# INFLUENCE OF PROCESS PARAMETERS OF THE ION SOURCE ON THE HYDROPHILIC PROPERTIES OF POLYMERIC MATERIALS

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https://doi.org/10.37904/metal.2024.4946

**Abstract**

Currently, polymers are a group of future-proof materials, which, in contrast metals, are characterized by low weight and also are easier to obtain and relatively cheap. However, due to their low surface energy, their use is often limited. Due to plasma technology, it is possible to modify the surface properties of polymers in a cost-effective and efficient way. During the last years, low temperature plasma surface functionalization of polymer materials has increasingly earned a high position in a wide range of application fields. This paper present the influence of ion etching technology on modyfication of the surface of polymers. An assessment of the impact of the operating parameters of the ion gun on the hydrophilic properties of polymers was presented. An analysis of the surface topography, chemical composition and wettability of polymer materials after the activation process was carried out.

**Keywords:** Polymer, plasma treatment, ion etching, hydrophilic properties of polymers.

## 1. INTRODUCTION

The variety of applications requires the use of polymers with different surface properties. Surface engineering offers many techniques for modifying surface properties, such as: glow discharge, corona discharge, X-ray radiation, photon, electron or ion beam bombardment. Using the above-mentioned techniques, it is possible to modify the surface properties of polymers in terms of [1]: hydrophobicity or hydrophilicity, surface morphology, surface energy, as well as produce functional groups, increase the adhesion of the deposited coating to the substrate, modify chemical properties, electrical conductivity, or remove contaminations.

Works on modifying the surface properties of polymers by ion beam bombardment was initially focused on improving mechanical properties and biocompatibility [2]. Changes in the electrical conductivity of polymers have also been studied to remove electrostatic charges from the surface [3]. Another work has shown that changes in the chemical structure and surface development can improve the adhesion between the polymer and the metal layer [4]. Also at the Surface Engineering Center (Łukasiewicz-ITeE in Radom) work was carried out on the use of plasma surface engineering techniques to modify polymer membranes [5], including work directly related to the use of ion beam treatment of polymer substrates.

The range of impact of the ion beam does not exceed several micrometers [6]. The ion beam penetrating polymer materials causes much greater changes than, for example, in the case of ceramics or metal. This is due to the fact that polymeric materials have a macromolecular structure, and therefore the strength of bonds in their molecules is much lower. Due to the fact that polymeric materials dissipate heat poorly, attention should be paid to the amount of energy delivered to their surface due to the possibility of melting processes, recrystallization of the crystalline phase or thermal aging. Polymer materials are most often modified using a beam of argon, oxygen, nitrogen, helium or xenon ions.

The effects of the ion beam on polymeric materials can be divided into: structural effects manifested by the release of hydrogen, cross-linking and degradation, and oxidation, as well as effects related to changes in functional properties, including mechanical properties, tribological properties, microroughness, adhesion, wettability, and biological properties. Ion beam impact on polymers may affect both their structure and chemical composition in the near-surface zone. The effect it brings depends not only on the type of ionized gas and the amount of energy supplied, but also largely on the molecular weight of the polymer, the structure of the macromolecule and its structure [7].

The presented research results are a part of work on improving the adhesion of functional coatings applied using the MS-PVD method to the surfaces of polymer membranes used in the water filtration process. Adhesion problems were revealed during operational tests of membranes with produced coatings. Therefore, attempts were made to use ion sources to modify the polymer surface immediately before the coating application process. **Figure 1** shows the diagram of the research concept.

