

Deposition of coating containing carboxylic acid groups on polyurethane foams with DBD plasma jet

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Abstract: The surface of three-dimensional (3D) porous polyurethane (PU) foam was functionalized by depositing a coating containing carboxylic acid groups with a dielectric barrier discharge (DBD) plasma jet fed with helium, acrylic acid (AA) and ethylene. The discharge ignited throughout the entire porous structure of the foam allows for a uniform surface functionalization and the increase of the heavy metal ions adsorption from water solution.

Keywords: DBD, plasma jet, coating deposition, PU foams, heavy metal ions adsorption.

1. Introduction

In recent years, atmospheric pressure cold plasmas (APCPs) have attracted growing interest in surface processing of materials thanks to the easy-to-handle apparatuses, their compatibility with continuous production processes and the absence of complex and expensive pumping systems, needed for low pressure operations [1-3]. One actual issue with APCP sources is the surface functionalization of complex 3D porous materials. Thanks to the possible ignition of the atmospheric pressure discharge also inside the sub-millimetric substrate pores, it is possible to treat uniformly the outer and inner surfaces of the substrates without affecting their bulk properties [4-12].

DBDs are one of the most common and utilized approaches to generate APCPs. They require the presence of at least one dielectric layer located in the current path between the metal electrodes to prevent the arc transition as well as the utilization of an alternated current (AC) high voltage (HV) power supply [13-15].

This contribution focuses on the utilization of an atmospheric pressure DBD plasma jet fed with helium, AA and ethylene to deposit thin films containing carboxylic acid groups [16] on the entire structure of 3D open-cell porous commercial PU foams. The possible utilization of treated samples for the adsorption of heavy metal ions from water solution is also evaluated.

PU foam was selected since it is an inexpensive, versatile polymeric material, characterized by high surface area, and high thermal stability [17-19].

2. Experimental section

The deposition was performed using an atmospheric pressure plasma jet with coaxial cylindrical DBD configuration. A glass tube was placed between the HV and ground electrode as dielectric barrier, the discharge gap corresponded to the 2 mm thick annular space formed between the HV electrode and the glass tube. The sample holder, located under the jet, was provided with a xy

translator to allow the displacement of the sample and the enlargement of the area interested by the deposition. The DBD was generated by applying a sinusoidal HV at 20 kHz and 1400 V_{rms} to a feed mixture of helium (7 slm), AA vapours, introduced with a bubbling system (22 ppm), and ethylene (200 ppm) for 90 min [16].

Commercial open-cell PU foam strips (length: 50 mm, width: 20 mm, thickness: 4 mm) with pore density of 45 ppi and porosity of about 97% were used as substrates. The coating was also deposited on glass slides for diagnostic purpose.

The chemical characterization of the PU before and after the plasma deposition was carried out using a small spot X-ray Photoelectron Spectroscopy (XPS), while the capacity of treated foams to adsorb heavy metal ions from water solution was evaluated with Anodic Stripping Voltammetry (ASV), by measuring the ion concentration before and after the immersion of the foams in solution. Most experiments were performed using cadmium ions.

3. Mainly results

As shown in Fig. 1, under the experimental conditions utilized in this work, during the deposition processes the plasma ignited throughout the entire porous structure of the 3D foam.

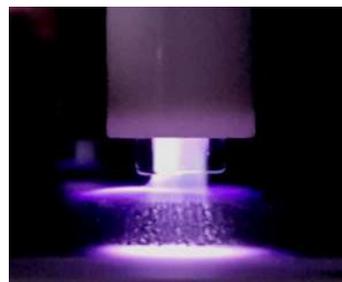


Fig. 1. Plasma plume during the deposition processes on PU foams

XPS analyses, performed in different positions of the foam (top, centre, and bottom), allowed to assess the good uniformity of the deposition in terms of chemical composition. As shown in Table 1, within the experimental uncertainty, the coating has the same composition than that deposited on the glass.

Table 1. Atomic composition of coating deposited on PU foams and glass slides

	PU (top)	PU (cross-section)	PU (bottom)	Glass
C (%)	73.5 ± 0.2	73.0 ± 0.8	73.2 ± 0.3	72.8 ± 0.5
O (%)	26.5 ± 0.3	27.0 ± 0.8	26.8 ± 0.3	27.2 ± 0.5
C-C/C-H (%)	47.2 ± 0.4	46.2 ± 1.8	46.3 ± 0.7	45.8 ± 0.9
C-O (%)	13.4 ± 0.2	13.9 ± 0.4	13.4 ± 1.0	14.4 ± 0.2
O-C-O/C=O (%)	4.0 ± 0.4	3.9 ± 0.5	4.0 ± 1.0	4.2 ± 0.3
COOH (R) (%)	8.9 ± 0.3	9.0 ± 0.3	9.4 ± 0.4	8.4 ± 0.2

The surface functionalization increased 12 times the capacity of the foam to adsorb cadmium ions when immersed, for 1 h, in aqueous Cd solution 500 µg/L at pH=7. The adsorption capacity increases also when the solution pH up to pH=8 (Fig. 2); for higher values the deposit decomposed.

The adsorbed ions could be released by immersion in acidic HCl solution at pH=2 and after rinse in distilled water, the foam was ready for a new adsorption experiments. The recyclability of the coating was good, since after 8 adsorption-release cycles any appreciable reduction of the adsorption capacity was not detected.

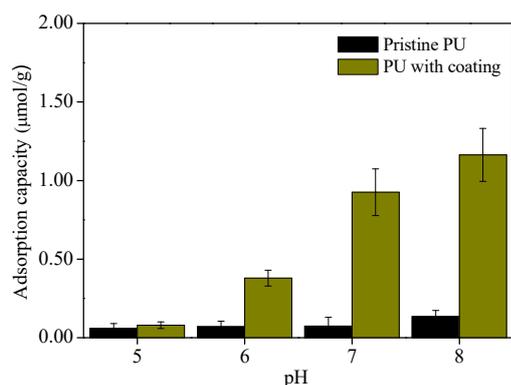


Fig. 2. Effect of the pH of the Cd solution on the adsorption capacity of pristine (black) and plasma treated (green) foams.

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5. References

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