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Preparation of PET track-etched membranes for membrane distillation by photo-induced graft polymerization

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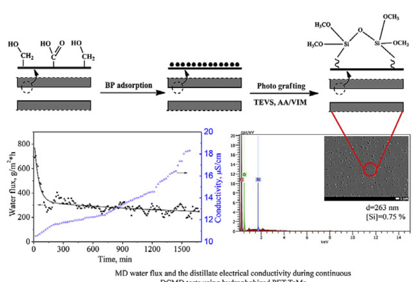
HIGHLIGHTS

- PET membranes were hydrophobized by photografting of triethoxyvinylsilane.
- Membranes were characterized by FTIR, SEM-EDX methods.
- The modified membrane exhibited improved contact angle and liquid entry pressure.
- The modified track-etched membranes can be used for water desalination via DCMD.

GRAPHICAL ABSTRACT



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ABSTRACT

New type of membranes with appropriate mechanical strength, thermal and chemical stability, high efficiency and hydrophobic surface are requisite for the development of membrane distillation (MD) applications. In this study hydrophobic track-etched membranes (TeMs) with pore size of 180 nm and thickness of 12 μm based on polyethylene terephthalate (PET) were prepared using photo-induced graft polymerization of silicon monomer such as triethoxyvinylsilane leading to increasing of contact angle up to 104°. The effect of monomers and additives concentration, time of grafting and aging on the surface morphology, pore size and contact angle were investigated by Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX) and goniometric analysis. The performance of the membranes was evaluated using direct contact membrane distillation (DCMD) process. The results show maximum permeate flux of 700 $g/m^2 \cdot h$ and 180 g/m^2 h (dT = 75 °C) during 24 h saline solution operation (15 and 30 g/l respectively) with efficiency up to 99.3%.

1. Introduction

Membrane Distillation (MD) is one of the membrane separation processes known for more than fifty years and still needs to be improved for its successful application. The main problems of MD are related to high energy consumption, high energetic and

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economic costs, the lack of membranes and modules for MD that can lead to flawless operation without simultaneous wetting or fouling of the membrane. The efficiency of the MD mostly depends on the type and characteristics of the membrane used, which is well studied in a numerous papers devoted with membranes suitable for MD [1–12]. For such application, membranes should have high porosity and hydrophobicity, low heat transfer flux and pore tortuosity, large pore size, uniform pore size distribution and optimal thickness, satisfactory thermal and chemical stability (in the case of chemicals separation) [12–15].

High hydrophobicity prevents wetting of membranes and provides better separation. High porosity, pore size and small thickness lead to high heat flux, which decreases with thickness rising. There is a conflict between the requirements of high mass transfer of thinner membranes and low heat transfer through the thicker membranes [16,17]. Nowadays, the most common types of membranes used in MD are hollow fiber membranes and flat sheet membranes of organic and inorganic origin. Although the hollow fiber membranes have a higher surface area, when flat sheet membranes have higher heat flux due to less thickness and less pore tortuous [1,15].

The most popular polymer materials for the production of membranes for MD are polytetrafluoroethylene, polypropylene and polyvinylidene fluoride since they have low surface energy [12,18–21]. However, their high cost and difficulties in module sealing are the major drawbacks. Moreover, other polymers such as polyesters, polyethylene, cellulose were tested in MD after coating with hydrophobic polymers, though they do not meet all the requirements for MD [13]. Thus, the search for new materials and membrane types suitable for MD is an urgent task.

In this work, track-etched membranes (TeMs) were tested in MD process. Astana branch of the Institute of Nuclear Physics has all appropriate technological base to design on a large scale of TeMs with well characteristics [22–24]. The main disadvantage of TeMs is low porosity (5–30%), along with that TeMs have calibrated pore size and excellent pore size distribution. Their pores are cylindrical shape without any tortuosity. Moreover, TeMs usually have a thickness of 5–24 μm [25–28]. Characteristics reviewed above make TeMs perspective for MD application, especially for accurate separation or concentration [29] of different liquids.

Toward this goal, TeMs based on poly(ethylene terephthalate) (PET) have been chosen as objects of research due to its appropriate chemical, physical, mechanical properties and convenient method of preparation. However, PET is a semi-hydrophobic polymer and for successful application in MD process its modification is required.

