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# Atmospheric pressure microwave plasma for aluminum surface cleaning

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### ABSTRACT

An atmospheric pressure, 2.45 GHz microwave plasma operating in ambient air was used to clean and activate aluminum surfaces. The effect of processing parameters on surface chemistry of aluminum has been studied to determine the minimal power and time needed to create clean surfaces. The contact angle measurements showed that the hydrophilicity greatly increases with increasing power and decreasing substrate speed. Fourier transform infrared spectroscopy shows that oxidative and thermal degradation is present during the plasma cleaning process. The authors' system using atmospheric pressure air plasma proves to be an efficient method for cleaning and activating metal surfaces without generating chemical waste and can be used to increase the adhesion of subsequent protective coatings.

## I. INTRODUCTION

Many metals, including aluminum alloys, require coatings to protect the metals from corrosion, wear, impact, and other sources of potential degradation.[1,2] Proper adhesion of these protective coatings to the metals is critical for their effectiveness. For decades, surface preparation predominantly consisted of cleaning the metal with chemical solvents.[3,4] However, recently, it has been shown that plasma-based technologies have great potential in surface preparation.[5] Not only can they be used to clean surfaces of any contaminants, but they can activate the surface with radicals and ions that can further increase the adhesion of the protective coatings and glues.

Initially, many of these techniques were developed using low-pressure plasmas.[6–9] However, the potential applications are limited because the parts need to be prepared in a vacuum system. This means that the parts need to be small enough, and they can only be treated in a batch process. To overcome the limitations associated with vacuum systems, many researchers are applying plasmas generated at atmospheric pressure. Atmospheric plasma systems can more easily be incorporated into assembly lines, enabling their use on a wide range of metal components.

Atmospheric pressure plasmas can be generated in a variety of ways[10–18] including dielectric barrier discharges (DBDs), direct current discharges, radio frequency plasma, and plasma-energized jets. All of these methods have been used to treat metallic surfaces.[19,20] To name some examples, a special type of DBD was successfully used to clean an oil-contaminated aluminum surface,[21] and Muñoz et al.[22] developed a surface-wave atmospheric plasma and studied the cleaning potentials of the postdischarge region of the plasma. Atmospheric plasma has shown promise as an efficient way to clean and activate metal surfaces without generating chemical waste and can be used to increase the adhesion of subsequent protective coatings. However, there are still limitations in the costs of the plasma sources (DBD, Surface-wave) and the gases (helium) needed to generate the plasma.

Here, we present an atmospheric pressure, 2.45 GHz microwave plasma system that can also be used to clean and activate aluminum surfaces simply using compressed air, with no need for He

or even Ar. Use of a 2.45 GHz microwave source is critical for reducing the costs of the plasma system, since these are widely manufactured (i.e., kitchen microwave ovens). This work investigates the contact angles and contaminants on aluminum surfaces as a function of the processing parameters to determine the minimal power and time needed to create clean surfaces with our system.

## II. EXPERIMENT

### A. Atmospheric pressure setup

A schematic of the ECAP (Evaporative Coatings at Atmospheric Pressure) setup[23–25] is shown in Fig. 1. While high temperatures that can evaporate materials are possible, it is also possible to run at lower temperatures. In the center of the torch, a 0.25 in. tungsten antenna is connected to a microwave coupler, where the microwave is delivered from a microwave power supply. Between the outer electrode with an inner diameter of 0.75 in. and antenna exists a quartz tube with an inner diameter of 0.625 in. to regulate the flow profile of the inlet gas as well as prevent arcing from the antenna to the torch body. The power of the input microwave can be adjusted up to 6 kW. A multiscrew stub tuner is used to minimize the overall impedance of the system thereby maximizing the power delivered to the plasma. The reflected power during experiments was always under 10%. Various gases enter at the bottom of the torch and flow to the tip of the antenna, where the plasma is ignited and maintained. The sample is held 9 mm above the end of the quartz tube and is allowed to move at an angle of 11° along the horizontal axis. Tilting the sample at an angle was important to get consistent cleaning. Initially, all the experiments were conducted at 0° with respect to the horizontal. Using this configuration resulted in nonuniformity in cleaning, which was attributed to a nonuniform air flow profile. In order to alleviate this issue, the entire stage was tilted to allow a more unidirectional flow of the gases. A set of stepper motors was used to move the samples across the plasma allowing for residence times ranging from 3 to 30 s.

