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DEPOSITION OF ACRYLIC ACID PLASMA POLYMER ONTO POLY(ETHYLENE TEREPHTHLATATE) NUCLEAR TRACK MEMBRANES

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Abstract. Polymerization of acrylic acid onto polyester membranes (polyethylene terephthlate) track membranes was carried out in radiofrequency plasma generated in parallel plate discharge configuration. The deposition of an acrylic acid film onto membrane surface was observed from Atomic Force Microscopy (AFM) investigations, also from the increase of the membrane thickness and of the membrane weight. In addition, a decrease of the membrane pores size for long time plasma treated samples was noticed. PET membranes treated in argon/acrylic acid plasma show transport properties which depend on the solution pH.

Key words: radiofrequency plasma, plasma polymerization, nuclear track membranes.

1. INTRODUCTION

Polymers are frequently used in separation processes of mixtures of gases, liquids etc, in the form of polymeric porous foils. One of the membrane types used in these processes are the track membranes. This work discusses the process of plasma modifications of polyethylene terephthlate track membranes (PET-TM). This type of membrane has specific characteristics, such as small thickness and high uniformity of pores, due to preparation techniques, as described elsewhere [1].

The field of applications for this type of membranes tends to be extended and for that reason it is required to tailor the membrane properties. Several methods, based on physical and chemical modifications of polymeric materials can be used, and one of the most important is the plasma treatment. A number of studies, devoted to the investigation of modification of polymeric foils by plasma graft polymerization of acrylic acid were recently published [2-4]. The aim of this paper is to present the modification of PET membrane characteristics and transport properties by exposure to argon/acrylic acid plasma. The plasma polymerization of acrylic acid onto PET membranes was investigated by AFM, thickness, pore diameter and water permeabilty measurements.

2. EXPERIMENTAL

The treatments were performed in a discharge chamber presented in Fig. 1 and

desribed in detail previously [5]. In addition, here the plasma gas is a mixture between argon and acrylic

acid vapors and has a specific color. The solution of acrylic acid is placed in a glass tube, outside the discharge chamber and the vapors are carried into the plasma by argon flow. The influence of plasma parameters (plasma duration) on PET membranes characteristics was investigated. Only one side of the membrane was treated.

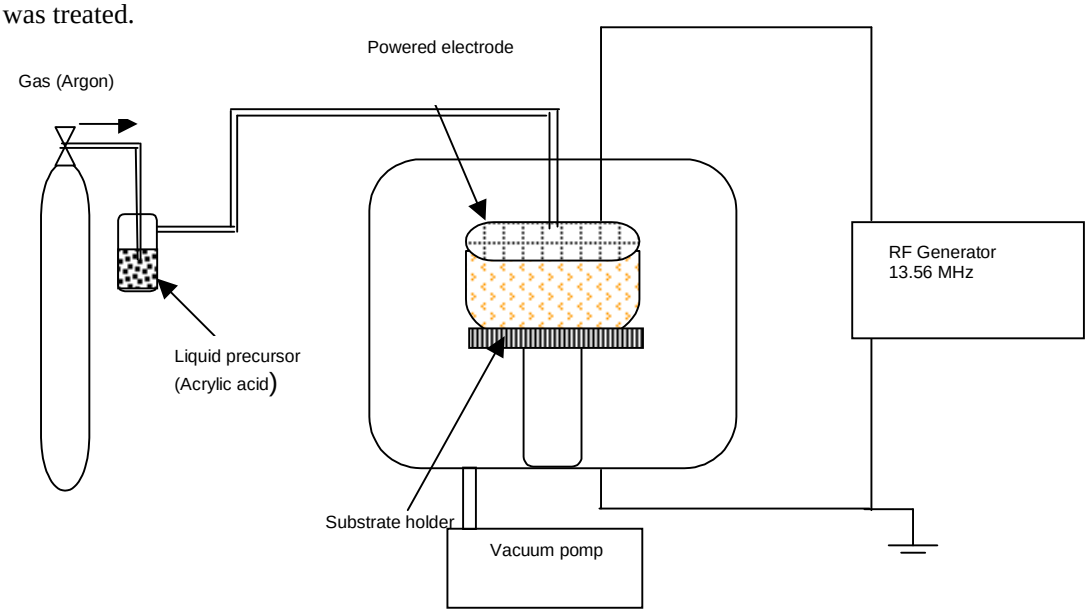

Fig. 1 - The experimental set-up.

