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Morphological, chemical and permeation characteristics of plasma modified polymeric track membranes

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Polyethylene terephthalate nuclear track membranes were subjected to radiofrequency low pressure plasma treatments in ammonia. The modification of morphology, chemical composition, and of water flow across membranes was investigated, in relation with the applied power, gas pressure, and treatment duration. The plasma treatments lead to modification of water permeability through membranes, opening a way for improving their transport properties.

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1. Introduction

The filtration processes are widely used in food industry, chemical industry, medicine, biology. The polymers are among the most important materials used for membranes production, due to their properties and the cost effectiveness. Various fabrication techniques were developed for polymeric membranes. In the phase inversion method, porous (sponge type) asymmetric polymeric foils, having tortuous pores of complicated shapes are obtained, usually with a large distribution of pores size . By irradiation of polymeric thin foils with high energy accelerated ions followed by chemical removal (wet etching in alkaline solutions) of the damaged material along the ions trajectories polymeric nuclear track membranes with linear pores are fabricated [1]. The nuclear track membranes are characterized by the narrow distributions of their pores size. The pores diameter, which depends on the type and energy of accelerated ions, ranges in the hundreds of nanometers domain.

In many cases, for obtaining polymeric membranes suitable for a certain group of applications, it is required to change and/or improve their initial properties such as pores size, surface topography, wettability, transport properties, adhesion, biocompatibility, etc. Thus, other techniques than the fabrication ones are welcome, that enlarge the applications field. Mainly, physical and chemical methods for modification of polymeric material are in view. Such as, the plasma treatments are versatile, low cost, clean and easy applicable. Along the time a number of studies regarding the modification of polymeric membranes in different plasma discharge configurations and conditions (type of gas, pressure, power) were reported [2 - 7].

This paper presents results regarding the modification of poly(ethylene terephthalate) track membranes (PET TM) by radiofrequency (RF) plasma treatments. The effect of ammonia plasma generated in a parallel plate discharge configuration on the basic characteristics of the membranes, namely morphology, surface topography, chemical composition, wettability, and water permeability was studied.

2. Experimental

PET TM membranes with 0.2 and 0.4 μm pore size and 10 μm thickness were exposed to a RF plasma generated in ammonia, in a plasma reactor provided with a capacitively coupled parallel plate discharge configuration. The experimental set-up was described in detail previously [8]. Treatments with radiofrequency power in the range 20-80 W, at pressures of 13.3-133 Pa were performed.

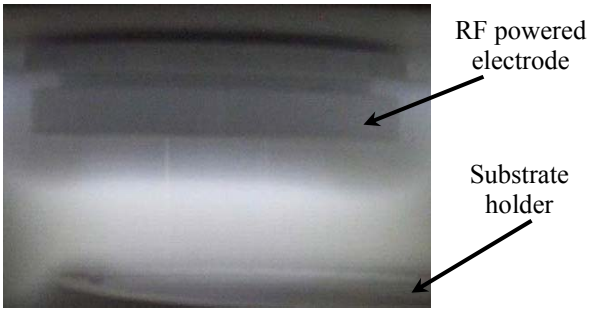

Fig. 1. Image of the discharge in ammonia during PET TM treatment (power 60W, pressure13.3 Pa).

An image of the discharge in ammonia for 60W power and 13.3 Pa pressure, showing how the membrane was positioned during the treatment is presented in Fig. 1. Only one side of the membrane was exposing to plasma.

The investigation of membrane characteristics before and after plasma treatment was carried out by a series of complementary techniques, as follows: Atomic Force

Microscopy (AFM, Q-Scope^{TM} Nomad^{TM}) for surface topography, microscopic goniometry for contact angle measurements, thickness electronic meter (Unit Tesa, Austria) for thickness measurements. In addition, the chemical composition at surface resulted from Electron Spectroscopy for Chemical Analysis (ESCA) spectra recorded with the spectrometer Riber SIA-100 provided with MAC-2 analyzer (MgK_a, 100 W, 15 kV, 20 mA); the position of peaks (the binding energy values) was calibrated against the C_{1s} standard peak (284.6 eV). Permeability modifications were studied by water filtration in an FMO-2 (Russian) installation at a pressure drop of $7*10^4$ Pa. Special precautions were not taken to avoid the sample contact with the open atmosphere prior to analyses.

