Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.988659

57 (2016) 3405–3413
February

Taylor & Francis
Taylor & Francis Group

Preparation and characterization of polyurethane (PU)/polyvinylidene fluoride (PVDF) blending membrane

Hao Dong[a,b], Kaijun Xiao[a,*], Xu Tang[a], Zhihui Zhang[a], Jiali Dai[a], Ranran Long[a], Wei Liao[a]

[a]*College of Light Industry and Food Sciences, South China University of Technology, 381 Wushan Road, Guangzhou 510640, P.R. China, Tel. +86 15013025984; email: 516410953@163.com (H. Dong), Tel./Fax: +86 20 87113843; email: fekjxiao@scut.edu.cn (K. Xiao), Tel. +86 20 87113843; email: 604339611@qq.com (X. Tang), Tel. +86 13710146130; email: 422029109@qq.com (Z. Zhang), Tel. +86 20 87113843; emails: 814031102@qq.com (J. Dai), 570323222@qq.com (R. Long), 314940253@qq.com (W. liao)*
[b]*Guangzhou Quality Supervision and Testing Institute, Guangzhou 510110, China*

Received 24 June 2014; Accepted 9 November 2014

ABSTRACT

In order to improve the hydrophilicity and mechanical properties of polyvinylidene fluoride (PVDF) membrane, polyurethane (PU) was blended into PVDF casting solution and then PU/PVDF blending membrane was prepared via the method of thermally induced phase separation (TIPS). The properties and surface structure of the blending membrane were characterized by means of contact angle test, mechanical properties test, Fourier transform infrared spectroscopy (FTIR), atomic force microscope (AFM), and differential scanning calorimetry (DSC). The results showed that the contact angle of PVDF membrane was decreased from 85.71˚ of pure membrane to 66.46˚of PU/PVDF blending membrane (PU of 2 wt.%), indicating that the hydrophilicity of blending membrane was significantly improved with the addition of PU. FTIR tests showed that the C=O stretching vibration absorption peak in aldehyde group (hydrophilic group) of PU/PVDF blending membrane was stronger than that of pure PVDF membrane, which can explain the increase in hydrophilicity of blending membrane. Moreover, mechanical properties test indicated that the mechanical strength of PU/PVDF blending membrane was increased remarkably when compared with that of pure PVDF membrane. The AFM results showed that the PU/PVDF blending membrane had lower roughness, manifesting its improved anti-fouling properties. In addition, DSC results indicated that the crystallinity of PVDF polymer matrix decreased with the introduction of PU.

Keywords: PVDF; PU; TIPS; Blending membrane; Hydrophilicity; Surface roughness

1. Introduction

Polyvinylidene fluoride (PVDF) is one of the most attractive polymer materials in membrane industry, especially in water treatment industry, due to its excellent stability and membrane-forming properties [1–3], therefore, it is widely used in the manufacturing of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and pervaporation (PV) membranes. However, due to the hydrophobic

---

*Corresponding author.

nature of PVDF, membranes fabricated with PVDF polymer have a high fouling tendency and declined permeability when they are exposed to protein-containing solutions, which can lead to a sharp drop of membrane's pure water flux and has become a severe drawback for their applications in food industry and water treatment [4–7]. In order to improve the hydrophilicity of PVDF membranes, several strategies, such as physical blending, chemical grafting, and surface modification, have therefore been investigated [8–10].

Recent studies on hydrophilic modification of PVDF mainly focused on blending hydrophilic organic materials as it has the advantage of easy preparation using phase inversion. Several hydrophilic organic materials have reported to modify PVDF, and some researchers have found that they can increase the water permeability of PVDF membranes with uniform pore size and pore distribution, which are mainly because of the increase in pore density as well as in the hydrophilicity of the membrane surface and inside the pores. But, the addition of organic hydrophilic materials usually reduces the membrane strength [11–15], making PVDF membranes easily to be damaged.

PU is a kind of hydrophilic high-molecular polymer that is formed by the reaction of the isocyanate and polyester or polyether polyol under certain conditions. From the point of molecular structure, PU can be considered as a kind of block polymer. As there are a large number of polar groups, PU emerges a great quantity of hydrogen bonds intramolecularly and intermolecularly, and forms a kind of three-dimensional reticular structure by physical cross-linking, resulting in several advantages of PU, such as high strength, anti-abrasion, and excellent mechanical properties [16,17]. In the meantime, plenty of hydrogen bonds in PU can also make it an extraordinary modification material in the preparation of PVDF membranes [18,19]. Zhou et al. [20] prepared a novel thermal-sensitive polyurethane (TSPU)/SiO_2 nanohybrid membrane via *in situ* nanohybrid method in wet phase inversion process, and results of AFM and SEM analysis showed that the mean size and the distribution of nanoSiO_2 particles in the TSPU matrix is relied on the SiO_2 content, FTIR study indicates that two chemical bonds of Si–C and Si–O–C occur between the organic and the inorganic phase. Using PU to replace other hydrophilic organic materials in PVDF membranes, not only keeps the advantage of hydrophilicity property, but also enhances the strength of the membrane.

