

## Facile optimization methods of polyvinyl chloride porous membranes with improved tensile strength

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### ABSTRACT

Polyvinyl chloride (PVC) flat sheet membranes with high tensile strength were fabricated via immersion precipitation phase inversion method used N,N-dimethylacetamide/dioctyl phthalate (DOP) as the mixed solvents. The influences of DOP content in mixed solvents and polyvinylpyrrolidone (PVP) addition on structure and performance of prepared PVC flat sheet membranes were investigated by morphology, pure water flux, porosity, and mechanical property. The results showed that the growth of the finger-like structure was promoted by introducing PVP, which could effectively increase the pure water flux of the membrane. With the increase of the DOP content, the cross-section structure became denser and the membrane surface pore size became larger. The increase of the DOP content brought about the increase of membrane hydrophilicity but decreased the membrane porosity and protein rejection. The obtained membrane exhibited the maximum tensile strength of 12.15 MPa as the DOP content reached to 10 wt.%.

*Keywords:* Polyvinyl chloride; Flat sheet membrane; Mixed solvent; Tensile strength

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### 1. Introduction

The traditional preparation method of microfiltration and ultrafiltration membranes was a non-solvent induced phase separation (NIPS) method, which endowed the membranes with high porosity, excellent permeability, but poor tensile strength [1,2]. The defect of membranes with poor tensile strength would restrict their wide application in the harsh environment and shorten the membrane service life, especially in a membrane bioreactor system [3]. There were two main methods to improve the membrane tensile strength through the reported literature. The first was the formulation optimization of the casting solution, which included the inorganic particles adding [4,5], polymer blending [6], solvent compounding [7], and so on. The other was the changes in the membrane preparation methods,

which included the thermally induced phase separation (TIPS) method [8], melt-spinning cold-stretching (MSCS) method [9], recombination reinforced method [10–12], and so on. In the past studies, both of the TIPS and MSCS methods were needed to operate at the high temperature, while the recombination reinforced method that used the supporting layer was complex. Compared with these methods, the formulation optimization of the casting solution was relatively simple and energy conservation, which was unnecessary to need high-temperature operation and complex reinforcement technology.

Especially, the solvent compounding method including two or more solvents and diluents as the mixed solvents, could obtain the high tensile strength membranes at the relatively low preparation temperature and improve the membrane surface hydrophilicity or hydrophobicity easily.

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Meanwhile, energy consumption could be reduced compared with TIPS and MSCS methods. Moreover, the process of membrane formation could be decided by the interaction between the mixed solvents and non-solvents, while the two or more solvents and diluents were competition relations. Especially, the polymer aggregation state and membrane pore structure could be jointly improved by all these interactions. These researches had been reported in the literature openly [13–16]. For example, Ma et al. [17] prepared the poly(vinylidene fluoride) (PVDF) flat sheet membranes used the *N,N*-dimethylformamide (DMF) and  $\gamma$ -Butyrolactone ( $\gamma$ -BL) as the mixed solvent. Their research found that the membrane structure changed from the cellular to spherulitic morphologies by varying the mass ratio of DMF/ $\gamma$ -BL and the highest tensile strength could reach 7.3 MPa. Li et al. [18] evaluated the evolution process of PVDF hierarchical morphology used the *N,N*-dimethylacetamide (DMAc) and dibutyl phthalate (DBP) as the mixed solvents. The superhydrophobic and self-cleaning surface could obtain when the DMAc/DBP mass ratio was 5/5 and the quenching time was 300 s at 25°C air atmosphere. Jin et al. [19] fabricated the polyvinyl chloride (PVC) ultrafiltration membrane through the combination of the TIPS and NIPS method used the diphenyl ketone (DPK) and DMAc/DMF as the mixed solvents. The prepared PVC membranes showed the bicontinuous spongy structure and had excellent tensile strength.

