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The effects of pretreatment condition of non-woven fabrics on the PVC-co-PVAc-OH membrane performances

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ABSTRACT

In this paper, flat-sheet membranes were prepared with PVC-co-PVAc-OH material/poly (ethylene glycol) 2000/dimethylformamide using different types of non-woven fabrics (NWFs) as substrate using phase inversion method. NWFs were immersed into organic solvent, and then exposed to a humid environment for certain time before casting a thin liquid film onto them. The effects of the substrate, NWFs, and the pretreatment method of the NWFs on the structure and performance of membranes were mainly studied. The types of NWFs and its pretreatment conditions have significant impacts on the performances of the membrane: firstly, types of solvent to immerse NWFs have little impact on final membrane performance; secondly, both pure water flux and the corresponding rejection increased, and then decreased dramatically, with longer immersion time; however, when the immersion time was more than 12 h, the surface of NWF was wrinkled slightly; finally, in order to prepare a membrane with high rejection, two approaches are possible: either prolonging the solvent evaporation time and increasing of the temperature or decreasing the relative humidity in the environment. In the experiment, the membranes were used to purify the Bovine serum albumin solution by the dead-end membrane module. And all the results were conformed to scanning electron microscopy observation, pore size distribution or water content of the membranes.

Keywords: Non-woven fabrics; Pretreatment conditions; Performances

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1. Introduction

Membrane-based separation is an increasingly viable, cost-effective separation technology, alternative or complementary to traditional unit operations, offering some inherent advantages. In the past decades, membrane filtration processes have found a wide range of applications in water treatment [1], medicine [2], human health [3], environmental protection [4,5], the food industry [6,7], and fermentation [8], and so on.

If polymer membranes are to be used in more challenging separations, they must not only exhibit good separation properties but also be durable [9]. For the plate-and-frame module, the strength of membrane is one of the greatest concerns. Higher tensile strength of the wet membranes possesses greater workability at the initial stage [10]; however, the increase of porosity leads to a decrease in membrane

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strength [11]. Non-woven fabrics (NWFs), made from molten plastic or plastic film by chemical, mechanical, heat or solvent treatment, are flat, porous sheets, and fabric-like material with large surface-to-volume ratio [12]. They can be developed into different types of multi-layer bonded structures, with a variety of bulk properties suitable for specific end-uses [13]. Due to their random network of overlapped fibers, multiple connected pores, and high thermal and chemical stability, NWFs have been used in many biomedical separations, as one of the most popular filtration media [14,15]. NWFs can also be used as substrates to support porous membranes in ultrafiltration or nanofiltration processes [16]. When a membrane is casted onto NWFs, it shows a big improvement in the strength properties for both tensile strength and compression capacity [17]. The flat-sheet membrane configurations are generally manufactured by casting the polymer solution on a polyester or polyethylene substrate, NWFs [18]. NWFs can be used as the substrate to improve the strength of the membranes, while, other properties of NWFs, such as a random filament orientation and numerous micropores [19], the fibers material, diameter/length, pore size distribution [20], air transmission coefficient and the surface roughness of NWFs etc, also play important role in membrane performance.

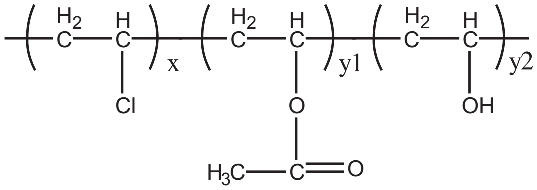
Furthermore, although rarely reported in the present literature, the effects of the pretreatment conditions of NWFs on membrane performances have to be given particular attention in the practical membrane-making process. Therefore it is very pertinent to quantify and study the influence of the pretreatment condition of NWFs on membrane performances, as this can provide a good basis for membrane-making process optimization.

In present experimental investigations, three types of (ethylene terephthalate) (PET) NWFs with different weight, thickness and air transmission coefficient, were initiated by phase inversion process for propagating the flat-sheet PVC-co-PVAc-OH membranes as substrate. In order to optimize the membrane preparation process, the types of NWFs and its pretreatment conditions (immersion solvent, immersion time, evaporation time, environmental humidity and temperature) of NWFs on membrane performances were systematically studied.

2. Experimental

2.1. Materials

Solvents, dimethylformamide (DMF), dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP), all of analytical grade, were purchased from Tianjin Fuchen Chemical Reagent Factory. Poly (ethylene glycol) with molecular weight of 2000 g/mol, i.e. PEG 2000, which was chosen as the additive in casting solution, and *N*-butanol used as santomerse were purchased from Beijing Chemical Engineering Factory. Substrates, three types of PET NWFs (A, B, C), were purchased from Beijing Ande Membrane Separation Technology Engineering (Beijing) Co., Ltd. Bovine serum albumin (BSA) used as reagent for determining the rejection of membrane was purchased from Beijing Microorganism Culture Medium Manufacturing Corporation, and its isoelectric point of pH was 4.8. Homemade PVC-co-PVAc-OH [21], modified from polyvinyl chloride-vinyl acetate (PVC-co-PVAc) material with hydroxyl group, was used as the membrane material. Its structure can be described elsewhere as follows [21]:



2.2. Preparation of the membranes

To start with, a certain proportion of PVC-co-PVAc-OH polymers and a given additive (PEG 2000) were dissolved in DMF to form a homogeneous solution, and the casting solution was kept in the vacuum oven at 60 ℃ for a certain time. At the same time, NWFs were put into deionized water to remove the impurities and then they were dried at the environmental temperature of 25 ℃, and then immersed in different solvents for certain time. Next, the immersed NWFs were evaporated for certain time under different temperature and relative humidity. In addition, the casting solution was casted onto NWFs with solvent by a casting blade under same environmental temperature and relative humidity. After exposuring a period of time the casted film along with the glass plate was gently immersed into the coagulation bath at a temperature of 20 ℃ with precipitation time of 30 min. Finally, the formed membrane was immersed into the deionized water bath for 24 h to remove residual solvent.

2.3. Membrane characterization

2.3.1. Flux and separation experiments

Pure water flux and rejection of BSA (with an average molecular weight of 67,000 g/mol) were conducted via a dead-end membrane module with an effective membrane filtration area of 24 cm^2. The experiments were measured at transmembrane pressure (TMP) of 0.2 MPa, and the results were calculated by Eqs. (1) and (2):

$$J = \frac{V}{A \times t} \tag{1}$$

where J is the abbreviations of pure water flux of the membrane ($\text{mL cm}^{-2}\,\text{h}^{-1}$), V is the total permeate volume during the experiment (mL) and A is the effective membrane area (cm^2), t denotes the operation time (h), respectively.

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

where R is the abbreviation of rejection of the membrane, C_p and C_f represent the concentration of the permeation and the feed solution (g L^{-1}), respectively. Moreover, the analysis of BSA was performed by using the UV spectrophotometer (HP 845l-A) at $\lambda = 280$ nm, the experimental set-up can be found in Wang et al. [22]. And all the experiments were repeated three times to ensure reproducibility of the results.

