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Enhancing hydrophilicity performance of polysulfone hollow fiber membrane by surface modification via UV-induced graft polymerization of HEA

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ABSTRACT

In order to enhance hydrophilicity performances, polysulfone (PSF) hollow fiber membrane was modified through graft polymerization with 2-Hydroxyethylacrylate initiated by ultraviolet radiation. The effects of irradiation time and monomer concentration on the grafting degree of the membranes were examined. Fourier transform infrared (FT-IR) spectra, X-ray photoelectron spectra, scanning electron microscopy, thermal gravimetric analysis, and different thermo analysis were used to characterize the chemical and morphological changes of the PSF membrane matrix surface. Static contact angle measurements showed that the hydrophilicity of PSF matrix was enhanced after grafting modification. Water flux and bovine serum albumin filtration experiments also show that the hydrophilicity and fouling resistance of the grafted membranes were obviously increased with increasing grafting degree.

Keywords: PSF membrane; Graft polymerization; UV radiation; Hydrophilicity; 2-Hydroxyethylacrylate

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1. Introduction

In recent decades, membrane technology is an attractive separation approach due to the fast- and energy-efficient process without phase change [1]. Polysulfone (PSF) hollow fiber membrane, a type of pressure-driven membrane process, has strong adaptability of technology, easy installation and simple operation, and no impact to environment [2]. Furthermore, as a kind of hollow fiber, it has the benefit of large loading density, simple module structure, and high specific surface area. All of the above advantages make it give rise to worldwide interest. Nowadays, PSF has been applied in many fields, especially in drinking water industry and wastewater treatment [3].

However, the low hydrophilicity of PSF matrix has become an obstacle for its potential application in industry and wastewater treatment [4,5]. Although many techniques have been employed to solve this problem, only few are successfully applied at the industrial level due to economic and technical obstacles. In recent years, graft polymerization on polymeric matrixes followed by functionalization

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monomer is widely used in order to achieve controllable structure and ideal properties [6]. Grafting polymerization can be initiated using electron beams, gamma radiation, plasma treatment, and chemical initiators [7–9]. Among these, major techniques designed to achieve surface modification of polymeric materials, endowing PSF matrix with hydrophilicity monomer by ultraviolet (UV) radiation-induced is a valuable and economical method for the modification of the hydrophilic properties of PSF surfaces [10,11]. UV-initiated grafting polymerization has several advantages: simplicity, cost-effective, and current industrial applications [12]. The UV-initiated grafting polymerization occurs on the surface of polymeric matrixes and the grafting degree can be controlled conveniently in grafting process [13]. Furthermore, the graft structure is built with covalent bonds, and the chemically stable properties can be expected.

In this work, PSF membrane was modified through graft polymerization of 2-Hydroxyethylacrylate (HEA) initiated by high energy UV. The factors influencing the grafting degree of HEA were discussed in detail. Hydrophilicity properties of original PSF and PSF-g-HEA were investigated using water and bovine serum albumin (BSA) solution. Both the thermal stability and fouling resistance of the PSF-g-HEA were systematically investigated in order to evaluate its potential for wastewater treatment.

2. Experimental

2.1. Materials

The monomer, 2-Hydroxyethylacrylate (HEA, purity ≥ 99%), was purchased from Tianjin Tianjiao Chemical Co., Ltd (Tianjin, China). PSF ultrafiltration (UF) hollow fiber membrane with a molecular weight cut-off (MWCO) of around 50,000 Da, which was kindly offered by Tianjin MOTIMO Membrane Technology Ltd (Tianjin, China), was used as matrix membrane. All reagents were used as received without further purification. Ultrapure water with a resistivity of 17.4 MΩ/cm was used in all experiments. All reagents and solvents were used as received. Properties of PSF hollow fiber membrane are shown in Table 1.

Table 1
Properties of PSF hollow fiber membrane

PSF hollow fiber membrane	
Filtration mode	Outside-in
Outer diameter (μm)	1,187
Inner diameter (μm)	709
Water permeability (L m^{-2} h^{-1} bar^{-1})	71.97
MWCO (Da[a])	50,000

[a] According to the manufacturer.

2.2. Preparation of PSF-g-HEA

The procedure for the preparation of PSF-g-HEA is as follows:

(1) Pretreatment: firstly, the PSF hollow fiber membranes of definite length were cleaned with ultrapure water for 24 h to remove any preservative agents like glycerol frequently used by membrane manufacturers. Secondly, the pretreated membranes were dipped in 0.13 mol/L BP/ethanol solution for 12 h to ensure the photosensitizer BP fully adsorbed onto the PSF substrate.