Thermally induced phase separation (TIPS) is a kind of method for preparation of polymer microporous membrane that uses phase separation way by controlling temperature [21,22]. In this work, the pure PVDF membrane and PU/PVDF blending membrane were prepared via the method of TIPS, the effects of PU on the pure water flux, hydrophilicity, and mechanical properties were discussed, which can provide theoretical basis and technical support for the preparation of PU/PVDF organic blending membrane.

2. Materials and methods

2.1. Materials and equipment

N,*N*-dimethylacetamide (DMAc, purity >99%) and dimethyl phthalate (DMP, purity >99%) were obtained from Fuyu Fine Chemical Co. Ltd (Tianjin, China). PVDF (FR904) was purchased from New Materials Co. Ltd (Shanghai, China). Bovine serum albumin (BSA, $M_w = 67{,}000$) was provided from Bio Life Science & Technology Co. Ltd (Shanghai, China). PU was obtained from Saideke Business Corporation (Guangzhou, China). A mixture of distilled water and ethanol was used as the nonsolvents for the membrane precipitation.

Vector 33 Fourier transform infrared spectrometer from Bruker Company (Germany) was used for FTIR analysis. AGS-10 KNI universal electronic tensile tester from Jin Island Company (Japan) is used for the mechanical properties test. Contact angle test of membranes by OCA15 surface contact angle meter from Dataphysics Company (Germany). DSC Q200 from TA Instrument Company (American) was used to test the crystalline of the membrane and Nanoscope IIIa atomic force microscope was obtained from Veeco Metrology Company (American) to test the surface roughness of membranes.

2.2. Preparation of PU/PVDF blending membrane

First of all, PVDF was dissolved into DMAc and DMP mixing solvent, then, the above mixture was stirred constantly for 4 h at 180°C to obtain homogeneous casting solution. The solution was still for 24 h to remove air bubbles and membrane was prepared by a flat membrane casting equipment (150-J, Tianjin, China). After exposing it in air for 15 s, the membrane prepared on glass was immediately immersed into the deionized water for 5–7 d and the PU/PVDF blending membrane was obtained. The process technology of PU/PVDF blending membrane is shown in Fig. 1. The preparation of pure PVDF membrane can refer to our previous researches [23–25].

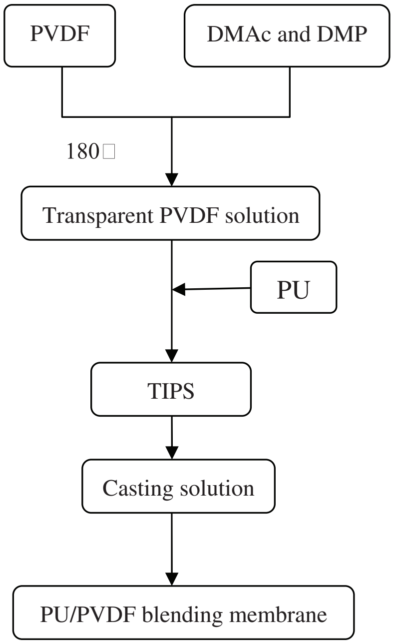

Fig. 1. Technological process of PU/PVDF blending membrane.

2.3. Characterization of PU/PVDF blending membrane

2.3.1. Pure water flux

The flux, the basic permeation property of membranes, was tested in a self-made UF unit (effective area = 50.3 cm^2) fed with pure water at 0.1 MPa. The flux at 25°C were calculated by the following equation:

$$J = V/(St) \qquad (1)$$

where V is the volume of permeate, S is the membrane area, and t is the operation time.

2.3.2. The rejection rate

The membrane rejection rate was tested in the same unit fed with BSA (20 mmol/L) at 0.1 MPa for 15–30 min. The BSA concentration in permeation solution and bulk solution were tested by a spectrophotometer. The rejection (%) was obtained by:

$$R = (1 - C_P/C_F) \times 100\% \qquad (2)$$

where C_P and C_F represent the BSA concentrations in permeation solution and bulk solution, respectively.

2.3.3. The mechanical properties

The tensile strength and elongation at break of the membranes were determined with a universal electronic strength measurement instrument. The measurements were carried out at room temperature and the stretch rate was 20 mm/min.

2.3.4. The static contact angle

The contact angles between water and the membrane surfaces were measured using a contact angle measurement apparatus according to the drop method. The smooth and clean parts of the membrane were chosen to measure the contact angles. The mean values were taken as the results after the contact angles measured four times on different parts of the membranes.

