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Atmospheric-Pressure Plasma Jet Surface Treatment for Use in Improving Adhesion

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September 2017

University of Oregon: Polymer Internship End-of-Term Report

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Abstract

Atmospheric-pressure plasma jets (APPJs) are a method of plasma treatment that plays an important role in material processing and modifying surface properties of materials, especially polymers. Gas plasmas react with polymer surfaces in numerous ways such as oxidation, radical formation, degradation, and promotion of cross-linking. Because of this, gas and plasma conditions can be explored for chosen processes to maximize desired properties. The purpose of this study is to investigate plasma parameters in order to modify surface properties for improved adhesion between aluminum and epoxy substrates using two types of adhesives. The background, results to date, and future work will be discussed.

Introduction

Plasmas have been found to have wide applications in materials processing and surface modification.[1] Plasma exhibits quite different properties from substances in the gaseous, liquid, or solid state. It is a highly reactive environment consisting of negatively charged electrons, highly charged positive ions, and neutral atoms or molecules. When these highly reactive, ionized species are introduced to a material's surface, the surface properties change.[2]

A specific type of plasma treatment, the atmospheric-pressure plasma jet (APPJ), has been developed and has shown many advantages in materials processing.[3] This portable, handheld instrument allows materials to be treated outside of a space and sample-size limiting vacuum. It also requires less equipment and thus, less maintenance, and allows for direct treatment on the line in industrial manufacturing settings.[4] As a whole, plasma treatment also has minimal waste, does not require volatile organic solvents or hazardous pressures, and produces reliable, consistent results.[2]

Figure 1 shows a design of an atmospheric-pressure plasma jet. It typically consists of a dielectric tube, made from glass, ceramic, or quartz, and contains two concentric electrodes separated by a small gap.[5] A typical APPJ will operate with radio frequency of 13.56 MHz applied to the central electrode and RF power of 250 W.[6]

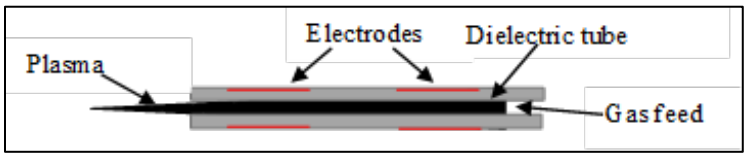

Figure 1. Basic APPJ schematic

A carrier gas will flow through the dielectric tube and between the two electrodes, igniting the plasma, allowing it be deposited downstream onto a surface.[2] Several different gases, or combinations of gases, can be used and will have different effects on material properties.[7] In addition to the processing gas, many other factors such as, pressure, power, length of treatment, and distance from source to material can play an important role in final material properties. [8]

In this work, a series of surface characterization techniques were used on aluminum 6061 substrates to help determine the effects of various plasma treatments. This paper outlines the experiments conducted to determine the optimal processing parameters to effectively increase surface activation and improve adhesion in commonly used substrates and adhesives within Los Alamos National Laboratory. In addition to the completed research, the ongoing experimental plan will be discussed.

Methods

The instrument used to perform all treatments was the PVA TePla PlasmaPen™, shown in Figure 2. Nitrogen gas was used in all plasma treatments. Surface characterization was performed on aluminum 6061 substrates to determine when a particular plasma treatment parameter would significantly affect the surface.

Figure 2. PVA TePla PlasmaPen™

X-Ray Photoelectron Spectroscopy (XPS)

Four samples and a baseline, shown in Table 1, were examined via XPS. This technique allows us to compare the elemental composition and chemical concentrations of untreated and plasma treated aluminum 6061 surfaces. All specimen were ultra-high vacuum (UHV) cleaned prior to treatment and were allowed to sit at room temperature and pressure after treatment for varying amounts of time, prior to XPS analysis.

Sample	Time Treated (s)	Distance from Al (mm)	Time after Treatment (h)
1	0	0	N/A
2	60	15	1
3	300	15	1
4	300	15	24
5	300	15	168

Table 1. Treatment parameters for specimen examined via XPS.

All spectra were collected with a 25W Al Kα x-ray source at a pass energy of 50 eV. 1000 μm x 1000 μm area scans were collected.

