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Preparation of PVDF/Al_2O_3 hybrid membrane via alkaline modification and chemical coupling process

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ABSTRACT

Polyvinylidene fluoride PVDF/Al_2O_3 hybrid membrane (PAHM) was prepared via alkaline modification and chemical coupling using PVDF modified by KOH in the solution of methanol as a membrane-forming polymer, using vinyl-trimethoxy-silicane as a coupling agent and aluminum isopropoxide (AIP) as an inorganic precursor, respectively. PAHM, linking PVDF and Al_2O_3 with chemical bond, was obtained by sol–gel method. FT-IR spectroscopy, surface contact angle testing, differential scanning calorimetry, and atomic force microscope were applied to characterize the PAHM. The effects of the coupling agent on the structure and properties of the hybrid membrane were also investigated. The results showed that the hydrophilicity of the modified PVDF were the best with 5 wt% of KOH solution at 60℃ for 30 min. When PAHM is prepared with 1% coupling agent, the average pore size and the pure water flux decreased compared to PAHM without coupling agent, while the rejection rate significantly increased. Along with the increase in AIP concentration, the tensile strength and elongation at break of PAHM gradually improved, but both of them have a reduction when AIP concentration reached to 10% by weight. Compared with the original PVDF membrane, the flux attenuation coefficient of PAHM prepared by alkali-coupling agent modification declined from 45 to 27%, which means the antifouling performance of membrane improved markedly.

Keywords: Modified PVDF; Alkali modification; Coupling agent; Hydrophilicity; Organic–inorganic hybrid membrane

1. Introduction

Polyvinylidene fluoride (PVDF) is known as one of the most attractive polymer materials in the microporous membrane industry. It is widely used in the manufacturing of reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and pervaporation (PV) membranes due to its extraordinary properties, such as excellent thermal stability and mechanical properties, high chemical resistance to aggressive reagents like organic solvents, acid, and bases, and excellent membrane-forming abilities [1–6]. However, due to the hydrophobic nature of PVDF, membranes fabricated from PVDF polymer have a

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high-fouling tendency and declined permeability when they are exposed to protein-containing solutions, which leads to a sharp drop in the membrane's water flux and has become a severe drawback for their application in food and pharmaceutical industry [7–10]. So, in order to improve the hydrophilicity of PVDF, it is necessary for us to have the PVDF modified.

Several strategies to improve the hydrophilicity of PVDF membranes have, therefore, been investigated such as physical blending, chemical grafting, and surface modification [11,12]. Recent studies on PVDF-blending modification mainly focused on blending polymers with hydrophilic materials as it has the advantage of easy preparation using phase inversion. Several hydrophilic organic materials have reported to modify PVDF, and they can increase the water permeability of a membrane with similar pore size and pore distribution due to an 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 membrane strength [13–16].

Inorganic materials have been known as a prospective additive for membrane separation processes due to their excellent mechanical properties and remarkable thermal properties, and these extraordinary properties of inorganic materials can be maintained under a wide variety of conditions, leading to a good separation performance [17–19]. Inorganic materials that can be blended with PVDF include SiO_2, ZrO_2, TiO_2, Al_2O_3, and some small molecular inorganic salts, such as lithium salts [20–23]. PVDF can be used as composites with these inorganic nanoparticles to improve the membrane separation performance, thermal ability, and membrane-forming ability by the combination of the basic properties of organic and inorganic materials. The strong affinity of Al_2O_3 nanoparticles to water makes it the best candidate material for hydrophilic modification of PVDF membrane [24]. PVDF and Al_2O_3 are not connected by chemical bonds for the most of the previous works, that is to say, the membranes have insufficient combination strength between the inorganic material and PVDF polymers, which results in low tensile strength of membrane.

In this work, the active groups, such as hydroxyl and carbonyl groups, were exposed after the modification of PVDF by alkali, and these active groups cross-linked with aluminum isopropoxide (AIP) through a coupling agent. Then, PVDF/Al_2O_3 hybrid membrane (PAHM) linking with the chemical bonds was prepared. The uniformity of the modified PAHM was improved, and the combined strength of organic and inorganic ingredients was enhanced; thus, this can increase the mechanical strength of the hybrid membrane and provide a new approach for preparing the organic–inorganic hybrid membrane containing chemical cross-linking bands.

