High-Reliability Adhesive Bonding of Polymeric Substrates Through Atmospheric Plasma Treatment

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ABSTRACT

Adhesively bonded joints are ubiquitous in both aerospace and medical applications given the advantages that they offer over their mechanical counterparts. Compared to fasteners, adhesives weigh less, take up less space, and can be applied much more efficiently in a large-scale manufacturing operation. There is also a wide range of properties that adhesives can offer in medical-device applications such as flexibility, biocompatibility, and sterilization compatibility. However, many substrates utilized in these high-reliability applications (e.g., PTFE and PEEK), are polymeric in nature, and do not generally form strong adhesive bonds in their native state. In this work, the effect of atmospheric plasma on seven polymeric substrates was studied. The substrates studied were PTFE, UHMWPE, nylon 6/6, PVC, FR4, phenolic, and POM. Surface energy measurements were collected as a function of time after treatment to quantify the effects of varied processing parameters. Lap-shear coupons were also tested to assess adhesive strength. Across all substrates (except for PTFE), the plasma treatment had a measurable effect on the surface energy along with the adhesive bonding strength. In some cases, the adhesive bond became stronger than the tensile strength of the bulk material and failures within the substrate were observed. The concept of plasma susceptibility was defined to quantify the strength change as a function of plasma dose. This work demonstrates the utility of using atmospheric plasma as a surface treatment for low-surface energy polymeric substrates that will be used in high-reliability applications to ensure optimal adhesive bond strength.

Key words: Atmospheric plasma, adhesive bonding, surface energy

INTRODUCTION

Polymers, by their nature, typically have relatively poor adhesive properties. This stems from the fact that polymers are often chemically inert, whilst also having low surface energies [1]. This combination of properties means that adhesives do not form strong bonds with polymeric substrates resulting in relatively low adhesive strength. This causes issues in high-reliability applications where low-weight polymeric substrates and adhesives are not only preferred, but required, over their heavier metallic fastener counterparts.

As such, polymers for structural applications are often pre-treated before any adhesive is applied to maximize the adhesive strength between substrates. Common pre-treatments include abrading, priming, and etching [2].

However, each of these methods have disadvantages that must be considered when treating for adhesion. For example, abrasion can have dimensional effects that can be deleterious for high-tolerance applications, and chemical etches produce hazardous waste streams. There can also be high labor costs associated with manual treatment, especially when masking steps are involved. Plasma treatment alleviates these issues with the added benefits of the option for automation (i.e., higher repeatability and quality), and in many cases no pre-cleaning is required. Plasma treatments also have the benefit of being a surface modification technique and do not affect the bulk properties of the substrate as typical penetration depths are on the order of 1 to 10 nm [3].

Atmospheric plasma treatment is carried out by ionizing a working gas (often a combination of compressed air, oxygen, or argon) to form a plasma that is impinged onto the surface of interest. The high-energy plasma has three main effects. The first being an ablative effect which can remove surface contamination (i.e., a purely mechanical effect). Secondly, the high-energy plasma can react with the surface and break existing covalent bonds and replace them with polar functional groups (i.e., functionalization) [4]. When oxygen or air are used as a working gas, these polar bonds typically contain oxygen that provide extra valence electrons to the surface, which are capable of covalently bonding to the applied adhesive or coating. This bonding potential substantially increases the adhesive strength to the substrate. The third and final effect is induction of configurational changes resulting in higher-energy states that are more amenable to forming bonds.

Published literature found that plasma treatment is a viable method for increasing the wettability and bond strength of a variety of polymers like PP, PET, polyamide, HDPE, PBT, PEEK, PVDF, and PA6 [5]. It has also been observed that by tuning the working gas, various effects can be achieved by placing specific functional groups on the surface [4].

The purpose of this study is to assess the effect of atmospheric plasma treatment used with compressed air. The effect of plasma surface treatment on adhesive bond strength for a variety of polymeric substrates was analyzed, including polytetrafluoroethylene (PTFE), a flame-retardant glass-reinforced epoxy laminate (FR4), polyoxymethylene (POM), nylon 6/6, canvas electric phenolic laminate (phenolic), polyvinylchloride (PVC), and ultra-high molecular weight polyethylene (UHMWPE).

