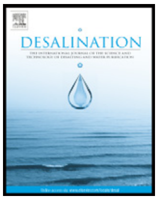
Desalination 289 (2012) 72–80

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



PES/SPAES blend membranes for nanofiltration: The effects of sulfonic acid groups and thermal treatment

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ARTICLE INFO

Article history:
Received 10 August 2011
Received in revised form 28 November 2011
Accepted 12 January 2012
Available online 8 February 2012

Keywords:
Sulfonated polymer
Blend membrane
Salt rejection
Charge

ABSTRACT

Polyethersulfone (PES)/sulfonated poly(arylene ether sulfone) (SPAES) blend membranes were prepared using a phase separation method. The miscibility of the PES/SPAES blend solution was confirmed through a differential scanning calorimetry (DSC) and the membranes containing a maximum of 3 wt.% of SPAES were selected for studying the effect of the sulfonic acid groups on the membrane performance. The increase of the solution viscosity through the addition of SPAES strongly affected the thickness of the top layer. The thermal treatment of the blend membranes caused the densification of the skin layer and reduced the pore sizes on the top layer. The changes on the membrane surface depending on the SPAES concentration and heating temperature were observed using an atomic force microscope (AFM). The roughness and contact angle decreased with an increase in the SPAES concentration in the membranes, while increases in the heating temperature increased the roughness and contact angle through membrane shrinkage. The increase of the SPAES concentration and heating temperature resulted in a decrease of the water permeability but a higher salt rejection. While the salt rejection gradually increased with the increase of the SPAES concentration, the thermal treatment only significantly affected the blend membrane with a high SPAES concentration.

1. Introduction

PES is an attractive membrane material for nanofiltration due to its excellent chemical, thermal and mechanical properties. However, the relatively hydrophobic character of PES results in membrane fouling. Membrane fouling caused by the adsorption of nonpolar solutes, hydrophobic particles or bacteria results in a higher energy demand, shorter membrane lifetime, and unpredictable separation performance [1]. Therefore, numerous methods to improve the hydrophilicity of materials have been developed such as bulk modification, surface modification, and polymer blending.

The introduction of ionic groups into membranes offers increasing hydrophilicity and charge effects that are expected to exclude solutes or colloids bearing the same charge sign, resulting in lower membrane fouling [2]. Much research regarding hydrophilic modification has been reported to enhance water flux and salt rejection [3–5]. Bowen et al. prepared membranes by blending polyetherimide (PEI) and sulfonated poly(ether ether ketone)(SPEEK). The addition of SPEEK improved the hydrophilic properties of the membrane, which led to an increase in the water permeability and a higher salt rejection [3]. Li et al. also applied polysulfone (PSf)/SPEEK blend membranes in the separation of low molecular weight dyes from alcohol based feeds. The addition of SPEEK leads to a more open membrane structure and consequently higher solvent fluxes. Due to the Donnan exclusion, the blend membranes showed the best retention for solutes with the same charge as the polyelectrolyte [4]. Different PSf were sulfonated in order to examine the performance for nanofiltration by Blanco et al.; they found that the higher sulfonation degree enhanced the rejection of nanosized solutes [5].

Blending hydrophobic polymers with sulfonated polymers during the casting solution preparation is a simple and effective method of creating charge throughout a membrane [4,6]. Sulfonated poly(arylene ether) sulfone (SPAES) exhibits high thermal and mechanical stability and excellent miscibility with PES. In this study, charged membranes prepared via blending SPAES and PES were used to investigate the effect of the blended polymers on water permeability as well as salt rejection. The blend membranes with an asymmetric structure were prepared by phase inversion method. Furthermore, various heating temperatures were applied in order to adjust the pore size of the membranes. The changes of the surface structure, roughness, and cross-section of the membranes were observed with reference to the SPAES content and heating temperatures.

2. Experimental

2.1. Materials

Sumika excel PES 4800G grade was purchased from Sumitomo Chemical (Japan) and used after drying in an oven at 100 °C for 12 h. Polyethylene glycol (PEG) Mw 10,000 was used as a pore-forming

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doi:10.1016/j.desal.2012.01.012

additive and purchased from Merck (Germany). The 4,4′-Dichlorodiphenylsulfone (DCDPS) and 4,4′-biphenol (BP) were used as the aromatic halide and diol, respectively, and were purchased from Tokyo Kasei (Tokyo, Japan); they were recrystallized from isopropyl alcohol (IPA) and dried in a vacuum oven for a minimum of 12 h at 120 °C. The DCDPS was converted to 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS; yield: 91.4%) using fuming sulfuric acid (28% free SO_3; Aldrich, USA). Sodium chloride (NaCl), sodium hydroxide (NaOH), toluene ($C_6H_5CH_3$), potassium carbonate (K_2CO_3), and dimethyl acetamide (DMAc) were obtained from Aldrich (USA) and were used as received. N-methylpyrrolidinonoe (NMP; Daejeong Chemical, Korea) was employed as a solvent for the membrane preparation.

2.2. Preparation of the PES/SPAES blend membranes

The SPAES was synthesized using direct copolymerization of sodium-salted SDCDPS, DCDPS, and BP via previously reported methods [7–9]. The degree of sulfonation of the prepared SPAES was controlled to 50% and its inherent viscosity was approximately 1.5 dL/g.