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) as the solvent. Bovine serum albumin (BSA, $M_w = 67{,}000$) was provided from Bio Life Science & Technology Co., Ltd. (Shanghai, China). AIP was from Sinopharm Chemical Reagent Co., Ltd. A mixture of distilled water and ethanol was used as nonsolvent for the membrane precipitation.

2.2. Preparation of hydrophilic PAHM

2.2.1. Process technology of Modified PAHM

The process technology of the modified PAHM is shown in Fig. 1.

2.2.2. Alkali modification of PVDF polymer

Firstly, KOH methanol solutions of l, 3, and 5% (wt) were prepared and then mixed with PVDF, respectively. The reaction was under the circumstances of thermostatic water-bath and magnetic stirring; the reaction was controlled at 40,

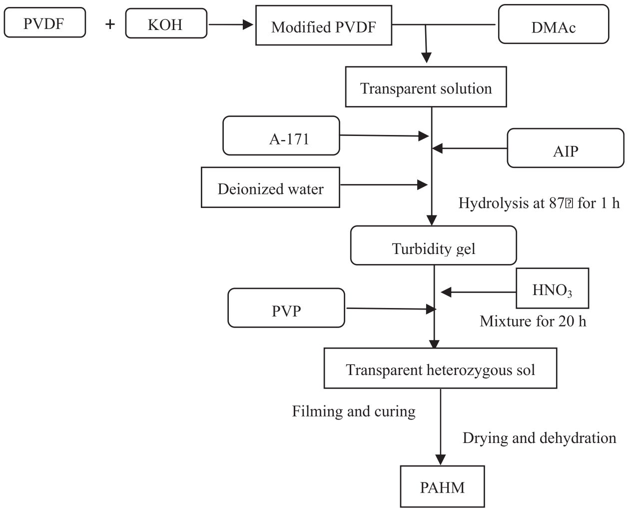


Fig. 1. Preparation route of modified PAHM.

60, and 80°C for 10, 30, and 60 min, respectively. Finally, the disposed PVDF was washed repeatedly to neutral by methanol and dried for about 24 h in the vacuum-drying oven at 70°C.

2.2.3. Cross-linking of PVDF polymer and AIP

PVDF was dissolved into DMAc solvent to prepare the casting solution, then, the defined amount of coupling agent and different concentrations of AIP were put into it, the PVDF polymer and AIP were cross-linked after the solution dissolved.

2.2.4. Preparation of PAHM

The above mixture was stirred constantly for 20 h at 87°C to obtain a homogeneous casting solution. The solution was kept still for 24 h to remove air bubbles and the membrane was prepared by a flat membrane casting equipment (150-J, Tianjin, China). After exposure in air for 15 s, the membrane prepared on glass was immediately immersed in the deionized water for 5–7 days and the PAHM was obtained.

2.3. Characterization of modified PAHM

2.3.1. Pure water flux of PAHM

The flux, the basic permeation property of membranes, was tested in a self-made ultrafiltration unit (effective area = 50.3 cm^2) fed with pure water at 0.2 MPa. The flux at 25°C (kg/(m^{2}h)) was calculated by the following equation:

$$J = V/(St) \tag{1}$$

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

2.3.2. The rejection ratio of PAHM

The same unit was fed with BSA at 0.2 MPa for 30 min, in order to obtain the membrane rejection. The BSA concentration in permeation solution and bulk solution was tested by a spectrophotometer. The rejection (%) was obtained by:

$$R = (1 - C_P/C_F) \times 100\% \tag{2}$$

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

2.3.3. The antifouling property of PAHM

The same unit was fed with BSA (1 g/L) at 0.2 MPa for 20 min, in order to obtain the antifouling property of the hybrid membrane. The flux attenuation coefficient (m) for pure water was obtained by the following equation:

$$m = (1 - J_1/J_0) \times 100\% \tag{3}$$

where J_0 and J_1 are the pure water fluxes of membrane before and after the BSA was ultrafiltrated, respectively. Smaller the m, better the antifouling property of membrane.

2.3.4. The static contact angle of PAHM

The contact angles between water and the membrane surfaces were measured using a contact angle measurement apparatus (OCA15, Germany), 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 were measured four times on different parts of the membranes [25].

2.3.5. FT-IR characterization

FT-IR analyzer (Vector 33, Germany) was employed to probe the chemical composition of the prepared membranes. The samples of the membrane were analyzed by transmission beam method.

