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Optimizing Aluminum Bonding: Exploring Surface Roughness and Contact Angle Effects through Plasma and Acid Etching Contrasts

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ABSTRACT: The use of adhesives to replace traditional techniques like welding and riveting has been on the rise in various industries as increasingly complex geometries and situations for bonding is required. It's well known in the scientific community that an adhesive bond is only as efficient as the surface preparation used beforehand. Plasma treatments have been shown to gently clean the surface by only removing the top-most layer from the adherend and "charging" the surface instead of berating it. Whereas chemical treatments "etch" the surface in hopes of increasing surface area by increasing surface roughness. This method can be difficult to control quantitatively and can generate waste leading to serious environmental concerns. This study aims to address the encountered differences between plasma treatments and acid etching on aluminum substrates for adhesive bonding. Treating the surface of adherends plays a crucial role in promoting a good bond between adhesive and adherend. In this study, the effects of plasma and acid treatments are categorized using surface roughness measurements as well as contact angle which have been shown to correlate to mechanical strength. When evaluating different surface treatments, it is notable to mention that not only surface roughness and contact angle play a role in determining which method is most effective but also the consequences of the treatment itself. It was found that although chemical etching was the most effective in increasing roughness and decreasing contact angle, it generates a large amount of waste and is not sustainable compared to plasma work which uses a renewable process. The results from this work provide a deeper understanding of the relationship between surface treatments and surface roughness/contact angle and how this relates to a stronger adhesive bond.

INTRODUCTION AND BACKGROUND:

The development and formulation of polymer adhesives have been a major topic of interest for materials and polymer science. This boom in interest regarding polymer adhesive science has motivated the formulation of adhesives tailored for unique purposes. Properties like adhesion strength, elasticity, chemical resistance, sustainability, and thermal capabilities can all be manipulated to fit a manufacturer's specific needs. Over the last few decades, adhesives have made their way into many prominent fields of industry and have proven their usefulness in construction, aerospace, automotives, microelectronics, and medicine [1]. In addition to being able to manipulate their properties as a material, adhesives also have the ability to substitute traditional bonding procedures like riveting, welding, soldering, and nailing [1]. The preference of adhesive bonding over traditional methods is supported by substantial research that demonstrates the advantages of adhesively bonded joints. In contrast to the high thermal bonding procedures mentioned, like welding and soldering, bonding via adhesives can be done in cold environments making it much more cost effective, less dangerous, and mitigating risks to damaging the structure of the material you are trying to bond. This is very important in industries that involve very sensitive materials like weapons design or microelectronics. Additionally, some adhesively bonded joints can be bonded using specific chemical or mechanical procedures. This can offer a myriad of advantages as other traditional bonding techniques permanently bond the materials in place. Furthermore, skills required to perform bonding such as welding, are also becoming a rare commodity because it takes a very specific skillset to do effectively. The use of adhesives eliminates this skill gap and reduces the workforce needed to achieve generally the same outcome. In addition to the skill set required for methods like welding, specialized equipment is also needed as well as substantial amounts of time which for obvious reasons can present its own unique challenges. Lastly, the flexibility and versatility of polymer adhesives can contribute to many complex geometries of bonding that just wouldn't be possible using traditional means. Traditionally, physical methods have been used to treat surfaces such as abrading, or chemical etching. As industries continue to overcome environmental concerns, it becomes increasingly more important to investigate alternatives to traditionally harmful methods like chemical etchings. Plasma cleaning provides a great alternative due to its relatively low cost, fast treatment, and minimization of harmful solvent waste. However, many industries are unwilling to change, as chemical etchings have historically produced better results in increasing mechanical strength [4]. Bonding surfaces can only be done once with a certain material to obtain quality data, which makes it both wasteful and time consuming. It's hypothesized in the scientific community that categorizing how good a surface is for bonding can be determined by the surface's contact angle and or surface roughness (Ra) value [4]. When the surface roughness of a sample increases, the effective surface area for bonding on that samples surface increases, meaning more adhesive can coat the surface. It's also thought that increasing the roughness of the surface could promote mechanical interlocking of each side of the adherend [12], the validity of saying that by increasing the surface roughness it will directly correlate to increasing mechanical strength of the bond is highly debated in the scientific community [12-13]. Surface roughness is calculated in terms of Ra (average roughness) or Sa (arithmetical mean height). Typically, researchers categorize surface roughness by Ra [12-13], but in this work, surface roughness is categorized by Sa. The difference between these two values is that in Ra measurements a stylist type instrument is dragged across the surface whereas in Sa measurements, a microscope is used to draw a mean plane on the surface and measure the arithmetical mean of the pits and valleys that are present on the surface. Sa values have been found to show much higher surface roughness values when compared to Ra values and therefore caution should be used when comparing the two [10]. For the purpose of this study, only Sa will be referenced when on the basis of surface roughness. With plasma treatments, a point of interest is that these techniques don't change the surface morphology, making them reusable, very controllable, and much faster. Rather than abrade or degrade the surface to create microstructures like in chemical etching does, it charges the surface which impacts wettability but has minimal impact on surface roughness. Plasma can be tuned to etch as well. An exact equation correlating surface energy and contact angle cannot be measured without the use of advanced anti-gravity equipment; however, it is well known that by decreasing the contact angle we can see a correlation to an increase of surface energy [7]. As according to Young's equation [9].

