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Preparation of PVDF/PVC composite membrane for wastewater purification

Qi Zhang, Shifeng Zhang, Yufeng Zhang, Xiaoyu Hu, Yingbo Chen*

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China
Tel. +86 22 8395 5357; Fax. +86 22 8395 5055; email: chenyingbo@tjpu.edu.cn

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ABSTRACT

Polyvinylidene fluoride (PVDF) membranes are widely used in waste water purification and desalination for the advantages of excellent separation performance and good mechanical stability. However, high cost and inert to modification limit their application in many fields. Here, we prepare a novel membrane containing PVDF and polyvinyl chloride (PVC) using phase inversion method. The influence of polymers ratios on the structure and performance of the membranes is investigated. The porosity of the membranes is tested using weight differential method. And the result shows that the porosity increases with adding more PVC in the composite membranes. The flux does not proportionally increase with increasing the amount of PVC in the composite membranes. With adding a small amount of PVC (1 and 5%), the flux is dramatically larger than that of pure PVDF membrane; then it goes down with adding more PVC (10–20%). In order to find out the mechanism of increment in flux with adding small amount of PVC, the composite membranes with varied amount of PVC are characterized using differential scanning calorimetry. Also the morphologies of the composite membranes are observed using scanning electron microscopy and mechanical strength of the composite membranes are recorded using a material testing machine.

Keywords: PVDF; PVC; Composite membrane; Flux

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1. Introduction

Poly (vinylidene fluoride) (PVDF) membranes are widely used in ultrafiltration [1], microfiltration [2,3], and membrane distillation [4,5] due to their advantages such as excellent chemical resistance, well-controlled porosity, and good thermal stability and favorable mechanical properties [6,7]. PVDF membranes always attract lots of attention due to all these properties. However, high cost and inert to modification limit their application in many fields.

A large number of studies have been carried out by domestic and foreign researchers on PVDF membrane in order to enhance the properties of PVDF membrane and widen its application. Bottino et al. [8] investigated the correlations between and the casting and coagulating solution and the characteristics and

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*Corresponding author.

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properties of the resulting PVDF membranes. The effect of additives on the morphology and transport properties of porous asymmetric PVDF ultrafiltration membrane was investigated by Yuliwati and Ismail [9]. Functional PVDF membrane with thermal sensitivity was also prepared via phase inversion of PVDF-g-PINPAAm [10]. Rajendran [11] reported PVDF/PVC-based blend electrolytes with EC/PC as plasticizers prepared using solvent-casting technique in lithium battery applications. However, PVDF/PVC composite membrane has rarely reported in the literature.

Poly(vinyl chloride) (PVC) is one of the most industrialized materials with low cost, environmentally friendly and excellent properties, whose industry is developed rapidly in the world and prospect is rather bright [12,13]. Blending [14,15] of polymers to prepare membrane is a useful method to improve membrane properties. Therefore, in this study, novel membranes are prepared via physical blending modification and the influences of polymers ratios on the structure and performance of the membranes are investigated. The present method to prepare PVDF/PVC composite not only reduces the cost of producing PVDF membranes, but enhances the membrane performance.

2. Experimental

2.1. Materials

PVDF and PVC were received from Tianjin Motimo Company. Dimethylacetamide (DMAc) was purchased from Tianjin Kermel Co. Ltd. Deionized water was used as coagulation.

2.2. Preparation of PVDF/PVC composite membranes

18wt% blend solution containing varied rations of PVDF/PVC (w/w) was prepared by dissolving the blend in DMAc with stirring for 9 h at 25℃. The rations of blends are PVDF/PVC = 100:0, 99:1, 95:5, 90:10, 80:20, 50:50, and 0:100. The polymer solution was put aside for deaeration, followed by scraping the viscous solution on a glass plate using a blade knife, the glass plate was then immediately transferred to the coagulation bath water, and soaked in water 24 h. A membrane was peeled from the glass and immersed in 70℃ hot water for 1.5 h to thermal set the membrane. Finally, the membrane was dried in vacuum oven at 60℃.

