Special Issue: Microfiltration and Ultrafiltration Membrane Science and Technology

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and Prof. Bart Van der Bruggen (University of Leuven)

EDITORIAL

Microfiltration and Ultrafiltration Membrane Science and Technology
I. C. Escobar and B. Van der Bruggen, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.42002**

REVIEWS

Nanoporous membranes generated from self-assembled block polymer precursors: *Quo Vadis*?
Y. Zhang, J. L. Sargent, B. W. Boudouris and W. A. Phillip, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41683**

Making polymeric membranes anti-fouling via "grafting from" polymerization of zwitterions
Q. Li, J. Imbrogno, G. Belfort and X.-L. Wang, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41781**

Fouling control on MF/ UF membranes: Effect of morphology, hydrophilicity and charge
R. Kumar and A. F. Ismail, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.42042**

EMERGING MATERIALS AND FABRICATION

Preparation of a poly(phthalazine ether sulfone ketone) membrane with propanedioic acid as an additive and the prediction of its structure
P. Qin, A. Liu and C. Chen, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41621**

Preparation and characterization of MOF-PES ultrafiltration membranes
L. Zhai, G. Li, Y. Xu, M. Xiao, S. Wang and Y. Meng, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41663**

Tailoring of structures and permeation properties of asymmetric nanocomposite cellulose acetate/silver membranes
A. S. Figueiredo, M. G. Sánchez-Loredo, A. Maurício, M. F. C. Pereira, M. Minhalma and M. N. de Pinho, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41796**

LOW-FOULING POLYMERS

Low fouling polysulfone ultrafiltration membrane via click chemistry
Y. Xie, R. Tayouo and S. P. Nunes, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41549**

Elucidating membrane surface properties for preventing fouling of bioreactor membranes by surfactin
N. Behary, D. Lecouturier, A. Perwuelz and P. Dhulster, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41622**

PVC and PES-*g*-PEGMA blend membranes with improved ultrafiltration performance and fouling resistance
S. Jiang, J. Wang, J. Wu and Y. Chen, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41726**

Improved antifouling properties of TiO_2/PVDF nanocomposite membranes in UV coupled ultrafiltration
M. T. Moghadam, G. Lesage, T. Mohammadi, J.-P. Mericq, J. Mendret, M. Heran, C. Faur, S. Brosillon, M. Hemmati and F. Naeimpoor, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41731**

Development of functionalized doped carbon nanotube/polysulfone nanofiltration membranes for fouling control
P. Xie, Y. Li and J. Qiu, *J. Appl. Polym. Sci.* 2015, DOI: **10.1002/app.41835**

SURFACE MODIFICATION OF POLYMER MEMBRANES

Highly chlorine and oily fouling tolerant membrane surface modifications by *in situ* polymerization of dopamine and poly(ethylene glycol) diacrylate for water treatment
K. Yokwana, N. Gumbi, F. Adams, S. Mhlanga, E. Nxumalo and B. Mamba, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41661**

Fouling control through the hydrophilic surface modification of poly(vinylidene fluoride) membranes
H. Jang, D.-H. Song, I.-C. Kim, and Y.-N. Kwon, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41712**

Hydroxyl functionalized PVDF-TiO$_2$ ultrafiltration membrane and its antifouling properties
Y. H. Teow, A. A. Latif, J. K. Lim, H. P. Ngang, L. Y. Susan and B. S. Ooi, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41844**

Enhancing the antifouling properties of polysulfone ultrafiltration membranes by the grafting of poly(ethylene glycol) derivatives via surface amidation reactions
H. Yu, Y. Cao, G. Kang, Z. Liu, W. Kuang, J. Liu and M. Zhou, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41870**

SEPARATION APPLICATIONS

Experiment and simulation of the simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed micelles
A. D. Vibhandik, S. Pawar and K. V. Marathe, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41435**

Polymeric membrane modification using SPEEK and bentonite for ultrafiltration of dairy wastewater
A. Pagidi, Y. Lukka Thuyavan, G. Arthanareeswaran, A. F. Ismail, J. Jaafar and D. Paul, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41651**

Forensic analysis of degraded polypropylene hollow fibers utilized in microfiltration
X. Lu, P. Shah, S. Maruf, S. Ortiz, T. Hoffard and J. Pellegrino, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41553**

A surface-renewal model for constant flux cross-flow microfiltration
S. Jiang and S. G. Chatterjee, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41778**

Ultrafiltration of aquatic humic substances through magnetically responsive polysulfone membranes
N. A. Azmi, Q. H. Ng and S. C. Low, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41874**

BIOSEPARATIONS APPLICATIONS

Analysis of the effects of electrostatic interactions on protein transport through zwitterionic ultrafiltration membranes using protein charge ladders
M. Hadidi and A. L. Zydney, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41540**

Modification of microfiltration membranes by hydrogel impregnation for pDNA purification
P. H. Castilho, T. R. Correia, M. T. Pessoa de Amorim, I. C. Escobar, J. A. Queiroz, I. J. Correia and A. M. Morão, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41610**

Hemodialysis membrane surface chemistry as a barrier to lipopolysaccharide transfer
B. Madsen, D. W. Britt, C.-H. Ho, M. Henrie, C. Ford, E. Stroup, B. Maltby, D. Olmstead and M. Andersen, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41550**

Membrane adsorbers comprising grafted glycopolymers for targeted lectin binding
H. C. S. Chenette and S. M. Husson, *J. Appl. Polym. Sci.* 2015, **DOI: 10.1002/app.41437**

Enhancing the antifouling properties of polysulfone ultrafiltration membranes by the grafting of poly(ethylene glycol) derivatives via surface amidation reactions

Haijun Yu,[1] Yiming Cao,[1] Guodong Kang,[1] Zhongnan Liu,[1,2] Wu Kuang,[1,2] Jianhui Liu,[1] Meiqing Zhou[1]

[1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China
Correspondence to: H. Yu (E-mail: yuhj@dicp.ac.cn)

ABSTRACT: A carboxylic acid group was introduced on the polysulfone (PSF) membrane surface through a Friedel–Crafts reaction. Then, three kinds of poly(ethylene glycol) (PEG) derivatives were chosen to be immobilized on the PSF membrane surface via amide bonds. The membrane surface morphology, chemical composition, and hydrophilicity were investigated with scanning electron microscopy, attenuated total reflectance Fourier transform infrared spectroscopy, and water contact angle. The results indicate that PEG derivative immobilization effectively improved the antifouling properties of the PSF membranes. We found that prolonging the Friedel–Crafts reaction time or choosing the proper PEG derivative [methoxy poly(ethylene glycol) 550] could increase the surface hydrophilicity effectively and thus render the modified membranes better antifouling properties. The long-term ultrafiltration experiment demonstrated the improvement of recycling properties and the reliability of the surface modification process. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41870.

