a light, threaded layered on top. It could also work well in space applications, guarding vessels from radiation without the added weight of mechanical fasteners. Many more coatings, laser patterns, and plastics must be tested to get the full scope of this

process. Perhaps different metal and plastic combinations would produce hybrids that would have substantially different properties and therefore be more suitable for other, unforeseen fields. The plastic-metal hybrid may even be a good substitute for other current hybrid systems that need a lighter or more flexible portion that a plastic can provide. Observing other industries will be the primary jump-off point for this section of research.

Even with the most hopeful outlooks for the future, there is still an enormous amount of work to be done further verifying the work done in this Thesis. Many issues arose along the way which may have skewed datasets. The manufacturing process for the Al was done by hand which, while done carefully, lead to uneven surfaces. Although this bias was accounted for with a leveling feature in the surface roughness measurement program, it may cause aberrations in the other printing processes. For instance, the change in surface depth, even as miniscule as it was, may cause the laser ablation focus to be slightly off where it needed to be. These initial shifts also were expanded in the polished samples, as grinding too much off one area left dips that later, finer grits did not reach. Unevenness was also occasionally introduced in the coatings if they were applied too thickly, causing the nozzle of the PRUSA to bump and shift in the initial layers of printing.

Furthermore, although many adhesion tests were done with each sample combination, many had to be thrown out due to either print errors or invalid output data from the adhesion tester. Many more experimental runs should be done to highlight trends that come from each combination. Although a work-around for the adhesion tester was devised, the results were still out of the device's approved range. To properly validate the data received, it is planned that an analog scale can be adapted to pull modified dollies with specific interchangeable weights. It would, of course, be better if samples with adhesion that could withstand the minimum 150 lbs could be more consistently created. Until then, other adhesion testing methods may be applied.

All of the validation also hardly scratches the surface of the other combinations that can be tried. As stated previously, out of the six polymers sourced for this experiment, only two were tested to completion, leaving CPE, ABS, PLA, and NGEN to sit in storage with largely unknown adhesion properties. The time in between prints also likely allowed moisture from the environment to be absorbed into filaments before printing, altering the properties and printability of the plastics. Water in the filament will boil, causing nonuniformity in the feed, while its presence in the final product decreases strength [42]. There are also a whole host of other commercial plastics that could be acquired and tested. The 6061 Aluminum could also be replaced with other types of Al or other metals all together. In the end, only two basic laser patterns were tested, leaving gaps in both pattern shape and ablation channel dimensions. Although it was initially intended, there is likely promise in combining the coatings and the laser patterns with the cuts acting as reservoirs for the coatings to anchor the plastic. If future work is retained to the six plastics, five Al surfaces (buffed, sand-blasted, glass-blasted, polished, and untreated), three laser patterns, two laser depths, four silanes, and another plastic coating on top, that leaves 1440 individual combinations to be tested, all of which would need to be pull-tested several

times over to validate their readings. All of this is to say that there is a lot of potential for iteration on this work that could be done. Although, even with more time to dedicate to this project for UTSI and ARL, many unpromising combinations may be avoided using the knowledge assembled in this Thesis, as well as having specific applications in mind.