PET membranes with a thickness of 9.5 µm and pore diameters of 0.2 µm were used. A series of complementary methods of investigations were used aiming to reveal the modifications induced by argon/acrylic acid plasma treatments. The topography of the membranes was characterized by Atomic Force Microscopy (AFM, Q-Scope^{TM} Nomad^{TM}). The thickness of the membranes was determined by an electronic meter of thickness (Unit Tesa, Austria). The effective pore size was calculated from the air flow rate values. The water permeability for different pH values was measured at a standard filtration installation FMO-2 (Russia)

3. RESULTS AND DISCUSSION

The surface properties of the membrane were studied by AFM. The image of untreated membranes presents a smooth surface and well defined pore shape (Fig. 2).

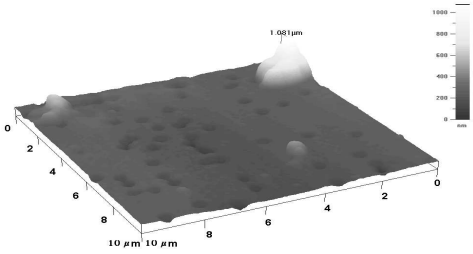

Fig. 2 - AFM image of a PET TM (0.2 µm pore diameter)

Samples of PET TM, glass and Si were exposed to plasma in the same time. The Si substrates were partially covered by a mask before starting the plasma treatment. After plasma treatments the mask was removed and the samples of Si were investigated by AFM, scanning both the covered and uncovered zones. Form height differences between these two areas it was concluded that deposition of a polymeric thin film occurs (Fig.3, a). The thickness of the deposited film on Si measured by AFM is small, reaching ~100 nm after 10 minutes plasma treatments which mean a deposition rate of 10 nm/min. The topography of the deposited thin film was also observed by AFM (Fig. 3, b). The polymeric film surface appears to be quite smooth and uniform.

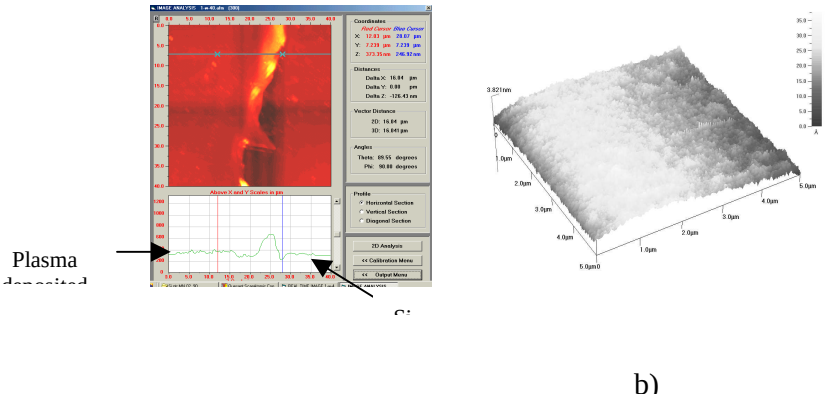

Fig. 3 - AFM images from Si substrate coated in acrylic acid plasma (60W, 10^{-1} torr): a) 10 min, b) 1 min.

The results of membrane thickness measurements are presented in Fig. 4. They show that after plasma treatment the thickness increases which entail again the idea that acrylic acid fed plasma deposits a thin film at the substrate surface. The thickness of the membrane reaches a maximum values for longer treatment time, in this case the average deposition rate was 0.04 μm/min. In Fig. 5 results regarding the behavior of the pores diameter are presented. The pores diameter show a decrease after plasma treatments, again after longer plasma time it was observe the most pronounced effect.