2.3.6. Morphological structure characterization of PAHM

The surfaces and microstructures of the membranes were examined by SEM (Nova Nanosem 430, Dutch). The membranes were frozen in liquid nitrogen and fractured, and the fracture surfaces were tested after they were disposed by vacuum dehydration. The surface structures were directly tested by SEM.

2.3.7. The porosity of PAHM

The porosity of PAHM was measured via density method: The Q of a certain area of the dry dehydrated membrane was weighed by electronic balance and the thickness of the membrane was measured by micro-calliper. The volume and density of the membrane were calculated, and there upon the porosity of PAHM was calculated by the following formula:

$$\varepsilon = (1 - \rho_1/\rho_2) \times 100\% \quad (4)$$

where ρ_1 is the density of membrane and ρ_2 is the density of PVDF (1.805 g/cm^3).

2.3.8. *Atomic force microscope analysis*

The surface roughness of the membrane indicates the difference in 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 polluted. In this study, the surface roughness was tested by Atomic force microscope analysis (AFM) (Nanoscope IIIa, USA).

2.3.9. *The mechanical properties*

The tensile strength and elongation at the break of the membranes were determined with a universal electronic strength measurement instrument (AGS-10 KNI, Japan). The measurements were carried out at room temperature and the stretch rate was 2 mm/min.

2.3.10. *Differential scanning calorimetry test and thermogravimetric analysis*

The melting point of PAHM was tested using a differential scanning calorimetry (DSC) analyzer (DSC Q200, the United States) to analyze the effect of hybridization on the properties of the prepared membranes. The measurements were carried out under the condition of N_2 with a speed of 10℃/min starting from −80℃, and the flow velocity of gas was 40 mL/min. The temperature of thermal decomposition was measured by a thermogravimetric analysis (TGA) (Q500, USA). The measurements were carried out using N_2 at a speed of 10℃/min from the room temperature, and the flow velocity of gas was 30 mL/min.

3. Results and discussion

3.1. *The effects of alkali-treatment on the hydrophilicity and the pure water flux of membrane*

The contact angle is an important property that can characterize the hydrophilicity of membrane materials. Generally, the smaller the contact angle, the better the hydrophilicity of membrane surface. PVDF, modified in different conditions, were fabricated into membranes and polymer concentration was kept at 17% (wt), and PVP was 4%. The effects of KOH concentration, reaction time, and reaction temperature on the modification of PVDF were investigated by measuring the contact angle and pure water flux. As shown in Figs. 2–4, the contact angle of modified PAHM decreased while the pure water flux increased, thus demonstrating that the hydrophilicity of PVDF membrane improves after alkali modification. It is shown that the main reason for this phenomenon is that the strong base when reacted with PVDF on the surface of the membrane, which can introduce hydrophilic polar-groups, such as hydroxide radical and carboxyl groups, improves the hydrophilicity of the PVDF membrane. The dissolubility of the polymer descended markedly and the color deepened along with the enhancing extent of PVDF modification. So the best modification process is using 5 wt% of KOH solution at 60℃ for 30 min in our work to obtain modified PVDF to investigate the preparation of PAHM.

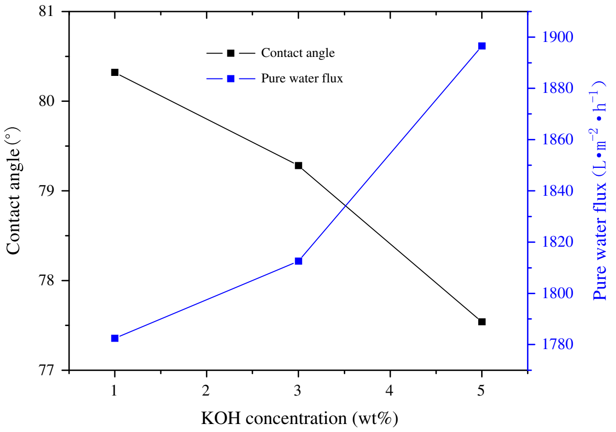


Fig. 2. Effect of KOH concentration (60℃, 30 min) on the contact angle and pure water flux of membrane.

