Tethering Methoxy Polyethylene Glycols to Improve the Antifouling Property of PSF/PAA-Blended Membranes

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ABSTRACT: Poly(acrylic acid) (PAA) was used as an additive to fabricate blended polysulfone (PSF) ultrafiltration (UF) membranes. Hexanediamine was used as a crosslinking agent to react with PAA and formed an active surface with amine group. Then, an end carboxyl group methoxy polyethylene glycol (MPEG) was grafted on the membrane surface via an amidation reaction. Water contact angle measurement indicated that the surface hydrophilicity of PSF/PAA-blended membranes and MPEG-modified membranes remarkably increased. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) was used to confirm the existence of PAA in the blended membranes and the change of chemical composition. Membrane surface and cross-sectional morphologies were observed by scanning electron microscope. The flux of pure water increased slightly after modification, while the rejection to bovine serum albumin had no obvious change. The improvement of antifouling property for MPEG-modified membrane was accordant with the increase of PAA content in PSF/PAA-blended membranes. Protein UF experiments revealed that membrane fouling, especially irreversible membrane fouling, was remarkably reduced due to the incorporation of MPEG. The long-term protein UF experiment demonstrated the improvement of recycling property and the reliability of modification.
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Key words: blend; surface modification; methoxy polyethylene glycol; antifouling; crosslinking

INTRODUCTION

Numerous applications of ultrafiltration (UF) membranes, such as in food and dairy processing,[1] biopharmaceutical recovery,[2] wastewater treatment,[3] and reverse osmosis pretreatment.[4] Special engineering plastics like poly(ether sulfone) (PES),[5] polysulfone (PSF),[6] poly(vinylidene fluoride) (PVDF),[7] and polyacrylonitrile (PAN)[8] have become important UF membrane materials because of their good performances such as high mechanical property, good heat-aging resistance, and chemical stability.[9] A major challenge to these membrane materials is membrane fouling which is caused by the nonspecific protein adsorption on the membrane surface and in the membrane pores due to the inherent hydrophobic characteristics of these membrane materials.[10,11] The contaminants in the water cause membrane fouling, which decreases the UF membrane lifetime and represents a major roadblock to wider adoption of membrane technology for water purification.[12,13] Furthermore, chemical cleaning of membranes results in cost increment and disposal of waste.

In general, fouling occurs on hydrophobic surfaces as a result of protein adsorption, denaturation, and aggregation at the membrane-solution interface.[14] Compared with hydrophobic membranes, the membranes with hydrophilic surface have great advantage in reducing protein adsorption and deposition.[15,16] To resolve the fouling problem, a number of approaches, such as coating,[17] blend,[18,19] surface graft polymerization,[20,21] and chemical modification[22–25] have been reported in the literatures to reduce the membrane fouling. A particularly effective hydrophilic polymer for surface modification is poly(ethylene glycol) (PEG) due to its excellent resistance to protein adsorption and inherent biocompatibility.[26] In recent years, the immobilization of PEG on material surface to improve the blood compatibility and minimize membrane fouling is well-documented in Refs. 27–29.

The majority of polymer UF membranes were prepared by immersion precipitation.[30] Therefore, an alternative approach to UF membrane hydrophilic modification involves the addition of an amphiphilic copolymer to the membrane casting solution along with the base material.[31–33] Some researchers have been introduced polymers with photo-active or chemical-active into UF membranes though polymer blending.[26,28,34] Carboxyl groups have chemical

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reactivity and could be used to further modification. For example, Xu and coworkers[26,28] have synthesized poly(acrylonitrile-*co*-maleic acid)s (PANCMA) and blend it with polyacrylonitrile to fabricate UF membrane. The carboxyl groups could react with PEG to obtain a hydrophilic membrane. But these additives should be synthesized by the researchers themselves and had not been commercial application. Poly(acrylic acid) (PAA) is a commercial polymer and has been intensively used as additives during preparation of PSF and PES UF membranes by phase separation methods.[35,36] It is a simple method that makes it possible to fabricate, at low price, membranes that contain active carboxyl groups and hydrophilicity while keeping the PSF and PES advantages.

However, although the effect of hydrophilization of the polymer membrane can clearly be observed, the stability of the modifying agent in the membrane matrix can be a problem.[37–39] For example, when PAA was blended directly with other polymer as described in the literature,[35] the elution of PAA was unavoidable due to its water dissolubility. It seems that an increase molecular weight of hydrophilic additive enhances the entanglements of the soluble additive chains with membrane material chains, thus improving the retention of additive chains in the membrane matrix. Since both chemical activity and stability should be achieved for polymer membranes using PAA as additive, sometimes crosslinking process is necessary.[36]

The goal of this research was to enhance the surface hydrophilicity of PSF UF membranes to improve their fouling resistance. In this study, we developed an easy method to fabricate hydrophilic and stable PSF UF membranes though a blend-crosslinking-grafting process. The PAA was first blended with PSF to obtain a blended PSF/PAA UF membrane, and a crosslinking step was then introduced using hexanediamine as crosslinking agent. Finally, an end carboxyl group polyethylene glycol methyl ether (MPEG) was grafted on the PSF/PAA-blended membranes though an amidation reaction. Water contact angles were measured to confirm the variation of surface hydrophilicity. The scanning electron microscopy (SEM) was used to observe the morphological changes of membrane before and after modification. The permeation and antifouling properties of modified membranes were evaluated using bovine serum albumin (BSA) as a model protein. The UF results indicated that the antifouling property of modified membrane was significantly improved.

