In Situ Crosslinking of Hyperbranched Polyglycerol in Casting Solutions and Its Effect on the Structure and Properties of Porous PVDF Membranes

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ABSTRACT: Porous membranes were prepared via phase inversion process from casting solutions composed of poly(vinylidene fluoride), hyperbranched polyglycerol (HPG), and *N,N*-dimethylacetamide. To seek a stable presence of HPG in the resulting membranes, it was crosslinked in the casting solutions using 4,4′-oxydiphthalic anhydride as the crosslinking agent. The membranes were characterized in terms of morphology, surface and bulk chemical compositions, water contact angle, porosity, water flux, and bovine serum albumin (BSA) adsorption experiments. The effects of HPG content and crosslinking degree on the membrane structure and properties were investigated. The increasing of crosslinking degree resulted in a significant improvement in HPG stability in the membrane matrix, and a remarkable enrichment of the crosslinked HPG at the separation surface was observed when the membrane was shaken in water at a relatively high temperature (60°C). This enrichment led to a decrease in the value of water contact angle and an improvement in fouling-resistance. To optimize the membrane performance, a small amount of poly(vinylpyrrolidone) (PVP) was used as an additive, and it was found that the addition of PVP led to a considerable increase in water flux. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 548–556, 2010

Key words: membrane; poly(vinylidene fluoride); hyperbranched; phase inversion

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has been widely used as a separation membrane material because of its excellent thermal stability as well as chemical stability against corrosive chemicals and organic compounds including acids, alkaline, strong oxidants, and halogens.[1,2] However, PVDF is susceptible to be fouled by proteins and oils because of its strong hydrophobicity, which limits its applications in many fields such as waste water treatment, biomedical technology, etc.[3] To improve the antifouling ability of PVDF membrane, different methods have been carried out. Basically, these methods include blending with hydrophilic polymers,[4–6] surface modification by grafting hydrophilic monomers,[7,8] and surface coating,[9] etc. Comparatively, blending presents a convenient approach for phase inversion process.

Hyperbranched polymers have received an increasing attention in recent years because of their unique structures and properties, compared with their linear analogues. The highly branched structure and a large number of terminal functional groups are two important features of hyperbranched polymers clearly distinguishing them from linear polymers.[10] As hyperbranched polymers can be obtained in one-pot synthesis from AB_m-type monomers, they are of great significance from the viewpoint of industrial applications.[11]

Hyperbranched polyglycerol (HPG), which has a stable, biocompatible polyether scaffold, high end group functionality as well as a highly branched architecture, was first synthesized by Frey and coworkers.[12–15] HPG is also highly hydrophilic due to the large amount of hydroxyl groups at the end of the HPG molecules. In our previous work,[16] HPG was used as a hydrophilic modifier for porous PVDF membrane. It was found that the HPG could improve the hydrophilicity of PVDF membrane effectively. However, it was observed that the HPG was prone to migrating out from the membrane matrix when the membrane was shaken in water at a relatively high temperature (60°C), indicating a not quite stable presence of HPG in the membrane matrix. Therefore, the hydrophilicity of the PVDF

membrane will decline in practical applications if the stability of the HPG is not enhanced.

In this study, to seek a stable presence of HPG in the resulting PVDF membrane, the HPG was added to the casting solution and consequently crosslinked using 4,4'-oxydiphthalic anhydride (ODPA) as the crosslinking agent. The effects of HPG content and crosslinking degree on membrane structures and properties were investigated. Specially, when shaking the membrane in water at a relatively high temperature, the dynamic migrating process of crosslinked HPG in the membrane matrix was simulated. The changes of the chemical compositions in the membrane bulk and the separation surface were measured by means of Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and elemental analysis. The hydrophilicity and fouling-resistance of the membrane surface were also investigated. To achieve a best membrane performance, poly(vinylpyrrolidone) (PVP) was used as an additive to tune the membrane structure.

EXPERIMENTAL

Materials

PVDF (FR-904) (M_n = 380,000) was obtained from Shanghai 3F new materials. 1,1,1-Tris(hydroxymethyl)propane and potassium methylate solution (MeOK) (3.7M in methanol) were purchased from Fluka and used as received. Glycidol and diglyme obtained from Aldrich were dried by 4A molecular sieve before use. Acetone, methanol, and N,N-dimethylacetamide (DMAc) are analytical grade. Tetrahydrofuran (THF) was dried by sodium before use. Acidic ion-exchange resin (732#) was supplied by ShangHai HuiZhu resin. PVP (K30) was purchased from ShangHai chemical reagent company. ODPA was purchased from Aldrich and used as received. Bovine serum albumin (BSA, Fraction V) was purchased from Aldrich, and the phosphate buffered saline (PBS, 0.01M, pH 7.4) was prepared by the addition of prepackaged buffer salts (Aldrich) to deionized water.