MATERIALS AND METHODS
Materials
Polymer sheets 1/8" thick of phenolic (P1206273), POM (P0203985), FR4 (P1205766), nylon 6/6 (P0401766), PTFE (P14042200), PVC (P1611009), and UHMWPE (P0601888) were procured from Alro and dry machined into five-fingered lap-shear panels (1 inch by 4 inches) in conformance with ASTM D3163 – Standard Test Method for Determining Strength of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading.

Solvents used for pre-cleaning samples, isopropanol (A464-1) and heptane (HX0076-1) were procured from Fisher Scientific.

For surface energy measurements, diiodomethane (158429-100G) was procured from Sigma Aldrich, and deionized water was made in house with an Aries ARS-102 High Purity Water System.

For lap-shear testing, the adhesive Loctite EA9320NA AERO was procured from Henkel. Glass bond beads (602583) with a maximum diameter of 4.9 mil were procured from Potters Industries.

Methods
To assess the effect of atmospheric plasma on the selected polymers, two properties were measured after treatment, namely surface energy and lap-shear strength. Given that specific mechanisms of surface modification could be different for each polymer, three treatment parameters were varied. These parameters were the interchangeable nozzle (22826 (14°), 22824 (5°), or 22892 (32°)), nozzle-to-surface length (6 mm or 10 mm), and nozzle velocity (50 mm/s or 150 mm/s). A graphic of this setup can be seen in Figure 1.
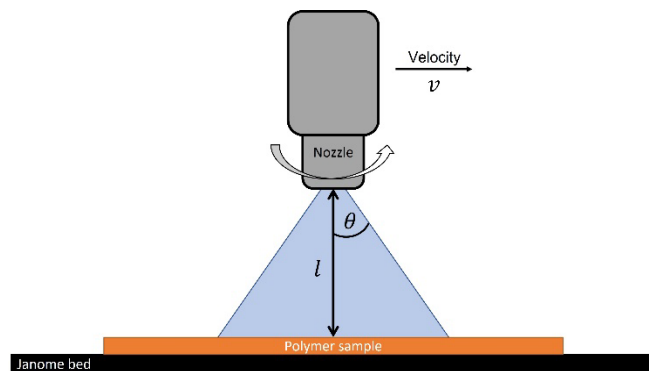

Figure 1: Treatment apparatus and definition of geometry variables

The combination of these parameters resulted in 12 unique test conditions for each material, plus one control condition (i.e., untreated). A treatment dosage was calculated using the following formula:

$$E = \frac{P}{2lv \tan \theta}$$

where: E is the energy dose [J/mm^2]
P is the power delivered by the plasma unit [W]
l is the nozzle-to-substrate length [mm]
v is the velocity of the nozzle [mm/s]
θ is the nozzle angle [°]

An index of these conditions is shown below in Table 1.

Table 1: Summary of test conditions. A control condition, C0, was also tested representing no plasma treatment

Condition	Nozzle angle [°]	Speed [mm/s]	Length [mm]	Dose [J/mm^2]
C0	N/A	N/A	N/A	0
C1	14	50	6	3.01
C2	14	150	6	1.00
C3	14	50	10	1.80
C4	14	150	10	0.60
C5	5	50	6	8.57
C6	5	150	6	2.86
C7	5	50	10	5.14
C8	5	150	10	1.71
C9	32	50	6	1.20
C10	32	150	6	0.40
C11	32	50	10	0.72
C12	32	150	10	0.24

Plasma Treatment Methods
The plasma treatment equipment consisted of a Plasmatreat RD1004 Openair-Plasma®-Rotation Jet mounted to a Janome JR503 3-axis desktop robot. The jet was coupled to an RCM-PCU rotation-monitoring system along with a PCM-PCU jet-pressure control module. A PCU-M Plasma Control Unit for control and monitoring of the plasma treatment process was used along with the FG5001 digital high frequency plasma generator.