(2) Grafting step: the pretreated PSF samples were then put into the monomer solution with a specified composition (HEA concentration ranged from 0.5 to 8 g/L, 0.0009 mol/L $FeCl_3$, and ethanol as solvent) in a thin polyethylene plastic bag. The membranes were ranged in good order and the oxygen of the system was purged by bubbling nitrogen for 10 min. Subsequently, UV radiation with a wavelength of 365 nm was adopted to initiate the graft polymerization (Fig. 1). In order to guarantee the uniformity of grafting, both sides of the samples were irradiated for the same time.

The grafting degree (DG) was calculated by the following equation:

$$DG = (W_1 - W_0)/(A \times 10) \tag{1}$$

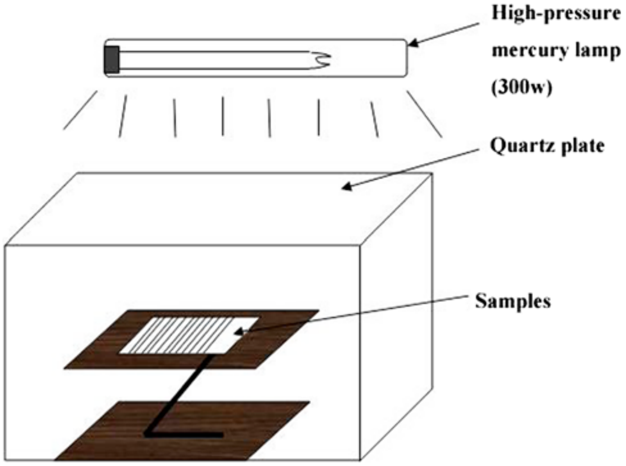

Fig. 1. The apparatus for photografting polymerization.

where W_0 and W_1 are the weights of PSF membrane matrix before and after grafting polymerization, respectively, A is the effective area of the membrane. All the results were the average of five parallel experiments.

2.3. Characterization of PSF-g-HEA

Infrared spectra were obtained with FT-IR spectra (VECTOR22, BRUKER Co.), and the measurements were carried out at a range of 3,000 to 1,000 cm^{-1}. High-energy resolution X-ray photoelectron spectra (XPS) analyses were conducted on a Kratos AXIS 165 spectrometer using monochromatic Al Ka X-rays. The contact angle (CA) measurements were performed on Cam 100 optical angle meter (YH-168A instruments Ltd, Japan). The surface morphology was analyzed using scanning electron microscope (QUANTA 200, FEI). The different thermo analysis was performed at a range of 0–800℃ for 10℃ min^{-1} under nitrogen protection on a NETZSCH STA409PC instrument (Netzsch, Germany).

2.4. Water permeation and fouling test experiments

The water permeation and fouling test experiments were carried out using a cross-flow filtration unit (Fig. 2) made in our laboratory. The cross-flow cell houses hollow fiber membrane module with an effective area of 18.63 cm^2. Pure water and BSA solutions of 0.50 mg/mL were employed as a feed for the evaluation of membrane performance. In all experiments, ultrapure water was utilized to characterize the pure water flux of original and modified membranes. Both the retentate and permeate solutions were recycled back to the feed tank to maintain a constant feed concentration. Pure water flux (J_w) and protein permeation (J_p) were evaluated at 0.1 MPa and at a flow rate of 110 L/h at 25 ± 1℃. J_w and J_p were calculated according to the following equation:

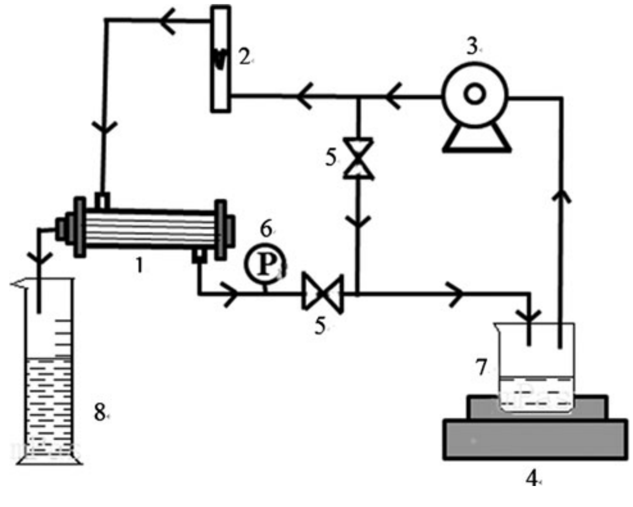

Fig. 2. The permeation and antifouling measurement device.
Notes: (1) the membrane modual, (2) rotameter, (3) high-pressure diaphragm pump, (4) electro-thermostatic water bath, (5) valve, (6) stainless steel vibration-proof pressure gauge, (7) pure water/feed solution, (8) graduated cylinder.

$$J_w(\text{L m}^{-2}\,\text{h}^{-1}\,\text{bar}^{-1}) = V_w/A\Delta t \tag{2}$$

$$J_p(\text{L m}^{-2}\,\text{h}^{-1}\,\text{bar}^{-1}) = V_p/A\Delta t \tag{3}$$

where V_w and V_p are the permeation volume of pure water and BSA solution, respectively, Δt is the operation time (h) and A is the effective area of the membrane (m^2).