INTRODUCTION

In recent years, ultrafiltration as a novel and powerful technology has been widely used in many areas, including wastewater treatment, protein separation, and dairy industry.[1–3] Membrane fouling caused by the nonspecific adsorption or deposition of protein molecules on the membrane surface or pore wall leads to a serious reduction of flux; this seriously restricted ultrafiltration applications.[4,5] It has been widely accepted that the surface chemical and physical properties (molecular weight cutoff, surface wettability, surface charge, and surface acidic/basic character) play dominant roles in determining the antifouling characteristics.[6] Compared with hydrophobic membranes, membranes with hydrophilic surfaces have great advantages in mitigating membrane fouling.[7,8]

Polysulfone (PSF) is a thermoplastic widely used for the production of ultrafiltration processes and gas separation for its excellent chemical, thermal, and mechanical stability.[9–11] However, the hydrophobic nature of the PSF ultrafiltration membrane leads to serious membrane fouling. The adsorption of protein on the membrane surface and pores can cause serious membrane fouling, and this can have a great impact on the efficiency and economics of the ultrafiltration process. To overcome such problems, PSF ultrafiltration membranes have been modified by the coating of hydrophilic polymers onto the PSF membrane surface,[12] blending,[3,13,14] grafting of hydrophilic polymers onto PSF membranes through radical reactions generated with low-temperature plasma,[15–17] ultraviolet radiation,[18,19] γ radiation,[20] or chemical reaction.[21–24] The incorporation of functional groups, such as carboxyl groups or sulfonic acid groups, into the polymer matrix has been demonstrated an effective strategy for providing an active site for surface modification.[25,26]

Poly(ethylene glycol) (PEG) is well known for its extraordinary ability to resist protein adsorption because of its hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in an aqueous medium.[27] For example, Xu and coworkers[28,29] prepared ultrafiltration membranes with excellent protein-adsorption resistance and biocompatibility properties through the covalent immobilization of PEG onto the polysulfone membrane surface. Compared to membranes with carboxylic acid, the membrane-grafted PEG had a higher pure water flux and favorable antifouling properties. However, because the end functional group of PEG was a hydroxyl group, the membrane had a low activity in the chemical reaction, and this seriously limited the application of PEG in the membrane modification process. Therefore, many PEG derivatives have
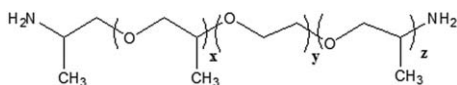
Figure 1. Structure of ED600 and ED2000 [O,O'-bis(2-aminopropyl) poly(propylene glycol)-*block*-PEG-*block*-poly(propylene glycol) (weight-average molecular weight = 600), Jeffamine ED600 $x + z = 3.6$, $y = 9.0$, O,O'-bis(2-aminopropyl) poly(propylene glycol)-*block*-PEG-*block*-poly(propylene glycol) (weight-average molecular weight = 2000), Jeffamine ED2000 $x + z = 6.0$, $y = 39$].

been developed, such as PEG with double bonds [poly(ethylene glycol methyl methacrylate) or poly(ethylene glycol double acrylate)][30–33] and PEG with some active groups (e.g., amino groups and carboxyl groups).[34] Compared with PEG, these derivatives have a higher reaction activity and can be used easily in membrane modification. However, these PEG derivatives are so expensive that they are not suitable for membrane modification. Therefore, a PEG derivative that is cheaper, easy to buy, or can be conveniently prepared should be used for membrane modification applications.

In this study, a carboxyl acid group was introduced on the PSF ultrafiltration membrane surface through a Friedel–Crafts reaction. Then, three kinds of PEG derivatives were chosen to be immobilized on the PSF membranes. The two kinds of PEG derivatives were commercial polymers that had amino groups on the end, and the other polymer was an end-carboxyl-group methoxy poly(ethylene glycol) 550 (MPEG550), which was synthesized in our laboratory. The surface morphologies and interior structures of these membranes were observed by scanning electron microscopy (SEM). The surface chemical composition and hydrophilicity improvement were analyzed by attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy and contact angle (CA) measurement, respectively. Their antifouling properties to bovine serum albumin (BSA) solution and permeation properties were studied by an end filtration model.

EXPERIMENTAL

Materials
PSF Udel-3500 (Amoco Co.) was dried at 110°C for 12 h before use. Solvents and reagents were purchased from commercial sources and were analytical grade. O,O'-Bis(2-aminopropyl) poly(propylene glycol)-*block*-PEG-*block*-poly(propylene glycol) with a molecular weight of 600 (Jeffamine ED600) and O,O'-bis(2-aminopropyl) poly(propylene glycol)-*block*-PEG-*block*-poly(propylene glycol) with a molecular weight of 2000 (Jeffamine ED2000) were purchased from Hunstman Co., Ltd. The molecular structures of ED2000 and ED600 are given in Figure 1. Compared with other PEG derivatives, ED600 and ED2000 are cheaper and easier to get. MPEG550 with a molecular mass of about 550 g/mol was purchased from Aldrich Co. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was purchased from Shanghai Medpep Co., Ltd. BSA was purchased from Aoboxing Biotechnology Limited Co. (Beijing, China). Anhydrous tin tetrachloride was purchased from Fluka and was used as received. Sodium hydroxide (NaOH), PEG with a molecular weight of 400 (PEG400), and dimethyl acetamide
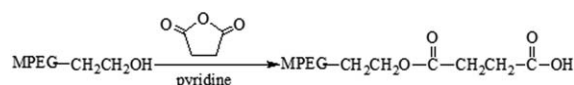
Scheme 1. Schematic illustration of the terminal carboxyl group MPEG synthetic process.

were all analytical grade and were used without further purification.

The end carboxylic acid MPEG550 was synthesized from methoxy poly(ethylene glycol) (MPEG) with a classical synthesis method according to ref. [35; this method is summarized in Scheme 1.

Preparation and Modification of the Membranes
PSF membranes were fabricated through an immersion precipitation method. Casting solutions were prepared by the dissolution of PSF (14 wt %) and PEG400 (6 wt %) into dimethylacetamide with vigorous stirring to form a homogeneous solution. After the removal of air bubbles, the casting solution was cast onto a clean glass plate with a casting knife with a 200-μm gate open. The nascent membrane was placed in air (25°C, 45–50% relative humidity) for 10 s and then immersed in running water for 24 h.

Before surface modification, the PSF ultrafiltration membranes were washed with 0.01 mol of NaOH solution to remove any chemicals and wetting agents absorbed on the membrane surface and then dipped in methanol for 24 h to eliminate water. The carboxylic group was grafted onto the membrane surface through the immersion of the membrane in the modified solution (60 mL of acrylic acid, 20 mL of phosphoric acid, and 11.44 g of anhydrous tin tetrachloride) for different reaction times and different temperatures. The modified membranes [polysulfone membranes with carboxylic groups (C-PSF membranes)] were cleaned with deionized water to remove residual acrylic acid. The C-PSF membranes were rinsed gently with deionized water before use. The preparation process of the C-PSF membranes is shown in Scheme 2.

Grafting of the PEG Derivative Chains on the Membranes
According to the chemical structure of the PEG derivatives, two methods were adopted in this experiment. In the first method, a 0.1 wt % EDC aqueous solution was composed of a sodium citrate buffer solution (100 mL, pH 4.7) with 100 mg of EDC. The C-PSF membranes were first immersed in an EDC solution for 4 h at 4°C to activate the carboxyl groups and then rinsed three times with deionized water.