Due to the special molecular structure of PVC, many kinds of common diluents (e.g. DBP, dioctyl phthalate (DOP), di(2-ethylhexyl)phthalate (DEHP), dioctyl adipate (DOA), and so on) exhibited different degrees of plasticizing effect to PVC resins. The plasticizing process was due to the penetrating of the plasticizer to the PVC macromolecule chains, and these liquid-solid two-phase system called gelation would melt and transform into one single solid phase in the appropriate preparation temperature [20]. These changes could improve the fluidity of PVC at low temperatures below the melting point and prevent degradation. However, the phase separation of the plasticizer and PVC resin did not occur when the temperature decreased to room temperature. Thus, the extraction process of plasticizer would change the aggregation state structure of PVC and lead to the shrink of prepared membrane size and membrane pores on the macro level, which would reduce the membrane pores connectivity and membrane permeability [21]. Based on the aforementioned discussion, the tensile strength of the prepared PVC membrane was increased after the plasticizing and extraction processes due to the changes in the aggregation state structure of PVC [21]. Therefore, the introduction of plasticizer into solvents as mixed solvents could improve the membrane mechanical properties to some extent. In previous works, there were few kinds of literature reporting the improvement of mechanical properties on PVC membranes by introducing the mixed solvents, which was used to improve the aggregation state structure of PVC and then optimized the membrane comprehensive performance.

In this article, the PVC flat sheet membranes were fabricated by introducing the DMAc/DOP as mixed solvents via immersion precipitation phase inversion method. The objective of this study was to improve the mechanical properties of PVC flat sheet membranes by the formulation optimization of casting solution. The influences of DOP content in mixed

solvents on structure and performance of prepared PVC flat sheet membranes were investigated by morphology, pure water flux, porosity, and mechanical property measurements.

## 2. Experimental

### 2.1. Materials

PVC (Fiber grade, DG-1000k, the average degree of polymerization is  $1,030 \pm 50$ ) resin was purchased from Tianjin Dagu Chemical Plant (Tianjin, China). Dioctyl phthalate (DOP, >99.5%) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. *N,N*-dimethylacetamide (DMAc, Analytical Reagent), ethanol (EtOH, Analytical Reagent) and polyvinylpyrrolidone (PVP, Analytical Reagent, K30, Mw = 10,000) were bought from Tianjin Guangfu Fine Chemical Research Institute. Bovine serum albumin (BSA, Analytical Reagent, Mw = 68,000) was supplied by Beijing Aoboxing Universeen Biotech Co., Ltd.

### 2.2. Preparation of PVC flat sheet membranes

The PVC flat sheet membranes were fabricated via the immersion precipitation phase inversion method. A defined mass ratio (listed in Table 1) of PVC, PVP, and DMAc/DOP were blended under constant mechanical stirring in a three-necked round-bottom flask for 4 h at 70°C. Then, the prepared polymer solutions were placed in the electric vacuum drying oven for 1 h at 70°C to remove air bubbles. Before casting the membrane, the casting solution, glass plate, and casting knife were kept consistent at 70°C for 30 min. After that, the membranes were cast on the glass plate with a 120  $\mu$ m casting knife through the automatic film applicator (Elcometer 4340), and then, the glass plates were immediately immersed into the water coagulation bath at room temperature. The prepared membranes were washed and stored in water, and next ethanol for at least 48 h to completely leach out the residual solvents, water-soluble additive, and DOP. Thus, the PVC flat sheet membranes were prepared subsequently. The compositions of coating dope solutions are shown in Table 1.

### 2.3. Membrane characterizations

#### 2.3.1. Morphology observation

Scanning electron microscopy (SEM TM3030, Hitachi Co., Japan) was used to investigate the morphology of surface and cross-section of prepared membranes. The membranes were immersed in liquid nitrogen for 10–15 s and were frozen. Then the frozen membranes were broken for cross-section observation. Samples were all gold-sputtered before testing.

