Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.797065

51 (2013) 3960–3969
May

Taylor & Francis
Taylor & Francis Group

Study on preparation and performance characteristics of polyvinyl chloride-co-vinyl acetate-modified membranes on the nonwoven fabrics

Wenjuan Li[a,b], Jing Zhang[a], Ye Xiao[c], Zhan Wang[a,*], Longyue Shi[a], Wentao Yang[a], Lina Cheng[a], Na Chen[a]

[a]*College of Environment and Energy Engineering, Beijing University of Technology, Beijing 100124, P.R. China*
Tel. +86 10 67396186; Fax: +86 10 6739 1983; email: wangzh@bjut.edu.cn
[b]*Patent Examination Cooperation Center of the Patent Office, SIPO, Beijing 100083, P.R. China*
[c]*School of Biological and Chemical Engineering, Beijing United University, Beijing 100023, P.R. China*

Received 3 May 2012; Accepted 10 April 2013

ABSTRACT

This work reports that membranes were cast from solution consisting of dimethylformamide, polyethylene glycol, and polyvinyl chloride-co-vinyl acetate (VC-co-VAc-OH) to prepare flat-sheet membranes on the nonwoven fabrics via phase inversion method. The influence of various factors (solid content, the content of additive, environmental temperature, relative humidity, evaporation time of solvent, coagulation temperature, and coagulation time) on membrane performance (the pure water flux and the retention of bovine serum albumin (BSA)) were studied in the film-forming process of the VC-co-VAc-OH membrane. The results showed that the membrane with higher pure water flux (289.6 mL $\mathrm{cm^{-2}\,h^{-1)}}$ and good retention of BSA (86.7%) can be prepared under optimized preparation conditions. In addition, the carbon dioxide gas, which was produced by a chemical reaction between glacial acetic acid in the casting solution and sodium carbonate in coagulation medium, can improve the antifouling ability of the membrane. The membrane prepared by chemical reaction under optimum conditions (the molar ratio between Na_2CO_3 and glacial acetic acid is 0.5:1) possess higher pure water flux (457.7 mL $\mathrm{cm^{-2}\,h^{-1}}$) and good retention of BSA (90.7%).

Keywords: VC-co-VAc-OH; Nonwoven fabrics; Properties; Chemical reaction

1. Introduction

One of the most important characteristics of ultrafiltration (UF) membranes is selectivity, i.e. the ability to separate the solute components differing in particle size or molecular weight. The importance of this characteristic is caused by the possibility to determine with its help, the principle applicability of filtration to different separation processes and also, to calculate the results of UF separation [1]. With rapid development of membrane distillation and membrane absorption technologies, the fabrication of hydrophobic microporous hollow fiber membranes has attracted

---

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

much attention in recent years. In the membrane distillation or membrane absorption system, the microporous membranes are used as a contactor to provide vapor/gas–liquid interfaces by allowing the vapor/gas to transfer through the membrane pores. Although the porous membrane only acts as a nonselective barrier, it plays an important role in determining the system performance. One of the technical challenges, membrane wetting, is associated with membrane properties, such as surface energy, pore size, and pore size distribution. Zhang [2] pointed out that the use of UF employing a polyvinyl chloride (PVC) membrane as a pretreatment for a reverse osmosis system treating the secondary water effluent at Scottsdale Water Campus was investigated. Membrane fouling tendency was evaluated, foulants were characterized, and chemical cleaning was optimized. Bierbrauer's work [3] reported the modification of PVC by partially replacing the chlorine atoms of the chains with moieties derived from fluorinated nucleophilic compounds: 4-fluorothiophenol, 3, 4-difluorothiophenol, and pentafluorothiophenol. Membranes were cast from tetrahydrofuran solutions of the modified PVCs and the permeability and diffusion coefficients of hydrogen, nitrogen, oxygen, carbon dioxide, and methane through the membranes were measured using permeation techniques. A novel method was proposed by Mei [4] to improve the hydrophilicity and permeation of PVC/polyacrylonitrile/SiO_2 composite hollow fiber membranes by the interfacial hydrolysis of PAN between PVC and SiO_2. Water contact angle and protein filtration were employed to evaluate the hydrophilicity and the antifouling performance of the membranes. The alkaline hydrolysis occurred in the composite HFMs, both water permeation and the antifouling performance were improved while the mechanical strength was still kept at a high level. Chen [5] found that blends of hydroxyl-terminated polybutadiene-based polyurethane (PU) and PVC membranes with various relative weight percentages were prepared by solution process. Thermal property, tensile strength, and intermolecular bonding of membranes were function of the contents of PVC and PU's hard segment. Hosseini [6] found that PVC/styrene–butadiene–rubber blend heterogeneous cation exchange membranes were prepared by solution casting technique using tetrahydrofuran as solvent and cation exchange resin powder as functional group. Membrane surface modification was carried out with silver nanoparticles in a vacuum reactor by argon plasma treatment to increase the performance.