Rejection of protein (R) was obtained for the original and modified membranes by measuring the concentrations of protein in the permeate at 280 nm using a TU-1901 UV/vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd). The rejection, R, is calculated according to the following equation:

$$R(\%) = (1 - C_{p,i}/C_{p,0}) \times 100\% \tag{4}$$

where $C_{p,i}$ and $C_{p,0}$ are the concentration of BSA in the permeate and feed solution (mg/mL), respectively.

After filtration of BSA, the membranes were washed with ultrapure water until the conductivity of the permeate solution was below 5 μs cm^{-1} and the water flux of the washed membranes was measured ($J_{1,i}$). In order to evaluate the fouling-resistant capability of the membranes, flux recovery was calculated using the following expression:

$$\text{FR}(\%) = (J_{1,i}/J_{w,i}) \times 100\% \tag{5}$$

3. Results and discussion

3.1. Graft polymerization of PSF-g-HEA

The degree of HEA grafting on PSF membrane matrix at different monomer concentrations as a function of irradiation time is given in Fig. 3. It could be observed that the degree of grafting increases with increasing irradiation time. As UV irradiation time increased, more active sites were excited on the PSF matrix, and more monomers were accessible to the surface radicals, resulting in the increase of grafting degree. However, with the irradiation time prolonged,

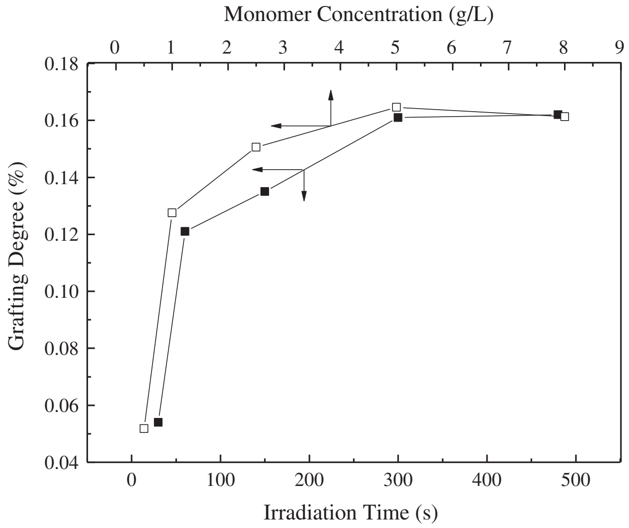

Fig. 3. The grafting degree (mg cm^{-2}) with different radiation time (s) and monomer concentration (g/L).

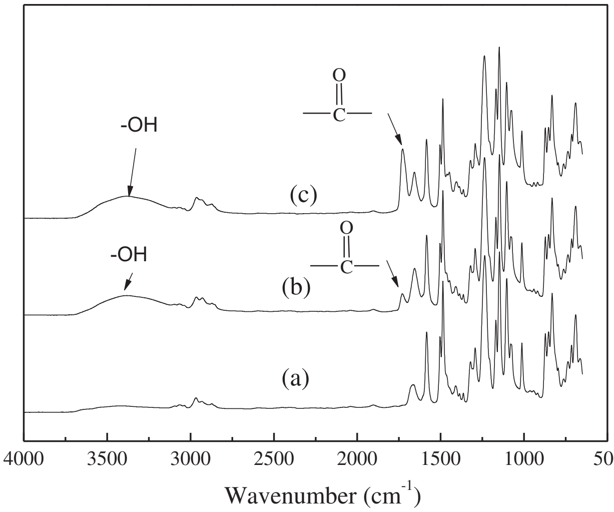

Fig. 4. FT-IR spectra of PSF membranes (a) original PSF (b) PSF-g-HEA (GD = 0.06 mg cm^{-2}), and (c) PSF-g-HEA (GD = 0.16 mg cm^{-2}).