2.3.2. Solvent evaporation rate constants

A gravimetric approach has been followed for determining the evaporation rate of the organic solvent during membrane preparation [23]. Every minute, the weight of NWFs plus the immersion solvent and glass plate were recorded to evaluate the changes of the solvents by the electronic balance (Sartorius, BS323S Max 320g) with the repeatability of 0.001 g and the linearity of ± 0.001 g. The solvent evaporation ability can be quantitatively evaluated by knowing the constant (b) of solvent evaporation rate [24]:

$$(w_t - w_\infty) = (w_0 - w_\infty)\exp(-bt) \tag{3}$$

where w_t, w_0 and w_∞ are the weight of NWFs at $t = t$, $t = 0$ and $t = \infty$ respectively; b called the constant of solvent evaporation rate, which is the slope of the linear part in the equation.

If we make $w = \frac{(w_t - w_\infty)}{(w_0 - w_\infty)}$, and then $bt = -\ln w$.

2.3.3. Calculation of the pore size distribution of the membrane

Pore size distribution of all membrane samples were determined by liquid–liquid interfacial contact method, which may be referred in other literature [25,26]. Before the start of the experiment, the membranes were equilibrated into *n*-butanol for some time to fill the pores with this solvent, and then with constant increment of pressure, water was used to displace *n*-butanol in the membrane. The pore *radii* (r) and the pore size distribution ($f(r)$) were determined by the following equations, respectively.

$$r_{pj} = \frac{2\sigma\cos\theta}{P_j} \tag{4}$$

$$f(r) = \frac{P_i(P_{i-1}Q_i - P_iQ_{i-1})}{(r_{i-1} - r_i)P_{i-1}\sum_{i=1}^{m}\frac{P_i}{P_{i-1}(P_{i-1}Q_i - P_iQ_{i-1})}} \tag{5}$$

where σ, θ, P, Q are the water/water saturated *n*-butanol interfacial tension, water/polymer contact angle, applied pressure and permeate flow rate, respectively.

2.3.4. Scanning electron microscopy

Morphologies of these air-dried PVC-co-PVAc-OH membrane samples can be investigated by SEM, and all the morphologies were obtained on an S-4300 SEM (Hitachi, Japan).

2.3.5. Water content

The water content (WC %) was calculated by the following equation [27]:

$$\text{WC}\ (\%) = \frac{w_w - w_d}{w_w} \times 100\% \tag{6}$$

where w_w and w_d are the weight of the membrane (g) before and after dried in the air before using them to filter the BSA solution, respectively.

3. Theoretical background of formation kinetics

The membrane formation kinetics is very important in understanding the formation mechanism of the membrane [28]. And the phase inversion process involves a phase separation of a polymer solution in polymer rich and lean phases, where the polymer solution is immersed in a non-solvent bath. The simplest system is formed by three components, polymer/solvent/non-solvent, which can be described by the ternary diagram [29].

The binodal curve delimitates the two-phase region, rich and lean polymer phases. The spinodal curve shows all the possible fluctuations lead to instability, and the region between binodal and spinodal corresponds to metastable compositions will bring phase separation. The point binodal and spinodal meet is referred to as the critical point. When the precipitation path crosses the binodal below the critical point, nucleation of a polymer rich phase may initiate the phase separation process, while if the precipitation path crosses the binodal above the critical point, nucleation of the polymer lean phase may occur. In microfiltration and ultrafiltration processes, membranes formed by instantaneous demixing have a porous top layer and are used [29].

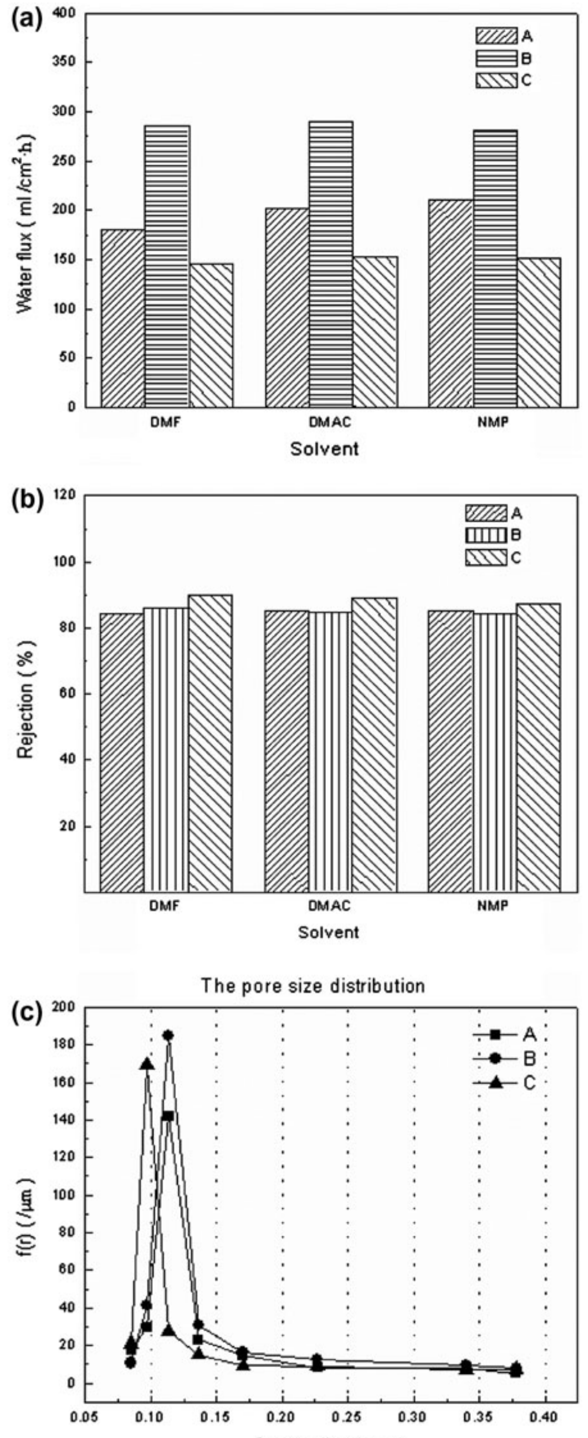


Fig. 1. Effects of immersion solvent of NWFs on membrane performances. (a) The pure water flux of the membrane; (b) The rejection of the membrane; (c) the pore size distribution of the membrane using DMF as the immersion solvent on the three types of non-woven (A, B, C). The pretreatment conditions of NWFs were described as follows: immersion time in solvent is 3 h, the evaporation time of the solvent is 2 min, the environmental temperature and relative humidity are 20℃ and 40%.

4. Results and discussion

The polymer concentration plays an important role in membrane performance. All of the steps were repeated for polymer concentration of 16 wt.% as described in literature [21]. PEG 2000 was chosen as an additive in our study, because its presence in the cast solution film can increase the porosity/permeability of the prepared membranes [30]. Moreover, to prepare a membrane with good performances, the environmental temperature [31], the relative humidity of the humid surroundings [32], the evaporation time, coagulating bath temperature [30] and precipitation time were also systematically measured.