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta Y$$

Figure 1: Youngs equation [9]

Where γ_{SL} refers to solid–liquid interfacial tension, which refers to the tension that is formed between the liquid and adherend surface. γ_S is solid–vapor surface tension, which refers specially to the tension between the adherend surface and the gas or vapor that encompass it. γ_L is the liquid-vapor tension, which refers to the tension between the liquid and surrounding gas or vapor. Within this equation, the terms γ_S and cos θY are simple to measure. However, the resulting terms are very complex and require a great deal of specialized instruments to measure [7]. However, we can qualitatively see that the closer θ gets to 0 the higher the surface energy is going to be and vice versa. Based on this assumption, we will accept the notion that they are correlated without explicitly needing to solve the equation, which fits the purposes of this study.

A common bonding substrate surface preparation technique is etching and or surface modification. Surface etching is a process that involves modification of a surface to promote adhesion strength and can be done in multiple ways including chemical cleaning, plasma cleaning (dry cleaning), and abrasion methods. The idea behind surface cleaning or "etching" is to increase the surface energy of the substrate and increase wetting of the adhesive by re-moving chemical and physical contaminants from the surface or changing the morphology of the surface [15]. Chemical etching is a process that is used mainly on metals to remove material from the substrate using strong chemical solutions, otherwise known as "etchants". This process has a long history dating back to 2500 BC where it was used in the processing of copper jewelry and ornaments by citric acid [16]. Currently, chemical etching is used in a variety of industries, such as aerospace and defense, to produce complex and highly accurate components from almost any metal. New techniques for cleaning surfaces such as chamber plasma etching, and the plasma pen or jet have also been developed. Since its inception nearly 50 years ago, plasmas have been used to etch very minute and complex details in silicon chip technology circuits [16]. The fact that a smart phone can fit in your pocket instead of needing to cart it around on wheels is thanks to plasma etching. Plasma cleaning works by taking various gases (typically oxygen, nitrogen, or air) and subjecting them to ionization via radiofrequency or microwaves. The resulting plasma is very reactive and is allowed to react with the surface to be cleaned. The plasma is great at oxidizing or reducing the surface which allows for removal of organic matter from the surface [17]. Typically, plasma treatment offers good selectivity without damaging the surface that is being cleaned, making it a powerful tool.

Plasma etching of bonding substrates has been shown to greatly improve the adhesion layer between metals by properly removing containments and charging the surface that aim to promote better adhesion through better surface bonding [13]. Plasma treatments can also be tailored by using different instruments. Plasma chambers generally include placing the sample in a sealed chamber that is then introduced to various gases.

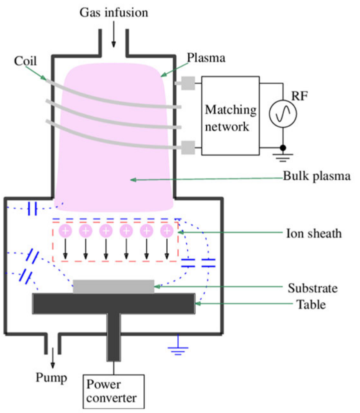

Figure 2: Diagram of a plasma chamber layout [18].