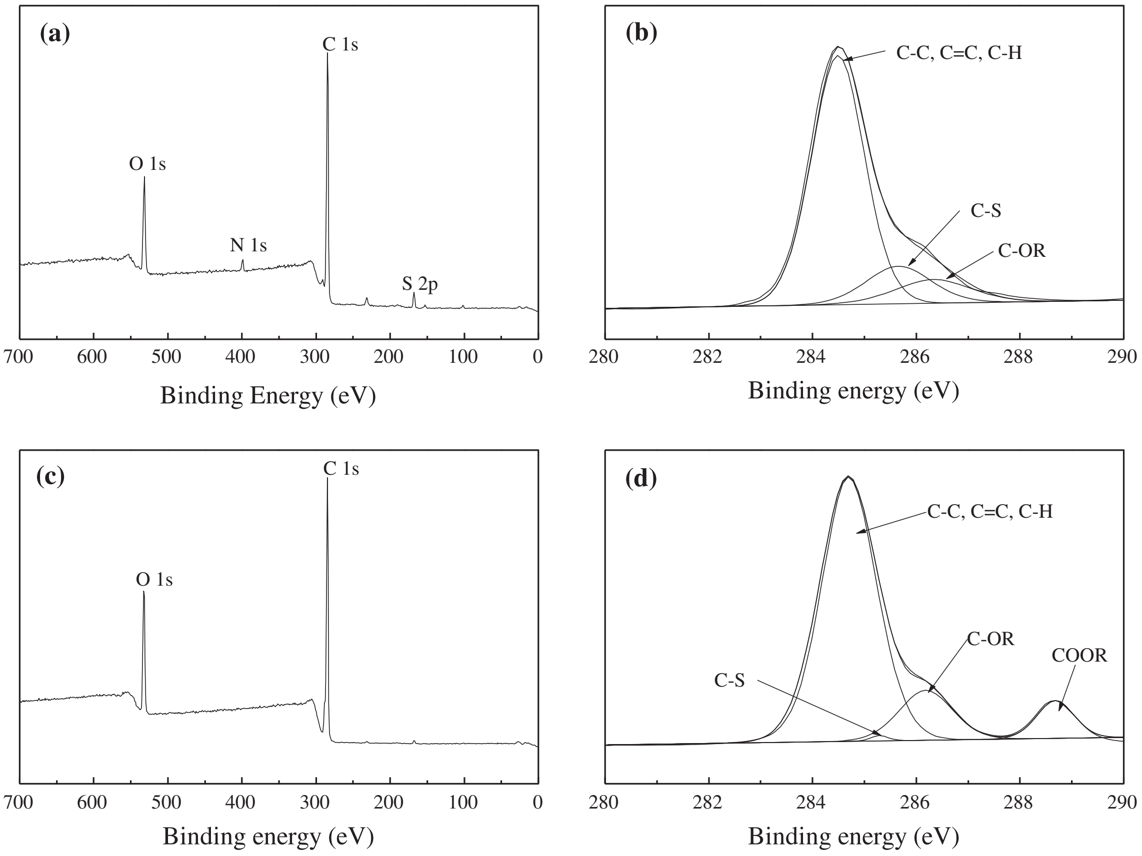

Fig. 5. Wide-scan and 1 s core-level spectra of the PSF and PSF-g-HEA membrane surface: ((a), (b) PSF, and (c), (d) PSF-g-HEA).