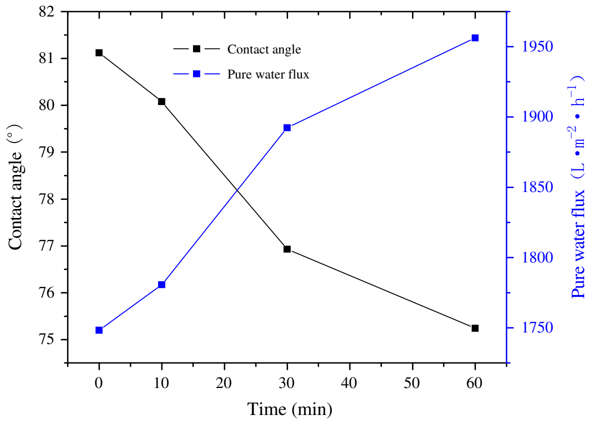


Fig. 3. Effect of reaction time (KOH 5 wt% KOH, 60℃) on the contact angle and pure water flux of membrane.

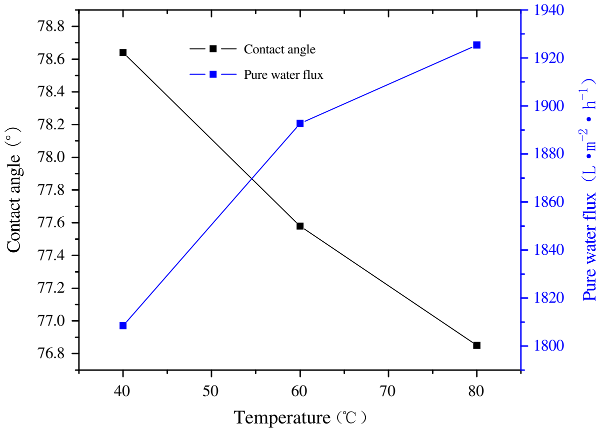


Fig. 4. Effect of reaction temperature (5 wt% KOH, 30 min) on the contact angle and pure water flux of membrane.

3.2. FT-IR spectra analysis of modified PVDF and PAHM

Fig. 5(a) presents the typical FT-IR spectra of modified PVDF. As indicated in Fig. 5(a), the peaks appearing at 1,644 cm^{-1} derive from the stretching vibration of C=C double bond, revealing the formation of the C=C double bond. So, the surface of PVDF processed by alkali can result in the C=C double bond. Meanwhile, the FT-IR spectra of the modified PVDF surfaces reveal the appearance of the peak at 3,000–3,500 cm^{-1}, which is associated with the hydroxyl group [26–29]. This is because when PVDF was disposed by a strong alkali solution, its defluorination was accompaniedby an oxidizing reaction [24,30]. It is thought that the primary reason why the contact angle of modified PVDF membrane decreased was the formation of the carbonyl group and the hydroxyl group, which can improve the hydrophilicity of the surface of membrane. As shown in Fig. 5(b), the appearance of the peak at 1,699 indicates that the carbonyl group was successfully introduced into PAHM. What is more, the peaks at 833 cm^{-1} and 758 cm^{-1} are the stretching vibration peaks of Si–O–Al, and the peak at 615 cm^{-1} is the bending vibration peak of Si–O–Al, manifesting that coupling agent was involved in the hybrid reactions via the hydrolysis with AIP.

3.3. Effect of coupling agent on the microstructure and separation property of PAHM

Fig. 6(a) and (b) are the SEM images of the surface of PAHM without coupling agent and with 1% coupling agent, respectively. As shown in Fig. 6(a), the PAHM without coupling agent possesses a microporous structure with bigger pore size and uneven micropores. In comparison, it can be seen from Fig. 6 (b) that the PAHM with 1% coupling agent maintains its microstructure; nevertheless, the micropores tend to be diminished and distributed evenly. Fig. 6(c) and (d) are the SEM images of the PAHM cross-section without coupling agent and with 1% coupling agent, respectively. As shown in Fig. 6(c), the cross-section of the PAHM without coupling agent has part macropores. However, it can be seen from Fig. 6(d) that the cross-section of PAHM with 1% coupling agent