3. Results and discussion

AFM images of PET TM surfaces, recorded after increased treatment durations in plasma are presented in Fig. 2 a-d, where the evolution of the topographical characteristics of the surface can be observed. In Figure 2a the surface of an untreated PET TM with 0.4 μm pore diameters looks flat and almost smooth, with well defined circular pore margins. After a short time (1 min) of ammonia plasma treatments at 60 W the surface remains flat but, on small scale, becomes rough (Figure 2 b), aspects characteristic to a etched surface. Further, at longer treatment times (5 min and 10 min, Figures 2c and 2d, respectively) the surface is less flat on large scale area, smoothes again and the pores margins are rounded, characteristic to a deposited surface. These images suggest that in ammonia plasma both etching and deposition may be possible: the surface etching is prominent first (Figure 2b), but the etching effects seem to be blurred later by a prevailing deposition process (Figures 2c, d). These results can be compared with the AFM studies on PET TM plasma treatments in air [8], when more spectacular changes of surface topography were observed, with large increase of surface roughness, and drastically changes of pore shape. One may conclude that ammonia plasma treatments are less aggressive then those in oxygen containing plasmas.

The results of thickness measurements performed on PET TM treated in ammonia plasma at different power values (20, 40, 60 and 80W), at a 13.3 Pa and 133 Pa discharge pressure, respectively are shown in Figure 3. Both decreasing and increasing of thickness were observed, depending on power and treatment time. The decrease of thickness is observed at low power (20 W), or for short treatment duration at high power (80 W). It is assigned to an etching process, leading to material removal from the membrane surface, supported by the AFM results. The increasing of membrane thickness is observed generally for long treatments times and high power plasmas (40, 60 W, and 80 W). The thickness increasing is a surprising result, because ammonia is a non polymerizable gas. The thickness increasing can only be explained by a re-polymerization process: the source of the precursor sustaining the deposition is the membrane itself, via the material removed by etching.

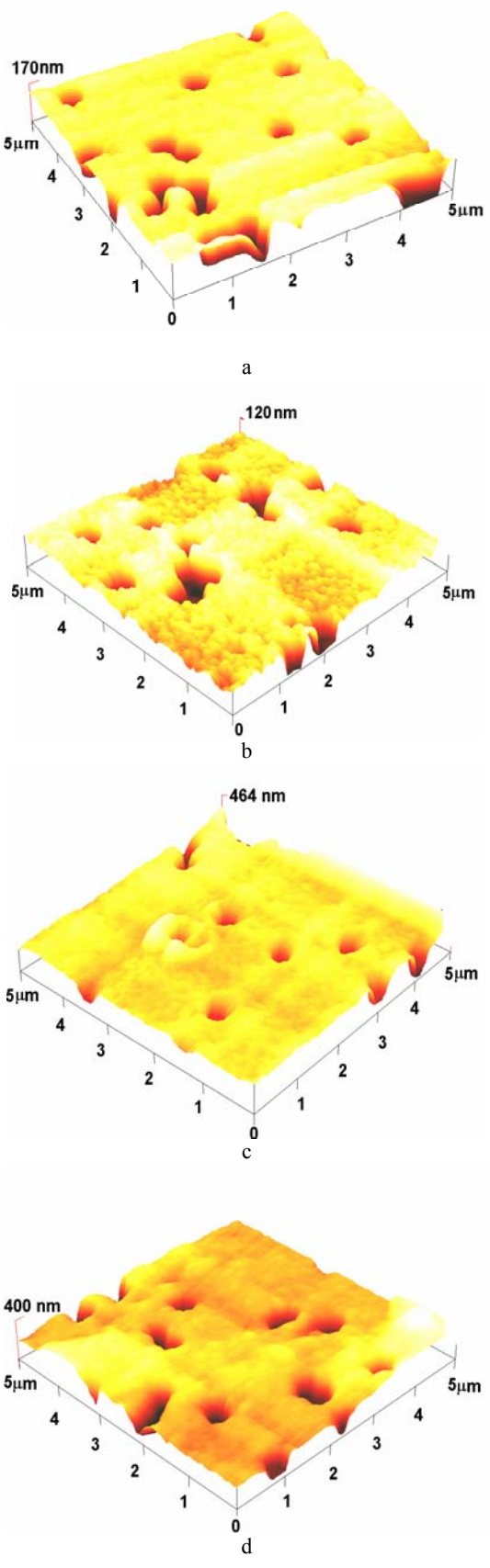

Fig. 2. AFM images of 0.4 μm pore diameter PET TM, illustrating the change of surface topography with the treatment (power 60W, pressure13.3 Pa) duration: a) untreated, b) 1 min c) 5 min, d) 10 min