2.3.5. FTIR characterization

FTIR analyzer was employed to probe the chemical composition of prepared membranes. Under 50°C, the PVDF, PU powder, pure PVDF membrane, and the PU/PVDF blending membrane were vacuum-dried for 3–4 h, then the samples were analyzed by transmission beam method.

2.3.6. AFM analysis

The surface roughness of membrane indicates the difference of surface morphology, which has a significant effect on the membrane's physical and chemical properties. The membranes with bigger surface roughness have higher permeability and are easy to be fouled. In this study, the surface roughness was tested by AFM [26,27].

2.3.7. DSC test

The melting point of PU/PVDF blending membrane was tested using a DSC analyzer to analyze the effect of hybridization on the properties of the prepared membranes. The measurements were carried out at the condition of N_2 with a speed of 10°C/min starting from −50°C, and the flow velocity of gas was 25 mL/min.

2.4. Statistical analysis

Data were analyzed using SPSS (SPSS Inc., Chicago, IL, USA) and presented as mean ± SD with triplicates. Significance was determined at $p < 0.01$ by analysis of variance (ANOVA) followed by Duncan's least significant test.

3. Results and discussion

3.1. Effects of PU form on the properties of PU/PVDF blending membrane

The PU molecule contains a large number of hydrogen bonds, so PU can be added into the PVDF casting solution to improve the hydrophilicity of PVDF membrane. In this paper, the effects of PU forms on the pure water flux, the BSA rejection rate, and mechanical properties of blending membranes were studied. Under the condition of the volume ratio of DMAc and DMP at 1:1, the thermally induced phase temperature of 180–210℃, PVDF contents of 18% and PU contents of 2%, the properties of blending membrane with different PU forms were presented in Table 1. From Table 1, we can see that the pure water flux and the BSA rejection rate of blending membrane with PU were higher than those of pure PVDF membrane, especially the blending membrane with A and B addition of PU, respectively, increasing from 283.8 L/m^2 h and 68.2% to 492.5 L/m^2 h and 96.8%, with the amplifications of 73.5 and 41.9%, respectively.

3.2. Effects of PVDF contents on the properties of PU/PVDF blending membrane

The polymer concentration affects the structure and performance of the membrane. The effect of PVDF contents on the pure water flux, the BSA rejection rate, and porosity of membrane were studied under the condition of the volume ratio of DMAc and DMP at 1:1, the thermally induced phase temperature at 180–210℃ and the PU contents of 2% (A, B components were added to the PVDF casting solution, respectively). The changes of pure water flux and the BSA rejection rate of the membrane with different PVDF contents are shown in Fig. 2. Fig. 2 shows that the pure water flux of membranes declined from 867 L/m^2 h with 14% PVDF to 365 L/m^2 h with 22% PVDF, while the rejection rate of membranes increased with the increase in PVDF contents.

3.3. Effects of DMP ratio in mixed solvent on the properties of PU/PVDF blending membrane

The effect of the ratio of DMP in solvent on the permeability of blending membrane were studied under the condition of the thermally induced phase temperature at 180–210℃, the PU contents of 2% and PVDF contents of 18%, and the results were shown in Fig. 3. As shown in Fig. 3, with the increase in DMP in solvents, the pure water flux of blending membrane decreases, while the BSA rejection rate increases accordingly. This is because when the DMP ratio (the proportion of solvent DMP in mixed solvent) in solvents increased, the villous porous structure replaced the closed pore structure on the surface of hybrid membrane, which influences the permeability of blending membrane. In this work, the DMP ratio of 50% was chosen.

3.4. Effects of PU contents on the properties of PU/PVDF blending membrane

Taking DMAc and DMP as diluents with the ratio at 1:1, maintaining the thermal transformation temperature at 180–210℃ and PVDF contents at 18%, the effect of different PU contents on the properties of the blending membrane were studied. Fig. 4 showed the change trend of pure water flux and BSA rejection rate of blending membrane with different PU contents. As Fig. 4 shows, with the PU contents increasing constantly, the pure water flux of the blending membranes increases first and then decreases, while

Table 1
Effects of the PU form on the properties of blending membrane*

PU form	The pure water flux (L/h m)	BSA rejection rate (%)	Tensile strength (MPa)	Elongation at break (%)
Pure PVDF membrane	283.8 ± 10.6^a	68.2 ± 1.2^a	3.47 ± 0.23^a	5.25 ± 0.15^a
Solidified PU	436.4 ± 8.5^b	92.3 ± 1.6^b	3.78 ± 0.41^b	5.92 ± 0.21^b
Half-solidified PU	467.3 ± 10.6^c	96.4 ± 1.2^c	3.82 ± 0.44^b	5.96 ± 0.23^b
Components A and B	492.5 ± 7.2^d	96.8 ± 1.5^c	6.12 ± 0.33^c	8.28 ± 0.08^c

*The data are expressed as means ± SD with triplicates. Values within the same column with different letters are significantly different at $p < 0.01$.

