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Preparation of PVDF/Al_2O_3 hybrid membrane via the sol–gel process and characterization of the hybrid membrane

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ABSTRACT

In this study we present a new method to prepare organic–inorganic hybrid polyvinylidene fluoride (PVDF)/Al_2O_3 membranes via *in situ* polymerization of aluminum isopropoxide (AIP) using the sol–gel process. FTIR analysis showed the existence of Al in hybrid membrane when AIP was added to the casting solution. The effects of AIP on the performances of hybrid membranes were investigated. The results showed that the pure water flux and the bovine serum albumin (BSA) rejection increased firstly and then decreased with increasing AIP content. When AIP content was 12 wt.%, compared with PVDF membrane without the addition of AIP, the pure water flux of hybrid membrane was increased by 83.4% and the BSA rejection was improved from 88.3 to 96.6%. In addition, other performances of the hybrid membrane such as hydrophilicity, mechanical properties, and antipollution were also improved.

Keywords: Polyvinylidene fluoride (PVDF); AIP; Organic–inorganic hybrid membranes

1. Introduction

Hybrid materials could combine basic properties of organic and inorganic materials and offer specific advantages for the preparation of artificial membranes with excellent separation performances, good thermal and chemical stability and adaptability to the harsh environments, as well as membrane forming ability. As new membrane materials, organic–inorganic hybrid materials have attracted more and more attentions [1–5].

Polyvinylidene fluoride (PVDF) is one of the most attractive polymer materials in water treatment industry due to its excellent chemical resistance, thermal stability, low toxicity, and good mechanical properties [6]. However, its hydrophobic characteristic that often leads to severe membrane fouling and the decline in permeability limits its application in water treatment [7,8]. Several strategies to improve the hydrophilicity of PVDF membranes have therefore been investigated such as physical blending, chemical grafting, and surface modification [9]. Recent studies on PVDF-blending modifications focused on blending polymers with inorganic materials.

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Inorganic materials that can be blended with PVDF include silica (SiO_2) [10], titanium dioxide (TiO_2) [11], zirconium dioxide (ZrO_2) [12], and some small molecule inorganic salts, such as lithium salts [13]. Initially, most of these modifications are the addition of nano-particles to the casting solutions to prepare the hybrid membranes. To promote the dispersion of the organic components in polymers, a sol–gel process was used to grow the inorganic phase in the polymer solution. The sol–gel technique has provided new opportunities for the preparation of organic–inorganic materials, which allows the formation of inorganic framework under mild condition and incorporation of minerals into polymers, resulting in increased chemical, mechanical, and thermal stabilities without obviously decreasing the properties of the polymers [14,15]. Furthermore, the remaining hydrogen bond clusters at the surfaces of the materials after the sol–gel reaction improve the membrane hydrophilicity and enhance the stability of the composite materials [16–20].

Since Al_2O_3 nanoparticle has high affinity to water, it is also used as a candidate for further hydrophilic modification of the PVDF membrane [10]. However, there are few reports on the preparation of PVDF/Al_2O_3 hybrid membrane by sol–gel process. It is known that aluminum alkoxides are very popular for the processing of alumina. Among the alkoxides, aluminum isopropoxide is currently used in the sol–gel processing of alumina [21]. In this work, PVDF/Al_2O_3 hybrid membranes were prepared by sol–gel process and phase inversion method. The effect of aluminium isopropoxide (AIP) on membrane structure and property were investigated.

2. Experimental

2.1. Materials

PVDF (FR904) was purchased from New Materials Co. Ltd. (Shanghai, China). *N*,*N*-dimethylacetamide (DMAc, purity > 99%) was obtained from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Bovine serum albumin (BSA) (BSA, $M_w = 67{,}000$) was provided from Bio Life Science and Technology Co., Ltd. (Shanghai, China). Polyvinylpyrrolidone (PVPK30) obtained from Beijing Chemical Plant was used as additives. AIP was from Sinopharm Chemical Reagent Co., Ltd.

2.2. Instruments

Vector 33 Fourier Transform Infrared Spectrometer from Bruker Company (Germany). AGS-10 KNI Universal Electronic Tensile Tester from Jin Island Company (Japan). OCA15 Surface Contact Angle Meter from Dataphysics Company (Germany). Nova Nanosem 430 scanning electron microscopy (SEM) from Dutch.

