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Preparation of Al_2O_3/PU/PVDF composite membrane and performance comparison with PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane

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ABSTRACT

In this study, Al_2O_3/polyurethane/polyvinylidene fluoride (Al_2O_3/PU/PVDF) composite membrane was prepared via the thermally induced phase separation process. Pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane were also prepared for comparison. These membranes were characterized by means of contact angle test, mechanical properties test, Fourier transform infrared (FT-IR) spectroscopy, atomic force microscopy (AFM), and differential scanning calorimetry (DSC). In addition, the separation performance of membranes was evaluated in terms of water flux and rejection ratio. The results showed that the Al_2O_3/PU/PVDF composite membrane had better hydrophilicity and mechanical properties compared with pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane. FT-IR test confirmed the introduction of the hydrophilic groups, such as hydroxyl and carbonyl, which are responsible for the enhancement of the hydrophilicity of Al_2O_3/PU/PVDF composite membrane. The AFM results showed that the Al_2O_3/PU/PVDF composite membrane had the lowest roughness, manifesting its improved anti-fouling properties. Furthermore, DSC results revealed that the crystallinity of PVDF polymer matrix decreased with the introduction of the functionalized Al_2O_3 nanoparticles.

Keywords: PVDF; PU; Hydrophilicity; Organic–inorganic composite membrane; AFM

1. Introduction

Polyvinylidene fluoride (PVDF) is one of the most extensively used membrane materials in water treatment due to its excellent stability and membrane-forming properties [1–3]; therefore, it is widely used in the manufacturing of microfiltration, ultrafiltration (UF), nanofiltration, reverse osmosis, and pervaporation membranes. However, its strong hydrophobic properties, resulting in severe membrane fouling and declined permeability, has limited its wide applications in water treatment, even some areas of food industry [4–6]. Consequently, several strategies, such as physical blending, chemical grafting, and surface modification, have been devoted to enhancing the hydrophilicity and anti-fouling properties of PVDF membranes [7–9].

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In order to increase the hydrophilicity of PVDF membrane, 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. For example, polyurethane (PU) is a kind of hydrophilic high-molecular polymer. Several advantages of PU, such as high strength, anti-abrasion and excellent mechanical properties, and plenty of hydrogen bonds, make it an extraordinary modification material in the preparation of PVDF membranes [10–12]. However, the addition of organic hydrophilic materials, even PU, usually reduces membrane strength [13–17]. Recent studies on hydrophilic modification of PVDF mainly focused on blending some inorganic materials such as zirconium dioxide [18], alumina [19], titanium dioxide [20], and lithium salts [21]. In particular, Al_2O_3 nanoparticle is one of the most promising candidates for the hydrophilic modification of PVDF membrane because of its high affinity to water [22]. Nevertheless, limited reports are available on the preparation of Al_2O_3-based composite membranes with PU.

In this work, ternary component composite Al_2O_3/PU/PVDF composite membrane was prepared via thermally induced phase separation (TIPS) process. In the meantime, pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane were also prepared via the method of TIPS, and the properties of these four kinds of membranes were compared with each other.

2. Materials and methods

2.1. Materials and equipments

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

Vector 33 Fourier transform infrared (FT-IR) spectrometer from Bruker Company (Germany) was used for FT-IR analysis. AGS-10 KNI Universal Electronic Tensile Tester from Jin Island Company (Japan) was used for the mechanical properties test. Contact angle test of membranes was carried out using OCA15 Surface Contact Angle Meter from Dataphysics Company (Germany). Differential scanning calorimetry (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 Al_2O_3/PU/PVDF composite membrane

PVDF was dissolved into DMAc and DMP mixing solvent to prepare the casting solution; then, the defined amount of AIP and different concentrations of PU were put into it. 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. After exposed in air for 15 s, the membrane prepared on glass was immediately immersed into the deionized water for 5–7 d and the Al_2O_3/PU/PVDF composite membrane was obtained. And the preparation of pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane can refer to our previous research [23–25].