Based on our preliminary study, we aimed at establishing optimized preparation conditions of the membrane which were achieved as follows: the content of additive was 4%, environmental temperature was 20℃, relative humidity was 40%, evaporation time was 30 s, coagulating bath temperature was 20℃, and precipitation time was 30 min. Moreover, filtration experiments were conducted under constant TMP of

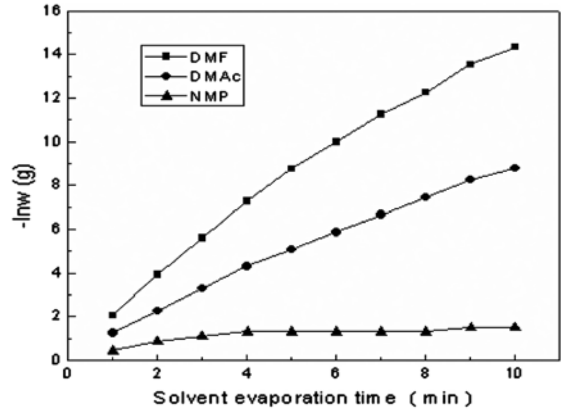


Fig. 2. Curve of evaporation rate for different immersion solvents from NWFs $\left(w = \frac{w_t - w_\infty}{w_0 - w_\infty}\right)$.

Table 1
The properties of different types of NWFs

	A	B	C
Material	PET	PET	PET
Weight (kg/m^2)	0.085	0.088	0.085
Thickness (mm)	0.099	0.106	0.094
Air transmission coefficient (cfmft^2)	4	5.8	2

0.2 MPa at 22°C. These conditions were also generally applied in the following study.

4.1. The selection of immersion solvent

In order to study the performance of different solvents on the NWFs, and then selected a more suitable immersion solvent, three types of NWFs were immersed into three different types of solvents (DMF, DMAc and NMP) for 3 h, and then they were evaporated for 2 min at environmental temperature of 20°C and relative humidity of 40%, respectively. After that, the polymer solution was cast onto the surfaces of the NWFs which worked as substrate of the membranes. Finally, the membrane properties, such as pure water flux, rejection, the pore size distribution and water content, were evaluated to determine the better substrate and immersion solvent. All experimental results were illustrated in Fig. 1. As presented in Fig. 1, when using different types of solvents as the immersion solvent, the variation tendency of the pure water flux and rejection of membrane were not obvious, in other words, the type of solvent has little impact on final performances of the membrane. In contrast, when using different types of NWFs as substrate, the variation tendencies of the membrane performances were obvious, especially for the pure water flux, which implied that a membrane with high pure water flux or separation performance can be successfully prepared by selecting the type of NWFs. For example, as shown in Fig. 2, when NWFs A or C was chosen as substrates, the membranes showed lower pure water flux than B at the same rejection. This can be explained by the different pore size of NWFs. According to Table 1, all three types of NWFs (A, B, C) were made of PET material with different properties. The air transmission coefficient for NWFs A, B and C were 4, 5.8 and 2 cfmft^2, respectively. It means that NWF B had the biggest pore size and possesses the smallest resistance to the fluid flow; therefore, the highest membrane flux could be obtained. This result showed good agreement with the value investigated in Fig. 1 (a) and (c). Furthermore, the rejection depends mainly on the pore radius of the skin layer, while the influence of NWFs' pore radius on the rejection of the membrane is very small.

The constant of solvent evaporation rate, describing the rate of solvent evaporation, is one of the important parameters to determine the attractiveness of the membrane-making process. Evaporation brings an essential change in polymer concentration of the casting solutions [23], and faster evaporation rates causing eventually lower diluting levels of the casting solvent. In order to study the influence of solvent evaporation on the structure of the membranes, the evaporation rates of different solvents from the surface of NWFs were determined using method of the gravimetry. Constants of evaporation rate (DMF, DMAc and NMP) were measured and the results were drawn in Fig. 2.

As shown in Fig. 2, to begin with, the sequence of curves slopes was b_{DMF} (0.0174) > b_{DMAc} (0.0101) > b_{NMP} (0.0022). So, the evaporation rate of DMF is the fastest in the three types of solvents, then is DMAc, and NMP is the last. This implies that, DMF can evaporate more fully from the surface of NWFs in the shortest time. It is worth to notice that, a very low evaporation

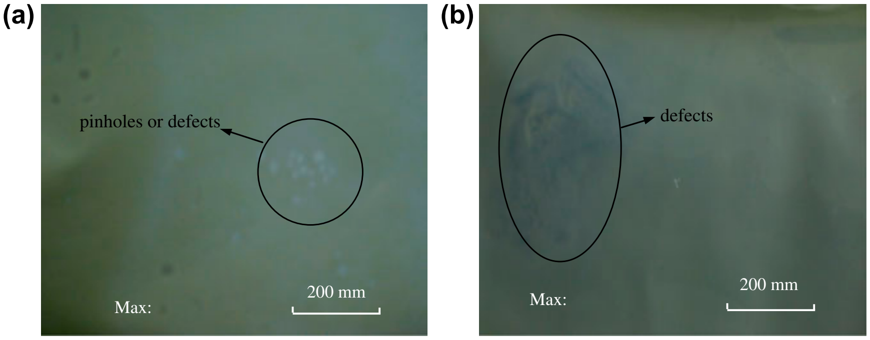


Fig. 3. The digital photo of top surface for parts of the PVC-co-PVAc-OH membrane, the roped areas are the examples of pinholes or defects. (a) DMAc as immersion solvent; (b) NMP as immersion solvent.

rate of solvent can lead the solvent to gather and concentrate on some areas of the surface of NWFs, and the coated polymer solution will be diluted by the congregated solvent causing pinholes or defects on the membrane surface as shown in Fig. 3 (using DMAc and NMP as solvent). Because DMF is highly volatile and evaporates easily from the surface of NWFs, when is used as immersion solvent, a uniform smooth membrane surface with less pinholes or defects can be formed in a relatively short period of time. This can save time, and be beneficial for industrial production processes. Considering the above factors, DMF was chosen respectively in future study.

4.2. The selection of immersion time of NWFs in solvent

In order to investigate the influence of immersion time of NWFs on the membrane performances, immersion time of 1, 5, 10, 15, 20–720 min in DMF were respectively applied to prepare the membrane using the above mentioned three types of NWFs as substrate; then the membrane performances were evaluated respectively, and the experimental results were presented in Fig. 4.

Fig. 4 shows the variations of pure water flux and rejection of the membrane as altered by the increase of immersion time. For example, when using NWF A as substrate, as the immersion time increased, both the pure water flux (from the initial lower value of 190.3 mL cm^{-2} h^{-1} changes quickly to a relative higher value of 354.7 mL cm^{-2} h^{-1} with 10 min immersion time, and then to 210.3 mL cm^{-2} h^{-1} with 30 min immersion time) and the corresponding rejection of BSA (from 82.3 to 90.7, then to 87.4%, correspondingly) changed drastically, increasing first, and then decreasing after 30 min. The explanation of these changes in both the membrane flux and rejection rate is not obvious. Moreover, the trends of flux and rejection were similar with the other two types of NWFs (B and C). Finally, it is worth to notice that, when the immersion time is longer than 12 h, the NWF surface would look slightly wrinkled.