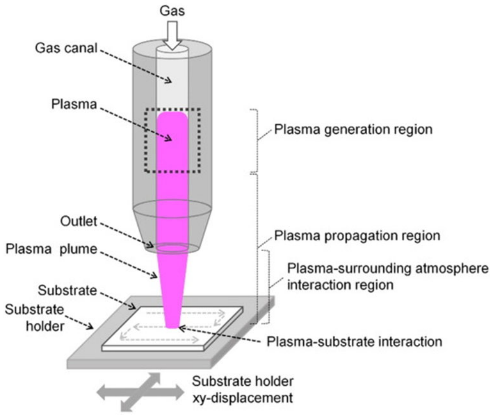

Figure 3: Diagram of a plasma pen layout [19].

Contrary to traditional plasma treatments involving a chamber, the plasma pen is a versatile instrument in that it can be used in open atmosphere and can treat smaller areas of the substrate, unlike the chamber where you subject the entire material to treatment. This could potentially save time and parts of the material because treatment on the whole substrate could potentially damage crucial elements. A plasma pen offers a plethora of advantages such as lower cost, smaller treatment areas, and shorter treatment time. The pen can be a viable option for industries who don't need ultra-strength bonding, as well as small sampling sizes, and quick treatment as to ensure good wettability for quick turnarounds needed to sustain a clean surface for bonding. Contrary to the idea that the plasma chamber is aiming to charge the surface of the subtract and increase wetting that way, acid etching aims to physically degrade the surface in a way that creates various microstructures that increase wetting through physical means such as pitting. It's a valuable technique that helps enhance adhesion between adhesives to metals through chemical corrosion [13]. The process itself utilizes the application of an acidic solution to the surface of the adherend. This in-turn removes a thin layer of material from the surface of the adherend which contains organic impurities [13]. The removal of this thin layer can also be engineered in a way as to create textured or a micro-roughened surface. This surface customization can be fine-tuned to fit the specific needs of the adhesive and promote mechanical interlocking of materials, increasing the utilization of space on the surface which usually increases surface wettability and therefore increases coating of the adhesive [13]. The industry of acid etching consists of endless varieties of various techniques set to accomplish the same task in different ways. In this study, P2 acid etching is used as it as shown to exhibit great properties while reducing the need for chromatic solvents [12].

Typical adhesive joints are categorized in 7 basic joint configurations, shown in figure 4, but many more iterations can be derived to serve purpose in their specific application. [14]. The use of these joints can help create uniform thickness of material and therefore distribute stresses and mechanical deformation uniformly, depending on the joint and material [14].

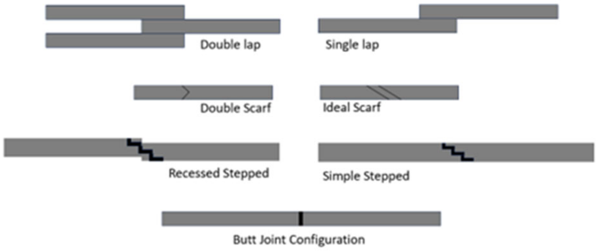

Figure 4: Diagram of typical adhesive joints.

For this study, an adaptation of the single lap shear joint is used for bonding. This adaption of the lap shear joint was engineered to minimize unwanted torsional stresses stemming from outside factors such as mechanical load frames during assembly, by cutting notches in each of the bonding areas. This modification allows for the distribution of uniform stress on the substrate and adhesive. The overall goal in this study is to demonstrate the differences plasma and acid etching have on the mechanical strength of a lap shear adhesive bond. And to further highlight the possibility that plasma cleaning has to replace acid etching in industry.

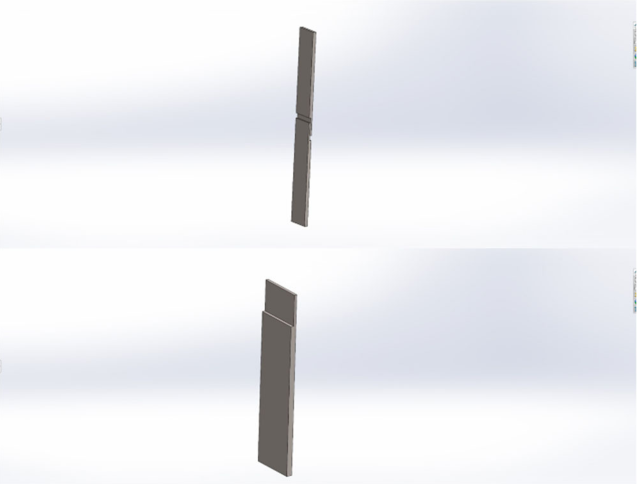

Figure 5: 3d model showing the lap shear used in study (bottom) as well as how they are orientated for bonding (top).