EXPERIMENTAL

Materials

Solvents and reagents were purchased from commercial sources and in analytical grade. PSF Udel-3500 (Amoco Company) was dried at 110°C for 12 h prior to use. PAA with a molecular weight of 450,000 g/mol was supplied by Aldrich. Hexanediamine was purchased from Sinopharm Chemical Reagent Co., 1-ethyl-3-(3-dimethyl amidopropyl) carbodiimide (EDC) was purchased from Shanghai Medpep Co.

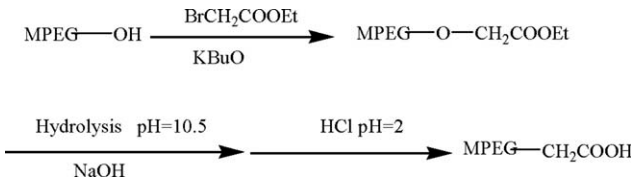

Figure 1 Synthesis route for the formation of MPEG-COOH.

The MPEG-COOH was synthesized from MPEG with method according to Ref. 40, which was summarized in Figure 1. The MPEG-COOH with the end carboxyl group was prepared and used as grafting modifier for its higher activity than MPEG. Furthermore, the MPEG-COOH had a superior stability in protein solution.[41]

Membrane preparation

Blended membrane preparation was followed the method according to Ref. 35. PSF and PAA were dissolved separately in DMF in a glass reactor equipped with a mechanical stirrer and thermostated at 90°C for more than 4 h. Afterward, the two solutions were mixed together in known proportions, and stirred for 120 min to form the casting dopes. The de-bubbled casting dope was cast on a glass plate with a steel knife and the plates were subsequently immersed into a deionized water bath at 20 ± 1°C and stored 12 h before crosslinking. The thickness of wet membranes was about 160 μm. The resulting membranes were designated as PSF/PAA-blended membranes.

Membrane modification

EDC was used to as a coupling reagent to activate the carboxyl groups in the PSF /PAA-blended membrane for 24 h at 4°C.[42] The EDC solution (0.1 wt %) was prepared by dissolving 100 mg of EDC in 100 mL of sodium citrate buffer solution at pH 4.7. Then, these EDC-activated membranes were reacted in 4 mg/mL hexanediamine solution at 4°C for 24 h. After the amidation reaction, the membranes were washed with deionized water. The resulting membranes were designated as N-PSF membrane.

A sample of 4 g end-carboxylic group MPEG was dissolved in a sodium citrate buffer solution (200 mL, pH 4.7), mixed with EDC (200 mg), and kept at 4°C for 5 h to activate the carboxyl groups. These

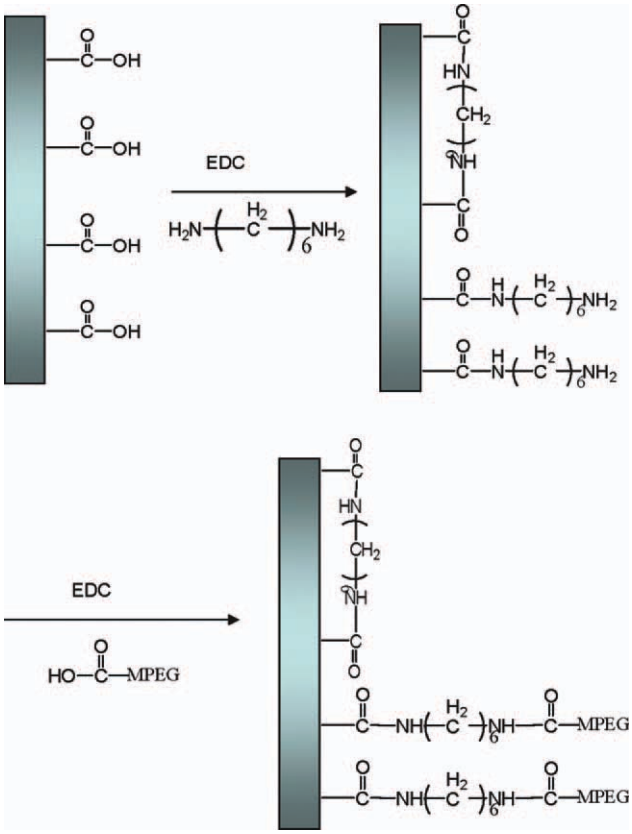

Figure 2 Fabrication process for the MPEG-modified membrane studied in this work. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

N-PSF membranes then were immersed into the end-carboxylic group MPEG solution (4 mg/mL) at 4°C for 24 h. After the amidation reaction, the membranes were washed with deionized water. The resulting membranes were designated as MPEG-modified membrane. Fabrication process for the MPEG-modified membrane is summarized in Figure 2.

According to Ref. 35, fabrication procedure was important for the properties of blended membranes. More transparent solutions were obtained by dissolved PAA and PSF separately. The complete dispersion of the solvent-swollen chains would enhance the entanglement of the compatible polymer chains in the casting dopes. With increase of the PAA content, the casting dopes turned to more and more cloud. When hydrophilic additives, such as poly (vinyl pyrrolidone) (PVP) and PEG, were blended directly with other polymer as described in the literature,[37] the elution of additive was unavoidable due to its water dissolubility in coagulation step and UF process. To overcome this obstacle, crosslinking was usually adopted as a method to form a crosslinking layer and enhance the stability of additives.[36,43] In this study, hexanediamine was used as a crosslinking agent to react with PAA and formed an active surface with amine group for further modification.

Membrane characterization

The surface and cross-sectional morphologies of membranes were observed by scanning electron microscope (Philips XL30E). In order to investigate the chemical changes between the original and modified membranes, a total reflection Fourier transform infrared (ATR/FTIR) spectroscopy (Eqoinox 55) was used.