To further investigate the effect of types of NWFs and immersion time on the structure of the porous membrane, the morphologies of the cross-section of membranes prepared using different types of NWFs and with different immersion time were illustrated in Figs. 5 and 6, respectively. It can be seen from Fig. 5, the pore size of the membrane had distinct structures, and became larger and then smaller when the different substrates of NWFs A, B, and C were used, respectively. The result of the pure water flux was

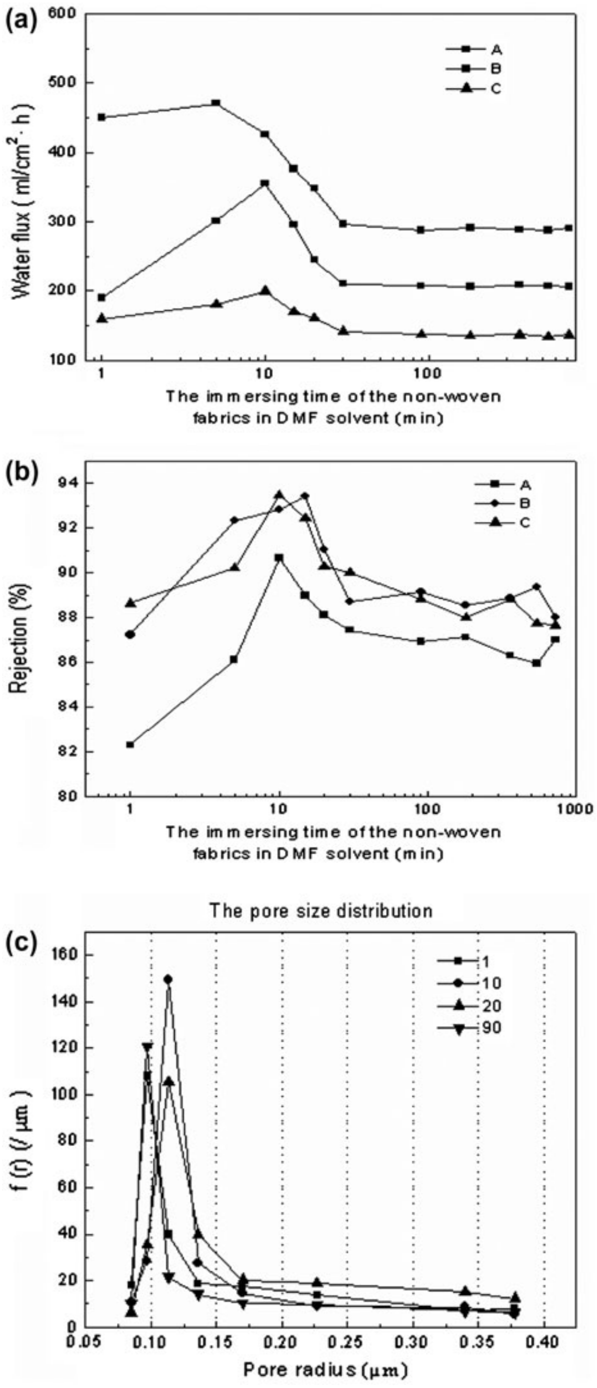


Fig. 4. Effects of the immersion time of NWFs in DMF solvent on membrane performances. (a) The pure water flux of the membrane; (b) the rejection of the membrane; (c) the pore size distribution of the membrane using NWF A as the substrate. The pretreatment conditions of NWFs were described as follows: the evaporation time of the solvent from the surface of NWFs is 2 min, the environmental temperature and relative humidity are 20℃ and 40%.

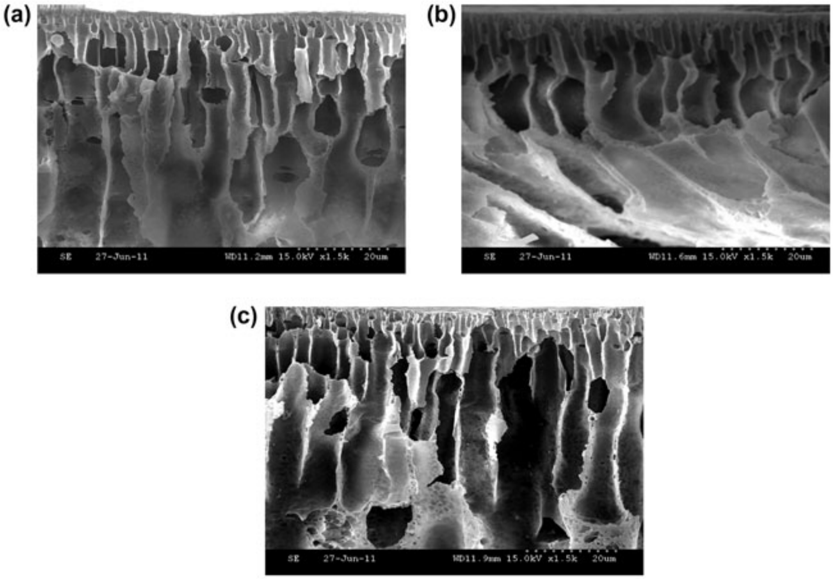


Fig. 5. The morphologies of the cross-section for the PVC-co-PVAc-OH membrane cast on NWFs A, B, C with the best immersion time in DMF solvent, respectively.

agreement with that from morphological observations. For example, when NWF B was chosen as substrate, the prepared membrane possessed higher flux and had the bigger pore size in comparing with NWF A and C, this confirms the conclusion drawn from Fig. 4 (c). As shown in Fig. 6, with the increase of NWFs immersion time, the pore size of the membrane changed dramatically, i.e. increased firstly, then decreased. The trend of pore size in morphology changes with the increase of immersion time conformed completely with the trend of the pore size distribution described in Fig. 4(c). Moreover, the observation of the SEM images was in coincident with the changes of the pure water flux. Therefore, the immersion time in solvent has an important influence on the pore sizes of the membrane.

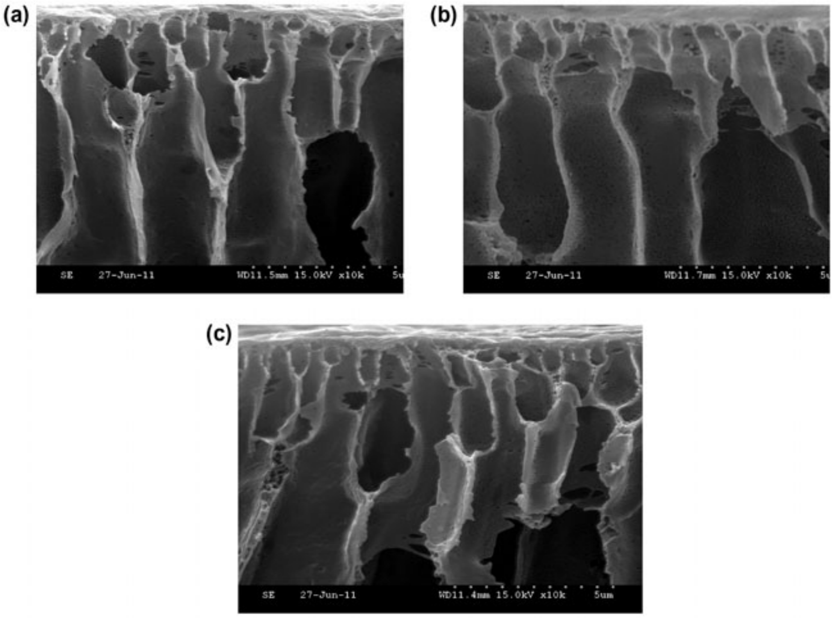


Fig. 6. The morphologies of the cross-section for the PVC-co-PVAc-OH membrane with different immersion time of NWF A in DMF solvent: 1, 10, 20 min, respectively.

