Journal of Membrane Science 320 (2008) 363–371

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers

Zhifeng Fan, Zhi Wang*, Ning Sun, Jixiao Wang, Shichang Wang

Chemical Engineering Research Center, School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering,
Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 14 January 2008
Received in revised form 8 April 2008
Accepted 10 April 2008
Available online 18 April 2008

Keywords:
Polysulfone ultrafiltration membrane
Polyaniline nanofibers
Blending
Permeability
Antifouling property

ABSTRACT

Polyaniline (PANI) nanofibers were used to improve hydrophilic property and permeability of polysulfone (PS) membrane. PS membrane and PS/PANI nanofibers blended membranes with different PANI–PS mass ratios (1, 5, 10, and 15 wt.%) were prepared by phase inversion process. The blended membranes showed similar bovine serum albumin (BSA) and albumin egg (AE) rejections to PS membrane. The blended membranes had larger porosity and better hydrophilic property than PS membrane, which caused the improvement of their permeability. Pure water fluxes of the blended membranes with PANI–PS mass ratios of 1 and 15 wt.% were 1.6 and 2.4 times that of PS membrane, respectively. During the filtration of BSA solution, the blended membranes had slower flux decline rate than PS membrane. Moreover, stable permeate fluxes of the blended membranes with PANI–PS mass ratios of 1 and 15 wt.% were 2.0 and 2.5 times that of PS membrane, respectively. Compared with PS membrane, mechanical property and thermal stability of the blended membranes with less PANI–PS mass ratio, e.g. 1 wt.%, had no obvious change. For the blended membrane with PANI–PS mass ratio of 15 wt.%, breaking strength increased 28% and elongation at break decreased 30.6%.

1. Introduction

Since polysulfone (PS) ultrafiltration (UF) membranes have high mechanical property, good heat-aging resistance, and chemical stability, they have been widely used in such diverse fields as water treatment, food processing, and biotechnology [1,2]. However, conventional PS UF membranes easily suffer serious membrane fouling and have low permeate flux, which partially results from the hydrophobic property of PS materials [3]. Hence, hydrophilic modification of PS UF membranes has attracted a great deal of interest in recent years. Such methods as plasma treatment [4,5] and graft polymerization [6,7] have been adopted to obtain hydrophilic UF membranes with high flux and low fouling.

Polymer blend is an important alternative to obtain new polymeric materials with designed properties, less complicate than developing new polymerization, and the least expensive [8]. Water-soluble polymer [9], charged polymer [10], and other hydrophilic polymers [11–14] have been used to prepare hydrophilic UF membranes through homogeneous blending [1]. In addition, multi-walled carbon nanotubes/PS heterogeneous blended membranes with high flux and rejection have been reported [15]. Accordingly, polymer blend is effective to modify conventional UF membranes and obtain membrane performance with low fouling and high flux.

As a desirable membrane material [16], polyaniline (PANI) (Fig. 1) has been used to prepare membranes for gas separation [17], pervaporation [18,19], and electrodialysis [20] because of its stability, relatively inexpensive cost, and simple acid–base doping chemistry [21,22]. Recently, PANI nanofibers have attracted a great deal of interest because of their appealing potential applications in nano/microelectronics, metallic corrosion protection, sensors, and actuators [23]. In addition, PANI nanofibers have been used to obtain superhydrophilic surface because of their high surface energy and hydrophilic property [24]. Polymer nanofibrous membranes have many attractive attributes like high porosity, interconnected open pore structure, and large surface area per unit volume [25–29], which are beneficial to the improvement of membrane permeability. Based on the above, we prepared a kind of composite UF membrane with PANI nanofibers top layer through filtration of PANI aqueous dispersion in our previous work [30]. Because PANI nanofibers layer had porous structure and hydrophilic property, the composite UF membrane had high flux and low fouling during the filtration of bovine serum albumin (BSA) aqueous solution. Accordingly, PANI nanofibers could be used to improve

---

* Corresponding author. Tel.: +86 22 27892155; fax: +86 22 27404496.
E-mail address: wangzhi@tju.edu.cn (Z. Wang).

0376-7388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2008.04.019

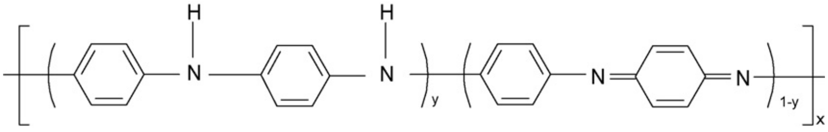

Fig. 1. General formula of polyaniline.

membrane permeability and antifouling property because of their hydrophilic property and nanofiber morphology.

Since polymer blend is effective to modify conventional UF membrane, which has been mentioned above, PANI nanofibers would be blended with PS to improve membrane performance and the method of immersion phase inversion would be used to prepare the blended membrane in this study. It is expected that the blended membrane might have stable structure and preferable performance. The effects of PANI–PS mass ratio on membrane structure and performance were investigated. The hydrophilic property and chemical composition of PS/PANI nanofibers blended membrane surface were characterized by contact angle measurement and X-ray photoelectron spectroscopy (XPS), respectively. The distribution of pore size was measured by differential scanning calorimeter (DSC) and the morphologies of blended membranes were observed by scanning electron microscope (SEM). The permeation and rejection performances of the membranes were tested, and the antifouling ability was evaluated through UF experiments using BSA as a model protein.