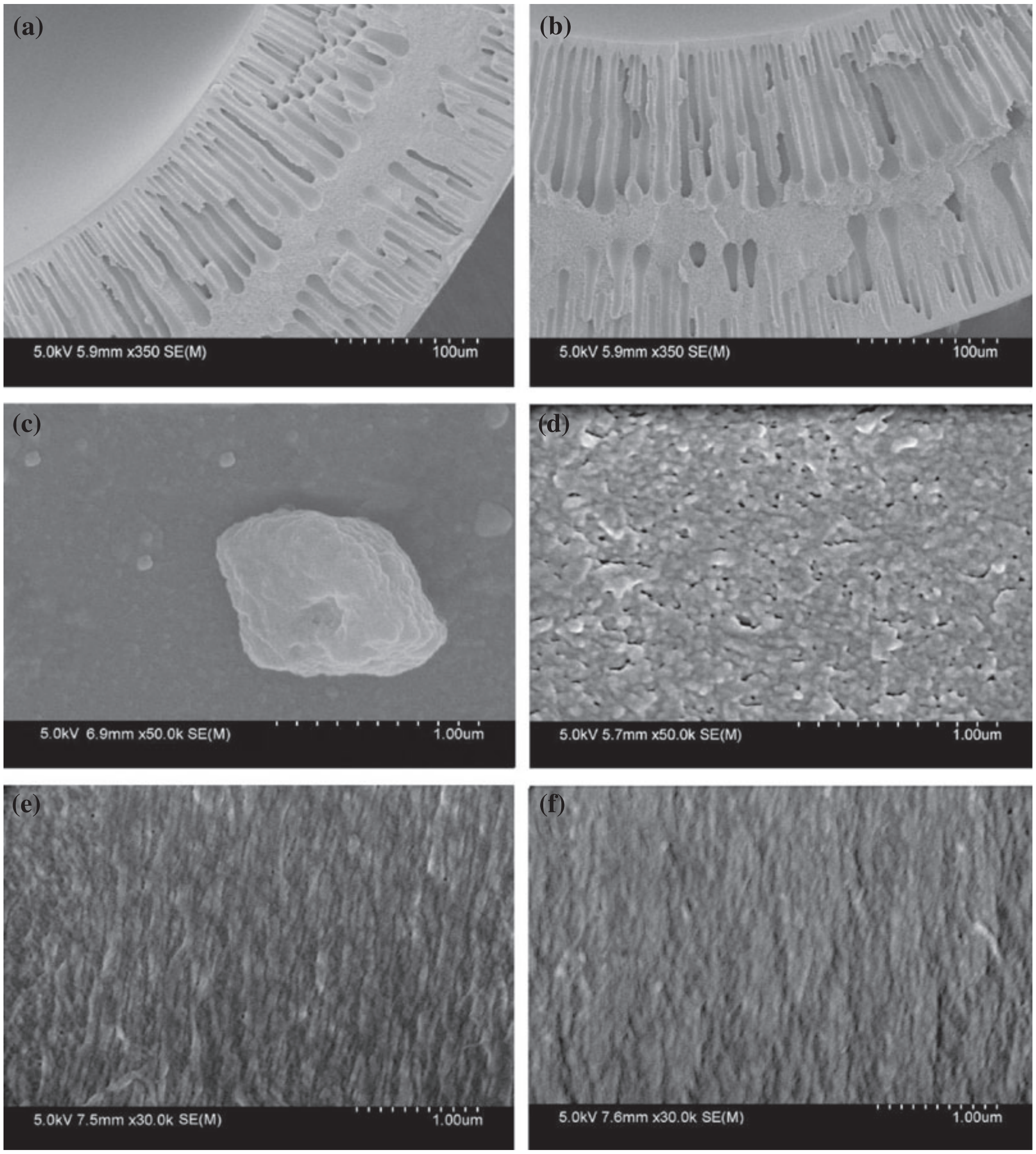

Fig. 6. SEM images for the (a), (c), (e) original PSF, and (b), (d), (f) PSF-g-HEA, respectively.

the consumption of initiator and monomer led to an asymptotic saturation of the grafting degree [14]. Thus, the irradiation time was set as 5 min in the following experiments. Grafting degree of PSF membrane matrix nearly increased proportionally with an increase in the monomer concentration up to 5 g/L, and then declined. This trend is believed to be related to higher concentrations of monomer available to react with the active sites on irradiated PSF membrane matrix, so that a higher grafting degree was achieved with the increase in monomer concentration. Furthermore, the grafting degree inclined to level off at higher concentration, which can be explained by the homopolymerization of HEA monomer. In fact, the grafting is monitored by a cumulative effect of the monomer diffusion within the polymer matrix, termination of the growing polymer chains, and the deactivation of the primary radicals. If the surface of PSF matrix was covered with the homopolymer, the diffusion of monomer into the inner area was hindered, resulting in the decrease of grafting degree with the subsequent increase in monomer concentration [15].

3.2. Characterization of PSF-g-HEA

After graft polymerization, we confirmed considerable chemical change of PSF membrane matrix by measuring FT-IR spectra. Fig. 4 shows the differential

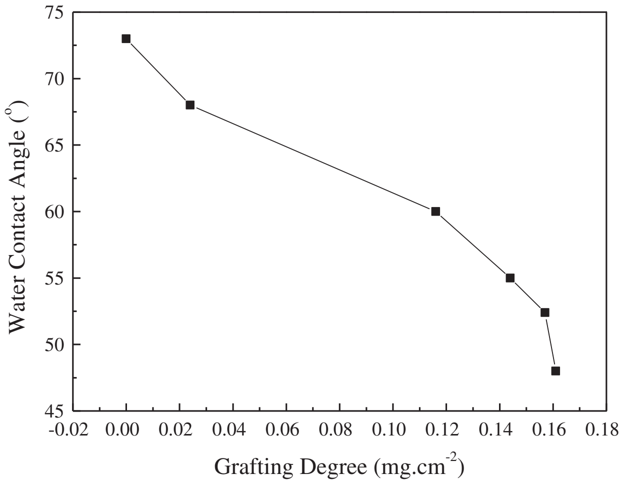

Fig. 7. The effect of grafting degree on water CA.

