Preparation, characterization and optimization of superhydrophobic PVDF-PVC composite membrane based on concentration change of casting solution

Dashuai Zhang1,2,3, Xiaoxue Lin1,2,3, Yan Zhang1,2, Xiaopeng Zhang1,2, Chen Li1,2, Yang Lin1,2, Tianyi Sun1,2, Linhua Zhu1,2, Qiang Lin1,2 and Zaifeng Shi1,2

1 Key Laboratory of Water Pollution Treatment and Resource Reuse, Hainan Normal University, Haikou, Hainan 571158, People’s Republic of China
2 College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou, Hainan 571158, People’s Republic of China
3 These authors contributed equally to this work.

E-mail: zaifengshi@163.com

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Abstract

The PVDF/PVC superhydrophobic composite membrane was prepared by non-solvent induced phase separation method. When the concentration of PVDF/PVC (= 85/15) is 4%, DMF can be used as a solvent to prepare PVDF/PVC superhydrophobic composite membrane by using the simple and applicable NIPS method. Through static contact angle and rolling angle, it was found that the maximum contact angle of PVDF/PVC composite membrane with low concentration can reach 152°, rolling angle is 3 degrees, and the surface potential energy is also relatively low about 8°. It was found by DSC that the crystallinity of PVDF/PVC composite membrane with low concentration was higher, SEM shows that the surface of 4% PVDF/PVC composite membrane has nano scale protrusion, and AMF finds that the surface of 4% PVDF/PVC composite membrane was high Surface roughness. When the surface roughness was high, the surface hydrophobicity is improved, the wetting problem was alleviated, the self-cleaning ability of the membrane is improved, and the membrane pollution is reduced. It was found that the 4% PVDF/PVC composite membrane prepared by low concentration method has a long-lasting self-cleaning performance and can be used as an organic coating in the field of self-cleaning.

1. Introduction

The superhydrophobic surface has been widely concerned because of its water repellency, anti-sticking, anticorrosion, self-cleaning [1–3] and other characteristics. Many animals and plants surface in nature have superhydrophobic property [4–6]. Inspired by the super-hydrophobic phenomenon in nature, scientists have designed many superhydrophobic surface preparation techniques to simulate natural self-cleaning surfaces [7–11], such as lithography methods [12], wet/dry etching [13–15], chemical vapor deposition [16, 17], sol–gel technique [18], electrochemical deposition [19], electrospinning [20], layer–by-layer deposition technique [21], templating [22], 3D printing [23], direct laser texturing [24], glancing angle deposition [25], anodization [26], polymer blends [27] etc. In this paper, polymer PVDF and PVC were used to prepare the superhydrophobic membrane.

Polyvinylidene fluoride (PVDF) and polyvinyl chloride (PVC) microfiltration membranes and ultrafiltration membranes are widely used in water treatment due to excellent chemical resistance and good thermal stability and favorable mechanical properties [28–30]. PVDF is soluble in N,N-dimethylformamide (DMF), which is miscible with water. The pore structure and hydrophobicity of the PVDF membrane prepared by simple and practical non-solvent induced phase separation method (NIPS) method can be well regulated [31, 32]. Also, PVC is one of the materials with the highest degree of industrialization at present, which has the
advantages of low price, excellent performance and long service life, and has the competitive advantage of commercial application. Its industry is developing rapidly all over the world, and its prospect is very broad [33–35]. Polymer blending was an effective way to improve membrane properties [36, 37]. Zhang et al [38] prepared PVDF/PVC composite membrane by blending method. It was found that PVC content had an effect on the hydrophobicity of the composite, the maximum contact angle of PVDF/PVC composite membrane however was only about 114°. Although PVDF and PVC blend improved the hydrophobicity of the membrane, it was not yet superhydrophobic. To further improve the hydrophobicity of the PVDF membrane, scholars have carried out a lot of research on the PVDF membrane.