Contact angle between water and membrane surface was measured with sessile drop method and a JC 2000C contact angle measurement instrument (Powereach Co., Shanghai, China) was used. A water droplet was placed onto the membrane surface, using a syringe, and the contact angle of the droplet was measured. At least 5 contact angles were averaged to get a reliable value.

Ultrafiltration experiments

A dead-end stirred cell filtration system was used to measure the flux of pure water and BSA fouling. The stirred cell (Model MSC300, Mosu Co., Shanghai, China) was connected with a nitrogen gas cylinder and solution reservoir. The cell had an inner diameter of 62 mm and a volume capacity of 300 mL. The effective area of the membrane was 30.2 cm^2. Nitrogen gas was used to maintain the system operation pressure. All the UF experiments were carried out at stirring speed of 400 rpm to minimize concentration polarization. After the membrane was fixed, the stirred cell and the solution reservoir were filled with deionized water. Each membrane was initially pressurized at 0.15 MPa for 30 min. Then, the pure water flux (J_{w1}) was measured after 15 min operation at 0.1 MPa. Next, 1.0 mg/mL BSA phosphate buffer saline (PBS, 0.1 mol/L, pH 7.0) was added to the reservoir and the flux (J_p) was evaluated after 30 min UF. Finally, the BSA solution was replaced by deionized water. The membrane was cleaned in stirred cell with deionized water for 20 min at speed of 400 rpm, and the water flux (J_{w2}) was measured again at 0.1 MPa. In the long-term UF process, the UF operations in a sequence of pure water, BSA solution, and water cleaning, were repeated four cycles to evaluate the flux recovery properties of modified membranes.

The water flux of membrane was calculated by the following equation:

$$J_w = \frac{V}{ADt} \tag{1}$$

where $V(L)$ was the volume of permeated water, A (m^2) was the membrane area, and Δt (h) was the operation time.

$$\mathrm{FRR} = \frac{J_{w2}}{J_{w1}} \times 100\% \tag{2}$$

The BSA rejection ratio, Re, was defined as follows:

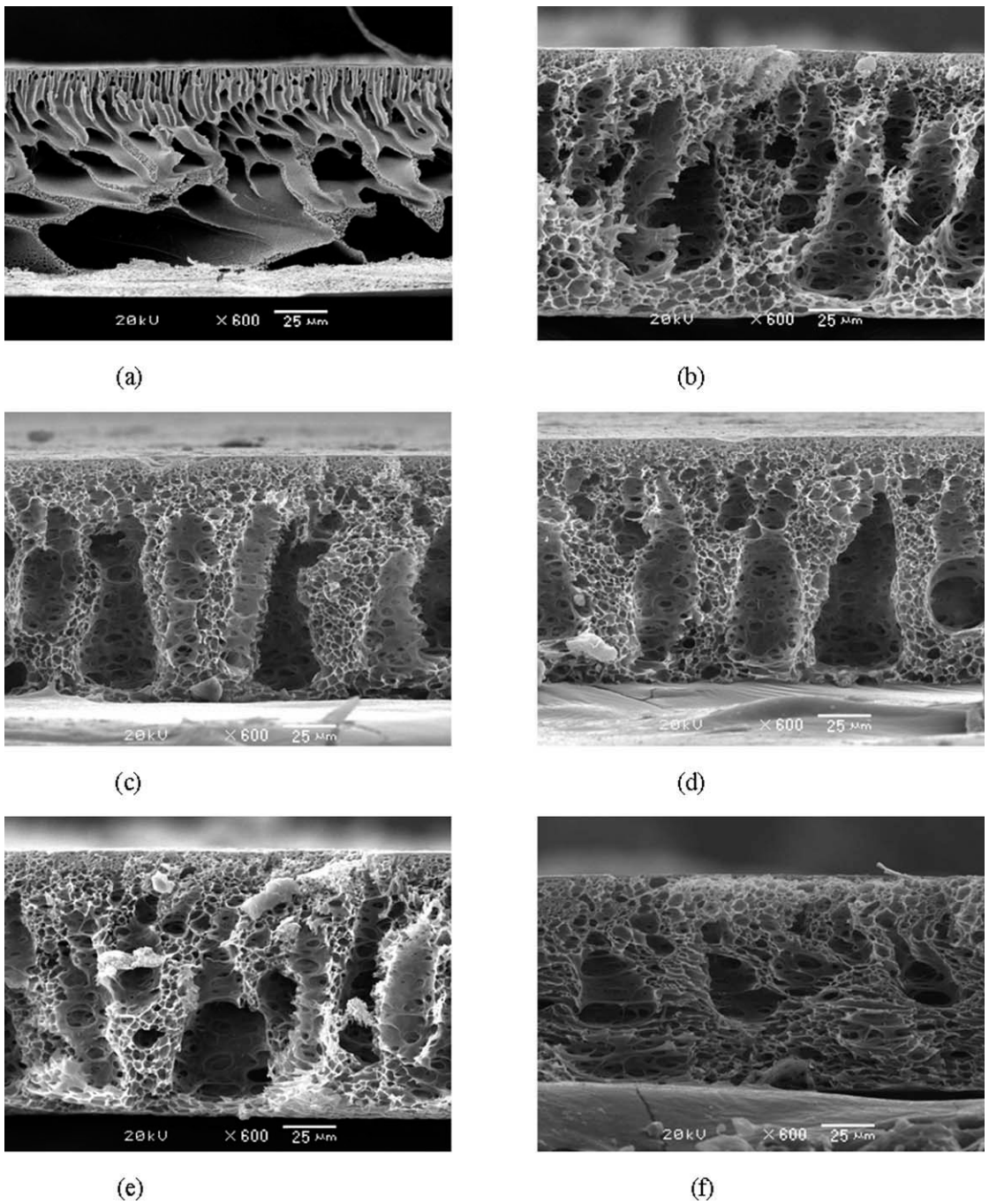

Figure 3 Cross-sectional SEM morphologies for PSF control membrane (a) and PSF/PAA-blended membranes with PAA content of 2.0 wt % (b), 4.0 wt % (c), 6.0 wt % (d), 8.0 wt % (e), and 10.0 wt % (f) in casting solutions.

$$Re(\%) = (1 - \frac{C_p}{C_b}) \times 100\% \quad (3)$$

where C_p and C_b (mg/mL) were BSA concentrations of permeate and feed solutions, respectively.