EXPERIMENTAL

Methods:

Preparation of Aluminum 6061 coupons in order to be used for P_2 acid etching involved subjecting them to dry sandblasting with a 220-grit aluminum oxide abrasive for 2 minutes in a uniform manner or until a matte finish on the surface was visually verified. The samples were then submersed in water to remove an access material and dried with nitrogen. A solution of 3.5% by weight Dirl-Lum 603 and water was created in an ultrasonic tank, the solution was heated to 65 °C and the coupons were immersed for 7.5 minutes. Upon completion of the cleaning the samples were removed and dried with nitrogen until no water remained. The P_2 solution was prepared using 14.2% by weight of Ferric Sulfate and 75.3% by weight of purified water, this solution was allowed to mix until all the ferric sulfate had been thoroughly dissolved and the solution became dark red in color. While still under constat stirring, 10.5% by weight of sulfuric acid was added to the solution slowly. This final P_2 solution was then preheated to 52 °C and the aluminum coupons bonding areas were fully immersed for 11 minutes. Upon completion of the 11 minutes, the coupons were removed and thoroughly rinsed with deionized water and dried under nitrogen until no water remained. Surface roughness measurements using a KeyenceVR6200 were conducted immediately after the drying of the coupons following treatment and shortly after contact angle measurements were attained. All contact angle measurements in the study were obtained using a Surface Analyst™ series 5001, a custom boot was 3D printed and swapped out for the default boot to ensure accuracy of contact angle measurements with the geometry of the coupon. This allowed for the coupon to be slid into the boot and tightened so that no movement would interfere with drops on the surface.

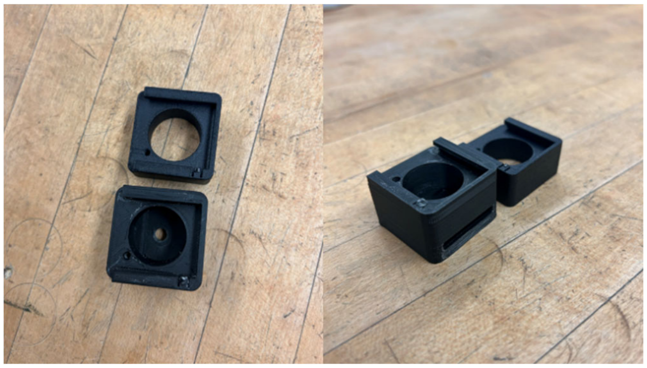

Figure 6: Custom 3d printed boot shown on the left and default manufacturer designed boot shown on the right.

Figure 7: Left to Right, P_2 acid etching setup, ultrasonic Dirl-Lum 603 solution, and Ferric sulfate precursor solution.

For plasma chamber treatments, coupons were placed horizontally into an IoN 100-40Q plasma chamber and subjected to varying wattages and allowed to remain in the chamber for times ranging from 1 minute to 25 minutes with wattages ranging from 100-500. Nitrogen plasma was used for all treatments regarding the plasma chamber. Immediately following plasma treatment, contact angle measurements were conducted. In addition, for degradation studies, the samples that were to be tested at a later date were wrapped in UHV aluminum foil to ensure the reduction of contaminants and preservation of the treatment itself.

Plasma Pen treatments were conducted using a PlasmaPen™ Atmosphere Plasma System. The pen itself was strapped to a support stand to ensure reproduceable cleaning and exposure of the pen to the surface of the substrate. Distances at which the pen was affixed varied as well as the time of exposure of treatment, shortly after treatment exposure contact angle measurements were obtained. For degradation studies, the samples that were to be tested at a later date were wrapped in UHV aluminum foil to ensure the reduction of contaminants.

For all surface roughness characterization, a Keyence VR6200 was used. When using this instrument, it was of the upmost importance that a completely level surface was used. This is simply because the optical microscope can confuse this uneven surface with actual structures and therefore mis-categorize it. If the sample was warped in the Z axis in any way it created a skewed height profile of the sample and miscalculated roughness values. For this studies purpose, the aluminum substrate 6061 is a very thick piece of metal that has been machined in a way as to prevent this.

Materials:

For the purposes of this study aluminum alloy 6061 was used for all surface preparation measurements. P_2 acid etching was conducted using Sulfuric Acid from Sigma Aldrich, Ferric Sulfate from Spectrum, and Dirl-LUM 603 from Bluewave Ultrasonics.