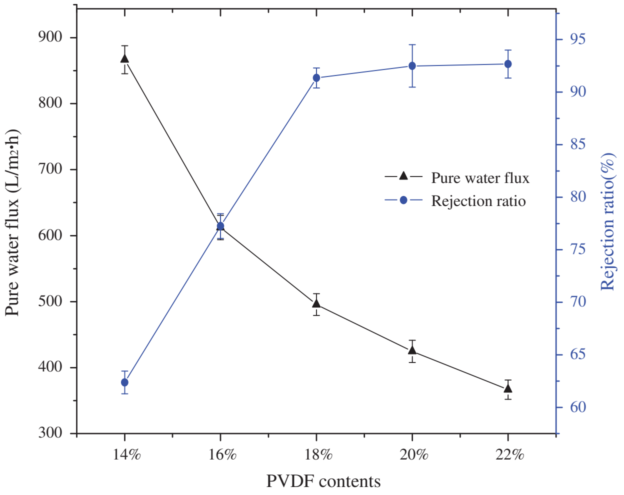

Fig. 2. Effect of the PVDF contents on the permeability of blending membrane.

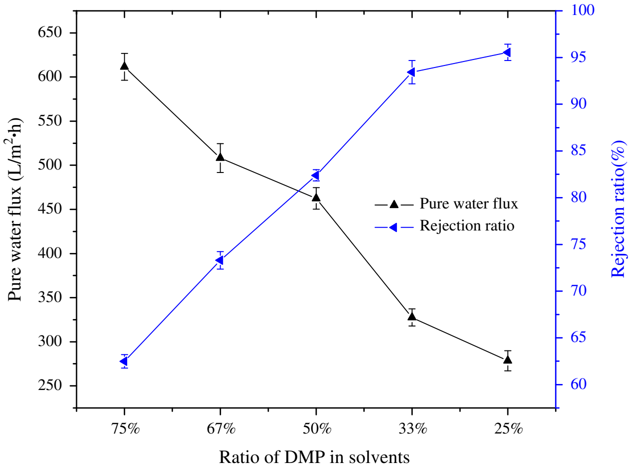

Fig. 3. Effect of the ratio of DMP in solvents on the permeability of blending membrane.

rejection rate first reduces then increased, and both achieves the best values when the PU content was 2%. This is because when the hydrophilic PU was added to the casting solution, the pure water flux of the blending membrane increases due to the water affinity of the PU, but when the PU content increases to a certain extent, the viscosity of PU highlights, which makes the high viscosity of the casting solution and results to the difficulty of forming membrane, that is why the porosity of blending membrane decreased (Fig. 5), and may lead to the decrease of the pure water flux of blending membrane. Above all, in this work, we chose the PU content of 2–3%.

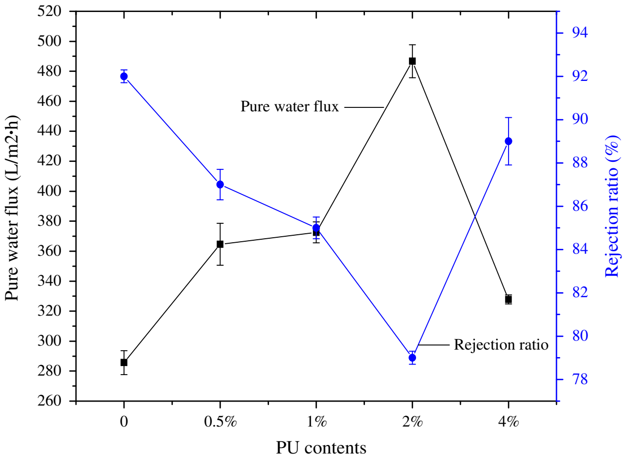

Fig. 4. Effect of PU contents on the permeability of blending membrane.

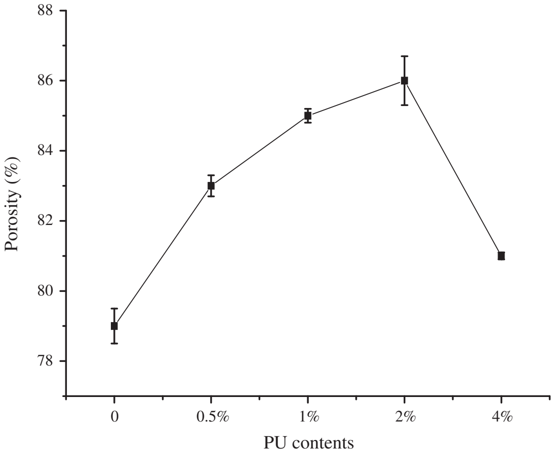

Fig. 5. Effect of PU contents on the porosity of blending membrane.