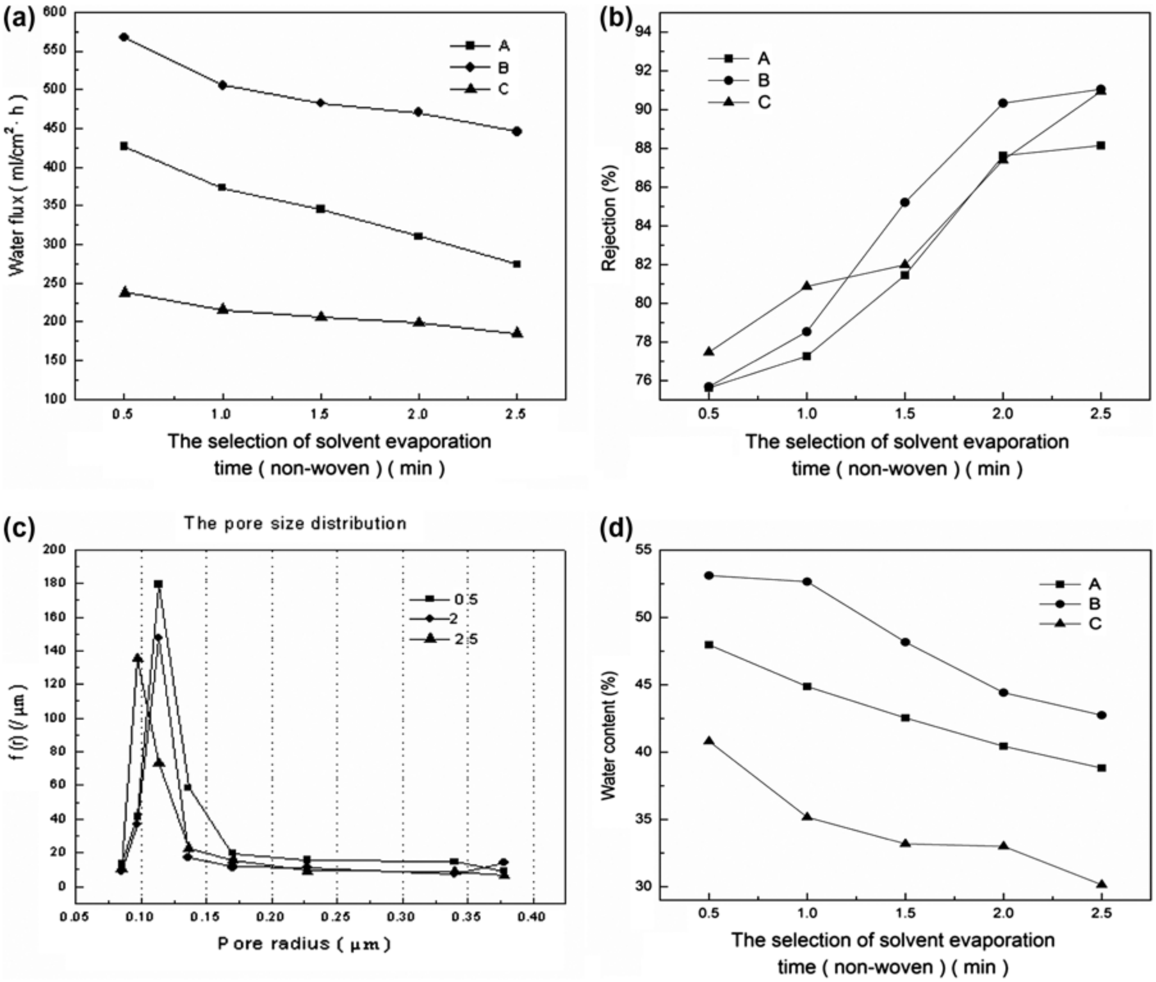


Fig. 7. Effects of the evaporation time of immersion solvent from the surface of NWFs on membrane performances. (The pretreatment conditions of NWFs were described as follows: immersion time of NWFs in DMF of 10, 5 and 10 min for NWFs, respectively, the environmental temperature and relative humidity are 20˚C and 40%, (a) the pure water flux of the membrane; (b) the rejection of the membrane; (c) the pore size distribution of the membrane using NWF A as the substrate; (d) the water content of the membrane).

Taking into account all these factors, we may safely draw the conclusion that when using the three types of NWFs (A, B, C) as substrate, immersion time in DMF of 10, 5, 10 min respectively, the membrane with best performance will be obtained. This conclusion was used in the following study.

4.3. Assessment of the wettability of the surface of NWFs

The wettability of NWF surface plays an important role in the membrane-making process, which was mainly influenced by the factors of evaporation time of volatile solvent, environmental temperature and the relative humidity. The casting polymer solution can be diluted by the non-volatilized solvent, when it is coated onto areas where the solvent congregates. As the casting polymer solutions were diluted, the polymer concentration incasting solution decreases slightly and the formed membrane showed a loose skin layer and bigger membrane flux [33]. This means

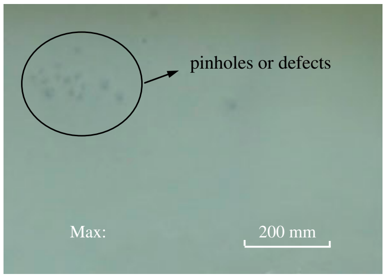


Fig. 8. The digital photo of top surface for parts of the PVC-co-PVAc-OH membrane made with evaporation time of the immersion solvent less than 1 min. The roped areas were examples of pinholes or defects.

