Hydrophilic Modification of Poly(vinylidene fluoride) Membrane with Poly(vinyl pyrrolidone) via a Cross-Linking Reaction

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ABSTRACT: A highly hydrophilic hollow fiber poly(vinylidene fluoride) (PVDF) membrane [PVDF-*cl*-poly(vinyl pyrrolidone) (PVP) membrane] was prepared by a cross-linking reaction with the hydrophilic PVP, which was immobilized firmly on the outer surface and cross-section of the PVDF hollow fiber membrane via a simple immersion process. The cross-linking between PVDF and PVP was firstly verified via nuclear magnetic resonance measurement on PVP solution after cross-linking. The hydrophilic stability of the modified PVDF membrane was evaluated by measuring the pure water flux after different times of immersion and drying. The anti-fouling properties were estimated by cyclic filtration of protein solution. When the cross-linking time was as long as 6 hr and the PVP content reached 5 wt %, the pure water flux (J_v) was constant as $\sim$ 600 L m^{-2} hr^{-1}. The hydrophilicity of the PVDF-*cl*-PVP membrane was significantly enhanced and exhibited a good stability. The PVDF-*cl*-PVP membrane showed an excellent anti-protein-fouling performance during the cyclic filtration of bovine serum albumin solution. Therefore, a highly hydrophilic and anti-protein-fouling PVDF hollow fiber membrane with a long-term stability can be prepared by a simple and economical cross-linking process with PVP. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) membrane has been widely used in many separation applications because of extraordinary mechanical property, high chemical resistance, and good thermal stability.[1] However, due to the low surface energy and hydrophobic characteristics, the membranes made from PVDF always suffer from fouling when applied in various separation and purification process of aqueous solution systems, such as drinking water production, waste water treatment, and bacteria filtration.[2]

The membrane with a hydrophilic surface is able to form a thin water boundary via the hydrogen bond to supply a strong repulsive force to the hydrophobic solutes.[3] Hence, a hydrophilic surface offers better fouling resistance as protein and many other foulants are hydrophobic in nature.[4] Therefore, a number of studies have been devoted to modify the PVDF membrane by improving the surface hydrophilicity to enhance the membrane lifetime and reduce the operation cost.[5,6] The modification methods include surface coating, surface grafting, and blending.[7-17] Among the various modification techniques, surface coating is the simplest way to improve the PVDF membrane hydrophilicity and the chemical treatment such as cross-linking can anchor the coated layer on the membranes to solve the instability problem.[3]

Because of the high hydrophilicity and biocompatibility, poly(vinyl pyrrolidone) (PVP) has been widely used in preparing polymer membranes to adjust pore size, produce hydrophilic surfaces and prevent fouling.[18] Cha and Yang found PVP addition was very effective to control the morphology of PVDF hollow fiber membranes.[19] Chen and Hong[20] combined PVP in blends with PVDF to prepare membranes via solution-casting and the results showed the increase of PVP caused the disappearance of

crystalline PVDF phases. Because PVP is water soluble which can be washed out during phase inversion processes, the main role of PVP in the blending with PVDF is pore forming agent rather than hydrophilic agent.[21] Xu et al.[22] prepared the hydrophilic PVDF-PVP ultrafiltration membrane by using $KMnO_4$ and KOH as oxidant and strong base to facilitate the hydrogen fluoride (HF) elimination from PVDF chains, and the PVP aqueous solution acted as a coating media. The modified membrane was promising and practical to further purify flavonoids from crude Ginkgo biloba extraction products. However, the alkaline treatment often destructs PVDF membrane structure, leading to lower its strength.[23]

Many researchers have focused on the cross-linking aqueous solutions of PVP through the irradiation and chemical interaction.[24,25] Kang et al.[26] reported that PVP can be immobilized with the microporous chlorinated polyvinyl chloride (CPVC) membrane using a cross-linking treatment. However, only a few reports analyzed the cross-linking between PVDF and PVP.[27,28] In this work, PVP was immobilized firmly on the outer surface and cross-section of PVDF hollow fiber microporous membranes (PVDF-cl-PVP) via the cross-linking reaction with potassium persulfate ($K_2S_2O_8$) as the cross-linking agent. The effects of PVP content and cross-linking time on the performance of PVDF-cl-PVP membranes were investigated. Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectrophotometer, scanning electron microscope (SEM), and contact angle (CA) meter were applied to determine the surface composition, morphology, and hydrophilicity of the PVDF-cl-PVP membranes, respectively. The hydrophilic stability of the modified PVDF membranes was evaluated by measuring the pure water flux after different times of immersion and drying. The anti-fouling properties were estimated by cyclic filtration of protein solution.