Filtered and desiccated in-house compressed air regulated to 5 bar was connected to the inlet of the PCU-M, and one of the three interchangeable nozzles was installed onto the jet depending on the conditions being tested. The polymeric coupons were mounted to the bed of the Janome desktop robot with a single strip of double-sided adhesive tape on the back (opposite the testing surface) to hold it in place during treatment.

Twelve unique programs were written for the Janome robot, one for each of the unique nozzle, speed, and length

combinations. Before every plasma treatment, polymer samples were wiped with a Kimtech Science™ Kimwipe™ dampened with heptane followed by a Kimwipe™ dampened with isopropanol. This was done to ensure that the polymers were not contaminated prior to treatment. For the sake of consistency, control samples were also wiped down with heptane and isopropanol. During treatment, the Janome would raster the nozzle across the entire coupon such that no overlap occurred. No polymer samples were treated more than once. The working parameters of the plasma treatment can be found in Table 2.

Table 2: Working parameters of the atmospheric plasma unit

Parameter	Value
Working gas	In-house compressed air
Inlet pressure	5 bar
Gas flow rate	47 L/min
Power	450 W
Rotation rate	2700 RPM
Voltage	280 V

Surface Energy Methods
Double sessile drop tests were carried out with the KRÜSS Mobile Surface Analyzer (MSA), and data analysis was conducted using the KRÜSS ADVANCE software version 1.12.

The MSA was programmed to dispense 2 µL drops of each solvent (water and diiodomethane) onto the sample, wait 2 seconds, and then measure the contact angles of each drop. The ellipse (Tangent-1) method was used to fit the profile of the drops and the baseline was checked for accuracy. The left and right drop contact angles were then calculated based on the measured drop profile and baseline position, both for the water and diiodomethane drops during each measurement and averaged for further calculation of the surface energy. See Figure 2 for an illustration of this process.
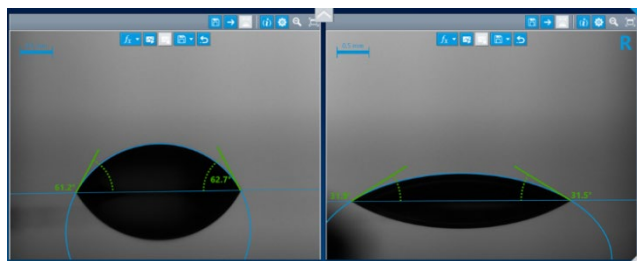

Figure 2: Contact angle measurements on polymeric coupons using Krüss MSA. Water (left), and diiodomethane (right)

The Owens-Wendt-Rabel-Kaelble (OWRK) model for determining surface free energy of a substrate was chosen due to its applicability to moderately polar surfaces with low charge, much like all polymers of interest in this study (except for UHMWPE). The OWRK model is a two-component model [6-8] that states that the surface energy of

a solid is composed of a dispersive component that accounts for Van der Waals and other non-site-specific interactions, and a polar component that accounts for dipole, hydrogen-bonding, and site-specific interactions.

The model combines Good's equation [9]:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2 \left(\sqrt{\sigma_s^D \sigma_l^D} + \sqrt{\sigma_s^P \sigma_l^P} \right)$$

and Young's equation [10]:

$$\sigma_s = \sigma_{sl} + \sigma_l \cos \theta$$

where: σ_{sl} is the interfacial surface tension [mN/m]
σ_s is the solid surface tension [mN/m]
σ_l is the liquid surface tension [mN/m]
σ_s^D is the dispersive component of the solid surface tension [mN/m]
σ_l^D is the dispersive component of the liquid surface tension [mN/m]
σ_s^P is the polar component of the solid surface tension [mN/m]
σ_l^P is the polar component of the liquid surface tension [mN/m]
θ is the angle between the solid and liquid [°]

with the result of the model being:

$$\frac{\sigma_l(\cos \theta + 1)}{2\sqrt{\sigma_l^D}} = \sqrt{\sigma_s^P \frac{\sigma_l^P}{\sigma_l^D}} + \sqrt{\sigma_s^D}$$

When using two liquids of known surface tensions, in this case water and diiodomethane, the equation can be solved as a system of two equations, one for each liquid, and the polar and dispersive components of the solid can be determined.