Synthesis and characterization of HPG

HPG (Fig. 1) was synthesized according to method reported in literatures.[12–15] The details of the HPG synthesis process has been given in our previous work.[16] The average molecular weight of HPG was determined by gel permeation chromatograph (WATERS-515, Waters) using THF as the solvent and polystyrenes as calibration standards. The hydroxyl values were determined by the following method: the product was dissolved in acetic anhydride (in pyridine) and refluxing for an hour, to assure a complete acetylation of the hydroxyl
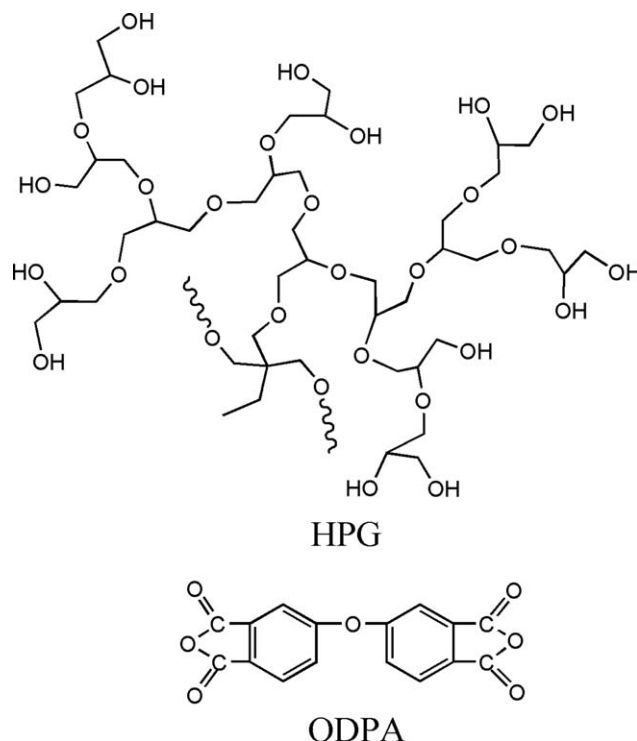

Figure 1 Molecular structures of HPG and ODPA.

groups. Then back titration was performed with a KOH solution (0.5M, in deionized water, standardized by potassium hydrogen tartrate, 99%, Acros) and the hydroxyl value was calculated. The synthesized HPG has an average molecular weight of 4832 with a narrow distribution of 1.48, and the hydroxyl value of the HPG is 305 mg KOH/g.

Preparation of membranes

Table I shows the sample ID of prepared PVDF membranes and their corresponding compositions in casting solutions. After stirring the mixture of PVDF/HPG/(PVP)/DMAc at 70°C for 24 h, a calculated amount of crosslinking agent (ODPA) was added to it and keep stirring for another 24 h at 70°C. After degassing under reduced pressure at 25°C for 30 min, the homogeneous casting solution was obtained. A typical phase inversion process was adopted to prepare PVDF membranes. The solution was cast on a glass plate, and then immediately immersed in a coagulation bath of deionized water and DMAc (50/50, w/w) mixture at 25°C. The solidified membranes were rinsed with deionized water for 48 h to remove solvents and then dried for 48 h at room temperature before characterization.

Characterization of membranes

The surface and cross-section (fractured in liquid nitrogen) morphologies of membranes were imaged

TABLE I
Compositions of Casting Solutions

Membrane ID	Casting solution composition (wt %)					Crosslinking degree (%)[a]
	PVDF	HPG	ODPA	PVP	DMAc	
M0	12.0	–	–	–	88.0	–
M-10h-20c	12.0	1.2	0.4	–	86.4	20
M-15h-20c	12.0	1.8	0.6	–	85.6	20
M-20h-20c	12.0	2.4	0.8	–	84.8	20
M-15h	12.0	1.8	–	–	86.2	–
M-15h-10c	12.0	1.8	0.3	–	85.9	10
M-15h-30c	12.0	1.8	0.9	–	85.3	30
M-15h-20c-pvp	12.0	1.8	0.6	2.0	83.6	20

[a] Calculated according to the mole ratio of anhydride/hydroxyl.

on a scanning electron microscopy (SEM) (FEI, USA) after sputter coated with gold. The surface compositions of membranes were characterized using attenuated total reflectance Fourier transform infrared spectroscopy (FTIR/ATR) (Vecter 22 FTIR, Bruker Optics, Switzerland) and XPS (PHI 5000c, Peking-Elmer instruments). The element content in membrane bulk was measured on an elemental analyzer (Vario EL III, Elementar). The hydrophilicity of the membrane top surface was characterized on the basis of water contact angle measurements (OCA20, Dataphysics, Germany) at 25°C. The porosity of membranes was determined by mercury porosimetry (Autopore IV9500, Micromeritics). The measurements of the flux were first carried out by loading the membranes (diameter: 60 mm) in test cell with water at a pressure of 0.15 MPa for 30 min, and then the membranes were subjected to pure water flux estimation at a transmembrane pressure of 0.1 MPa for 30 min. The pure water flux (J_w, L/(m^2 h)) is determined as: $J_w = \frac{Q}{A\Delta t}$, where Q, Δt, and A is the quantity of collected permeate, the testing time, and the membrane area respectively.[17] The BSA adsorption experimental procedure was as follows: A piece of crosslinked film (3.5 × 4.0 cm^2) was immersed in a solution of phosphate buffered BSA solution (10 mL, pH = 7.4) at 25 ± 0.5°C for 24 h and a shaking speed of 150 rpm to reach the absorption equilibrium. The amount of the adsorbed protein was determined by measuring the difference between the concentration of albumin in the solution before and after adsorption using UV–vis spectrometer (HP 8453, USA) via the absorbance at 280 nm.[18]