EXPERIMENTAL

Materials
PVDF hollow fiber membranes with internal and external radius of 1.3 and 1.8 mm were prepared by using thermally induced phase separation method. PVP (K30, $M_w = 35,000$) was purchased from Boai Nky Pharmaceuticals Ltd. (Henan, China). The PVP was dried in vacuum at $(60 \pm 1)°C$ for 8 hr before used. Potassium persulfate ($K_2S_2O_8$), sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), and bovine serum albumin (BSA = 67,000, IEP = 4.7) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China).

Cross-Linking Process
PVDF hollow fiber membranes were rinsed successively with ethanol and pure water for 1 hr, respectively. Then, the PVDF membranes were soaked in the aqueous solution containing $K_2S_2O_8$ (0.4 wt %) and PVP (0.1, 0.5, 1, 3, 5, 10 wt %) at $(90 \pm 1)°C$. After different periods (2, 4, 6, 16, 24 hr), the PVDF membranes were washed with water for 24 hr to remove residual PVP and then dried under vacuum for 24 hr and weighted.

The increased mass of PVDF membrane (Δm, g m^{-2}) was calculated as follows:

$$\Delta m = \frac{w_2 - w_1}{A} \tag{1}$$

where w_1, and w_2 are the weight of nascent and modified PVDF membrane (g), respectively. A is the outer surface area of the PVDF membrane (m^2).

Membrane Characterizations
FTIR spectroscopy was carried out by a Nicolet 6700 FTIR spectrometer with an ATR (California, USA) attachment to investigate the chemical compositions of PVDF membranes. Each spectrum was collected by cumulating 64 scans at a resolution of 4 cm^{-1}.

^{19}F-nuclear magnetic resonance (NMR) cryoporometry measurements were carried out on a NMR spectrometer (600 MHz, JEOL JNM-ECA-600) at 14.09 Tesla. The region 30 to -430 ppm was shown.

The outer surfaces and cross-sections of the PVDF hollow fiber membranes were observed by SEM (JEOL JSM7401) under standard high-vacuum conditions. All of the samples were preserved in liquid nitrogen, then deposited on a copper holder and sputtered with gold prior to SEM.

Dynamic CA between water and PVDF hollow fiber membranes was measured and calculated on a CA meter (OCA 20, Germany) at 25°C. Water (2 μL) was carefully dropped on dry samples with an automatic piston syringe and photographed. The CA value of each sample was measured at three various positions for each sample.

A self-made dead end filtration set-up was applied to characterize the filtration performance of nascent and modified PVDF membranes. All of the membranes were initially immersed in pure water for 1 hr. The filtration experiments were conducted at room temperature ($25 \pm 0.5°C$) and a constant operation pressure of 0.1 MPa. The pure water flux (J_v, L m^{-2} h^{-1}) was used to express the rate at which water permeated the membrane and defined as the permeate water volume per area per unit of time.

$$J_v = \frac{V}{A\Delta t} \tag{2}$$

where V, A, and Δt are the permeate water volume (L), membrane area (m^2), and permeation time (hr), respectively.

Stability
The hydrophilic stability of modified PVDF membranes was evaluated by two methods. On the one hand, the pure water flux of the nascent and modified PVDF membranes after different times of immersion and drying was measured and compared. On the other hand, the PVP leaching percentage of modified PVDF membranes was calculated.

After the nascent and modified PVDF membranes were immersed in pure water for 1 hr, the averaged pure water flux ($J_{v,0}$) was determined. Then, the membranes were dried under vacuum at 50°C for 24 hr and the pure water flux was measured again and recorded as $J_{v,i}$ (i indicates the number of times the immersion and drying procedure occurred).

The dried nascent and modified PVDF membranes with 10 cm of length were weighed, noted as w_1 and w_2, respectively. Subsequently, the modified PVDF membranes were soaked in pure water at 25°C. After 72 hr, the membranes were dried under
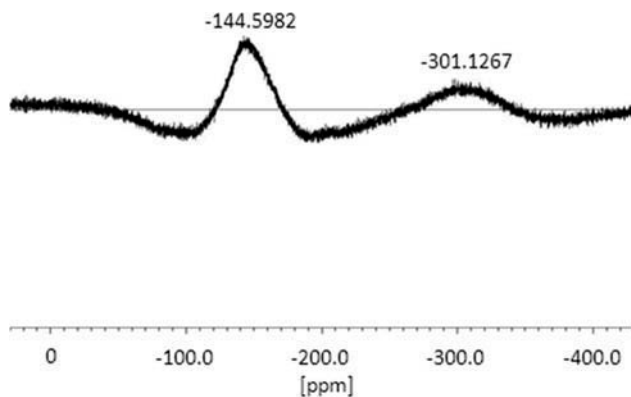
Figure 1. ^{19}F-NMR spectrum of PVP solution after cross-linking process (5 wt % PVP, 6 hr).

vacuum at 50°C for 24 hr and weighted (w_3). The leaching percentage (LP, wt %) of PVP from the PVDF membranes can be calculated by eq. (3):

$$LP\% = \frac{w_2 - w_3}{w_2 - w_1} \times 100\% \qquad (3)$$

where w_1 is the mass of nascent PVDF membrane (g), w_2 and w_3 are the mass of modified PVDF membrane before and after immersion in pure water (g), respectively.