The surface morphology and pore structure of the membrane could be modified by polymer mixing, adding nanoparticles and coating to improve the hydrophobicity of the membrane [39–42]. As a semi-crystalline polymer, the precipitation of PVDF in the process of phase separation is controlled by liquid-liquid phase separation and solid-liquid phase separation. It has been found that the formation of the liquid core in the casting solution with low polymer concentration is much faster than that of crystal core. Therefore, the liquid-liquid phase separation plays a leading role, and some crystal cores grow slowly, forming nano-sized spherical particles [32]. The surface micro/nanostructure roughness is an effective way to improve surface hydrophobicity. Therefore, the membrane with low polymer concentration has the potential for strong hydrophobicity.

In this study, PVDF/PVC composite membrane was prepared by NIPS, and the superhydrophobic PVDF/PVC composite membrane was prepared by changing the concentration of PVDF/PVC casting solution. In the preparation of PVDF/PVC composite membrane, the addition of PVC increased the hydrophobicity of the membrane and reduced the cost of PVDF membrane. Also, the self-cleaning experiment of PVDF/PVC composite membrane shows that the composite membrane has a long-lasting self-cleaning performance. It has potential application prospects in the fields of antifouling self-cleaning equipment, membrane distillation, oil-water separation, gas separation, total evaporation and so on.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF, FR904, Shanghai 3F New Materials Technology Co. Ltd); dimethylformamide (DMF, Aladdin Reagent Co., Ltd); polyvinyl chloride (PVC, Aladdin Reagent Co., Ltd); deionized water (self-made).

2.2. Methods

2.2.1. Membranes preparation

PVDF and PVC were dried in vacuum at 60 °C for 12 h before use. PVDF/PVC blends were dissolved in DMF and stirred at 60 °C for 6 h to prepare different concentrations of PVDF/PVC (85:15) (4%, 8%, 12%, 14% and 16%) and degassed by ultrasonic for more than 1 h.

The composite membrane was prepared by NIPS method. The blend was placed on the stainless steel plate automatic membrane coating machine MEMCAST™ (Porometer Ltd, Belgium) with a knife gap 200 μm.

The cast membrane was exposed in air for 10 s and then immersed into a 25 °C pure water coagulation bath for 5 min. After the casted membrane solidified, it was ultrasonicated in anhydrous ethanol for 0.5 h, washed with deionized water, and then soaked in deionized water for 12 h. The residual solvent was removed and dried at room temperature. Finally, the membrane was dried in a vacuum oven at 60 °C for 6 h before characterized.

2.2.2. Surface morphology of the membrane

Morphology of PVDF membranes surface were investigated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The surface morphology of the composite membranes was characterized by JS7100F field emission SEM (JEOL, JPN) with 5 kV accelerating voltage. Before SEM characterization, samples were sprayed with a thin layer of gold. The surface roughness of the membrane was measured by AFM (Nanosurf AG), using Tap190Al-G silicon as a probe, scanning at an area of 10 μm × 10 μm at a speed of 1 Hz. The surface roughness (Ra) of the membrane was analyzed by SPIP™ Analysis software.

2.2.3. Crystallization of membrane

The crystal structure of the sample was determined by Wide Angle x-ray Diffraction (WAXD), using an x-ray diffractometer (Ultima IV, Rigaku, Japan) with a Cu Kα radiation source (1.54 Å), the diffraction angle was 5° ~ 65°. The crystallinity of the sample was determined by Differential Scanning Calorimeter (DSC), using an x-ray diffractometer (Netzsch-STA 449 F3, Netzsch, Germany). The test conditions are as follows: In the atmosphere
of high purity nitrogen, the flow rate of nitrogen in carrier gas was 20 ml min\(^{-1}\), the membrane of 10–12 mg was cut, the Al crucible was used, the heating rate was 10 °C min\(^{-1}\), and the temperature was raised from 30 °C to 400 °C. The crystallinity of the sample can be calculated by the area of the endothermic peak of the DSC by equations (1), (2).

\[ \Delta H = \frac{S_p}{m} \times 100\% \]  

Where \( m \), \( S_p \), \( \Delta H \) represents polymer mass (g), melting peak area (J) and melting enthalpy (J g\(^{-1}\)) of polymer, respectively.

\[ X_p = \frac{\Delta H}{w \times \Delta H_m} \times 100\% \]  

Where \( X_p \), \( \Delta H_m \), \( w \) represents the crystallinity (%), the standard enthalpy (J g\(^{-1}\)) and the percentage content of the polymer, respectively. The standard enthalpy of PVDF is 104.7 J g\(^{-1}\) [43].

