Journal of Membrane Science 486 (2015) 195–206

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Improved antifouling properties of polyethersulfone membrane by blending the amphiphilic surface modifier with crosslinked hydrophobic segments

Yanan Liu [a,b], Yanlei Su [a,b], Xueting Zhao [a,b], Yafei Li [a,b], Runnan Zhang [a,b], Zhongyi Jiang [a,b,*]

[a] Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

ARTICLE INFO

Article history:
Received 8 January 2015
Received in revised form
18 March 2015
Accepted 19 March 2015
Available online 27 March 2015

Keywords:
Amphiphilic modifier
Melamine formaldehyde
Surface segregation
Antifouling membrane
Ultrafiltration

ABSTRACT

In this study, a novel structured amphiphilic modifier with crosslinked hydrophobic segments was synthesized and used to fabricate antifouling membranes. The amphiphilic modifier (MF-g-PEG*n*) was synthesized by etherification of melamine formaldehyde (MF) prepolymer with polyethylene glycol (PEG), and blended in polyethersulfone (PES) matrix to prepare membranes *via* a nonsolvent induced phase separation method. The hydrophilic polyethylene oxide (PEO) segments in the modifier were enriched at membrane surface through spontaneous surface segregation, endowing membranes with improved antifouling properties. The hydrophobic MF segments in the modifier were entangled with PES chains for robust anchorage of PEO segments. Moreover, the presence of MF-g-PEG*n* reduced the thermodynamic stability of the casting solution, endowing the membranes with high porosity. The separation performance of membranes was evaluated using bovine serum albumin (BSA) aqueous solution as model system. During the filtration process, the flux recovery ratios (FRR) after BSA aqueous solution separation of the PES control membrane and PES/MF-g-PEG6000 (0.36 wt%) were 70.8% and 91.6% respectively. The pure water fluxes of membranes were improved from 60.7 L m^{-2} h^{-1} for the PES control membrane to 164.7 L m^{-2} h^{-1} for PES/MF-g-PEG6000 (0.36 wt%), and all the membranes possessed 100% rejection efficiency.

1. Introduction

As one of the most promising and capable separation processes in many industries, ultrafiltration (UF) has been widely applied in the field of wastewater treatment, food processing and protein separation [1]. Compared with traditional separation methods, UF possesses a great number of advantages such as highly selective separation, continuous and automatic operation, easy scale-up and low space requirement, and in particular low energy cost. However, in UF process, the complex interactions between membrane materials and various foulants in the feed solution often lead to the attachment, accumulation or adsorption of foulants on membrane surface and/or in membrane pores, which cause serious membrane fouling [2]. Membrane fouling will cause a sharp decline in flux and increase the maintenance and operation cost, which limits the wide application of membrane technology [3]. Therefore, construction of antifouling membrane surfaces is always an important issue.

Several methods have been explored to decrease the interaction force between foulants and membrane surface, such as surface coating [4–6], surface grafting [7–9]and surface segregation [10,11]. Among them, surface coating and surface grafting both suffer from the drawback that the internal pores of the membrane remain unmodified and are still susceptible to fouling. Comparatively, the surface segregation offers a novel and efficient method, because it ensures the in situ modification of membrane internal pores as well as the membrane surface. The surface segregation technique can be described as follows: amphiphilic modifier (consisted of hydrophobic backbones and hydrophilic side chains) is first blended with membrane-forming polymer in membrane casting solution, and during the subsequent phase inversion process, the hydrophilic segments of the modifier are segregated to the membrane surface and pore surface spontaneously whereas the hydrophobic segments are firmly entangled with the membrane matrix [11,12].

Many researchers have used the surface segregation method to engineer antifouling UF membrane surface. Our previous works used Pluronic F127 to modify the membrane surface [13,14].

* Corresponding author at: Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel.: +86 22 27406646; fax: +86 22 23500086.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

http://dx.doi.org/10.1016/j.memsci.2015.03.045
0376-7388/

The membranes blending with Pluronic F127 exhibited higher hydrophilicity, wettability and lower protein adsorption in comparison with the control membrane. Li et al. synthesized amphiphilic zwitterionic copolymer poly(vinylidene fluoride)-graft-poly(sulfobetaine methacrylate) (PVDF-g-PSBMA) by atom transfer radical polymerization (ATRP) and used as additive to improve hydrophilicity and antifouling properties of PVDF membranes [15]. As we know, the hydrophilic segments and hydrophobic segments in the amphiphilic modifier play different roles in modifying the membranes. The hydrophilic segments modify the membrane surface to decrease the interaction force between foulants and membrane surface, and the hydrophobic segments have strong interaction with the membrane matrix and ensure the stable existence of hydrophilic segments on membrane surface. Furthermore, the length of hydrophilic segments and hydrophobic segments [16,17], the species of hydrophilic segments [13,15] and the structure of hydrophobic segments [18] have an important influence on the surface segregation process. So far, most efforts were focused on designing the hydrophilic segments of the amphiphilic modifier such as polyethylene oxide (PEO) [14,19–24], polyvinylpyrrolidone (PVP) [16,25], zwitterionic polymers [15,26,27], polyacrylic acid (PAA) [28], etc, however, few efforts were focused on the influence of the hydrophobic segments in the amphiphilic modifier on the membrane performances [18]. Theoretically, the interaction between hydrophobic segments and membrane matrix is closely related to the assembly behavior of amphiphilic modifier during phase inversion process. Accordingly, designing modifiers with novel structure for efficient surface segregation is an important research issue.

