ON THE DYNAMICS OF THE TOP LAYER OF POLYSULFONE MEMBRANES DURING PLASMA TREATMENT

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ABSTRACT

Air plasma treatments of asymmetric polysulfone membranes (top layer: pore radius 200 nm, thickness 10 μm, porosity 10^{-4}) have been performed in a capacitively coupled RF discharge (experimental conditions: RF power W=10-40 watt, pressure p = 0.8-1.5 torr, exposure time t=1-30 minutes). The effects of treatments on the membranes, have been investigated by permeation of gases and liquids. Mass gravimetry, infrared absorption spectroscopy and contact angle measurements have been used to complete the information. The results indicate structural changes of membranes (regarding chemical composition, pores size, thickness of top layer) due to ablation and repolymerization of ablated material.

1. INTRODUCTION

A review of the possibilities to affect polymeric membrane properties by plasma action has been performed previously [1]. These possibilities refer to plasma polymerization of specific monomers, with reduction of pore's size, or simply plasma treatments in nonpolymer-forming gases. In the case of plasma treatments with nonpolymer-forming gases it was shown that membrane properties can be modified by etching the surface polymeric material [2] or by other processes as plasma polymerization of etched material.

We have performed radio-frequency (RF) plasma treatments of polysulfone membranes in air. The results indicate that in our experimental conditions, plasma treatment is associated with redeposition of ablated material as a thin layer on the membrane surface. This takes place in a competitive process between plasma ablation and polymerization.

2. EXPERIMENTAL

2.1 Membrane preparation

The samples submitted to treatments were asymmetric porous polysulfone membranes prepared by phase inversion. By this technique membranes consisting of a thin top layer (pore diameter d_1=0.24 μm) over a spongy support layer (thickness 0.7 mm) were formed in a single step.

2.2 Plasma treatment

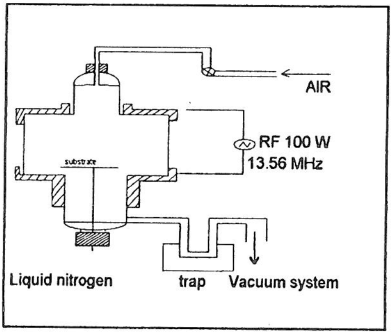

Fig. 1 The experimental set-up

The treatments were performed in a capacitively coupled planar RF discharge (13.56 MHz) in a cylindrical reactor having 9.5 cm internal diameter, 1000 cm^2 walls aria and a plasma volume of 1500 cm^3. The samples were placed on a metallic holder floating in the plasma. The experimental set up is presented in Fig. 1. The experimental conditions were: pressure value p=1 torr, RF power values W=10-50 watt, treatment duration 1-30 min.

2.3 Techniques of analysis

The mass variation of membranes, as effect of treatments, has been measured with a laboratory balance (precision 5 μg). The rate of mass change was subsequently calculated.

The permeation of gases was investigated by measuring the flow rates of a gas (nitrogen), due to a pressure gradient, between two compartments separated by a treated sample. The medium pressure over the membrane was in the range 1-100 torr. From these data the reduced permeabilities (gas flux / unit of surface * unit of differential pressure) have been calculated.

The flux of water was measured with a filtering cell (pressure range 1-5 bar). Using the measured values of the water flow, the hydrodynamic permeabilities (water flux/ unit of surface * unit of differential pressure) have been calculated.

The infrared spectra were obtained by a Specord 75 IR spectrophotometer in the range 4000-400 cm^{-1}.

The contact angle measurements were performed directly by measuring the contact angle of a water drop laying on the membrane surface with a microscope

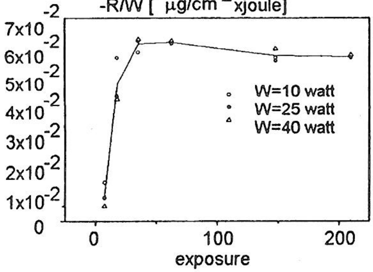

Fig. 2 Gravimetry results

3. RESULTS AND DISCUSSION

During the treatments a continuous decrease of mass of samples is observed. The more appropriate parameter to describe the mass loss process was found to be W*t (RF power times treatment duration), named below as exposure. This is shown in Fig. 2 where the points corresponding to various power and time values are laying on the same curve.

The use of exposure is beneficial for representing the air permeation results too. This can be seen in Fig. 3 where the dependencies of gas reduced permeability on W*t are shown. In Fig.4 the water flux versus exposure is shown.

If the gravimetry and permeation results are compared to each other, it is observed that in all cases the treatments at low exposure values are associated

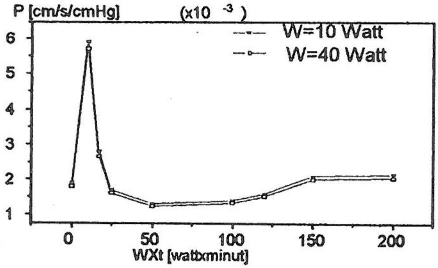

Fig. 3 Air permeability

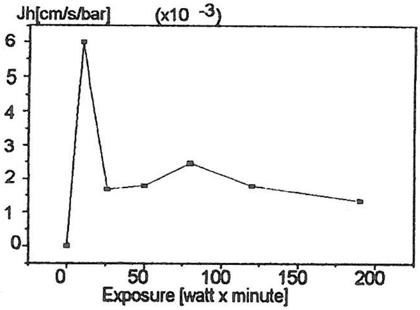

Fig. 4 Hydrodynamic flux

with strong variations in mass loss rate. On the other side permeation rates (air and water) as well as treatments at high exposure values are associated with stable values of mentioned parameters (figs. 2, 3, 4).