RESULTS AND DISCUSSION

Morphology studies

The SEM images of the separation surface and cross-section of membranes with different HPG content are shown in Figure 2. It can be seen that the pure PVDF membrane has a homogeneous separation surface with very few pores. When HPG is added, a separation surface with more porous structure is obtained. It can also be seen that the number of pores with larger diameter increases slightly with the increasing of HPG content. At the meantime, honeycomb-like structures are obtained in the membrane matrix, as can be seen from the cross-section images. The size of the honeycomb-like voids in the membrane matrix is larger than that in the pure PVDF membrane. Usually, when pure water is used as the coagulation bath, asymmetric large voids will appear in the cross-section. At the same time, as reported by Nunes and Sforqa,[4] and Hester and Mayes,[6] the presence of a hydrophilic polymer in the casting solution might be expected to increase the affinity of the casting solution and precipitant, enhancing solvent–nonsolvent exchange and creating the conditions for instantaneous demixing and associated microvoid formation. As large microvoid in the membrane substructure will impair the mechanical properties and make the membrane unsuitable for high-pressure applications,[19–21] a mixture of solvent (DMAc) and water (50/50, w/w) was used as coagulation bath in this work. According to Strathmann,[22] the presence of solvent in the coagulation bath decreases the activity of both the solvent in the casting solution and the water in the coagulation bath, enhancing the conditions for delayed demixing and suppressing the macrovoid formation, and consequently the honeycomb-like structure was obtained, which still showed a asymmetric characteristic.

The SEM images of the membranes with different HPG crosslinking degree, but the same content of HPG is shown in Figure 3. It can be seen that a lower HPG crosslinking degree results in a higher porosity at the separation surface. This is because the lower the crosslinking degree, the larger the amount of uncrosslinked HPG in the casting solutions. Consequently, the amount of uncrosslinked HPG acting as the pore forming agent increases during the immersion precipitation process, leading to a
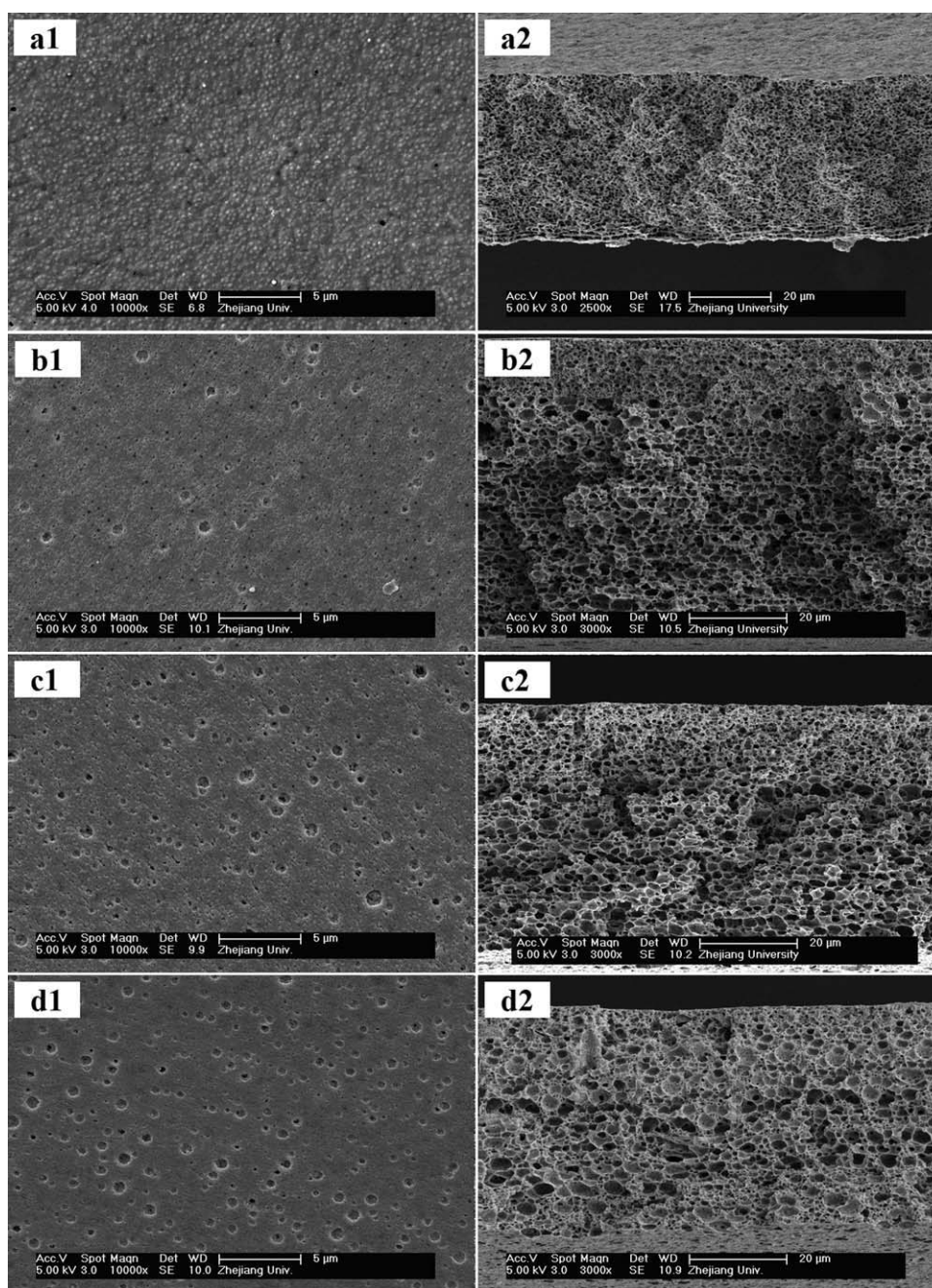
Figure 2 Separation surface (left) and cross-section (right) SEM micrographs of membranes: (a) M0, (b) M-10H-20c, (c) M-15H-20c, and (d) M-20H-20c. (The crosslinking degree is fixed at 20%).