3.5. Hydrophilicity of PU/PVDF blending membrane

The contact angle is an important property that can characterize the hydrophilicity of membrane materials. In a general way, the hydrophilicity of membranes is better with smaller contact angles. The contact angles between water and the membrane surfaces were measured using a contact angle measurement apparatus according to the drop method. The results were shown in Table 2. From Table 2, we can see that the contact angle and the average pore size of membrane with PU was significantly lower than that without PU, and with the increase in PU contents, the contact angle and the average pore size of blending membranes decreases continuously, that is to say, the hydrophilicity of membranes was increased gradually,

Table 2
Effects of PU contents on the hydrophilicity of PU/PVDF blending membrane*

PU contents (%)	Contact angle (˚)	Average pore size (μm)
0	85.71 ± 2.55^a	0.110 ± 0.006^a
0.5	73.42 ± 1.87^b	0.069 ± 0.003^b
1	71.35 ± 2.20^c	0.053 ± 0.005^c
2	66.46 ± 2.62^d	0.048 ± 0.008^d
4	66.20 ± 3.42^d	0.046 ± 0.007^d

*The data are expressed as means ± SD with triplicates. Values within the same column with different letters are significantly different at $p < 0.01$.

we can come to the conclusion that the introduction of PU indeed improved the hydrophilicity of blending membranes. But when the PU contents exceed to 2%, the contact angle of blending membranes changed unobviously.

3.6. Mechanical properties of PU/PVDF blending membrane

The mechanical properties of blending membranes with different PU contents were presented in Table 3. From Table 3, it is apparently seen that the tensile strength and elongation at break of blending membranes with PU were higher than those without PU, and with the increase in PU contents, the tensile strength of blending membranes showed a trend of decrease after the first increase, while the elongation at break increased continually. These behaviors indicate that adding an appropriate amount of PU to a PVDF solution can improve the membrane's mechanical properties.

3.7. FTIR analyses

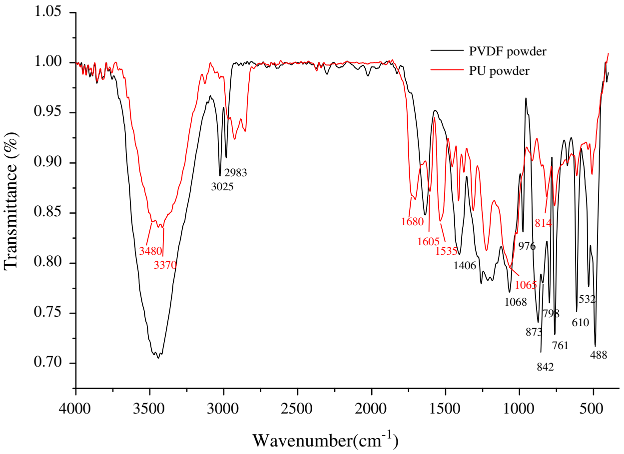

Fig. 6. FTIR spectra of PVDF and PU powder.

The FTIR and FTIR of the sample powder and membranes were shown in Figs. 6 and 7. The black lines in Fig. 6 indicated the infrared spectra of the PVDF powder. The absorption peaks at 488, 610, 761, and 976 cm^{-1} are the characteristic peaks of α-crystal shape. The absorption peaks at 532 and 842 cm^{-1} are the characteristic peaks of β-crystal shape. The red lines in Fig. 7 indicated the infrared spectra of the PU powder. The intense absorption peak at 1,680 cm^{-1} indicated the N–N stretching vibration, and the band at 1,680 cm^{-1} was the C=O stretching vibration. The bands at 1,605, 1,535, and 814 cm^{-1} were assigned to the N–H deformation vibration. In addition, the band occurring at 1,065 cm^{-1} was the

Table 3
Effects of PU on the mechanical properties of PU/PVDF blending membrane*

PU contents (%)	Tensile strength (N)	Elongation at break (%)
0	3.47 ± 0.23^a	5.28 ± 0.27^a
0.5	4.21 ± 0.35^b	5.95 ± 0.25^b
1	5.28 ± 0.28^c	6.37 ± 0.14^c
2	6.36 ± 0.16^d	8.48 ± 0.20^d
4	5.10 ± 0.22^e	6.36 ± 0.11^c

*The data are expressed as means ± SD with triplicates. Values within the same column with different letters are significantly different at $p < 0.01$.

