

Preparation and Characterization of Superhydrophobic Modification of Polyvinylidene Fluoride Membrane by Dip-Coating

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Abstract: The superhydrophobicity polyvinylidene fluoride (PVDF) membranes were modified *via* reducing surface energy by dip-coating perfluoroalkyl methacrylic copolymer (Zonyl 8740) onto the membranes prepared on mat glass. The chemical component of the unmodified and modified PVDF membranes surface was investigated by ATR-FTIR. Morphology and hydrophobicity of the unmodified and modified PVDF membranes were examined by scanning electronic microscopy and water contact angle, respectively. The effects of concentration of Zonyl 8740, coating time, conditions of heat treatment on hydrophobic capability of PVDF membranes were investigated. The results showed that the water contact angle increased from 141° to 151° by the dip-coating modification, therefore getting superhydrophobic PVDF membrane. Moreover, the porosity and the morphology of modified PVDF membrane were unchanged by the dip-coating modification. This results suggested that the hydrophobicity stability of the modified PVDF membrane was also good.

Keywords: Polyvinylidene fluoride, Superhydrophobic, Coating modification, Perfluoroalkyl methacrylic copolymer, Membrane preparation.

1. INTRODUCTION

In recent years, a great interest attention has been directed to the superhydrophobic surfaces due to the conceivable application in micro fluidics system, surface self-cleaning, material biocompatibility and so on [1-3]. During the last decades, much more research has been devoted to superhydrophobic membranes for using in many of novel applications such as membrane distillation [4], membrane absorption [5-6], membrane self-cleaning [7] and membrane fouling control [8-9].

Therefore, lots of different techniques including plasma etching [10], chemical vapor deposition [11], sol-gel methods [12], electrospinning [13-14], phase separation and plasma treatment [16], have been developed to make superhydrophobic membranes. These methods mainly depend on two ideas: one is making a roughness surface on a low surface energy material; the other is modifying a rough surface with a material of low surface energy [14].

PVDF is a popular material in membrane application due to its advantages such as excellent mechanical

property, easy process ability, exceptional chemical stability and good thermal stability [14]. Hence, with the superhydrophobic property, the PVDF membranes will be able to be used more widely in the future.

Fluorinated polymers are regarded as low surface energy materials owing to its repellent property for oil and water [17]. Perfluoroalkyl methacrylic copolymer (Zonyl 8740) is a kind of cationic fluoride, and can be used to obtain super water-repellent films [18-19]. Farhadi prepared the anti-ice surface by spin-coating Ag nano-particles and subsequently dip-coating with a thin film of Zonyl 8740 [20]. Hsieh fabricated superhydrophobic carbon fabric by decorating carbon nanotubes onto microsized carbon fibers and subsequent fluorination surface treatment [21].

In our previous study, PVDF hydrophobic membrane was prepared by copying with rough glass, and the WCA of PVDF membrane was 141° [22]. However, the WCA of the PVDF membrane was less than 150° and membrane performance was not investigated. This study aims to research the feasibility of obtaining the superhydrophobicity of PVDF membranes simply by coating low surface energy materials (Zonyl 8740) onto the membrane prepared on mat glass.

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2. EXPERIMENTAL

2.1. Materials

Polyvinylidene fluoride (PVDF), type761A, Arkema (China) Investment Co., Ltd; N,N-Dimethylacetamide (DMAc) (AR), Tianjin Kemiou Chemical Reagent Co., Ltd.; Ethanol (AR), Tianjin Kemiou Chemical Reagent Co., Ltd.; Zonyl 8740, Shanghai Dupont Industrial Co., Ltd.

2.2. Preparation of PVDF Membranes

The PVDF powder was dried at 100 °C under vacuum for 24 h before used. The PVDF solution (10 wt.%) with DMAc as the solvent was prepared at 60 °C for 12h. The casting solution was placed at 60 °C for about 24h to release the gas bubbles in the casting solution. Then the membranes were obtained with the casting solution on the rough glass, 30 °C water bath as coagulant for 24 hours and cleaned and dried later.

2.3. Zonyl 8740 Coating on the Surface of PVDF Membranes

2.3.1. Zonyl 8740 Coating Solution Preparation

Zonyl 8740 solution for coating purpose was prepared by mixing Zonyl 8740 and ultra-pure Milli-Q water at room temperature to form a homogeneous solution. The concentration of Zonyl 8740 ($C_{\text{Zonyl8740}}$) was varied from 0.5wt.% to 6wt.%.