2.3. Characterization of membranes

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 (J, L m^{-2} h^{-1}) at 25°C was calculated by the following equation:

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

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

2.3.2. Rejection ratio

The same unit was fed with BSA at 0.1 MPa of 15–30 min in order to obtain the membrane rejection ratio. The BSA concentration in permeation solution and bulk solution were tested by a spectrophotometer. The rejection ratio (R, %) was obtained by the following formula:

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

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

2.3.3. Anti-fouling property test

To study the anti-fouling property of the membranes, the change of water flux as a function of time was recorded and the attenuated coefficient m was calculated as follows:

$$m = (1 - J_2/J_1) \times 100\% \quad (3)$$

where J_1 and J_2 are the pure water fluxes before and after filtering BSA solution, respectively.

2.3.4. 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. 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.

2.3.6. FT-IR characterization

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

2.3.7. Atomic force microscopy analysis

The surface roughness of membrane indicates the difference of surface morphology, which has a significant effect on the membrane 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 microscopy (AFM).

2.3.8. DSC test

The melting point of membranes 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 l0℃/min starting from −50℃, 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 $p < 0.01$ or 0.05 by analysis of variance followed by Duncan's least significant test.

3. Results and discussion

3.1. Effect of AIP content on the permeability performance of Al_2O_3/PU/PVDF composite membrane

The pure water flux and the BSA rejection ratio of Al_2O_3/PU/PVDF composite membranes with different concentration of AIP are shown in Table 1. As can be seen in Table 1, the permeability of the Al_2O_3/PU/PVDF composite membrane initially increased and then decreased with the increasing AIP content, resulting in maximum values at the AIP content of 8%, which are 842 L h^{-1} m^{-2} of pure water flux and 84.4% of rejection ratio, respectively. The p-value test for the results was highly significant ($p < 0.01$), which indicated that the pure water flux and the BSA rejection ratio of PVDF membranes were highly significant based on AIP content. Compared with the membrane without AIP, the pure water flux and the BSA rejection ratio increased 196% and 24%, respectively. This result could be due to the enhancement on the hydrophilicity of the membranes with the addition of AIP. However, when the AIP concentration exceeded the limitation, the Al_2O_3 nanoparticles would form large aggregates to block the pores of the membranes, resulting in decreases in the flux.

3.2. Hydrophilicity of membranes

The contact angle, which can affect the flux and anti-fouling ability of membrane, 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, as can be seen in Table 2, the contact angle of membrane with PU was significantly lower than that without PU, and

Table 1
Permeability performance of Al_2O_3/PU/PVDF composite membrane*

AIP content (%)	Pure water flux (L m^{-2} h^{-1})	Rejection ratio (%)
0	284 ± 12[a]	68.6 ± 1.6[a]
4	563 ± 27[b]	79.0 ± 0.9[b]
8	842 ± 44[c]	84.1 ± 0.7[c]
12	678 ± 41[d]	83.5 ± 1.1[c]

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

Table 2
Effects of PU on the hydrophilicity of membrane*

PU contents (%)	Contact angle (°)
0	85.80 ± 2.55[a]
0.5	72.55 ± 1.26[b]
1	70.42 ± 2.21[c]
2	66.45 ± 2.60[d]
4	66.33 ± 1.56[d]

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

with the increase of PU contents, the contact angle of blending membranes decreases continuously, that is to say, the hydrophilicity of membranes was increased gradually, we can say 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 ($p > 0.05$). In the mean time, the contact angles of pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PU/PVDF composite membrane in their optimal processes were also determined. The contact angle of pure PVDF is 85.80°, while PU/PVDF and Al_2O_3/PU/PVDF membrane have contact angles of 66.51° and 64.62°, respectively. The Al_2O_3/PU/PVDF composite membrane appeared to be more hydrophilicity than pure PVDF membrane, which was consistent with our previous work in our laboratory [23,24]. It can also be inferred from Table 3 that the enhancement of the hydrophilicity is due to the addition of PU.

3.3. Mechanical properties of membranes

The mechanical properties of four kinds of membranes in their optimal processes, including tensile strength and elongation-at-break, are listed in Table 4. Compared with the pure PVDF membrane, the PU/PVDF blending membrane had slightly higher tensile strength and elongation-at-break, while the Al_2O_3/PVDF membrane had lower tensile strength but much larger elongation-at-break. This could be explained by two aspects. On the one hand, the introduction of AIP was favorable for the formation of the finger-like pore in the membrane support surface, resulting in decrease in the tensile strength of the membrane. On the other hand, nano-Al_2O_3 particles possess high mechanical strength which could enhance the mechanical properties of the membrane. It is worth noting that the Al_2O_3/PU/PVDF composite membrane had the largest tensile strength and elongation-at-break as shown in Table 4. This could be due to the presence of PU, which served as a coupling agent and significantly improved the compatibility between the inorganic filler Al_2O_3 and polymer matrix (PVDF). The force exerted on the polymer matrix could be well