Drop Shape Analyzer (DSA)

DSA was used to examine surface energy and wettability of aluminum 6061 surfaces before and after plasma treatments, summarized in Table 2. Distance and time of treatment were varied among samples. Samples were measured immediately after treatment (time after treatment = 0 h).

Sample	Time Treated (s)	Distance from Al (mm)
1	5	10
2	30	10
3	300	10
4	30	5
5	30	50

Table 2. Treatment parameters for specimen examined via DSA.

Before plasma treatment, aluminum surfaces were cleaned thoroughly with isopropyl alcohol and allowed to dry for at least 5 minutes. Contact angle was measured with water and diiodomethane before treatment on the cleaned surface, and immediately after treatment for comparison of before and after results.

Results and Discussion

X-Ray Photoelectron Spectroscopy (XPS)

The first region of interest is copper, shown in Figure 3. Both copper and copper oxides appear in treated samples, and the concentration increases with respect to intensity of plasma treatment. There are no traces of copper or copper oxides in the untreated sample. After review of the instrument specification, it was determined the presence of copper is attributed to copper in the pen tip in the APPJ instrument.

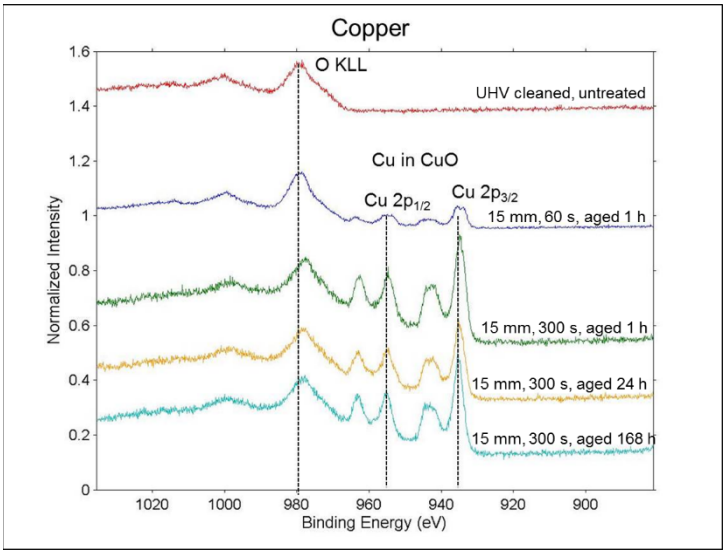

Figure 3. Cu XPS region: copper and copper oxides appear in treated samples. The pen tip is copper and the concentration of copper increases with respect to the length of plasma treatment.

Figure 4 shows the oxygen 1s region of the 5 samples. A peak shift to a lower binding energy is observed in the treated samples with respect to length of treatment, and begins to shift back towards higher binding energies as the time after treatment increases. This is attributed to the formation of metal oxides during treatment. Metal oxides occur at lower binding energies and metal carboxyls at higher binding energies.

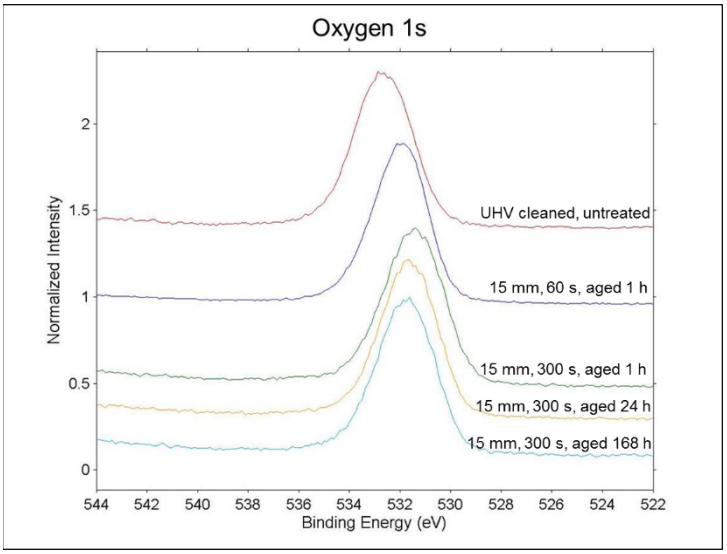

Figure 4. O1s XPS region: peak shift observed indicating metal oxides longer treated samples, and a combination of metal oxides and carboxyls in the shorter treated sample. The 300 s samples have a peak shift towards higher binding energies, with respect to the time after treatment.