The IR spectra have been obtained for two situations: a) pellets of polysulfone material mixed with prepowdered KBr (1 mg polysulfone / 50 mg KBr) and b) a film deposited on a KBr support placed near the membrane during plasma treatment. The spectra are presented in Fig. 5. As can be noticed in the case a) the spectrum presents a lot of overlapped maxima which are difficult to be unraveled. However, according to the references [3] most of them can be ascribed to the deformation and ring vibrations of the aromatic groups. The peak at 1153 cm-1 is ascribed to the symmetrical stretching of the sulfonyl group -SO2-. One observes from the spectrum (case b) that the deposited film is chemically different from the initial polysulfone material. It shows only a few isolated maxima which most likely due to some chemical radicals containing S atoms originating from the initial polysulfone material (maxima at 480, 620-750 and 1116cm-1 ascribed to the vibrations of S-S , C-S and S=O bonds).The contact angle measurements show a decrease of values meaning the increase of

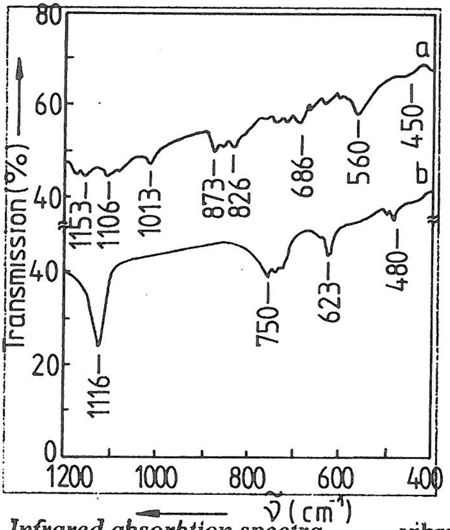

Fig. 5 Infrared absorbtion spectra

wettability by comparison with the untreated membranes (Fig. 5). However these results are difficult to be interpreted because the chemical change of surface during the treatment is accompanied by changes of rugosity and pore dimensions suggested also by an important hysteresis effect (not displayed in the Fig. 5).

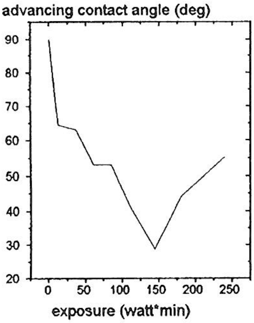

Fig. 6 The contact angle

All these results are indicating that during the treatment the top layer of polysulfone membrane is modified, perhaps destroyed by plasma ablation, followed by the reconstruction of a structure with different properties. The decrease of permeation rates at high exposure values suggests that a new top layer is rebuilt probably by repolymerization of ablated material.

The dependence of gas permeation rate on the mean pressure over the membrane allows the pore diameter to be calculated using the method described in [4]. This method gives the average pore diameter for homogenous membranes. In the case of asymmetric membranes, consisting of layers with highly different permeabilities, one obtains by use of this method the mean pore diameter of the layer with lowest permeability (the top layer). The results of the calculations are shown in Fig. 7. This parameter displays strong variations in the early stage of treatment period that are followed by a large plateau.

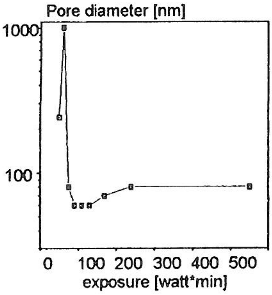

Fig. 7 Pore diameter

By assuming that the maxima of curves from Figs. 3, 4, correspond to the complete top layer destruction by plasma ablation then the maximum observed in the dependence of pore diameter on exposure (Fig. 7) represents the support pore diameter. The density of pores for the membrane, considered in this stage homogeneous, has been computed. Subsequently, by applying the model of two series resistances [4] the thickness of the top layer was calculated for different exposure values.(Fig. 8).

All these results prove the existence of structural changes of polysulfone asymmetric membranes during plasma treatments. The first stage of process is

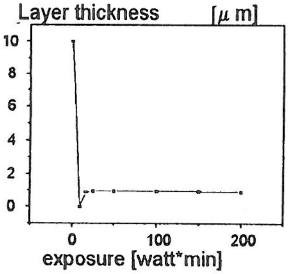

Fig. 8 Layer thickness

associated with an increase of pores radius and decrease of the thickness of active layer due to ablation processes. So, it seems that in the early stage of treatments strong variations in membrane characteristics are related to the top layer destruction. Subsequently a new top layer, with different properties is rebuilt and remains stable even when the membrane is loosing continuously its mass.

CONCLUSIONS

The permeation rate measurements indicate that, at least three stages of treatments exists: *i*) a stage corresponding to the destruction of top layer of the porous structure (low W*t, 0-10 watt·min), *ii*) an intermediate stage corresponding to rebuilding of a new top layer (moderate W*t, 10-100 watt·min), *iii*) a subsequent stage corresponding to a stabilized new top layer (pore radius 20 nm, thickness 0.8 μm) for W*t larger than 100 watt·min.

The other results (IR spectroscopy, values of the contact angle) confirm that the new top layer have different properties (regarding aspect, chemical composition) in comparison with the initial one.

The described dynamics of the top layer can be explained by the competition between ablation and synthesis of the layer by plasma polymerization of ablated material.

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