RESULTS AND DISCUSSION

Characterization of the PSF/PAA-blended membranes and MPEG-modified membranes

The cross-sectional morphologies of PSF control and PSF/PAA-blended membranes are shown in Figure 3. All the membranes exhibited the typical asymmetric structure of UF membranes with a top dense layer, a porous sublayer and fully developed macropores at the bottom. According to the study of Boom et al.,[44] the addition of a high molecular weight polymer to a casting dope would suppress the macrovoid formation. The changes in the membrane structure and characteristics would be caused by the system property modification due to the presence of PAA. The most important feature in the SEM studies is the absence of clear polymer–

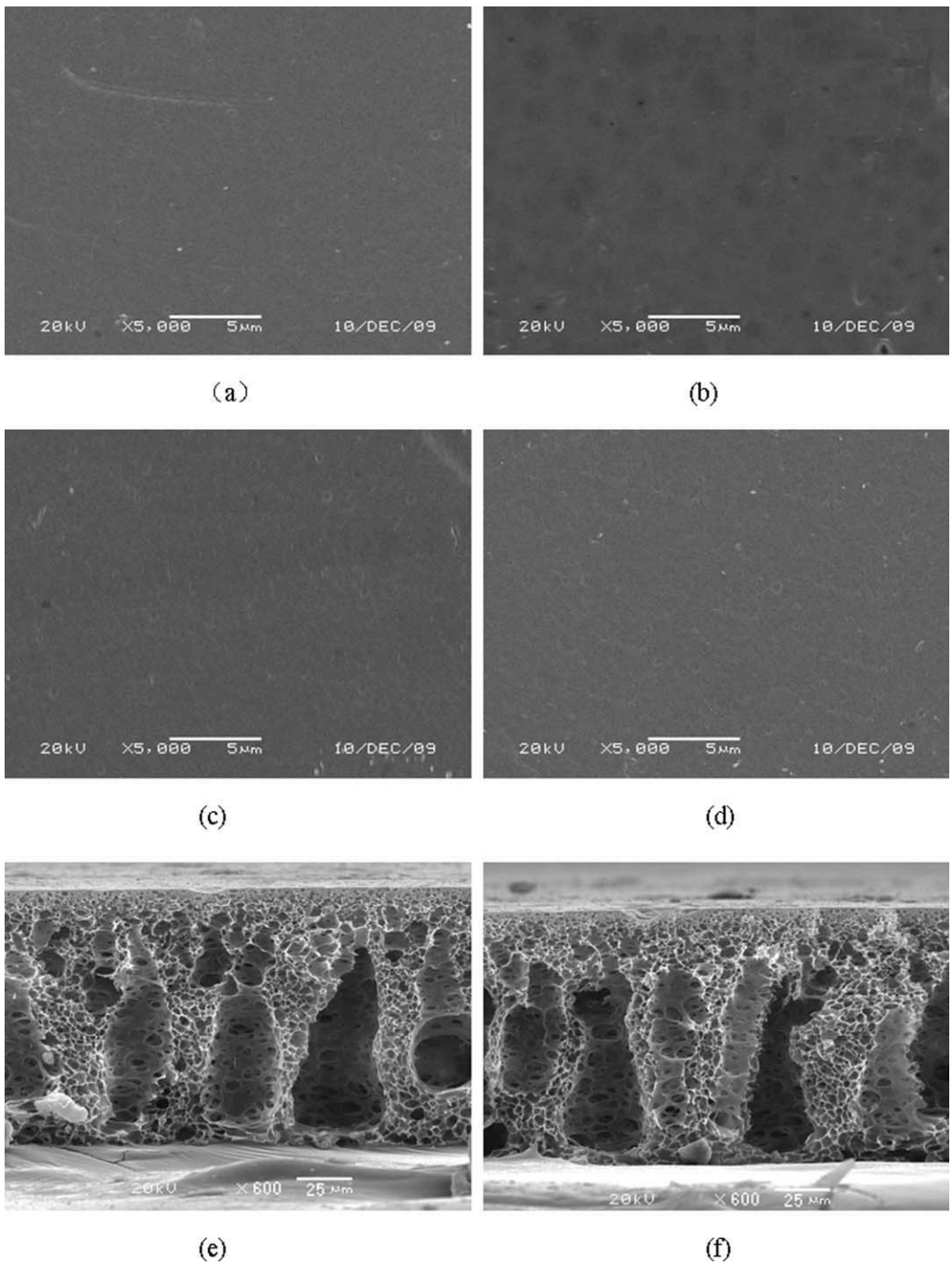

Figure 4 Surface morphologies of PSF control membrane (a), PSF/PAA-blended membrane (PAA 4.0 wt % in casting solution) (b), N-PSF membrane (PAA 4.0 wt % in casting solution) (c), MPEG-modified membrane (PAA 4.0 wt % in casting solution) (d), cross-sectional SEM morphologies for PSF/PAA-blended membranes (e), and MPEG-modified membranes (f) with PAA content of 6.0 wt % in casting solutions.