LIST OF REFERENCES

- [1] A. Terekhov, B. Canfield, J. Jones, T. Moeller and L. Costa, "Ultrafast Laser Fabrication of Capillary Electrospray Emitter Arrays," *Lasers in Eng.*, Vol. 0, pp. 1–7, vol. 0, pp. 1-7, 2020.
- [2] T. Schmitz, L. Costa, B. Canfield, J. Kincaid, R. Zameroski, R. Garcia, C. Frederick, A. Rossy and T. Moeller, "Embedded QR code for part authentication in additive friction stir deposition," *Manufacturing letters*, vol. 35, no. 1, pp. 16-19, 2023.
- [3] L. Costa, K. Lansford, D. Rajput and H. W., "Unique corrosion and wear resistant identification tags via LISITM laser marking," *Surface & Coatings Technology*, vol. 203, no. 14, pp. 1984-1990, 2023.
- [4] I. Gibson, D. Rosen, B. Stucker and M. Khorasani, *Additive Manufacturing Technologies*, 3rd Edition ed., Cham: Springer, 2021.
- [5] J. Kozak and K. P. Rajurkar, "Hybrid machining process evaluation and development," in *2nd international conference on machining and measurements of sculptured surfaces*, Krakow, 2000.
- [6] Team Xometry, "Plastic: Definition, Types, Properties, Applications, Advantages, and Disadvantages," Xometry, 21 April 2023. [Online]. Available: <https://www.xometry.com/resources/materials/what-is-plastic/>. [Accessed 20 April 2024].
- [7] R. P. Bohara, S. Linforth, T. Nguyen, A. Ghazlan and T. Ngo, "Anti-blast and -impact performances of auxetic structures: A review of structures, materials, methods, and fabrications," *Engineering Structures*, vol. 276, p. 115377, 2023.
- [8] R. Rahmani, M. Antonov and M. Brojan, "Lightweight 3D printed Ti6Al4V-AlSi10Mg hybrid composite for impact resistance and armor piercing shielding," *Journal of Materials Research and Technology*, vol. 9, no. 6, p. 13842–13854, 2020.
- [9] Solidworks Corporation, "Solidworks 3D CAD," Dassault Systèmes, [Online]. Available: <https://www.solidworks.com/product/solidworks-3d-cad>. [Accessed 6 September 2022].
- [10] Onshape, "Onshape CAD," Onshape, [Online]. Available: <https://www.onshape.com/en/>. [Accessed 14 November 2022].
- [11] Ultimaker, "UltiMaker Cura," Ultimaker, [Online]. Available: <https://ultimaker.com/software/ultimaker-cura/>. [Accessed 16 September 2022].
- [12] I. Daniel and O. Ishai, *Engineering Mechanics of Composite Materials*, 2nd Edition ed., Oxford, New York: Oxford University Press, Inc., 2006.
- [13] S. Ebnesajjad, *Surface Treatment of Materials for Adhesive Bonding*, Waltham: Elsevier Inc., 2014.
- [14] Prusa Polymers, *Prusament PETG Technical datasheet*, 2023.

- [15] Prusa Polymers, *Prusament PVB Technical datasheet*, 2022.
- [16] Prusa Polymers, *Prusament PLATechnical datasheet*, 2022.
- [17] colorFabb, *colorFabb_nGen Technical datasheet*, 2023.
- [18] Eastman, *Eastman Amphora™ AM3300 3D Polymer*, 2015.
- [19] Ultimaker, *CPE Technical datas sheet*, 2018.
- [20] Ultimaker, *ABS Technical datas sheet*, 2018.
- [21] K. Muralova, J. Kovar, L. Klakurkova, J. Bednar, L. Benes and R. Zahradnicek, "Analysis of surface morphology and topography of pure aluminium machined using WEDM," *Measurement*, vol. 114, pp. 169-176, 2018.
- [22] K. PHILLIPS, H. GANDHI, E. MAZUR and S. SUNDARAM, "Ultrafast laser processing of materials: a review," *Advances in Optics and Photonics*, vol. 7, no. 4, pp. 684-705, 2015.
- [23] R. Osellame, G. Cerullo and R. Ramponi, *Femtosecond Laser Micromachining: Photonic and Microfluidic Devices in Transparent Materials*, Berlin: Springer, 2012.
- [24] B. K. Nayak and M. C. Gupta, "Self-organized micro/nano structures in metal surfaces by ultrafast laser irradiation," *Optics and Lasers in Engineering*, vol. 48, pp. 940-949, 2010.
- [25] E. Bormashenko, *Physics of Wetting: Phenomena and Applications of Fluids on Surfaces*, Boston: Dr Gruyter, 2010.
- [26] Prusa, "Original Prusa i3 MK3S+ 3D printe," Prusa Research a.s., [Online]. Available: <https://www.prusa3d.com/product/original-prusa-i3-mk3s-3d-printer-3/>. [Accessed November 2022].
- [27] R. Hernandez, D. Slaughter, D. Whaley, J. Tate and B. Asiabanpour, "ANALYZING THE TENSILE, COMPRESSIVE, AND FLEXURAL PROPERTIES OF 3D PRINTED ABS P430 PLASTIC BASED ON PRINTING ORIENTATION USING FUSED DEPOSITION MODELING," in *Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference*, Austin, 2016.
- [28] M. Trpkoš, "All In One 3D Printer test," Thingiverse, 19 November 2017. [Online]. Available: <https://www.thingiverse.com/thing:2656594>. [Accessed 26 June 2023].
- [29] Z. Gaa, "Smart compact temperature calibration tower," UntiMaker Thingiverse, 24 December 2017. [Online]. Available: <https://www.thingiverse.com/thing:2729076>. [Accessed 6 July 2023].
- [30] All3dP, "How to Use a Temp Tower in Cure - Simply Explained," All3dP, 25 June 2023. [Online]. Available: <https://all3dp.com/2/temp-tower-cura-tutorial/>. [Accessed 6 July 2023].
- [31] B. Zhang, H. Yang, H. Liu, J. Hao and X. Liu, "Crystallographic features and microstructure evolution of sandwich warm laser polishing: The case of aluminum foil," *Applied Surface Science*, vol. 573, no. 1, p. 151557, 2022.