Antifouling Performance
BSA was used as a model protein to evaluate the anti-fouling property of PVDF membranes and BSA filtration step was performed and repeated. In BSA filtration cycle, a BSA solution (0.1 g L^{-1}), prepared by dissolving BSA in phosphate-buffered saline (PBS, PH = 7.4) solution was filtered by the tested membranes under the pressure of 0.1 MPa for 1 hr. The flux of BSA solution was measured by successively sampling for every 5 min. in 30 min. The PBS solution was made from a mixture of NaH$_2$PO$_4$·2H$_2$O and Na$_2$HPO$_4$·12H$_2$O. Then, the membranes
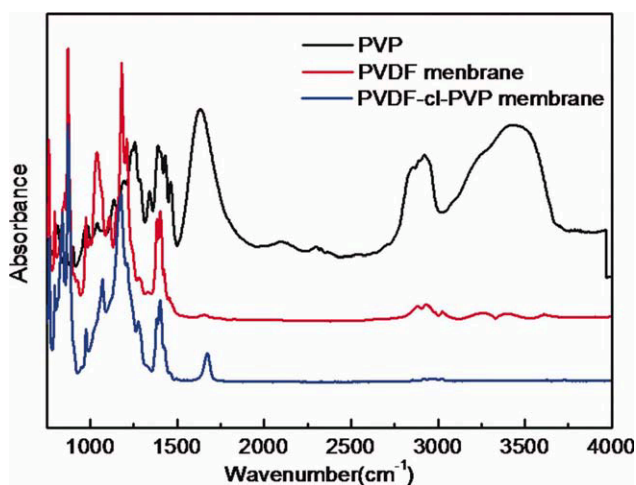

Figure 2. ATR–FTIR spectra of PVP polymer, outer surfaces of PVDF membrane and PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
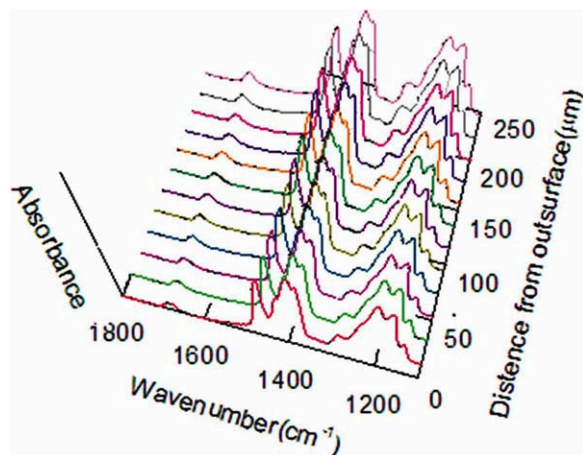

Figure 3. Mapping-FTIR spectra of cross section of PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were washed by 0.5 mol L^{-1} NaOH solution for 30 min and rinsed with pure water for the same period. After that, the flux of BSA solution was measured again. The experiment was stopped after six cycles.

RESULTS AND DISCUSSION

Characterization of the Cross-Linked PVDF-*cl*-PVP Membrane
In this study, a simple immersion method was performed and the cross-linking process between PVDF and PVP occurred with K$_2$S$_2$O$_8$ as the cross-linking agent. PVP immobilized on and in the PVDF hollow fiber membrane was confirmed initially by NMR and FTIR spectra.

^{19}F NMR spectrum for the solution containing 5 wt % PVP after the cross-linking reaction for 6 hr is shown in Figure 1. The immersed solution contained ^{19}F, indicating a cross-linking between PVP and PVDF rather than an adsorption of PVP on the PVDF membrane. As a result, PVP can be immobilized firmly on and in the PVDF membrane through the chemical bond. PVP was immobilized on the outer surface of PVDF membrane, which was confirmed by ATR–FTIR spectra in Figure 2. Compared with nascent PVDF membrane, additional adsorption centered at 1670 cm^{-1} (C=O) could be observed from the spectrum of the modified PVDF membrane (PVDF-*cl*-PVP), which was consistent with that of PVP polymer. It demonstrated that PVP was immobilized on the outer surface of PVDF membrane through adsorption and cross-linking. The spectra of the cross-section of PVDF-*cl*-PVP membrane were measured by Mapping-FTIR technique, as shown in Figure 3. Through the whole cross-section of PVDF-*cl*-PVP membrane, an obvious characteristic peak at 1670 cm^{-1}was attributed to the bending vibration of carbonyl group (C=O), which originated from PVP. During the immersion, cross-linking held the atoms in PVDF and PVP molecules together. Thus, PVP entered into the inner of PVDF membrane and cross-linked with the PVDF in the cross-section of membrane.