In the present study, we synthesized a novel structured amphiphilic modifier (MF-g-PEG*n*) with hydrophilic PEO segments and crosslinked hydrophobic melamine formaldehyde (MF) segments. And the amphiphilic modifier was blended in PES to improve the antifouling properties of the prepared membranes. The functional groups of MF-g-PEG*n* copolymers were confirmed by Fourier transform infrared spectroscopy (FTIR), the chemical structures were analyzed by ^{1}H nuclear magnetic resonance (^{1}H NMR), and their thermodynamic properties were measured using a differential scanning calorimetry (DSC). The surface chemical compositions of the prepared membranes and surface segregation of PEO segments were characterized using X-ray photoelectron spectroscopy (XPS). Moreover, the morphology of the prepared membranes was investigated by the scanning electron microscope (SEM) and atomic force microscope (AFM), and the interaction force between the model foulant bovine serum albumin (BSA) and the membrane surface was measured by AFM with BSA-immobilized tip. Finally, the water permeability and antifouling properties of membranes were evaluated.

2. Experimental

2.1. Materials

Melamine (AR) and 37 wt% formaldehyde aqueous solution was purchased from Kermel Co. and Aladdin Co. respectively. Polyether sulfone (PES) (6020P, M_w 59,000, flake form) was purchased from BASF Co. (Germany) and dried at 110 °C for 12 h before using. Polyethylene glycol (PEG) with average molecular weight of 1000, 2000, 4000 and 6000 respectively were received from Guangfu Fine Chemical Research Institute (Tianjin, China). *N*-methyl pyrrolidone (NMP) and bovine serum albumin (BSA) were all purchased from the local reagent corporation and were of commercially analytical grade.

2.2. MF-g-PEGn synthesis

Synthesis of MF could be divided into two steps, preparation of MF prepolymer and polycondensation of MF prepolymer [29]. To make MF soluble in organic solvents, one of the most efficient methods was to etherify it with alcohols [30]. PEG with alcoholic hydroxyl group could etherify MF prepolymer to obtain MF-g-PEG*n*, where *n* indicated the average molecular weight of PEG. All synthesis reactions in this study were performed under an identical condition, while the average molecular weight of PEG was varied to obtain surface segregation modifiers with different structures. One representative example was shown to synthesize MF-g-PEG2000 as follows:

20.0 mmol melamine and 60.0 mmol 37 wt% formaldehyde solution were poured into a round-bottomed three-necked flask equipped with a mechanical stirrer. The reaction temperature was kept at 60 °C, and pH value of the aqueous solution was adjusted to 10–11 with 10 wt% NaOH aqueous solution. When the mixture became transparent, the prepolymer solution of MF was obtained and kept stirring for 30 min. Then under agitation, 30 mL deionized water and 1.0 mmol PEG2000 were added to the prepolymer solution. The mixture was heated to 75 °C and pH of the mixture was adjusted to 4–5 with 5 wt% hydrochloric acid solution. After pH adjustment and temperature rise, the reaction was continued with stirring for 5 h. At the time of reaction completion, the product was under vacuum rotary evaporation at 60 °C, then was dried completely at 60 °C for over 72 h. The products were characterized by Fourier transform infrared spectrometer (FTIR, VERTEX70), ^{1}H nuclear magnetic resonance (^{1}H NMR, INVOA-500), and the thermal properties of them were measured using a differential scanning calorimetry (DSC, 200F3, NETZSCH Co.) at a heating and cooling rate of 10 °C/min under a nitrogen (N_2) atmosphere.

2.3. Membrane preparation

The blend membranes of PES and MF-g-PEG*n* were prepared by the nonsolvent induced phase inversion (NIPS) method, using NMP as solvent and water as the nonsolvent coagulation bath. Casting solutions containing PES, MF-g-PEG*n*, pore-forming agent PEG2000 and NMP according to the compositions listed in Table 1. The solutions were stirred for 4 h at 60 °C and then left for 6 h to ensure complete release of bubbles. Then, the casting solutions were cast on glass plates with a steel knife maintaining a uniform thickness of 300 μm and immersed into a water coagulation bath. The resultant membranes were designated as PES/MF-g-PEG*n* (*w*) membranes, where *n* indicated the average molecular weight of PEG in MF-g-PEG*n* copolymers and *w* indicated the addition amount of MF-g-PEG*n* during the membrane preparation process. All membranes were kept in deionized water to eliminate any residual solvent prior to utilization. The PES membranes were prepared as control membranes following a similar procedure.

Table1
Composition and water contact angle of different membranes.

Membrane	PES (wt%)	PEG2000 (wt%)	MF-g-PEG*n* (wt%)				NMP (wt%)	WCA (°)
			*M*1	*M*2	*M*4	*M*6		
1	18	18	–	–	–	–	74.00	70.2 ± 1.6
2	18	18	–	0.18	–	–	73.82	68.2 ± 1.9
3	18	18	–	0.36	–	–	73.64	67.6 ± 1.1
4	18	18	–	0.54	–	–	73.46	69.5 ± 1.3
5	18	18	–	0.72	–	–	73.28	67.9 ± 1.2
6	18	18	–	0.90	–	–	73.10	68.9 ± 1.6
7	18	18	0.36	–	–	–	73.64	67.7 ± 1.5
8	18	18	–	–	0.36	–	73.64	68.2 ± 1.8
9	18	18	–	–	–	0.36	73.64	69.7 ± 2.1