Moreover, in order to improve the strength and hydrophilicity of the PVC material, a new membrane material, polyvinyl chloride-co-vinyl acetate (VC-co-VAc-OH) material, can be obtained by embedding the molecular chain of vinyl acetate fragments in PVC material and introducing the hydroxyl group to VC-co-VAc material. However,at present, very few literatures report on the production of membranes using the modified Vc-co-VAc-OH material via phase inversion method. The modified VC-co-VAc-OH was used as a material via phase inversion method to prepare flat-sheet membranes in this paper and establish the suitable membrane-making conditions on the nonwoven.

2. Experimental

2.1. Materials

Solvents — dimethylformamide (DMF) and glacial acetic acid (CH_3COOH) — were purchased from Tianjin Fuchen Chemical Reagent Factory. Additives — polyethylene glycol (PEG) (200, 600, 1000, 2000, 20000), coagulants — Na_2CO_3, and $NaHCO_3$, and N-butanol used as santomerse were purchased from Beijing Chemical Engineering Factory, nonwoven fabrics were from Beijing Ande Membrane Separation Technology Engineering. Bovine serum albumin (BSA), used as reagent for determining the retention of membrane, was purchased from Beijing Micro-organism Culture Medium Manufacturing Corporation, and its isoelectric point of pH is 4.8. Home-made VC-co-VAc-OH was used as membrane material [7].

2.2. Preparation of membranes

Firstly, a certain proportion of VC-co-VAc-OH polymers and a given additive PEG were dissolved in DMF to form homogeneous solution, and the casting solution was placed in the vacuum oven at 60℃ for three days. At the same time, the nonwoven were put into deionized water to remove the impurities on its surface, dried at low temperature, and then immersed in solvent for later use. Secondly, the thin liquid film was cast on nonwoven or a clean glass plate by a casting blade under the temperature of 25℃ and relative humidity of 40%, and then, the casted film along with the glass plate was gently immersed into coagulation bath with a temperature of 25℃ for 30 min. Finally, the formed membrane was moved from the coagulation bath and stored in the deionized water bath for 24 h to remove residual solvent.

2.3. Reaction mechanism

In the coagulation bath, carbon dioxide can be produced by the reaction between the glacial acetic acid in the casting solution and the salt in coagulation bath [8–13]. The corresponding reaction equation can be expressed as follows:

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \uparrow$$

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2 \uparrow$$

In general, the movement of bubbles is influenced by various forces (drag, pressure, etc.) in the viscous liquid, and it is a nonlinear, complex, unstable process. In this article, the pore size distribution of the membrane is controlled by changing the CO_2 intensity.

2.4. Membrane characterization

2.4.1. Flux and separation experiments

The experimental set-up and the calculation method for the pure water flux and the retention of BSA can be found elsewhere [10].

2.4.2. Calculation of the pore size distribution of the membrane

The pore size distribution of the membrane was determined by a modified bubble point method, which may be referred in other literatures [11,13]. Also, the pore size distribution and appearance can be investigated by scanning electron microscopy.