higher porosity at the separation surface. In the meantime, the increase in crosslinking degree gives rise to the increase in viscosity of the casting solutions, which leads to a slight reduction in the size of the honeycomb-like voids, and therefore, the porosity in the membrane matrix decreases from 73.9 to 65.7% when the crosslinking degree increases from 0 to 30% (Table II).

To optimize the membrane structure, a small amount of PVP was used as an additive. By comparing the images in Figures 3(c) and 4, in which the membranes have the same HPG content and cross-

linking degree, it can be clearly seen that the addition of PVP results in a significant increase in the porosity of both the separation surface and the membrane bulk. The bulk porosities of these two membranes measured by mercury porosimetry are 68.5 and 76.4%, respectively (Table II).

Surface and bulk compositions of modified membranes

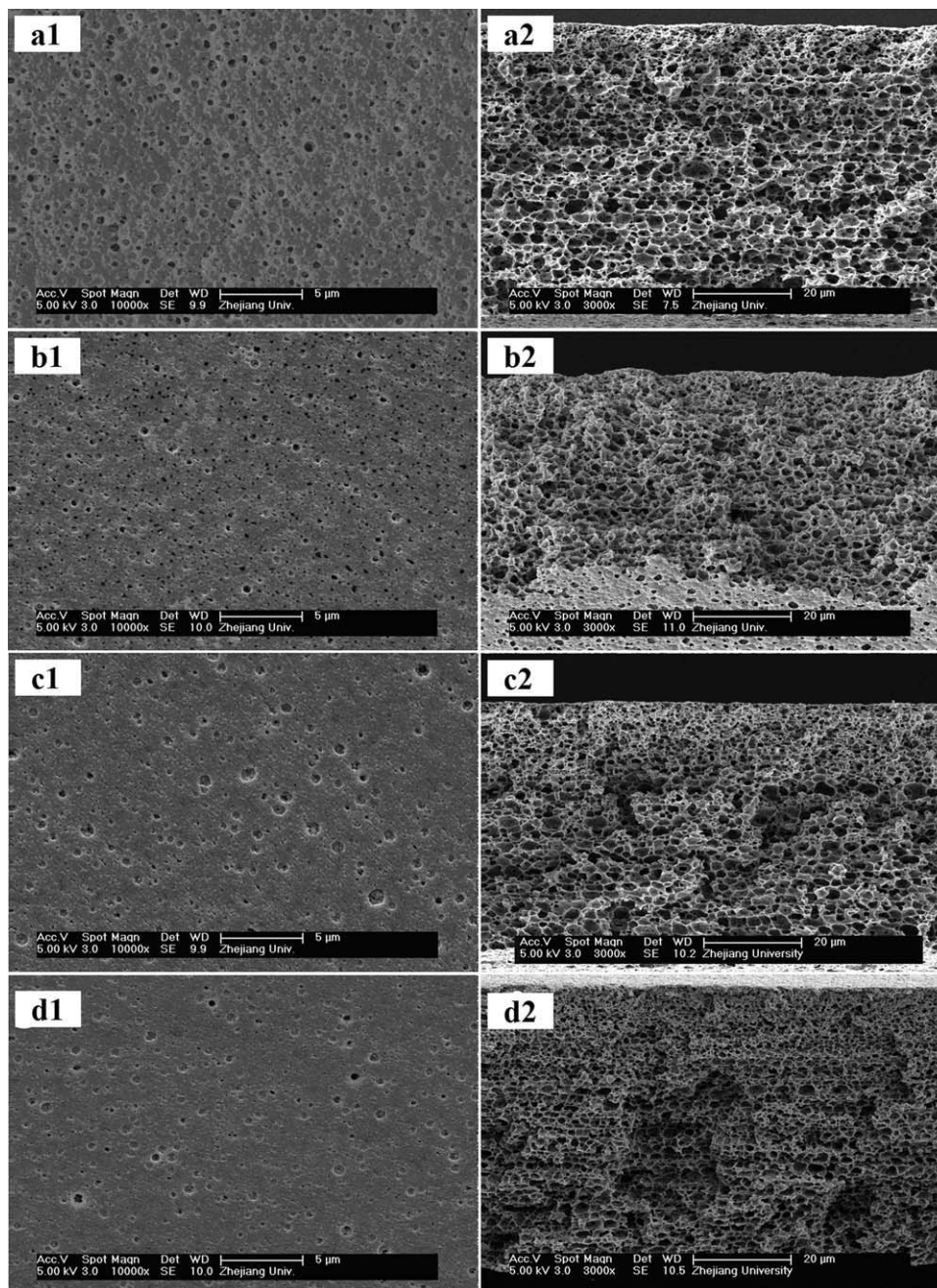Table III shows the variety of O/F atomic ratio in casting solution, membrane matrix, and at the

