Journal of Membrane Science 454 (2014) 144–154

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Poly(vinylidene fluoride)/poly(acrylic acid)/calcium carbonate composite membranes via mineralization

Suo-Hong Zhi, Ling-Shu Wan, Zhi-Kang Xu *

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 7 August 2013
Received in revised form
24 October 2013
Accepted 7 December 2013
Available online 14 December 2013

Keywords:
Poly(vinylidene fluoride)
Composite membrane
Mineralization
Alternate soaking process
Calcium carbonate

ABSTRACT

Organic–inorganic composite membranes were prepared via calcium carbonate ($CaCO_3$) mineralization induced by poly(vinylidene fluoride) (PVDF)/poly(acrylic acid) (PAA) blend membranes. PAA was used as a polyanionic macromolecule in the blend membranes to generate $CaCO_3$ particles by an alternate soaking process (ASP). The mineralization condition was optimized based on the concentrations of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) solutions used for ASP, the number of ASP cycles, and the PAA content in the blend membranes. Structures and surface hydrophilicity of the composite membranes were characterized in detail by FTIR-ATR, FESEM, EDX, XRD and water contact angle. Results confirm that $CaCO_3$ particles consisting of calcite and vaterite dispersed uniformly in/on the membranes. The membrane hydrophilicity increased dramatically due to the intrinsic wettability of these $CaCO_3$ particles. In addition, the $CaCO_3$ particles also caused the collapse of PAA chains in the membrane pores. Therefore, pure water fluxes of the membranes were improved about three times. Furthermore, the mineralized membranes even showed a high rejection (99.85%) of Congo red, which makes them potential in dye-polluted wastewater treatment.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is one of the most extensively used materials for ultrafiltration, microfiltration and pervaporation membranes due to its excellent antioxidation, good thermal stability, and high hydrolytic resistance as well as fine mechanical property [1–3]. However, the hydrophobicity of PVDF is a conspicuous drawback for membranes because it is liable to cause membrane fouling in water treatment [4]. Therefore, extensive efforts have been devoted to improve the surface hydrophilicity of PVDF membranes through a variety of methods such as surface grafting, inorganic compositing, and polymer blending. Techniques used in the surface grafting include plasma treatment [5,6], UV-induced polymerization [7], electron beam irradiation [8,9], and living/controlled radical polymerization [10,11]. In the blending and compositing methods, amphiphilic copolymers [12,13] and inorganic particles [14–21] were often used as hydrophilic additives for PVDF membranes. Organic–inorganic composite membranes were fabricated from PVDF and inorganic nanoparticles with good hydrophilicity. These nanoparticles include Al_2O_3 [14,15], SiO_2 [16,17], TiO_2 [18–20] and montmorillonite (MMT) [21]. However, the membrane hydrophilicity usually failed to improve, because most inorganic particles were buried in the membrane matrix. Another problem is that these particles were easy to agglomerate and resulted in non-uniform distribution in the membranes. Therefore, it remains a major challenge to achieve uniform dispersion of inorganic particles in/on the membranes. Furthermore, compared with the organic–inorganic composites generated via biomineralization in nature, it is also questionable about the stability of the inorganic particles on the hydrophobic surface of PVDF membrane, especially for those not subject to chemical bonds.

It is generally acknowledged that, for biomineralization occurring within living organisms, the organic components (biomacromolecules such as proteins) direct the nucleation, growth habit and orientation of inorganic particles. Therefore, the formed biominerals usually have high stability because they interact strongly with the organic matrices and then result in a hybrid structure. As one of the most abundant biominerals, calcium carbonate ($CaCO_3$) has been widely studied in recent years to mimic the process happening in nature. It is now well-known that

---

Abbreviations: $CaCO_3$, calcium carbonate; PVDF, poly(vinylidene fluoride); PAA, poly(acrylic acid); ASP, alternate soaking process; $CaCl_2$, calcium chloride; Na_2CO_3, sodium carbonate; MMT, montmorillonite; MPPM, microporous polypropylene membrane; DMAc, dimethylacetamide; MD, mineralization degree; FT-IR/ATR, Fourier transform infrared/Attenuated total reflection spectrometer; FESEM, field emission scanning electron microscope; EDX, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction analysis; WCA, water contact angle; J_w, pure water flux; J_R, pure water flux of cleaned membranes; *FRR*, flux recovery ratio; K_{sp}, solubility product

* Corresponding author. Tel.: +86 571 8795 2605; fax: +86 571 8795 1773.
E-mail address: xuzk@zju.edu.cn (Z.-K. Xu).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.12.011

the mineralization of $CaCO_3$ in organism is based on the principle of matrix media. As a general principle, the assembly of minerals starts with the concentration of Ca^{2+} and then the nucleation of $CaCO_3$ closely associated with polyanionic macromolecules [22]. Poly(acrylic acid) (PAA) is one of the common polyanionic macromolecules. It has been extensively studied as the matrix media to generate $CaCO_3$ particles through electrostatic interaction between carboxyl groups and calcium ions in solution [23,24]. These features provide a new guide for designing organic–inorganic composite membranes with ideal performance, because PAA has usually been grafted on the membrane surfaces or blended with polymers to fabricate hydrophilic membranes with pH stimulus-responsibility [25–27]. However, PAA is not a perfect additive for hydrophilic modification due to its swelling property in water. The introduction of $CaCO_3$ particles with PAA as polyanionic macromolecules could avoid the disadvantage of PAA, because the $CaCO_3$ particles made the PAA chains to collapse [28,29].