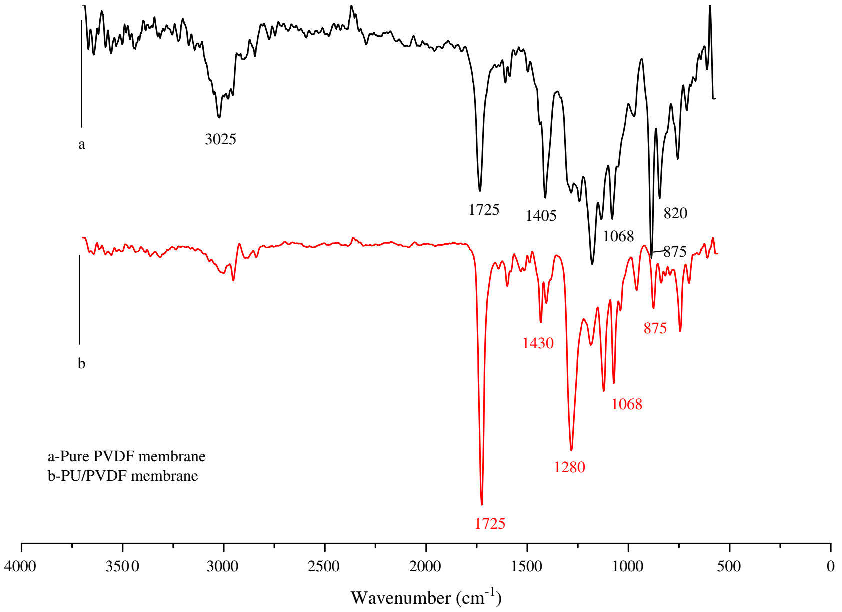

Fig. 7. ATR-IR spectra of PVDF and PU/PVDF blending membranes.

C–H stretching vibration. Line (a) and (b) in Fig. 7 showed the infrared spectrogram of pure PVDF membrane and PU/PVDF blending membrane, respectively. It can be obtained from the line (a) that most absorption peaks in PVDF powder were reserved in the pure PVDF membrane, such as 1,068, 1,405 and 3,025 cm^{-1}, indicating that the preparation technology of PVDF membrane has no impact to the chemical bond in the molecule of PVDF. It also has no obvious change to the chemical structure of PU/PVDF blending membrane after adding PU, with the phenomenon that the absorption peaks at 875, 1,068, and 1,430 cm^{-1} are reserved. However, a new absorption peak at 1,725 cm^{-1} occurred and its absorption strength is stronger than pure PVDF membrane. This may be a cause of the C=O stretching vibration absorption peak in aldehyde group. It showed that the number of aldehyde was increased markedly with the introduction of aldehyde group and the introduction of PU. Aldehyde is the hydrophilic group, which explains why the hydrophilic of PU/PVDF blending membrane is stronger than pure PVDF membrane. In addition, the new absorption peak at 1,280 cm^{-1} of blending membrane demonstrates that the mechanical properties of blending membrane have a certain improvement after the combination with two phases by doping PU.

3.8. *AFM analyses*

Fig. 8 was the AFM images of pure PVDF membrane (A) and PU/PVDF blending membrane (B). It is obvious that the surface roughness of blending membrane with PU were decreased, from 228 nm of the pure PVDF membrane reduced to 47 nm of PU/PVDF blending membrane, that is to say, the anti-fouling property of PU/PVDF blending membrane is better than that of pure PVDF membrane. In the mean time, it is also explained why the hydrophilicity and pure water flux of PU/PVDF blending membrane were better than those of pure PVDF membrane.

3.9. *DSC characterization*

The DSC curves for the pure PVDF membrane and blending membrane with PU contents of 2% were revealed in Fig. 9. Compared with the pure PVDF membrane, the melting point of PU/PVDF blending membrane slightly decreased and the molten enthalpy dropped from 50.03 to 48.32 J/g, which indicates the crystallinity decrease in PU/PVDF blending membrane. This is because the introduction of PU weakened the strong interaction of PVDF molecular chain and reduced the degree of order of PVDF, resulting in the decrease in crystallinity.