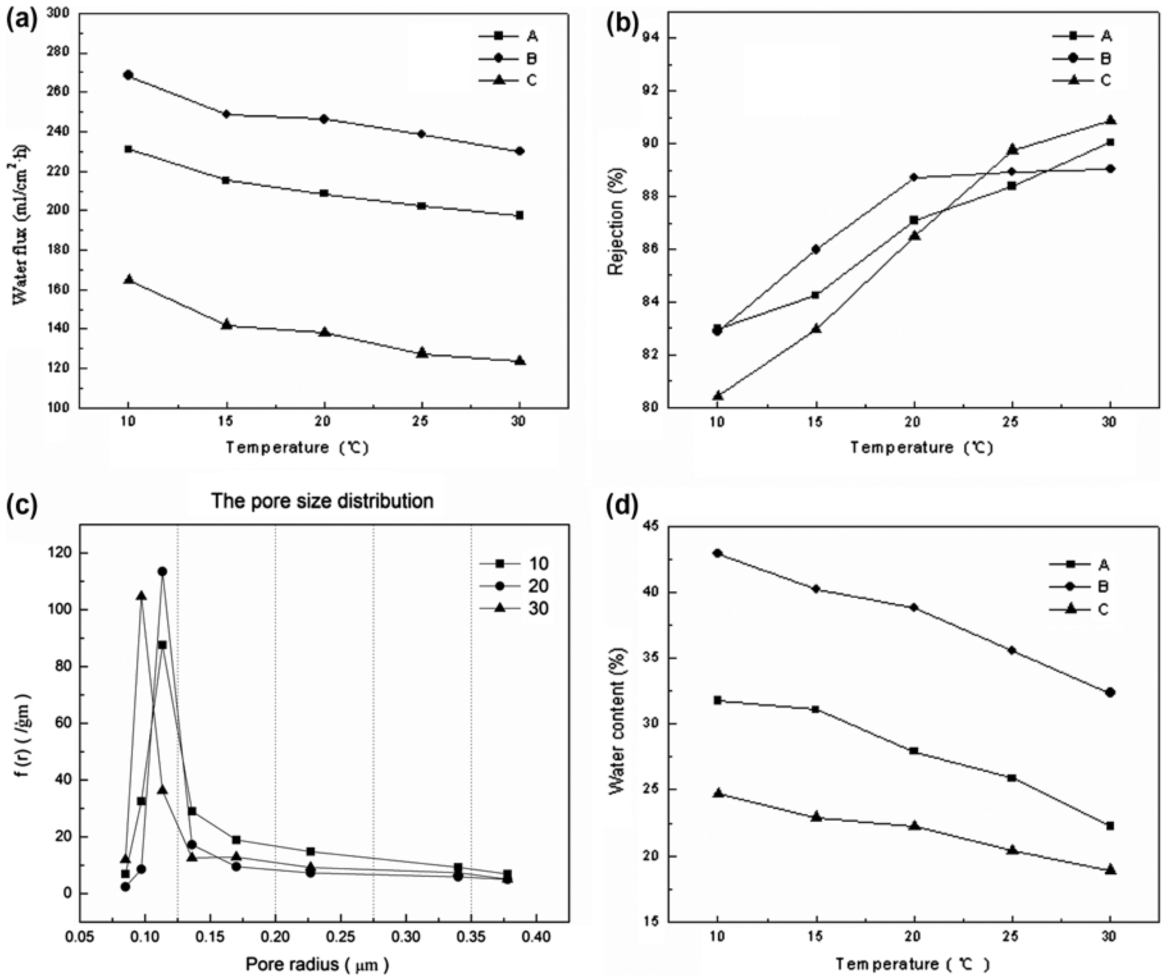


Fig. 9. Effects of the environmental temperature on membrane performances. (The pretreatment conditions of NWFs were described as follows: the immersion time of NWFs in DMF were 10, 5 and 10 min for NWFs, respectively, the environmental temperature and relative humidity are 20℃ and 40% (the membrane were made under the conditions of 30℃ and 40%), (a) the pure water flux of the membrane; (b) the rejection of the membrane; (c) the pore size distribution of the membrane using NWF A as the substrate; (d) the water content of the membrane).

that, a decrease in polymer concentration can promote the liquid-liquid phase separation, and facilitate the formation of a pore structure with better connectivity, leading to enhance the water flux and decrease the rejection of the membrane [33]. So, these three factors were discussed in this chapter and the experimental results were shown in Figs. 7–10, respectively.

As shown in Fig. 7(c), the pore size of the membrane is decreasing with the increasing of the evaporation time of the NWFs in air. This can be explained by the fact that adsorbed DMF on the NWFs after evaporation can be used as the solvent which can dilute the casting solution and thus have some impact on the phase inversion process. So, shorter evaporation time, higher adsorbed DMF on the NWFs, relative lower solid content in membrane casting solution, and the obtained membrane will possess bigger pore size.

With the increase of polymer concentration, the viscosity of the casing solution increases, the non-solvent is more difficult to diffuse into the casting solution, the speed of membrane formation decreases, the time of phase separation delay longer and results in decreasing of the finger-like structure in the membrane. Moreover, the rearrangement of the chain segment also will take longer time with the polymer concentration increased, and make the formation process slowing down; this can increase the sponge-like structure in the membrane.

When putting the NWFs with the cast polymer film into coagulation bath, the solvent rapidly diffuses out from the cast polymer film, while the enter rate of

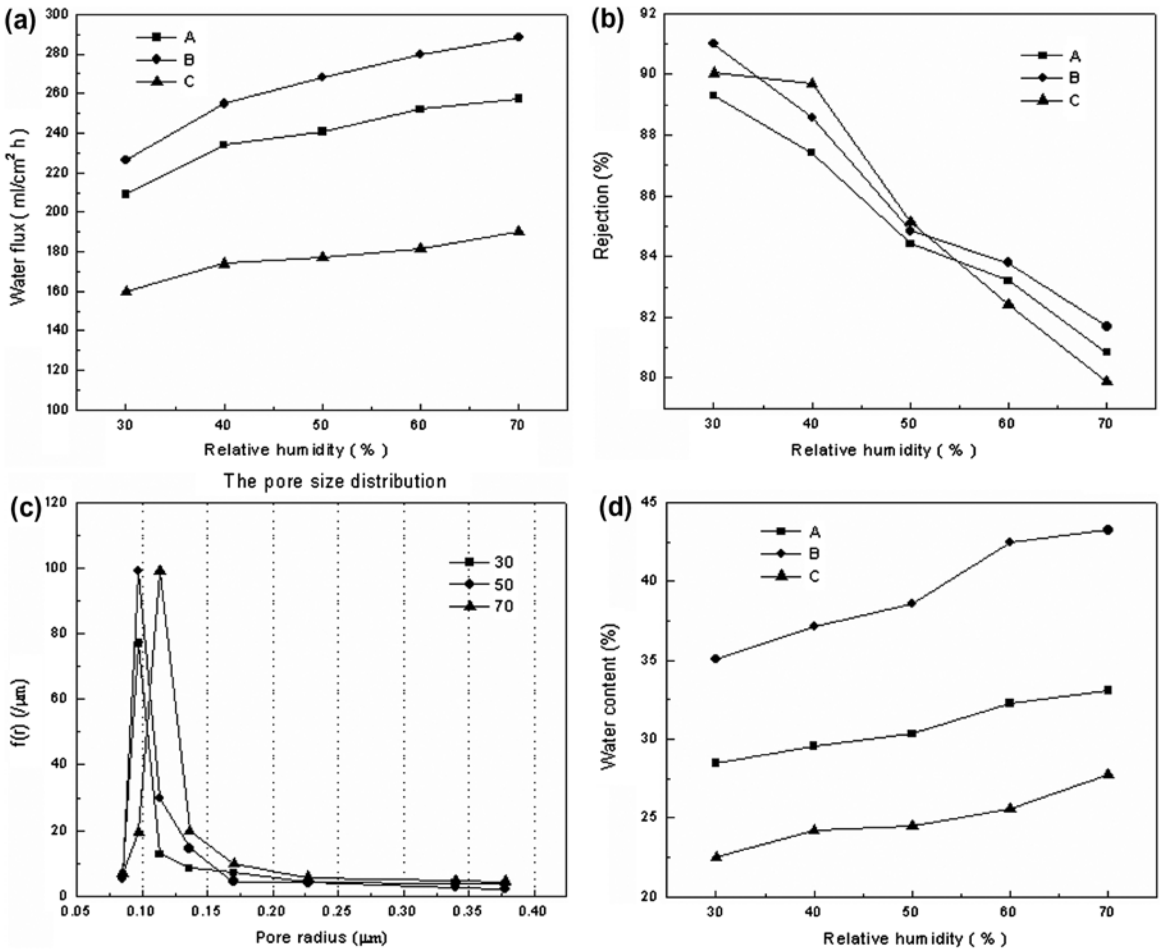


Fig. 10. Effects of the relative humidity on membrane performances. (The pretreatment conditions of NWFs were described as follows: the immersion time of NWFs in DMF were of 10, 5 and 10 min for NWFs, respectively, the environmental temperature and relative humidity are 20℃ and 40% (the membrane were made under the conditions of 30℃ and 40%), (a) the pure water flux of the membrane; (b) the rejection of the membrane; (c) the pore size distribution of the membrane using NWF A as substrate; (d) the water content of the membrane).

the precipitant into the casting solution very low. At this time, polymer concentration increase rapidly in the surface layer, this results in crystallization gelation and forms the homogeneous dense membrane. With the increase of polymer concentration, the precipitation of phase separation is more required, and more coagulation time is needed, therefore, the casting solvent far away from the interface have sufficient time to enter into the crystallization gelation zone, and then the crystallization gelation line gradually moves up, which can be observed in Fig. 11 and more dense membrane will be formed.