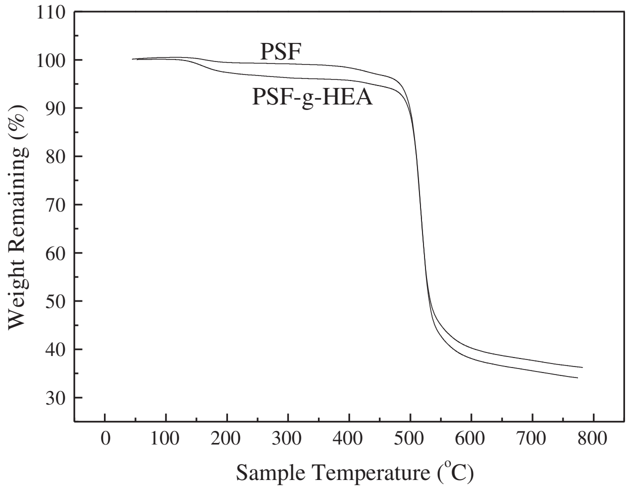

Fig. 8. TG curve of original PSF and PSF-g-HEA.

spectrum which is obtained from the original PSF membrane matrix and PSF-g-HEA with different DG; the spectrum was in good agreement with the original PSF. Compared with the original PSF matrix, the obvious appearance of an absorption peak at a wavenumber of 1,672 cm^{-1} was attributed to the stretching vibrations of C=O and the intensity of the peak increases with increasing of grafting degree [16]. Further characterization of PSF-g-HEA was conducted by XPS analysis. Compared to the original PSF, an additional peak could be observed at 288.4 eV because of the presence of COOR group in the grafted PSF sample [17] (Fig. 5). The FT-IR and XPS spectra suggested that the HEA was successfully grafted onto the PSF matrix after graft polymerization.

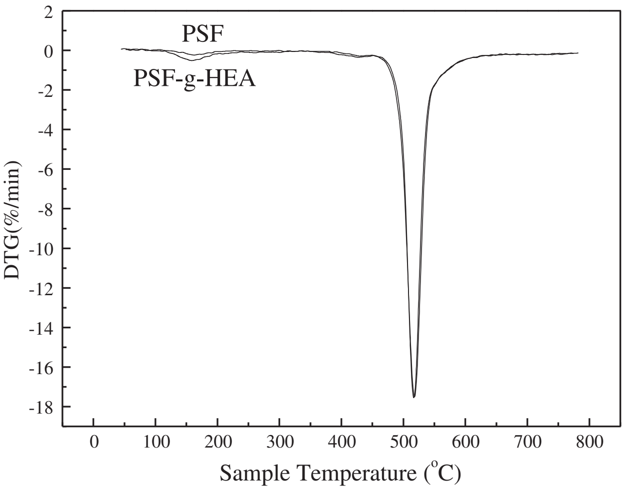

Fig. 9. DTG curve of original PSF and PSF-g-HEA.

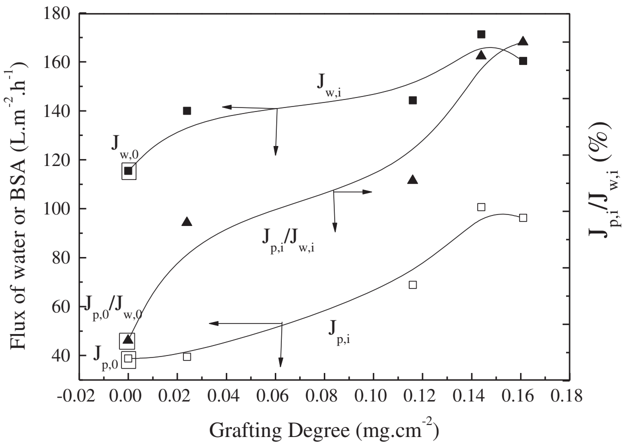

Fig. 10. The effect of grafting degree on the permeation performance of the membrane.