3. Results and discussion

In the preliminary experiments, it has been found that when the casting solution casts directly onto the non-woven, the top and bottom surfaces of the obtained flat membrane are uneven, and its performance is not stable. Therefore, the non-woven fabrics are pretreated before using. The non-woven fabrics will be submerged in DMF for a certain period of time; whether the non-woven fabrics can fully attach to the glass depends on the adsorption force of the liquid, and then the non-woven fabrics remains unstable for a certain period of time. After the pretreatment, the surface of obtained membrane becomes smooth.

3.1. Impact of casting solution content on the membrane properties

The composition of casting solution, including polymer concentration, additive species, and concentration were studied during membrane-making process preparation. In this section, preparation conditions of membrane were performed at a temperature of 20℃, relative humidity of 50%, evaporation time of 45 s, coagulation temperature of 20℃, coagulation time of 24 h, and stored in deionized water bath for 24 h. And, the filtration experiments are conducted under constant transmembrane pressure of 0.2 MPa at 22℃.

3.1.1. Polymer concentration

The polymer concentration plays an important role in membrane properties. All of these steps, which can be seen from Fig. 1(a), were repeated for difference polymer concentration ranges from 12 to 20 wt.%, the pure water flux sharply decreases from 430.6 to 6.3 $\mathrm{mL\,cm^{-2}\,h^{-1}}$, while the retention evidently increases from 6.3 to 96.1%; and when the concentration is greater than 18%, the flux is very low, far less than 100 $\mathrm{mL\,cm^{-2}\,h^{-1}}$, while there is a significant increase in retention from 6.3 to 96.1%; when the concentration is below 14%, the retention is less than 70%; it can be find clearly that with the solid content of 16%, the pure water flux is 266.0 $\mathrm{mL\,cm^{-2}\,h^{-1}}$ and retention of BSA is 90.2%, which is a better result. As shown in Fig. 1(b), both the water content and pore radius decrease as the polymer concentration increases, with the solid content of 16%, the water content and pore radius were 42.9% and 109.0 nm, respectively. This is the fact that the decrease in polymer concentration can promote the liquid–liquid phase separation and restrain crystallization of polymer, and the pore structure with better connectivity is obtained leading to increased water flux and decreased retention [14].

From what has been discussed above, we may safely draw the conclusion that the solid content of 16% can be taken for a better condition to prepare membrane, and this conclusion was put into use in the later study.

3.1.2. Impact of additive

PEG has good biocompatibility and low toxicity, and also, one of the most common hydrophilic polymers. Therefore, PEG of different molecular weights is chosen as an additive in our study.

3.1.2.1. The species of PEG. Presence of low molecular weight PEG additive in the cast solution film increases porosity/permeability and simultaneously, thermal/chemical stability of the prepared membranes. On the other hand, using cold coagulation bath, despite increasing the thermal/chemical stability of the prepared membranes, results in reduction of membranes porosity/permeability. From another

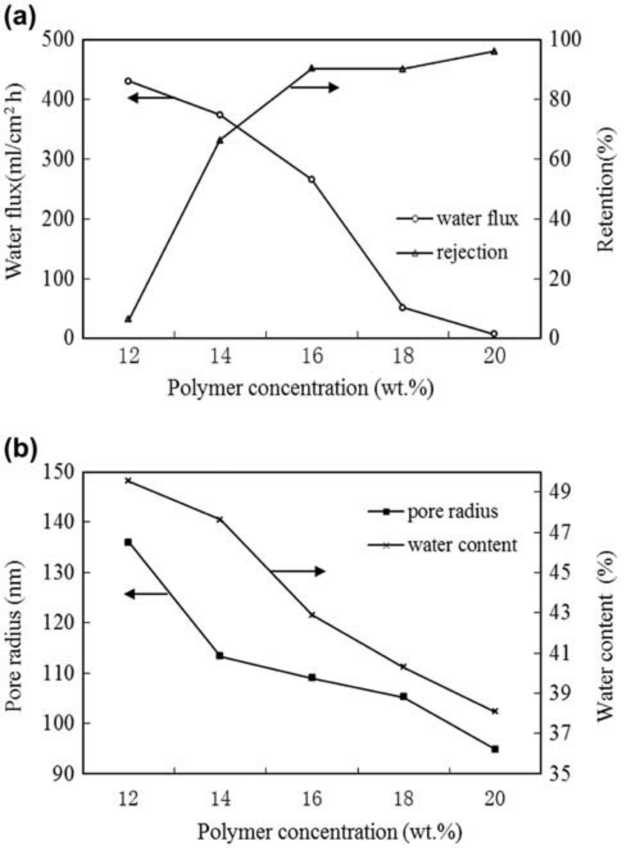

Fig. 1. Effect of the polymer concentration on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

point of view, the presence of PEG increases the viscosity of the cast film.