polymer phase separation in the solidified materials. This feature may indicate a good interpenetration of PSF and PAA chains in the asymmetric membranes. With the PAA content increased from 0 to 10.0 wt %, the finger-like structure decreased when compared with the PSF control membrane [Fig. 3(a)]. Similar structures of PSF/PAA-blended membranes were shown in other references.[35,36] The sponge-like structure appeared at the higher content of PAA in the membrane. This phenomenon was probably caused by phase separation, responsible for the formation of the membranes' asymmetric structure, being retarded by the hydrophilic nature of PAA in casting solution.[45] Similar phenomenon had been reported by Jung and Nam.[46,47]

Figure 4 presents the surface and cross-sectional morphologies of PSF control and modified membranes. There were no significant morphological

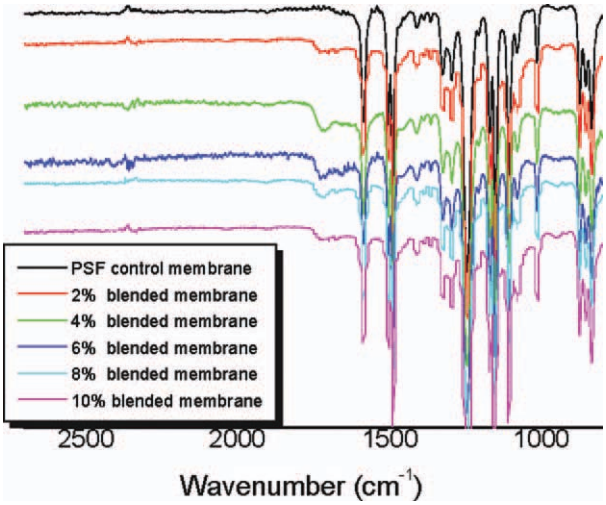

Figure 5 ATR/FTIR spectra of PSF control membrane (a), and PSF/PAA-blended membranes with PAA content of 2.0 wt % (b), 4.0 wt % (c), 6.0 wt % (d), 8.0 wt % (e), and 10.0 wt % (f) in casting solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

variations between PSF control and modified membranes. It was thus inferred that surface modification did not appreciably change the morphology of PSF UF membrane. In fact, grafting was a surface modification technology under mild conditions, which would probably have negligible effect on the membrane structure.

Figure 5 presents FTIR/ATR spectra of PSF control membrane and blended PSF/PAA membrane. For the PSF/PAA blend membranes, a new characteristic peak was observed, which was centered at 1728 cm^{-1} and attributed to the carboxylic acid group in PAA. The characteristic peak was related to PAA content in the PSF/PAA-blended membrane. In Figure 4, the characteristic peak intensity had an increase trend when the PAA content increased from 0 to 4.0 wt %, and then showed a decrease when the PAA content further increased. The result indicated that the PAA content in the blended membranes had a maximum value when the PAA content reached 4.0 wt % in casting solution. The decrease in the characteristic peak intensity, when the PAA content relative to total polymers in the casting solution increased, indicates a significant loss in PAA in the coagulation (and washing) step.

Figure 6 is FTIR/ATR spectra of PSF control membrane, PSF/PAA-blended membrane, N-PSF membrane and MPEG-modified membrane. The spectrum of the PSF/PAA-blended membrane showed an absorbance band at 1728 cm^{-1}, which was the characteristic peak for carboxyl group in carboxylic acid. When the PSF/PAA-blended membrane was reacted with hexanediamine in the presence of EDC, carboxylic acid groups in the polymer chain formed amide bonds with the primary amines of hexanediamine [scheme is shown in Fig. 6(b)]. The amide bond peaks were observed at 1660 and 1540 cm^{-1}, which correspond to C=O stretching (amide I) and N—H in-plane bending (amide II),[48,49] respectively. Meanwhile, the characteristic peak of carboxylic acid disappeared. For the MPEG-modified membrane, two additional absorptions are observed, which are centered at 943 and 2880 cm^{-1} and attributed to the CH_2 rock and C—C stretch, and the CH_2 symmetric stretch of MPEG, respectively.[50] At the same time, a slight increase in peak intensity at 1660 and 1540 cm^{-1} were evident in Figure 6(d).

The hydrophilicity of PSF/PAA-blended membranes and MPEG-modified membranes were characterized though the measurement of water contact angle. As carboxylic group of PAA was a hydrophilic group, PSF/PAA-blended membranes would show a higher hydrophilicity than PSF control membrane.[38,51] Figure 7 showed the relationship between the water contact angle and the PAA content in casting dope. When the PAA content was increased from 0 to 4.0 wt %, the water contact angle of PSF/PAA blend membrane was dropped from 75° to 64°. However, it had a slight increase from 64° to 72° when the PAA content was further increased from 4.0 to 10.0 wt %. Water contact angle related to the PAA content of the PSF/PAA-blended membrane. Generally, contact angle decreased with the increase of PAA mass ratio in PSF/PAA-blended membrane. A smaller water contact angle meant a higher PAA content in the PSF/PAA-blended membranes and a