#### 2.3.2. Permeation performance experiments

The pure water flux was measured in cross-flow filtration mode at 0.1 MPa pressure and was calculated by Eq. (1):

$$J = \frac{V}{At} \quad (1)$$

Table 1  
Compositions of casting dope solutions

Membrane ID	PVC/wt.%	PVP/wt.%	DMAc/wt.%	DOP/wt.%
M1	16	0	74	10
M2	16	10	74	0
M3	16	10	69	5
M4	16	10	64	10
M5	16	10	59	15
M6	16	10	54	20

where  $J$  is the permeation flux of membrane ( $L/(m^2 h)$ ),  $V$  is the quantity of permeation ( $L$ ),  $A$  is the effective area of membrane ( $m^2$ ), and  $t$  is the testing time ( $h$ ).

The filtration experiments were then carried out by 1 g/L BSA solution. The concentration of feed solution and permeate solution were determined by UV spectroscopy at a wavelength of 280 nm, using a PERSEE TU-1801 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.). The separation efficiency of the membrane was defined by Eq. (2):

$$R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \quad (2)$$

where  $C_f$  and  $C_p$  are the concentration of protein in the feed and the permeate solution, respectively.

### 2.3.3. Apparent viscosity of the polymer solutions

The viscosities of the casting solutions with different compositions and temperatures of casting solutions were determined by a rotational viscometer (SNB-1, Shanghai FangRui Instrument Co. Ltd.).

### 2.3.4. Porosity

The membrane porosity was defined as the pores volume divided by the total volume of the porous membrane. It can be determined by the gravimetric method. The membrane sample with 20 mm × 20 mm was immersed in the n-butyl alcohol for at least 24 h. Then the n-butyl alcohol that attached to the membrane surface was wiped by filter paper. After that, the weight of the wet membrane was measured. The weight of the dry membrane was measured after drying in an electric blast drying oven for 10 h at 60°C. The porosity was calculated according to Eq. (3):

$$\varepsilon(\%) = \frac{(W_1 - W_2) / \rho_1}{(W_1 - W_2) / \rho_1 + W_2 / \rho_2} \times 100\% \quad (3)$$

where  $W_1$  is the weight of wet membrane (g),  $W_2$  is the weight of dry membrane (g),  $\rho_1$  is the n-butyl alcohol density ( $\rho_1 = 0.81 \text{ g/cm}^3$ ),  $\rho_2$  is the PVC density ( $\rho_2 = 1.40 \text{ g/cm}^3$ ).

### 2.3.5. Static water contact angle

The static water contact angle of PVC flat sheet membranes was measured by a contact angle measuring instruments

(DSA100, KRUSS, Germany). The measurements were carried out at room temperature (relative humidity: 50%). A drop of the water with 0.5  $\mu\text{L}$  was dropped on the top surface of the sample with 60 mm × 10 mm, then a video was created. The different images from the video determined the contact angle at the same time of 10s. Each sample was measured five times at different areas of the membrane to evaluate the average value.

### 2.3.6. Measurement of mechanical property

The membrane mechanical properties were measured by Electromechanical Universal Testing Machine (CMT4204, MTS Systems, China). At room temperature, the membrane samples were cut to the size of 80 mm × 10 mm. Then, the gripping range and the tensile rate were set as 50 mm and 20 mm/min, respectively. Each sample was tested five times to evaluate the average value.

## 3. Results and discussion

### 3.1. Apparent viscosity of polymer solutions

In the immersion precipitation phase inversion process, the double diffusion process was carried out between the non-solvent in the coagulation bath and solvent in casting solution when the casting solution was immersed into the coagulation bath, which determined the obtained membrane structure to a large extent. The apparent viscosity of casting solutions was one of the important factors influencing the double diffusion rate and the formation of the pore structure in the membrane formation process. The low apparent viscosity would speed up the double diffusion rate and be promoted the growth of pore structure in the immersion precipitation phase inversion process. The apparent viscosity of PVC casting solutions with different DOP content in the mixed solvent is shown in Fig. 1. It could be seen that the apparent viscosity of the PVC casting solution increased with the increase of the DOP content in the mixed solvent. In general, the double diffusion rate between the solvent in the casting solution and the non-solvent in the coagulation bath would be reduced when the apparent viscosity of the casting solution increased.