The surface and cross-section morphologies of PVDF membranes before and after modification were examined by SEM at magnification of ×3000. As displayed in Figures 4(a) and 5(a),
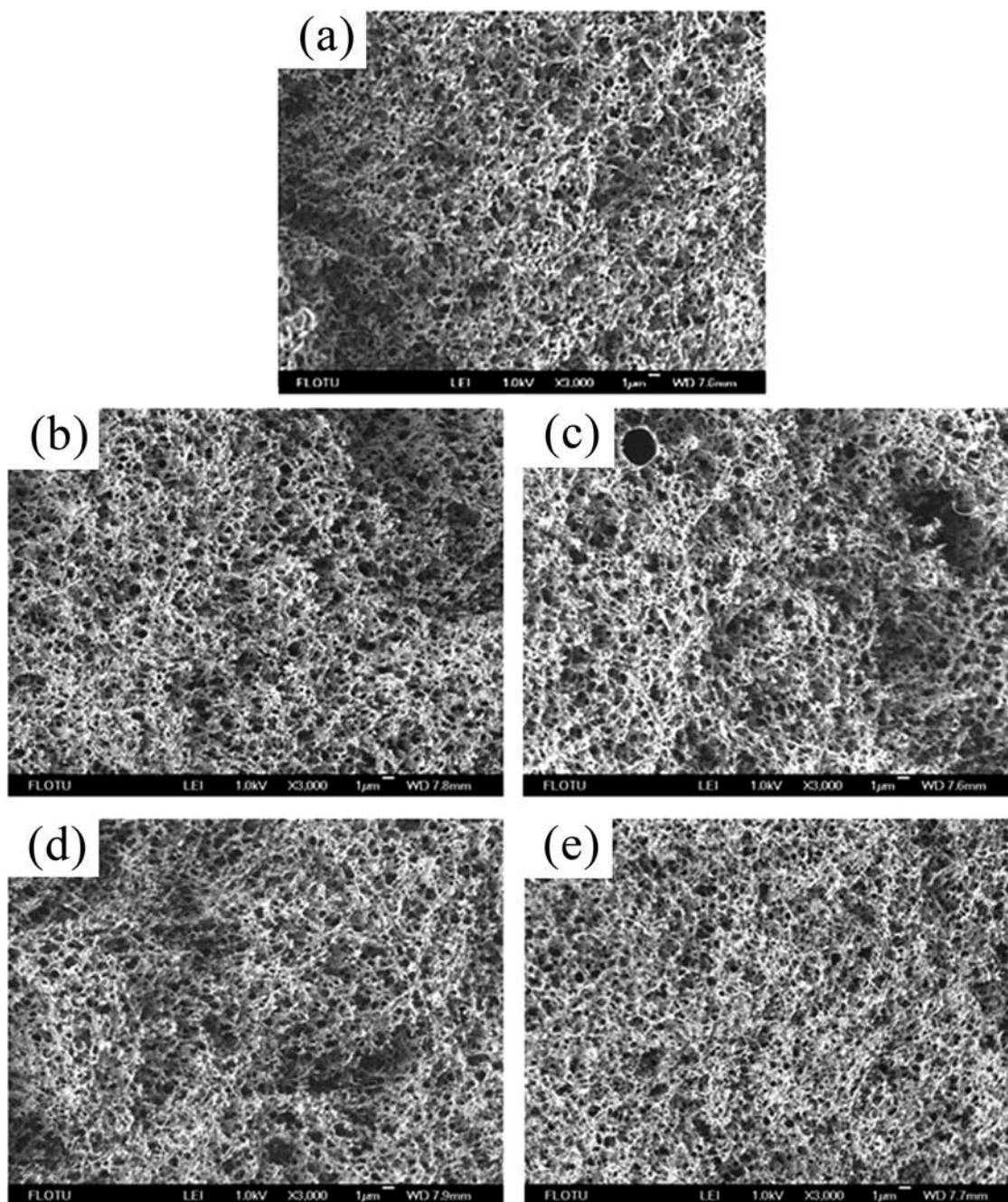
Figure 4. Cross-section morphologies of (a) PVDF membrane, (b) PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr), (c) PVDF-*cl*-PVP membrane (5 wt % PVP, 24 hr), (d) PVDF-*cl*-PVP membrane (10 wt % PVP, 6 hr), and (e) PVDF-*cl*-PVP membrane (10 wt % PVP, 24 hr).

the PVDF membrane showed a porous cross-section morphology with a porous skin layer. Compared with the nascent PVDF membrane, the number of opening pores on the cross sections and the outer surfaces of PVDF-*cl*-PVP membranes appeared to be reduced due to the coverage of PVP. As shown in Figure 5, the pores of outer surface of PVDF-*cl*-PVP membrane become smaller with the increase of PVP content and cross-linking time. As the PVP content and cross-linking time increased to 10 wt % and 24 hr, respectively, the membrane surface pores were almost fully covered [Fig. 5(e)]. As the PVP content increased, the amount of

PVP which was cross-linked with PVDF and fixed onto the PVDF membrane increased.

