Preparation of hydrophobic PVDF/PVC/nano-graphite composite membrane and its self-cleaning properties

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Abstract
In this study, novel physical blending modified membranes are prepared using the non-solvent induced phase separation method, the influences of nano-graphite and Poly(vinyl chloride) (PVC) incorporated into the hydrophobic performance of the polyvinylidene fluoride (PVDF) membrane were investigated. The composite membrane was prepared not only reduces the cost of producing PVDF membrane, but also enhances the hydrophobicity of the membrane. The addition of nano graphite and PVC accelerated the phase transformation of PVDF and changed the crystal structure of PVDF. Therefore, the surface roughness of the composite membrane is changed, and the hydrophobicity of the composite membrane is enhanced compared with the original PVDF membrane. The crystal structure and crystallinity of the composite membranes can be analyzed by WAXD and DSC, the surfaces morphology of the composite membranes were characterized by SEM and AFM, the wetting and hydrophobicity of the composite membrane by CA and SFE. The experimental results show that adding a small amount of nano inorganic substance (nano graphite) to the (PVDF-PVC) blend polymer is an effective method to prepare and improve the hydrophobic performance of the blend polymer membrane. The PVDF-PVC/nano-graphite prepared in the experiment not only improves the hydrophobic performance of the PVDF membrane, but also reduces the cost of the composite membrane through the addition of PVC. Meanwhile, the membrane has a durable self-cleaning performance, which widens the applications of PVDF membranes.

1. Introduction
Poly (vinylidene fluoride) (PVDF) microfiltration and ultrafiltration membranes have been widely used in water treatment. As a promising material for ultrafiltration, microfiltration, and membrane distillation\textsuperscript{[1, 2]}, PVDF has drawn much attention for its excellent chemical resistance, well-controlled porosity, good thermal stability and favorable mechanical properties\textsuperscript{[3]}. Furthermore, PVDF membranes were prepared by simple and applicable NIPS method, which can be well regulated and controlled the pore structure and hydrophobic properties of the PVDF membranes\textsuperscript{[4]}. However, high cost and poor hydrophobicity limit their application. In order to improve the hydrophobicity of the PVDF membrane, a large number of studies have been reported by domestic and foreign researchers on the PVDF membrane.

Poly(vinyl chloride) (PVC) membranes were widely used in ultrafiltration due to excellent chemical resistance and good thermal stability and favorable mechanical, physical properties\textsuperscript{[5]}. PVC membranes always attract lots of attention due to all these properties in water treatment. Furthermore, PVC is one of the most industrialized materials with inexpensive, excellent properties and long use lifespan, whose industry is developed rapidly in the world and prospect is rather bright\textsuperscript{[6]}. Although PVC has many advantages as a
material for membranes, the poor hydrophobicity is the major drawback which limits their application in water treatment [7].

To strong hydrophobic membranes, people mixing hydrophobic polymers, changing the composition of coagulation bath, grafting hydrophobic macromolecules, prepare hydrophobic coatings, and incorporate nanoparticles. The surface morphology and pore structure of the membrane was significantly changed by simply incorporating nanoparticles, such as silica, montmorillonite or clay nanoparticles, into the polymer materials, which enhanced the hydrophobicity of the membrane [8, 9]. Polymer blending was one of the effective ways to improve the hydrophobicity of membrane [10]. Qi Zhang et al. PVDF/PVC composite membrane was prepared by polymer blending. The effect of polymer ratio on the structure and properties of the membrane was studied. The results show that PVC content can affect the hydrophobicity of the composite [11]. Through the preparation of PVDF and PVC blend membrane, not only the hydrophobicity of PVDF membrane can be improved, but also the cost of PVDF membrane can be reduced. The application field of PVDF membrane is extended.

In this study, novel membranes are prepared via physical blending modification, the influences of nano-graphite incorporated into and polymers ratios on the hydrophobic performance of the composite membranes are investigated. The NIPS method to prepare PVDF/ PVC/nano-graphite composite not only reduces the cost of producing PVDF membranes but also improves the hydrophobicity of the membranes. Furthermore, through self-cleaning experiments, PVDF/PVC/nano-graphite membrane has a durable self-cleaning performance and has potential applications in membrane distillation, self-cleaning devices, and other fields.