3. Characterization of PVDF/PVC composite membrane

3.1. Pure water flux

Pure water flux the membrane was tested using a membrane cell with cross-flow mode. The permeate was collected every 5 min for half an hour. The pressure between the feed and permeate side was fixed at 0.1 MPa, and the flux was calculated according to Eq. (1):

$$F = V/(A \times t) \tag{1}$$

where F is the membrane flux (L/m^{2}h), V the volume of permeate at time t, and A the effective filtration area of the membrane (24 cm^2).

3.2. Porosity

The porosity of the membrane is tested by weight differential methods. The weight of wet membrane was recorded followed by drying in vacuum oven at 60℃ till constant weight. The weight of the dried membrane was also records, and the porosity of membrane was calculated according to Eq. (2):

$$P = (W_w - W_d)/W_w \tag{2}$$

The weight of both wet and dried membranes was tested for 5 times to get an average number.

3.3. Water contact angle

The contact angle of the membranes was measured using a microscopy system. Deionized water (5 μl) was dropped perpendicularly onto the surface of the films placed on a horizontal glass sheet using a microcylinder. The images of water drops on the surface were then observed using Scalar video loupe (VL-11s) and analyzed using the Sigma TV II program.

3.4. Mechanical properties

The mechanical properties were studied using a material testing machine (YG605). A piece of membrane with 1 × 4 cm was cut to fit the clamp of the machine. Five samples were recorded to calculate an average value.

3.5. Morphological and structural analysis

Scanning electron microscopy (SEM) images were examined using SEM (Quanta 200). Prior to the analysis,

Table 1
Thermal and mechanical property of PVDF/PVC composite membranes

Sample	T_m (PVDF) (℃)	ΔH (PVDF) (J/g)	T_g (PVC) (℃)	Break strength (N)
PVDF	173.9	74.39	–	21.0
1% PVC	174.4	76.14	–	14.6
5% PVC	175.1	77.69	–	16.2
10% PVC	171.2	76.36	82.5	10.6
20% PVC	171.7	71.85	80.8	8.2
50% PVC	171.3	67.94	81.2	10.6
PVC	–	–	87.2	8.8

the membranes were coated with a thin shell of gold by sputter deposition. Differential scanning calorimetry (DSC) spectra were determined using a PERKIN ELMER DSC7 at a heating rate of 10℃/min over a temperature range from room temperature to 300℃.

4. Results and discussion

Table 1 lists the thermal and mechanical properties of the composite membranes. The melting temperatures of PVDF in the composite slightly increases with small amount of PVC (1 and 5 wt.%). While it decreases about 3℃ when more PVC is added in the composite. It can be concluded that small amount of PVC in the composites is favorable to the crystallization of PVDF. Litter PVC might play a role as nucleating agent for the crystallization of PVDF. However, more PVC in the composite declines the behavior of PVDF crystalline due to their bad compatibility. The change of enthalpy of PVDF melting has similar trends to the alteration of melting temperature. On the other sides, glass transition temperature (T_g) of PVC

Table 2
Porosity, flux, and contact angle of PVDF/PVC composite membranes

Sample	Porosity	Flux (L/m^{2}h)	Contact angle (°)
PVDF	0.12	0.33	116.7
1% PVC	0.20	1.33	110.1
5% PVC	0.46	1.79	110.8
10% PVC	0.31	0.80	109.7
20% PVC	0.36	1.66	113.4
50% PVC	0.51	6.30	71.4
PVC	0.54	0.66	72.6