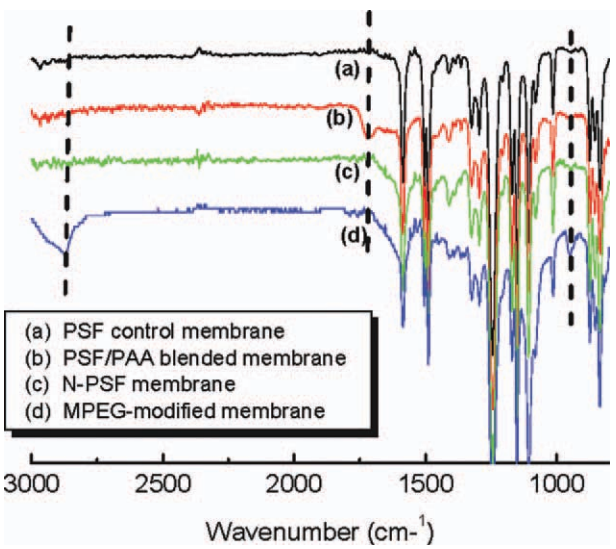

Figure 6 ATR/FTIR spectra of PSF control membrane (a), and PSF/PAA-blended membranes (PAA 4.0 wt % in casting solution) (b), N-PSF membrane (PAA 4.0 wt % in casting solution) (c), and MPEG-modified membrane (PAA 4.0 wt % in casting solution) (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

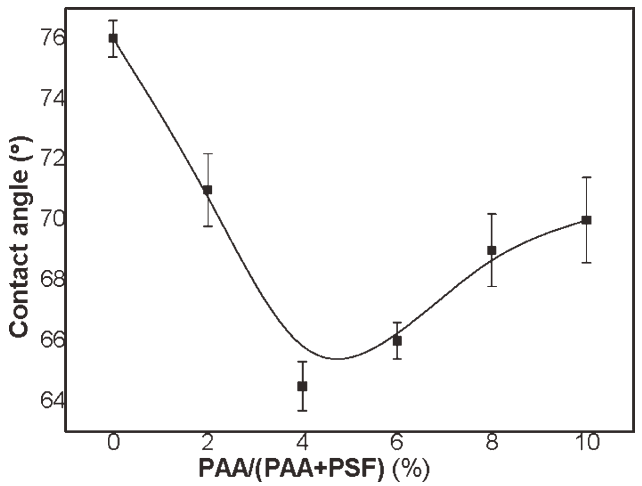

Figure 7 The contact angles for PSF/PAA-blended membranes as a function of PAA content in casting solution.

higher carboxylic group content on the membrane surface. The result indicated that a significant loss in PAA in the coagulation (and washing) step when PAA content exceeded 4.0 wt %. It seemed that an increase in the proportion of insoluble PSF enhanced the entanglements of the soluble PAA chains with PSF chains, thus improving the retention of PAA chains in the membrane matrix. In this study, PAA had a high-molecular weight (45,000), which increased the chance of formation of PSF/PAA aggregation. The result was accordance with that of ATR/FTIR in Figure 7.

The effect of PAA content in casting solution on contact angles of MPEG-modified membranes is shown in Figure 8. It can be seen that all MPEG-modified membranes showed lower contact angles than those of PSF/PAA-blended membranes in the same PAA content of the casting solution. Among them, the membrane with 4.0 wt % PAA manifested the lowest value of 54.5°, which indicated the highest hydrophilicity. The decrease tendency of water contact angles was consistent with the results of PSF/PAA-blended membranes, which was shown in Figure 7. These results indicated that there was a substantial increase of surface hydrophilicity for MPEG-modified membrane due to surface modification. The improvement of hydrophilicity meant a higher antifouling property in BSA UF.

Permeation and separation property of the MPEG-modified membranes

UF experiments were carried out to investigate the permeability of the PSF/PAA-blended membrane and the MPEG-modified PSF membranes. Table I shows the formulations of casting solutions and water flux of PSF/PAA-blended membrane. It was found that with the increase of PAA content from 0 to 10.0 wt %, a decline of the pure water flux for PSF/PAA-blended membranes was observed from 170.6 to 126 L/m^2 h. This was attributed to morphology changes of the membrane skin layer, e.g. the increasing thickness of the skin layer. Meanwhile, the rejection ratio of BSA was decreased from 95% to 89.1%.

Table II shows the flux variation of the modification process. There were several factors affecting the water permeability of the membrane, such as the thickness of dense top layer, the property (pore radius and pore density), and the hydrophilicity of the membrane. The flux change could be explained by the balance between the pore-covering effect of the grafted chains and the increase hydrophilicity. It was generally accepted that, through surface grafting of MPEG, improvement in the hydrophilicity of UF membrane may bring some increase to the water permeation flux.[26,28] Meanwhile, the grafting of MPEG would block the membrane pore, which caused the decrease of pure water flux. Results of UF experiments of MPEG-modified membranes are showed in Table II. It was found that membrane flux could be slightly increased by the introduction of MPEG. In this study, the increase of membrane hydrophilicity played a major factor for the variation of pure water flux.

Stability of the MPEG-modified membrane

The stability of MPEG-modified membrane was studied by the following methods: the modified membranes were washed with deionized water drastically for two weeks, and then measured the variation of pure water flux and water contact angles.

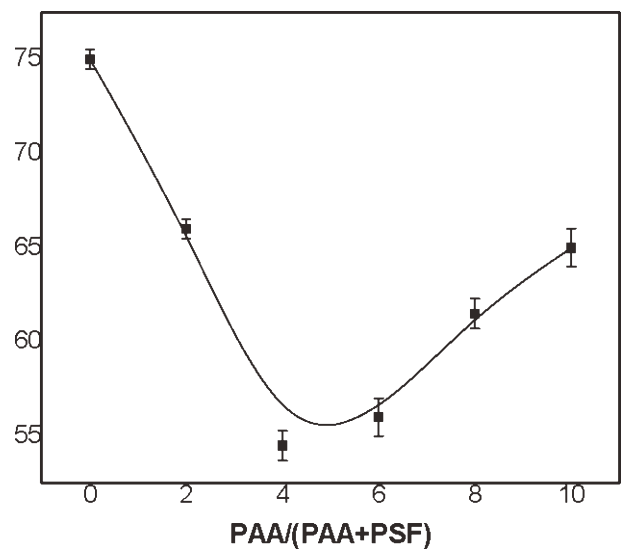

Figure 8 The contact angles for MPEG-modified membranes as a function of PAA content in casting solution.