It is seen that carbon is present in the untreated sample, potentially indicating poor cleaning or contamination after cleaning. The carbon concentration decreases with treatment as the plasma removes organics on the material surface. The C1s spectra is shown in Figure 5.

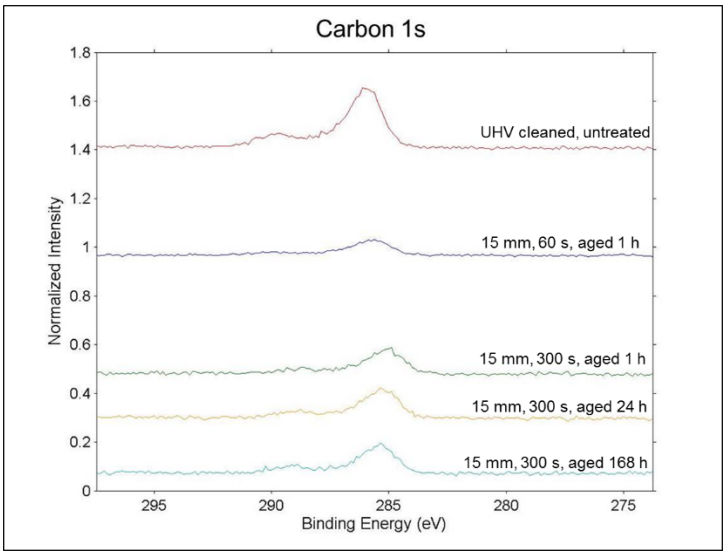

Figure 5. C1s XPS region: carbon concertation decreased in the longer treated samples.

The aluminum XPS spectra shows aluminum metal and aluminum oxide present in the untreated sample. As the treatment time increases, the oxide peak becomes suppressed within the metal peak, as shown in Figure 6. This could potentially be from the presence of copper, which has a peak around the 75 eV binding energy, creating convoluted peak overlapping.

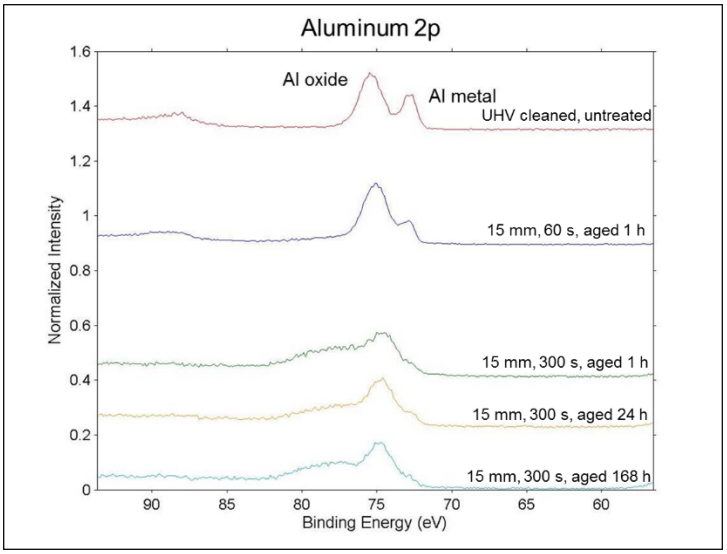

Figure 6. . Al2p XPS region: aluminum and aluminum oxide is present in the UHV cleaned and shorter treated sample. The oxide becomes suppressed with longer treatment time.

As shown in the XPS results and Table 3, the copper pen tip causes copper to be sputtered across the substrate surface. Additionally, longer treatment times have a significant effect on the surface chemistry. The reactivity of the air to samples did not have an effect within a week, but there was evidence of growth of silicon and flourine on the sample surface.