Figure 3 Separation surface (left) and cross-section (right) SEM micrographs of membranes: (a) M-15H, (b) M-15H-10c, (c) M-15H-20c, and (d) M-15H-30c. (The HPG/PVDF ratio is fixed at 15%).

separation surface. The O/F ratios in the membrane matrix and at the separation surface increase with the increasing of HPG content and crosslinking degree, but they are all smaller than those in the corresponding casting solutions. This phenomenon suggests that uncrosslinked HPG partially dissolves into the coagulation bath during the immersion precipitation process. However, the loss of HPG can be suppressed by increasing the crosslinking degree. As can be seen from Table III, the amount of HPG remaining in the membrane bulk of M-15h, in which

TABLE II
Porosity and Water Flux of Membranes

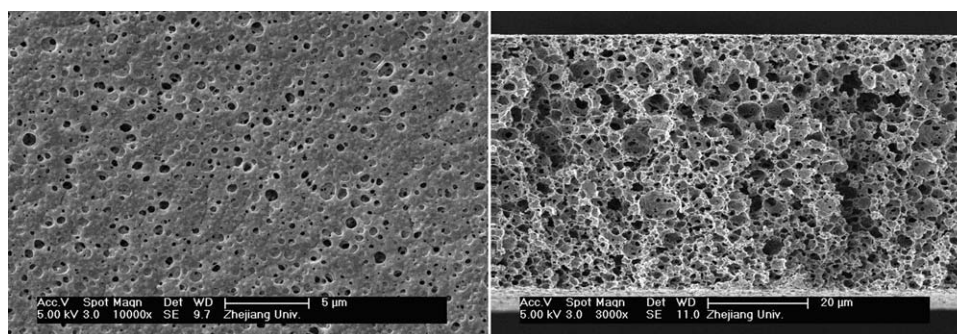| Membrane ID	Porosity (%)	J_w (0.1 MPa) (L/m^2 h)
M0	59.5	–
M-10h-20c	66.1	62.6
M-15h-20c	68.5	95.8
M-20h-20c	73.1	143.4
M-15h	73.9	275.8
M-15h-10c	70.2	174.7
M-15h-30c	65.7	73.9
M-15h-20c-pvp	76.4	461.8

Figure 4 Separation surface (left) and cross-section (right) SEM micrographs of M-15H-20c-pvp.

the HPG is not crosslinked, is only 48 mol %, whereas that of M-15h-30c, in which the HPG crosslinking degree is 30%, is as high as 85 mol %.

To investigate the stability of HPG in the membrane matrix, membranes with different HPG crosslinking degree were shaken in water at a relatively high temperature (60°C), and the changes of O/F ratio as a function of treatment time are shown in Figure 5. As for M-15h (a), in which the HPG is not crosslinked, the O/F ratio decreases quickly, and after 30 days of treatment, there is almost no HPG remaining, indicating an unstable presence of HPG in the membrane matrix. With the increasing crosslinking degree of HPG, the stability of HPG increases. For example, in the beginning of the treatment, there is only a slight decrease of O/F ratio for M-15h-30c which has a 30% crosslinking degree of HPG, and after that, the O/F ratio begins to level off, suggesting the stable existence of HPG in membrane matrix. These results indicate that crosslinking is an effective approach to keep the HPG from leaching out from the membrane matrix, and therefore, leading to a long-term modification of the membranes.

The effects of the treatment on the changes of the chemical compositions at the separation surface were also investigated. M-15h-20c was chosen as a sample membrane and shaken in water at 60°C for different time span. The changes of chemical compositions at the membrane separation surface measured by FTIR/ATR and XPS are given in Figures 6 and 7. In Figure 6, there are two overlapped absorption peaks around 1100 cm^{-1} attributed to the stretching vibrations of C—O bonds in —C—OH and C—O—C groups, respectively. The broad absorption centering at 3384 cm^{-1} is the typical stretching vibrations of hydroxyl groups in hydrogen-bond state. It can be clearly seen that the strength of the peak at 3384 cm^{-1} increases when the treatment time increases, suggesting the increase in surface coverage of HPG. In Figure 7, three major emission peaks can be observed at 292.4 eV for C(1s), 538.7 eV for O(1s), and 693.2 eV for F(1s), respectively. Intensity of O(1s) peak increases with the increase of treatment time. The O/F ratio calculated according to the area of O(1s) peak and F(1s) peak is 0.153 after 30 days of treatment, much higher than that of the membrane matrix (0.092), as shown in Figure 5(c).