2. Experimental

2.1. Materials

The PVDF polymer (Solef FR904) was purchased from Shanghai 3F New Materials Technology Co.(China). Dimethylformamide (DMF, >99.5%), PVC and graphite (>99.95% metals basis, ≥325mesh) was purchased from Aladdin reagent co., Ltd; China Deionized water was used as coagulation.

2.2. PVDF/PVC composite membranes preparation

PVDF polymer and PVC polymer were vacuum dried at 60 °C for 12 h before use. 12 wt% blend solution containing varied ratios of PVDF/PVC (w/w) was prepared by dissolving the blend in DMF with stirring for 24 h at 60 °C. The rations of blends are PVDF/PVC = 100:0, 95:5, 90:10, 85:15, 80:20, 70:30, 50:50, and 0:100. The polymer solution degassed for more than 24 h at room temperature.

PVDF polymer, PVC polymer and graphite were vacuum dried at 60 °C for 12 h before use. Different concentrations of nano-graphite (0, 0.1, 0.5, 1, and 2 wt%, which were marked as M-0, M-0.1, M-0.5, M-1, M-2 respectively) was first added into DMF by ultrasonic mixing for 2 h, and 12 wt% Blend solution PVDF/PVC (w/w = 85/15) (10.2 wt% PVDF and 1.8 wt% PVC) were dissolved into the above solution. The above solutions were stirred at 60 °C for 12 h, and then degassed at room temperature for more than 24 h.

Flat sheet composite membranes were prepared by the NIPS method. At room temperature, the degassed solution was cast on automatic membrane coater MEMCAST™ (Porometer Ltd, Belgium) of stainless steel plate with a knife gap of 100 μm.

The cast membrane was exposed in air for 30 s and then immersed in DMF/H2O(=6:4) coagulation bath for 24 h. Rinse with distilled water, then immerse in fresh distilled water kept for 24 h to remove residual solvents, and it was dried at air temperature. Finally, the membrane was dried at 60 °C for 12 h in a vacuum oven before use.

2.3. Membrane scanning electron microscopy (SEM) analysis

The surfaces morphology and the cross section (the fracture mode of liquid nitrogen is adopted) of the composite membranes were characterized by JSM-7100F field emission scanning electron microscopy (JEOL, JPN).

2.4. Membrane atomic force microscopy (AFM) analysis

The membrane surface roughness was measured by adopting AFM (atomic force microscopy, Nanosurf AG). The measurements were carried out with a silicon probe (Tap 190Al-G) over a 10 μm × 10 μm area at a scanning rate of 1 Hz. The collected data were analyzed using SPIP™ Analysis software and the root-mean-square roughness (Ra) for each sample was reported.
2.5. x-ray diffraction (XRD) and differential scanning calorimeter (DSC)

The crystal structure and crystallinity of the samples can be analyzed by wide-angle x-ray diffraction (WAXD). Its (Ultima IV, Rigaku, Japan) test condition were Cu Kα radiation source (0.154 nm), A 0.02 step in 2θ/count, beam voltage of 40 kV and beam current of 40 mA. The diffraction angles were recorded in the 2θ range 5° to 60° and the scanning speed was 3°/min.

The crystallinity can be determined by XRD diffraction curve and by peak-sharing program. Traces can be used for the peak-sharing and calculation. The software is a self-contained x-ray diffractometer. The calculation is based on the following formula:

$$X_c = \frac{S_l}{S_c + S_a} \times 100\%$$  \hspace{1cm} (1)

where $S_c$ is the integral area of amorphous peak and $S_a$ is the integral area of amorphous peak.