2.3.2. Coating of Zonyl 8740 onto the PVDF Membranes

The membranes were dip-coated in the coating solutions with different concentration for a predetermined period of time ranging from 0h to 50 h. Then the coated membranes were dried in the vacuum, with the time of heat treatment ranging from 1h to 8h and the temperature of heat treatment ranging from 30 °C to 110 °C. At last the membranes were rinsed and dried. These membranes were labeled as modified PVDF membranes.

2.4. Membrane Characterization

2.4.1. Scanning Electron Microscopy (SEM)

SEM images were taken by the Hitachi s-4800 Scanning Electron Microscope operated at 5 kV. Before collecting the SEM images, all samples of PVDF membranes were coated with gold.

2.4.2. Water Contact Angle Measurement (WCA)

Static WCA were tested with the JYSP-180 optical water contact angle measuring device at room

temperature. A droplet of single 5 μ L ice water was used as the measure droplet. All the WCA data were averaged with five measurements to minimize experimental errors at different locations of membrane surface.

2.4.3. Fourier Transformed Infrared Spectroscopy (ATR-FTIR)

The properties of the unmodified and modified PVDF membranes were analyzed with ATR-FTIR (SENSOR37). The surface infrared spectra of the unmodified and modified PVDF membranes were collected between 400 cm^{-1} and 4000 cm^{-1} .

2.4.4. Membrane Porosity

Membrane porosity (ε) was obtained by gravimetric method. Some dry membranes were placed into ethanol at room temperature for 24h in order to fill the pores with ethanol completely. Then, the ethanol out side of the membranes was removed by rubbing away and the weight of the wet membranes (W_w) was measured. After the membranes were dried, the weight of dried membranes (W_d) was measured. ε was calculated by Eq. (1).

$$\varepsilon = \frac{W_w - W_d}{S \times d \times \rho} \times 100\% \quad (1)$$

Where S is represented as the area of the membrane (cm^2); d is used as the thickness of the membrane (cm); the ethanol density is represented by ρ (0.789g/ cm^3).

2.4.5. The Hydrophobicity Stability of Modified PVDF Membrane

The modified PVDF membranes were fully immersed into de-ionized water and alcohol respectively at different time (from 0h to 24h). Then the membranes were brought out of the solvents, cleaned in pure water and dried by vacuum after predestined time. And the static WCA of the modified PVDF membranes was tested.

3. RESULTS AND DISCUSSION

3.1. Effects of Modification Condition on Hydrophobicity of Modified PVDF Membranes

3.1.1. Effect of Coating Time on Hydrophobicity

The figure indicates that as the coating time increases, the WCA of modified PVDF membranes approaches the maximum (144°), and then does not change (Figure 1). The WCA of the modified PVDF

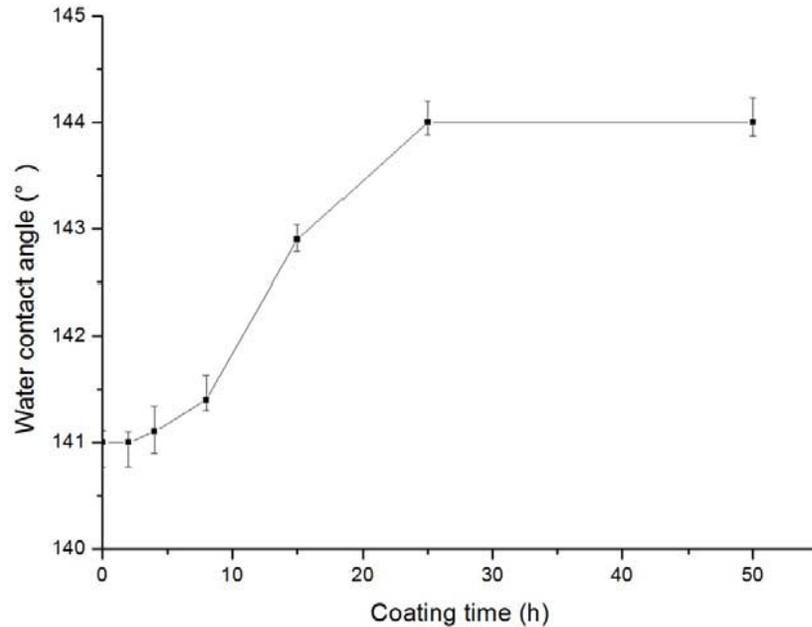


Figure 1: Effect of coating time on the hydrophobicity (Zonyl 8740 concentration was 2wt.%, the temperature of heat treatment was 30 °C).

