Journal of Membrane Science 423–424 (2012) 362–370

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties

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ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form
24 July 2012
Accepted 20 August 2012
Available online 27 August 2012

Keywords:
Nanocomposite membrane
Mesoporous silica
Antifouling
Irreversible fouling

ABSTRACT

Fouling is regarded as the bottleneck in membrane filtration process. One of the practical strategies to decrease fouling is the use of advanced anti-biofouling membrane material. In this study, mesoporous silica (MS) particles was synthesized as inorganic fillers, and fabricated with polyethersulfone (PES) to achieve nanocomposite membranes with antifouling properties by phase inversion method. The effect of the MS particles on the microstructure and properties of the resulting hybrid membranes were investigated by scanning electron microscopy (SEM), thermal gravitational analysis (TGA), and ultrafiltration (UF) experiments. The results indicated that the nanocomposite membrane with 2% MS exhibited excellent hydrophilicity, water permeability and good antifouling performance. In addition, the TGA results showed that the introduction of the MS particles improved the thermal stability of the nanocomposite membranes. The protein adsorption on the membrane surface decreased significantly from 45.8 μg/cm^2 to 21.4 μg/cm^2 when the MS content increased from 0% to 2%. Most importantly, the protein UF experiments revealed that the incorporation of MS particles reduced membrane fouling, especially irreversible fouling, which reduced dramatically. No benefit was gained from higher MS content (4%), which resulted in significant particle agglomeration.

1. Introduction

Ultrafiltration technology has found wide application for concentration, purification and fractionation of various products in many fields such as the food, medical and biotechnological industries, or as a pre-treatment stage prior to reverse osmosis treatment [1]. However, most commercial ultrafiltration membranes are made from hydrophobic polymers such as polyethersulfone (PES), polysulfone (PS), polypropylene (PP) and polyvinylidene fluoride (PVDF) [2,3], which are susceptible to membrane fouling caused by the deposition of organic pollutants on the membrane surface or adsorption into the membrane pores. Membrane fouling is still a major problem, which impacts the operating costs of UF and restricts its practical application [4]. Membrane fouling includes reversible and irreversible fouling. Reversible fouling can be easily removed by hydraulic cleaning such as backwashing and cross-flushing. However, irreversible fouling can only be overcome by chemical reagents, and repeated chemical cleanings may reduce the membrane performance. Membrane fouling causes a decline in flux and increased energy consumption, while the necessary chemical cleaning procedures add costs and decrease membrane life. Therefore, many investigators tried to find ways to reduce membrane fouling, especially irreversible fouling, to improve the cost effectiveness of UF membranes.

Generally, making membranes more hydrophilic is a common strategy to reduce membrane fouling. Much effort has been devoted to improving hydrophilicity of the conventional hydrophobic membranes by using various techniques, including coating [5,6], grafting hydrophilic species onto the membrane surfaces [7,8], and blending with hydrophilic polymer or inorganic fillers [9,10]. Among these methods, blending with inorganic particles has attracted a great deal of interest due to availability of different types of functional inorganic particles. A variety of inorganic fillers such as titanium dioxide (TiO_2), alumina (Al_2O_3), zirconium (ZrO_2), silica (SiO_2) and Fe_3O_4 have been used to fabricate inorganic–polymer composite membranes [11–16]. Many of these studies indicate that membrane modification enhanced performance, by improving water permeability, mechanical strength, and fouling resistance. However, some researchers report that the non-porous particles tend to migrate to the membrane surface during the phase separation process [14], which leads to a decrease in the effective filtration area of the membrane. Furthermore, the impermeability of the nonporous particles blended into

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http://dx.doi.org/10.1016/j.memsci.2012.08.029

the polymer matrix does not directly contribute to the enhancement of the membrane transport properties, so the improvement in membrane permeability has been quite limited.

Mesoporous silica (MS) has been studied extensively for various applications due to its high surface areas, narrow pore size distributions and adjustable mesopore sizes [17,18]. MS has been found to increase the permeability of mixed matrix membranes without sacrificing their selectivity due to its good compatibility with the polymer matrix, and it has been widely used to fabricate nanocomposite gas separation membranes to enhance both gas permeability and selectivity [19–21]. For instance, mesoporous silica sphere-polysulfone mixed matrix membranes were prepared for the separation of H_2/CH_4 and CO_2/N_2 mixtures. The thermal stability and mechanical performance of the membranes were enhanced by the incorporation of the particles and H_2/CH_4 separation performance was optimized by blending 8 wt% MS into the polymer [22]. However, no-one has investigated the utilization of mesoporous silica for the preparation of mixed matrix ultrafiltration membranes.