### B. Sample preparation

The substrates were prepared by cutting 7075-T6 aluminum alloy plates into rectangular pieces with a length of 50 mm, a width of 25 mm, and a thickness of 2.5 mm. Samples were characterized as received and after coated with oil. For the coated samples, $15 \mu l$ of machine oil (20WT Quaker State) was used to coat half of the surface of the sample ($25 \times 25$ mm$^2$). A nonwoven wiper was used to spread the oil droplet onto the surface to ensure full coverage of the oil.

### C. Characterization

The hydrophilicity of the surfaces was measured through contact angle measurements using a Rame-Hart 250-F1 goniometer. A $1 \mu l$ droplet of distilled water was dropped onto the plasma treated and as-received surfaces, and the water contact angle between the solid–liquid and liquid–air interface was measured.

Characterization of the chemical species present on the surfaces was performed using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker ALPHA). The ATR-FTIR absorption spectra were recorded from 400 to 4000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. Presented data are an average of 24 spectra. All data were background subtracted using FTIR absorption of air as the background spectrum. For some samples, the background subtracted spectrum was normalized to the C—H$_2$ peak at 1453 cm$^{-1}$ of the untreated sample.

## III. RESULTS AND DISCUSSION

The cleaning effectiveness of the ECAP system was first demonstrated with the use of an argon/nitrogen gas mixture. Plasmas were stabilized in the ECAP using a microwave power of 600 W and a mixture of 20 l/min Ar and 10 l/min N$_2$. To better visualize the cleaning effectiveness of the ECAP system, a red dye was mixed into the oil before coating the aluminum sample [Fig. 2(a)]. Once the plasma was stabilized, the aluminum samples were passed through the plasma at 0.83 mm/s, and the oil was removed through oxidation by the plasma [Fig. 2(b)]. From these images, it is visually clear that the plasma removed the oil with a path width of approximately 10 mm. Additionally, oil was partially removed in the 15 mm band adjacent to the plasma plume.

These results were very encouraging to show that the ECAP, with its cheaper power source, could effectively remove a large amount of oil from a metal surface. Additionally, the use of Ar/N$_2$
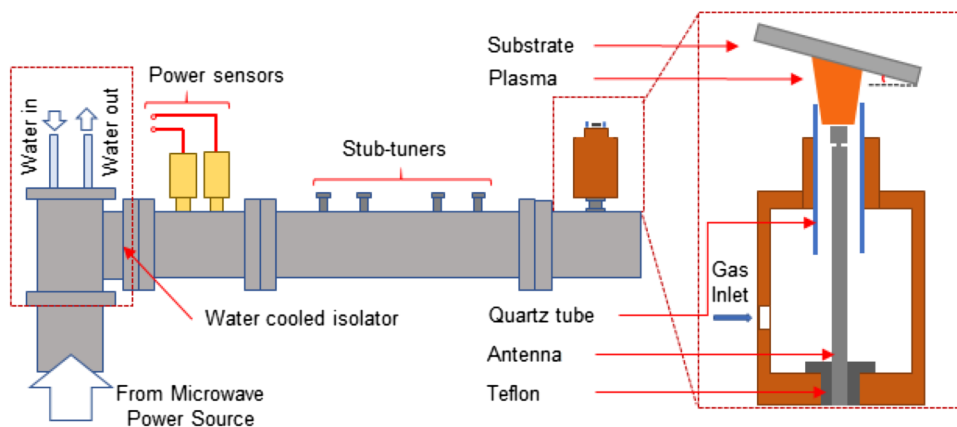