RESULTS AND DISCUSSION

Plasma Chamber:

3 sets of aluminum coupons were each measured for contact angle immediately following the creation of the plate from machining. Each of these coupons were treated and set aside in UHV aluminum foil to remain at rest until the time interval to which they were going to be measured arose. It was hypothesized that storing them in this UHV foil would help remedy the aging of the treatment by keeping it free of moisture and outside contamination. As evident in figure 8 the results show that after treatment with the plasma chamber not only is the average contact angle of each substrate drastically reduced, but this reduction in contact angle is also sustained for a great period of time after treatment making it a very versatile technique.

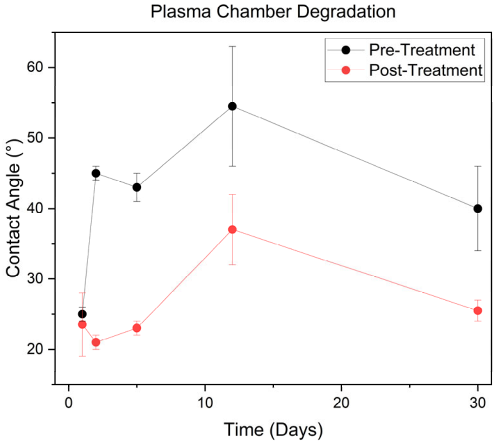

Figure 8: Before and After treatment of the plasma chamber degradation at 100 watts for 2 minutes.

Ideally, the lower the contact angle on the substrate, the higher wettability it's going to have, creating for a stronger bond. However, there reaches a threshold where reducing it any further would have minimal effects on wettability and therefore bonding. The threshold for this was determined to be 20 degrees. The effects of varying the power and time were also researched in attempts to lower the contact angle even further than the treatment of 100 watts at 2 minutes that was shown in figure 8. Shown in figure 9 below, the effect that changing the power is quite minimal. However, its thought by researchers that increasing the power might increase the charge on the surface as well as physical berate the surface, giving it enhanced properties of both physical etching and plasma etching [21]. In this study, this effect was not observed as the plasma chamber that was used in this research could not sustain reaching power above 500 watts.

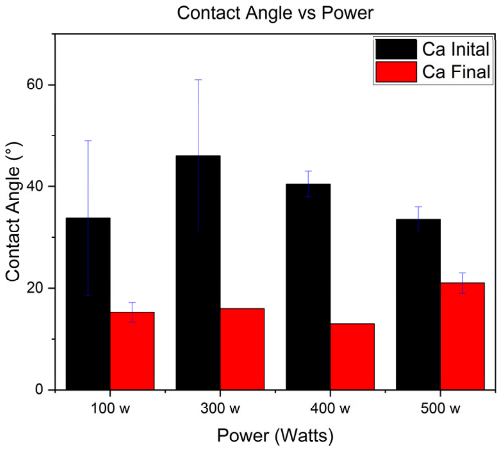

Figure 9: Effects of varying power outputs on contact angle at a constant time of 2 minutes within the plasma chamber.

Illustrated in figure 10, changing the time the sample was in the chamber had a greater effect on contact angle than changing the power from 100-500 watts. As shown in figure 10, the samples surface can get to as low as 6° when left in the chamber for 25 minutes instead of 2. However, as previously mentioned, the difference between 6° and 15° is very minimal on the effects of surface wettability in the sense that in both situations, almost the entire surface of the substrate is being covered. So, it was determined that increasing power up to 500 watts was not beneficial, and that increasing the time in the chamber had a much greater effect on the contact angle than the wattage.

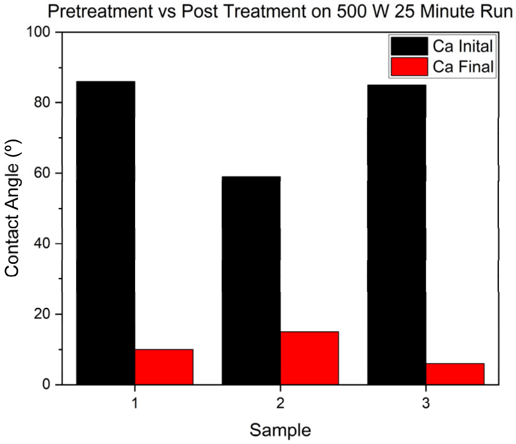

Figure 10: Effects of a changing time from 2 minutes to 25 minutes at 500 watts on contact angle.