The flux and the rejection of the membrane are key parameters in membrane filtration and they were determined influence by membrane casting solution and the preparation condition. For example, higher gelation rate result in looser skin layer of the membrane and higher flux and lower rejection of the membrane. And as the polymer concentration increased, the pure water

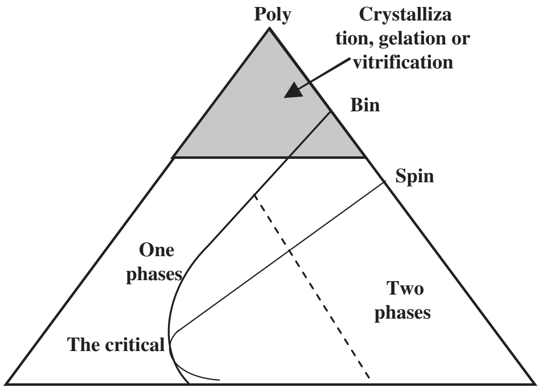


Fig. 11. Schematic phase diagram for ternary systems.

flux decreased, BSA rejection increased, which has the same trend as the literature elsewhere [34].

It can be seen from Fig. 7(a) and (b) that, on one hand, at a fixed evaporation time from the surface of NWFs for the immersion solvent, the membrane made using NWF B as substrate also has a higher pure water flux than the other two types NWFs (A, C); on the other hand, it becomes apparent that, with an increase in the solvent evaporation time, the pure water flux of the all membranes decreased while the rejection obviously increase. Take the substrate A for example, the flux decreased from 426.1 to 273.9 mL cm^{-2} h^{-1} and the corresponding rejection increased from 75.6 to 88.1%. This is confirmed by the experimental data (see Fig. 7 (c)), with the evaporation time increased from 0.5 to 2.5 min, the maximum pore size distribution of the membrane changed from 0.113 to 0.097 μm.

Water content of membranes is an indirect indication of their hydrophilicity and flux behavior [27]. As shown in Fig. 7(d), the water content of membranes decreased with the increase of the evaporation time of immersion solvent from the surface of NWFs. This is in agreement with the results observed for the trend of the pure water flux and rejection shown in Fig. 7(a, b), i.e. with the decrease of both the pore size and the water content, the pure water flux decreased, and simultaneously the rejection increased. Finally, a conclusion can be drawn from Fig. 7, that, a membrane with good performances can be obtained with an evaporation time of 1.5–2 min.

In addition, some details were worth to be noticed: when the evaporation time of the immersion solvent from the surface of NWFs was less than 1 min, the wetness of NWFs can not be kept uniform around the whole surface. In such a situation, if the casting solution was coated onto NWFs, a large number of pinholes or defects can be formed on the membrane surface as shown in Fig. 8. With 2 min evaporation time of the immersion solvent, a membrane with good performances could be prepared, and 2 min can be taken as an optimized evaporation time for practical applications.

It has generally been accepted that the evaporation of the wet NWFs is a very important step in the process of membrane preparation. From the discussion above, it can be pointed out that, as the solvent evaporation time increases, the casting solution would be less diluted, thus leading to a decrease in the pure water flux and the increase of the rejection. A similar situation appeared when the temperature increases or the relative humidity in the environment decreases. Take NWF A in Figs. 9 and 10 for example, When the environmental temperature increased from 10 to 30℃, variations of the pure water flux (from 268.4 to 229.9 mL cm^{-2} h^{-1}) and the corresponding rejection (from 82.9 to 89.0%) are modest, while simultaneously, the pore size and the membrane water content are gradually reduced (from 31.8 to 22.2%). With the decrease of the water content and the porosity of the membrane, the pure water flux decreased. Furthermore, smaller pore sizes promote more macromolecular material to be hold back by the membrane, and as a consequence the rejection of the membrane should increase. However, when the relative humidity increased from 30 to 70%, the pure water flux increased from 226.1 to 288.5 mL cm^{-2} h^{-1},while the corresponding rejection decreased from 91.0 to 81.7%, showing variation trends which are opposite to that of the environmental temperature.

5. Conclusion

Flat-sheet membranes were manufactured from PVC-co-PVAc-OH material and DMF solvent onto NWFs using phase inversion method. The membrane properties and morphologies were greatly influenced by types of NWFs and their pretreatment conditions. Experimental results show that:

Firstly, types of immersion solvents have little impact on the final membrane performances; while, the flux of membranes and its morphologies were greatly influenced by the type of NWFs, but had almost no influence on the BSA rejection. The reasons may be attributed to the special structure of NWFs, especially the air transmission coefficient which reflects the pore size of NWFs.

Secondly, as the immersion time were longer, both the pure water flux and the corresponding rejection of BSA increased quickly, then decreased dramatically, and almost kept constant when the evaporation time was larger than 30 min. Also the immersion time could not be longer than 12 h in order to keep a smooth surface of the NWF. SEM images showing the morphology of the cross sections of the membrane and the pore size distribution were examined and the results were consistent with the measurements of pure water flux and rejection.

Finally, either the increase of the evaporation time of the solvent, the increase of the environmental temperature, or the decrease of the relative humidity in the environment, resulted on a pure water flux decrease, accompanied by an increased in the rejection. This is because, when the casting polymer solution is coated onto the wet areas, it can be diluted by the non-volatilized solvent, and under the conditions discussed above, the diluted degree of the casting polymer solution decreases, allowing the preparation of a membrane with a low pure water flux and high rejection rate.

Overall, when using NWFs as substrate, the desired membranes with high flux and excellent rejection of BSA could be manufactured by properly controlling the pretreatment conditions. This proved that the PVC-co-PVAc-OH material can be applied to industrial production.