### 3.2. Morphology of PVC flat sheet membranes

The cross-section morphologies of prepared PVC flat sheet membranes are shown in Fig. 2. It could be seen that

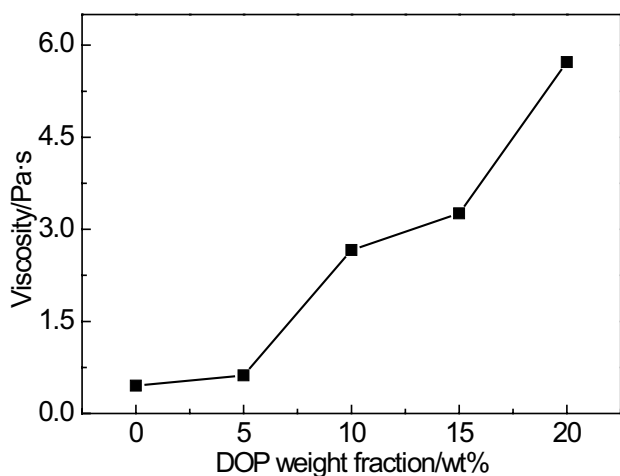


Fig. 1. Apparent viscosity of PVC casting solution with DOP content ( $T = 70^{\circ}\text{C}$ ).

the M1 membrane was composed of the finger-like structure closed to the top surface and the dense structure without obvious pores closed to the bottom surface. When the glass plate with the casting solution was immersed in water coagulation bath, the existence of DOP in mixed solvents that was insoluble in water would hinder the double diffusion between the DMAc solvent in the casting solution and the water in coagulation bath to a certain extent, which would restrain the growth of the finger-like pores and form the M1 cross-section structure. Compared with the M1 membrane, the M4 membrane that used the PVP as the additives was formed the finger-like structure and this finger-like structure crossed through the whole cross-section of the M4 membrane. Meanwhile, there produced thick sponge-like porous structure between these finger-like pores. This was because the hydrophilic PVP additives made the double diffusion rate increase in the phase inversion process which promoted the growth of the finger-like pores. Moreover, the density of the finger-like pores was decreased and the sponge-like

structure between the finger-like pores was formed due to the increment apparent viscosity of casting solution with the addition of PVP additives.

From Fig. 2b1, c1, and d1, the cross-section of PVC flat sheet membranes prepared with DMAc/DOP mixed solvents and PVP additives showed the typical finger-like structure. When the solvent was only DMAc, the finger-like pore structure almost crossed through the whole cross-section of the M2 membrane. However, the cross-section of the M6 membrane increased to three layers of finger-like pore structures as the DOP content reached to 20 wt.%, and the density of finger-like pores increased. This was due to the changes in the apparent viscosity of casting solution with the addition of DOP. When the solvent was only DMAc, the relatively low apparent viscosity increased the double diffusion rate between DMAc in casting solution and the water in the coagulation bath which promoted the growth of the finger-like pores. But the apparent viscosity of casting solution increased with the increase of the DOP content from 0 to 20 wt.% (Fig. 1). The relatively high apparent viscosity would reduce the double diffusion rate in the phase inversion process which would restrain the growth of the finger-like pores and form the multi-layers of finger-like pore structures.

The surface morphologies of prepared PVC flat sheet membranes are shown in Fig. 3. It could be seen that a lot of little pitting was uniformly distributed on both of the top and bottom surfaces of the M1 membrane, which was due to the extraction of DOP. In contrast, the M2 membrane prepared only with DMAc solvent possessed of smooth and compact top surface without obvious pores, while the bottom surface was more roughness than the top surface and distributed a lot of open pores. The top surface of the M4 membrane became rough and appeared some open pores when the DOP content increased to 10 wt.%. The bottom surface of the M4 membrane also had some open pores, but the porosity was lower than that of the M2 membrane. As the DOP content reached to 20 wt.%, the top surface of the prepared M6 membrane possessed of few big pores, but the bottom surface became rough without obvious open pores compared with the M4 membrane. When the glass plate with