To our knowledge, there are rare reports focusing on the mineralization of $CaCO_3$ in/on membranes [30]. Most recently, we grafted PAA on the surfaces of microporous polypropylene membrane (MPPM) and then fabricated MPPM/$CaCO_3$ hybrid membranes with superhydrophilicity and ultrahigh water permeability [28]. However, we think it should be more suitable for practical application if PAA is simply blended with a polymer for membrane fabrication [29], rather than grafted on a fabricated membrane. Therefore, we aim to develop PVDF/$CaCO_3$ composite membranes by depositing $CaCO_3$ particles both on the membrane surfaces and in the membrane pores via blending and then mineralization. PVDF/PAA blend membranes were prepared by the immersion precipitation method. A small amount of PAA was added as polyanionic macromolecule for the subsequent mineralization. We determined the optimized mineralization condition and studied the distribution of $CaCO_3$ particles in the resulted membranes. We also explored the permeation and rejection as well as adsorption properties of the mineralized membranes in detail.

2. Experimental

2.1. Materials

PVDF ($M_n = 1.53 \times 10^5$, $M_w/M_n = 2.3$) was purchased from Solvay Solexis Inc. (Belgium). PAA ($M_w = 450{,}000$, $M_w/M_n = 1.2$) was a commercial product of Aladdin Reagent Company (China). Anhydrous Na_2CO_3 and dimethylacetamide (DMAc, AR grade) were obtained from Sinopharm Chemical Reagent Co. Ltd. Anhydrous $CaCl_2$ was received from Quzhou Juhua Chemical Company (China). Ultrapure water was produced with an ELGA LabWater system (France) and used in all experiments.

2.2. Preparation of PVDF/PAA blend membranes

PVDF/PAA blend membranes were fabricated by the typical immersion precipitation method. PVDF (15 wt% based on the weight of casting solution) and PAA (0 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt% based on the PVDF weight) were dissolved in DMAc at 60 °C by stirring for 12 h and kept for 12 h without stirring to completely release air bubbles. These solutions were cast onto clean glass plates using a casting knife, and then immersed into water bath for phase separation. Temperature of the water bath was kept at 35 °C. After the membranes detaching from the glass plates, they were taken from the bath and subsequently soaked in ultrapure water for at least 24 h. To avoid the shrinkage of membrane pores, the samples were immersed in ethanol aqueous solution with different concentrations for dehydration and then soaked in *n*-hexane overnight. Finally, the membranes were dried in air at room temperature for subsequent mineralization.

2.3. Mineralization of PVDF/PAA blend membranes

ASP was applied to membrane mineralization. A dry membrane was soaked in ethanol for 10 min, and then immersed in ultrapure water for 30 min. The membrane was sequentially immersed in $CaCl_2$ aqueous solution for 30 s, rinsed with ultrapure water for 30 s, immersed in Na_2CO_3 aqueous solution for 30 s, and rinsed again with ultrapure water for 30 s. The above four steps were considered as one cycle. We changed the mineralization degree by varying the cycle numbers. Finally, the mineralized membrane was immersed in ethanol aqueous solution with different concentrations for dehydration and dried in vacuum oven at room temperature. The mineralization degree (*MD*) of membrane was calculated as follows:

$$MD = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_1 and W_2 are the weight of PVDF/PAA membrane before and after mineralization, respectively.

2.4. Structure characterization and property determination

The cloud points of the casting solutions were measured at 25 °C for obtaining the thermodynamic phase diagram. PVDF and PAA were dissolved in DMAc for 24 h. Deionized water was added to the solution by a pipette until visual turbidity was achieved. Composition at the cloud point was calculated by weight.

The apparent viscosity of PVDF/PAA casting solution was measured using a rotational viscometer (NDJ-79, Electrical Machinery Plant, Tongji University, China). All measurements were performed at a shear rate of 176 s^{-1} and 60 °C.

Attenuated total reflection/Fourier transform infrared (ATR/FT-IR) spectrometer (Nicolet Nexus 470, USA) was used to detect the chemical composition of the membrane surface. Thirty-two scans were taken for each spectrum at a resolution of 2.0 cm^{-1}.

Membrane morphologies were observed by field emission scanning electron microscope (FESEM, Hitachi S4800, Japan) under vacuum. Both the surface and the cross-section of membrane were then sputtered gold for 90 s before observation. The distribution of the calcium element on/in the membranes was also examined by energy dispersive X-ray spectroscope (EDX).

X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max-2550PC X-ray diffractometer (Panalytical, Netherlands).

Hydrophilicity of the membrane surface was evaluated by water contact angle (WCA) measurement. WCA was measured by the sessile drop method using a CTS-200 system (Mighty Technology Pvt. Ltd., China) at room temperature. The volume of droplets was 2.0 μL.

Zeta potential of the membrane surface was measured using electrophoretic light scattering spectrophotometer (Malvern, Zetasizer Nano ZS, England). Polystyrene latex particles (diameter: 50 nm) for mobility monitoring particles were dispersed in a 10^{-3} M KCl solution at 25 °C. The pH value was adjusted to 7.0 with NaOH aqueous solution.

The tensile strength and elongation of the membranes were evaluated by a tensile test instrument (RGM-4000, Shenzhen REGER Instrument Co. Ltd., China). The test was carried out at a strain rate of 5 mm/min at 25 °C. The membrane samples were prepared in rectangular shape with a gauge length of 40 mm and a width of 10 mm. The thickness was measured exactly by a thickness gauge (CH-1-S/ST, Shanghai Liuling Instrument Plant, China).

Download English Version:

https://daneshyari.com/en/article/633938

Download Persian Version:

https://daneshyari.com/article/633938

Daneshyari.com