2.2.4. Superhydrophobic properties of PVDF/PVC composite membrane

The wettability and hydrophobicity of the composite membrane can be known by measuring the contact angle (CA) of the composite membrane. Using the CA goniometer (OCA15EC, SCA20 software, Germany), the CA of the membrane was determined by the sessile drop method. The sample was placed on the test bench and dripped with 3 μl liquid (water, diiodomethane or glycerol). The different positions of each membrane sample were measured 5 times, and a reliable average value was obtained. The cos \( \theta \) transformation of Young’s equation [44] as follows (3):

\[ \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \]  

Where \( \gamma_{SV} \), \( \gamma_{SL} \), \( \gamma_{LV} \) represents the surface tensions of membrane and air, membrane and liquid, and liquid and air, respectively. It can be seen from formula (3) that when liquid and air are fixed, the larger \( \theta \) is, the more difficult for solid surface to be wetted; on the contrary, the smaller \( \theta \) is, the easier for solid surface to be wetted. The surface free energy (SFE) of the membrane surface can be obtained via the static CA measurements employing Lifshitz-van der Waals/acid-base method (LW/AB). Using three different liquid water (polar), glycerol (polar) and methylene diiodine (non-polar), the contact angles of the three solutions were input into SCA20 software to calculate the SFE of the membrane. The calculation formula is as follows (4,5) [45]:

\[ \gamma_m^T = \gamma_m^LW + \gamma_m^{AB} \]  

\[ \gamma_m^{AB} = 2 \sqrt{\gamma_m^LW \gamma_m^{OP}} \]  

Where \( \gamma_m^T \), \( \gamma_m^LW \), \( \gamma_m^{AB} \) and \( \gamma_m^{OP} \) represents the total SFE, the Lifshitz-van der Walls interactions, the acid-base interactions, the electron-acceptor parameter and the electron-donor parameter of the membrane, respectively.

3. Results and discussion

3.1. Surface morphology of PVDF/PVC composite membrane

The surface morphology of PVDF/PVC composite membranes with different concentrations were studied. The surface morphology of the prepared membrane was imaged by SEM (figure 1). Figures 1(a)–(d) showed that the concentration of the composite membrane was 4% and 8%, and nano-spherical particles were formed on the surface of the composite membrane. Compared with figures 1(a)–(d), it was found that the number of nanospheres on the surface of the composite membrane with a concentration of 4% was more than 8%. Figures 1(e)–(j) showed that the formation of nanospheres on the surface of the composite membrane disappeared with the increase of the concentration of the composite membrane (12%, 14%, 16%).

Through SEM image observation, we found the 4% PVDF/PVC membrane surface were covered by larger amount of nanospheres as compared to other concentrations. The average diameter of the nanospheres was about 100 nm and uniformly distributed on the surface of PVDF/PVC membrane. To better understand the surface condition of the 4% PVDF/PVC composite membrane, AFM was done. The surface was shown in figure 2, with the mean roughness (Sa) and root mean square roughness (Sq) of 175.88 nm and 239.6 nm, respectively. AFM shows that there were micro- and nano-scale structures on the surface of PVDF/PVC membrane.