The AFM and thickness measurements indicate that the ammonia treatment of PET TM lead to a complex phenomenon which involves both etching and re-deposition processes. It is known that during the process of pores fabrication by chemical etching, a reduction of the polymeric chains length occurs, the resulting fragments being dissolved in the alkali solution. At the end, a material with a lower molecular weight is formed at surface. Possible, this low molecular weight material, easier to be removed by plasma, is the source for re-deposition of a layer, presumable with a low density, over the more etching resistant crystalline phase of membrane.

The curves in Fig. 4 present the results of ESCA investigations of the plasma treated membranes. The curves were obtained from the O_{1s}, N_{1s} and C_{1s} peaks belonging to the respective species, which were identified in the spectra. They show the changes of the chemical composition at the membrane surface. The N_{1s}/C_{1s} and O_{1s}/C_{1s} ratios increase in the early treatment stage and reach a plateau with a slight tendency to decrease for long treatment times. The presence of N_{1s} peak proves that during the PET TM treatment in ammonia plasma, uptake of nitrogen with formation of nitrogen-carbon bonds occurs. The presence of O_{1s} peak is normal in the untreated membranes (oxygen is part of the ethylene terephthalate molecule), but its increase proves on further oxidation of the polymer surface. Most likely the oxidation appears when carrying the samples out in air, because is presumable than the abstraction of oxygen from the surface by H atoms and NH radicals is active during the plasma treatment. The stabilization of the surface chemical composition at long treatment duration points out again on re-deposition, indicating that for long treatment durations layers having similar compositions are formed on surface.

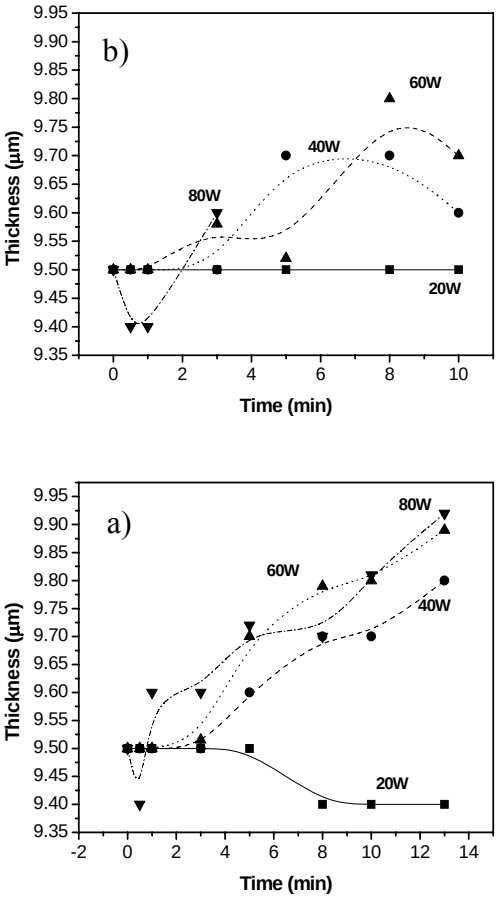

Fig. 3. The dependence of membrane thickness on the treatment power and time: a) pressure13.3 Pa, b) pressure 133 Pa.

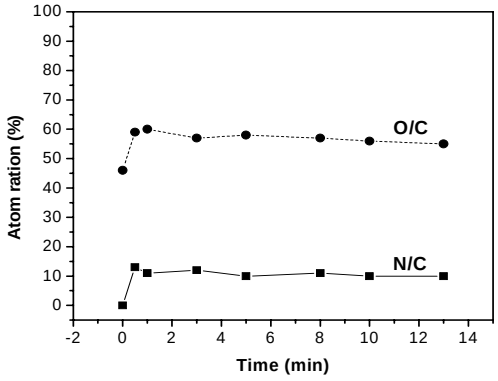

Fig. 4. The dependence of the relative content of atoms at surface on the treatment time (power 40 W, pressure 13.3 Pa).