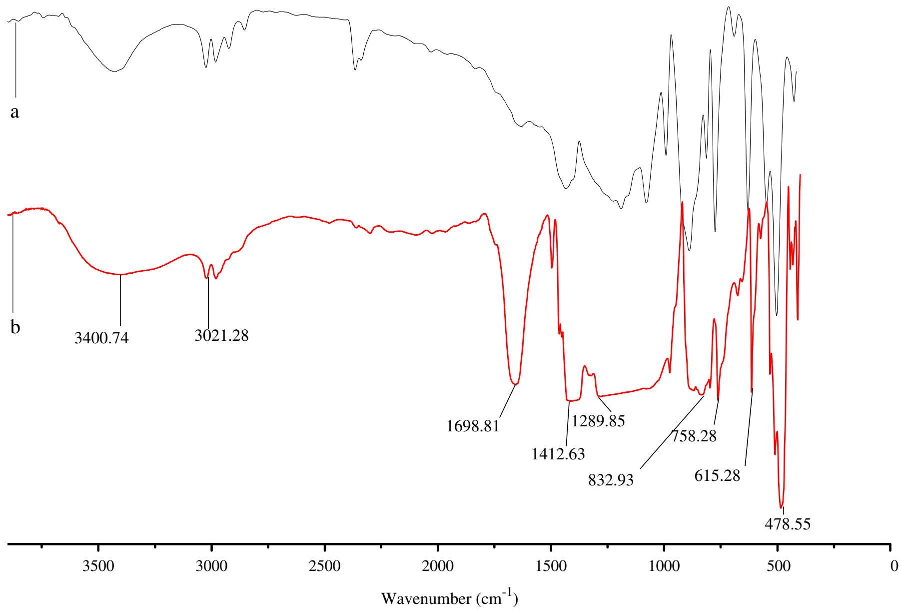


Fig. 5. FT-IR spectra of modified PVDF (a) and modified PAHM (b).