In high purity nitrogen atmosphere, the flow rate of carrier gas nitrogen is 20 ml min$^{-1}$. Samples of 9–12 mg membrane were cut and heated at 10 °C min$^{-1}$. The temperature was raised from 30 °C to 400 °C. The endothermic peak on DSC spectra was caused by melting of the crystalline part of the polymer. The enthalpy of the endothermic peak was related to the crystallinity. The crystallinity was calculated by formulas (2), (3).

$$\Delta H = \frac{S_l}{m} \times 100\%$$  \hspace{1cm} (2)

Where $m$ (g) is the mass of the polymer, $S_l$ (J) is the melting peak area of the polymer, and $\Delta H$ is the melting enthalpy (J/g) of the polymer.

$$X_p = \frac{\Delta H}{w \times \Delta H_m} \times 100\%$$  \hspace{1cm} (3)

Where $X_p$ is the crystallinity (%), $\Delta H$ is the melting enthalpy (J/g) of the polymer, $\Delta H_m$ is the standard enthalpy (J/g) of the fully crystallized polymer, and $\Delta H_m$ is the percentage of the polymer in the solid content, the standard enthalpy of PVDF is 104.7 J g$^{-1}$ [12].

2.6. Contact angle (CA) and surface free energy (SFE) analysis

To understand the wetting and hydrophobicity of the composite membrane, we measured the contact angle (CA) on the surface of the composite membrane. The CA of the membranes was measured by using the sessile drop method with CA goniometer (OCA15EC, Germany) integrated with SCA20 software at room temperature. The membrane samples were placed on a flat platform and 3 μl droplets of water, glycerol and diiodomethane were dripped onto the surface of the membrane. At least five measurements were measured at different locations of each membrane sample and an average value to get a reliable value. The wettability $g$ of the membrane surface can be expressed by CA, and the wettability of a solid surface can be expressed by CA, $\theta$, which is governed by Young’s equation: Young’s equation as follows.

$$\gamma_s = \gamma_{SL} + \gamma_L \cos \theta$$  \hspace{1cm} (4)

Where $\gamma_s$, $\gamma_{SL}$ and $\gamma_L$ represents the surface tensions between solid membrane(m) and air, between solid membrane and liquid(L), between liquid and with air, respectively.

The method of Lifshitz-van der Waals/acid-base (LW/AB) was adopted. The surface free energy (SFE) of the membrane surface can be obtained by CA. Using Lifshitz van der wall (non-polarity) and Lewis acid-base (polarity) measurements, three probe solutions water in polar solution, glycerol in polar solution and diiodomethane in non-polar solution (water surface tension $\gamma = 72.80$ mN m$^{-1}$, glycerol surface tension $\gamma = 64.00$ mN m$^{-1}$ and diiodomethane surface tension $\gamma = 50.80$ mN m$^{-1}$), The initial CA on the prepared membrane was determined respectively [13].

The total SFE (mN m$^{-1}$) of a membrane was calculated by equations (5), (6):

$$\gamma_{m}^T = \gamma_{m}^{LW} + \gamma_{m}^{AB}$$  \hspace{1cm} (5)

$$\gamma_{m}^{AB} = 2\sqrt{\gamma_{m}^{L} \gamma_{m}^{W}}$$  \hspace{1cm} (6)

Where $\gamma_{m}^{T}$ indicates the total SFE of the membrane, $\gamma_{m}^{LW}$ indicates the Lifshitz-van der Walls interactions of the membrane (dispersive component), $\gamma_{m}^{AB}$ indicates the acid-base interactions of the membrane (polar component), $\gamma_{m}^{L}$ and $\gamma_{m}^{W}$ are the electron–acceptor and electron–donor components of the solid surface tension, respectively.

$$\gamma_L (1 + \cos \theta) = 2(\sqrt{\gamma_{m}^{LW} \gamma_{m}^{LW}} + \sqrt{\gamma_{m}^{L} \gamma_{m}^{W}} + \sqrt{\gamma_{m}^{L} \gamma_{m}^{W}})$$  \hspace{1cm} (7)

