

# Atmospheric Plasma Surface Modification of Polytetrafluoroethylene Films

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## ABSTRACT

This work details the use of atmospheric-pressure dielectric barrier discharge plasmas to enhance the adhesion of thin metal coatings to surfaces of polytetrafluoroethylene (PTFE) films. Prolonged exposure to the energetic species in a He-O<sub>2</sub> plasma discharge leads to a decrease in water contact angle, indicating either a chemical restructuring of the PTFE surface, and/or changes in the morphology of the surface. Our initial results show a maximum decrease in water contact angle (WCA) of approximately 25° after only 10 seconds of He-O<sub>2</sub> plasma exposure. Scanning electron microscopy imaging performed on plasma-treated surfaces reveal changes in morphology, indicating physical etching and roughness changes caused by the plasma. Preliminary scratch test results indicate improved adhesion of metal films to the surface of the polymer.

**Keywords:** atmospheric plasma, polytetrafluoroethylene, metal deposition

## 1 INTRODUCTION

Polytetrafluoroethylene (PTFE) is a widely studied and used material due to its inert nature and chemical stability. However, these same attributes also render PTFE surfaces difficult to modify and functionalize. Developing a treatment method that would allow for the surface functionalization of PTFE with the same ease and variety as other industrial polymers like polyethylene would be a useful and valuable technology for a number of industries. Primary interests would focus on augmenting and enhancing PTFE's desired features like bacterial resistance, biocompatibility, high-temperature stability, and hydrophilicity [1, 2].

Numerous methods exist for polymer surface modification including wet-chemical and mechanical treatments, flame exposure, and exposure to ions, plasmas, and UV radiation, among others [3, 4]. Specifically, atmospheric-pressure (AP) plasma treatments have proven as successful as the above processes in modifying the surface chemistry of a variety of polymers [1, 2], but also possess the added advantage of a quick and scalable process without the need

for vacuum systems. Previous studies have focused on the effects of atmospheric plasmas [1,5,6], atmospheric pressure plasma assisted liquid deposition [7], and the results of sputter-coating on as-received PTFE substrates [8]. In this study we demonstrate the effects of plasma-induced surface modification of PTFE on the adhesive behavior of a commercial epoxy and a metallic thin film.

## 2 EXPERIMENTAL

### 2.1 Materials

Polytetrafluoroethylene sheets (Goodfellow, 0.1 mm thick) were cleaned before use by soaking them in ethanol for 15 minutes, then allowing them to air dry.

The polyurethane adhesive used for the peel tests was Dev-Con 2 (Devthane), which was kept at low temperature in a standard freezer for 5 minutes immediately before mixing to slow the polymerization process and allow for an extended working time.

### 2.2 Experimental Procedures

Plasma surface modification was performed using an atmospheric pressure dielectric barrier discharge system, with the bottom electrode in a roller configuration (Fig.1). The system (Sigma Technologies, model APC2000) is equipped with two electrodes with a total working area of approximately 0.065 m<sup>2</sup>. For plasma treatment, the carrier and reactive gases were injected into the electrodes at atmospheric pressure and allowed to diffuse, forming a filamentary glow discharge. The system includes two aluminum slotted electrodes, which have a working distance of 1.2 mm from the rotating alumina ground electrode.

Helium was used to initiate and generate the plasma at atmospheric pressure before the reactive gas was introduced to the system, and for this study the He flow rate was set at 12,000 sccm. Oxygen was used as a reactive gas at flow rates from 50 to 1000 sccm. The operating frequency of the applied voltage was 90 kHz with power densities varying between 6.2 kW/m<sup>2</sup> and 12.4 kW/m<sup>2</sup>. Plasma exposure times of the polymer surfaces ranged between 2 seconds and 2 minutes.

### 3 RESULTS

#### 3.1 Surface Chemistry and Morphology

For the metallization process, a gold-palladium alloy was used and sputtered on the polymer surface using a Hummer XP Sputter Coater. Samples were placed inside the sputtering chamber and evacuated to ~30mTorr. The sputter chamber was then backfilled with Ar to a pressure of 55mTorr (7.33 Pa). A DC voltage of 1.3 kV was then supplied to the electrode, yielding sputtering plasma.

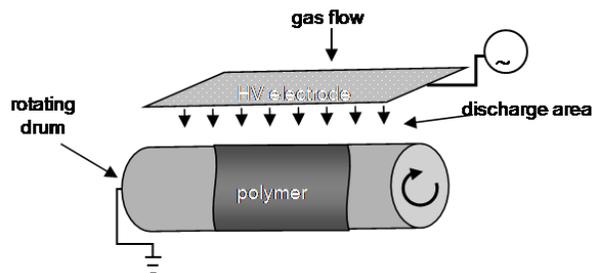


Figure 1. Atmospheric plasma system setup.