Table 3
Hydrophilicity of three kinds of membranes in their optimal process*

Membranes sample	Contact angle (°)
Pure PVDF	85.80 ± 2.12
PU/PVDF	66.51 ± 1.65
Al_2O_3/PU/PVDF	64.62 ± 2.42

*The data are expressed as means ± SD with triplicates.

Table 4
Mechanical properties of the membranes*

Membranes sample	Tensile strength	Elongation-at-break (%)
Pure PVDF	5.3 ± 0.3[a]	6.4 ± 0.6[a]
PU/PVDF	5.5 ± 0.5[b]	9.6 ± 0.8[b]
Al_2O_3/PVDF	4.7 ± 0.6[c]	49.3 ± 0.5[c]
Al_2O_3/PU/PVDF	7.8 ± 0.2[d]	51.1 ± 0.9[d]

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

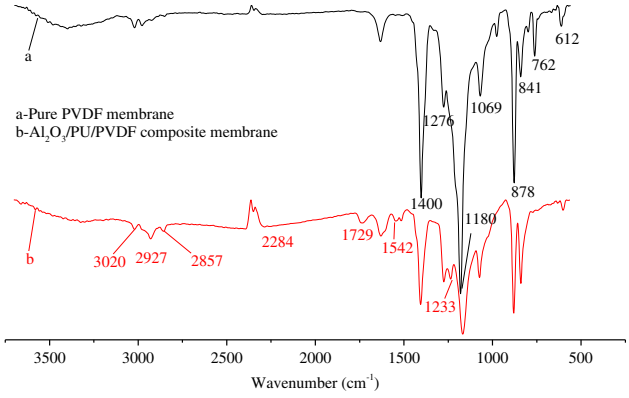

Fig. 1. FT-IR spectra of pure PVDF membrane and Al_2O_3/PU/PVDF composite membrane.

transferred and consumed by the inorganic filler, resulting superior tensile strength and large elongation-at-break.

3.4. FT-IR analyses

Under the 50°C, the PVDF, PU powder, pure PVDF membrane, and the Al_2O_3/PU/PVDF composite membrane were vacuum-dried for 3–4 h. The FT-IR of membranes was analyzed using a FT-IR spectrophotometer, respectively, and the chemical structure was determined. As shown in Fig. 1, it could be found that the characteristic absorption peaks of PVDF at 1,276, 1,180, 1,069, and 841 cm^{-1} were also presented in the spectra of the Al_2O_3/PU/PVDF composite membrane. This indicated that the structures of the PVDF were well preserved. By the comparison of the spectra of PVDF membrane and Al_2O_3/PU/PVDF composite membrane, the peaks at 2,857, 2,927, and 3,020 cm^{-1} were observed in the latter, which were assigned to –OH group. In addition, the peak at 1,729 cm^{-1} could be assigned to C=O double bond, which was also a new peak in Al_2O_3/PU/PVDF composite membrane.