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Nomenclature

A — the effective membrane area (cm^2)
b — the solvent evaporation rate constant
C_f — the concentration of the feed solution (g L^{-1})
C_p — the concentration of the permeation solution (g L^{-1})
$f(r)$ — the pore size distribution
J — pure water flux of the membrane (mL cm^{-2} h^{-1})
P — the applied pressure (Pa)
Q — permeate flow rate (kg/s)
R — the abbreviation of rejection of the membrane (%)
radii (r) — the pore size (μm)
t — the operation time (h)
V — the total permeate volume during the experiment (mL)
w_0 — the weight of NWFs at evaporation time $t = 0$ (g)
WC % — water content
w_d — the weight of the membrane after dried in the air (g)
w_w — the wet weight of the membrane (g)
w_t — the weight of NWFs at evaporation time $t = t$ (g)
w_∞ — the weight of NWFs at evaporation time $t = \infty$ (g)

Greek symbols

σ — the water/water saturated n-butanol interfacial tension (N m^{-1})
θ — water/polymer contact angle (°)

References

[1] C. Wang, F. Yang, L. Liu, Hydrophilic and antibacterial properties of polyvinyl alcohol/4-vinylpyridine graft polymer modified polypropylene non-woven fabric membranes, J. Membr. Sci. 345 (2009) 223–232.

[2] S. Patrick, M.D. Ramsey, S. Francis, M.D. Nuthalapaty, L.M.D. George, Contemporary management of preterm premature rupture of membranes (PPROM): A survey of maternal-fetal medicine providers, Am. J. Obstet. Gynecol. 191 (2004) 1497–1502.

[3] B.H. Park, Y. Chang, Y. Lee, Targeting of membrane type1-matrix metalloproteinase (MT1-MMP) using superparamagnetic nanoparticles in human liver cancer cells, Colloids Surf. A 313 (2008) 647–650.

[4] T. Xu, Electrodialysis processes with bipolar membranes (EDBM) in environmental protection—A review, Resour. Conserv. Recycl. 37 (2002) 1–22.

[5] T. Liu, The application of membranes in environmental protection, Desalination 62 (1987) 149–164.

[6] C. Charcosset, Preparation of emulsions and particles by membrane emulsification for the food processing industry, J. Food Eng. 92 (2009) 241–249.

[7] N.D. Lawrence, S.E. Kentish, A.J. O'Connor, Microfiltration of skim milk using polymeric membranes for casein concentrate manufacture, Sep. Purif. Technol. 60 (2008) 237–244.

[8] M. Kanai, V. Ferre, S. Wakahara, A novel combination of methane fermentation and MBR—Kubota submerged anaerobic membrane bioreactor process, Desalination 250 (2010) 964–967.

[9] C. Omole, S.J. Miller, J.K. William, Increased molecular weight of a cross-linkable polyimide for spinning plasticization resistant hollow fiber membranes, Macromolecules 41 (2008) 6367–6375.

[10] P. Chen, T. Kuo, J. Kuo, Novel chitosan–pectin composite membranes with enhanced strength, hydrophilicity and controllable disintegration, Carbohydr. Polym. 82 (2010) 1236–1242.

[11] S. Kuiper, R. Brink, W. Nijdam, Ceramic microsieves: Influence of perforation shape and distribution on flow resistance and membrane strength, J. Membr. Sci. 196 (2002) 149–157.

[12] M.C. Porter, Handbook of industrial membrane technology, published in the United States of America by Notes Publications, 1990, p. 53.

[13] Y. Tyan, J. Liao, R. Klauser, Assessment and characterization of degradation effect for the varied degrees of ultra-violet radiation onto the collagen-bonded polypropylene non-woven fabric surfaces, Biomaterials 23 (2002) 65–76.

[14] C.C. Wang, F.L. Yang, L.F. Liu, Hydrophilic and antibacterial properties of polyvinyl alcohol/4-vinylpyridine graft polymer modified polypropylene non-woven fabric membranes, J. Membr. Sci. 345 (2009) 223–232.

[15] S. Ni, P. Lee, A. Fessehaie, Enrichment and biofilm formation of anammox bacteria in a non-woven membrane reactor, Bioresour. Technol. 101 (2010) 1792–1799.

[16] C. Wang, F. Yang, F. Meng, High flux and antifouling filtration membrane based on non-woven fabric with chitosan coating for membrane bioreactors, Bioresour. Technol. 101 (2010) 5469–5474.

[17] S.S. Homaeigohar, K. Buhr, K. Ebert, Polyethersulfone electrospun nanofibrous composite membrane for liquid filtration, J. Membr. Sci. 365 (2010) 68–77.

[18] F.F. Stengaard, Preparation of asymmetric microfiltration membranes and modification of their properties by chemical treatment, J. Membr. Sci. 36 (1988) 251–275.

[19] G. Wu, S. Lin, C. Yang, Preparation and characterization of high ionic conducting alkaline non-woven membranes by sulfonation, J. Membr. Sci. 284 (2006) 120–127.

[20] C. Burger, B.S. Hsiao, B. Chu, Nanofibrous materials and their applications, Annu. Rev. Mater. Res. 36 (2006) 333–368.

[21] W. Li, X. Ye, Z. Wang, The preparation and performance characteristics of polyvinyl chloride-co-vinyl acetate modified membranes, Energy Procedia 5 (2011) 1158–1162.

[22] S. Wang, Z. Wang, Y. Zhang, Experimental study of the control of pore sizes of porous membranes applying chemicals methods, Desalination 177 (2005) 7–13.

[23] I. Glavchev, R.N. Nikolov, P. Valchev, Determination of evaporation rates of mixed solvents with the formation of thin films for membranes, Polym. Test. 22 (2003) 529–532.

[24] T. Matsuura, S. Sourirajan, Fundamentals of Reverse Osmosis, NRCC, Ottawa, 1985, p. 136.

[25] W. Albrecht, K. Kneifel, T. Weigel, Preparation of highly asymmetric hollow fiber membranes from poly(ether imide) by a modified dry–wet phase inversion technique using a triple spinneret, J. Membr. Sci. 262(1–2) (2005) 69–80.

[26] G. Capannelli, F. Vigo, S. Munari, Ultrafiltration membranes–characterization methods, J. Membr. Sci. 15 (1983) 289–313.

[27] G. Arthanareeswaran, D. Mohan, M. Raajenthiren, Preparation and performance of polysulfone-sulfonated poly(ether ether ketone) blend ultrafiltration membranes. Part I, Appl. Surf. Sci. 253 (2007) 8705–8712.

[28] Q. Zheng, P. Wang, Y. Yang, Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process, J. Membr. Sci. 279 (2006) 230–237.

[29] P.S. Machado, A.C. Habert, C.P. Borges, Membrane formation mechanism based on precipitation kinetics and membrane morphology: Flat and hollow fiber polysulfone membranes, J. Membr. Sci. 155 (1999) 171–183.

[30] E. Saljoughi, M. Amirilargani, T. Mohammadi, Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes, Desalination 262 (2010) 72–78.

[31] T. Young, J. Huang, W. Chuang, Effect of evaporation temperature on the formation of particulate membranes from crystalline polymers by dry-cast process, Eur. Polym. J. 38 (2002) 63–72.

[32] H.C. Park, Y.P. Kim, H.Y. Kim, Y.S. Kang, Membrane formation by water vapor induced phase inversion, J. Membr. Sci. 156(2) (1999) 169–178.

[33] A.F. Ismail, A.R. Hassan, Formation and characterization of asymmetric nanofiltration membrane: Effect of shear rate and polymer concentration, J. Membr. Sci. 270 (2006) 57–72.

[34] X. Li, C. Chen, J. Li, Formation kinetics of polyethersulfone with cardo membrane via phase inversion, J. Membr. Sci. 314 (2008) 206–211.