2.3. Membrane preparation and characterization

Firstly, PVDF was dissolved in DMAc at 70°C with strong stirring to a concentration of 17 wt.%. Different AIP concentrations (0–20%, by weight of PVDF) were added into PVDF solution, and the mixture was stirred at 70°C again for 1 h to get a homogenous PVDF/AIP solution, and then, the deionized water as well as nitric acid was dropped into the solution in a molar ratio of 5/0.13/1 (H_2O/HNO_3/AIP). Finally, 4% of PVP (by weight of solution) was added as additives. The above mixture was stirred for 20 h at 85°C to obtain homogenous casting solution. The solution was degassed for 24 h and then was poured onto a glass plate with the membrane blade at room temperature. After exposed in air for 15 s, the casting solution on glass was immediately immersed in the water bath and stand for 5–7 days, and then, the hybrid PVDF/Al_2O_3 membrane was dried in the air and was obtained.

FT-IR was employed to investigate the composition of the resultant membranes. The surface structure of the membranes was examined by SEM. The permeation properties of membranes were tested in a self-made ultrafiltration unit (effective area = 50.3 cm^2) fed with pure water at 0.1 MPa. The same unit was fed with BSA in order to obtain the rejection ratio of membranes. The contact angles between water and the membrane surfaces were measured using a contact-angle measurement apparatus according to the drop method. The tensile strength and elongation-at-break of the membranes were determined with a universal electronic strength measurement instrument.

3. Results and discussion

3.1. FT-IR analyses

The FT-IR spectra obtained are shown in Fig. 1. Typical peaks of the α-phase PVDF crystals appeared at 488, 612, 762, and 978 cm^{-1}, and the bands at 509 and 840 cm^{-1} corresponded to β-phase PVDF crystals [22–25]. From Fig. 1(b), it is apparently seen that the α-phase crystal bands weakened or disappeared with the AIP addition, while the β-phase crystals bands somewhat increased. The presence of the absorption band at 1596 cm^{-1}, ascribed to the stretching mode of Al–O–Al, suggested the existence of Al_2O_3 in the hybrid membrane [26]. It might suggest that the generating Al_2O_3 had an effect on crystalline of PVDF

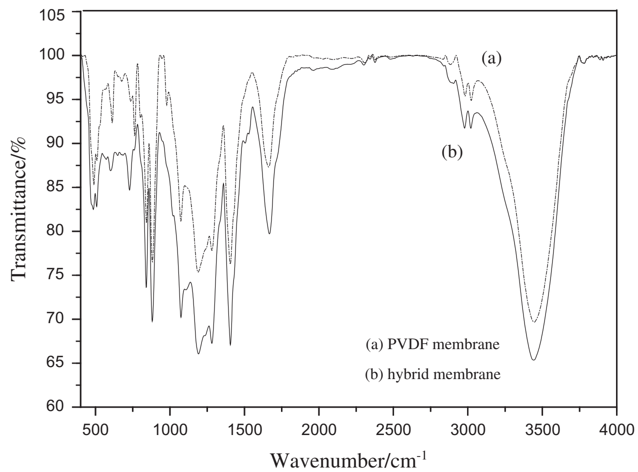

Fig. 1. FT-IR spectra of PVDF and PVDF/Al_2O_3 hybrid membranes.

molecule. In addition, new bands were observed at 601 and 1502 cm^{-1} which implied the interaction between PVDF and Al_2O_3.

3.2. Surface morphology

Fig. 2 shows the SEM images of PVDF and PVDF/Al_2O_3 hybrid membrane surfaces. It can be seen that the micropores were distributed on membrane surfaces with different additions of AIP. Fig. 2(b–d) shows a smaller pore size and higher porosity. Apparently, a homogeneous with uniformly sized pore membrane was obtained, when the content of AIP was 12% (Fig. 2(d)).