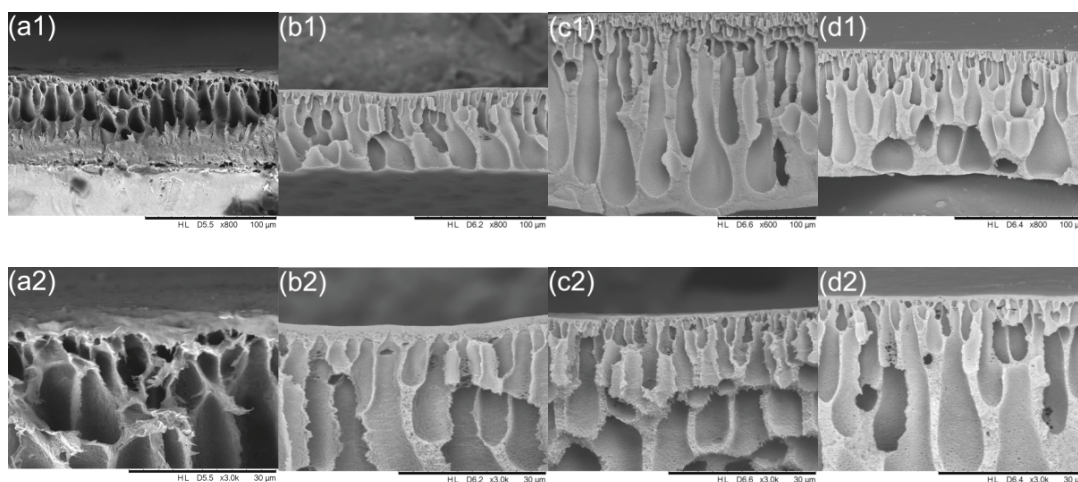


Fig. 2. Cross-section morphologies of PVC flat sheet membranes. (a) M1, (b) M2, (c) M4, and (d) M6; 1-cross section and 2-partial enlargement of cross section).