The EDC-activated C-PSF membranes were incubated in an aqueous solution containing an excessive amount of ethylenediamine solution (10 mg/mL) at 4°C for 24 h to produce an aminated PSF membrane. These aminated PSF membranes then were immersed into the end carboxylic acid MPEG solution (4 mg/mL MPEG, 1 mg/mL EDC) at 4°C for 24 h.

In the second method, EDC-activated C-PSF membranes were immediately immersed in ED2000 and ED600 solutions (4 mg/mL), respectively. All of the modified membranes were rinsed three times with deionized water.
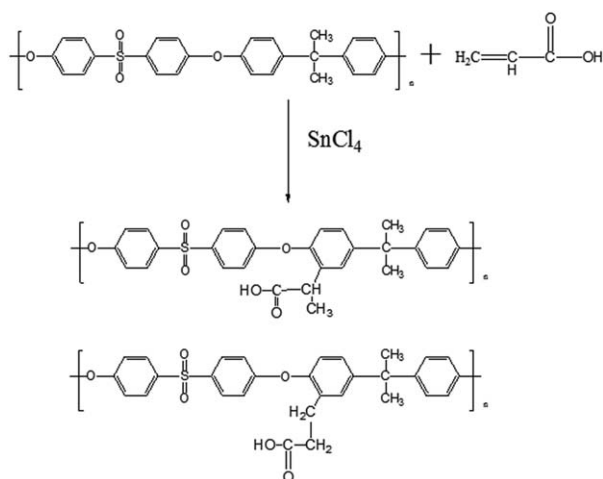
Scheme 2. Reaction schemes for the grafting of the PSF ultrafiltration membrane by acrylic acid.

Characterization of the Modified Membranes

Water CA measurements have been used commonly to characterize the relative hydrophilicity or hydrophobicity of modified membrane surfaces. A CA goniometer (JC2000C CA Meter, Powereach Co., Shanghai, China) was introduced to measure static CAs at room temperature. An average value of five measurements was taken to report. The surface and cross-sectional morphologies of modified and PSF membranes were observed by SEM with a KYKY-2800 scanning microscope.

Total reflection FTIR spectroscopy (Equinox 55) was introduced to investigate the chemical changes between the PSF and PEG-immobilized ultrafiltration membranes and to confirm the immobilization of PEG on the membrane surface.

Determination of the Concentration of the Surface-Grafted AAc

The grafting density of carboxylic on the surface of the PSF membrane was evaluated with the toluidine blue O (TBO) dye method.[36,37] The TBO dye specifically interacted with the carboxyl groups on the PSF membrane. A calibration curve was first generated from the optical density of the TBO solutions of known concentrations at 633 nm measured on a UV spectrophotometer (Shimadzu Mini-1240). The membranes with an area of 4 cm^2 were placed in a TBO solution (pH 10) for 5 h under constant agitation at room temperature. The PSF membranes were rinsed with an excess amount of 0.1mM NaOH solution to remove the noncomplexed TBO molecules. The stained membranes were then dried before they were immersed into 50% acetic acid; this made the TBO from the carboxyl acid groups of the PSF membranes desorb from the surface. The calculation was based on the assumption that 1 mol of TBO had complexed with 1 mol of the carboxyl acid groups of the grafted AAc polymer. At least three TBO amounts were averaged to get a reliable value.

Ultrafiltration Experiments

A dead-end stirred cell filtration system was used to measure the flux of the pure water and BSA fouling. The stirred cell was connected with a nitrogen gas cylinder and solution reservoir.

The cell had an inner diameter of 64 mm and a volume capacity of 300 mL. The effective area of the membrane was 32.15 cm^2. Nitrogen gas was used to maintain the system operation pressure. A stir plate was used at 350 rpm to minimize the concentration polarization. After the membrane was fixed, the stirred cell and solution reservoir were filled with deionized water. Each membrane was initially pressurized at 0.15 MPa for 30 min with deionized water. Then, the pure water flux (J_{w1}) was measured after 15 min of operation at 0.1 MPa. Next, 1.0 mg/mL BSA phosphate buffer saline (PBS, 0.2M, pH 7.0) was added to the reservoir, and the flux (J_p) was evaluated after 30 min of ultrafiltration. Finally, the BSA solution was replaced by deionized water. The membrane was cleaned in the stirred cell with deionized water for 20 min, and the pure water flux (J_{w2}) was measured again. In the long-term process, the ultrafiltration operations in a sequence of pure water, BSA solution, and water cleaning, were repeated four times to evaluate the flux-recovery properties of the membranes.

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

$$J_w = \frac{V}{A\Delta t} \tag{1}$$

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

The BSA rejection ratio (R_e) was defined as follows:

$$R_e(\%) = \left(1 - \frac{C_p}{C_b}\right) \times 100\% \tag{2}$$

where C_p and C_b are the BSA concentrations of the permeate and feed solutions (mg/mL), respectively:

$$\eta = \frac{J_{w1}}{J_0} \tag{3}$$

where η is the relative water flux and J_0 and J_{w1} are the pure water fluxes of the PSF membrane before and after the modification process (L m^{-2} h^{-1}), respectively. The flux recovery ratio (FRR) was calculated as follows:

$$\text{FRR} = \frac{J_{w2}}{J_{w1}} \times 100\% \tag{4}$$

where J_{w1} and J_{w2} (L m^{-2} h^{-1}) are the pure water flux of the PSF membrane before and after the BSA fouling–cleaning experiment, respectively.

RESULTS AND DISCUSSION

Chemical and Morphological Characterization of the PSF and PSF-Based Modified Membranes

ATR–FTIR measurement was performed to confirm the successful grafting reaction of the PEG chains onto the PSF membrane surface. Figure 2 shows the FTIR spectra of the PSF, C-PSF, ED600, ED2000, and MPEG550 immobilized membranes. The spectrum of the C-PSF membrane [Figure 2(b)] showed an absorbance band at 1725 cm^{-1}, which was the characteristic band for C=O of the carboxylic acid. Compared with the FTIR spectrum of PSF, there were new adsorption peaks at 944 cm^{-1} in the spectra of the ED600, ED2000, and MPEG550
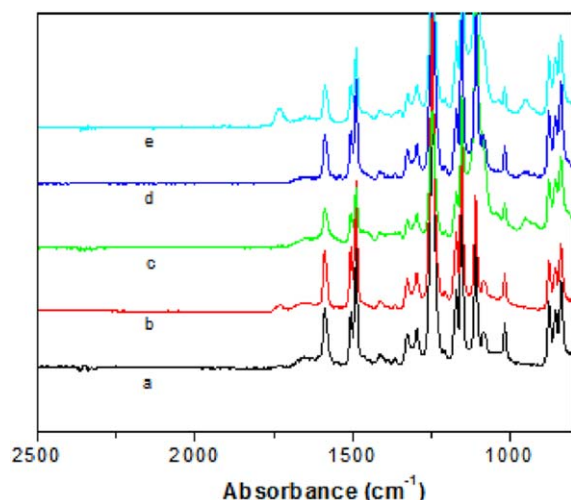
Figure 2. FTIR–ATR spectrum of the (a) PSF control membrane and (b) PSF-*g*-acrylic acid membrane (reaction time = 40 min), (c) PSF-*g*-ED600 membrane (reaction time = 40 min), (d) PSF-*g*-ED2000 membrane (reaction time = 40 min), and (e) PSF-*g*-MPEG membrane (reaction time = 40 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

