



Synthesis and characterization of porous composite membranes with hydrophilic/hydrophobic sides



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ABSTRACT

Hydrophilic/hydrophobic polymer composite membranes have known a growth of interest in various separation processes, such as desalination of water, pervaporation, reverse osmosis, gas separation, micro- and nanofiltration. In this work we obtained porous hydrophilic/hydrophobic composite membranes by RF magnetron sputtering deposition of polytetrafluoroethylene-like (PTFE) thin films on one side of a polyethylene terephthalate (PET) track etched membrane, used as a porous substrate. The results show that the obtained PTFE material containing various CF_x bonds is present both on the membrane surface and in its pores as a thin film, without completely covering of the pores in-depth. We proved that the membrane presents one hydrophilic side (PET) and one hydrophobic side (PTFE), with flowing characteristics (tested for gas) maintained even in the situation when the pores seems completely covered with PTFE material on the surface.

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1. Introduction

One of the most serious problems of the actual society is the fresh water shortage which seems to become critical by 2020 [1]. Most of the proposed solutions for solving this issue are based on separation processes (electrolysis, evaporation, distillation). In particular those based on polymeric membranes benefit of advantages regarding low cost, energy efficiency, and space saving, recommending them for various applications [2–4]. Membrane separation systems based on reverse osmosis and nanofiltration have been widely used for sea water desalination, wastewater treatment and pharmaceutical industry [5,6]. Nevertheless, they present important drawbacks related to the low filtration rate, high operation pressure, and fouling due to both inorganic sediments and biofilm formation. Another promising technology for such applications is based on Membrane Distillation (MD) process. This separation process has many attractive characteristics as compared to those mentioned above, such as high rejection rate of ions in solution, low operation temperature and pressure, and higher permeate quality. Due to these operational parameters, the process is a cost effective one, and requires less demands for the membrane properties [7]. This allows the use of less expensive materials such as polymers, which solves as well the usual problems related to corrosion of the active element. Another important advantage is the relatively larger membrane pores which prevents the pores blocking upon biofilm formation.

Among the Membrane Distillation processes, direct contact membrane distillation (DCMD) present the simplest configuration: the hot solution (feed) is in direct contact with the hot membrane surface, where the evaporation takes place [8]; the key parameter is the pressure difference which moves the vapors from the hot feed side to the cold permeate side, and they condense inside the membrane pores [4]. Therefore, the retention of gas phase inside the membrane pores in DCMD process is an essential condition for insuring a continuous process. In order to prevent the wetting of the pore channels, the membranes used in DCMD process should be hydrophobic. The most popular polymeric membranes used in these processes are polyethersulfone [9], polypropylene, polytetrafluoroethylene (PTFE) [10] and polyvinylidene fluoride porous membranes [11,12]. At the same time, these hydrophobic materials present high resistance to mass transfer and high thermal conductivity which allows the heat loss across the membrane [4], limiting the DCMD process. On the other hand, hydrophilic materials generally possess higher thermal resistance than hydrophobic ones [13]. Therefore, the use of bulk hydrophilic porous materials in combination with an efficient hydrophobization process of the surface is an open challenge for distillation membranes with improved performances. The hydrophobic covering of the hydrophilic membrane surface can be realized by several methods implying plasma utilization, such as surface functionalization by fluorine containing radicals [14], coating and grafting [15–17]. While the surface functionalization present the drawback of hydrophilic recovery, the plasma coating [18] seems an efficient alternative for synthesis of porous composite membranes with hydrophobic component starting from hydrophilic ones [19]. This approach has been

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investigated by plasma polymerization of fluorine containing precursors, such as vinyltrimethylsilicon/carbon tetrafluoride and octafluorocyclobutane [20].

In the present work, we present an alternative approach to prepare hydrophobic/hydrophilic composite membranes. We start from a hydrophilic PET porous support with pores generated upon ion irradiation, the so-called PET-track membranes, PET TM, on which we deposit a hydrophobic layer of PTFE material. Such track-etched membranes were employed in various membrane separation processes like pervaporation, reverse osmosis, nanofiltration and microfiltration and gas separation [21–24]. Magnetron sputtering technique is used here for covering of PET-TM hydrophilic membrane surface by using a polytetrafluorethylene target. The main purposes are the synthesis and investigation of the resulted composite membranes in respect to hydrophobic PTFE layer properties, thickness, morphology, topography, chemical composition, permeation and wettability.

2. Experimental

2.1. Materials and methods

Track etched polyethylene terephthalate membranes (PET TM) of 10.0 μm thickness with an effective pore diameter of 95 nm and pore density of $1.3 \times 10^9 \text{ cm}^{-2}$ were used as supports in this study. The PET TM membranes were prepared by heavy ions bombardment of a PET film with krypton accelerated at an energy of $\sim 3 \text{ MeV/nucleon}$ in a U400 cyclotron, followed by physico-chemical treatment in an alkali solution with a surface-active addition [25]. The membrane samples were cut in circular form with diameter of 10 cm prior the experiments. Flat silicon substrates were used as well in order to evaluate the deposition rate of the process and the surface properties of the PTFE films. The magnetron targets were prepared from PTFE rod (Goodfellow) machined according to the technical specifications of the magnetron sputtering source (diameter: 25 mm, thickness: 3.18 mm). They were cleaned by ultra-sonication in ethanol before using and submitted to a presputtering process prior used for deposition in order to clean the surface.