The SPAES and PES were dissolved in NMP to prepare 20, 23, and 25 wt.% casting solutions. Each solution contained 0, 1, 2, and 3 wt.% of SPAES based on the total solution. The content of PEG was fixed to 5 wt.% in all polymer solution. The blend membranes are referred to as $\#_1$–$\#_2$ herein, where $\#_1$ and $\#_2$ indicate the total polymer concentration and SPAES concentration in the solutions, respectively. For example, the 23-1 sample represents a 23 wt.% PES/SPAES solution containing 1 wt.% SPAES.

The casting solution was poured onto a clean glass plate at room temperature and it was automatically cast on a glass plate using a casting knife film applicator (Elcometer, England) and an auto bar coater (Gist Co. Ltd., Korea) with a membrane thickness of approximately 150 μm. The casting speed was controlled to 50 mm/s. The glass plate with the cast film was immersed in a water bath after a retention time of 10 s. A thin polymeric membrane film was separated from the glass after few minutes of immersion in the water. The membranes were washed in a water bath for 24 h and then all residual additives and solvents were completely removed through immersion in a methanol bath for 12 h using the solvent-exchange method. In order to evaluate the thermal effect on the membrane surface morphology and permeation and separation properties, the membranes were dried at room temperature, 80 °C and 150 °C for 2 h and some samples were stored in the water bath without drying.

2.3. Characterization

The polymer solution viscosity was measured using a viscometer (Brookfiled HBDV-1, USA). The miscibility of the PES and SPAES was confirmed using thermogravimetric analyzer (TGA; TGA Q50, TA Instruments, USA) at a heating rate of 20 °C/min. The changes in the glass transition temperature (Tg) depending on the concentration of SPAES were evaluated using a DSC (DSC Q20, TA Instruments, USA) at a heating rate of 10 °C/min. The cross-section and surface morphology of the membranes were observed using a field emission scanning electron microscopy (FE-SEM, Philips XL30 S FEG, Netherlands). The specimens were prepared by fracturing the membranes in liquid nitrogen. The samples were placed on a mount and then sputter coated with gold. The compositions of the specimen's cross section were analyzed using an electron probe microanalyzer (EPMA; Jeol, JXA-8100, Japan) with a wavelength dispersive spectrometer (WDS). A non-contact atomic force microscopy (AFM) was performed with a scanning probe microscope (XE-100, PSIA, USA). The cantilever of the SSS-NCH was made out of Si with a spring constant of 42 N/m and a guaranteed tip radius of curvature is less than 5 nm. The roughness was measured on a scan area of 100 nm × 100 nm. The root-mean-squared (RMS) roughness was calculated after flattening. The dynamic contact angles of the membranes were measured using the Wilhelmy plate technique (Sigma 70, KSV Co., Finland). The dipping liquid used was double purified water. In this way the dynamic contact angle of the membranes based on the SPAES concentration and thermal treatment were determined. The basic equation for the Wilhelmy plate method is:

$$F = mg + P\gamma_{LV}\cos\theta - F_b, \tag{1}$$

where F is the total force, m is the plate mass, g is the acceleration of gravity, F_b is the buoyancy force, P is the membrane area, and γ_{LV} is the surface tension of the double purified water. Filtration experiments were performed at 25 °C in a Teflon cross-flow cell (CF042, Sterlitech Co., USA) using a flat sheet membrane with an effective surface area of 33.15 cm^2. The operating pressure was fixed at 4 bars. Sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$) solution with a concentration of 1000 ppm was used as the feed solution. The permeation cell was allowed to equilibrate for at least 30 min. The water permeabilities were expressed as $L/(m^2 \cdot h \cdot bar)$. The salt concentration in the permeate was determined using a conductivity meter (HQ 14 d portable conductivity meter, HACH, USA). The salt rejection (R) was calculated using the following equation:

$$R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100, \tag{2}$$

where C_{feed} and $C_{permeate}$ are the concentration of the feed solution and permeate solution respectively. The schematic drawing of the nanofiltration test apparatus is shown in Fig. 1.

3. Results and discussion

3.1. Miscibility of the PES/SPAES

Casting solutions containing different PES/SPAES compositions were prepared for the membrane fabrications. The effect of the SPAES concentration on the solution viscosity was examined using a viscometer. When the SPAES concentration increased from 0 to 4 wt.% of total solution, the solution viscosity increased greatly from 5800 to 12,200 cP due to the high viscosity of SPAES. This increasing viscosity affects the membrane morphologies and permeation properties, independent of the charge effect of SPAES. The viscosity changes depending on the SPAES concentration and are shown in Fig. 2.

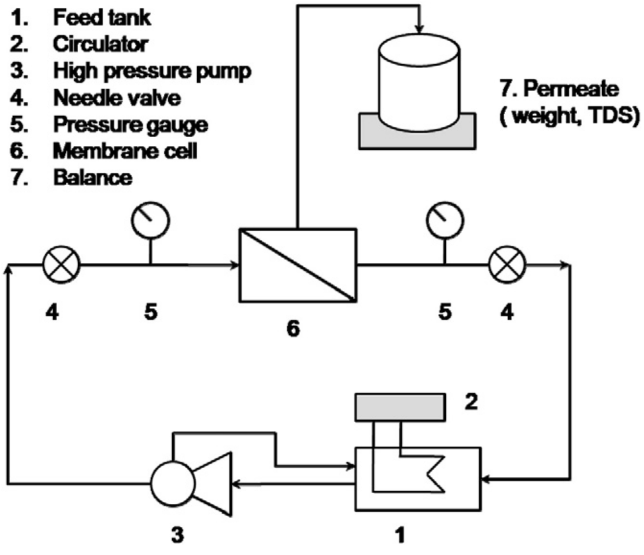

Fig. 1. Schematic drawing of a flat sheet membrane test apparatus.