immobilized membranes [Figure 2(c–e)]. These were characteristic bands of the PEG derivatives. Compared to ED600 and MPEG550, ED2000 was more difficult to immobilize on the membrane surface; therefore, the intensity of the 944-cm^{-1} band of the ED2000 membrane was relatively weak. Furthermore, the intensity of the 1108-cm^{-1} band for C—O stretching vibrations was enhanced by PEG chain immobilization. There was also an adsorption peaks at 1729 cm^{-1} in the spectrum of the MPEG550 immobilized membrane; this was the characteristic band for C=O in the carboxyl end group MPEG550. We found that with the surface modification method of the Friedel–Crafts reaction followed by the grafting process, the PEG chains were successfully grafted onto the PSF membrane.

The hydrophilicity or hydrophobicity of each membrane could be easily obtained by water CA measurement, although it was difficult to definitely interpret the surface properties for the porous membranes. Figure 3 presents the water CAs of the PSF control membrane and the modified PSF membranes. The control PSF membrane had the highest CA of 75°; this indicated that it had the lowest hydrophilicity. The modified membranes had lower CAs in comparison with the PSF control membrane. The variation of the water CAs indicated that the introduction of PEG derivatives effectively enhanced the membrane surface hydrophilicity. The PSF membrane modified by MPEG550 had the lowest CA (49°), and the others modified by ED600 and ED2000 had similar CA values. These were around 54°. The hydrophilicity was determined by the hydrophilic ethylene glycol unit density on the membrane surface. The greater the number of hydrophilic ethylene glycol units there were on the membrane surface, the better the hydrophilic properties in the measurement were. Compared with ED600, ED2000 had a longer PEG chain, and this could provide a better hydrophilicity. On the other hand, ED2000 was more difficult to graft onto the membrane with the longer chain. Therefore, ED2000 and
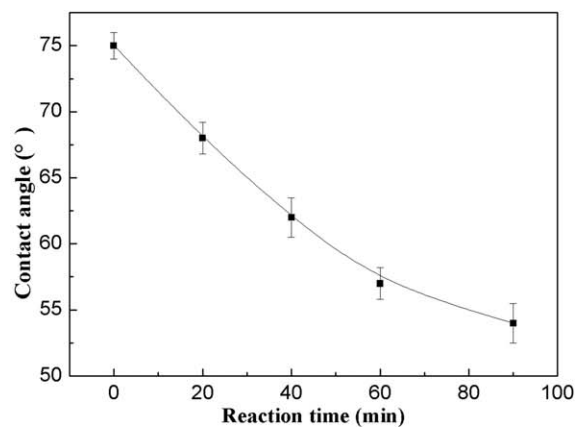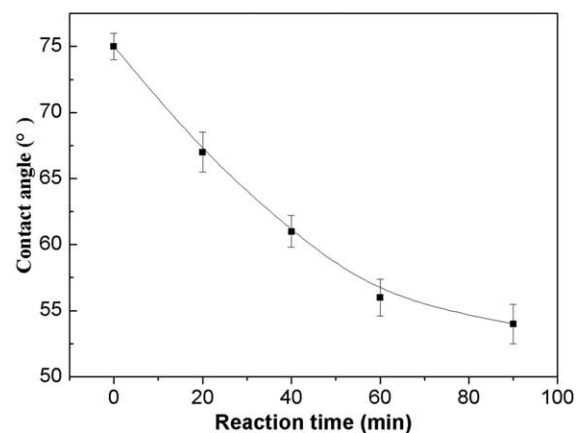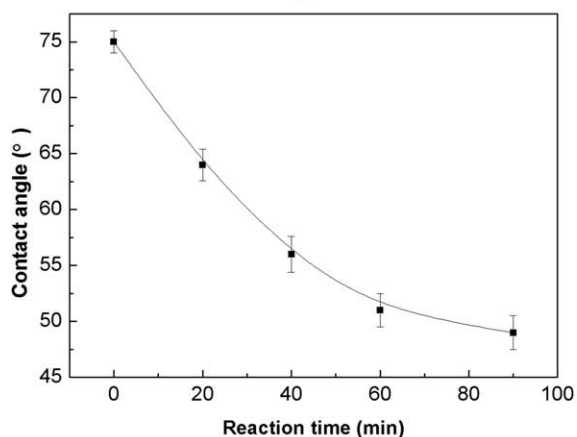
Figure 3. Effect of the reaction time on the surface hydrophilicity of the modified PSF membranes. (a) ED600, (b) ED2000, and (c) MPEG550.

ED600 showed the same results in the CA measurement. A similar result from this phenomenon was also reported by another researcher.[28] Meanwhile, ED600 and ED2000 contained not only hydrophilic ethylene glycol units but also hydrophobic propylene glycol units at the same time. The propylene glycol units showed hydrophobic properties on the membrane surface.
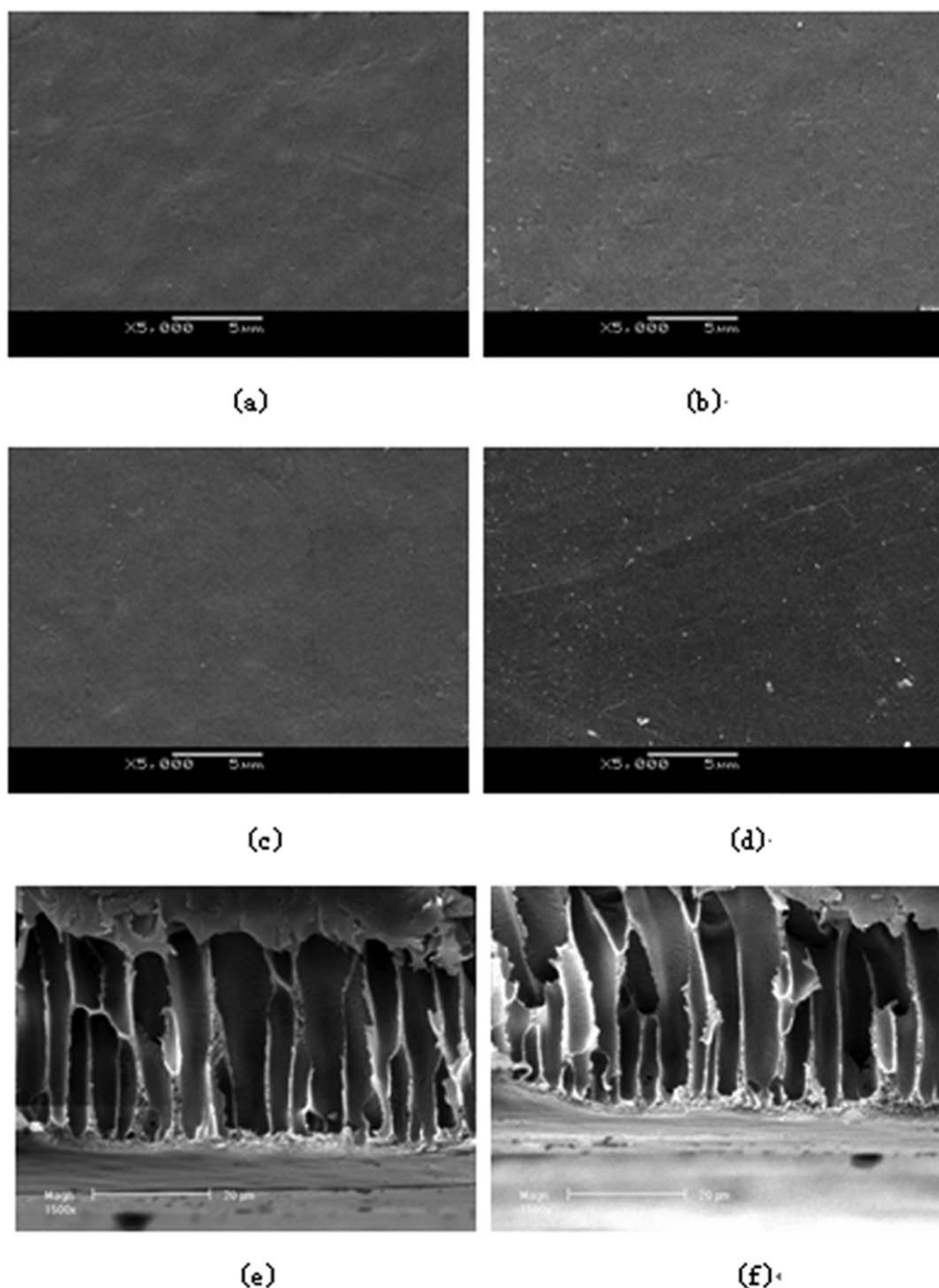
Figure 4. Surface and cross-sectional morphology of the (a) PSF control membrane (5000×), (b) ED600 membrane (5000×), (c) ED2000 membrane (5000×), (d) MPEG550 membrane (5000×), (e) PSF control membrane (1500×), and (f) MPEG550-modified membrane (1500×).