The morphologies of the original PSF membrane matrix and PSF-g-HEA membrane were observed by FESEM and typical images are shown in Fig. 6. It can be seen that the PSF membrane has a typical double layer cross-sectional structure, with each layer of the membrane consisting of a dense top and a finger-like support layer. The outer surface of PSF membrane matrix was smooth and uniform, while the outer surfaces of grafted membranes became rough. Compared with the outer surface of the PSF membrane matrix, the inner surface was uneven, which might be due to the roughness or shallow sunken nature of the inner surface. However, morphological changes for the inner surfaces and cross-section of grafted membranes were not as obvious as those of the outer surfaces after grafting polymerization. All the morphological changes of both surfaces and cross-section indicated

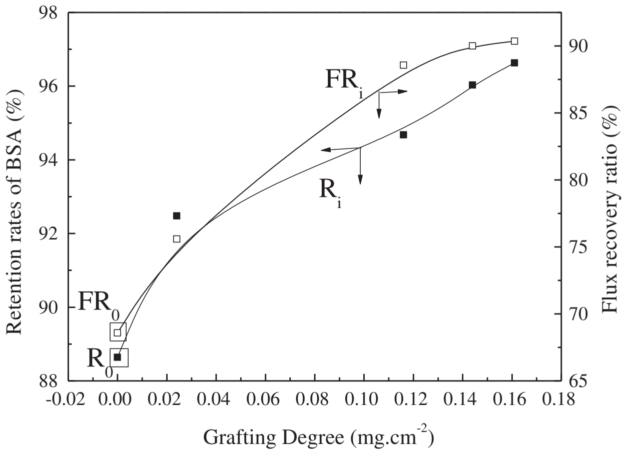

Fig. 11. The effect of grafting degree on the retention rates of BSA and flux recovery ratio.

that grafting was carried out on the outer surface of the PSF membrane.

As shown in Fig. 7, the CA of the PSF membrane matrix decreased with the subsequent increase of the grafting degree. Water CA of PSF-g-HEA exhibited a decrease from 73° to 47° with the grafting degree increasing from 0 to 0.16 mg cm^{-2}, which indicated that the hydrophilicity of the original PSF matrix surface was greatly improved after graft polymerization [18].

In order to study the stability of the PSF-g-HEA against thermal conditions, the thermal gravimetric analysis (TG) and different thermo analysis (DTG) were carried out in the temperature range of 0 and 800℃ at 10℃ /min (Figs. 8 and 9). The thermal decomposition of the modified sample consisted of three steps, including dehydration process and the decomposition of HEA grafted chain and PSF matrix. The dehydration process corresponding to the first peak was due to the evaporation of water adsorbed in the membrane. The second DTG peak and the weightless peak in the TG curve were the results of the decomposition of the HEA-grafted chain, the peak value appears in the 402.75℃, which was not obvious enough due to the low grafting degree, showing that the modified membrane had good thermal stability. For the third peak which was the decomposition of PSF matrix, it can be seen the peak value of the modified PSF was close to the original membrane, which means the heat resistance of the PSF-g-HEA was reduced only a very small amount.

3.3. Performance of PSF-g-HEA

Pure water flux and permeability of BSA solution measurements of selected PSF-g-HEA membranes as a function of grafting degree are presented in Fig. 10. $J_{w,0}$ and $J_{p,0}$ were the permeation of pure water and BSA for the unmodified membrane, respectively. It could be seen that pure water flux increased rapidly with the grafting degree. Pure water flux increased from 115.41 to 171.25 L m^{-2} h^{-1} when the grafting degree increased from 0 to 0.144 mg cm^{-2}. In addition, the permeability of BSA solution also showed a similar trend, which indicated that the permeability of PSF-g-HEA membranes was higher than that of the typical PSF hollow fiber membranes. This was because grafting of HEA improved the hydrophilicity of the membrane, and exactly for that reason, the $J_{p,i}/J_{w,i}$ value also increased with the increasing of grafting degree. When the grafting degree of PSF-g-HEA was over a critical value, the pore size was narrowed, resulting in the slight decrease in pure water flux with the subsequent increase of grafting degree [19, 20].

In addition, as shown in Fig. 11, the separation performance increased with increasing of grafting degree in a trend similar to that of the fouling resistance. The rejection ratio of the PSF-g-HEA membranes increased from 88.64 to 96.63% and the flux recovery ratio increased from 68.58 to 90.36% when the grafting degree increased from 0 to 0.16.

4. Conclusions

In this work, a novel modified hollow fiber membrane PSF-g-HEA was obtained by UV radiation-induced graft polymerization. The HEA was grafted on the outer surfaces of the PSF matrix membrane. The grafted membrane under 0.1 MPa showed a pure water flux of 171.25 L m^{-2} h^{-1}, which was 1.48 times of the original membrane, when the grafting degree was 0.144 mg cm^{-2}. Compared to the original PSF matrix membrane, the flux recovery rate and the rejection rate also increased, implying that the hydrophilicity, fouling resistance, and the separation performance were improved significantly at the same time, which makes the application range of the membrane further expanded.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1081628.

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References

[1] C.Y. Feng, K.C. Khulbe, T. Matsuura, A.F. Ismail, Recent progresses in polymeric hollow fiber membrane preparation, characterization and applications, Sep. Purif. Technol. 111 (2013) 43–71.