FIG. 1. Schematic of ECAP plasma system. The length of the antenna and cavity are set such that the high field point where breakdown occurs is at the end of the antenna. A set of stepper motors (not shown) rasters the substrates over the plasma. For these experiments, the substrates were suspended at an angle of 11° off the plane parallel to the torch as shown here.
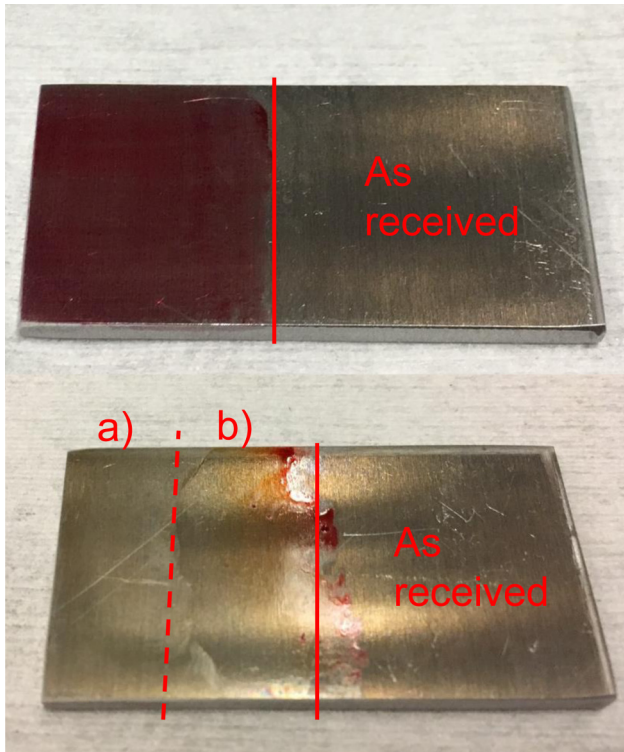
**FIG. 2.** Images of oil + red dye on aluminum coupons before (top) and after (bottom) plasma cleaning. The plasma was rastered over the right edge of the sample (a) that resulted in a completely cleaned surface. The region adjacent (b) was partially cleaned. Plasma condition was 600 W power, 20 l/min Ar + 10 l/min $N_2$, and a sample speed of 0.83 mm/s.



**FIG. 3.** Contact angle measurements of water on (a) as-received aluminum and (b) plasma cleaned aluminum using 600 W power, 20 l/min air and a sample speed of 2.5 mm/s.

gas mixture was encouraging since it is significantly cheaper than helium. However, argon is still more expensive than what many manufacturing facilities will desire. Therefore, we studied the stability of the plasma using compressed air instead of $Ar/N_2$. A brief study of the contact angle measurements of contaminated samples postplasma treatment was conducted to verify their efficacy. The results indicated an average contact angle of 20.32° ± 10.04° with $Ar/N_2$ plasma and 8.86° ± 0.06° with air plasma treatment. The maximum sample temperature measured using thermistors for either gas mixture was approximately 190 °C. From this, it was evident that air plasma was more efficient at surface cleaning. This can be attributed to higher oxygen and hydroxyl radicals present in an air plasma. These radicals play a significant role in chemically removing the contaminants present on the surface.[26]