Sample	C1s	O1s	Mg2p	Al2p	Cu2p3
UHV cleaned	26.43	47.11	0.82	25.64	0.00
15 mm, 60 s, 1 h	9.18	56.09	1.56	30.63	2.54
15 mm, 300 s, 1 h	11.02	50.12	3.92	23.59	11.34
15 mm, 300 s, 24 h	13.30	49.77	5.36	23.40	8.18
15 mm, 300 s, 168 h	13.09	48.11	7.76	21.22	9.82

Table 3. Atomic concentrations observed from XPS.

Treating the samples for 300 s was determined to be too long of a treatment due to the high copper concentrations present and the suppressed aluminum peaks. Additionally, while the time that the samples are exposed to room atmosphere after treatment did not have a large impact on the XPS results, it will still be considered in further studies in an effort to develop a standard treatment procedure.

Drop Shape Analyzer (DSA)

As described in Table 2, the aluminum specimens were treated at various distances and times in order to closely examine the surface energy of the material as it relates to duration and distance of treatment. The untreated aluminum samples had an average water contact angle (WCA) of 82.82° and calculated surface energy of 24.29 mN/m. One of the five untreated samples is shown in Figure 7.

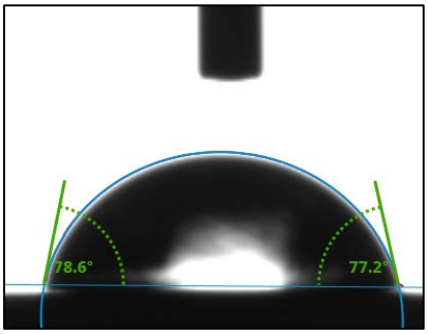

Figure 7. Untreated Al 6061 water contact angle measurement.

The results of water contact angle and surface energy with respect to time of exposure, are summarized in Table 4. It was found that as time increases, the water contact angle decreases, and thus surface energy and wettability increases. It was also determined that 5 seconds was too short of a treatment time to have a significant effect on the surface energy.

Sample	WCA (°)	Surface Energy (mN/m)
10 mm, 5 s	69.15	39.58
10 mm, 30 s	35.78	62.65
10 mm, 300 s	18.20	72.01

Table 4. WCA and surface energy averages for time related treatments.

Distance was varied for substrates treated for 30 s, and the results are summarized in Table 5. When the pen tip was 50 mm away from the substrate, there was minimal effect on the wettability and surface energy. However, when the surface was treated at a close 5 mm, the actual use of the pen became difficult and surface area covered was not maximized.

Sample	WCA (°)	Surface Energy (mN/m)
5 mm, 30 s	26.71	66.82
10 mm, 30 s	35.78	62.65
50 mm, 30 s	63.55	46.21

Table 5. WCA and surface energy averages for distance related treatments

Continuing Work

To test adhesive strength between bonded, plasma-treated substrates, an Iosipescu shear adhesive test will be performed. From preliminary data, a design of experiment will be created to efficiently perform adhesive testing. The substrates and adhesives that will be tested are shown in Table 6.

Substrate	Adhesive
Aluminum (Al 6061 alloy)	Silicone (Dow Corning® 3110)
Fully cured epoxy (EPON™ Resin 828 & JEFFAMINE® T-403)	Epoxy adhesive (EPON™ Resin 828 & EPIKURE® Curing Agent)

Table 6. Testing will be performed on aluminum and epoxy substrates bonded with silicone and epoxy adhesives.

In addition to substrate and adhesive, other factors that will be in the experimental design include: time of exposure, distance from substrate, and time after treatment. These will be considered continuous variables and will be assigned a high and low value. The experiment will include three replicates as mechanical adhesive testing is shown to have some data scatter.

This data will be analyzed and used to determine the optimal parameters for each specific set of adhesives and substrates. Furthermore, extended experiments with other adhesives or substrates may be performed as well as examining the properties of materials when processing gases other than nitrogen are used. An aluminum pen tip was ordered to avoid sputtering copper across aluminum surfaces, however this problem has not been resolved for use with other substrates.

Conclusion

APPJ treatment with nitrogen improves surface energy and changes elemental composition of the surface. XPS shows the presence of copper and change in oxides with treatment to aluminum and DSA shows that wettability and surface energy increases with the increase in treatment time or decrease in treatment distance. These surface changes may lead to improvements in adhesion which will be determined by shear adhesive testing.

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