From the results given in Figure 5–7, it can be inferred that, during the treatment time, two processes will probably take place. One is the dissolving of the uncrosslinked HPG into water, and the other is the migrating of the crosslinked HPG from membrane bulk to the membrane surface to minimize the interfacial energy between the membrane and

TABLE III
Comparison of O/F Atomic Ratio in Casting Solution, Membrane Matrix, and at the Separation Surfaces

Membrane ID	O/F ratio			
	Casting solution[a]	Membrane matrix[b]	HPG remaining degree (mol %)[c]	Membrane surface[d]
M-10h-20c	0.103	0.072	70	0.042
M-15h-20c	0.162	0.125	77	0.073
M-20h-20c	0.215	0.153	71	0.081
M-15h	0.122	0.059	48	0.031
M-15h-10c	0.143	0.083	58	0.052
M-15h-30c	0.171	0.146	85	0.087

[a] Calculated from the O/F ratio of (HPG + OPDA)/PVDF in casting solution.
[b] Elemental analysis.
[c] HPG remaining degree = (O/F)$_{\text{membrane matrix}}$/(O/F)$_{\text{casting solution}}$.
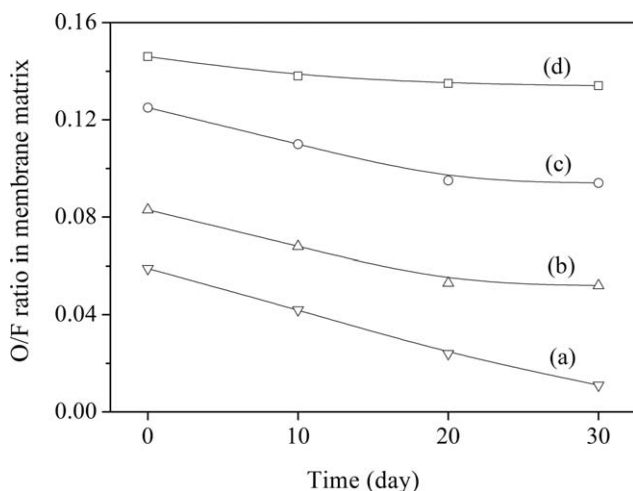[d] XPS.

Figure 5 Changes of O/F ratio in membrane matrix after shaken in water at 60°C for different time span: (a) M-15h, (b) M-15h-10c, (c) M-15h-20c, and (d) M-15h-30c.

water.[23] In the beginning, the main process is the dissolving of the uncrosslinked HPG into water. After all of the uncrosslinked HPG has been dissolving into water, the migration becomes the controlling process, leading to the enrichment of crosslinked HPG at the membrane surface.

Water contact angle analysis

The water contact angle of the membrane surface was also found to be influenced by the HPG content and the crosslinking degree. Figure 8 shows the changes of water contact angle of membranes with different HPG content after shaken in water for different period of time. The initial contact angle of
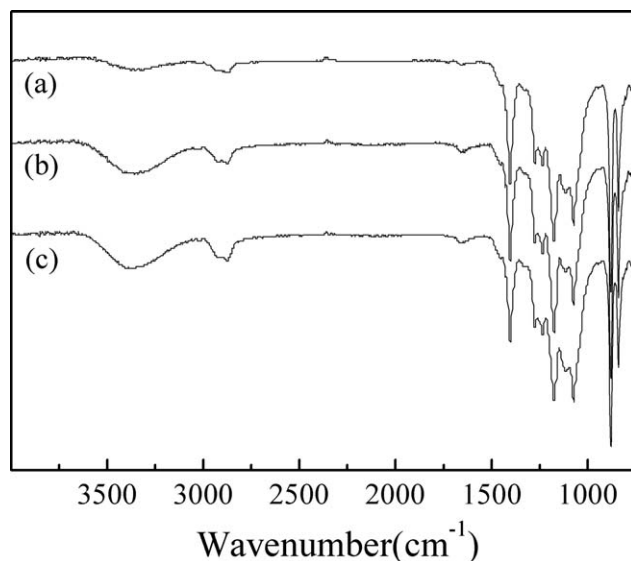

Figure 6 FTIR/ATR spectra of the M-15h-20c after shaken in water for (a) 0 day, (b) 20 days, and (c) 30 days at 60°C.
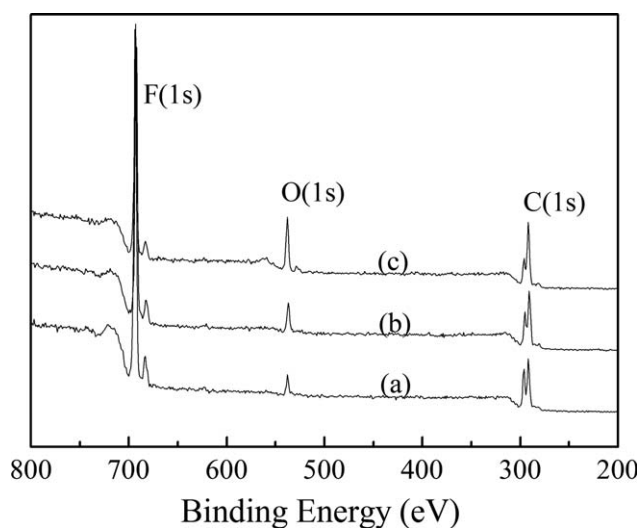

Figure 7 Changes of the chemical compositions of the separation surface of M-15h-20c after shaken in water for (a) 0 day, (b) 20 days, and (c) 30 days at 60°C.