The ESCA and thickness measurements corroborate with the contact angle measurements which show, as well, the stabilization of the surface for long treatment times [8]. The contact angle measurements indicated that 20 W and short time treatments increase the wettability, with the surface becoming more hydrophobic for longer treatments. The treatments conducted at high power and long time have led in all cases to surfaces more hydrophobic than the initial ones, pointing out again on the presence of a redeposited material with the same defined chemical nature.

Generally, the water permeability through porous media shows a dependence on the filtration time, with an initial value at the start of the process. For the 20 W treated PET TM the initial water permeability exhibits a rapid growth for short treatment times followed by stabilization with tendency to decrease for longer treatment times (Figure 5). This behaviour is related to the membrane etching, effective in changing its thickness (Fig. 3) and pore size and wettability, especially in the early stage of treatment. At higher discharge power (60 W, Fig. 5) one observes a gradual growth of the water permeability, reaching a plateau toward the long treatment time region. This corresponds to transport through membranes with redeposited layers and higher pores, layers which are gradually reconstructed at longer treatment times. As concerning the dependence of water permeability on the filtration time, this is presented in Fig. 6

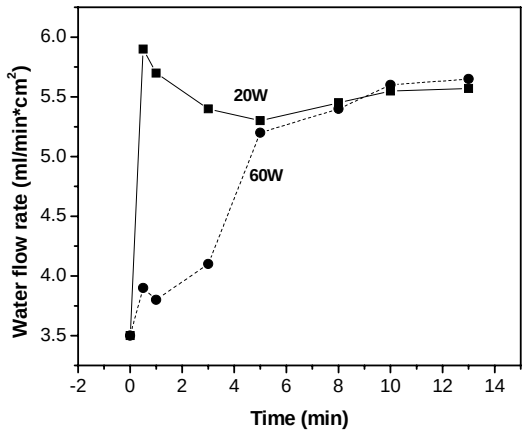

Fig. 5. Dependence of the initial water flow rate of PET TM on the treatment time, for 20 W and 60 W discharge powers (pressure 13.3 Pa).

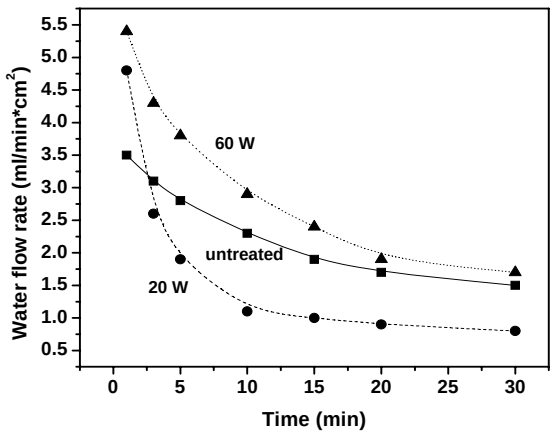

Fig. 6. Dependence of the water flow rate on the filtration time for untreated PET TM and membranes treated (time 5 min, pressure 13.3 Pa) at 20 W and 60 W.

for untreated PET membrane and for 5 minutes ammonia plasma treatment PET TM at 20W and 60W power values. During the filtration process the water permeability generally decreases. The decrease is slower for the membranes treated at higher power (60 W), for which a redeposited layer is expected to exist. Moreover, in this case the water permeability remains higher than for the untreated membranes, which outline that improved filtration performances can be obtained by plasma treatments.

4. Conclusions

The treatments of poly (ethylene terephthalate) nuclear track membranes in ammonia plasma affect the surface topography, causing roughening and enlargement of pores, modify the membranes thickness, and change the chemical nature of the uppermost surface layer. The AFM, thickness, ESCA and contact angle measurements indicate that these changes are realized via a mechanism including membrane etching and redeposition of the etched material, with reconstruction of a new layer at membrane surface. These processes depend on the applied power and the treatment time.

The transport properties of the treated membranes were also changed due to modification of membrane structure and surface chemical composition. Depending on the treatment parameters the water permeability may be improved compared to that of the initial membrane, which can lead to filtration systems with increased efficiency.

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