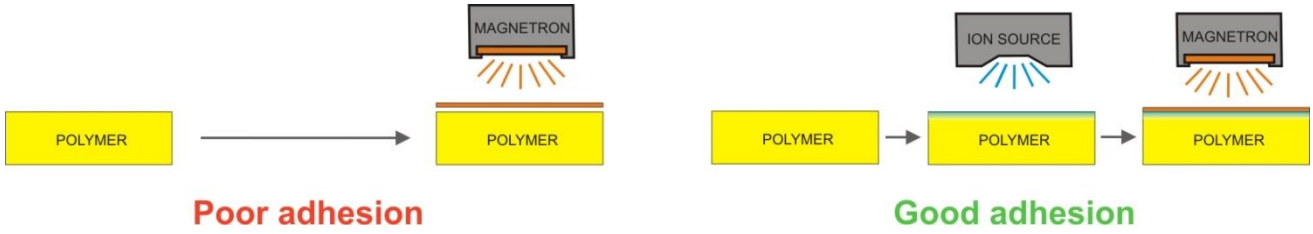


**Figure1** Scheme of the concept of improving the adhesion of functional coatings to polymer substrates.

## 2. EXPERIMENT

### 2.1 Preparation and parameters of experiments

The experiments were performed using the FlexLine device, designed and built at Łukasiewicz-ITeE in Radom, equipped with a continuous substrate transport system using the roll to roll method (**Figure 2a**). In an experiment, polymer samples were treated by modular ion beam sources eH400HC (**Figure 2b**) from KRI® (gridless End-Hall ion sources with hollow cathode) [8, 9, 10], with various operating parameters (discharge current Id=2.0A; 2.5A; 3,5A). Argon and oxygen were used as the ionized gas. The tests were performed at a pressure of p=5×10-3mbar, stabilized with argon. All processes had a fixed exposure time (t = 5min.). Polyamide (PA) samples with dimensions: Ø25.4×6mm and Rz=650nm were used for testing. The samples were placed under the ion sources at a distance of approximately l = 200 mm.

a  b 

**Figure 2** FlexLine device: a) general view, b) eH400HC - modular ion sources in operation.

### 2.2 Samples characterisation

Polyamide samples exposed to the ion beam were studied for changes in surface topography, chemical composition and, above all, for changes in the contact angle. To obtain images of surface topography and roughness tests, a Q-Scope 250 atomic force microscope from Quesant Instrument Corporation, was used. The chemical composition of solid poliamide samples were studied using a Hitachi field emission scanning electron microscope, SU-70, equipped with an EDS X-ray microanalyzer from Thermo Scientific. Wettability (H2O) tests of native and activated polymer samples were carried out by measuring the contact angle using the lying drop method using a tensiometer of the Ł-ITeE design.

## 3. RESULTS

### 3.1 Topography studies

In all cases of activation, a decrease in the Rz roughness value was recorded in relation to the native sample (from 19% to 32% in both Ar and O2). Based on the 3D visualization of the surface topography, it can be concluded that for activation at a discharge current of Id = 2.5A (for both Ar and O2), the surface is smoother while maintaining similar Rz values than in other cases. The topography of the tested samples and the roughness test results are shown in (**Figure 3**).