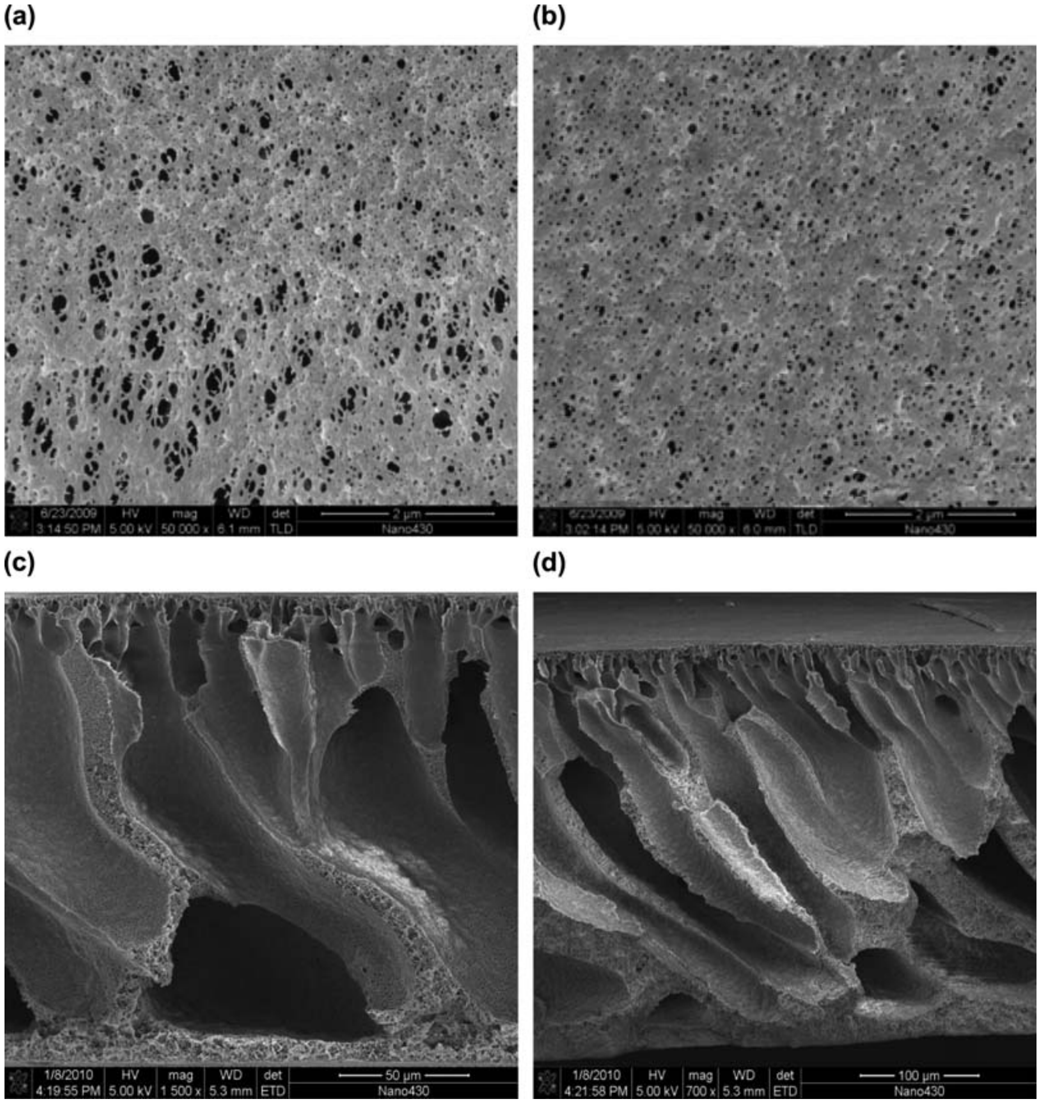


Fig. 6. SEM images of the surface and fracture structures of PAHM.

has long and thin holes and regular shape of pore lumen, and the connectivity among pores is relatively higher. These phenomena demonstrate that coupling agents play an important role in the increase of the interphase compatibility.

Table 1 presents several properties of membrane with 1% coupling agent. After adding coupling agent, the average pore size and water flux of PAHM decreased, but the rejection rate increased, which are corresponding to the SEM images of the surface and cross-section structures of PAHM. This is probably because the coupling agent can promote the consistency of inorganic and organic phases, which is helpful for the nanometer particles to evenly disperse in the PVDF polymer. Several researches have demonstrated that the coupling agent is the main factor that affects the quantity, particle size, distribution, and dispersity of inorganic particles; it can enhance the compatibility and consistency of inorganic and organic phases [31,32].

Table 1
Effect of coupling agent on membrane characteristics

Membrane sample	Without coupling agent	With 1% coupling agent
Water flux ($L\,h^{-1}\,m^{-2}$)	3,102	1,982
Rejection rate (%)	28	95
Average pore size (μm)	0.105	0.053
Porosity (%)	87	85

3.4. Aggregation of modified PAHM with alkali-coupling agent

Fig. 7 presents the AFM images of the hybrid membranes with different AIP contents. As shown in Fig. 7(a), we can hardly see isolated Al_2O_3 particles as the organic phase were mutually cross-linking with the inorganic phase. As the content of the AIP increase to 8 wt%, we can see from Fig. 7(b) that the Al_2O_3 of small particle size and PVDF formed an interpenetrative net structure. As the content of the AIP reach 16 wt%, the size of the inorganic particles became bigger, and the spherical Al_2O_3 particles formed a sheet of continuous net structure with PVDF permeating in the polymer and aggregation of inorganic particles becomes larger.

3.5. Mechanical properties of alkali-coupling agent modified PAHM

The effects of the contents of AIP and coupling agent on the mechanical properties of modified PAHM are shown in Fig. 8. The elongation at break and tensile strength initially increased with the increase of AIP addition and then declined as the AIP concentration was further increased. At the peak value, when the AIP concentration was 10%, the elongation at break and tensile strength reached the maximums. In the process of the formation of Al_2O_3 by sol–gel polymerization of AIP, there were interactions between Al_2O_3 and PVDF. Al_2O_3 could act as a cross-linking point in PAHM to link the polymeric chains [33] and increase the rigidity toughness of polymeric chains, and thereby produce an improvement in the elongation at break and tensile strength. But a higher content of the nanoparticles leads to a higher density of accumulation, which makes the hybrid membrane crisp and results in bad mechanical properties. In addition, both the elongation at break and tensile strength of the PAHM with coupling agent were higher than those without coupling agent; this is because the chemical bonds were formed between Al_2O_3 and PVDF with the coupling agent adding into the PAHM. This can improve the interaction of