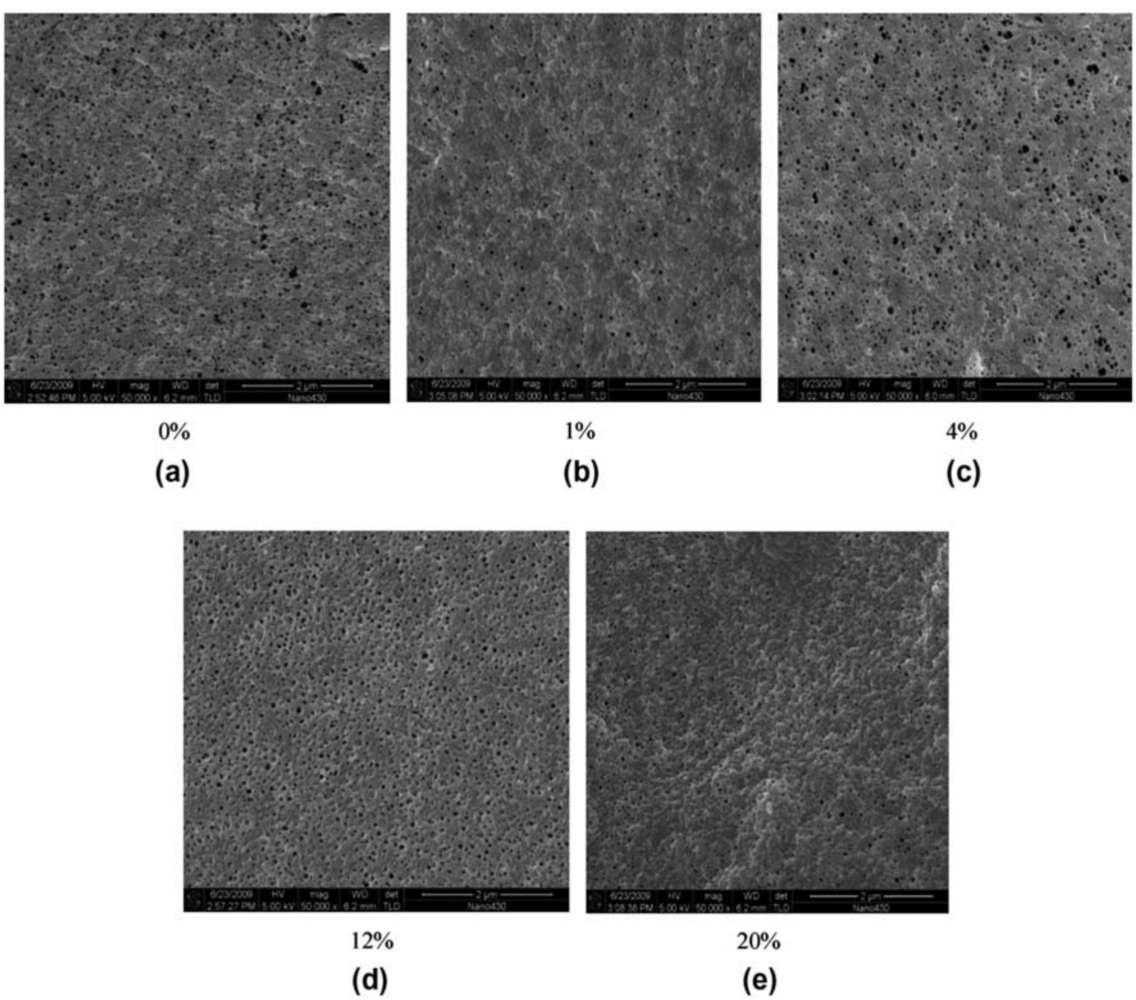

Fig. 2. SEM images of hybrid films with different alumina content (×50,000).

Table 1
Contact angle of PVDF/Al_2O_3 hybrid membranes with different AIP content

Sample number	*W* (AIP) (%)	Contact angle (°)
1	0	81.0
2	2	79.75
3	4	74.37
4	8	71.75
5	12	69.53
6	16	72.58
7	20	82.75

3.3. Hydrophilicity of membranes

The contact angle data of PVDF/Al_2O_3 hybrid membranes with different AIP concentration was listed in Table 1. It can be seen that the membrane hydrophilicity is reduced by the addition of AIP. This fact is due to the presence of Al_2O_3 nanoparticles generated by hydrolysis of AIP containing an amount of hydroxyl groups, responsible of the hydrophilicity increase. However, the contact angle increased when the AIP concentration exceeded 12 wt.%. This may be because that precipitation inhibited the dispersion of nanoparticles resulting in decrease of hydroxyl groups number.

3.4. Ultrafiltration performances

The pure water flux and the BSA rejection of hybrid membranes were examined. As shown in Fig. 3, the pure water flux increased with the increase in the addition of AIP and achieved a maximum value when the AIP concentration was 12%. Compared with PVDF membrane without AIP addition, the pure water flux of hybrid membrane was increased by 83.4% at 12 wt.%. However, higher AIP concentration led to the decrease in the flux. An increase in hydrophilicity of membrane by the addition of AIP enhanced the flux greatly. However, high AIP concentration (16 wt.%) produces highly viscous casting solution (623 pa s), which slowed down the formation process of hybrid membrane and resulted in the growth of macrovoid [27,28]. Consequently, the flux was decrease. When AIP content was increased, the BSA rejection was also gradually increased initially and then decreased. At 12 wt.%, the rejection was improved from 88.3% (without AIP addition) to 96.6%. Therefore, both flux and rejection can be improved by the appropriate amount of the addition of AIP.