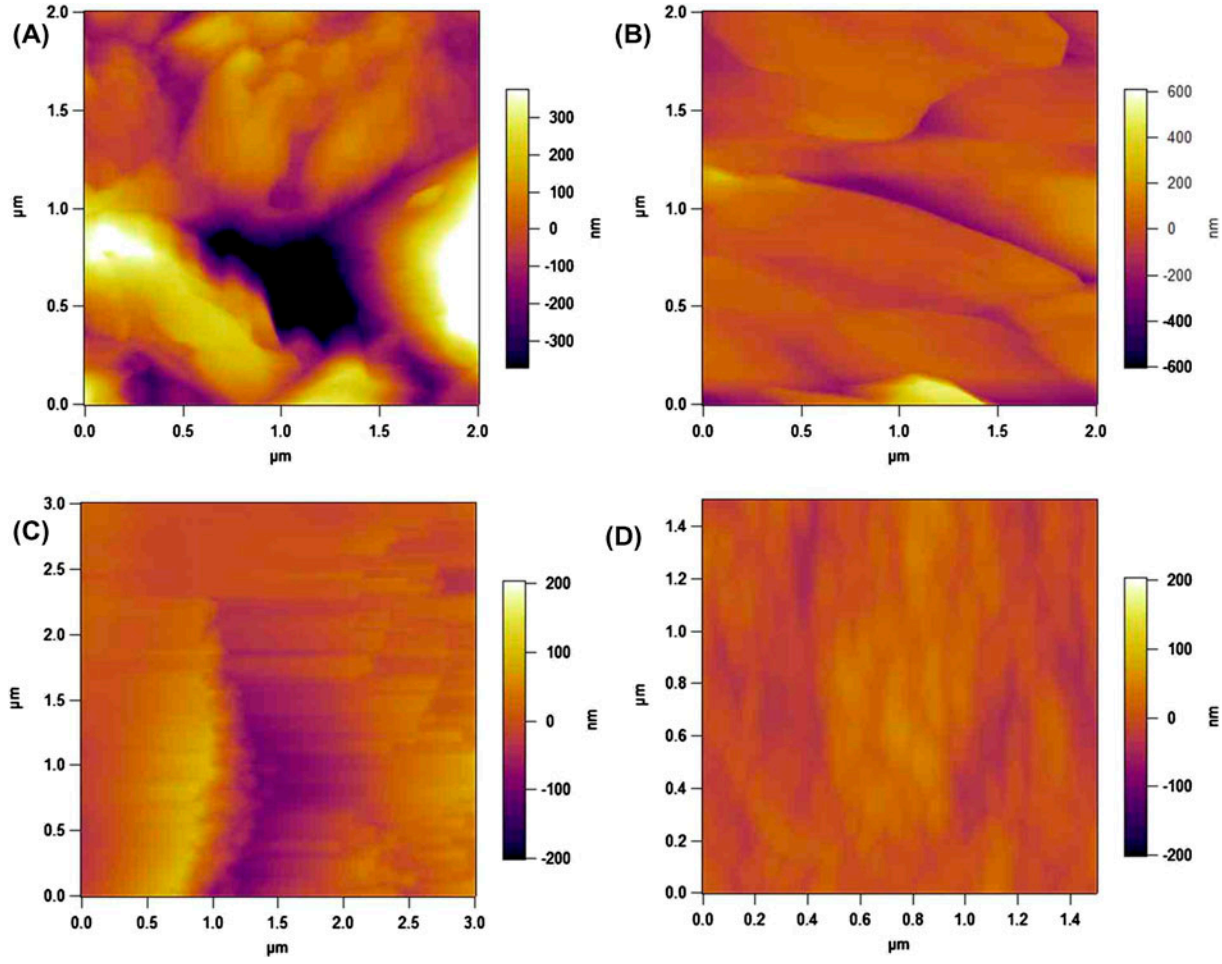

Fig. 2. AFM images of (A) pure PVDF membrane, (B) PU/PVDF blending membrane, (C) Al_2O_3/PVDF hybrid membrane, and (D) Al_2O_3/PU/PVDF composite membrane.

The FT-IR results indicated that some hydrophilic groups such as hydroxyl group, carbonyl group, and aldehyde were formed with the addition of PU and AIP, which was consistent with the contact angle results.

3.5. AFM results

Fig. 2 shows the AFM images of the four membranes. The surface roughness of the membrane was determined accordingly. Apparently, the Al_2O_3/PU/PVDF composite membrane was smoother than PU/PVDF and Al_2O_3/PVDF membrane. The Al_2O_3/PU/PVDF composite membrane had a roughness of 5 nm, while the pure PVDF membrane has a roughness of 228 nm. In general, a low roughness value of the membrane leads to a decrease in efficient filtration area, but an increase in anti-fouling performance of the membrane [22]. Three-dimensional AFM images of the four membranes were also shown in Fig. 3. It was further demonstrated that the membranes with PU (Fig. 3(B) and (D)) were smoother than those without PU (Fig. 3(A) and (C)). This could be due to the fact that PU could crosslink Al_2O_3 and PVDF or fuse itself together with PVDF.