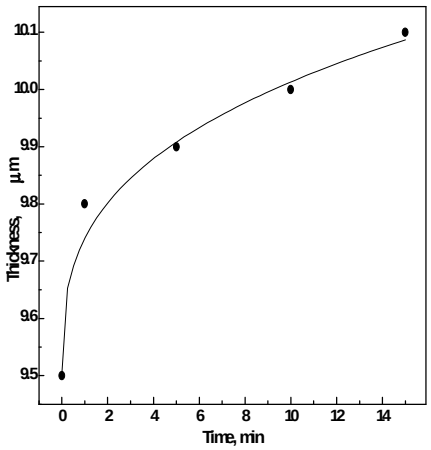

Fig. 4 - Thickness dependence on treatment duration , for PET TMwith 0.2 µm initial pores diameter).

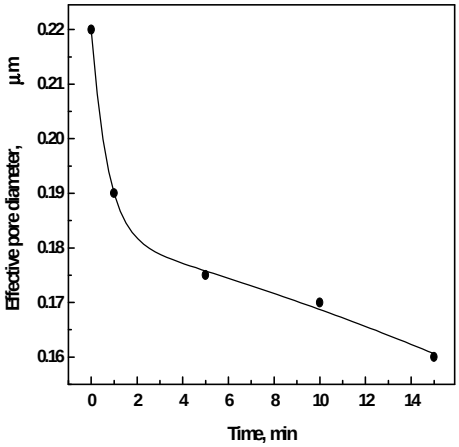

Fig. 5 - Dependence of pors diameter on duration of acrylic acid plasma treatment (for PET *TM with 0.2 µm initial pores diameter).*

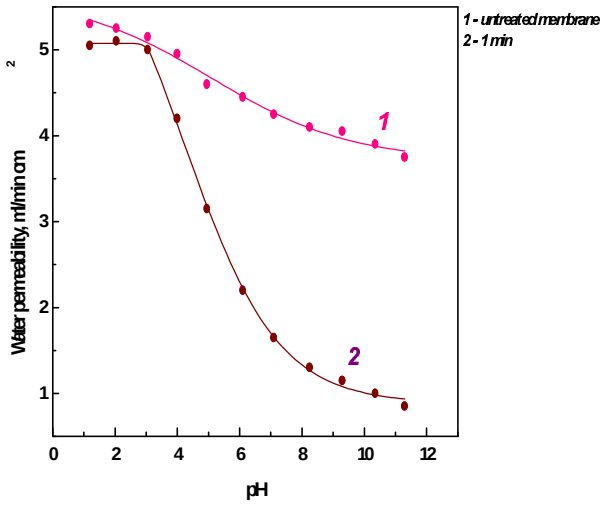

Fig. 6 - Dependence of water permeability upon solution pH for PET TM (0.2µm) for: 1 – untreated sample and 2 –samples treated in acrylic acid.

Modification of the transport properties [5] by plasma treatments was also observed. Changes in transport properties of PET TM treated in acrylic acid plasma are presented in Fig. 6. The dependence of water permeability on solution pH shows an interesting behavior. For small values of pH (up to 4) the water permeability of treated samples do not present noticeable modifications from the untreated membranes. For higher values of pH the water permeability decreases drastically for

the treated membranes as compared to the untreated ones. This behavior is explained by changing in molecular conformational states of the deposited layer. The macromolecules of plasma polymeric thin film present a compacted or extended conformation depending on pH [4].

4. CONCLUSIONS

Acrylic acid plasma treatments of PET TM modify the surface and morphological characteristics of the membrane, as well as transport properties. After plasma exposure at the membrane surface is deposited a thin polymeric film. Due to this deposition process the thickness of the membrane increases and the pore size decreases. In both cases maximum values were obtained after longer treatment time.

The water permeability of the composite membranes formed by polymerization of acrylic acid depends upon solution pH. Such a behavior of the membrane is explained by change of the conformational state of macromolecules of the deposited layer, which may cause the change of the pore diameter.

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