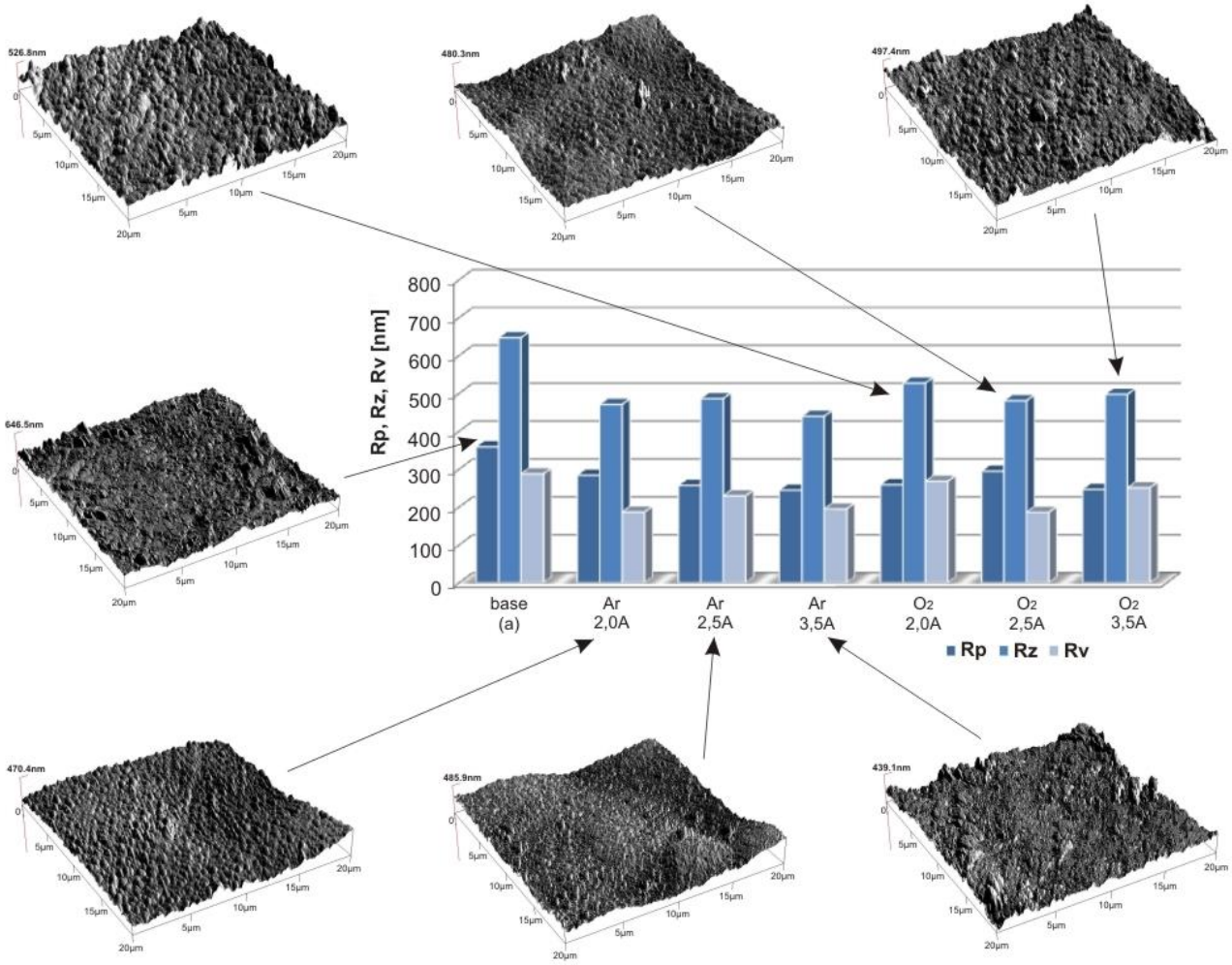


**Figure 3** Comparison of surface topography and roughness on the tested polyamide (PA) samples: unactivated base (a) with those activated in Ar and $O_2$ for three discharge current values: Id =2.0A, 2.5A and 3.5A

### 3.2 Chemical composition and microstructure studies

The research analyzed the content of carbon (C), oxygen (O), nitrogen (N) and argon (Ar) in the atomic composition. In all analyzed cases, a decrease in carbon content of 8.6÷13.7% at. can be observed. and an increase in oxygen content by 5.9÷6.9% at. and nitrogen by 1.8÷7.6% at. The greatest decrease in carbon content (by 13.7% at.) with a simultaneous increase in oxygen (by 6.1% at.) and nitrogen (by 7.6% at.) was recorded for etching in oxygen and discharge current Id = 3.5A. the lowest decrease in carbon content (by 8.6÷8.7% at.) with a simultaneous increase in oxygen (by 6.7÷6.5% at.) and nitrogen (by 1.8÷2.2% at.) was recorded for etching in argon and discharge current Id = 2.5A and 3.5A. In other cases, the compositions had intermediate values at a similar level. No study found argon content in the surface composition. **Figure 4** shows a comparison of the chemical compositions of the measured surfaces of PA samples.