From these tests, it was determined that stable air plasmas could be generated using microwave power as low as 300 W and 20 l/min air (data not shown). While visual tests are appealing, to quantify the cleaning effectiveness, contact angle measurements were needed. Therefore, contact angle measurements were performed on oily aluminum samples that were cleaned with an air plasma (600 W, 20 l/min air, 2.5 mm/s) (Fig. 3). These images clearly show that the water droplet on the plasma cleaned surface
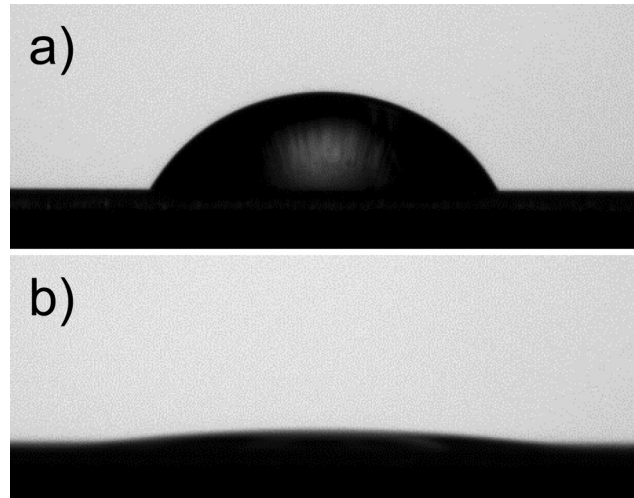
had lower contact angles than even the as-received aluminum sample (no oil). These results indicate that the surface was significantly more hydrophilic due to the removal of hydrophobic oils.

In order to optimize the atmospheric plasma processing conditions for cleaning, the hydrophilicity of the aluminum as a function of the plasma microwave power between 400 and 800 W was measured (20 l/min air, 2.5 mm/s) and can be seen in Fig. 4. From these experiments, it can be seen that the contact angle decreases for all of the plasma treated samples compared to the as-received and oil-contaminated controls. However, for the 400 W sample, the decrease in contact angle was limited and visual inspection showed oil still on the surface at these treatment speeds. For the samples with microwave powers between 500 and 800 W, the contact angles were between 20° and 36°, and there was no visible sign of oil on the surface. For all of these conditions, the oil was effectively cleaned from the aluminum surfaces.

It is known that increasing the microwave power increases both the gas temperature and the electron density, thus the radical density. Therefore, the cleaning potential of higher microwave power plasmas may be due to a combination of oxidative degradation from the oxygen radicals in the plasma as well as thermal degradation. Further tests were done at 600 W, as this power seemed to have slightly better results than 500 W but was low enough that the temperature on the surface of the aluminum could be minimized.

The substrate speed is also a critical parameter in determining the cleaning effectiveness of the atmospheric plasma. A slower speed results in an increased residency time under the plasma torch. In a manufacturing setting, the metals should be exposed to the plasma for the minimum time needed to fully clean the samples. Cleaning longer will result in wasted time and increased temperatures in the material. Therefore, contact angle measurements were performed on samples that were cleaned with substrate speeds from 0.417 to 8.33 mm/s (600 W, 20 l/min air) (Fig. 5). As
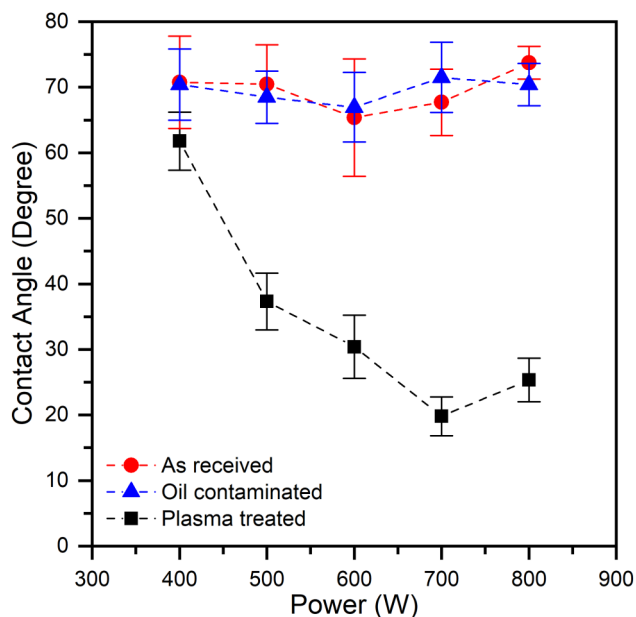
**FIG. 4.** Contact angle measurements of cleaned aluminum as a function of microwave power using 20 l/min air plasma and a substrate speed of 2.5 mm/s. Error bars are determined from ten measurements of the same droplet.
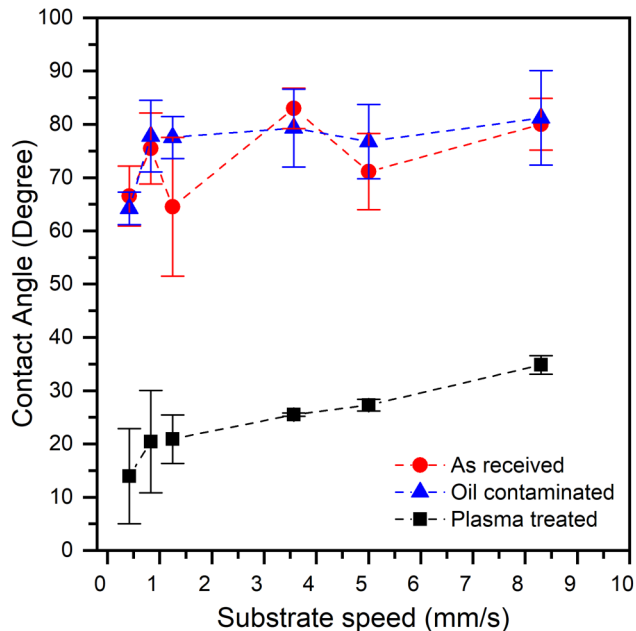