PTFE layers deposition on the PET TM support was conducted in a spherical stainless steel vacuum chamber evacuated by a turbomolecular/rotary pumping system down to a base pressure of $1 \times 10^{-2} \text{ Pa}$. The pressure in the chamber was monitored by a Pfeiffer gauge and the gas flow rates are controlled by electronic mass flow controllers (Bronkhorst Instruments). The chamber is equipped with a magnetron sputtering source (Kurt J. Lesker) and a second capacitively-coupled plasma source, as well with other ports for various plasma diagnostic systems, as shown in Fig. 1.

The magnetron source was mounted at 45° and 6 cm distance in respect to the substrate holder, which serves also as grounded electrode. The substrate holder is rotating during the deposition in order to insure thickness uniformity over large area. The PTFE target mounted in the magnetron is sputtered by igniting a discharge in argon flow (100 sccm) at RF power of 50 W and working on a pressure of $6.8 \times 10^{-1} \text{ Pa}$. In order to insure various thicknesses of the PTFE layers, the deposition time was varied from 10 to 35 min. The second plasma source has a shower-like electrode through which the gases are injected. In the present experiment, it was used only for cleaning the carbon-based residuals from the chamber walls, by a low pressure oxygen discharge ($7.9 \times 10^{-1} \text{ Pa}$, 50 W).

2.2. Membranes characterization techniques

Atomic Force Microscopy (AFM) technique was used to analyze the surface topography of the initial and PTFE-like coated membranes. AFM images were recorded with a Park Systems XE-100 microscope operating in non-contact mode, for various areas; herein we present data recorded over areas of $5 \times 5 \mu\text{m}^2$. Scanning Electron Microscopy (SEM)

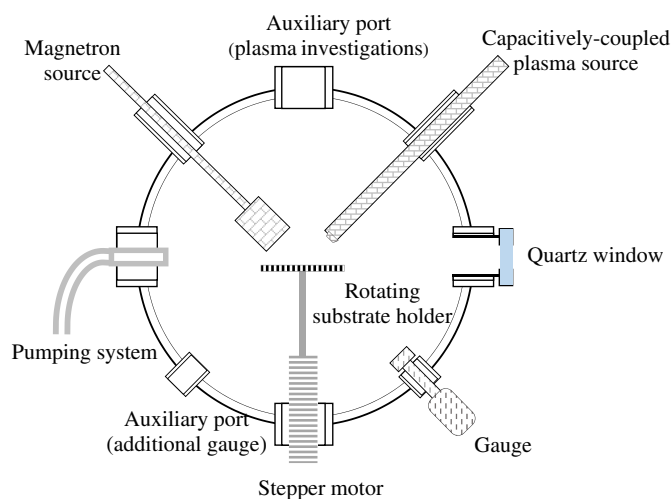


Fig. 1. Schematic of the experimental set-up used for the synthesis hydrophobic/hydrophilic composite membranes.

technique was used to investigate the samples microstructure, and to evaluate the modification of pores geometry upon plasma deposition. SEM measurements were performed on a Hitachi SU-8020 (Hitachi High-Technologies, Japan) ultra-high resolution microscope operating at low accelerating voltage (3 kV) in order to avoid damaging the polymeric samples. Before analyses, the composite membranes samples were covered with a thin gold layer deposited by vacuum thermal evaporation to prevent charges accumulation.

Chemical bonds of the deposited PTFE-like layer were investigated using a JASCO 6300 FTIR spectrometer. The spectra of film deposited on Si were recorded in transmission mode in the range $400\text{--}4000 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} and an average number of 128 scanning, while that of PTFE target was performed with attenuated total reflectance module by using the same measuring parameters. X-ray Photoelectron Spectroscopy (XPS) analyses were performed on a K-Alpha Thermo Scientific (USA) spectrometer equipped with a hemispherical analyzer. For the excitation of photoelectrons, X-ray radiation of an aluminum anode (AlK_{α} , 1486.6 eV) generated at a tube voltage of 12 kV and current emission of 3 mA was used. Survey spectra were recorded to determine the elemental composition of the porous composite membrane surface, while high resolution spectra for C1s, F1s, O1s and N1s binding energy regions were measured in order to evaluate the chemical bonding of the material.

The gas-dynamical pore diameter (effective pore diameters) of the initial membranes and of the composite membranes were determined from the gas permeation tests, using air as a standard gas. The air flux passed through the initial and coated membranes, which defines the membrane permeability to gas, was measured through an area of 1 cm^2 of the membrane at a pressure drop of $2 \times 10^4 \text{ Pa}$ by using a float flowmeter. The effective pore diameter was calculated with an error of 3% using the Knudsen formula [26], which describes the free molecular flow of the gas through the pores. Such approximation is valid when the pores have diameters below 200 nm, which fits the conditions in the present paper. The amount of the polymer deposited on the membrane was found by gravimetry by measuring the mass gain of the sample upon deposition of PTFE layers.

Water contact angles measurements were carried out at room temperature by a contact angle goniometer CAM 101 (KSV Instrument Ltd) equipped with a CCD camera. Distilled water droplets of $2 \mu\text{L}$ volume each were released manually on the membrane surface for contact angle measurements; each reported value was obtained upon averaging 20 measurements.

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