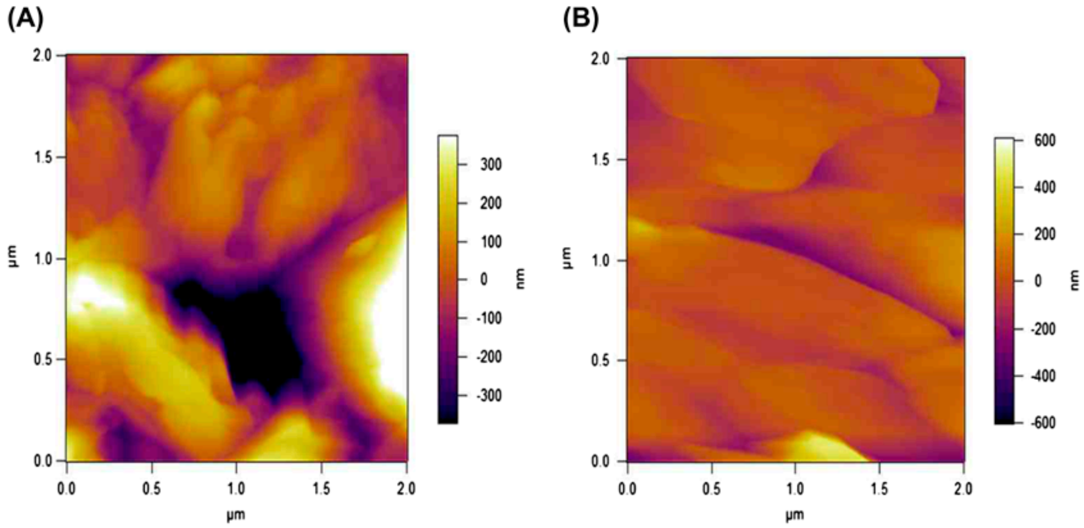

Fig. 8. AFM images of prepared membranes. (A) Pure PVDF membrane; (B) PU/PVDF blending membrane.

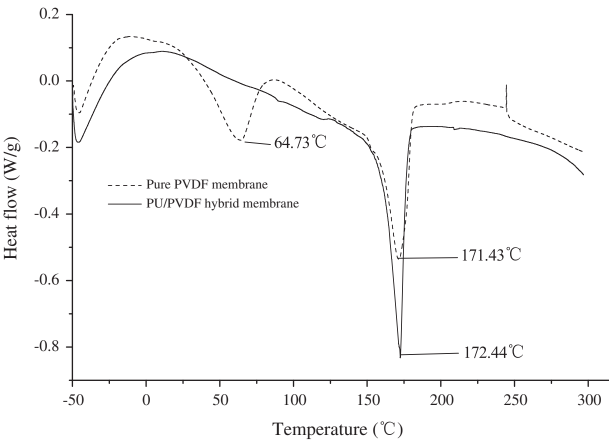

Fig. 9. DSC curves of pure PVDF membrane and PU/PVDF blending membrane.

4. Conclusions

(1) The pure PVDF membrane and PU/PVDF hybrid membrane were prepared via the TIPS method. The optimized processing technology of hybrid membrane were obtained by single factor experiment, and the optimized processing technology were as follows, adding A and B addition of PU, respectively, 16–18% PVDF contents, the ratio of DMP in solvents was 50 and 2% PU contents.

(2) The hydrophilicity property of blending membrane was better than those of pure PVDF membrane. With the increase in PU contents, the hydrophilicity of membranes was increased gradually, but when the PU contents exceed to 2%, the hydrophilicity of hybrid membranes changed unobviously. Furthermore, the introduction of PU can strengthen the mechanical properties of blending membrane in a certain extent. In addition, FIIR showed that the hydrophilic aldehyde group was formed with the introduction of PU, which implied the interaction between PVDF and PU.

(3) AFM and DSC tests indicated that the surface roughness and crystalline of blending membrane were decreased.

Acknowledgments

The authors gratefully acknowledge the funding provided by the National Natural Science Foundation of China (21176092), National "Twelfth Five-Year" Plan for Science & Technology Support program of China (2011BAE16B04) and the university-industry cooperation program of Guangdong (2010B090400512).

References

[1] L. Sauguet, C. Boyer, B. Ameduri, B. Boutevin, Synthesis and characterization of poly(vinylidene fluoride)-g-poly (styrene) graft polymers obtained by atom transfer radical polymerization of styrene, Macromolecules 39 (2006) 9087–9101.

[2] X.L. Li, K.J. Xiao, S.Y. Guo, Preparation and characterization of hybrid PVDF/Al_2O_3 membrane, J. S. Chin. Univ. Technol. (Nat. Sci. Ed.) 38(7) (2010) 112–116.

[3] B. Deng, M. Yu, X. Yang, B. Zhang, L. Li, L. Xie, J. Li, X. Lu, Antifouling microfiltration membranes prepared from acrylic acid or methacrylic acid grafted poly(vinylidene fluoride) powder synthesized via preirradiation induced graft polymerization, J. Membr. Sci. 350 (2010) 252–258.

[4] Y.C. Chiang, Y. Chang, A. Higuchi, W.Y. Chen, R.C. Ruaan, Sulfobetaine-grafted poly(vinylidene fluoride) ultrafiltration membranes exhibit excellent antifouling property, J. Membr. Sci. 339 (2009) 151–159.

[5] E. Yuliwati, A.F. Ismail, T. Matsuura, M.A. Kassim, M.S. Abdullah, Effect of modified PVDF hollow fiber submerged ultrafiltration membrane for refinery wastewater treatment, Desalination 283 (2011) 214–220.

[6] M. Khayet, T. Matsuura, Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation, Ind. Eng. Chem. Res. 40 (2001) 5710–5718.

[7] Y. Wei, H.Q. Chu, B.Z. Dong, X. Li, S.J. Xia, Z.M. Qiang, Effect of TiO_2 nanowire addition on PVDF ultrafiltration membrane performance, Desalination 272 (2011) 90–97.