membranes is stable with the coating time less than 8h or greater than 25h, while the change of the WCA of the modified PVDF membranes is obvious when the coating time is from 8h to 25h. This fact may be explained that with the coating time increasing from beginning to 25h, the degree of modify is saturated, which results in decreasing the surface energy of modified PVDF membranes and increasing the WCA of the modified PVDF membranes.

3.1.2. Effect of Heat Treatment on Hydrophobicity

The WCA of the modified PVDF membranes increases with the increase of the heat treatment temperature from 30 °C to 100 °C. And the dependence of the time of heat treatment on the WCA of the modified PVDF membranes shows that with the time of heat treatment extending from 1h to 8h the WCA of the modified PVDF membranes becomes bigger (Figure 2). It is because the adhesion between PVDF membrane

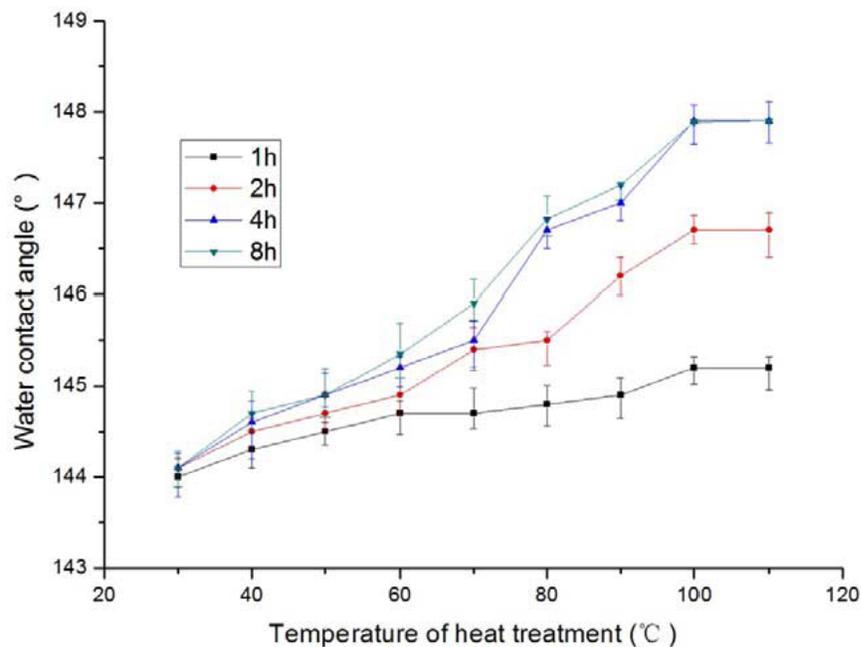


Figure 2: Effect of heat treatment on the hydrophobicity (Zonyl 8740 concentration was 2wt.%, the coating time was 25h).

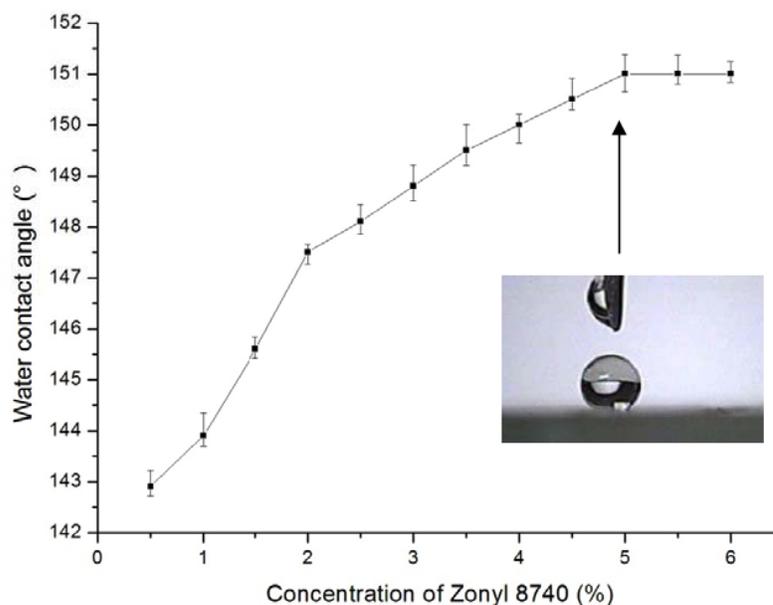


Figure 3: Effect of the concentration of Zonyl 8740 on the hydrophobicity (the coating time was 25h, the time of heat treatment was 4h, the temperature of heat treatment was 100 °C)