After the PVDF membranes were immersed in the PVP solution with the cross-linking agent $K_2S_2O_8$, the weight increased and the values of weight increase per area (Δm) depended on the PVP content and cross-linking time. Table I shows the dependence of Δm on PVP content and cross-linking time. It could be seen that prolong the cross-linking time can increase Δm, but the increasing rate of Δm slowed down at a long time of the crosslinking. The Δm increased rapidly at the beginning and
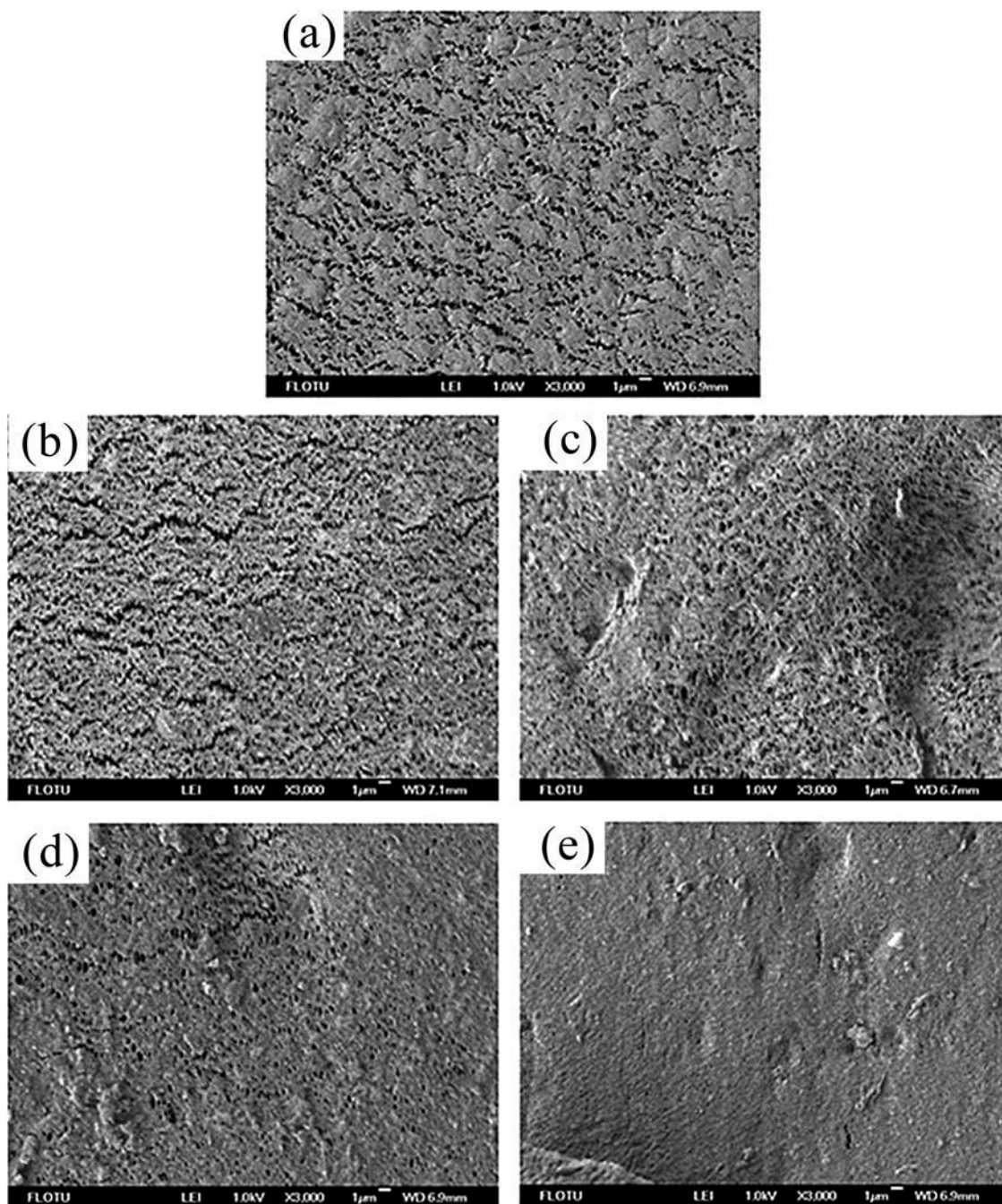
Figure 5. Outer surface morphologies of (a) PVDF membrane, (b) PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr), (c) PVDF-*cl*-PVP membrane (5 wt % PVP, 24 hr), (d) PVDF-*cl*-PVP membrane (10 wt % PVP, 6 hr), and (e) PVDF-*cl*-PVP membrane (10 wt % PVP, 24 hr).