One of the most frequently used methods for membrane hydrophobization is covering their surface by hydrophobic polymer layer using different techniques, such as plasma treatment, coating or graft polymerization [27,30–35]. Herewith, two tasks can be solved simultaneously: changing the surface energy and controllably reducing the average pore diameter to the optimum value. Polysiloxanes as well as fluorine-containing polymers and copolymers with a hydrophobic nature are the most often used ones [15]. The difficulties in modification consist in the formation of a strong bond between membrane surface and hydrophobic polymers leading to hydrophobic stability in liquids over time.

In our paper we consider a simple method of photo-induced graft polymerization of silicon compounds on PET TeMs for successful application of such kind of membranes for desalination process.

2. Experimental part

2.1. Chemicals

Triethoxyvinylsilane (TEVS), acrylic acid (AA), N-vinylimidazole (VIM), benzophenone, sodium hydroxide, sodium chloride, N,N-dimethylformamide and dichloroethane were purchased from Sigma-Aldrich. Monomers were cleaned from inhibitors by passing through alumina oxide column. Acrylic acid was distilled under vacuum. Deionized water (18.2 MΩ) obtained from four-stage water purification system Akvilon D-301 was used in all the experiments.

2.2. Preparation of the membrane and their modification

TeMs were prepared in two-step process. 12 μm thick PET films («Mitsubishi Polyester Film», Germany) were irradiated using the DC-60 accelerator (Astana branch of the Institute of Nuclear Physics in Kazakhstan) by $^{84}Kr^{15+}$ ions with an energy of 1.75 MeV/nucleon and ion fluence of $4.3 \cdot 10^7$ ion/cm^2. Then membranes with different pore diameters were obtained by mean of chemical treatment in 2.2 M NaOH at 85 °C at a certain time. Prepared membranes were dried and kept between paper sheets in the air.

Hydrophobization of PET TeMs was achieved by photoinduced graft polymerization of triethoxyvinylsilane. PET TeMs (10 × 15 cm) were ultrasonicated in water and acetone for extraction any impurities of organic and inorganic origin. Then samples were kept in N,N-dimethylformamide 5% benzophenone solution according to the procedure described in Ref. [36], washed in ethanol and dried. After that, samples were put into dichloroethane solutions of the monomer with concentrations from 5 to 30%. N-vinylimidazole or acrylic acid was also added to solutions in an amount of 0.3–6.6% acting as “initiator” for the grafting process of silicon monomers. The reaction mixture was purged with argon to remove dissolved oxygen and tightly closed with a polyethylene film. The UV-irradiation was carried out for 15–120 min under UV lamp OSRAM Ultra Vitalux E27 (UVA - 315–400 nm - W = 13.6 W, UVB - 280–315 nm - W = 3.0 W). The samples were washed first in dichloroethane and then in hot water to remove all ungrafted homopolymer, dried at 50 °C and weighed to determine the degree of grafting.

2.3. Membrane characterization

FTIR spectra were recorded to study chemical properties on Agilent Technologies Cary 600 Series FTIR Spectrometer with Single Reflection Diamond ATR accessory (GladiATR, PIKE). Measurements were taken in the range of 400–4000 cm^{-1}. All spectra (32 scans at 4.0 cm^{-1} resolution) were recorded at a room temperature. Spectra analysis was conducted by using Agilent Resolution Pro.

JEOL JSM-7500F scanning electron microscope (SEM) was used for characterization of pore diameters and morphology before and after PET TeMs modification. EDX analysis was performed on Hitachi TM 3030 with microanalysis system Bruker XFlash MIN SVE at 15 kV.

The effective pore sizes of inner diameter of pores were also estimated by gas permeability.

Water contact angle (CA) of the samples was evaluated using Digital Microscope 1000× magnification at a room temperature. CA was evaluated using static drop method. Drop volumes of deionized water were 15 μL and the average CA value was obtained by measuring the same sample at five different positions. CA was evaluated using a goniometric method based on dimensions of the drop by equation (1): θ

$$tg\theta = \frac{2h \cdot r}{r^2 - h^2} \quad (1)$$

where, θ - contact angle (°), r - the radius of contact area of the drop with surface (mm), h - drop height (mm).

Liquid Entry Pressure (LEP) was evaluated using deionized water