**FIG. 5.** Contact angle measurements as a function of the substrate speed in plasma. As-received measurements were made on the end of the sample that was not covered in oil or plasma cleaned. Error bars are determined from ten measurements of the same droplet.

anticipated, decreasing the substrate speed (increasing treatment time) results in improved cleaning (lower contact angle). However, at all speeds tested, oil was not visually observed. Even at the fastest speed tested, the contact angle of the oily sample is greatly decreased from 81° to 35° after cleaning.

To better determine whether the oil was completely removed, ATR-FTIR was used to characterize the chemical functionalities present on the surface of the samples before and after cleaning (Fig. 6). These data show that initially, for the oil-contaminated surface without plasma exposure, only C—H vibrational peaks are present, indicating that there are primarily hydrocarbons in the initial system. For the sample that had been exposed by plasma at a speed of 5.5 mm/s (20 l/min air, 600 W), all of the peaks had disappeared, which denotes a complete removal of the oil layer. For the sample treated with a speed of 8.33 mm/s, the intensity of C—H peaks decreases significantly, indicating that much of the oil is removed. However, carbon–carbon double bond and carbonyl peaks emerged as an intermediate product of the degradation process. These results indicate that the sample is not fully cleaned under these conditions. The presence of carbon double bonds and carbonyl peaks indicate the effects of both oxidative and thermal degradation routes.

To further understand the oil degradation mechanism, aluminum samples with thick oil layers were partially cleaned by 400 W, 20 l/min air plasma at substrate speeds of 0.833–5 mm/s (30 to 5 s exposure time; Fig. 7). These samples had excess oil and were treated at a low power to insure that the oils were not completely removed. Since ATR spectra are plotted against an arbitrary intensity, these
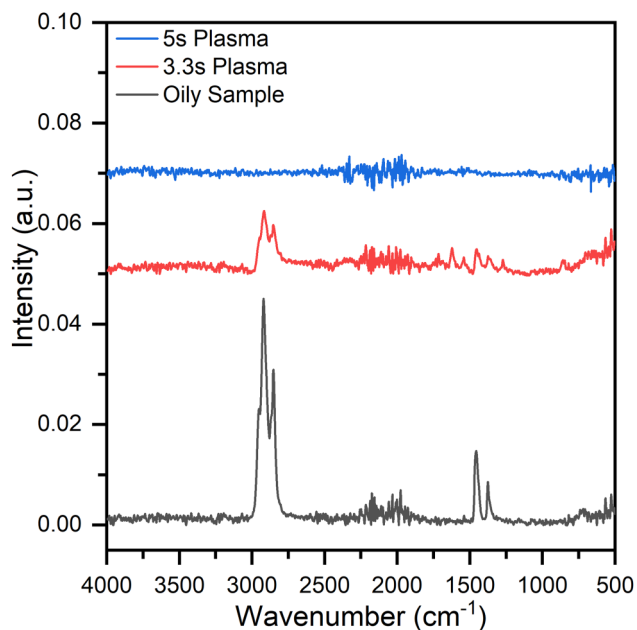