then leveled off after 6 hr. At the beginning of the cross-linking, the concentration gradient of PVP between membrane and the solution bulk was large, which caused a high mass transfer coefficient. When the mass transfer and reaction reached equilibrium, Δm was constant. It caused more PVP cross-linked with PVDF on and in the PVDF membrane per hour. It was also obvious that the Δm increased with the increase of PVP content and approached a constant value when the PVP content exceeded 5 wt %. Besides, for the PVDF membrane which was immersed in the solution without $K_2S_2O_8$ (2.98 g m^{-2}) (PVDF*

membrane), the Δm value was much smaller than that of PVDF-*cl*-PVP membrane (3.53 g m^{-2}). $K_2S_2O_8$ initiated the self-cross-linking of PVP and the cross-linking between PVP and PVDF, resulting in the increase of Δm.
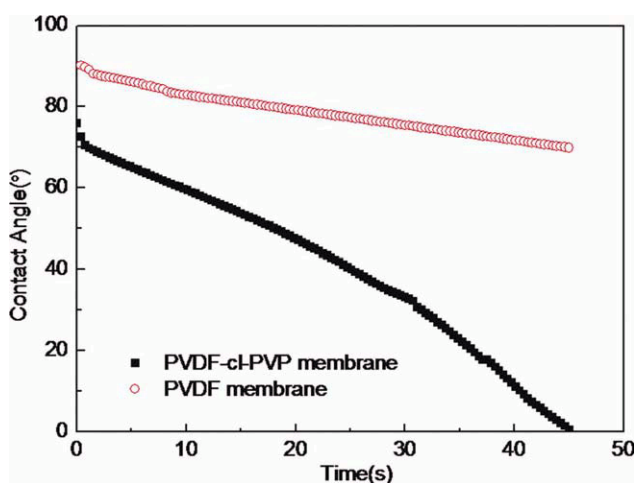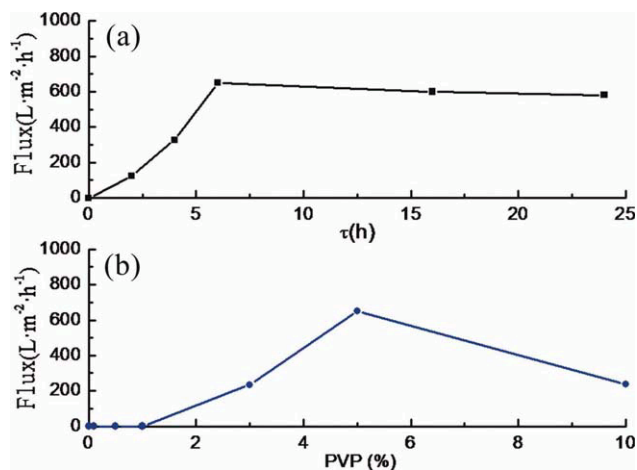
Hydrophilicity and Stability

The surface hydrophilicity is one of the main factors which affects the water flux and anti-fouling performance of membrane. Static CA was often used to evaluate the membrane hydrophilicity. However, water droplets could gradually

Table I. Dependence of Δm on Crosslinking Time and Content of PVP in the Immersed Solution

Membrane	Cross-linking time (hr)	PVP content (wt %)	Δm (g m^{-2})
PVDF*	6	5 (without cross-linking agent)	2.98
PVDF-cl-PVP	2	5	2.50
PVDF-cl-PVP	4	5	3.26
PVDF-cl-PVP	6	5	3.53
PVDF-cl-PVP	16	5	4.67
PVDF-cl-PVP	24	5	5.49
PVDF-cl-PVP	6	0.1	2.43
PVDF-cl-PVP	6	0.5	4.07
PVDF-cl-PVP	6	1	4.68
PVDF-cl-PVP	6	3	3.26
PVDF-cl-PVP	6	10	4.58

PVDF* represents the PVDF membrane after immersed in the PVP solution without cross-linking agent.

Figure 7. Dependence of pure water flux of PVDF-cl-PVP membrane on cross-linking time (5 wt % PVP) and PVP content (6 hr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

penetrate into the pores of surface induced by the capillary force. Hence, it is not accurate to evaluate the surface hydrophilicity of membrane only by analyzing static CA value.[29] In addition, the dynamic CA shows the decrease of CA with time and the CA values of membrane with great hydrophilicity should decrease rapidly.[30] In this work, the dynamic CA values of the outer surface of modified membranes were measured to characterize the hydrophilization effect of cross-linked PVP on PVDF membranes. As shown in Figure 6, the initial CA value of PVDF membrane was 90°, which was obviously higher than that of the PVDF-cl-PVP membrane with PVP content of 5 wt % and cross-linking time of 6 hr (77°). When the water dropped on the surfaces for more than 30 sec, the CA values of PVDF membrane kept constant at about 70°. However, the CA of the

Figure 6. Dynamic CAs of PVDF membrane and PVDF-cl-PVP membrane (5 wt % PVP, 6 hr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PVDF-cl-PVP membrane decreased rapidly. After 45 sec, a large part of the water droplet could penetrate into the PVDF-cl-PVP membrane and the CA value was close to zero. The results demonstrated that the hydrophilicity of the PVDF membrane was improved significantly by the cross-linking process with PVP.