TABLE I
The Composition and Permeation Properties of PSF/PAA-Blended Membrane Casting Solutions

Membrane	PAA (g)	PSF (g)	DMF (g)	PEG-400 (g)	PAA/(PAA + PSF) (%)	Pure water flux (L/m^2 h)	BSA rejection (%)
1#	0	15	79	6	0	170.6	95.2
2#	0.3	14.7	79	6	2	164.0	91.6
3#	0.6	14.4	79	6	4	150.0	92.3
4#	0.9	14.1	79	6	6	142.6	91.1
5#	1.2	13.8	79	6	8	134.0	89.7
6#	1.5	13.5	79	6	10	126.0	89.1

The results showed that the pure water flux and water contact angles had not obvious changes.

It was considered that the stability of the modified membrane originated from the crosslinking process. Before the crosslinking process, when the polymer chains were rapidly frozen into membranes by coagulation in water, the PSF and PAA would remain entangled to a large extent and the entangled PAA chains would be much less extractible from the vitrified PSF matrix. Although a good interpenetration of PSF and PAA chains in the asymmetric membranes, a gradually dissolution of PAA in the aqueous media during the membrane washing and storage steps could not be avoided.[35,36] After crosslinking process with hexamethylendiamine, the PAA was formed a reticulate structure in the blended membranes. To examine this hypothesis, a PSF/PAA-blended membrane and a PEG-modified membrane were immersed into DMF, separately. After 1 h, the PSF/PAA-blended membrane was completely dissolved, and the PEG-modified membrane still remained some residues, which was not dissolved in DMF. These results indicated that the crosslinking process could make the stability of PAA significantly enhanced.

Effect of PAA content on the antifouling property of modified membranes in protein UF process

Generally speaking, flux decline in protein UF is attributed to two main sources: concentration polarization and membrane fouling. In this study, concentration polarization could be alleviated by rigorous stirring (400 rpm) near the membrane surface.[29] Fouling occurs in two common ways: cake formation and adsorption of foulants. Fouling due to cake fouling is generally reversible by water flushing, which was defined as reversible fouling (R_r). Fouling due to the adsorption of foulants is essentially irreversible which occurs on both the membrane surfaces and pore walls, which was defined as irreversible fouling (R_{ir}). The flux decline caused by protein fouling in UF process was defined as total fouling (R_t).

TABLE II
Permeation and Antifouling Properties of Control PSF Membrane and MPEG-Modified Membranes

Membrane number	Relative flux (J_{w1}/J_0)	FRR (%)	BSA Rejection Ratio (%)
7#	1.09	80.59	94.4
8#	1.15	86.52	96.8
9#	1.13	81.01	94.2
10#	1.05	78.02	92.9
11#	1.09	77.93	92.1

$$R_t = \frac{J_{w1} - J_p}{J_{w1}} \quad (4)$$

$$R_r = \frac{J_{w2} - J_p}{J_{w1}} \quad (5)$$

$$R_{ir} = \frac{J_{w1} - J_{w2}}{J_{w1}} \quad (6)$$

A summary of R_r, R_{ir}, and R_t of the MPEG-modified membrane and PSF control membrane were shown in Figure 9. A decreased R_t could be observed with an increase of PAA concentration from 0 to 10.0 wt %, which indicated that the MPEG-modified membrane could maintain a higher flux in BSA UF process. When the PAA concentration was increased from 0 to 4.0 wt %, R_{ir} of the MPEG-modified membrane was dropped from 0.61 to 0.13. However, it had a slight increase from 0.13 to 0.22 when the PAA concentration was further increased from 4.0 wt % to 10.0 wt %. Meanwhile, R_r exhibited a slight increase. These results indicated that MPEG immobilization on membrane surface had remarkably reduced both total and irreversible fouling. In other words, reversible fouling (R_r), which could be removed by hydraulic cleaning, became the dominate factor responsible for the flux loss after the modification.

These results indicated that the MPEG-modified membrane could keep a higher flux in BSA UF process and had a superior flux recovery after hydraulic cleaning. As we known, when protein molecule contacted with the membrane surface, water molecules