and Zonyl 8740 is stronger as the temperature of heat treatment is higher or the time of heat treatment is longer, and 100 °C of heat treatment temperature, 4h of heat treatment time are chosen as the heat treatment conditions. It is similar to the results reported by Farhadi and Hsieh [20,23].

3.1.3. Effect of Concentration of Zonyl 8740 on Hydrophobicity

The influence of the concentration of Zonyl8740 ($C_{\text{Zonyl8740}}$) on the hydrophobicity of the modified PVDF membranes is shown in Figure 3. It reveals that the effect of $C_{\text{Zonyl8740}}$ on the hydrophobicity of the modified PVDF membranes is notable. With $C_{\text{Zonyl8740}}$ ranging from 0.5wt.% to 6wt.%, the WCA of PVDF membranes increased from 141° for virgin PVDF membranes to the maximum WCA with 151° (at $C_{\text{Zonyl8740}} = 5\text{wt.}\%$) (Figure 3). It is noted that $C_{\text{Zonyl8740}}$ with 5wt.% is enough, and it is not useful to use much high concentration of Zonyl8740 to decline the surface energy of PVDF membranes, only resulting in depositing on the surface of the modified PVDF membranes uselessly.

3.2. Membrane Performance

3.2.1. Morphology of Membranes

The top-surface, bottom-surface and cross-sectional structure of the membranes before and after coated with Zonyl 8740 of 5wt.% are shown in Figures 4-6. Figure 4 presents the top-surface of PVDF membranes before and after coated with Zonyl 8740. From Figure

4a1 and b1, the SEM image of the membrane after the modification is similar to the membrane before the modification. As Figure 4a2 and b2 shown, the pore size of the unmodified PVDF membrane (100-120nm) is bigger than the modified PVDF membrane (90-100nm). The PVDF membrane before and after coated with Zonyl 8740 displays a porous structure on the bottom-surface (Figure 5). The cross-section SEM images of PVDF membranes before and after coated with Zonyl 8740 are shown in Figure 6, where the PVDF membranes before and after modification have a finger-like structure near the top-surface and a sponge-like and drop shape cavity structure near the bottom-surface (Figs. 6a1 and b1). In fact, the formation of drop shape cavities in the bottom-surface can be related to the slow phase-inversion because of the rough glass substrate [24]. From Figure 6a2 and b2, the cross-section near top skin layer of the modified PVDF membrane (600-700nm) is thicker than the unmodified PVDF membrane (400-500nm), which can be associated to the modification. As Figure 6a3 and b3 show, there is no difference of the cross-section near bottom skin layer of membranes that before and after coated with Zonyl 8740. It can be concluded that the morphology of membrane after modification is not altered obviously by the dip-coating modification.

3.2.2. The Surface Chemical Component Analysis of Unmodified and Modified PVDF Membranes

The surface chemical component analysis of unmodified and modified PVDF membranes was confirmed by FTIR-ATR. The ATR-FTIR spectra of the