#### 2.3 Analytical Techniques

Changes in sample hydrophilicity were assessed by observing water contact angles, using the sessile-drop method, with standard water contact angle (WCA) procedures (ASTM D5946-04). Contact angles were calculated using the Young-Laplace fitting technique coupled with the auto-fitting software CAM 2008 (KSV Instruments).

Near-surface compositional depth profiling was performed using a Kratos Axis Ultra 165 X-ray photoelectron spectroscopy (XPS) system equipped with a hemispherical analyzer. A 100 W monochromatic Al K $\alpha$  (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area with a take-off angle of 90°. The pressure in the XPS chamber was held between 10<sup>-9</sup> and 10<sup>-10</sup> Torr. Elemental high resolution scans for C1s, O1s, and F1s were taken at a pass energy of 20 eV.

Changes in surface morphology were observed using scanning electron microscopy (SEM). A field-emission electron microscope (FEI NOVA NanoSEM 600) was operated in a low-vacuum detection mode, with chamber pressures held between 50-90 Pa. The low-vacuum mode of operation allows for beam currents up to 15KeV without damaging the sample at working distances between 8-15 mm.

Peel testing was carried out according to ASTM D-1876, using the Dev-con 2 polyurethane adhesive. Samples were cut into 0.0254m by 0.2286m strips, with 0.0762m tabs, and were peeled at a rate of 0.254m/min, using an MTS Synergie-1000lbs (500N load cell).

Scratch testing was performed on the metalized films to determine their adhesive strength using a nanoindenter (Nanoindenter XP, MTS Systems Corp), with a Berkovich tip.

Water contact angle measurements (Figs. 2a,b) showed a maximum drop in contact angle of approximately 25°, with the greatest effect occurring after a few seconds of exposure, then leveling out after that, indicating that atmospheric plasma treatments are effective even at short exposure times (Figure 3). A likely explanation for the leveling of the WCA is that under the plasma conditions used, no further sites are activated thus a saturation point is reached within a few seconds of exposure.

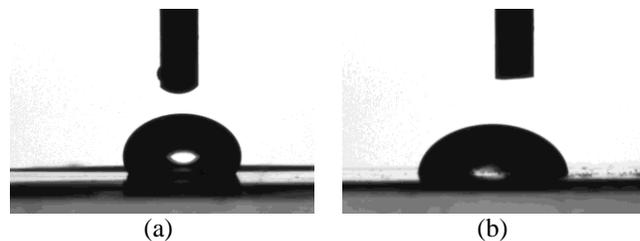


Figure 2: WCA micrographs of (a) untreated and (b) plasma treated PTFE.

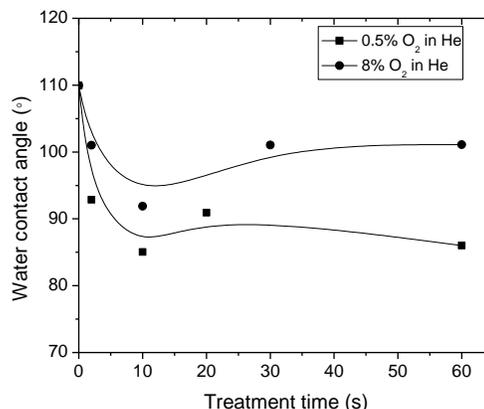


Figure 3: Effects of plasma exposure on WCA.

XPS analysis of plasma treated surfaces revealed a minor increase of about 2% in the atomic concentration of surface oxygen (O 1s) as shown in Figure 4, however, the major peaks were assigned to C 1s and F 1s (not shown). This result is not surprising given the high strength of the C-F bond due to its partial ionic character. Nonetheless, the increase in surface oxygen groups is still detectable, and indicates that the plasma treatment is indeed capable of breaking C-F bonds on the PTFE surface at atmospheric pressure. Further plasma parameter optimization will be carried out to achieve higher oxygen levels.

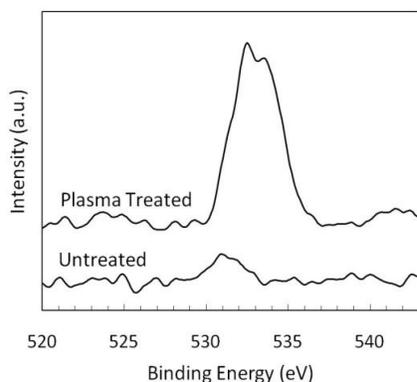


Figure 4: XPS results showing the O 1s peak of untreated and plasma treated PTFE.

Scanning electron microscopy did not reveal any significant changes in surface morphology (Figures 5a, b), indicating that plasma effects on the surface, such as wettability, are chemical rather than morphological. This is supported by the XPS results.