Surface roughness measurements were also conducted on the treated samples. However, with plasma treatments, the surface of the sample isn't being destroyed so it's expected that surface roughness will remain the same. This, however, is not what was observed. It was observed that post treatment actually showed a reduction in surface roughness. This is most likely due to the fact that the surface is being deep cleaned and everything is being completely removed making for a more uniform surface free of external contamination.

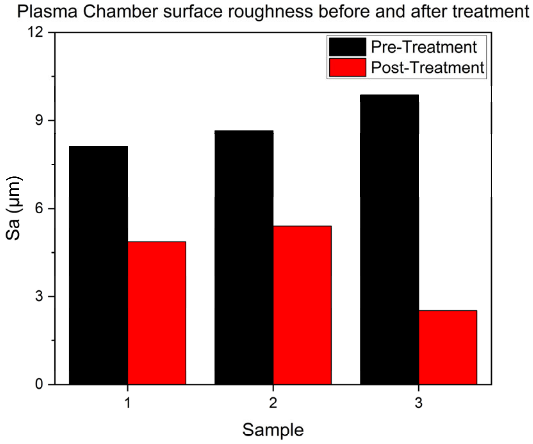

Figure 11: Effects of plasma chamber treatment on surface roughness.

The results from studying the plasma chamber conclude that it is a powerful technique capable of both increasing surface wettability and smoothing the surface of the adherend.

Acid Etching:

Following the setup of the P_2 acid etching procedure as mentioned in the methods section, 3 samples were etched, and both contact angle and surface roughness measurements were conducted on the samples. In order to keep the surface as clean as possible for optical measurements conducted on the Keyence for surface roughness, the order in which measurements were sampled was as follows: the substrate was to be analyzed on the Keyence for surface roughness firstly immediately following treatment, and then would be subjected to contact angle measurements immediately following SA measurements. The Keyence is a very sensitive optical device and can pick up very minute impurities on the surface and skew measurements, therefore this order of testing is crucial to ensure quality data. As expected, the surface roughness values of the substrate post treatment seemed to skyrocket in comparison to the other treatments. This is simply because with acid etching, the surface of the substrate is being eaten away and therefore creating an uneven surface.

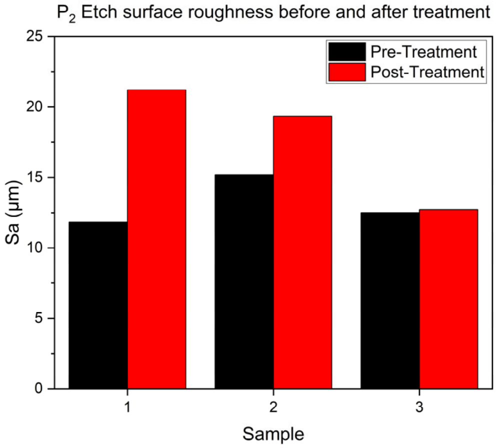

Figure 12: Effects of P_2 acid etching treatment on surface roughness.

These effects of surface roughness were consistent over a 25-hour interval insinuating that the samples could be fresh for as little as 25 hours and possibly beyond. This could have big implications for industry as samples could be treated and transported without having an extremely small window for bonding. It was hypothesized that the reason why surface roughness was even changing at all during this time was simply due to the fact that the sample kept being exposed to the environment over and over again after each measurement, possibly picking up unwanted containments on the surface. This same trend followed contact angle measurements, virtually no change was seen in the measurements over this 25-hour period even after being exposed to water droplets multiple times.