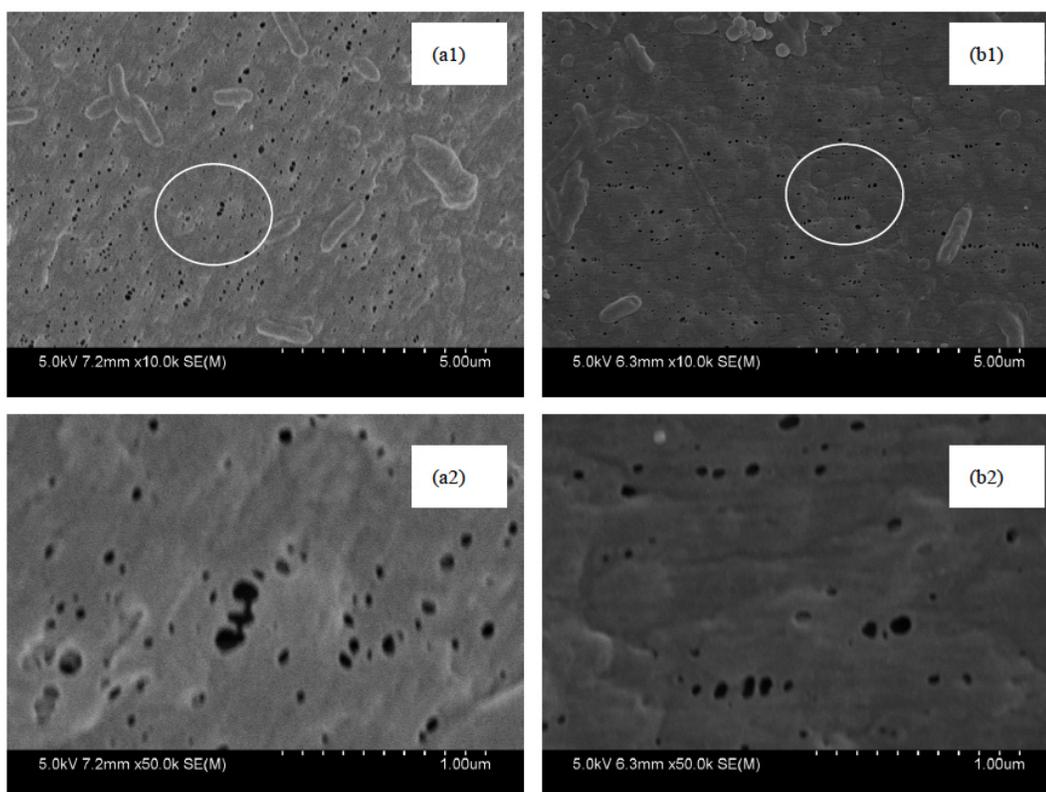


Figure 4: SEM micrographs of top-surface PVDF membranes before and after coated Zonyl 8740: (a) Unmodified PVDF membrane; (b) Modified PVDF membrane; (1) at a magnification of 10,000 \times ; (2) at a magnification of 50,000 \times .