2. Experimental

2.1. Materials

Polysulfone was manufactured by Dalian Polysulfone Plastic Limited Company and used as a membrane material. PANI nanofibers were prepared by chemical oxidative polymerization, according to the method reported in the literature [31]. The average diameter and length of the PANI nanofibers used in the experiment were 43 and 259 nm, respectively, which were determined by transmission electron microscopy and ImageJ software [30,32]. BSA with molecular weight 67,000 was electrophoretically pure and purchased from Tianjin Zhenjiang High-technology Company. Albumin egg (AE, molecular weight 43,000) and polyethylene glycol (PEG, molecular weight 35,000) were supplied by Sigma–Aldrich. Pure water was produced by a reverse osmosis system and its conductivity was less than 10 μs/cm. Aniline was purified by distillation under a reduced pressure. Ammonium peroxydisulfate (APS), methanol, hydrochloric acid, sodium hydroxide, and dimethylacetamide (DMAC) were of analytical grade and used as received.

2.2. Preparation of PS/PANI nanofibers blended membrane

Membranes were prepared by immersion phase inversion method. Casting solutions were prepared as follows. Firstly, PANI nanofibers were dispersed in DMAC, and the dispersion was sonicated for about 30 min using an ultrasonic device (KQ-100VDE, China). Then, PS was dissolved in the dispersion and vigorous stir was carried out at room temperature to prepare PS/PANI nanofibers blended solutions with different composition. For all the blended solutions, the mass ratio of PS to total blended solution was 15 wt.%, and PANI–PS mass ratio was varied: 0, 1, 5, 10, and 15 wt.%. The casting solutions were kept for 24 h to allow complete release of bubbles, then cast on a glass plate with a steel knife to get wet films of 300 μm thickness, exposed to air for 30 s, and immersed in a coagulation bath of pure water. The membranes formed and subsequently were washed thoroughly with pure water to remove residual solvent and kept in pure water before testing. All of the membranes were prepared under environmental humidity of 60% and temperature of 25 °C.

2.3. Characterization of PS/PANI nanofibers blended membrane

2.3.1. Membrane chemical composition and morphology analysis

The chemical composition of PS/PANI nanofibers blended membrane surface was analyzed by XPS (PHI-1600) using Mg Kα as the radiation source. Survey spectra were collected over a range of 0–1100 eV and the takeoff angle of photoelectron was set at 90°. PHI-MATLAB soft was used to analyze the XPS spectra. The surface and cross-section morphologies of PS/PANI nanofibers blended membranes were observed with SEM. SEM (XL30, Phillips) was used to get images of 500 magnifications and SEM (JEOL6700, Japan) was used to obtain images of 10,000, 20,000, and 50,000 magnifications. For the SEM observation, the membrane samples were cut into appropriate sizes and the surfaces were coated with gold by a sputter coating machine. Membrane surface roughness could be estimated from the AFM images. Surface topography of the membrane was tested by atomic force microscopy (AFM, Digital Instrument, D3100M MMAFM/STM).

2.3.2. Contact angle measurement

Contact angle measurement is widely used to characterize the hydrophilic property of polymeric surfaces, including polymeric membranes [33]. In the experiment, contact angle between water and membrane surface was measured with sessile drop method and a contact angle measurement instrument (JY-82, China) was used. A water droplet was placed onto the membrane surface, using a syringe, and the contact angle of the droplet was measured. The values reported are averages of five separate measurements on the same membrane.

2.3.3. Pore size and porosity measurements

The pore size was determined by the frozen temperature of water in porous membrane using DSC measurements [34]. The DSC apparatus was a Pyris Diamond differential scanning calorimeter equipped with a liquid nitrogen-cooling accessory and calibrated with indium (PerkinElmer, USA). The membrane sample of 10–20 mg was put in a sealable aluminum pan and one drop of pure water was added to maintain the sample in an excess of water. Then, the pan was cooled down to 258 K at a rate of 0.5 K/min, which was slow enough to maintain the thermodynamic equilibrium. From DSC thermograms and Eqs. (1)–(3), the pore radius distribution curves were obtained [35]:

$$R_{\mathrm{P}}\,(\mathrm{nm}) = -\frac{64.67}{\Delta T} + 0.57 \tag{1}$$

$$W_{\mathrm{a}}\,(\mathrm{J/g}) = -5.56 \times 10^{-2}\,\Delta T^2 - 7.43\,\Delta T - 332 \tag{2}$$

$$\frac{\mathrm{d}V}{\mathrm{d}R_{\mathrm{P}}} = \frac{m}{64.67\,k}\,\frac{\Delta T^2}{W_{\mathrm{a}}}\,Y \tag{3}$$

where R_{P}, ΔT, W_{a}, m, k, V, and Y are pore radius, temperature shift, apparent energy of water solidification, sample weight, cooling rate, pore volume, and heat flow, respectively.