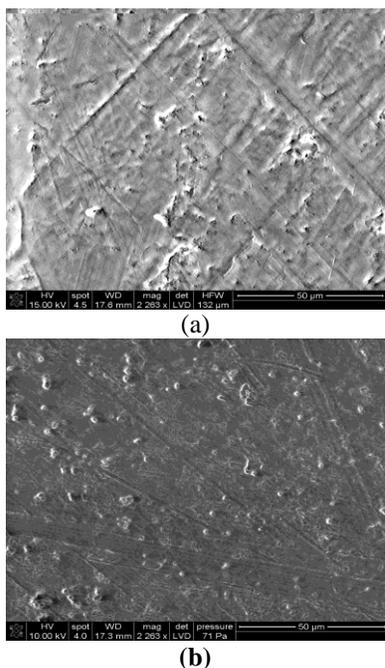


Figure 5: SEM images of (a) untreated and (b) plasma treated PTFE films.

### 3.2 Adhesion Strength

Adhesion tests were carried out as a means to verify the effectiveness of the plasma modification via peel tests with a polyurethane adhesive. Figure 6 shows the peel strength of untreated and plasma treated films. The results reveal two orders of magnitude increase in peel strength compared to control samples. This supports the argument that the plasma is responsible for the mild oxidation of the PTFE surface by enhancing the bonding between the surface and the adhesive.

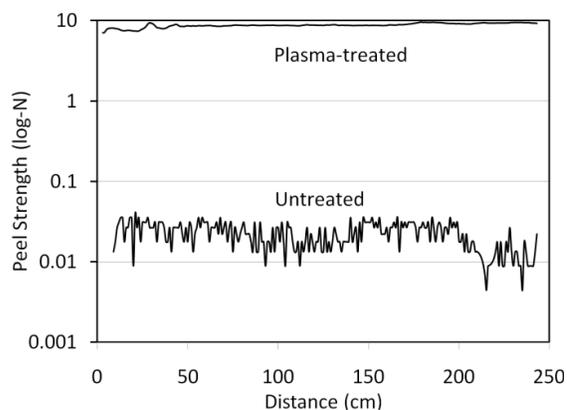


Figure 6: Increase in adhesive strength of PTFE sheets using a polyurethane adhesive.

Based on these results, the increased adhesion between the polymer surface and a metallic film was investigated by scratch tests. Au-Pd alloy films (50 nm) were sputtered on the surface of untreated and plasma treated PTFE samples. An applied load ramp from 0.05 mN to a maximum of 5 mN was used to scratch the surface of the metallized polymer surface. Scratch profiles and post-profiles (not shown) indicated plastic and elastic components attributed

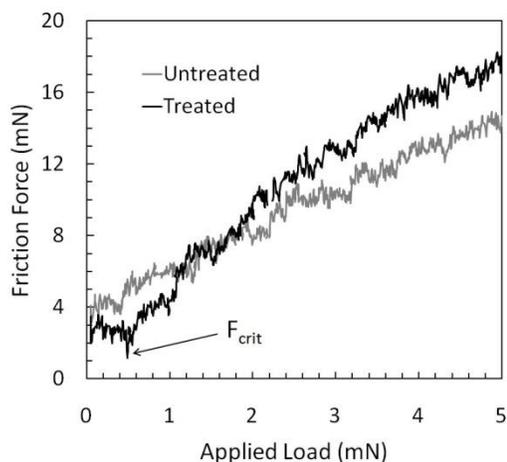


Figure 7. Friction force as a function of applied load during scratch tests for untreated and plasma treated samples, and the corresponding critical force ( $F_{crit}$ ).

to the mechanical properties of the bulk polymer. In order to obtain a value for a critical load corresponding to the failure of the metal/polymer interface, the friction force as a function of applied load during the scratch was inspected as shown in Figure 7. We defined the critical load here as the applied load at which the slope of Figure 7 changes. For the plasma treated sample,  $F_{crit}$  was 0.55 mN whereas for the untreated sample a change in slope was undetected so  $F_{crit}$  was assumed to be negligible. These preliminary results suggest that the force required to penetrate the metallic film is less for the untreated sample, arguably due to a weaker adhesion to the polymer surface. Nonetheless, more testing

is required to fully characterize and quantify the adhesive behavior and strength.

## 4 CONCLUSIONS

In this study we used an atmospheric plasma treatment to modify the surface of PTFE. Chemical analysis showed minor chemical modification by the addition of oxygen chemical groups. However, peel testing showed a two orders-of-magnitude increase in the adhesion strength of PTFE to a polyurethane adhesive. Scratch testing was used to investigate the adhesion of a thin Au/Pd film to the plasma-modified surface. Preliminary results indicate that the plasma treatment does improve the metal adhesion to the surface. Future studies will include further exploration of various plasma parameters including applied power, gas composition, and exposure time, as well as aging studies to determine the stability of the newly modified surfaces over time. Once an optimized plasma profile is developed, masks will be employed to selectively modify the surface and create a variety of patterns.

## 5 ACKNOWLEDGEMENTS

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