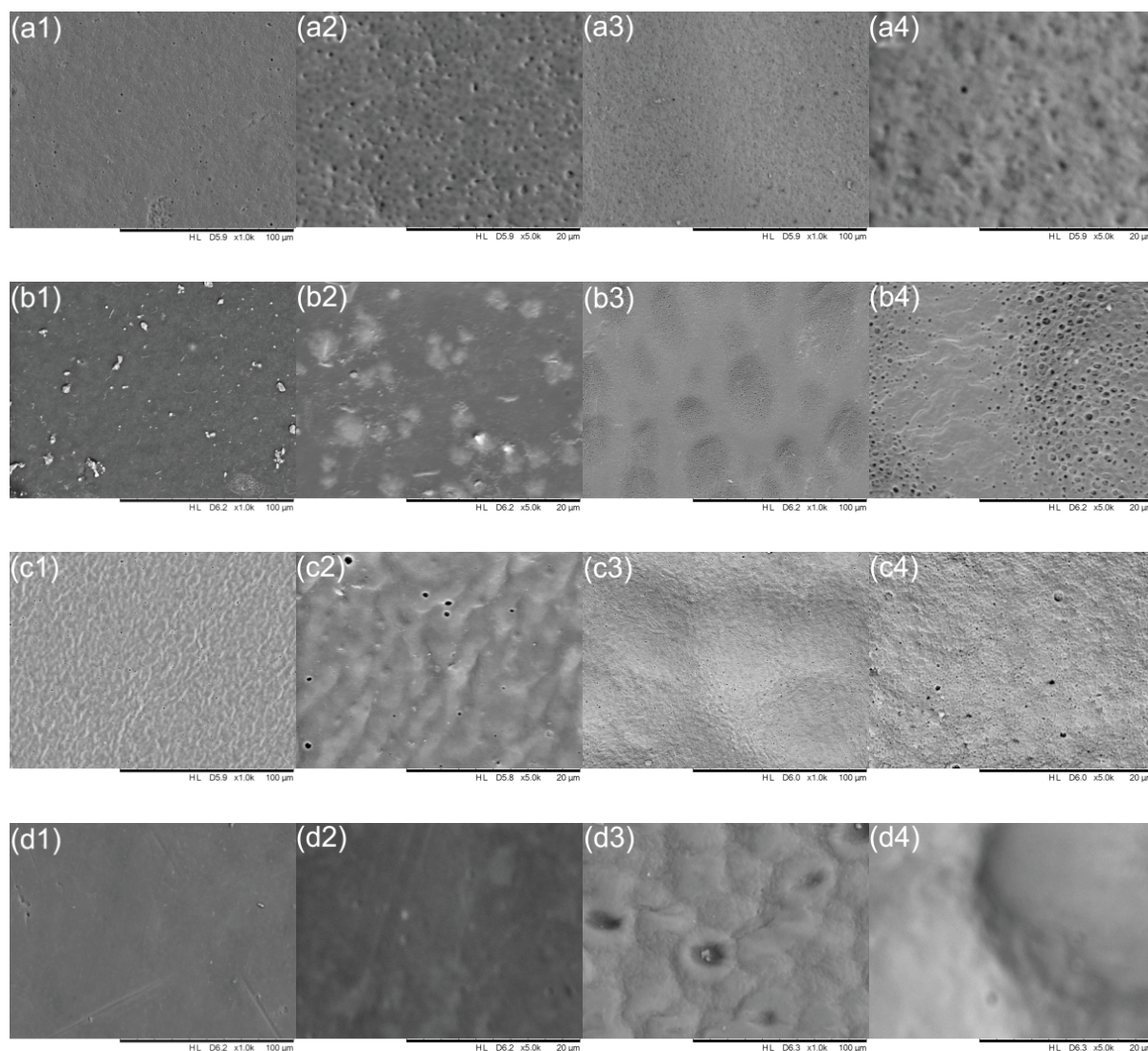


Fig. 3. Surface morphologies of PVC flat sheet membranes (a) M1, (b) M2, (c) M4, and (d) M6; 1-top surface, 2-partial enlargement of the top surface, 3-bottom surface, and 4-partial enlargement of the bottom surface).

casting solution came into water coagulation, the double diffusion changed the DOP concentration in the whole casting membrane and formed the higher DOP concentration in the membrane lower side than that in the membrane upper side. Meanwhile, the excessive use of DOP for the M6 membrane reduced the gelation speed and formed the soft membrane in the water coagulation bath. When the soft membrane immersed into ethanol, the aggregation state structure of PVC changed, which revealed that the M6 membrane was shrunk on the macro-level after the DOP extraction. Thus, the shrink of the M6 membrane formed the rough structure on the bottom surface.

### 3.3. Permeability of PVC flat sheet membranes

The different contents (0, 5, 10, 15, and 20 wt.%) of DOP in the casting solution were used to fabricate the PVC flat sheet membrane. The static water contact angle of the prepared

membrane top surface is shown in Fig. 4. It could be seen that the contact angle on the top surface decreased with the increase of the DOP content in the casting solution. This was due to the changes in the surface structures, aforementioned. The apparent viscosity of the casting solution increased with the increase of the DOP content in casting solution and the double diffusion process between the DMAc solvent in casting solution and the water in the coagulation bath became slow. Therefore, the smooth and compact top surface for the M2 membrane turned to a porous top surface for M4 and M6 membranes from Fig. 3. After the DOP extraction, these membranes of M2, M3, M4, M5, and M6 membranes were shrunk in different degree on the macro-level, and the original position of DOP in the membranes formed the little pitting and some pore structures on the membrane surface. Consequently, the membrane roughness increased with the increase of the DOP content in casting solutions. Due to the addition of hydrophilic PVP, the prepared PVC porous