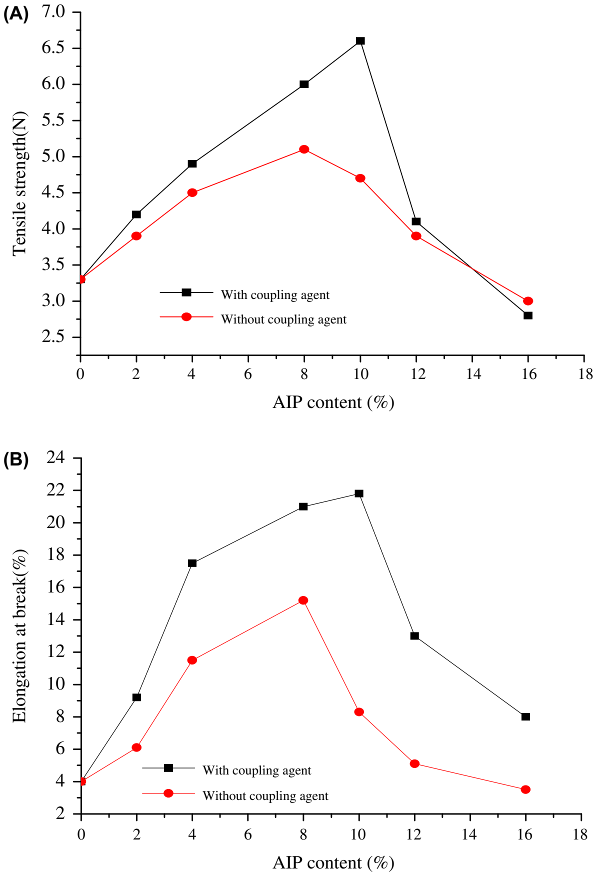
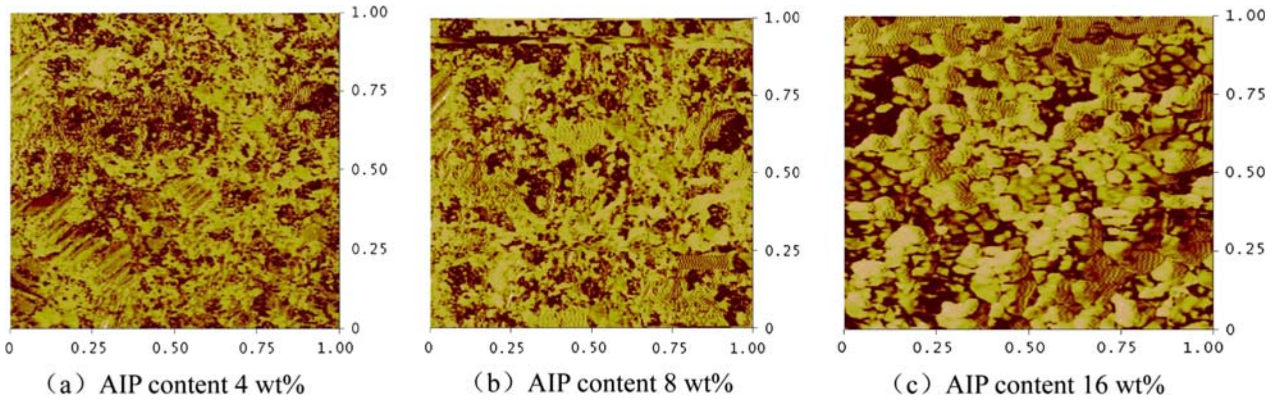


Fig. 8. Effect of coupling agent on mechanical properties of PAHM with different AIP contents.



（a）AIP content 4 wt%　（b）AIP content 8 wt%　（c）AIP content 16 wt%

Fig. 7. AFM images of modified PAHM with different AIP contents.

inorganic and organic compositions. These results also accommodate with the SEM images.

3.6. Antifouling property of alkali-coupling agent modified PAHM

Membrane fouling causes the permeation flux to decline drastically and flux reduction coefficient of membranes is one of the important indicators for membrane fouling. Table 2 illustrates the flux change for PVDF and PAHM using pure water and BSA solution as feeds, respectively. As shown in Table 2, when compared with pure PVDF membrane, the flux reduction coefficient of PAHM prepared by the alkali-coupling agent method declined from 45 to 27%, which indicates that the antifouling performance of membrane improved markedly. The main mechanism of membrane fouling is thought to be caused by undesirable formation of deposits on membrane surfaces [34,35]. A hydrophobic membrane surface formed due to better hydrophilicity of Al_2O_3 in PAHM inhibited the adsorption of deposits and caused the formed deposits to easily fall off, and hence greatly improved the membrane antifouling ability.