Where $\gamma_{m}^{LW}$ indicates the Lifshitz–van der Waals interactions of the liquid; $\gamma_{m}^{L}$ and $\gamma_{m}^{W}$ refer to the electron–acceptor and electron–donor components (indicating acid–base interactions) of the liquid surface tension, respectively.
The calculation of all components of the total SFE of a Polymer ($\gamma_{m}^{LW}$, $\gamma_{m}^{L}$, and $\gamma_{m}^{S}$) is possible when equation (7) is applied for three liquids with known values of $\gamma_{m}^{LW}$, $\gamma_{m}^{L}$, and $\gamma_{m}^{S}$, which can be obtained from the database of goniometer SCA20, and thus the total SFE can then be computed using equations (5), (6).

3. Results and discussion

3.1. FE-SEM of the composite membrane
Study of morphological changes associated with the nano-graphite addition of PVDF/PVC membrane. The surface and cross-sectional morphologies of the prepared membranes were taken imaged by SEM, as shown in figure 1.

The surface was the PVDF/PVC membranes. It was dense with no visible pores. Compared with the original PVDF/PVC membrane (M-0), addition of nano-graphite increased the surface roughness of the membrane, especially when the concentration of nano-graphite is more than 1 wt%. It was reported that the addition of graphene could increase the surface roughness of PVDF membranes.

It was reported that as a semi-crystalline polymer, PVDF precipitation in the phase-in-version process is controlled by both liquid-liquid demixing and solid-liquid demixing accompanying with crystallization the interlinked spherulitic structure [14]. However, it was found from the SEM result shows that And the that with adding PVC in the PVDF membrane, the PVDF/PVC (85:15) composite membranes had unapparently interconnected pellet structure, and the surface formed a macroporous structure with a small number of microspheres.

When the mass concentration of nano-graphite is less than 0.5%, the surface pore size and pore density decreased with increasing amounts of nano-graphite; But with continues to increasing amounts of nano-graphite, the surface pore size and pore density gathering force and the surface structure becomes open and loose. The gaps on the surface were the biggest in the case of M-2 ((figures 1(m) and (n)) and the size were around 5–30 μm.

As seen in the cross-sectional images, the membrane consists of macroporous and spongy porous layers from top to bottom. With the addition of graphene, the macrowood structure extended. The formation of macropores may be attributed to the good compatibility between the solvent (DMF) of the membrane and the solvent (H$_2$O) of the coagulation bath when the membrane was immersed in the coagulation bath. The mutual diffusion speed of the solvents is very fast and the instantaneous exchange occurs [15].

Based on the surface and cross-section SEM images, The composite membrane is spongy, porous and unapparently interconnected pellet structure. Compared with the original PVDF/PVC membranes (M-0), the surface roughness of nano-graphite has a certain change. The surface roughness of nano-graphite changed to a certain extent. The surface pore size and pore size density first decreased and then increased with the increase of nano-graphite. When the concentration of nano-graphite was higher than 1% wt%, the traces of nano-graphite could be clearly seen on the surface of the membrane. As a result, the sponge porous features was obtained for the PVDF/PVC/nano-graphite composite membrane.

3.2. AMF of the composite membrane
The roughness of membranes surfaces was shown in figure 2. Consistent with the SEM, the surface roughness of nano-graphite changed to a certain extent. The surface roughness density first increased and then decreased with the increase of nano-graphite. The average surface roughness values (Ra), which were quantified over a 10 μm × 10 μm samples, were 224, 290, 352, 425, 202 nm for M-0, M-0.1, M-0.5 M-1, and M-2, respectively. The addition of graphene induced the emergence of irregular particulates out of the surface, when the concentration of nano-graphite was higher than 1 wt%, the traces of nano-graphite could be clearly seen on the surface of the membrane.