On the other hand, MPEG550 only had hydrophilic ethylene glycol units, and this showed a better hydrophilic modification result. Therefore, the difference in the PEG derivative chemical structure led to different CA results.

The morphological changes of the PSF ultrafiltration membranes before and after modification by the PEG derivatives were examined by SEM, as shown in Figure 4. There were no significant morphological variations between the PSF control and the modified membranes. A characteristic morphology of asymmetric membrane consisting of a dense top layer and porous sublayer with a fingerlike structure was observed for all of the modified membranes. There was no appreciable morphological variation between the PEG-modified membranes and the unmodified PSF membrane. It was, thus, inferred that the surface modification did not appreciably change the morphology of the PSF ultrafiltration membrane. In fact, grafting was a surface modification technology under mild conditions, which would probably have had a negligible effect on the membrane structure.
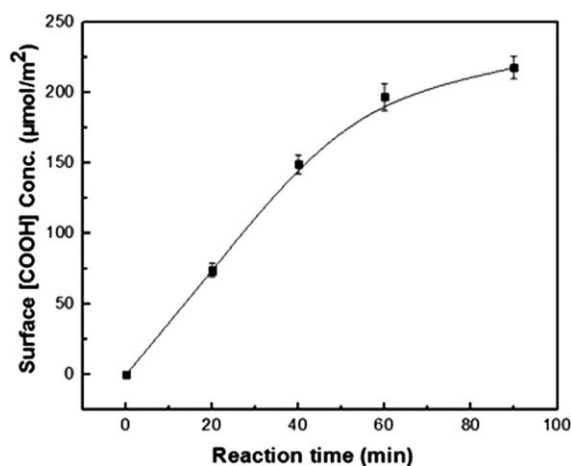
Figure 5. Effect of the reaction time used on the surface graft concentration of the carboxyl groups on the PSF-*g*-acrylic acid surface.

Determination of the Carboxyl Group Concentration on the C-PSF Membrane Surface by Reaction with TBO

The surface concentration of the carboxyl groups (in micromoles per square meter) was determined from the uptake of TBO. TBO is a positively charged blue-colored dye that can form a stable complex with COO─ groups in basic solutions through electrostatic interactions with a complex ratio of 1:1.[36,38] Figure 5 shows the effect of the reaction time on the grafting of acrylic acid on the membrane surface. The concentration of the surface-grafted carboxyl acid groups increased with increasing reaction time for the grafting reaction, whereas the increasing rate slowed down slightly at long times, with the most significant increase being observed at a reaction time of 1.5 h. With increasing reaction time, acrylic acid had more of a chance to react with PSF, and a higher acrylic acid concentration was achieved. At the same time, with increasing time of the Friedel–Crafts reaction, the increasing coverage of the membrane surface led to a decrease in the reaction rate. Thus, the rate of the increasing acrylic acid was slow at long times.

Effect of the Reaction Temperature, Reaction Time, and Kinds of Grafting Polymer on the Membrane Separation and Permeation Performance

In this study, the relative pure water flux through the membrane and R_e of the modified membranes were measured as a function of the membrane modification. Table I reveals the effect of the reaction temperature on the separation and permeation performance. When the reaction temperature was below

Table II. Effect of the Reaction Time and Grafting of the PEG Derivatives on the Performance of the Modified PSF Membrane

Membrane	Reaction time (min)	Grafting monomer	Relative flux (J_{w1}/J_0)	R_e (%)	FRR (%)
4	0	—	1	91.1	51.4
5	20	ED600	1.03	89.7	60.8
6	40	ED600	1.01	88.5	69.1
7	60	ED600	0.88	90.8	72.2
8	90	ED600	0.84	92.0	74.1
9	20	ED2000	1.00	92.1	63.0
10	40	ED2000	0.94	87.7	70.0
11	60	ED2000	0.90	88.2	72.0
12	90	ED2000	0.88	90.2	75.1
13	20	MPEG550	1.06	91.3	70.4
14	40	MPEG550	1.04	88.1	76.0
15	60	MPEG550	1.15	87.3	88.0
16	90	MPEG550	1.03	89.3	95.0

40°C, with increasing temperature, the reactive flux first decreased to 0.85 and then increased to 0.95. Meanwhile, the rejection rate decreased with increasing temperature. At 50°C, the modified membranes shrank seriously, and the modified membrane was difficult to test. It was thus concluded that the acrylic acid grafting process caused damage to the membrane pore. Therefore, the reaction temperature was fixed at 30°C in the following experiments.

Table II presents the variation of the pure water flux, antifouling property, and R_e with modified membranes. The membranes were first pressured at 0.15 MPa for 30 min, and a relatively steady water flux was obtained. Then, the feed was switched to a BSA solution, and the flux showed a sharp decline. The BSA ultrafiltration was maintained for 30 min at 0.1 MPa; then, the membranes were cleaned with deionized water for 20 min.