In this work, water was filtrated through each membrane rinsed at 0.1 MPa for at least 30 min until a steady flux (J_v) was achieved. The effects of cross-linking time and PVP content on J_v of the PVDF-cl-PVP membrane were shown in Figure 7(a,b), respectively. The J_v of the PVDF membrane without cross-linking process showed a minimal value of 0 L h^{-1} m^{-2}. An increase of J_v was observed when the PVDF membrane was cross-linked with PVP, which was attributed to the improvement of membrane hydrophilicity. As shown in Figure 7(a), the pure water flux of PVDF-cl-PVP membrane increased rapidly as the cross-linking time increased from 0 to 6 hr, and J_v was almost constant along with a further increase in the immersion time. The pure water flux of the PVDF-cl-PVP membrane increased from 0 to 650 L h^{-1} m^{-2} as the PVP content increased from 0 to 5 wt % but decreased obviously with further increasing the content of PVP, which can be seen in Figure 7(b). This could be ascribed to the decrease of the pore sizes caused by the crowded PVP. When the cross-linking time and PVP content were 6 hr and 5 wt %, respectively, the J_v of PVDF-cl-PVP membrane was higher than 600 L m^{-2} h^{-1}.

The hydrophilic stability of PVDF-cl-PVP membrane was evaluated by two methods. On the one hand, the pure water flux of PVDF membrane and PVDF-cl-PVP membrane after different number of times the immersion in water and drying in vacuum was measured and compared. On the other hand, the PVP leaching percentages of PVDF-cl-PVP membranes were calculated. Figure 8 demonstrates the pure water flux of PVDF membrane and PVDF-cl-PVP membrane after different times of immersion and drying. $J_{v,i}$ ($i = 0, 1, 2, 3, 4, 5, 6, 7$) was defined as the pure water flux of the membrane after i time (s) of
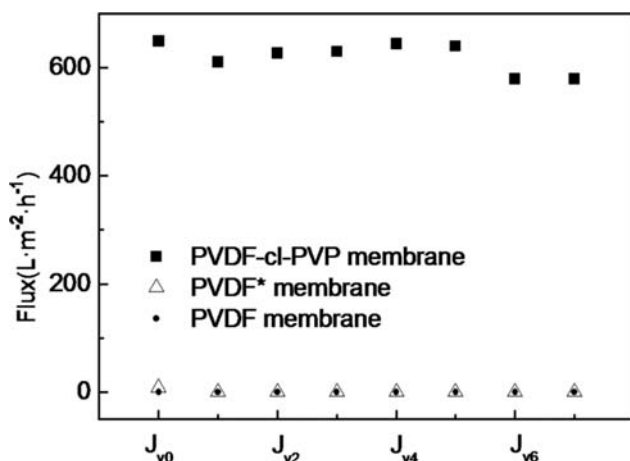
Figure 8. Pure water flux of PVDF membrane, PVDF* membrane (5 wt % PVP, 6 hr) and PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr) after different number of times the immersion and drying occurred.

immersion in water and drying in vacuum. Less pure water permeated through the PVDF membrane and PVDF* membrane. However, after immersion in pure water and dried in vacuum for seven times, $J_{v,0-7}$ of the PVDF-PVP membrane exhibited the stable value as 600 L m^{-2} h^{-1}.

The LP values can verify the cross-linking reaction and quantitatively determine the PVP content leached from the membrane before and after immobilization.[31] The results of PVDF* membrane and PVDF-*cl*-PVP membrane with different PVP contents are shown in Figure 9. The LP values of PVDF-*cl*-PVP membranes were much lower than that of PVDF* membrane. When PVDF* membrane was immersed in water, the residual PVP on PVDF membrane may leach into the water owing to the hydrophilicity of PVP. Thus, PVDF* membrane showed a large LP exceeding 55%. The PVP on and in PVDF-*cl*-PVP membrane would not leach because of the crosslinking, which resulted in a small value of LP. Additionally, as the PVP content increased from 5 to 10 wt %, the amount of PVP extracted from the PVDF-*cl*-PVP membrane increased from 5.6 to 8.0 wt %. This study clearly demonstrated that PVP was immobilized on and in PVDF membrane firmly after the cross-linking process. Therefore, the hydrophilicity of PVDF-*cl*-PVP membrane was maintained without sacrificing the hydrophilicity from leaching of PVP, which strongly supported the results of the permeation experiment shown in Figure 8.