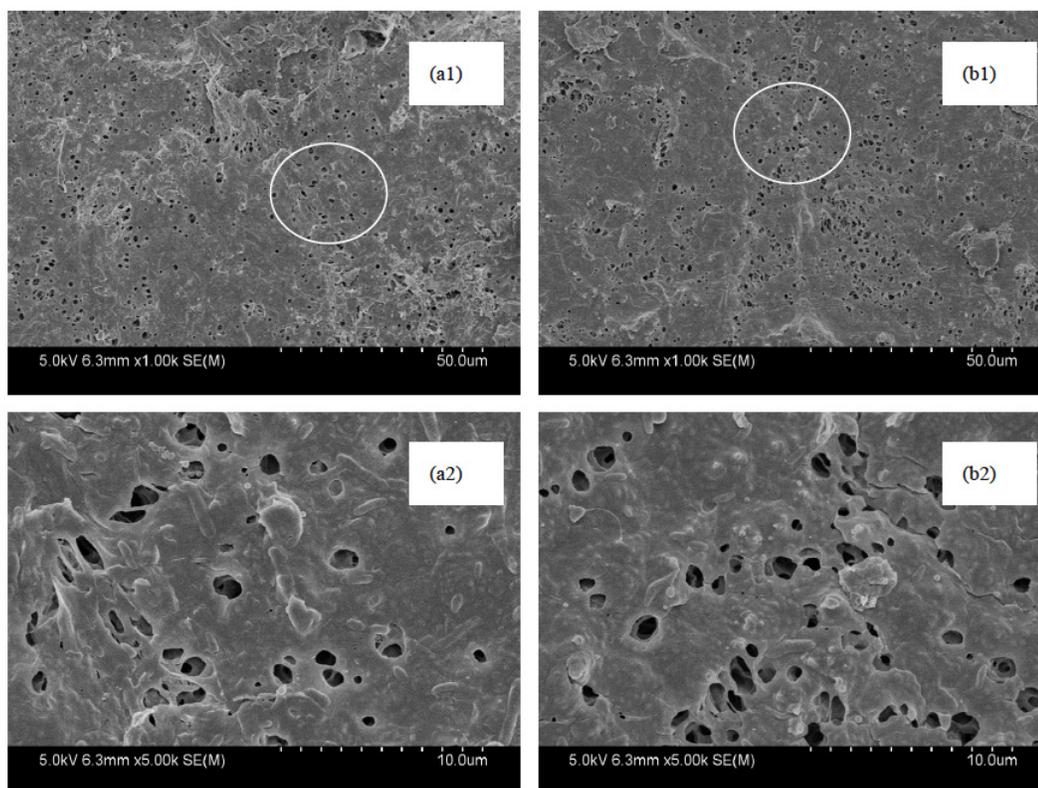


Figure 5: SEM micrographs of bottom-surface PVDF membranes before and after coated Zonyl 8740: (a) unmodified PVDF membrane; (b) modified PVDF membrane; (1) at a magnification of 1,000 \times ; (2) at a magnification of 5,000 \times .