The membranes were made with different species of PEG (200, 600, 1000, 2000, 20000) under the conditions of polymer concentration of 16 wt.%, additive of 4 wt.%, evaporation time of 30 s, temperature of 25˚C, relative humidity of 50%, coagulation temperature of 20˚C, and the solvent evaporation time of about 1 min on the nonwoven.

The addition of PEG with higher molecular weight leads to the improvement of hydrophilicity for the membrane. From Fig. 2a, molecular weight of PEG altered from 200 to 20000, the retention of BSA continuously increased, and the pure water flux increased when the molecular weight of PEG is not more than 2000, then, from PEG 2000 to 20000, the flux decreased. When the PEG is of smaller molecular weight, it has good solubility, and using PEG 2000 will have a suitable exchanging rate of solvent and pure water in the coagulation bath, and then, the membrane with better performance is made as shown in Fig. 2(a) and (b). On contrast, when the PEG is of higher molecular weight, as PEG 20000, it leaches out slower and more additive gets entrapped in the polymer matrix resulting in polymer aggregates to form a thicker and denser layer, then, the pure water flux will decrease and the retention increases. Then, when using PEG 2000 as the additive, the formed membrane has the highest pure water flux and good retention of BSA. Thus, PEG 2000 is the optimal additive and will be used in the latter study.

3.1.2.2. The concentration of additive. With the increase of additive content on one hand, as the porogen dissoluted numerously in the coagulation bath, macroporosity can be formed in the membrane [15,16], while on the other hand, it can promote a compatibility between the film and the other components in the original casting solution system, which is conducive to the formation of microporous films.

It can be known from Fig. 3(a) along with the increase of the additive content (PEG 2000) that the pure water flux of the membrane decreases firstly and then increases,with 4% content, a maximized pure water flux can be obtained, and the retention is

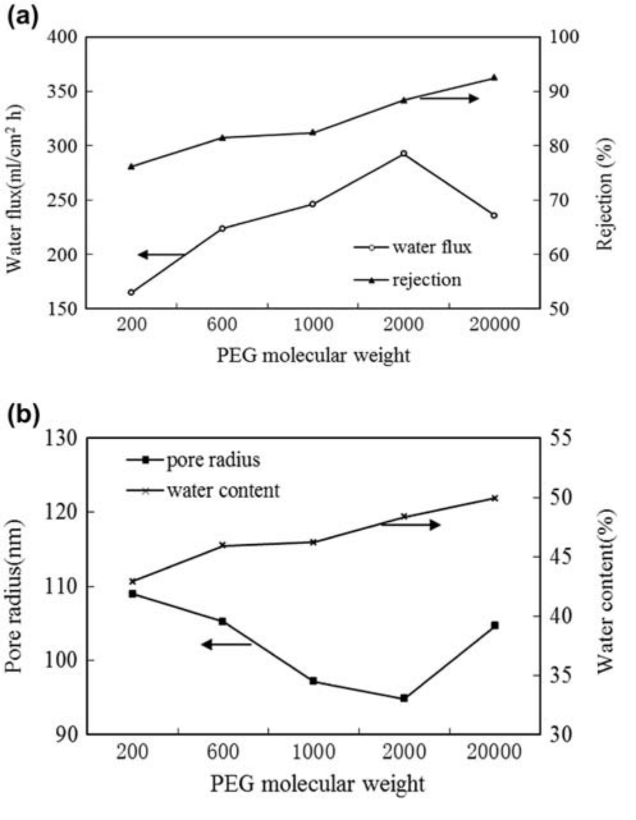

Fig. 2. Effect of the molecular weight of PEG on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

relatively higher in the meantime. The values of pore radius and water content in Fig. 3(b) reveal that the membrane prepared at the additive content of 4% possesses higher pore density and suitable pore size. Therefore, in the content of 4%, the ratio of additive is better and great amount of microporosity can be prepared. Henceforth, a better additive concentration can be achieved, and it is 4%.