Surface energy calculations were carried out automatically in the ADVANCE software. Values for the polar component, dispersive component, and the total surface energy were all gathered from the ADVANCE software, as well as any associated error calculations.

Lap-Shear Methods
Within five minutes of plasma treatment, lap-shear panels were adhesively bonded with Loctite EA9320NA AERO.

Batches of adhesive were mixed 10 g at a time in a 50 mL polypropylene container with a polystyrene spatula. Parts A and B were weighed to a ratio of 10:1.9 on a Mettler Toledo ML503T analytical scale to the nearest 0.01 g and bond beads were added at 0.04% by weight total. The mixtures were then hand-mixed for 30 seconds before being inserted into a Thinky ARE-310 planetary mixer. The mixer profile was set such that the first stage was a mix at 2000 RPM in planetary mode, and then a secondary stage at 2200 RPM in centrifuge mode.

The mixed adhesive was applied to the bonding end of the lap-shear coupons with a polystyrene spatula to cover approximately ¾" to accommodate the expected ½" overlap. The coupons were then mated and placed in a custom-designed fixture to hold together 15 sets of coupons with a ½" overlap, per ASTM D3163, during curing. The fixture was then placed into a pre-heated Blue M DC-1406F convection oven set at 85 °C for 2 hours. Once cured, the bonded panels were then separated at the built-in break notches with a bandsaw to obtain five individual lap-shear coupons per panel.

Mechanical testing of the samples was carried out on an Instron 5585 frame with a calibrated Instron 2K load cell (2518-111) all controlled using the Instron Bluehill Universal software. Before each sample, the load was zeroed then the samples were mounted into wedge-lock grips. The gauge length was zeroed, and the samples were pulled at a rate of 0.05 in/min to failure and the maximum force experienced by the bond joint at failure along with the failure mode (e.g., adhesive, or cohesive) was recorded.

RESULTS AND DISCUSSION
Effect of Atmospheric Plasma on Surface Energy
Double sessile drop tests were carried out on the samples to determine the effect of various atmospheric plasma treatments on their surface energies. Generally, adhesives will wet better to high-surface-energy substrates, which is normally a prerequisite for a reliable adhesive bond. It is for this reason that many polymers typically have poor adhesive properties; their surface energies tend to be low resulting in poor wetting and subsequent low adhesive strength.

For each unique condition, five data points were collected and averaged to calculate the surface energies of the polymers. Surface energy testing was conducted on 2.5 cm by 10 cm rectangular coupons separate from the lap-shear panels.

In Figure 3, the surface energies of seven polymer samples are shown as a function of the plasma dose received. Generally speaking, except for PTFE, the strongest treatments resulted in the most significant changes in surface energy.

When considering the relationship between plasma dose and surface energy of the treated samples, there does not seem to be a strong correlation, i.e., there is a significant increase from pre-treatment to post-treatment, but the magnitude of the dose does not appear to have a large effect. This, however, does not appear to be the case with UHMWPE where there is a steady increase in surface energy as the dose increases until it plateaus at its maximum value over the dosage range tested. In terms of wettability, this suggests that even low doses of plasma treatment can have significant effects on how an adhesive will wet to a surface.

The most effective conditions for each material were then selected and plotted in Figure 4 in a way to show the