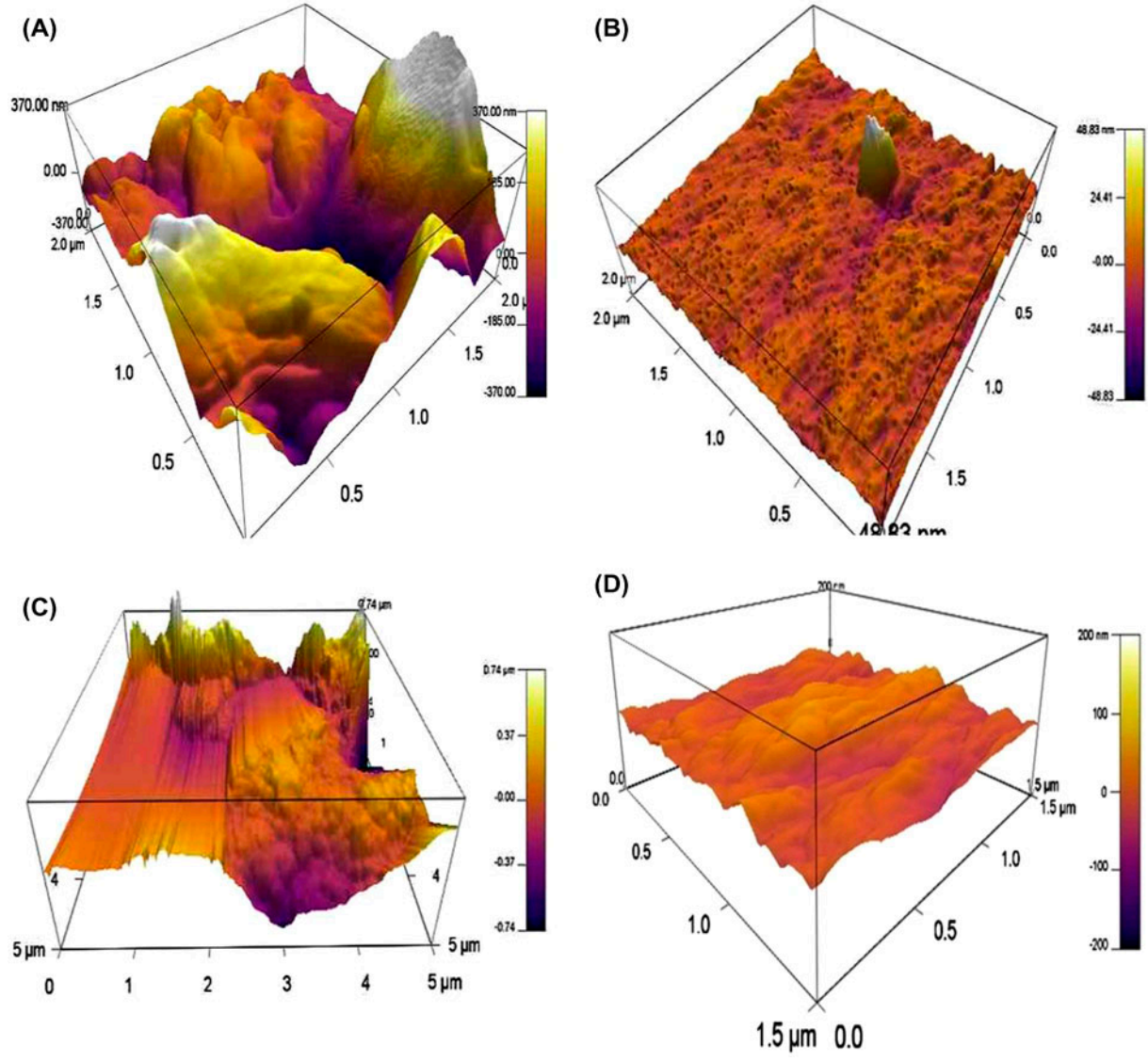

Fig. 3. Three-dimensional AFM images of (A) pure PVDF membrane, (B) PU/PVDF blending membrane, (C) Al_2O_3/PVDF hybrid membrane, and (D) Al_2O_3/PU/PVDF composite membrane.

