Applied Surface Science 256 (2010) 1825–1831

Contents lists available at ScienceDirect

Applied Surface Science

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

The influence of sulfonated polyethersulfone (SPES) on surface nano-morphology and performance of polyethersulfone (PES) membrane

Ahmad Rahimpour [a,*], Sayed Siavash Madaeni [b], Shahla Ghorbani [c], Abbas Shockravi [c], Yaghoub Mansourpanah [d]

[a] *Nanobiotechnology Research Laboratory, Faculty of Chemical Engineering, Babol University of Technology, Shariati Street, Babol, Iran*
[b] *Membrane Research Center, Department of Chemical Engineering, Razi University, Kermanshah, Iran*
[c] *Faculty of Chemistry, Teacher Training University, Tehran, Iran*
[d] *Department of Chemistry, Faculty of Science, Lorestan University, Khorramabad, Iran*

ARTICLE INFO

Article history:
Received 28 June 2009
Received in revised form 6 October 2009
Accepted 7 October 2009
Available online 14 October 2009

Keywords:
Polyethersulfone
Sulfonated polyethersulfone
Membrane preparation
Hydrophilic surface

ABSTRACT

In this research, firstly sulfonation of polyethersulfone (PES) was carried out and then polyethersulfone (PES)/sulfonated polyethersulfone (SPES) blend membranes were prepared with phase inversion induced by immersion precipitation technique. polyvinylpyrrolidone (PVP, 2 wt% concentration) was added in the casting solution as pore former. SPES was characterized by FT-IR and UV–visible spectra, ion exchange capacity and swelling ratio. The characterization of SPES polymer indicates that the sulfonic acid groups were produced on PES polymer. Also, the prepared PES/SPES blend membranes were characterized by contact angle, AFM, SEM and cross-flow filtration for milk concentration. The contact angle measurements indicate that the hydrophilicity of PES membrane is enhanced by increasing the SPES content in the casting solution. The SEM and AFM images show that the addition of SPES in the casting solution results in a membrane with larger surface pore size and higher sub-layer porosity. The mean pore size of the membrane increased from 98 nm for PES membrane to 240 and 910 nm for 50/50 and 0/100 PES/SPES blend membranes, respectively. The pure water flux and milk water permeation through the prepared membranes are increased by blending PES with SPES. Moreover, the protein rejection of PES/SPES blend membranes was lower than PES membrane.

1. Introduction

Phase inversion process has been widely adopted as a method for preparation of asymmetric polymeric ultrafiltration membrane [1–3]. Membrane based separation process have become important unit operations for concentration and purification of macromolecular solution. Ultrafiltration is a fractionation technique that can simultaneously separate and concentrate macromolecules or colloidal substances in process steams. The asymmetric membranes used in ultrafiltration (UF) are generally made from polymers such as cellulose acetate, polysulfone and polyethersulfone [4–6]. Polyethersulfone (PES) is widely used membrane material, because of high glass transition temperature which has high mechanical, thermal and chemical resistances [7–10]. However, the polyethersulfone is hydrophobic and sensitive to many organic solvents. Membrane surface properties often cause intense fouling when solutions containing substances like proteins are filtered. Therefore the modification of PES membrane is necessary for reducing the membrane fouling. An increase in the membrane hydrophilicity appears to be a good way to improve the membrane resistance to solvent alteration and to fouling as well. The different method for modification of PES membrane can be list as follows: addition of hydrophilic polymer to the membrane materials dope [11–12], immobilization of polymers with hydrophilic segments by photo-polymerization or adsorption [13]. The functional groups of hydrophilic monomers such as acrylic acid and N-vinyl-2-pyrrolidone could be grafted onto the PES membrane surface by plasma initiation polymerization [14–15]. This changes the surface properties of PES membranes such as hydrophilicity and roughness. Sulfonated polymers were considered to be much more resistant to fouling [16–17]. A more complex method of sulfonation via metalation–sulfination–oxidation steps was proposed by Kerres et al. [18,19]. The sulfonation of three different polysulfones by sulforic acid was studied by Blanco et al. [20]. The sulfonated polymers must be capable to forming asymmetric membranes with required mechanical, thermal, chemical and separation properties. The cheapest reagent for sulfonation would be oleum (SO_3 dissolved) in pure sulforic acid or sulforic acid (98%), which could be used as both reactant and solvent. few researchers have been studied on the sulfonation of polymers with this reagent [21].

---

[*] Corresponding author. Tel.: +98 912 8093155; fax: +98 111 3220342.
E-mail address: ahmadrahimpour@yahoo.com (A. Rahimpour).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.10.014

The main objective of this research was the sulfonation of polyethersulfone (PES) and investigation of changes in PES membrane properties by blending with this sulfonated polyethersulfone (SPES). The morphology, performance and hydrophilicity of SPES/PES blended membranes were also investigated.

2. Experimental

2.1. Material

Polyethersulfone (PES Ultrason E6020P with Mw = 58,000 g/mol) and dimethylacetamide (DMAC) were supplied by BASF Company. Sulforic acid (98%) and polyvinylpyrrolidone (PVP, with Mw = 25,000 g/mol) from Merck were used. 2-Propanol (IPA) was obtained from Miko Company. Distilled water was used throughout this study.