Antifouling Performance

The antifouling performance of the PVDF-*cl*-PVP membrane was evaluated by testing the filtration performance for a major protein, BSA. The hydrophilicity of membrane usually demonstrates a good correlation with the membrane performance during protein filtration.[5] In this study, the functionalization of the cross-linked PVDF membrane with PVP has made the PVDF membrane highly hydrophilic and having efficient performance on resisting the protein adsorption. The relative flux values of PVDF membrane and PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr) during the cyclic filtration of 0.1 g L^{-1} BSA solution are
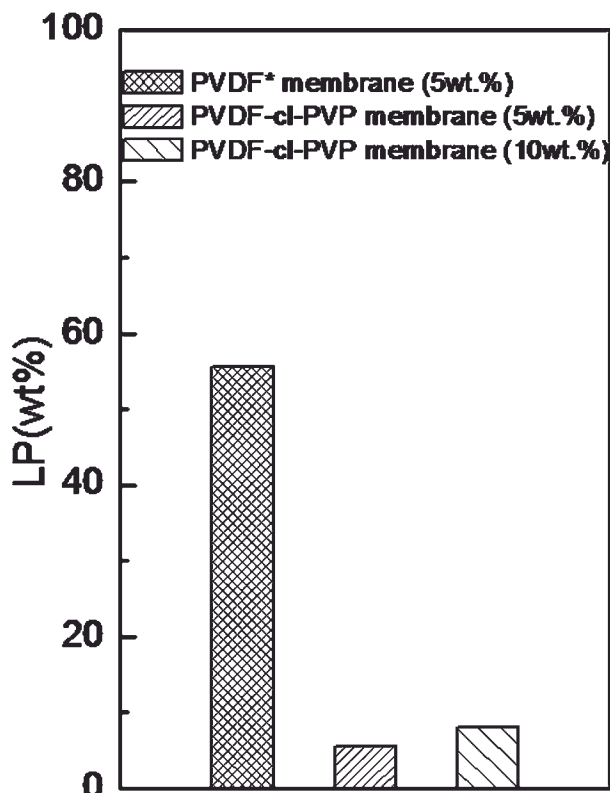

Figure 9. Amount of PVP leached from PVDF* membrane and PVDF-*cl*-PVP membrane with different PVP content (6 hr).

illustrated in Figure 10. For each circle, the permeate flux of PVDF membrane and PVDF-*cl*-PVP membrane declined rapidly at the start of filtration and the relatively steady permeation flux was finally observed at the later stage of each filtration circle, suggesting that the adsorption/deposition and the back diffusion of the protein molecules reached an equilibration. Compared with the nascent PVDF membrane, the PVDF-*cl*-PVP membrane exhibited the slower flux decline and the
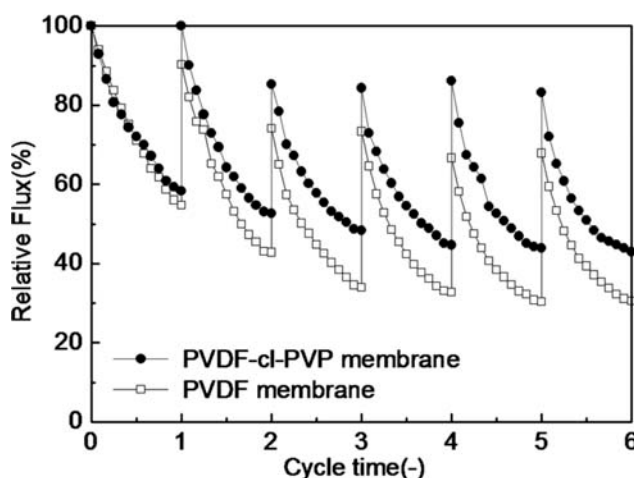
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Figure 10. Relative flux of PVDF membrane and PVDF-*cl*-PVP membrane (5 wt % PVP, 6 hr) during the filtration of 0.1 g L^{-1} BSA solution.

higher final steady permeate flux. As the times of filtration cycle increased, the difference of flux between PVDF membrane and PVDF-*cl*-PVP membrane enlarged. The results confirmed that the cross-linking of PVDF membrane with PVP efficiently reduced the membrane fouling during the cyclic protein filtration.

CONCLUSIONS

In this study, a highly hydrophilic and anti-protein-fouling PVDF hollow fiber membrane with a good stability was prepared by a simple and economical cross-linking process with PVP. The cross-linking between PVDF membrane and PVP was firstly verified through NMR measurement on the PVP solution after cross-linking reaction. FTIR and SEM analysis confirmed that PVP was successfully cross-linked on and in the PVDF membrane. The PVDF-*cl*-PVP membrane became highly hydrophilic and the water CA value approached to zero degree after 45 s. The pure water flux of the PVDF-*cl*-PVP membrane with 5 wt % of PVP content and 6 hr of cross-linking time increased to ~ 600 L m^{-2} h^{-1} and exhibited a good stability due to the small amount of PVP leached from the membrane. With conducting the cyclic experiment for BSA solution filtration, the PVDF-*cl*-PVP membrane proved a better antifouling performance than the nascent PVDF membrane.

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