3.6. Anti-fouling properties of the membranes

It was known that membrane fouling could result in permeability decline and shorten the membrane lifespan. To evaluate the anti-fouling properties of membranes, the initial flux, contamination flux, and the flux attenuation coefficient were calculated as shown in Table 5. The Al_2O_3/PU/PVDF composite membrane had a lower flux attenuation coefficient of 28.21% as compared with the three other membranes, that is, the pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membrane, indicating that the Al_2O_3/PU/PVDF composite membrane had better anti-fouling properties. The membrane fouling is mainly due to the formation of deposits on membrane surface and is closely related to the roughness of external membrane surface [26,27]. The smooth surface of the Al_2O_3/PU/PVDF composite membrane resulted in the low penetration coefficient and the better anti-fouling properties.

3.7. DSC analysis

The DSC curves of the pure PVDF, PU/PVDF, and Al_2O_3/PU/PVDF membrane are shown in Fig. 4. The melting point and molten enthalpy of the Al_2O_3/PVDF hybrid membrane were measured to be 170.7°C and 47.5 J/g, respectively, [24] as reported in our previous work. Compared with the pure PVDF and PU/PVDF membrane, Al_2O_3/PU/PVDF composite membrane had the lower melting point. It should also be noted that the Al_2O_3/PU/PVDF composite membrane exhibited lower molten enthalpy, which indicated the decrease of crystallinity in the Al_2O_3/PU/PVDF composite membrane. This is due to the formation of the interpenetrated network structure between the inorganic Al_2O_3 and polymer chains in the Al_2O_3/PU/PVDF composite membrane. The Al_2O_3 particles were uniformly dispersed into the polymer matrix, which could interrupt the polymer chain packing and subsequently resulted in the decrease of crystallinity.

Table 5
Anti-fouling properties of the membranes*

Membrane sample	Initial flux ($L\ m^{-2}\ h^{-1}$)	Contamination flux ($L\ m^{-2\ -1}$)	Flux attenuation coefficient (%)
Pure PVDF	284 ± 12	152 ± 30	46
PU/PVDF	846 ± 21	575 ± 26	32
Al_2O_3/PVDF	882 ± 25	526 ± 41	40
Al_2O_3/PU/PVDF	1,028 ± 42	738 ± 33	28

*The data are expressed as means ± SD with triplicates.

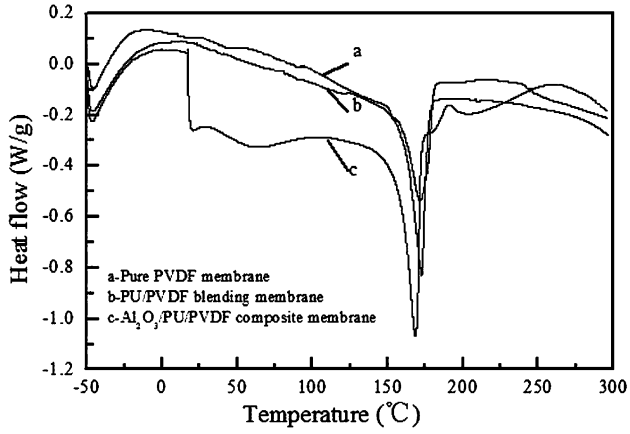

Fig. 4. DSC curves of the membranes.

4. Conclusions

Al_2O_3/PU/PVDF composite membranes were prepared by thermally induced phase inversion separation process. The introduction of the AIP and PU into polymer casting solution greatly affected the properties of the composite membranes. Based on this study, it can be concluded as follows:

(1) Al_2O_3/PU/PVDF composite membranes exhibited better hydrophilicity and mechanical properties compared with the pure PVDF membrane, PU/PVDF blending membrane, and Al_2O_3/PVDF hybrid membranes. The Al_2O_3/PU/PVDF composite containing 2 wt.% of PU had the excellent separation performance.
(2) FT-IR results confirmed that the hydrophilic groups, such as carbonyl and hydroxyl group, were successfully introduced in Al_2O_3/PU/PVDF composite membranes, which greatly improved mechanical properties and hydrophilicity, as indicated by the decrease in the contact angle.
(3) The roughness of the Al_2O_3/PU/PVDF composite membrane was measured to be 5 nm which was much lower than that of PU/PVDF blending membrane and Al_2O_3/PVDF hybrid membrane. It can be confirmed that the Al_2O_3/PU/PVDF composite membrane had better anti-fouling properties.
(4) DSC results indicated that the melting point of Al_2O_3/PU/PVDF composite membrane slightly decreased and that the molten enthalpy significant decreased, indicating the decrease of crystallinity in Al_2O_3/PU/PVDF composite membrane.

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