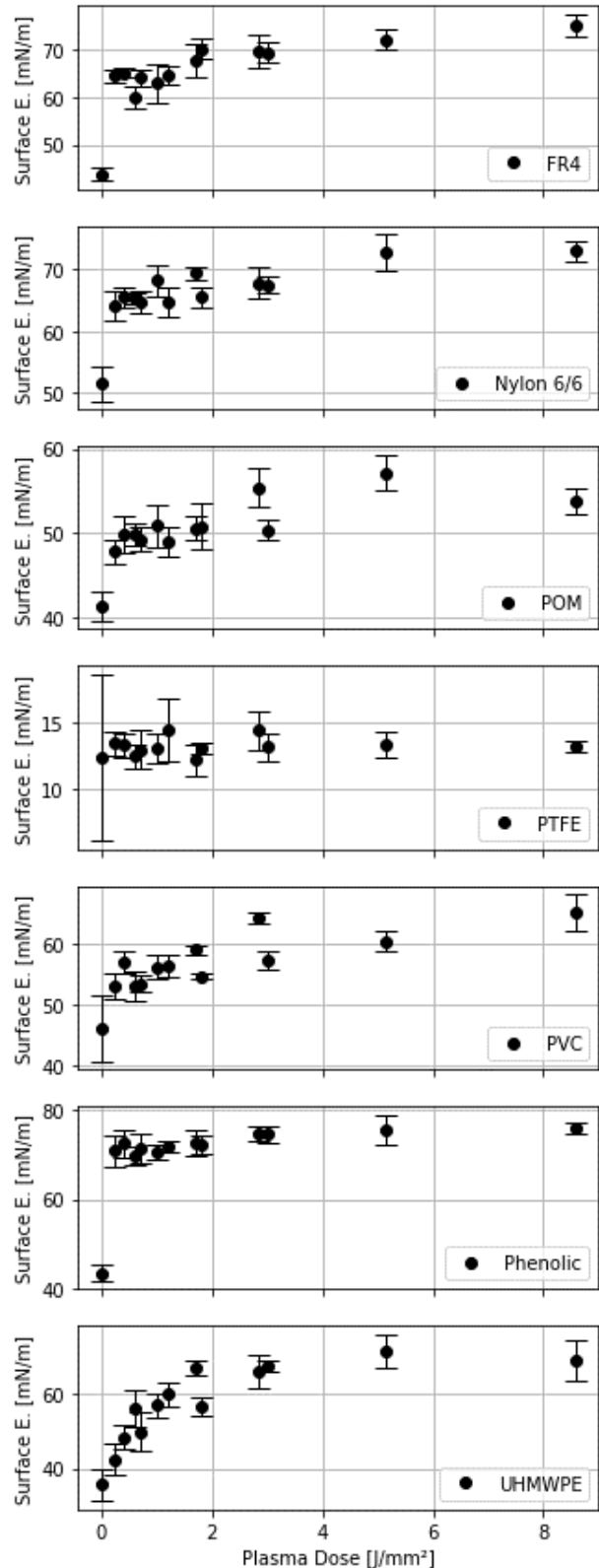composition of the surface energy separated into its polar and dispersive components.

Figure 3: Total surface energy of polymer samples as sum of the measured polar and dispersive components with error bars representing 1 standard deviation
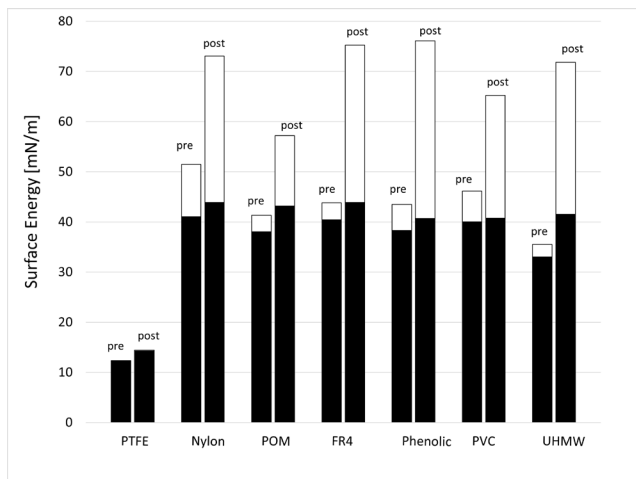
Figure 4: Surface energies of pre- (left) and post- (right) treated polymeric coupons split into their dispersive (black) and polar (white) components

Except for PTFE, which did not seem to be affected by the plasma treatment, all materials experienced a significant increase in the total surface energy. This is thought to be due to the high binding energy of the fluorine-carbon bonds. It has been observed that plasma treatment of fluorinated polymers generally results in an etching effect rather than a surface functionalization [11]. Although all materials did see a slight increase in the dispersive component of the surface energy, the majority of the increase can be attributed to the polar component of the surface energy. This is consistent with our understanding of the mechanisms under which the plasma affects the material by adding polar functional groups like hydroxyl, amino, carboxylic, or carbonyl groups [4].