The relative water fluxes and rejection rate before and after the grafted PEG derivatives were measured as a function of the transmembrane pressure, and the typical results are shown in Table II. As shown in Table II, when ED600 and ED2000 were grafted onto the PSF membranes, a slight decline of the relatively pure water flux was observed from 1.03 to 0.84. Meanwhile, when MPEG550 was grafted on the PSF membranes, the water flux was slightly higher than that of PSF membrane. On the other hand, when the Friedel–Crafts reaction time was

Table I. Effects of the Reaction Temperature on the Performance of the ED2000-Modified Membrane

| Membrane	Acrylic acid (mL)	Phosphoric acid (mL)	Anhydrous tin tetrachloride (g)	Reaction temperature (°C)	Relative flux (J_{w1}/J_0)	R_e (%)
1	60	20	11.44	30	0.85	91.0
2	60	20	11.44	40	0.93	41.2
3	60	20	11.44	50	a	a

a, the membrane was seriously shrunken at this temperature and was difficult to test.
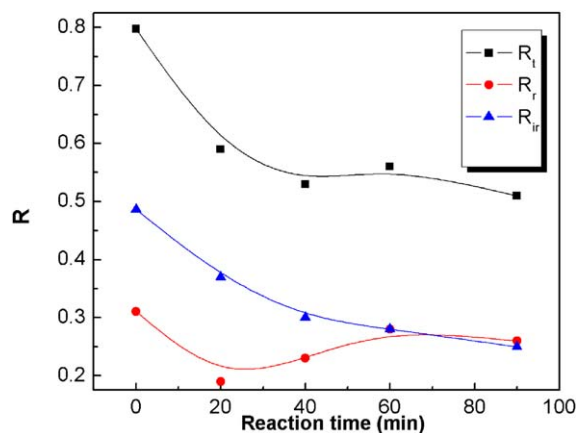
Figure 6. Summary of the R_t, R_r, and R_{ir} values of the ED600 membranes as a function of the reaction time in acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prolonged, the BSA rejection rate of the modified membranes were decreased from 91.1 to 87.7% and then raised to 92%. The pure water flux was affected by the membrane pore radius and surface hydrophilicity; this, therefore, increased the pore radius, and the hydrophilicity could increase the pure water flux. On the other hand, R_e was only affected by the membrane pore radius, and the smaller pore radius could increase the R_e of membranes. In the process of grafting the carboxylic acid, the membrane pore was enlarged; this contributed to the decrease in the BSA rejection rate and the increase in the relative pure water flux. When the Friedel–Crafts time was prolonged, the number of PEG derivatives grafted onto the membrane surface increased. After PEG derivatives were grafted onto the C-PSF membrane surface, the membrane pores were blocked to some extent; this played a dominant role in the water flux and led to a decrease in the water flux and an increase in the BSA rejection rate.[5] Compared with the membranes grafted with ED600 and ED2000, the membranes grafted with MPEG550 obtained a higher water flux. This was due to the fact that after modification, the membranes immobilized
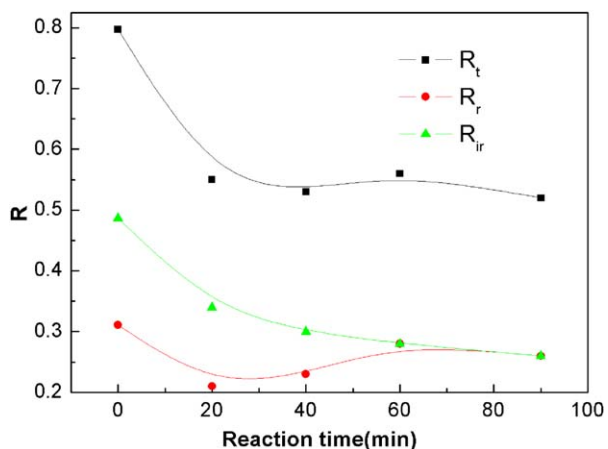
Figure 7. Summary of the R_t, R_r, and R_{ir} values of the ED2000 membranes as a function of the reaction time in acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
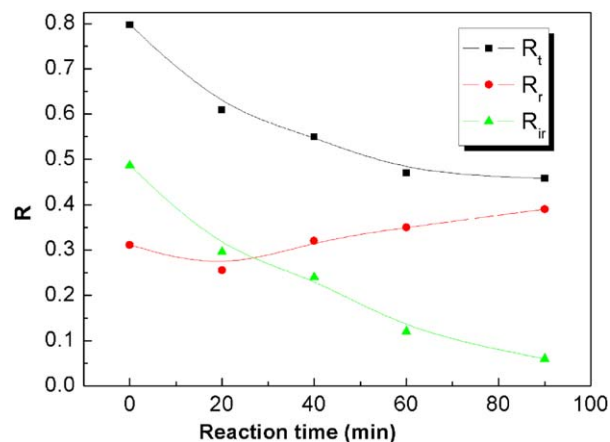

Figure 8. Summary of the R_t, R_r, and R_{ir} values of the MPEG550 membranes as a function of the reaction time in acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with MPEG550 had a higher hydrophilicity than ED600 and ED2000, which was in accordance with the results of the contact angles.

Antifouling Characteristics of the Modified Membranes
Membrane fouling, which causes a severe decrease in the flux, induces an increase in the production costs by increasing the energy consumption and the cleaning frequencies. To study the effect of PEG derivative grafting on the antifouling characteristics, BSA was used as a model protein. In most cases, the concentration polarization and membrane fouling were considered to be the two main sources for membrane flux decline in protein ultrafiltration. The influence of the concentration polarization could be weakened by an increase in the flow rate of liquid over the membrane. However, fouling is difficult to reduce and is irreversible. Generally speaking, membrane fouling is caused by the following three mechanisms: pore constriction within the membrane pores, pore blocking at the membrane surface, and cake formation on the membrane surface[39,40] Fouling caused by the adsorption of foulants occurs on both the membrane surfaces and pore walls and cannot be cleaned by water washing. In this study, the BSA rejection of all of the membranes were above 87%; this indicated that only a small amount of BSA entered the membrane pores. So the irreversible fouling was mainly caused by pore blocking. When PEG derivatives were immobilized on the membrane surface, the PEG chain covered the membrane surface and decreased the hydrophobic area of the membrane surface. When the reaction time was short, the PEG chain density on the membrane surface was relatively low. PEG chains were not enough to cover the membrane surface and inhibit the protein adsorption. Then, a part of BSA could still easily penetrate the PEG layer and be adsorbed onto the hydrophobic membrane surface. The PEG chain density at the membrane surface was relatively higher with prolonged reaction time. With higher PEG chains content, the BSA adsorption sites at the membrane surface were reduced, and a concentrated PEO layer was formed.