PES is one of the most common ultrafiltration membrane materials due to its outstanding mechanical strength, excellent thermal and chemical stability [7–11]. In the present study, ordered mesoporous silica was synthesized and was used to fabricate MS–PES nanocomposite membranes. The main advantage of our research is related to the use of silica with an ordered mesoporous structure. The application of mesoporous particles should improve the filler-polymer compatibility and enhance the particle dispersion in the matrix. In addition, the porous nature of the fillers gives them a high affinity to water, which should enhance the water content of the membrane and facilitate water transport through the membrane. Furthermore, the functional –OH group on the mesoporous silica should improve the hydrophilicity of the membrane and have adverse effect on the fouling resistance of the membrane. The aim of this study was to fabricate and characterize PES–MS mixed matrix membranes and to determine the optimum loading of inorganic filler to produce an enhancement in terms of permeability and antifouling properties. A series of experiments, such as SEM, water contact angle (CA) and TGA, were carried out for membrane characterization. The mechanism of membrane antifouling performance improvement caused by incorporation of MS was studied and an optimal loading of MS was proposed.

2. Experimental

2.1. Materials

PES (E6020P, BASF Co., Germany) was dried at 110 °C in an oven overnight prior to use in the casting solution preparation. *N*,*N*-dimethylformamide (DMF), poly ethylene glycol (PEG, M_w=400), cetyltrimethylammonium bromide (CTAB),tetraethylorthosilicate (TEOS), absolute ethanol, bovine serum albumin (BSA) and hydrochloric acid (36–38%) were obtained from Sigma Aldrich. Other regents were all of analytical grade and used without further purification. The water used in all experiments was distilled water. BSA solution (1 g/L, pH 7.0) was prepared using 0.2 M phosphate buffer solution.

2.2. Synthesis of mesoporous silica

The synthesis of mesoporous silica followed a similar process to that reported by Cai et al. [23]. Typically, 2.1 mL of sodium hydroxide aqueous solution (2 M) was mixed with 288 mL distilled water. Then, 0.6 g of CTAB was added and the mixture was heated at 80 °C while stirring until a clear solution was obtained. To this clear solution, 3 mL of TEOS was added dropwise with vigorous stirring. The reaction mixture was then stirred at 80 °C for 2 h. The product was centrifuged, washed with excess distilled water and then dried at ambient temperature. Finally, to extract CTAB from the MS, the synthesized product was refluxed in a solution of 150 mL ethanol and 2 mL hydrochloric acid (36–38%) at 78 °C for 12 h, centrifuged, washed with the distilled water, and then dried in an oven at 50 °C. The extraction process was repeated several times to completely remove the template (CTAB), and the prepared MS particles were obtained in powder form.

2.3. Preparation of MS/PES composite membrane

Different amounts (0%, 1%, 2% and 4% based on the solution weight) of dry mesoporous silica particles were added into DMF, the solution was ultrasonicated for 30 min to ensure good dispersion of the particles. 10% of PEG-400 and 18% of PES were then dissolved in the solution while stirring for 24 h at 60 °C until a uniform solution was obtained. The casting solution was then degassed at 60 °C overnight without stirring to completely remove any gas bubbles. The solution was then cast onto a glass plate to produce a flat sheet membrane (200 μm thick) by the phase inversion method. The fabricated membranes were immersed in fresh distilled water to remove all the residual solvent and pore-forming agent before characterization. The resultant membranes were kept in water prior to ultrafiltration experiments. Table 1 shows the compositions of the casting solution.

2.4. Characterization

The nitrogen sorption isotherm was obtained on a Micromeritics ASAP 2020MC instrument at −196 °C. The specific surface area of mesoporous silica was calculated using the multiple-point Brunauer Emmett Teller (BET) method. The pore size distribution was determined from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) specimens were prepared using a cryostat-microtome (Ultracuts, Reichert Leica), and were picked up by a copper films (200 mesh, ProSciTech).

Morphological structures of the prepared PES membranes were examined using a scanning electron microscope (SEM, JSM-6300F, JEOL). The membrane samples were frozen and fractured in liquid nitrogen, and both the surface and cross section of the samples were gold sputtered for observation. Elemental mapping was conducted with the SEM microscope equipped with energy-dispersive X-ray spectroscopy (EDX).

The hydrophilicity of the membrane was determined by measuring the contact angle of the membrane surface with a contact angle goniometer (CAM200, KSV Instruments Ltd). At least five water contact angles at different locations on the membrane surface were recorded to get a reliable value.

The membrane porosity ε (%) was defined as the volume of the pores divided by the total volume of the porous membrane. The porosity of the different membranes was calculated using Eq. (1) [24].

$$\rho(\%) = \frac{(W_w - W_d)/D_w}{(W_w - W_d)/D_w + (W_d/D_p)} \times 100\% \quad (1)$$

Table 1
PES nanocomposite membranes with different MS contents.

No.	PES (wt%)	PEG-400 (wt%)	DMF (wt%)	MS* (wt%)
M0	18	10	72	0
M1	18	10	71	1
M2	18	10	70	2
M3	18	10	68	4

* The percentage of MS is based on the total amount of casting solution.