Effect of Time on Treatment Effects
To assess the time scales over which plasma treatment is effective, surface energy measurements were collected over the course of 200 hours after the C1 treatment (i.e., a dose of 3.01 J/mm^2), and the results can be seen in Figure 5.

For all cases, except for PTFE, a significant increase in surface energy is observed immediately after treatment followed by a steady decline over the course of many days. Even after several days, the surface energies never fall back to their untreated values. Based on our understanding of the mechanisms occurring during the treatment, a combination of three things may be happening [4]. First, the plasma can have an ablative effect physically removing contamination or surface molecules. Second, covalent bonds can be broken and reformed causing a more permanent change to the polymer. Third, there can be conformational changes occurring within the polymer that cause a temporary increase in the energy of the state until relaxation back to the equilibrium state can occur. Theoretically, all three effects would not be considered permanent as samples can become re-contaminated, the newly formed functionality can react, and relaxation in the polymer to its equilibrium state would reverse and conformational changes. However, it is clear from the data that even over the course of 200 hours, the surface energies
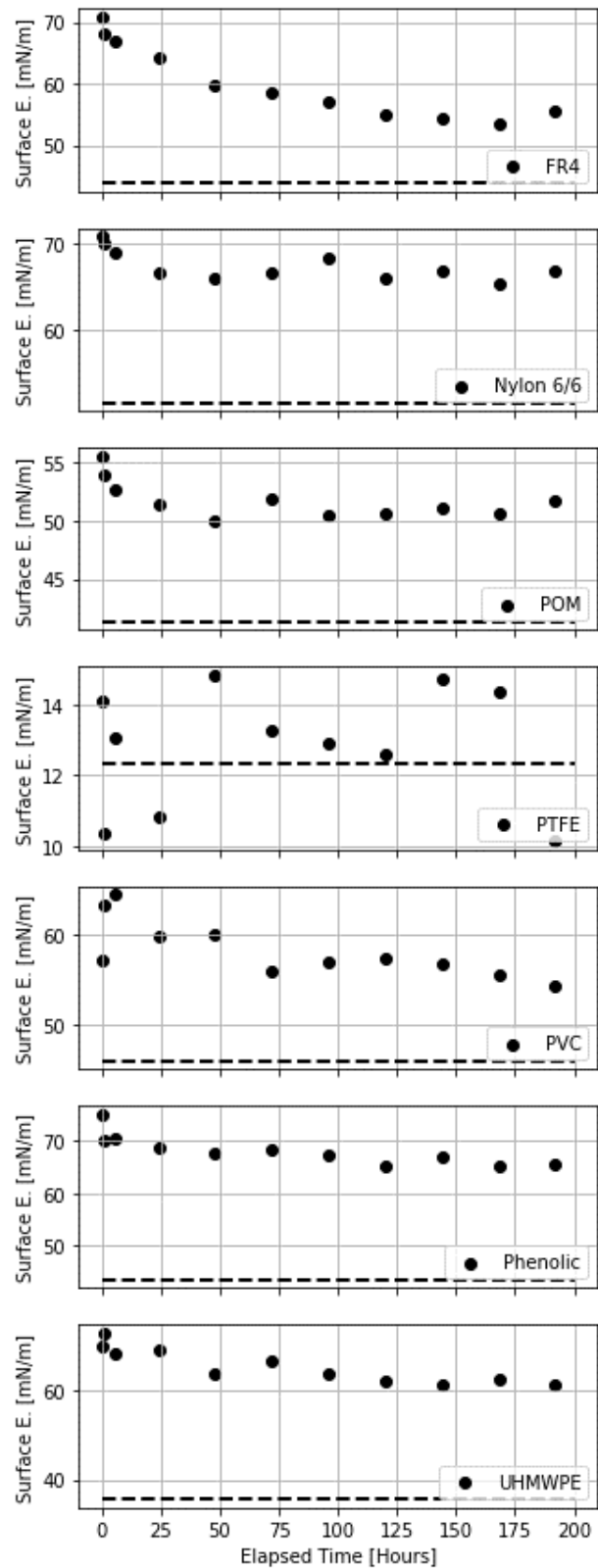