3.3. XRD and DSC of the composite membrane
The PVC is an amorphous compound and has no peak on the XRD curve, so the XRD diffraction pattern of the PVDF/PVC membrane shows only the peak of the crystalline polymer PVDF. Figure 3(0) shows the XRD diffraction patterns of the PVDF/PVC membrane. For pristine PVDF/PVDF (PVDF) membrane, the diffraction peaks at 18.5°, 20.1° and 22.9 °(2θ), which corresponded to γ-form of PVDF [16]. For the PVDF/PVC/nano-graphite composite membranes, the peak of 18.5° shifted to 18.3°, the peak of 20.1° shifted to 19.9°and the peak of 22.9° shifted to 22.7° two new peak at 26.56° and 26.58° appeared. The peak of 18.3° and 19.9° and 26.56° were the characteristic peaks of α-form of PVDF [9]. The peak of 26.58° were the characteristic peaks of nano-graphite. Figure 3 shows the XRD diffraction patterns of the PVDF/PVC/nano-graphite membrane. The diffraction peaks of nano-graphite and PVDF/PVC were compared. The integral area of the nano-graphite diffraction peak is obviously higher than that of PVDF/PVC diffraction peaks, which indicates that there is no
obvious crystallization of PVDF/PVC. Moreover, the integral area of the nano-graphite diffraction peak increased with the increase in the nano-graphite concentration. Therefore, the incorporation of nano-graphite results in the transformation of PVDF crystals from gamma-shaped to alpha-shaped in the step-by-step process. Previous studies reported that the incorporation of graphene nanosheets had impacts on the PVDF crystallization. Due to the special affinity between PVDF and carbon surface, the graphene nanosheets worked as

Figure 1. The SEM images of the composite membranes surfaces morphology of PVDF-PVC membranes with different nano-graphite concentrations: (a)–(c) 0%, (d)–(f) 0.1%, (g)–(i) 0.5%, (j)–(l) 1% and (m)–(o) 2%, respectively. Left: 100 magnification of the surface. Middle: 1000 magnification of the surface. Right: 1000 magnification of the cross-section
nucleating agents for PVDF precipitation and led to the PVDF crystalline transition \([17, 18]\). After the nano-graphite addition, the lamellar splay morphology appeared in the surface. The traces of sheet nano-graphite could be clearly seen on the surface of the membrane, with the increase of nano-graphite, when the concentration of nano-graphite was higher than 1 wt%.

The PVC is amorphous compound, XRD and DSC curves have no peak, PVDF is crystalline polymer. The derivative peaks of different crystalline peaks of PVDF occur on the XRD curve, and the melting peaks occur on the DSC curve. The integral area of the melting peak is equal to the heat absorbed by PVDF during the melting process. It was found that the crystallinity of the composite membranes increased firstly with the increase of the concentration of nano-graphite (table 1). When the concentration of nano-graphite reached 1 wt% the crystallinity values of DSC and XRD reached the maximum, which matched the results of SEM. The crystallinity calculated by DSC and XRD is different, but the trend is the same. The change of nano-graphite concentration changes the kinetic process and thermodynamic properties, but the effects of the two changes on the structure and properties of the membranes are consistent. The crystallinity calculated by DSC includes all the
20% PVC was added into the PVDF composite membrane, the maximum degree of contact angle was 113.4°, membrane, the contact angle of the composite membrane surface increased from 71.4° to 113.4°. The composite membrane was observed. With the addition of different proportion of PVC to the composite membrane, different amounts of PVC to PVDF, the effect of the amount of PVC in the composite on the hydrophobicity of the membrane hydrophobicity was evaluated by the CA and SFE measurements. Zhang Qi et al. 3.4. Hydrophobic properties of composite membrane The membrane hydrophobicity was evaluated by the CA and SFE measurements. Zhang Qi et al. by adding different amounts of PVC to PVDF, the effect of the amount of PVC in the composite on the hydrophobicity of the composite membrane was observed. With the addition of different proportion of PVC to the composite membrane, the contact angle of the composite membrane surface increased surface from 71.4° to 113.4°. When 20% PVC was added into the PVDF composite membrane, the maximum degree of contact angle was 113.4° [13]. The incorporation of inorganic nanoparticles into the dope solution was reported to change the CA of the PVDF membrane [19]. In this experiment, inorganic nanoparticles and PVC were added to observe the CA the change of in PVDF membrane.