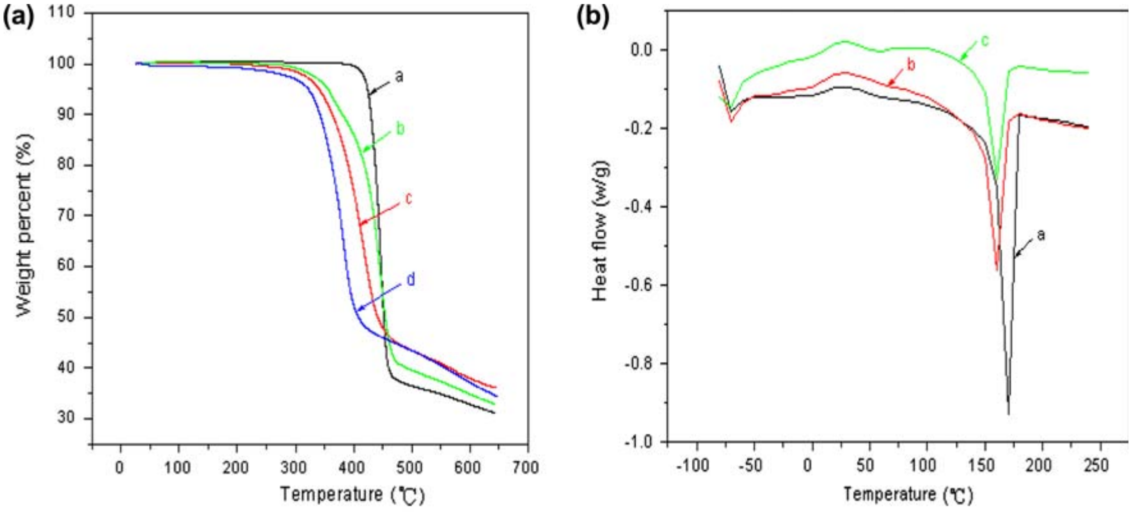
Table 2
The flux reduction coefficient of pure PVDF membrane and modified PAHM

Sample	Pure PVDF membrane	Modified PAHM
Initial flux ($L\,h^{-1}\,m^{-2}$)	1,746	3,580
Contamination flux ($L\,h^{-1}\,m^{-2}$)	956	2,630
The flux attenuation coefficient (%)	45	27

3.7. TGA and DSC analysis

The thermostability of PVDF, modified PVDF, modified PAHM, and pure PVDF membrane were measured by TGA and their thermogravimetric curves are presented in Fig. 9(a). The temperature of thermal decomposition moved to a lower temperature after the modification of PVDF. This is because there is the C=C double bond formed by the removal of HF after PVDF is modified by alkali. The temperature of thermal decomposition of modified PAHM was lower than that of pure PVDF membrane. It is mainly because the adding of inorganic particles weakens the interaction of high polymer chains.

The DSC curves for the pure PVDF membrane, modified PVDF membrane, and modified PAHM are revealed in Fig. 9(b). Compared with the pure PVDF membrane, the melting point of modified membrane slightly decreased and the molten enthalpy dropped obviously, which indicates the crystallinity decrease of modified PVDF. This is because the symmetrical structure on main chain formed double bond and triple



(a) PVDF
(b) Modified PVDF
(c) Pure PVDF membrane
(d) Modified PAHM

(a) Pure PVDF membrane
(b) Modified PVDF membrane
(c) Modified PAHM

Fig. 9. TGA curves of modified PAHM and DSC curves of modified PVDF membrane.

bond structures after PVDF removed HF in the condition of alkalinity, which destroys the quondam degree of order of polymer, resulting in the decrease of crystallinity.

4. Conclusions

(1) The modified PAHM was prepared using the method of alkali-coupling agent modification. FT-IR spectroscopy proved that the C=C double bond and the hydrophilic groups, such as hydroxyl group and carboxyl group were successfully introduced to the modified PVDF and PAHM, which enhances the chemical bond between PVDF and Al_2O_3 of the hybrid membrane, and hence greatly improved the mechanical properties and hydrophilicities of these membranes.

(2) The average pore size and the pure water flux decreased and the rejection rate significantly increased when PAHM was prepared with 1% coupling agent.

(3) Along with the increase in the AIP concentrations, the tensile strength and elongation at break of PAHM gradually improved, and both of them have a reduction when AIP concentration reached to 10% by weight.

(4) Comparing to the pure PVDF membrane, the flux attenuation coefficient of PAHM prepared via alkaline modification and chemical coupling process, declined from 45 to 27%, which means the antifouling performance of membrane improved markedly.

Acknowledgments

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