Figure 5: Surface energy of plasma-treated polymers over time after treatment. Measured values (●), initial untreated SFE (--)

of all samples, with the exception of PTFE, do not drop back down to the original un-treated values. This suggests that either the time scales over which the return to the original values is much longer than tested here, or there are some permanent mechanisms at play.

It should also be noted that all time trial experiments were carried out with a single plasma dose. In this case, a dose of 3.01 J/mm^2. It is unclear whether the rate at which the surface energy drops is a function of the plasma dose and should be the focus of future work.

Effect of Atmospheric Plasma on Lap-shear Strength
In high-reliability adhesive-bonding applications, the adhesive strength of the bond is an important property as it, along with few others like the coefficient of thermal expansion and modulus, can ultimately be the root cause of a failure.

To assess the effect of atmospheric plasma treatment on the adhesive bond strength of polymers, lap-shear samples of the aforementioned polymers were bonded and assessed over the established treatment conditions.

Lap-shear data for five of the selected polymers can be seen plotted in Figure 6. During testing of the control samples, both laminate materials, the FR4 and phenolic, experienced failure within the bulk and not at the adhesive interface, and therefore were not included as it was unclear how any changes in the adhesive strength could be quantified (i.e., the adhesive bond was already stronger than the bulk material); however, the MSA data does suggest that an increase would occur.

During testing, it was important that the coupon failure mode be tracked such that a valid comparison could be made. In this case, adhesive failure was the desired failure mode such that the adhesive strengths could be compared. In the case of PVC, although adhesive failure was observed for the control sample, all plasma-treated samples experienced a tensile failure within the bulk of the coupon, suggesting that the plasma treatment increased the adhesive strength to be greater than the bulk material (which is desirable in an adhesive bond). For that reason, any bond strengths listed here should be taken as a lower bound on the actual adhesive strength.

All samples, except for the PTFE, experienced significant increases in adhesive strength after plasma treatment, and over the dosages tested had a 2-4 times increase in adhesive strength. In most cases, this increase appears to exhibit a linear relationship between the dose and the resulting adhesive strength. The lack of change in the PTFE samples is consistent with the MSA results suggesting that PTFE is not as susceptible to the plasma treatment.