To describe the membrane fouling process, three parameters were introduced, including the total fouling ratio (R_t), reversible
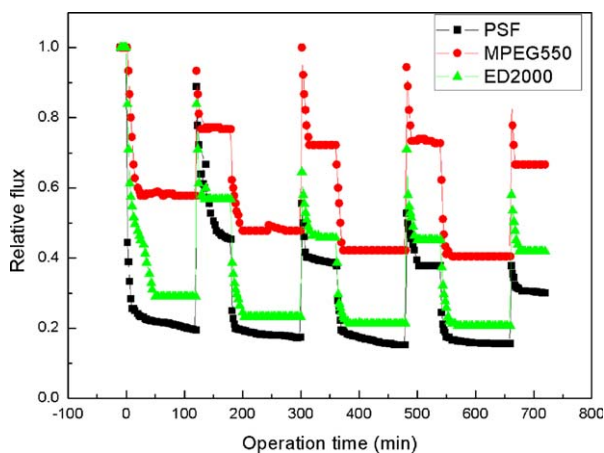
Figure 9. Effect of the reaction time and kinds of PEG derivatives on the recycling properties of the modified PSF membrane and PSF membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fouling ratio (R_r), and irreversible fouling ratio (R_{ir}), which was the degree of total flux loss caused by total fouling:[41]

$$R_t = \frac{J_{w1} - J_p}{J_{w1}} \qquad (5)$$

This parameter was used to indicate the degree of flux loss, which is the degree of reversible flux loss caused by reversible fouling:

$$R_r = \frac{J_{w2} - J_p}{J_{w1}} \qquad (6)$$

The reversible fouling was caused by reversible BSA adsorption on the membranes and led to reversible fouling, which could be eliminated by hydraulic cleaning:

$$R_{ir} = \frac{J_{w1} - J_{w2}}{J_{w1}} \qquad (7)$$

This was the degree of irreversible flux loss caused by irreversible fouling. It was irreversible BSA adsorption on the membrane surface, which caused irreversible fouling and could not be cleaned out by hydraulic cleaning. In practical application, irreversible fouling caused seriously flux loss and could not be removed by simple hydraulic cleaning. The membrane with the smallest R_{ir} value could achieve the most flux recovery after hydraulic cleaning. A summary of R_t, R_r, and R_{ir} of the PSF and ED600- and ED2000-modified membranes is shown in Figures 6 and 7. R_t of the

ED600-modified membrane decreased from 0.8 to 0.54 with an increase in the reaction time from 20 to 90 min, and correspondingly, R_{ir} decreased from 0.486 to 0.26, whereas R_r exhibited an no obvious difference trend. On the other hand, when the reaction time was prolonged, R_t and R_{ir} of the ED2000-modified membrane both decreased to 0.52 and 0.26, respectively, whereas R_r also showed no significant change. A lower R_t value meant lower total flux loss, and this indicated that the modified membranes could maintain a relative high flux in BSA ultrafiltration process. These results indicated that the immobilization of ED600 and ED2000 on the PSF membrane could partly reduce both the total and irreversible fouling. The result of ATR–FTIR spectroscopy indicated that the immobilization amount of ED2000 was smaller than that of ED600. The short PEG chain with less hydrophilic —CH_2—CH_2—O— segments brought about relatively a low hydrophilicity on the membrane surface compared to that of long PEG chains. On the other hand, a long PEG chain was difficult to react with carboxylic acid on the membrane surface. Therefore, although ED2000 had a longer PEG chain, which led to difficulty in immobilization on the membrane surface.[28] The relatively low immobilization amount of ED2000 caused a similar antifouling properties of the ED600-modified membrane.

Figure 8 shows a summary of the R_t, R_r, and R_{ir} of the PSF- and MPEG550-modified membrane. We observed that R_t of the MPEG550-modified membrane decreased from 0.8 to 0.458 with increasing reaction time from 20 to 90 min, and correspondingly, R_{ir} decreased from 0.486 to 0.06, whereas R_r exhibited a slight increase. Compared with the ED600- and ED2000-modified membranes, the MPEG550-modified membrane had a lower R_{ir} value; this was due to the difference in the hydrophilicity values among MPEG550, ED600, and ED2000. A lower R_{ir} meant a smaller amount of adsorbed protein could not be removed through hydraulic cleaning. That is, a greater part of fouling was reversible, and this was an exhibition of membranes with better antifouling properties as desired for practical applications. There were propylene glycol units, which were hydrophobic segments in the chemical structures of ED600 and ED2000 (Scheme 1). The hydrophobic segments decreased the hydrophilicity values of the ED600- and ED2000-modified membranes and the BSA molecule.

Recycling Properties of the Modified Membranes Through the Immobilization of PEG Derivatives on the PSF Membrane Surface

The relative low R_{ir} value of the modified membrane indicated that the membrane could be reused for several runs. To test the

Table III. Comparison of the Hydrophilization of the Prepared PSF Membrane with the Literature

Membrane type	Pure water flux (L m^{-2} h^{-1})	R_e (%)	FRR (%)	Ref.
CaCO$_3$-blended PSF	60 (at 200 kPa)	90.0	51.0	42
N-Propyl phosphonic chitosan blended PSF	230 (at 200 kPa)	94.0	74.0	43
Polyaniline-blended PSF	230 (at 200 kPa)	98.0	78.5	44
N-Succinyl chitosan blended PSF	228 (at 200 kPa)	93.5	70.0	45
Poly(acrylic acid) blended PSF	170 (at 100 kPa)	96.8	86.5	5
TiO$_2$-blended PSF	61 (at 200 kPa)	93.0	68.0	46
PEG-modified PSF	230 (at 100 kPa)	89.3	95.0	This study

recycling potential of the modified membrane, a further investigation was carried out through a long-term ultrafiltration with four runs. Figure 9 presents the time-dependent relative flux of the PSF membrane and modified membrane with MPEG550 and ED2000. As shown in Figure 9, the modified membrane with MPEG550 was retained at 66.7% after four cycles of BSA solution ultrafiltration for 8 h, whereas the relative flux of the PSF membrane decreased to 32.5% after four cycles. At the same time, the modified membrane with ED2000 decreased to 41.9% for 8 h of BSA ultrafiltration. The recycling properties of the PSF membranes was significantly enhanced; this indicated that the modified membranes could be reused for a longer time with only simple hydraulic cleaning.

Comparison of the Prepared Membranes with Some in the Literature

Table III compares the pure water flux, BSA rejection rate, and FRR values of this membranes with those of the literature data.[5,42–46] A comparison of all the membranes was made under similar feed conditions. With this comparison, we found that these membranes offered the highest FRR values.

CONCLUSIONS

PSF ultrafiltration membranes with enhanced fouling-resistance abilities were prepared by the immobilization of the PEG derivatives on the membrane surface. The ATR–FTIR spectroscopy results confirmed that the PEG derivatives were effectively immobilized on the PSF membrane surface. Compared with the PSF control membrane, the modified membranes showed a higher hydrophilicity, which was shown by the CAs. Ultrafiltration experiments indicated that the MPEG550-modified membranes considerably increased the water permeability and antifouling properties. The better antifouling properties rendered the modified membranes a longer operation lifespan. After four cycles of BSA solution (1.0 mg/mL), the relative flux of the MPEG550-modified membrane was retained at 66.7%; this was obviously higher than those of the ED2000-modified membrane and PSF control membrane.