**FIG. 6.** ATR-FTIR spectrum of oil-contaminated and plasma cleaned surface. Five-second plasma corresponds to a speed of 5 mm/s, and 3.3 s plasma exposure corresponds to 8.33 mm/s.
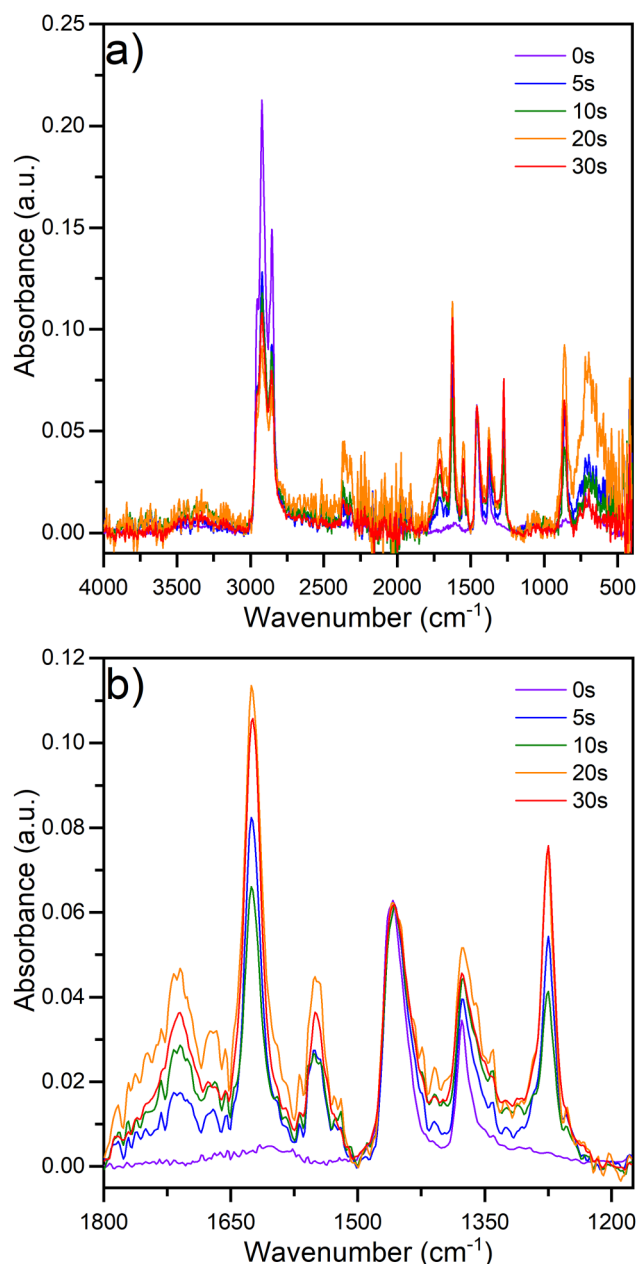
FIG. 7. (a) ATR-FTIR spectra of oil cleaned from aluminum with a 400 W air plasma at speeds ranging from 0.833 to 5 mm/s normalized to the C—H$_2$ peak at 1453 cm$^{-1}$ of the untreated sample. (b) Magnification of the ATR-FTIR spectra from 1200 to 1800 cm$^{-1}$. For the untreated oil sample, only the CH$_3$ and CH$_2$ peaks were present. For the plasma treated samples, C═O, C═C, and C—OH peaks are prevalent indicating both oxidative and thermal degradation of the oil.
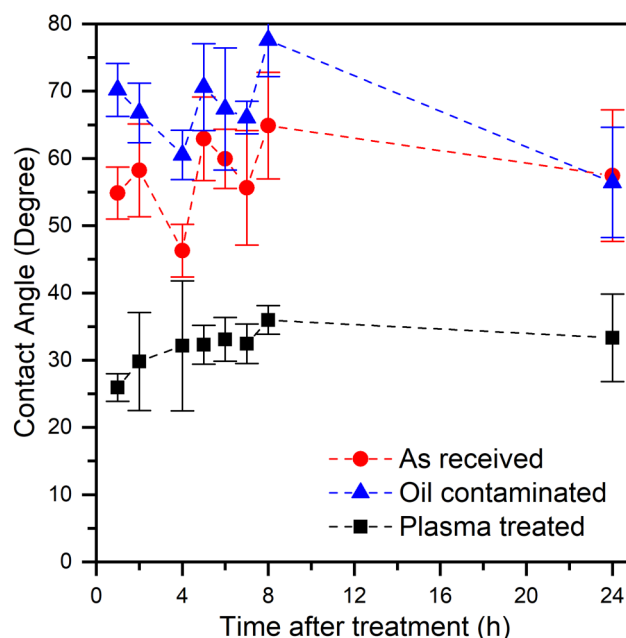