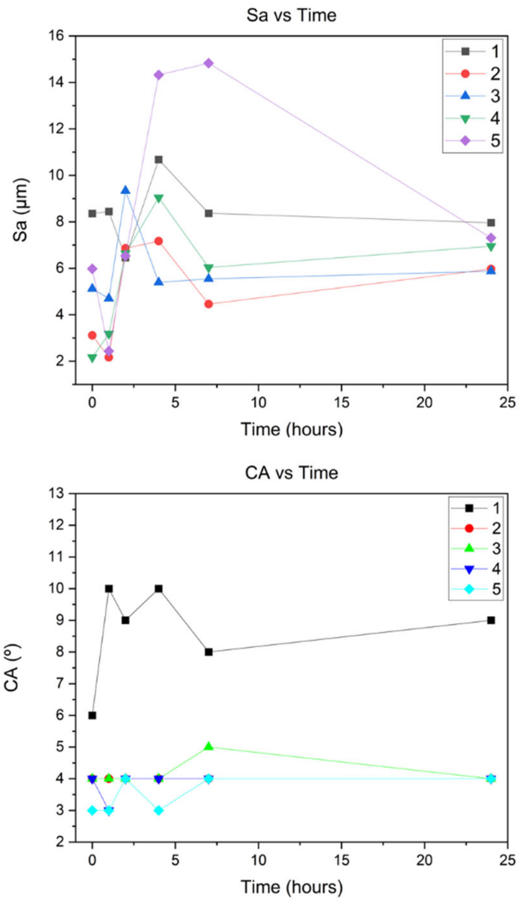

Figure 13: Aging study on the effects of time on contact angle (bottom) and surface roughness (top) of P_2 treated samples.

Contact angle measurements for P_2 etching showed values much lower than that of plasma work, measuring to as low as 3 degrees as shown in figure 13. After measuring the contact angle, it seemed that the instrument wasn't truly picking up the lowest angle as the droplet would continue to spread out after the measurement was taken. So, it could very well be possible that the measurements on some of these samples were in fact below 3 degrees. This delayed onset of the spreading of the drop could be attributed to the deep microstructures formed from the etching and the water slowly making its way into filling these microstructures, giving the illusion that its continuing to spread. However, this could be very beneficial in bonding strength as the adhesive will have plenty of opportunities to migrate its way into the deep crevices formed from the etch. As visualized in figure 14, the act of P_2 etching has large impacts on the contact angle of the treated surface and can result in measurements that are near 0 and too low for the instrument to even measure, unlike plasma treatments, this same measurement of contact angle can be reapplied to the same surface with essentially the same results, this is simply because the water just evaporates off the surface without having to worry about it messing with the charge on the surface. However, with surface roughness it looks like these essentially return to the pre-treatment values, this is hypothesized to be attributable to leaving the surface out in the open and it collect surface impurities like dust and other contaminants from the water that the sensitive microscope is picking up on.

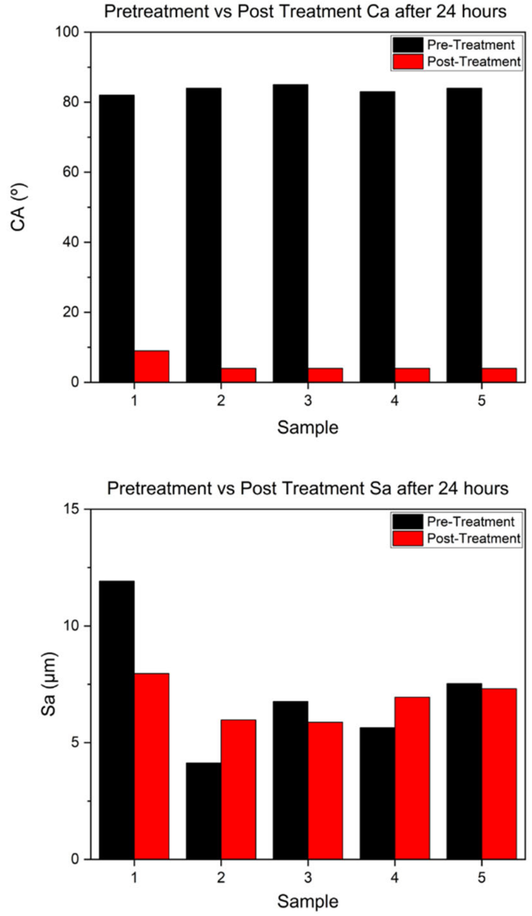

Figure 14: Effects of P_2 etching on samples pretreated and post treated after 24 hours.

Plasma Pen:

Using the same logic regarding the plasma chamber with greater time exposed to the plasma resulting in lower contact angle it was decided that this measurement would not be taken. However, with the plasma pen introduces a new variable of height variation. Unlike the plasma chamber where it is a completely enclosed space and the entire sample gets treated evenly, the plasma pen is an open atmosphere and produces a small beam of plasma. Because this beam isn't a fixed source it needs to be fixed to maintain an even exposure. The pen itself was positioned to a retort stand at heights ranging from 0.4 cm to 3.2 cm, this treatment was also varied by 10 seconds or 20 seconds to try and capture a glimpse to how changing time might affect the contact angle. Looking at figure 11, it can be seen that changing the time had virtually no effect on the resulting contact angle. The time difference between the two times might not have been enough to see a real difference. However, when looking at the distance away from the pen, it can be observed that this has almost a linear relationship with contact angle and that the closer the sample is to the pen the lower the contact angle. It was evident that the pen produced much higher contact angle results than that of the respective techniques of the chamber and acid etch, but ease of use of the instrument is a big selling point and could be very impactful if the researcher or industry only desires a certain contact angle.