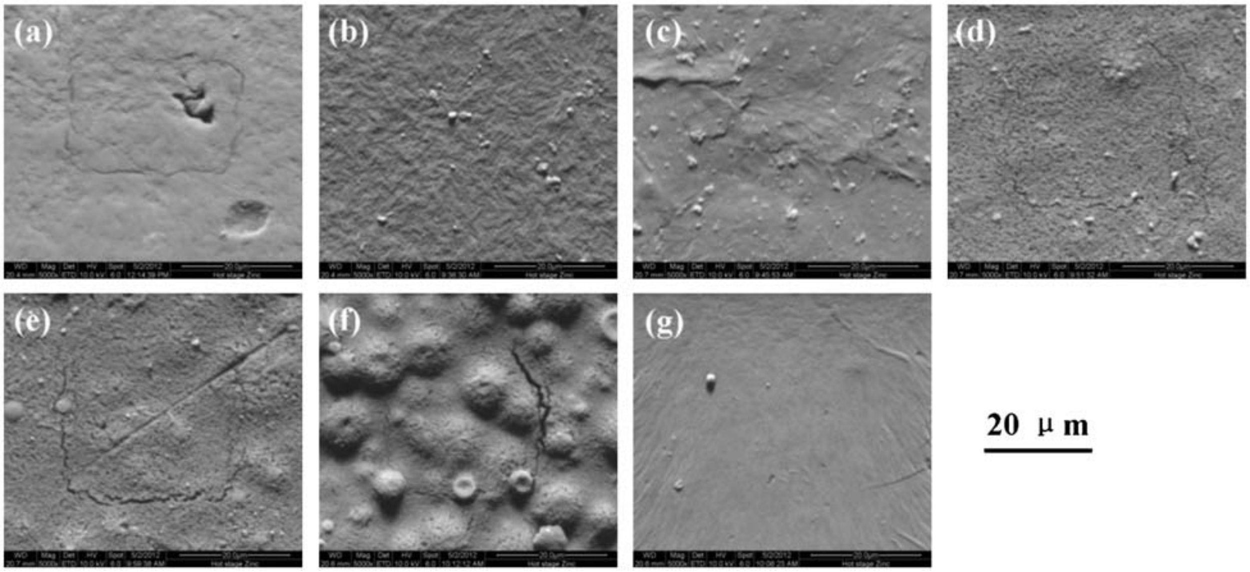

Fig. 1. SEM images of PVDF-PVC composite membranes with (a) no PVC, (b) 1% PVC, (c) 5% PVC, (d) 10% PVC, (e) 20% PVC, (f) 50% PVC, and (g) 100% PVC.

decreases when it mixes with PVDF in a large amount (>10 wt.%). It means motivation of PVC chains becoming easier when mixed with PVDF. The break strength of the membranes has a decreasing trends with more PVC added in the membranes. Nevertheless, membrane with small amount of PVC in the composite has relatively higher strength, especially the one with 5 wt.% PVC. Since the mechanical strength of PVDF membrane (21.0 N) is much higher than that of PVC membrane (8.8 N), adding of PVC in the composite membrane would decrease its strength. On the other side, small amount PVC facilitates the crystallization of PVDF, which causes a higher mechanical strength. Thus, the two factors results in the best mechanical strength of the composite membrane with 5% PVC.

The changes of porosity, flux and contact angle of the composite membranes with polymer ratios are listed in Table 2. The porosity increases with the content of PVC in the composites membranes except for that of 5% PVC. The increment of porosity of the composite membrane is contributed to the individuality of porous structure formation of amorphous PVC (porosity 0.54). The special high porosity of the composite membrane with 5% PVC may be due to the formation of interfacial voids between the crystals of PVDF and PVC (see Fig. 1(c)). High porosity of the composite membrane with 5% PVC responses to its high water flux (1.79 L/m^2h). However, the water flux of the composite membrane with more than 10% PVC also shows high values (1.66 and 6.30 L/m^2h for 20 and 50% PVC respectively). This high flux is due to the phase separation of the blends during the formation of membrane. The structures can be seen clearly from Fig. 1(e) and (f). The two components forms bi-continuous structures and even cracks in the composite membrane with 50% PVC. Water contact angles of the composite membrane also decrease with more PVC in the membranes. The decline of the surface energy of the membranes would helpful for enhancing the anti-resistance property of composite membranes.

5. Conclusion

In conclusion, PVDF/PVC composite membrane was prepared by phase inversion of a blends solution with varied polymer ratios. It was noticed that small amount of PVC (1 and 5 wt.%) plays a role as nucleating agent for PVDF and enhances the melting temperature and enthalpy of PVDF crystals. The composite membrane with 5 wt.% PVC has relatively high break strength, porosity, and water flux. Water contact angle also decreases by 6° with adding 5% PVC. The composite membrane with small amount PVC would have better performance and widen the applications of PVDF membranes.

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