[2] H.M. Xu, J.F. Wei, X.L. Wang, Nanofiltration hollow fiber membranes with high charge density prepared by simultaneous electron beam radiation-induced graft polymerization for removal of Cr (VI), Desalination 346 (2014) 122–130.

[3] C. Charcosset, Membrane processes in biotechnology: An overview, Biotechnol. Adv. 24 (2006) 482–492.

[4] J. Wang, Y. Xu, L. Zhu, J. Li, B. Zhu, Amphiphilic ABA copolymers used for surface modification of polysulfone membranes, Part 1: Molecular design, synthesis, and characterization, Polymer 49 (2008) 3256–3264.

[5] D.S. Wavhal, E.R. Fisher, Modification of polysulfone ultrafiltration membranes by CO_2 plasma treatment, Desalination 172 (2005) 189–205.

[6] A. Bhattacharya, B.N. Misra, Grafting: A versatile means to modify polymers: Techniques, factors and applications, Prog. Polym. Sci. 29 (2004) 767–814.

[7] H. Susanto, M. Ulbricht, Photografted thin polymer hydrogel layers on PES ultrafiltration membranes: Characterization Stability, and influence on separation performance, Langmuir 23 (2007) 7818–7830.

[8] S. Mok, D. Worsfold, A. Fouda, T. Matsuura, Surface modification of polyethersulfone hollow-fiber membranes by γ-ray irradiation, J. Appl. Polym. Sci. 51 (1994) 193–199.

[9] A. Schulze, B. Marquardt, S. Kaczmarek, R. Schubert, A. Prager, M.R. Buchmeiser, Electron beam-based functionalization of poly(ethersulfone) membranes, Macromol. Rapid Commun. 31 (2010) 467–472.

[10] J.P. Deng, L.F. Wang, L.Y. Liu, W.T. Yang, Developments and new applications of UV-induced surface graft polymerizations, Prog. Polym. Sci. 34 (2009) 156–193.

[11] J.Y. Wang, Y.Y. Xu, L.P. Zhu, J.H. Li, B.K. Zhu, Amphiphilic ABA copolymers used for surface modification of polysulfone membranes, Part 1: Molecular design, synthesis, and characterization, Polymer 49 (2008) 3256–3264.

[12] H.J. Yu, Y.M. Cao, G.D. Kang, J.H. Liu, M. Li, Q. Yuan, Enhancing antifouling property of polysulfone ultrafiltration membrane by grafting zwitterionic copolymer via UV-initiated polymerization, J. Membr. Sci. 342 (2009) 6–13.

[13] M.N. Abu Seman, N. Hilal, M. Khayet, UV-photografting modification of NF membrane surface for NOM fouling reduction, Desalin. Water Treat. 51 (2013) 4855–4861.

[14] J.Q. Meng, J.H. Li, Y.F. Zhang, S. Ma, A novel controlled grafting chemistry fully regulated by light for membrane surface hydrophilization and functionalization, J. Membr. Sci. 455 (2014) 405–414.

[15] H.L. Zheng, J.Y. Ma, C.J. Zhu, Z. Zhang, L.W. Liu, Y.J. Sun, X.M. Tang, Synthesis of anion polyacrylamide under UV initiation and its application in removing dioctyl phthalate from water through flocculation process, Sep. Purif. Technol. 123 (2014) 35–44.

[16] Q. Wang, L.Y. Liu, W.T. Yang, A novel and facile approach for preparing composite core–shell particles by sequentially initiated grafting polymerization, Polymer 48 (2007) 6581–6588.

[17] Q. Shi, J.Q. Meng, R.S. Xu, X.L. Du, Y.F. Zhang, Synthesis of hydrophilic polysulfone membranes having antifouling and boron adsorption properties via blending with an amphiphilic graft glycopolymer, J. Membr. Sci. 444 (2013) 50–59.

[18] S.N. Li, J.F. Wei, L. Wang, H. Yang, A. Wang, Y.X. Nie, Phthalate esters removal using modified fiber prepared by two-step electron beam irradiation of methacrylate monomer onto polypropylene substrate, Desalin. Water Treat. 52 (2014) 5470–5478.

[19] H. Yamagishi, J.V. Crivello, G. Belfort, Evaluation of photochemically modified poly(arylsulfone) ultrafiltration membranes, J. Membr. Sci. 105 (1995) 249–259.

[20] Z.M. Liu, Z.K. Xu, J.Q. Wang, J. Wu, J.J. Fu, Surface modification of polypropylene microfiltration membranes by graft polymerization of N-vinyl-2-pyrrolidone, Eur. Polym. J. 40 (2004) 2077–2087.