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer. The precipitation during phase separation is controlled by liquid-liquid and solid-liquid phase separation, and forms an interconnected spherulite structure accompanied by crystallization [32]. With the increase of PVDF/PVC concentration in the casting solution, the formation of was influenced by the thermodynamic properties of the system. With the increase of polymer
concentration in the casting solution, phase separation is more likely to occur in the casting solution. Based on phase diagram, with the increase of polymer concentration, the more unstable the system is, the more likely phase separation occurs [46]. The crystallization and liquid-solid phase separation are more likely to occur in the membrane casting solution system, which also indicates that liquid-liquid phase separation occurs when the polymer concentration is low.

**Figure 1.** SEM images of PVDF/PVC membranes with concentration of (a), (b) 4%, (c), (d) 8%, (e), (f) 12%, (g), (h) 14%, (i), (j) 16%, magnified at 5000 (a), (c), (e), (g), (i) and 40 000 (b), (d), (f), (h), (j) respectively.
The SEM results show that micro-nanospheres appear on the surface of PVDF/PVC membrane with 4% and 8% concentration of casting solution, when 4% and 8% PVDF/PVC was immersed in coagulation water bath, the solvent DMF and non-solvent water at the membrane/bath interface are at equilibrium, resulting in instantaneous liquid-liquid separation on the membrane surface. Although from a thermodynamic point of view, the liquid-solid separation was more likely to occur. However, the formation of liquid nuclei was much faster than that of crystal nuclei in low polymer concentration cast solutions. In the process of the liquid-liquid phase separation, some nuclei grow slowly and form nano-microspheres.

When the polymer concentration increases to 12%, 14% or even 16%, it is known from the thermodynamic properties that the system tends to generate liquid-solid phase separation. On the other hand, the viscosity of the polymer increases greatly and the exchange rate of DMF/H₂O decreases. The polymer in the casting liquid has time to generate the crystal nucleus for liquid-solid phase separation [47]. The liquid-solid phase separation generates many polymer crystal nuclei, and further develops with the phase separation. The crystal nucleus grows up to form spherical particles. The spherical particles continue to grow until the particles connect with each other, and then solidify.

3.2. XRD and DSC of the composite membrane
Amorphous PVC has no peak in XRD curve. Figure 3 shows the XRD diffraction pattern, and the XRD peaks of PVDF membrane and PVDF/PVC membrane coincide. The diffraction peaks of PVDF (PVDF/PVC) membranes are 18.5°, 20.1°, 22.8° and 26.56°(2θ) respectively, corresponding to the γ-form of PVDF [48]. The results show that the crystal structure of PVDF was not affected by PVC.

Similarly, the heat absorbed by PVDF/PVC membrane during melting was equal to the peak area of PVDF melting peak. The results showed that with the increase of PVDF/PVC concentration, the crystallinity of the composite membrane first decreased and then increased (table 1). When the concentration of PVDF/PVC was 12%, the crystallinity of DSC was the lowest. The crystallinity calculated by DSC includes all crystal particles in the membrane (including microcrystals and conventional large crystals). When the concentration of PVDF/PVC was 4% and 8%, a large number of microcrystals appear on the surface of the membrane, so the crystallinity of 4% and 8%PVDF/PVC membrane was higher than that of 12%. Furthermore, the crystallinity of the PVDF/PVC composite membrane with 4% concentration was more than 8%, indicating that the surface microcrystal of the PVDF/PVC composite membrane with 4% concentration is more than 8%, which was consistent with the SEM result. With the increase of the concentration of PVDF/PVC in the casting solution, when the concentration of PVDF/PVC reaches 14%, the crystallinity of large particles increases significantly, and the crystallinity of the composite membrane increases with the increase of the concentration of PVDF/PVC in the casting solution.
3.3. Superhydrophobic properties of PVDF/PVC composite membrane

The hydrophobicity of the PVDF/PVC membrane was evaluated by CA and SFE tests. The CA (water, glycerol and diiodomethane) and the SFE of composite membranes with different PVDF/PVC concentrations were listed in table 2. The values of CA and SFE decreased with the increase of the concentration of PVDF/PVC in the coating solution. At 4% blend concentration, the membrane was superhydrophobic as indicated by CA of 152° and SFE of 7.56 mN m\(^{-1}\), and consistent with the CA value of water [49].