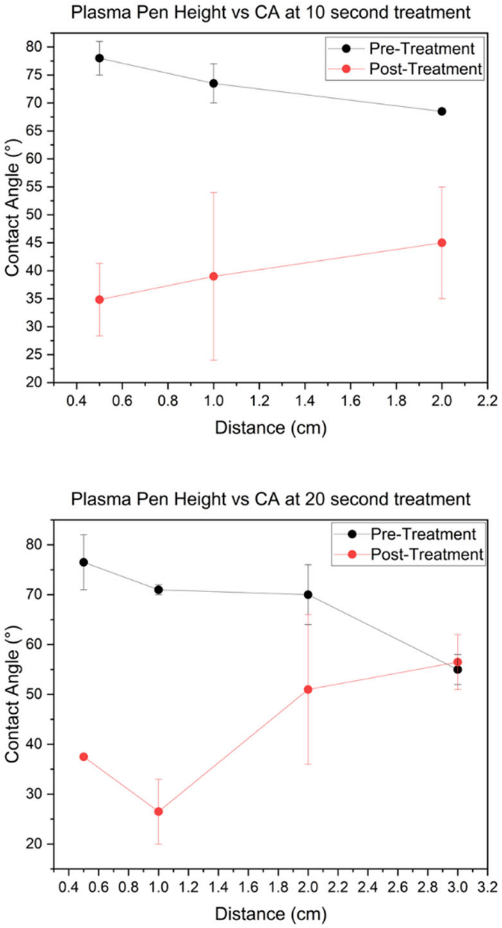

Figure 15: Effects of varying height measurements of the plasma pen on contact angle at different time intervals for treatment.

The pen has shown to provide fast and reliable results when trying to increase the wettability of surface. However, compared to its counter part of the chamber, the effects of the treatment last substantially less making it so a manufacturer would need a system if they were to do bonding instead of being able to outsource the work due to the short expiration date. As shown in figure 16 an experiment was conducted using a pen height of 1 cm and 20 seconds of treatment time. The results showed that the initial contact angle measurements were on par with that of the chamber, but quickly decayed as each hour passed by. Resulting in almost a complete negation of treatment by the end of 50 hours.

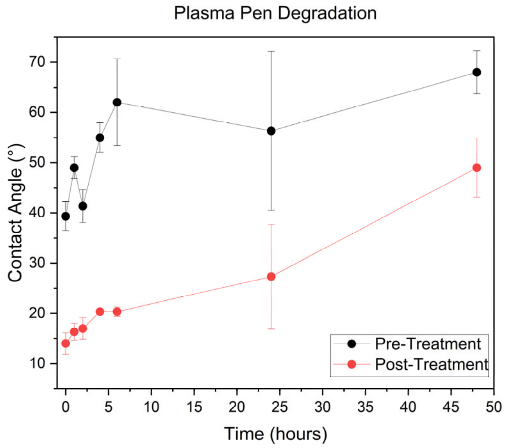

Figure 16: Plasma pen degradation experiment at 1 cm for 20 seconds.

It's obvious from this study that while it's possible to achieve low contact angles with this method, its essential that bonding take place immediately following the procedure to ensure maximum effectiveness of the treatment. With the pen comes the unique advantage of selectivity, meaning if there is a big part or only a certain area of the part needs to be cleaned, the pen can offer a service to pinpoint exactly which location needs to be cleaned with subjecting the entire sample to the source.

CONCLUSION:

With each treatment comes their own unique advantages and disadvantages, it's clear that with a growing interest in the needs for surface treatments, plasma treatments can offer a solid foundation to pave the way for future surface research. From the results, it was concluded that plasma treatments aim to impress when considering environmental concerns and versatility. But when looking at an expense or highest quality treatment, acid etching might come out on top. From the results its evident that acid etching can provide some more desirable roughness, contact angle, and preservability with surface contact. However, the extent to which these differences are important are directly related to the effect it has on bonding strength. This bonding strength is a subject for further research that will be conducted in the next paper. Substrates will be bonded and mechanically tested after treatment in order to compare the treatment's effect on adhesion strength for our specific substrate-adhesive system.

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