membrane surfaces decreases from 88° to 53° with the increase of HPG content from 0 to 20 wt %. By shaking the modified membranes in water, the water contact angle of membrane surfaces increases slightly in the first 15 days and then decreases gradually with the increase of treatment time. This phenomenon reflects the changes of the chemical compositions of the separation surfaces. As XPS results have shown, at the later stage of the treatment process, there is a considerable surface enrichment of HPG, which makes the surface more hydrophilic, resulting in the decrease in water contact angle.
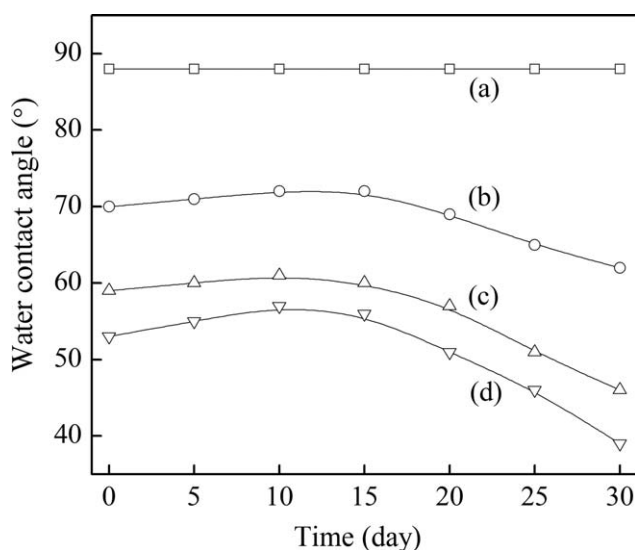

Figure 8 Changes of water contact angle of membranes with different HPG content after shaken in water for different time span at 60°C: (a) M0, (b) M-10H-20c, (c) M-15H-20c, and (d) M-20H-20c. (The crosslinking degree is fixed at 20%).
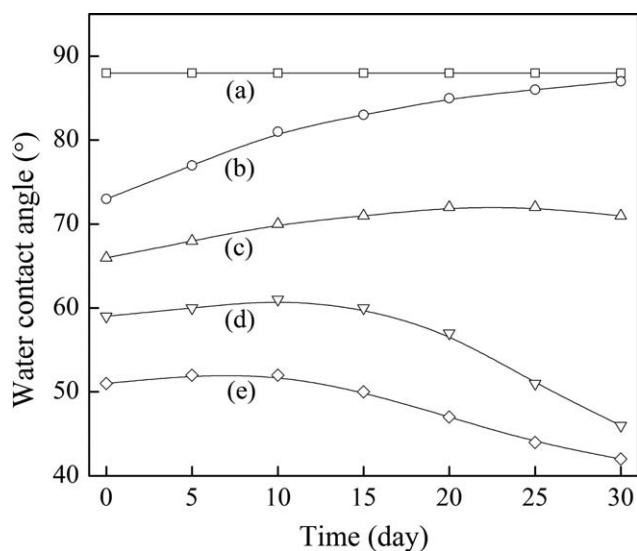
Figure 9 Changes of water contact angle of membranes with different crosslinking degree after shaken in water for different time span at 60°C: (a) M-15H, (b) M-15H-10c, (c) M-15H-20c, and (d) M-15H-30c. (The HPG/PVDF ratio is fixed at 15%).

Figure 9 shows the changes of water contact angle of membranes with different HPG crosslinking degree as a function of treatment time. The initial water contact angle decreases apparently with the increasing of HPG crosslinking degree. This should be ascribed to the increasing amount of the remaining HPG at the separation surfaces, as shown in Table III. However, the water contact angle of M-15h [Fig. 9(b)], in which the HPG was not crosslinked, increases quickly, and after 30 days of treatment, it is very close to that of the pure PVDF membrane. As the elemental analysis results have shown, HPG is unstable in the membrane matrix if it is not crosslinked and will dissolve out of the membrane matrix gradually, leading to the increase in water contact angle. The water contact angle of M-15h-10c [Fig. 9(c)], in which the HPG was crosslinked by 10%, also increases gradually within the treatment time, although the accretion is less than that of M-15h. When the crosslinking degree is increased to 20% or above [Figure 9(d,e)], the water contact angle only shows a slight increase in the beginning of the treatment, and then decreases gradually. These results are in good consistence with the XPS and elemental analysis.

Water flux of membranes

The water fluxes of all the membranes are listed in Table II. As the pure PVDF membrane has a relatively dense surface [Fig. 2(a1)], its water flux was not obtained within the measurement time. The addition of HPG results in a considerable improvement in water flux, and the water flux increases

with the increasing of HPG content, which is due to the increase in the pore size on membrane surface and the porosity of the membrane matrix, as shown in Figure 2. Also, it has been seen from Figure 3 that the increased crosslinking degree of HPG results in a decrease in the porosity of both the membrane surface and the membrane matrix, leading to the reduction in water flux. By comparing the membranes between M-15h-20c and M-15h-20c-pvp, in which the membranes have the same HPG content and crosslinking degree, it can be seen that the water flux increases significantly by the addition of PVP. This should be ascribed to the substantial improvement in the porosity of membrane surface and the membrane matrix, and the connectivity between the internal pores, induced by the addition of PVP. These results are of great significance because, on one hand, the HPG can act as a modifier to enhance the hydrophilicity, and on the other hand, by using PVP as an additive, the membrane structures can be controlled. Therefore, these two polymers can work together to achieve in an optimum membrane performance.