The CA values (water, glycerol, and diiodomethane) and the SFE values on the membrane were listed in table 2. With the increase of nano-graphite concentration in the PVDF/PVC dope solution, the CA increases first and then decreases with the increases in the nano-graphite concentration, contributed to the decrease of SEF first and then increases. At M-1, a good hydrophobic surface with a SFE of 18.97 mN/m was obtained, which was consistent with the result that the water CA value is very low [20].

Similar morphology was also observed for the surfaces of the membranes in figure 1(SEM) and figure 2(AFM). The CA values of the surface were affected by the concentration of nano-graphite. The higher water CA value for M-1 (137°) implied its strongly hydrophobicity. The roughness of the surface increases first and then decreases with the increases in the nano-graphite concentration (figure 2) contributed to the increase in hydrophobicity. Adding a proper amount of hydrophobic nano-graphite into the coagulation bath was supposed to improve the hydrophobicity of the composite membrane.

In the present study, the water CA increased first and then decreased with the increase of PVC content in PVDF/PVC composite membrane. When the ratio of PVDF to PVC is 85:15, the contact angle of PVDF/PVC composite membrane is the largest, which was 108°. Adding hydrophobic nano graphite into PVDF/PVC/nano-graphite composite membrane changed the hydrophobicity of PVDF/PVC composite membrane. With the increase of the content of nano-graphite in the composite membrane, the CA increases first and then decreases. When 1.0% nano-graphite (M-1) was added into PVDF/PVC/nano-graphite composite membrane, the maximum degree of water CA was 137° and the corresponding SFE was 18.97 mN/m.

3.5. Mechanical properties of composite membranes Table 3 shows the membrane thickness (mm) value of the composite membrane increased with the nano-graphite addition, but the Tensile stress at break (MPa), Elongation at break (%) and LEPw (MPa) value of the composite membrane decrease with the nano–graphite addition. In addition, in the case of M-0.5, all values changed most significantly. However, when nano-graphite increases to 1%, the Young’s modulus (MPa) value of the composite membrane is the highest. Compared with the original PVDF membrane, the composite membrane still has a certain mechanical strength [21]. The experimental results show that with the increase of

| Membrane | XRD(Crystallinity %) | DSC(Crystallinity %) |
|-----------|-----------------------|-----------------------|
| M-0       | 27.33                 | 36.54                 |
| M-0.1     | 29.32                 | 38.32                 |
| M-0.5     | 33.04                 | 38.63                 |
| M-1       | 33.50                 | 38.89                 |
| M-2       | 24.53                 | 33.58                 |

| Membrane | Water CA (°) | Glycerol CA (°) | Diiodomethane CA (°) | Surface free energy |
|-----------|--------------|-----------------|----------------------|---------------------|
| M-0       | 107.9 ± 1.3  | 101.0 ± 1.5     | 56.5 ± 0.2           | 30.74               |
| M-0.1     | 114.6 ± 0.7  | 109.5 ± 1.2     | 58.7 ± 0.7           | 29.59               |
| M-0.5     | 121.3 ± 0.5  | 120.3 ± 0.7     | 71.1 ± 0.9           | 22.21               |
| M-1       | 137.05 ± 0.9 | 130.6 ± 0.4     | 77.2 ± 1.3           | 18.97               |
| M-2       | 103.2 ± 1.0  | 93.4 ± 1.1      | 52.1 ± 0.8           | 33.02               |

microparticles in the membrane. The calculated crystallinity is high, while WAXD only has diffraction peaks for some perfectly crystallized crystals, so the calculated crystallinity is lower.
nano-graphite, the mechanical strength of the composite membrane does not increase as expected, but decreases. It was found that the hydrophobicity of the composite membranes was improved by adding nanographite by changing the surface roughness of the composite membranes. However, the mechanical strength and pore properties of the composite membranes still need further study.