[8] S.S. Madaeni, S. Zinadini, V. Vatanpour, A new approach to improve antifouling property of PVDF membrane using *in situ* polymerization of PAA functionalized TiO_2 nanoparticles, J. Membr. Sci. 380 (2011) 155–162.

[9] A. Sotto, A. Boromand, R.X. Zhang, P. Luis, J.M. Arsuaga, J. Kim, B.V. Bruggen, Effect of nanoparticle aggregation at low concentrations of TiO_2 on the hydrophilicity, morphology, and fouling resistance of PES–TiO_2 membranes, J. Colloid Interface Sci. 363 (2011) 540–550.

[10] B. Jung, Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration, J. Membr. Sci. 229 (2004) 129–136.

[11] J. Marchese, M. Ponce, N.A. Ochoa, P. Prádanos, L. Palacio, A. Hernández, Fouling behaviour of polyethersulfone UF membranes made with different PVP, J. Membr. Sci. 211 (2003) 1–11.

[12] A.L. Ahmad, M.A. Majid, B.S. Ooi, Functionalized PSF/SiO_2 nanocomposite membrane for oil-in-water emulsion separation, Desalination 268 (2011) 266–269.

[13] H. Dong, K.J. Xiao, W.S. Liu, S.Y. Guo, Enhancement of ultrafiltration with a γ-Al_2O_3 ceramic membrane by an electrical field, Desalin. Water Treat. 49 (2012) 234–239.

[14] Z.H. Meng, H.L. Liu, Y. Liu, J. Zhang, S.L. Yu, F.Y. Cui, N.Q. Ren, J. Ma, Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized in PVDF·Al_2O_3 membrane for dechlorination of monochloroacetic acid, J. Membr. Sci. 372 (2011) 165–171.

[15] M. Zhang, Q.T. Nguyen, Z. Ping, Hydrophilic modification of poly(vinylidene fluoride) microporous membrane, J. Membr. Sci. 327(1–2) (2009) 78–86.

[16] X.S. Wei, The thermostability and its improvement of polyurethane elastomers, Chinese J. Chem. Propellants Polym. Mater. 1(6) (2003) 13–15.

[17] H.F. Tian, Y.X. Wang, L. Zhang, C.Y. Quan, X.Z. Zhang, Improved flexibility and water resistance of soy protein thermoplastics containing waterborne polyurethane, Ind. Crops Prod. 32 (2010) 13–20.

[18] J.R. Meng, G.Z. Liang, L. Zhao, H.Y. Qin, The development of casting polyurethane elastomer, Chinese J. of Chin. Elastomerics 11(4) (2001) 39–43.

[19] T. Liu, L. Ye, Synthesis and properties of fluorinated thermoplastic polyurethane elastomer, J. Fluorine Chem. 131 (2010) 36–41.

[20] H. Zhou, Y. Chen, H.J. Fan, H.H. Shi, Z.Y. Luo, B. Shi, The polyurethane/SiO_2 nano-hybrid membrane with temperature sensitivity for water vapor permeation, J. Membr. Sci. 318 (2008) 71–78.

[21] A.H. Cui, Z. Liu, C.F. Xiao, Y.F. Zhang, Effect of micro-sized SiO_2-particle on the performance of PVDF blend membranes via TIPS, J. Membr. Sci. 360(1–2) (2010) 259–264.

[22] W.Z. Ma, J. Zhang, X.L. Wang, S.M. Wang, Effect of PMMA on crystallization behavior and hydrophilicity of poly(vinylidene fluoride)/poly(methyl methacrylate) blend prepared in semi-dilute solutions, Appl. Surf. Sci. 253(20) (2007) 8377–8388.

[23] K.J. Xiao, M. Lei, F.T. Li, Preparation of mesoporous membranes and its separating performance, Chinese J. Mod. Food Sci. Technol. 25(2) (2009) 168–171.

[24] K.J. Xiao, P. Xiong, Study on structures and properties of PVDF membrane prepared by mixed diluents, Chinese J. Chin. Plast. Ind. 38(12) (2010) 10–13.

[25] K.J. Xiao, L. Yuan, W.S. Liu, L. Li, X.H. Zhou, Y.R. Yin, Performances of PAN/PS blend membrane under action of electric field, J. S. Chin. Univ. Technol. (Nat. Sci. Ed.) 37 (2009) 85–89.

[26] M. Hirose, H. Ito, Y. Kamiyama, Effect of skin layer surface structures on the flux behaviour of RO membranes, J. Membr. Sci. 121(2) (1996) 209–215.

[27] X. Qian, R. Cheng, Applications of atomic force microscopy to characterization of synthetic membranes, Chin. J. Membr. Sci. Technol. 24(2) (2004) 62–67.