BSA adsorption

BSA is often used as a model protein to evaluate the antifouling capability of membranes.[24] In a batch system, BSA adsorption tests were carried out to investigate the membrane fouling potential caused by the membrane surface-protein interaction. Figure 10 compares the BSA adsorption of pure and modified membranes. The amount of protein adsorbed on M-15h-20c is much less than that on pure PVDF membrane (M_0) and this phenomenon becomes more apparent when it comes to a higher BSA concentration. Furthermore, the BSA absorbance
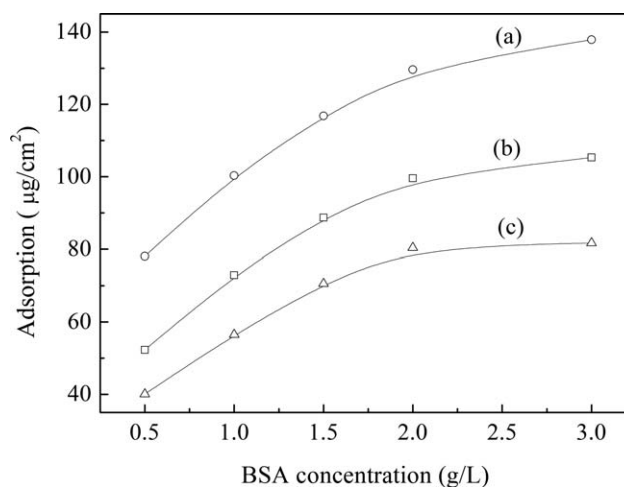

Figure 10 Amount of BSA adsorbed per unit area of (a) pure PVDF membrane, (b) M-15h-20c, and (c) M-15h-20c after shaken in water for 30 days.
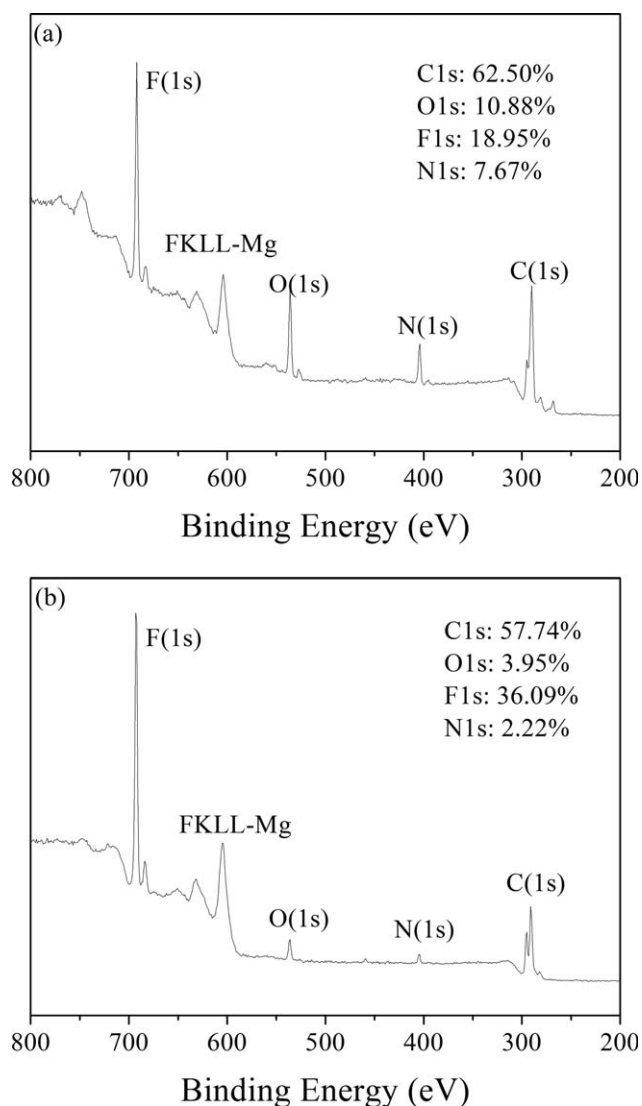
Figure 11 BSA adsorption on the membrane surfaces measured by XPS: (a) pure PVDF membrane and (b) M-15H-20c after shaken in water for 30 days.

decreases greatly after M-15h-20c was shaken in water for 30 days. As XPS and water contact angle analysis results have suggested, the crosslinked HPG enriches the membrane surface after shaken in water at a relatively high temperature (60°C). This enrichment at the membrane surface will weaken the membrane surface-protein interaction, which results in less protein absorbance on the membrane surfaces. The BSA adsorption behavior of the membranes was also observed by XPS (Fig. 11). From the change of the surface content of N atom, which belongs to BSA, it can be clearly seen that the antifouling ability of the modified membrane is improved remarkably.

CONCLUSIONS

PVDF membranes with growing hydrophilicity were fabricated by phase inversion process. HPG was added to the casting solution and consequently cross-linked with ODPA for a stable presence of HPG in the resulting membranes and improved membrane performance. Higher porosity at the separation surface and in the membrane matrix was obtained when increasing the HPG content, which led to higher water flux. However, a higher HPG crosslinking degree resulted in a decrease in the porosity of both the surface and the bulk, leading to the reduction in water flux. On the other hand, the water flux can be considerably improved by the addition of a small amount of PVP. XPS and elemental analysis results indicated that excellent HPG stability in the membrane matrix could be achieved by crosslinking in the casting solutions, and it was found that there was a remarkable enrichment of the crosslinked HPG at the separation surface after the membrane was shaken in water at 60°C, resulting in a decrease in water contact angle and improved fouling-resistance.

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