### 3.6. Self-cleaning properties of deposited PVDF/PVC/nano-graphite membrane

Figure 4 shows the images of 0.03 ml water droplets on membranes surface with different nanographite concentrations. When the water drops was dripped on the PVDF/PVC/nano-graphite (M-1) membrane, the CA is 137° (figure 4(M-1)), and the contact area with the solid surface is small. According to the Cassie-Baxter model, when water droplets drop on the PVDF/PVC membrane doped with 1.0% nanographite (M-1), and the ‘cavitation’ was formed between the water droplet and the M-1 membrane surface. For a part of water droplet sitting on air, the contact area between water droplets and M-1 membrane decreases, the adhesion strength between water droplets and M-1 membrane surface decreases, and the dirt particles on the rough surface are easy to be taken away by water droplets. This was further confirmed by self-cleaning test [22].

The self-cleaning test of the M-1 membrane was shown in figure 5. The self-cleaning performance of the self-standing M-1 membrane was investigated by spraying graphite powder onto the surface of a tilted membrane (tilting angle ~15°) [23]. Randomly spraying the graphite powder onto the surface of the tilted film, While rolling down, the water droplets formed spheres and can easily roll off with the dirty particles, leaving a clean surface as shown in figure 5(a). The measured static contact angle of M-1 membrane after the self-cleaning test is about 137°, still showing the good hydrophobic nature of the membrane. The M-1 membrane with durable self-cleaning property provided, showing great potential for applying to a variety of fields.

| Membrane | membrane thickness (mm) | Tensile stress at break (MPa) | Elongation at break (%) | LEPw (MPa) | Young’s modulus (MPa) |
|-----------|-------------------------|-------------------------------|-------------------------|------------|----------------------|
| M-0       | 0.068 ± 0.002           | 2.678 ± 0.108                | 147.500 ± 11.726        | 2.00       | 1.81 ± 0.03         |
| M-0.1     | 0.072 ± 0.001           | 2.197 ± 0.073                | 90.000 ± 7.746          | 1.69       | 2.44 ± 0.09         |
| M-0.5     | 0.100 ± 0.002           | 1.229 ± 0.037                | 54.167 ± 5.845          | 0.95       | 2.28 ± 0.03         |
| M-1       | 0.107 ± 0.002           | 1.098 ± 0.035                | 32.500 ± 4.183          | 0.85       | 3.38 ± 0.11         |
| M-2       | 0.142 ± 0.003           | 0.749 ± 0.034                | 28.333 ± 2.582          | 0.58       | 2.64 ± 0.12         |

Figure 4. Static contact angle of the prepared membranes with different nano-graphite concentrations.

Table 3. Mechanical properties of composite membrane.
4. Conclusion

In order to reduce the cost of producing PVDF membranes, we use PVDF casting solution, adding 15% cheaper PVC, the price of PVC is about a quarter of that of PVDF. Compared with PVDF membrane, the cost is expected to be reduced by about 10%. For the sake of enhancing membrane hydrophobic performance. By adding hydrophobic modified nano-graphite and PVC incorporated into the dope solution to prepare composite membranes prepared via NIPS method. The nano-graphite and PVC addition accelerated the phase inversion process and change the PVDF crystal. The modified membrane was the surface roughness of nano-graphite and PVC has a certain change, so enhanced the membrane hydrophobicity. The addition of graphene induced the emergence of irregular particulates out of the surface, when the concentration of nano-graphite was higher than 1 wt%, the traces of nano-graphite could be clearly seen on the surface of the membrane. The PVDF composite membrane, the CA increases first and then decreases with adding more PVC and nano-graphite in the composite membranes. When 1.0% nano-graphite graphene (M-1) was added into PVDF/PVC/nano-graphite composite membrane, the maximum degree of water CA was 137° and the corresponding SFE was 18.97 mN · m⁻¹. Also, the self-cleaning experiments have proved that PVDF/PVC/nano-graphite membrane has a lasting self-cleaning performance, and has potential application prospects in membrane distillations, versatile protective clothings, self-cleaning devices, etc.

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