By observing the surface morphology of the membrane in figure 1, it was found that the surface roughness of the membrane decreases with the increase of PVDF/PVC concentration, which leads to the decrease of hydrophobicity. It can be inferred that the concentration of PVDF/PVC has an effect on the surface CA value. The water CA value of 4% is 152°, which indicates that it has super hydrophobicity. It was found that there were dense nano-spherical particles on the membrane surface by SEM and AFM. XRD (figure 3) showed that the crystal structure of PVDF is not affected by PVC. DSC (table 2) results showed that microcrystalline existed on the surface of PVDF/PVC composite membrane with low concentration.

In this study, the concentration of the polymer blend casting solution is the main factor affecting the composite membrane. By changing the concentration of PVDF/PVC in DMF, it was found that the PVDF/PVC composite membrane prepared with 4% casting solution was superhydrophobic. The concentration of PVDF/PVC casting solution has an effect on the CA of the composite membrane, and the CA of water in the PVDF/PVC composite membrane decreases with the increase of the concentration of PVDF/PVC casting solution.

| Membrane | Water CA (°) | Glycerol CA (°) | Diiodomethane CA (°) | Surface free energy (mN m\(^{-1}\)) |
|-----------|--------------|-----------------|----------------------|----------------------------------|
| 4%        | 152.3 ± 0.8  | 150.2 ± 0.4     | 102.5 ± 0.6          | 7.76                             |
| 8%        | 118.5 ± 0.5  | 116.4 ± 1.1     | 61.5 ± 0.2           | 29.72                            |
| 12%       | 93.2 ± 0.4   | 90.1 ± 0.7      | 47.1 ± 1.3           | 35.97                            |
| 14%       | 92.1 ± 0.3   | 88.7 ± 0.4      | 46.5 ± 0.9           | 33.36                            |
| 16%       | 90.3 ± 1.0   | 86.4 ± 0.8      | 45.8 ± 0.6           | 36.87                            |
When the concentration of the casting solution was 4%, the CA of PVDF/PVC composite membrane was the highest, its value was 153°, and the SFE value was 7.56 mN·m⁻¹.

3.4. Mechanical properties of membranes
Table 3 shows mechanical properties of the composite membranes. As can be seen from the table 3, the membrane thickness (mm) value of the composite membrane increases with the increase of PVDF/PVC casting solution concentration, but the tensile stress at break (MPa), elongation at break (%) and liquid entry pressure of water (LEPw, MPa) value of the composite membrane first increase then decrease with the PVDF/PVC casting solution concentration. When the PVDF/PVC casting solution concentration is 12%, the mechanical properties of 12% were the best. Compared with PVDF membrane, the PVDF/PVC composite membrane has certain mechanical strength [50].

Table 3 shows that the concentration of PVDF/PVC casting solution increase, the mechanical properties of the composite membrane increase at first and then decrease. This was due to the fact that with the increase of the concentration of PVDF/PVC casting solution, the mechanical properties of the composite membrane first increase with the concentration of the casting solution, but when the casting solution continues to increase, the membrane becomes brittle according to our method, so the mechanical properties of the composite membrane decrease. With the increase of polymer concentration, the dense layer was easier to form, thus it was easier to prevent the exchange of solvents between the coagulation bath and the sublayer, affecting the formation of sublayer macropores and sponge structure, thus affecting the mechanical properties of the membrane [51]. From the results of the membrane thickness, when the concentration of the casting solution increases to 12%, 14% or even 16%, the thickness of the membrane basically does not change, but the thickness of the membrane was mainly affected by the sublayer structure of the membrane. The change of the membrane thickness shows that the sublayer thickness of the membrane decreases with the increase of the concentration of the casting solution, and the mechanical properties of the membrane are mainly affected by the sublayer structures of the membrane. Therefore, when the concentration of the casting solution continues to increase, the mechanical properties of the membrane decrease. At the same time, the experimental results also show that the membrane becomes more brittle with the increase of the concentration of the casting solution. The mechanical properties of the composite membrane were the best when the concentration of PVDF/PVC was 12%.