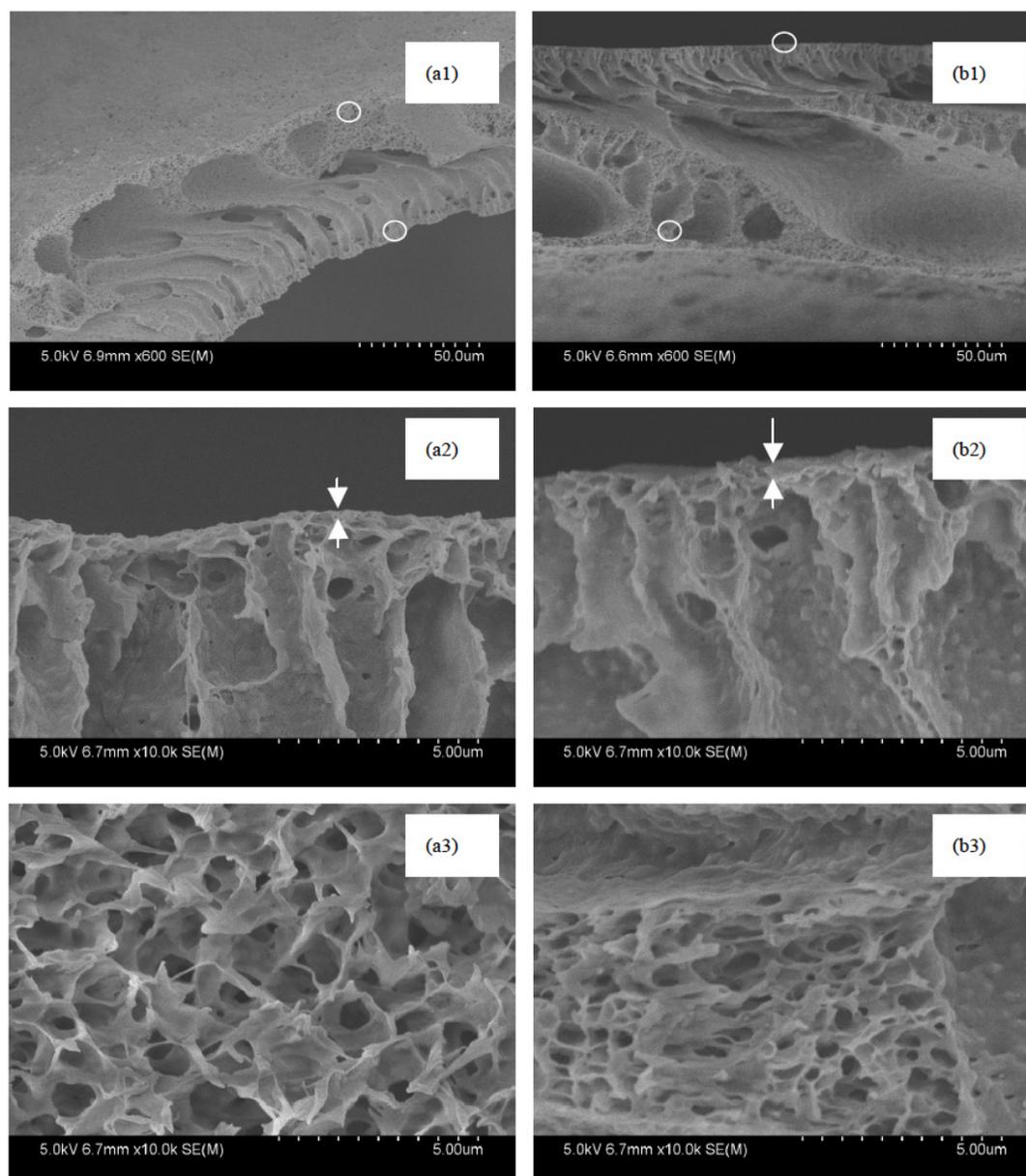


Figure 6: SEM micrographs of cross-section PVDF membranes before and after coated Zonyl 8740: (a) unmodified PVDF membrane; (b) modified PVDF membrane; (1) cross-section; (2) cross-section near top skin layer; (3) cross-section near bottom skin layer.

unmodified and modified PVDF membranes are illustrated in Figure 7. It can be seen that the characteristic peak at 1175 cm^{-1} corresponds of asymmetrical stretching of CF_2 . The characteristic peaks at 839 cm^{-1} and 874 cm^{-1} , and the characteristic peak at 1071 cm^{-1} represent the amorphous phase and crystal phase of PVDF severally [25]. The absorbance peak observed at 1403 cm^{-1} represents to the vibration absorption peak of CH_2 groups. Compared with the spectra of the unmodified membrane, the new peak at 1732 cm^{-1} in Figure. 7b corresponds to the absorption peak of $\text{C}=\text{O}$, which may be caused by dip-coating Zonyl 8740 on membrane. The result confirmed that,

there was Zonyl 8740 coated on the modified PVDF membrane surface.

3.2.3. Effect of Modification on Membrane Porosity

The gravimetric method was carried out in order to prove that the modification has not substantially changed the membrane porosity [8]. The result reveals that the membrane porosity is not altered significantly after dip-coating of the Zonyl 8740 (Figure 8). It also can be seen by comparing the SEM images in Figures 5 and 6, the modification does not significantly change the membrane porosity of the membrane coated by Zonyl 8740.

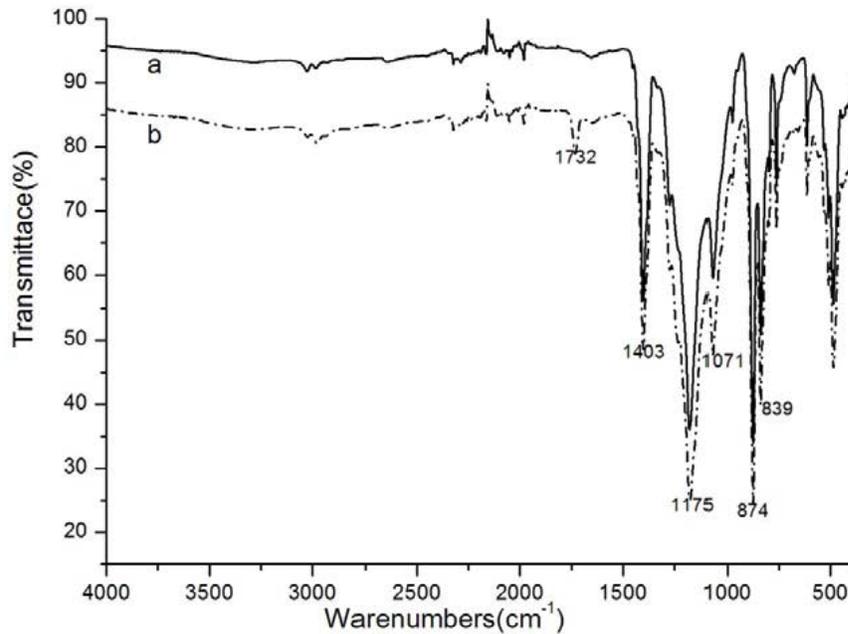


Figure 7: FTIR-ATR spectra of PVDF membranes (a) unmodified membrane; (b) modified membrane.