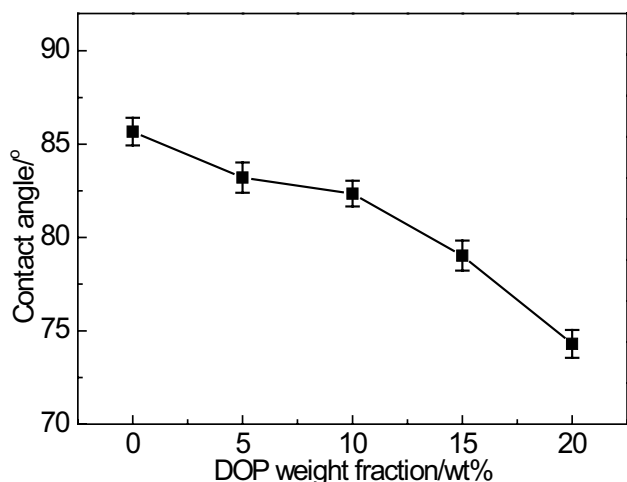


Fig. 4. Effects of different DOP content on top surface contact angle of PVC flat sheet membranes (testing temperature: 20°C).

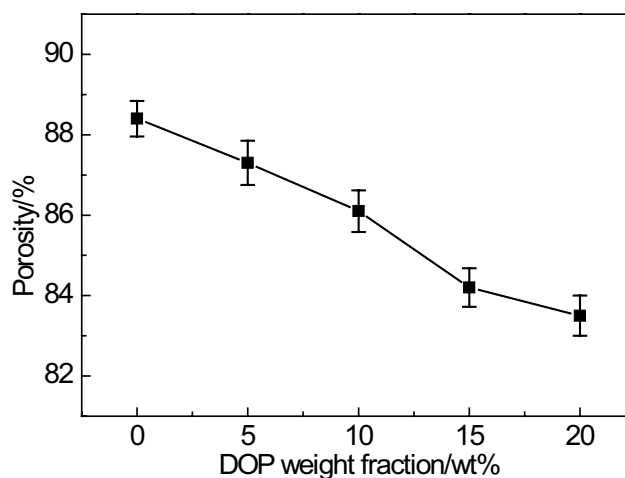


Fig. 5. Effects of different DOP content on porosity of PVC flat sheet membranes (testing temperature: 20°C).

membranes presented a hydrophilic surface. For the hydrophilic surface, the increase of membrane surface roughness could improve the membrane hydrophilicity. Hence, the static water contact angle on the top surface decreased with the increase of the DOP content in the casting solution.

Fig. 5 shows the porosity of prepared PVC flat sheet membranes with different DOP content. It was found that the membrane porosity decreased with the increase of the DOP content in mixed solvents. This was because the cross-section of prepared PVC flat sheet membranes changed from one layer of finger-like structure for the M2 membrane to three layers of finger-like structures for the M6 membrane. There produced more sponge-like pore structures between finger-like structures. Meanwhile, the shrinkage degree of prepared PVC membranes increased with the increase of the DOP content in mixed solvents. These changes led to a slight decline in the porosity of prepared PVC flat sheet membranes.

The pure water flux and the protein rejection of prepared PVC flat sheet membranes with different DOP content are shown in Fig. 6. It could be seen that the prepared M2 membrane with DMAc solvent had higher pure water flux and the protein rejection than that of other prepared membranes with DMAc/DOP mixed solvents. The pure water flux increased slightly and the protein rejection decreased with the increase of the DOP content from 5 wt.% to 20 wt.%. As we all know, the membrane rejection depended more on the denseness of the skin layer than on the structure of the cross-section [10,22]. The increase of the DOP content in mixed solvent decreased the double diffusion rate and formed the open pores structure on the top surface from the surface morphologies in Fig. 3, which reduced the denseness of the skin layer and further reduced the protein rejection. For the prepared M2 membrane with DMAc solvent only, the finger-like pore structure almost crossed through the whole cross-section which would reduce the membrane filtration resistance. The formation of open pores on the top surface would decrease the membrane filtration resistance, while the sponge-like structure between the multi-layers finger-like