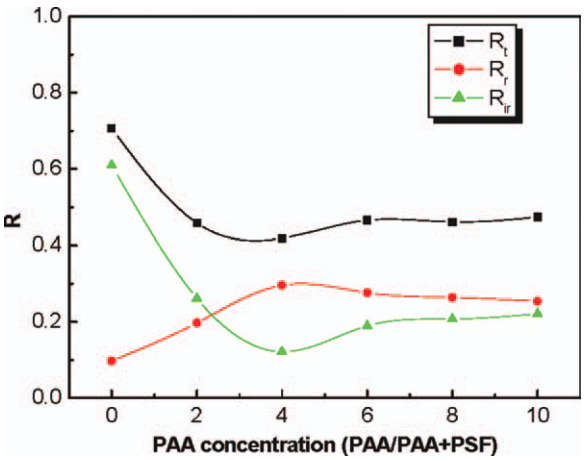

Figure 9 Total, reversible, and irreversible fouling ratio (R_t, R_r, R_{ir}) of MPEG-modified membrane with different PAA concentration of 0, 2.0, 4.0, 6.0, 8.0, and 10.0 wt % in casting solution, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between protein and the membrane surface would be replaced. In this process, conformation of protein molecule would change, which was considered to be one of the driving forces for protein adsorption and the reason of irreversible membrane fouling. The antifouling property improvement of MPEG-modified membrane was due to the appearance of hydrophilic MPEG on the membrane surface. For PSF control membrane, BSA molecules could directly adsorb onto the hydrophobic surface; but when MPEG was introduced, the protein adsorption sites were substantially disappeared and the amount of adsorbed BSA was considerably declined on membrane surface and in membrane pore. Furthermore, after a hydrophilic MPEG layer was formed, the chance for protein molecules to contact membrane surface were dramatically reduced,[29] thus irreversible fouling and subsequently total fouling were decreased.

The results of ATR/FTIR and contact angles indicated that the PSF/PAA-blended membrane (4.0 wt %) had the highest carboxylic group density. With the increase of the content of PAA in PSF/PAA-blended membrane, the PSF/PAA-blended membrane had more active sites for immobilization of MPEG on the membrane surface. Thus, the MPEG density on the membrane surface was consistent with the PAA content in the blended membranes. With the density of MPEG immobilized on the membrane surface increasing, the protein adsorption site was significantly reduced and formed a hydrophilic layer. Hydrophilic layer exclude the protein to avoid the substantial entropy loss caused by the entrance of large protein molecules into the MPEG layer.[52] Therefore, less protein would be absorbed at the interface of the membrane surface and the bulk solution, which rendered the membranes "easy to clean."

Comparison of PSF and MPEG-modified membranes in protein fouling process

In the practical application, the UF membranes should keep long-term antifouling property. The excellent antifouling property endows the MPEG-modified UF membranes with potential application in protein separation and purification for a long time without significant decrease of separation performance. Four times of BSA solution (1 mg/mL) UF with the cleaned membranes were carried out, and the results are shown in Figure 10.

Figure 10 presents the time-dependent flux of PSF control membrane and MPEG-modified membrane with 4.0 wt % PAA content for 10 h. After four times of BSA UF with a total operation time of 10 h and corresponding four times of hydraulic cleaning, the pure water flux of blend membrane was maintained at 157.1 L/(m^2 h), 83.1% of the initial value, while the pure water flux of PSF control membrane was only 59.71 L/(m^2 h), 35% of the initial value. The results indicated that the recycling property of the MPEG-modified membranes was significantly improved, and it was also indicated that the crosslinking through hexamethylendiamine had a relatively remarkable stability, which was due to the crosslinking between PAA and hexamethylendiamine.

CONCLUSIONS

A novel blend-crosslinking-grafting process was exploited for the modification of PSF UF membrane.

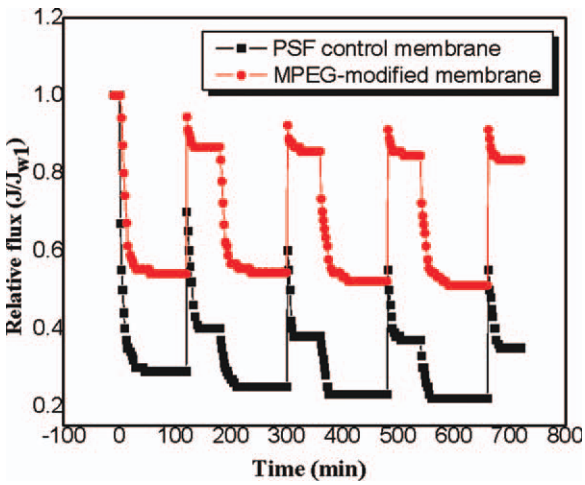

Figure 10 Time-dependent flux of PSF control membrane and MPEG-modified membrane (PAA 4.0 wt %) in casting solution during a process of five recycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

More specifically, PSF and PAA at a given weight percentage were dissolved in DMF separately, and then mixed to form casting solution. Hexamethylendiamine was used as a crosslinking agent and formed an amination of the membrane surface. Finally, an end carboxyl group MPEG was grafted though an amidation reaction. The stable residence of MPEG was validated by water contact angle and ATR/FTIR measurement. The MPEG-modified membranes showed higher hydrophilicity and superior resistance to protein fouling compared with PSF control membranes. The increase of hydrophilicity or adsorption peak intensity resulted in higher PAA content in the PSF/PAA-blended membranes and better antifouling property for MPEG-modified membranes. When the PAA content of blended membrane was 4.0 wt %, the flux recovery ratio of MPEG-modified membrane reached as high as 83.1%. The improved recycling property rendered the MPEG-modified membranes with favorable long-term utilization. Furthermore, the MPEG-modified membranes exhibited ideal permeation performance in protein process.

NOMENCLATURE

A	Effective membrane area (m^2)
C_b	Concentration of BSA in feed solution (mg/mL)
C_p	Concentration of BSA in permeate solution (mg/mL)
J_0	Pure water flux of membranes before modification (L/m^2 h)
J_{w1}	Pure water flux of membranes after modification (L/m^2 h)
J_p	Flux of membranes in BSA UF (L/m^2 h)
J_{w2}	Pure water flux of membranes after hydraulic cleaning (L/m^2 h)
V	Volume of permeated water (L)
R_r	Degree of reversible flux loss
R_{ir}	Degree of irreversible flux loss
R_t	Degree of total flux loss
W_1	Weight of dried PSF membrane before modification (g)
W_0	Weight of dried PSF membrane after modification (g)
Δt	UF time (h)
η	Relative water flux

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