- [32] ASTM International, "D4541-22 Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers," ASTM International, West Conshohocken, 2022.
- [33] ASTM International, "D2651-01 Standard Guide for Preparation of Metal Surfaces for Adhesive Bonding," ASTM International, West Conshohocken, 2016.
- [34] Keyence, "3D Surface Profiler VK-X3000 Series," Keyence, 2024. [Online]. Available: <https://www.keyence.com/ss/products/microscope/vk-x3000/>. [Accessed 29 February 2024].
- [35] Elcometer, "Automatic Pull-Off Adhesion Tester," Elcometerusa, 2015. [Online]. Available: <https://www.elcometerusa.com/Elcometer-510-Model-S-Automatic-Adhesion-Gauge-20mm-Kit.html>. [Accessed 11 November 2022].
- [36] Elcometer, "User Guide: Elcometer 510 S Adhesion Tester," Elcometer, 2019.
- [37] Tapemonster, "Intertape - Double Sided Paper Tape," Intertape Polymer Group, [Online]. Available: <https://www.tapemonster.com/products/double-sided-masking-tape?variant=9046543171620>. [Accessed 14 July 2024].
- [38] Permatex, *Permatex Clear RTV Silicone Adhesive Sealant Technical Data Sheet*, Solon, 2019.
- [39] Huntsman, *ARALDITE® 2015-1*, The Woodlands: Huntsman Advanced Materials, 2021.
- [40] Huntsman, *ARALDITE® 2035 A/B High Temperature Adhesive*, The Woodlands: Huntsman Corporation, 2023.
- [41] Huntsman, *Araldite Rapid two component fast cure epoxy adhesive*, Basel, Switzerland: Huntsman Advanced Materials, 2011.
- [42] P. Kakanuru and K. Pochiraju, "Moisture Ingress and Degradation of Additively Manufactured PLA, ABS and PLA/SiC Composite Parts," *Additive Manufacturing*, vol. 36, p. 101529, 2020.

VITA

Christian Sharpe was born and raised in Williamsburg, Kentucky, as the first child to Michael and Regina Sharpe, who supported him every step of the way. After graduating by taking every advanced course he could at Whitley County High School and some dual-credit courses at the University of the Cumberland, a desire to learn more pushed him to higher education. The search for a strong engineering school ended at the Tickle College of Engineering at the University of Tennessee Knoxville. There he made plenty of friends that would culminate in being paired with his current advisor Dr. Moeller during senior design. That chance encounter led to pursuing a Master's Degree at the University of Tennessee Space Institute. He could not pass up the chance to continue his studies at a good school with a good advisor, so in graduating with his Master's he went on to retain his research towards a doctoral degree. He could have only done it with the enormous help of his family and friends, whom without he would have never made it out of the foothills of Kentucky to see the rest of the world.