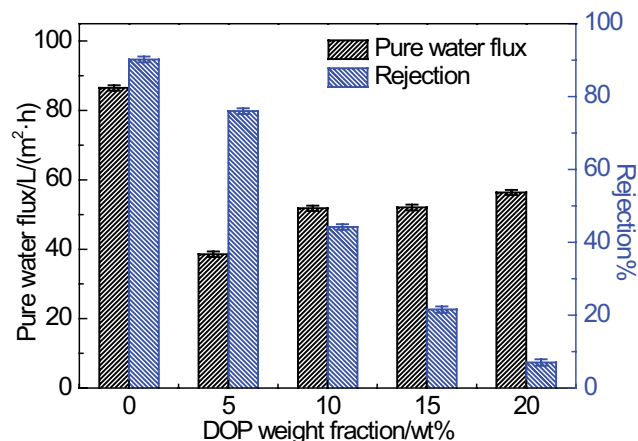


Fig. 6. Effects of different DOP content on pure water flux and protein rejection of PVC flat sheet membranes (testing temperature: 20°C).

structure would increase the membrane filtration resistance. Thus, the pure water flux increased slightly with the increase of the DOP content from 5 wt.% to 20 wt.% in this study.

### 3.4. Mechanical properties of PVC flat sheet membranes

Fig. 7 shows the tensile strength of prepared PVC flat sheet membranes with different DOP content. It could be seen that the tensile strength increased firstly and then decreased with the increase of the DOP content in casting solution from 0 to 20 wt.%. The existence of the DOP in casting solution reduced the membrane solidification speed. The penetrating of the DOP molecule into the PVC macromolecule chains increased the flexibility of the chain segment. The plenty of solidification time made the PVC macromolecule chain along the direction of the double diffusion, which increased the molecular chain regularity. The extraction of a small amount of DOP had little impact on the aggregation state of the PVC molecular chain. Thus,

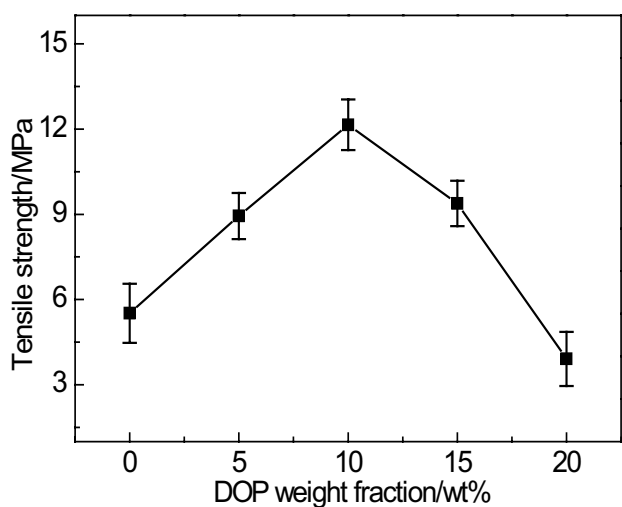


Fig. 7. Effects of different DOP content on tensile strength of PVC flat sheet membranes.

the tensile strength increased with the increase of the DOP content in the casting solution. However, the extraction of overmuch of DOP could significantly change the aggregation state of the PVC molecular chain structure and caused the shrink of the membranes (Fig. 3d2), which reduced the membrane uniformity. Therefore, the stress concentration point became more during the testing process and the tensile strength decreased. The maximum tensile strength (12.15 MPa) obtained as the DOP content reached to 10 wt.%. At the same time, the pure water flux was up to 51.80 L/(m<sup>2</sup> h).

#### 4. Conclusion

The PVC flat sheet membranes with high tensile strength were fabricated via immersion precipitation phase inversion method used DMAc/DOP as the mixed solvents. On the one hand, the growth of the finger-like structure was effectively promoted with the addition of PVP, resulting in increasing the membrane pure water flux. On the other hand, with the increase of the DOP content in the mixed solvents, the cross-section structure became denser and the membrane surface pore size became larger. The increase of the DOP content brought about the increase of membrane hydrophilicity but decreased the membrane porosity and protein rejection. The membrane obtained the maximum tensile strength of 12.15 MPa as the DOP content reached 10 wt.%.

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