FIG. 8. Contact angle measurements as a function of the time after plasma treatment. Error bars are determined from ten measurements of the same droplet.

spectra have been normalized to the CH$_2$ peak of the oily sample. Therefore, we are not looking at the removal of peaks but, instead, looking at the relative ratio of the chemical functionalities to the undegraded CH$_2$ groups, which is the primary functional unit in

unreacted oil. The peaks present in the ATR spectra have been identified based on previously published results.[27–29]

From these results, it can be clearly seen that after exposure to air plasma, there is a large increase in peaks related to the formation of C═O, C—OH, and C═C bonds relative to the CH$_2$ bonds. During oxidative degradation, oxygen and hydroxyl radicals attack the hydrocarbon oils resulting in the formation of the C═O and C—OH functional groups. In thermal degradation, however, oxygen is not present in large quantities, and instead, char is formed and can be identified by the presence of C═C bonding. By analyzing these results, it is assumed that both oxidative and thermal degradation are present during the plasma cleaning process.

Another important consideration for manufacturing-relevant surface treatment processes is to study the aging of the surface after cleaning. To study how long the surface remained hydrophilic after initial treatment (600 W, 20 l/min air, 2.5 mm/s), samples were cleaned and the contact angle was measured several times throughout the next 24 h (Fig. 8). From these experiments, the contact angle increased from 26° to 33° as the aging time evolves from 1 to 24 h. This result is promising since other atmospheric plasma activated aluminum surfaces can only sustain hydrophilic surfaces for a few hours,[18,19] which is shorter than what is needed in an industrial setting.

## IV. CONCLUSION

In this article, we have shown the use of a 2.45 GHz microwave generated atmospheric air plasma process to clean and

activate aluminum surfaces. The cleaning effect of the plasma treatment has been reported showing that even thick layers of machine oil can be cleaned successfully with the microwave discharge plasma in air at 600 W power and substrate speed of 2.5 mm/s. The contact angle measurements showed that the hydrophilicity greatly increases with increasing power and decreasing substrate speed. Such hydrophilic surface activation can improve the adhesion properties of protective coatings and glues onto the treated surfaces. Additionally, the chemical analysis of the oils after partial cleaning indicated that both oxidative and thermal degradation mechanisms are active during this process. Lastly, it was determined that the aluminum metals remained hydrophilic for at least 24 h after treatment. This system is promising for the surface treatment of aluminum alloys and other metals due to the lower cost of the microwave sources compared to competitive processes, the use of compressed air as the plasma gas, and the reduction of chemical waste compared to current chemical processes. Further investigation of the plasma parameters and gas phase chemistry will be studied to obtain a more thorough understanding of the processes involved.

## ACKNOWLEDGMENTS

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