2.2. Sulfonation method of PES

Sulfonation of PES was performed by sulforic acid (98%) as sulfonating agent and solvent. A 100 ml glass reactor, equipped with a magnetic stirrer a condenser and a nitrogen inlet/outlet was charged with PES powder, and sulfuric acid (98%). The temperature for polymer dissolution was 20 °C. The reported reaction time was the total time for polymer dissolution and reaction. SPES was gradually precipitated into ice-cold de-ionized water under rapid stirring, and the resulting precipitate was recovered by filtration and washed repeatedly with de-ionized water [22–23]. Generally, a fraction of the sulfonated PES could dissolve in cold water, if the sulfonation degree was high enough. In this study, the sulfonated PES was insoluble in water and was totally recovered by precipitation. Finally, the SPES was dried under vacuum at 40 °C overnight.

2.3. Characterization of synthesized SPES

FT-IR spectra were recorded on a Perkin-Elmer RXI over the range of 400–4000 cm^{-1}. UV–visible spectra were performed by Perkin-Elmer Lambda 25. The reaction monitoring was carried out in a stirred quartz cell at room temperature. The polymer concentration was equilibrated to obtain a valid absorbance.

The ion exchange capacity (IEC) was determined by suspending 0.3 g of SPES in 30 ml of 2 M NaCl solution for 24 h to liberate the H^+ ions. Then, the titration was done with standardized 0.1 M NaOH solution using phenolphthalein as an indicator. The IEC is defined as the ratio of exchanged H^+ (in ml equiv. g) to the weight of the dried polymer. The IEC was calculated according to the equation:

$$\text{IEC (mequiv./g)} = \frac{V_{\text{NaOH}} - V_{\text{NaCl}}}{1000W_{\text{dry}}} \qquad (1)$$

V_{NaOH}, V_{NaCl} and W_{dry} are volume of NaOH, volume of NaCl and weight of dry PES, respectively. Degree of sulfonation (DS) is the fraction of monomer unit which is sulfonated (ion exchangeable) after reaction. If we assume that all the sulfonic groups in the film are accessible (i.e. ion exchangeable), the average sulfonation degree (DS) can be calculated from the IEC. So that, the average number of DS equal is to ratio of DS to IEC:

$$M_0 + 103\text{DS} = \frac{1000\text{DS}}{\text{IEC}} \qquad (2)$$

where M_0 232 g/mol is the mass unit of the initial polymer (and 103 is the molar mass of the SO_3Na group). Thus, the DS can be obtained from the following equation:

$$\text{DS} = \frac{M_0\text{IEC}}{1000 - 103\text{IEC}} \qquad (3)$$

The sample films were soaked in water for 24 h and weighted immediately. These wet films (W_{wet}) were dried for 24 h at 60 °C and the dry weights were determined. From the dry and wet weights of the samples, the percent water contents were calculated using the following equation [24]:

$$\text{SW} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad (4)$$

2.4. Membrane preparation

The membranes were prepared via phase-separation process using immersion precipitation technique. The blend homogeneous solutions based on PES and synthesized SPES polymers were prepared by dissolving two polymers at different compositions in DMAC as solvent in the presence of PVP at 2 wt% concentration as pore former. The solution was cast on a smooth glass using a film applicator at room temperature and moved toward non-solvent bath for immersion precipitation. The non-solvent was only water. In order to guarantee complete phase separation, the membranes were stored in the coagulation bath for 24 h. As the final stage, each membrane was dried by placing between two sheets of filter paper for 24 h at room temperature. The dried membrane thickness was measured by a digital caliper device which confirmed that the membrane thickness was maintained around 150 μm.

2.5. Characterization of membrane

2.5.1. Contact angle measurements

In order to examine variations in the surface wetting characteristics of the PES membrane as a function of SPES concentration, water contact angle was measured for membrane surface using a contact angle measuring instrument [G10, KRUSS, Germany]. This represents the membrane hydrophilicity. De-ionized water was used as the probe liquid in all measurements. To minimize the experimental error, the contact angles were measured at five random locations for each sample and the average number was reported.

2.5.2. Scanning electron microscopy (SEM)

A scanning electron microscope was used to inspect the top of surface as well as cross-sectional morphology of the membrane. Cambridge scanning electron microscope (SEM, CamSca MV2300) was employed in this work. The membranes were cut into small pieces and cleaned with filter paper. The pieces were immersed in liquid nitrogen for 60–90 s and were frozen. Frozen fragments of the membranes were broken and kept in air for drying. The dried samples were gold sputtered for producing electric conductivity. After sputtering with gold, they were viewed with the microscope at 15 kV.

2.5.3. Atomic force microscopy (AFM)

Microscopic observation of surface and roughness of the prepared membrane was performed by an atomic force microscope. The AFM device was DualSope™ scanning probe-optical microscope (DME model C-21, Denmark). Small squares of the prepared membranes (approximately 1 cm^2) were cut and glued on glass substrate. The membrane surfaces were imaged in a scan size of 5 μm × 5 μm. The pore sizes were measured by inspecting line profiles of different low valleys (i.e. pores) and high peaks (i.e. nodules) on the AFM images at different locations of a membrane surface. Then the mean pore size of membranes was calculated.

2.5.4. Flux and retention

The pure water, non-skim milk permeation and protein retention properties of membranes were investigated with a