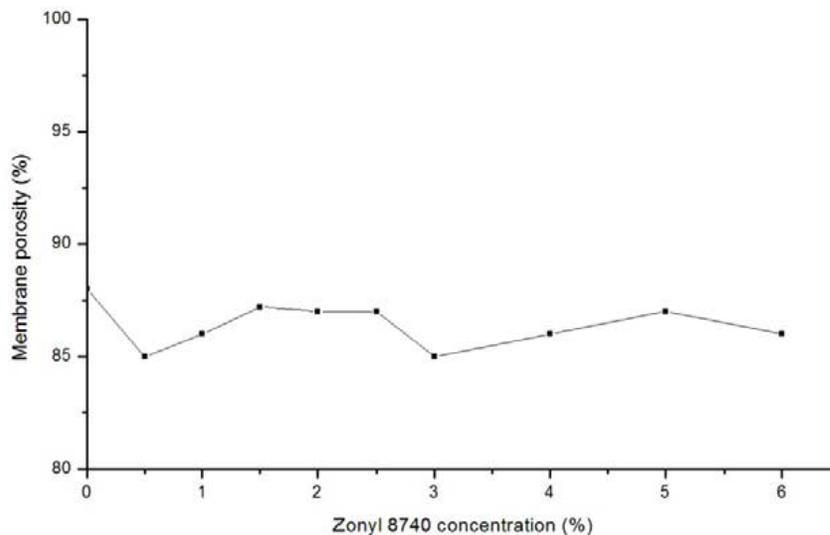


Figure 8: Effect of Zonyl 8740 concentration on PVDF membrane porosity.

3.2.3. The Hydrophobicity Stability of Modified PVDF Membrane

Figure 9 shows the variation of WCA on the modified PVDF membrane with immersion period. As can be seen in Figure 9, a slight decline of WCA indicates that the modified PVDF membrane possesses a long stability, since the WCA exceeds 150° with immersion period for 24 h. Also, the anti-alcohol ability of modified PVDF membrane is good with immersion period for 24h because the WCA is more than 150° . These results confirm (i) the fairly good hydrophobicity stability of Zonyl 8740 and (ii) the strong adhesion between PVDF membrane and Zonyl

8740 after heat treatment. It was also reported that the superhydrophobicity of the surface coated Zonyl 8740 is stable due to the good stability of Zonyl 8740 against ethylene glycol and water [23].

4. CONCLUSIONS

The super-hydrophobic PVDF membranes were obtained *via* reducing the surface energy by coating Zonyl 8740. By controlling the concentration Zonyl 8740, coating time and heat treatment, the membrane with the WCA of 151°C was obtained. The PVDF membrane before coated with Zonyl 8740 exhibited

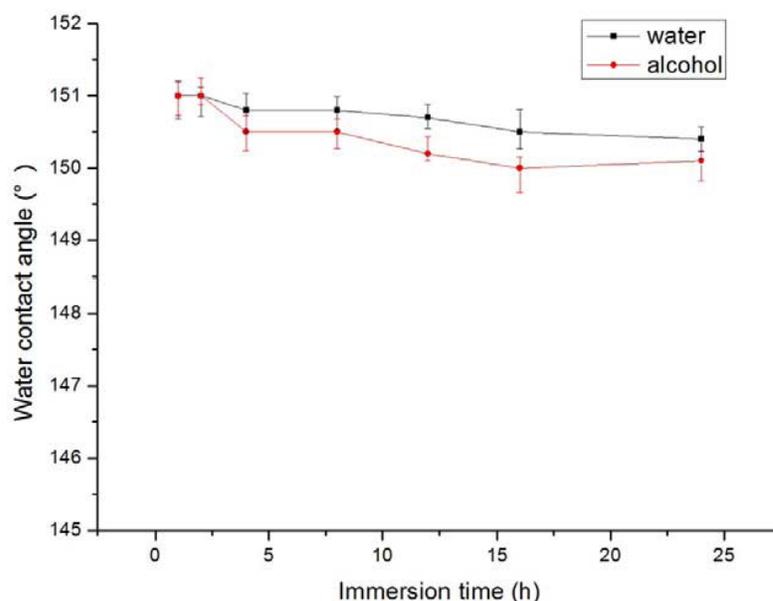


Figure 9: The hydrophobicity stability of modified PVDF membrane.

finger-like structure and displayed a very open pore structure, and the membrane morphology was intact after coated with Zonyl 8740. The results showed that the modified PVDF membranes also had unchanged membrane porosity and good hydrophobicity stability. The super-hydrophobic PVDF membrane could be obtained by the follow feasible conditions: mat glass of substrate, 10% of PVDF concentration in casting solution, 100 °C of heat treatment temperature, 4h of heat treatment time and 5% of Zonyl 8740 as coating solution.

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