ACKNOWLEDGMENTS

REFERENCES

1. Arunkumar, A.; Etzel, M. R. *J. Membr. Sci.* **2015**, *475*, 340.

2. Liu, T. Y.; Zhang, R. X.; Li, Q.; Van der Bruggen, B.; Wang, X. L. *J. Membr. Sci.* **2014**, *472*, 119.

3. Maruf, S. H.; Pellegrino, A. R. G. J.; Ding, Y. F. *J. Membr. Sci.* **2014**, *471*, 65.

4. Li, K.; Liang, H.; Qu, F. S.; Shao, S. L.; Yu, H. R.; Han, Z. S.; Du, X.; Li, G. B. *J. Membr. Sci.* **2014**, *471*, 94.

5. Yu, H. J; Cao, Y. M; Kang, G. D; Liu, J. H; Li, M. *J. Appl. Polym. Sci.* **2012**, *124*, 123.

6. Li, W; Zhou, J; Gu, J. S; Yu, H. Y. *J. Membr. Sci.* **2010**, *115*, 2302.

7. Wei, X.; Wang, R.; Li, Z. S.; Fane, A. G. *J. Membr. Sci.* **2006**, *273*, 47.

8. Yu, H. Y.; He, X. C.; Liu, L. Q.; Gu, J. S.; Wei, X. W. *Water Res.* **2007**, *41*, 4703.

9. Wu, H. Q.; Tang, B. B.; Wu, P. Y. *J. Membr. Sci.* **2014**, *451*, 94.

10. Zhao, Y. F.; Zhu, L. P.; Yi, Z.; Zhu, B. K.; Xu, Y. Y. *J. Membr. Sci.* **2013**, *440*, 40.

11. Sinha, M. K.; Purkait, M. K. *J. Membr. Sci.* **2013**, *437*, 7.

12. Hyun, J; Jang, H; Kim, K; Na, K; Tak, T. *J. Membr. Sci.* **2006**, *282*, 52.

13. Eren, E.; Sarihan, A.; Eren, B.; Gumus, H.; Kocak, F. O. *J. Membr. Sci.* **2015**, *475*, 1.

14. Shi, Q.; Meng, J. Q.; Xu, R. S.; Du, X. L.; Zhang, Y. F. *J. Membr. Sci.* **2013**, *444*, 50.

15. Kim, H.; Kim, S. S. *J. Membr. Sci.* **2006**, *286*, 193.

16. Wavhal, D. S.; Fisher, E. R. *J. Membr. Sci.* **2002**, *209*, 255.

17. Iwata, H.; Ivanchenko, M. I.; Miyaki, Y. *J. Appl. Polym. Sci.* **1994**, *54*, 125.

18. Kilduff, J. E.; Mattaraj, S.; Pieracci, J. P.; Belfort, G. *Desalination* **2000**, *132*, 33.

19. Pieracci, J. P.; Crivello, J. V.; Belfort, G. *J. Membr. Sci.* **2002**, *202*, 1.

20. Mok, S.; Worsfold, D. J.; Founda, A.; Matsuura, T. *J. Appl. Polym. Sci.* **1994**, *51*, 193.

21. Blanco, J. F.; Nguyen, Q. T.; Schaetzel, P. *J. Membr. Sci.* **2001**, *186*, 267.

22. Pospiech, D; Eckstein, K; Haussler, L; Komber, H; Jehnichen, D; Grundke, K. *Macromol. Chem. Phys.* **1999**, *200*, 1311.

23. Yoshikawa, M.; Tsubouchi, K.; Guiver, M. D.; Robertson, G. P. *J. Appl. Polym. Sci.* **1999**, *74*, 407.

24. Anke, N; Staude, E; Belfort, G. *J. Membr. Sci.* **1997**, *133*, 57.

25. Che, A. F.; Nie, F. Q.; Huang, X. D.; Xu, Z. K.; Yao, K. *J. Polymer* **2005**, *46*, 11060.

26. Ye, P.; Xu, Z. K.; Che, A. F.; Wu, J.; Seta, P. *Biomaterials* **2005**, *26*, 6394.

27. Ma, X. L.; Su, Y. L.; Sun, Q.; Wang, Y. Q.; Jiang, Z. Y. *J. Membr. Sci.* **2007**, *292*, 116.

28. Nie, F. Q.; Xu, Z. K.; Ye, P.; Wu, J.; Seta, P. *J. Polym.* **2004**, *45*, 399.

29. Xu, Z. K.; Nie, F. Q.; Qu, C.; Wan, L. S.; Wu, J.; Yao, K. *Biomaterials.* **2005**, *26*, 589.

30. Liu, B. C.; Chen, C.; Li, T.; Crittenden, J.; Chen, Y. S. *J. Membr. Sci.* **2013**, *445*, 66.

31. Chang, Y.; Shih, Y. J.; Ruaan, R. C.; Higuchi, A.; Chen, W. Y.; Lai, J. Y. *J. Membr. Sci.* **2008**, *15*, 165.

32. Ju, H.; McCloskey, B. D.; Sagle, A. C.; Kusuma, V. A.; Freeman, B. D. *J. Membr. Sci.* **2009**, *330*, 180.

33. Sagle, A. C.; Van Wagner, E. M.; Ju, H.; McCloskey, B. D.; Freeman, B. D.; Sharma, M. M. *J. Membr. Sci.* **2009**, *340*, 92.

34. Kang, G. D.; Liu, M.; Lin, B.; Cao, Y. M.; Yuan, Q. J. *Polymer* **2007**, *48*, 1165.

35. Geckeler, K; Bayer, E. *Polym. Bull.* **1980**, *3*, 347.

36. Uchida, E; Uyama, Y; Ikada, Y. *Langmuir* **1993**, *9*, 1121.

37. Ma, Z. W.; Kotaki, M.; Ramakrishna, S. *J. Membr. Sci.* **2006**, *272*, 179.

38. Lei, Y; Chao Yin, R. X; Zhuo, R. X; Leong, K. W; Mao, H. Q; Kang, E. T; Neoh, K. G. *Biomacromolecules* **2003**, *4*, 157.

39. Katsoufidou, K.; Yiantsios, S. G.; Karabelas, A. J. *J. Membr. Sci.* **2005**, *266*, 40.

40. Mockel, D; Staude, E; Guiver, M. D. *J. Membr. Sci.* **1999**, *158*, 63.

41. Pieracci, J.; Crivello, J. V.; Belfort, G. *J. Membr. Sci.* **2002**, *202*, 1.

42. Nair, A. K.; Isloor, A. M.; Kumar, R.; Ismail, A. F. *Desalination* **2013**, *322*, 69.

43. Kumar, R.; Isloor, A. M.; Ismail, A. F.; Matsuura, T. *J. Membr. Sci.* **2013**, *440*, 140.

44. Fan, Z.; Wang, Z.; Sun, N.; Wang, J.; Wang, S. *J. Membr. Sci.* **2008**, *320*, 363.

45. Kumar, R.; Isloor, A. M.; Ismail, A. F.; Matsuura, T. *Desalination* **2013**, *318*, 1.

46. Zhang, G.; Lu, S.; Zhang, L.; Meng, Q.; Shen, C.; Zhang, J. *J. Membr. Sci.* **2013**, *436*, 163.