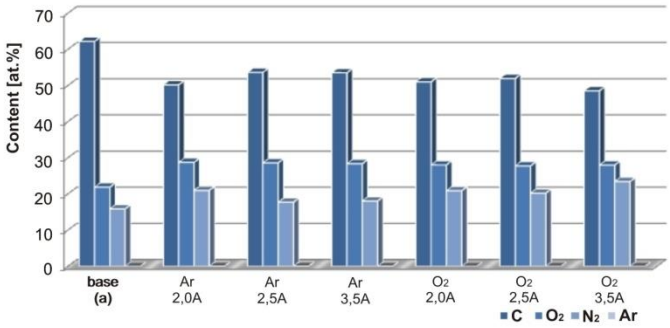


**Figure 4** Comparison of the chemical compositions measured on the surface of the tested polyamide samples, activated in Ar and $O_2$, for three discharge current values: Id = 2.0A, 2.5A and 3.5A with the composition of the native sample (a)

### 3.3 Wettability studies

Wettability tests on polyamide samples activated in Ar showed a decrease in the contact angle value by approx. 15% for Id=2.0A (up to 55.1º) and approx. 45% for Id=2.5A and 3, 5A (up to 36.4º). Activation in $O_2$ causes greater change in the contact angle of 55% (to the value of 29.2º ÷ 31.5º) for all tests.

Measurements were performed on the day of activation, after removing the samples from the process chamber, and then verified approximately two weeks after activation. These studies allowed to assess the durability of the effects achieved during activation in the form of a decrease in the contact angle, i.e. obtaining more hydrophilic properties of activated polymer surfaces. **Figure 5** shows a comparison of the contact angle test results on polyamide samples activated in Ar and O2, for all current values Id = 2.0A, 2.5A and 3.5A.

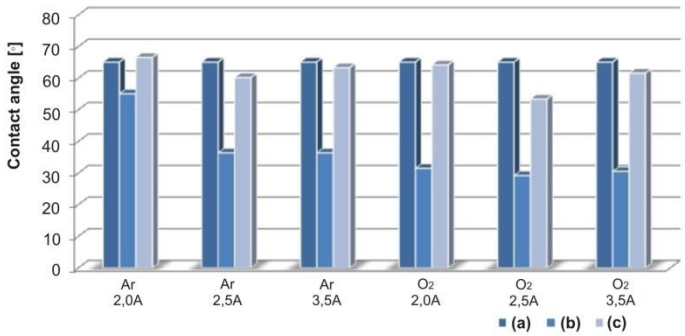


**Figure 5** Comparison of the contact angle test results on polyamide sample activated in Ar and O2 and three discharge current values Id=2.0A, 2.5A and 3.5A.: (a) before activation, (b) on the activation day, (c) 14 days after activation process

## CONCLUSION

The experiment was aimed at verifying the impact of the ion beam on a polyamide (PA) substrate in terms of surface topography, changes in chemical composition and changes in hydrophilic properties. The presented research results are part of work related to improving the adhesion of functional coatings applied using the MS-PVD method to the surfaces of polymer membranes used in the water filtration process.

Based on the obtained test results, in all cases a decrease in surface roughness Rz was found after the activation process. At the same time, for the discharge current Id=2.5A (for Ar and O2), a smoother surface was observed while maintaining similar Rz values than in the other cases, which may indicate changes in the surface structure of the polymer.

The examination of the chemical composition showed in all cases a decrease in carbon content with a simultaneous increase in oxygen and nitrogen content. This indicates the breaking of polymer chains and the formation of free radicals, which increases the ability to attach atoms near the surface. In this case, oxygen and nitrogen from the atmosphere are added after the samples are removed from the process chamber.

Wettability tests showed better hydrophilic properties after the ion beam activation process. It was also shown that in most cases this effect is unstable and after a long time the contact angle returns to a value close to the initial one. Only in the case of activation in oxygen for a discharge current of Id=2.5A, the contact angle does not return to the initial level and remains at a level approximately 20% lower than the initial level, which indicates a permanent improvement in hydrophilic properties.

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