It was observed that the magnitude of change that each polymer experienced was not uniform across all samples. For example, nylon 6/6 experienced just over double the
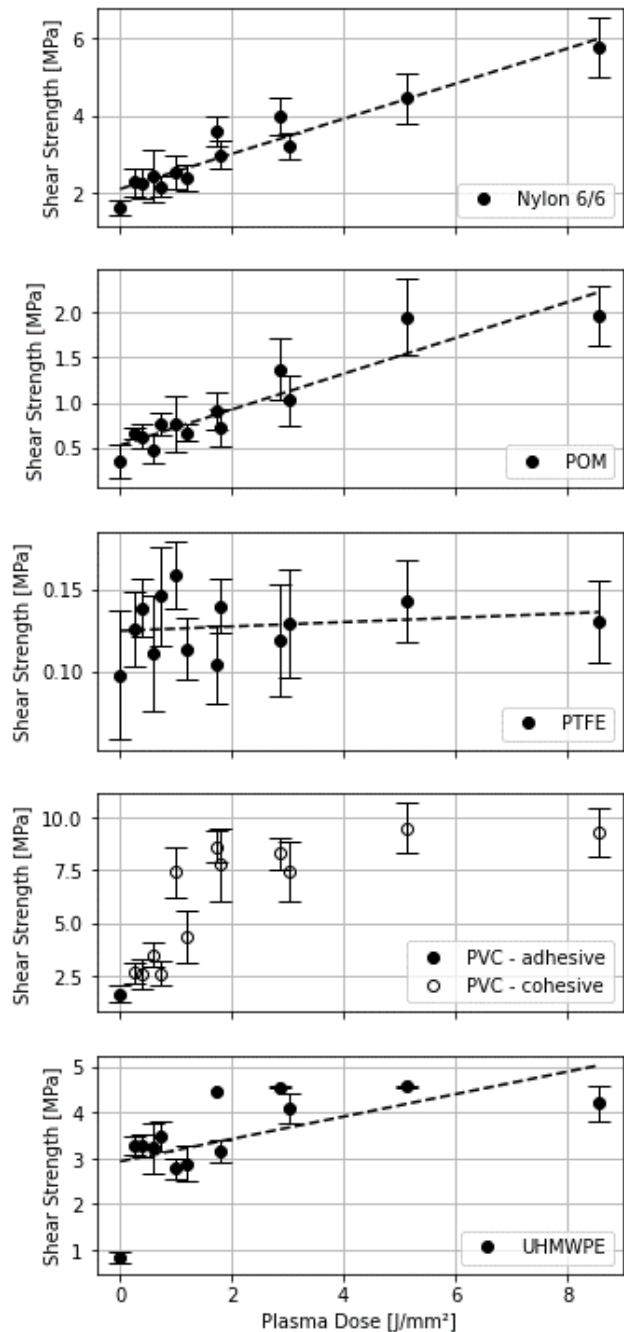

Figure 6: Lap-shear strength as a function of plasma-treatment dose. Measured adhesive strengths (●), cohesive strengths (○), linear best fit (--). Error bars represent one standard deviation

improvement that POM experienced for the same doses. This suggests that some polymers are more susceptible to the plasma treatment than others. In this manner, we define a "susceptibility" for each polymer which is equivalent to the slope of the best-fit line which represents how much change can be expected per unit dose; the higher the susceptibility, the more of a change in the strength given the same plasma dose. Since this work only dealt with a single adhesive, it is unclear at this point if this quantity is dependent on the adhesive properties as well and should be the focus of future

work. Calculated susceptibilities for the five polymers tested can be seen in Table 3. PTFE has a susceptibility of 0.00 N/J, which is consistent with the previous MSA findings in this work. After PTFE, in increasing susceptibility, we have POM, UHMWPE, nylon 6/6, then PVC with the highest susceptibility. Also, as a reminder, all plasma-treated PVC samples experienced bulk substrate failure, indicating that the reported susceptibilities represent a lower bound of the actual values.

Table 3: Susceptibility of selected polymers

Polymer	Susceptibility [N/J]
PTFE	0.00
POM	0.20
UHMWPE	0.24
Nylon 6/6	0.45
PVC	0.90[†]

[†] Denotes lower bound due to failure modes exhibited by lap-shear samples

Defining a susceptibility in this manner could be beneficial when considering that more intense plasma treatments can also have other effects that may be undesired (e.g., melting, degradation). By defining this susceptibility, we can maximize the adhesive strength of the resulting bond while preventing too intense of a treatment by tuning the dose.

At this point, it is unclear how high the increase in shear strength can become with increasing plasma dose. Given the finite number of sites that can be functionalized, it is thought that in all cases, there is a maximum shear strength that could be obtained regardless of dose. Further work would need to be carried out to extend the range of doses tested.

CONCLUSIONS
The results from this study indicate that atmospheric plasma treatment can have a significant impact on the wettability of adhesives to polymer substrates and the resulting adhesive strength of the bond.

Surface energy measurements indicate that although a significant change is seen immediately after treatment, the full effect is only semi-permanent and to obtain the most reliable bond, adhesive bonding should occur as soon as possible after treatment, preferably within a few hours.

Since adhesive strength appears to be a function of plasma dose, a susceptibility was defined to quantify the increase in adhesive strength observed per unit dosage for each polymer and can be used to tune the treatment to maximize bond strength while minimizing other deleterious effects (e.g., degradation).

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