3.5. The self-cleaning experiment of membrane
Figure 4 shows the sessile drop of water on the membrane surfaces with different PVDF/PVC casting solution concentration. The CA of the 4% membrane was 152° as shown in figure 4, and the contact area between water droplets and membrane surface is the smallest. Assuming that the water droplet on 4% membrane follows Cassie-Baxter model, ‘cavitation’ was formed between the water droplet and the 4% membrane surface. As there are parts of water droplet sitting on air, the contact area between water droplets and the 4% membrane decreases, the adhesion strength between water droplets and the 4% membrane surface decreases, and the dirt particles on the membrane surface are easily taken away by the water droplets. The self-cleaning test further confirmed this [52]. The self-cleaning test of the 4% membrane as shown in figure 5, the self-cleaning performance of the 4% was investigated by spraying nano-graphite powder on the surface of the membrane (tilt angle <5°)[53]. The graphite powder was randomly sprayed on the inclined membrane surface, and when water droplets were added to the membrane surface, the water droplets form spheres, the graphite powder and water droplets roll down at the same time (figure 5(a)). After cleaning, the CA of the 4% membrane is about 152°, which still shows good superhydrophobicity. Therefore, the 4% membrane has long-lasting self-cleaning performance and shows great application potential in many fields.

| Membrane | Membrane thickness (mm) | Tensile stress at break (MPa) | Elongation at break (%) | LEPw (MPa) |
|----------|-------------------------|-----------------------------|-------------------------|------------|
| 4%       | 0.040 ± 0.014           | 0.330 ± 0.015               | 11.667 ± 2.582          | 0.22       |
| 8%       | 0.067 ± 0.008           | 0.846 ± 0.019               | 20.883 ± 3.764          | 0.57       |
| 12%      | 0.086 ± 0.005           | 2.957 ± 0.071               | 156.677 ± 5.164         | 1.97       |
| 14%      | 0.069 ± 0.008           | 2.664 ± 0.044               | 85.833 ± 9.174          | 1.77       |
| 16%      | 0.073 ± 0.010           | 2.382 ± 0.119               | 84.167 ± 8.612          | 1.6        |
4. Conclusions

In order to reduce the production cost of PVDF membrane and improve its hydrophobicity, PVDF/PVC composite membrane was prepared by adding PVC into PVDF coating solution by NIPS method \(^{[54]}\). The hydrophobicity of the composite membrane was studied by changing the concentration of PVDF/PVC casting solution. The experimental results show that the CA in the composite membrane decreased with the increase of PVDF/PVC concentration. By observing the surface morphology of (SEM) thin membranes in figure 1, it was found that the surface roughness decreases with the increase of PVDF/PVC concentration. The reason was that when the concentration of PVDF/PVC was high, there were crystal nuclei in the casting solution, and liquid-solid phase separation is more likely to occur on the surface of the membrane, forming spherulites with large cross-linked particles. However, when the concentration of PVDF/PVC was low, there was no crystal nucleus in the casting solution, and the instantaneous liquid-liquid separation is more likely to occur on the surface of the membrane, resulting in the formation of nano-sized spherical particles. The 4% PVDF/PVC composite membrane has the maximum water CA at 152°, and the correspond SFE was 7.76 mN m\(^{-1}\). At the same time, the self-cleaning experiment of PVDF/PVC composite membrane shows that the composite membrane has a long-lasting self-cleaning performance. It has potential application prospects in the fields of antifouling self-cleaning equipment, membrane distillation, gas separation and so on.

![Figure 4. The CA of the membrane prepared by different concentrations of PVDF/PVC casting solution.](image)

![Figure 5. (a) The self-cleaning surface test of 4% membrane; (b) The sessile drop of water on 4% membrane after the self-cleaning test (CA ~ 152°).](image)
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Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Dashuai Zhang https://orcid.org/0000-0003-0618-1685

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