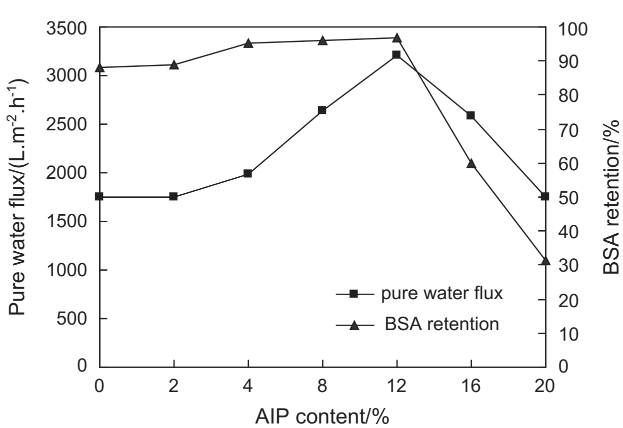

Fig. 3. Effect of AIP content on pure water flux and the BSA rejection of hybrid membranes.

3.5. Mechanical properties

The tensile strength and elongation-at-break of the membranes are listed in Table 2. AIP addition had no obvious effect on the tensile strength of hybrid membranes. The elongation-at-break initially increased with the addition of AIP and then declined as the AIP concentration was further increased. At the peak value, when the AIP concentration was 12%, the elongation-at-break was increased by 46.1%. These behaviors indicate that adding an appropriate amount of AIP to a PVDF solution can improve the membrane's mechanical properties. In the process of the formation of Al_2O_3 by polymerization of AIP, there were interactions between Al_2O_3 and PVDF. Al_2O_3 could act as a cross-linking point in hybrid membranes to link the polymeric chains [29] and increase the rigidity of polymeric chains and thereby resulting in an improvement on the elongation-at-break.

3.6. Antifouling performance

Membrane fouling caused the permeation flux to decline drastically. Fig. 4 illustrates the flux change for PVDF and PVDF/Al_2O_3 membranes using pure water and BSA solution as feeds. Fig. 4 shows that the permeation fluxes of water and BSA solution for the two membranes declined as the filtration time increased. However, for hybrid membrane, the fluxes reached a steady value at 20 and 50 min, respectively. While the fluxes of PVDF membrane declined continuously and the rates of flux decline were 33.7 and 40.0%, respectively, for pure water and BSA solution, compared with which, they were only 23.2 and 26.3% for the hybrid membrane. This shows that the PVDF/Al_2O_3 hybrid membrane had a more favorable antifouling performance. The main mechanism of mem-

Table 2
Mechanical properties of hybrid membranes with different AIP contents

W (AIP) (%)	Tensile strength (*N*)	Elongation-at-break (%)
0	26.04	23.52
2	23.22	32.47
4	21.81	30.11
8	25.78	31.79
12	25.13	34.36
16	24.83	28.04
20	24.17	21.48

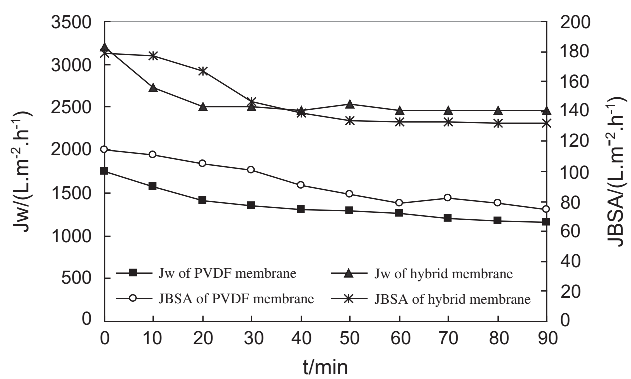

Fig. 4. Pure water and BSA solution fluxes of PVDF and PVDF/Al_2O_3 hybrid membranes change with time.

brane fouling is thought to be caused by undesirable formation of deposits on membrane surfaces [30,31]. A hydrophobic membrane surface formed due to better hydrophilicity of Al_2O_3 in hybrid membrane inhibited the adsorption of deposits and caused the formed deposits easily fall off and hence greatly improved the membrane antifouling ability.

4. Conclusions

Organic–inorganic PVDF/Al_2O_3 hybrid membranes were prepared by sol–gel and phase inversion process. AIP was directly added into the PVDF casting solution. During the blending process, the AIP could be hydrolyzed and polymerized, and inorganic Al_2O_3 nanoparticles were formed, meanwhile the hybridization with PVDF proceeded. PVDF membrane characteristics were changed by the addition of AIP. The hydrophilicity of hybrid membrane was improved and the elongation at break increased due to the strong interactions between the polymer chain and the hydrophilic group of the hydrolyzed AIP. The pure water flux and the BSA rejection increased firstly and then decreased with increasing AIP content. At 12 wt.%, compared with pure PVDF membrane, the pure water flux of hybrid membrane was increased by 83.4% and the BSA rejection was improved from 88.3 to 96.6%. Furthermore, the hybrid membrane had a higher antifouling ability.

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