3.2. Impact of preparation conditions on the membrane characteristics and its morphologies

The influences of preparation conditions, such as surrounding temperature, relative humidity of atmosphere, evaporation time of solvent, temperature of medium, and coagulation time on the membrane characteristics are investigated. In this section, the composition of casting solution are performed with an additive of PEG 2000, polymer concentration of 16 wt.%, and additive content of 4 wt.%. And, filtration experiments are conducted under constant transmembrane pressure of 0.2 MPa at 22℃.

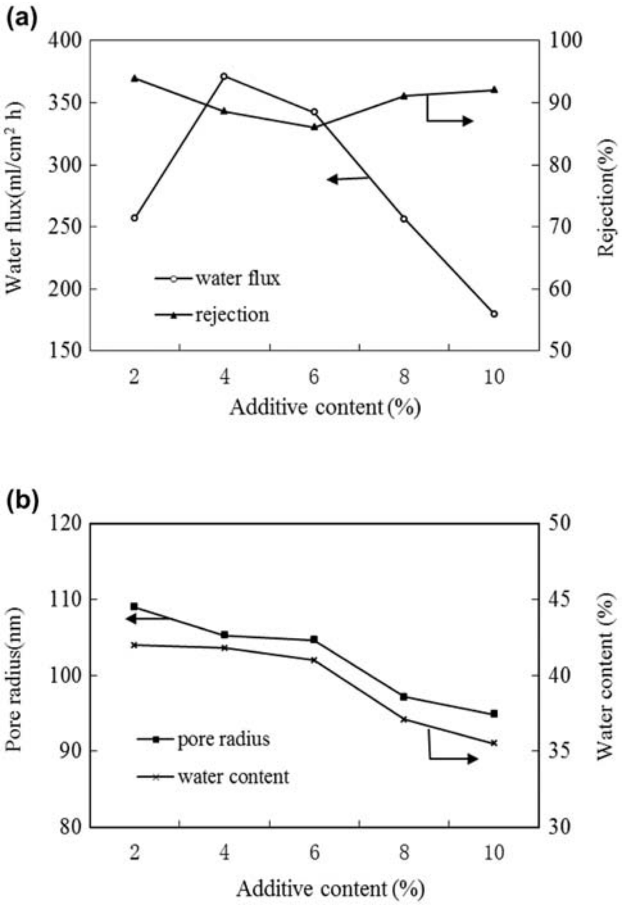

Fig. 3. Effect of concentration of additive on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

3.2.1. Temperature

Environmental temperature is one of the important parameters in membrane-making process, the temperature can affect the morphology of polymer molecules in the solution, the affinity between polymer and solvent, the evaporation speed of solvent, and so on. The solubility of the polymer in solution will change with changing temperature, so the impact of temperature must also be examined.

As the temperature increases, the solubility of the polymer becomes better, the viscosity of casting solution lowers, and the casting solution can easy be leveled to form a membrane with smooth surface, while the faster solvent evaporation eases the formation of a small pore structure. Through the comprehensive analysis of Fig. 4, it is observed that when temperature changed from 5 to 45℃, the rejection did not change much, but the water flux decreased from 300 to 240 $\mathrm{mL\,cm^{-2}\,h^{-1}}$, and the decrease of the water flux was not great from 5 to 25℃; since 25℃ is more close to the room temperature, better overall performance can be observed at 25℃.

3.2.2. Relative humidity

The relative humidity played a very important role in the phase inversion kinetics of the polymer membrane [17]. The increase of the permeability of the membrane could be attributed to a more porous structure.

In our system, five porous membrane samples were prepared during various relative humidities of the evaporation surroundings and the evaporation time was 2 min. Pure water flux and retention of BSA are presented in Fig. 5(a). The results show that the pure water flux of the membrane was increased with an increasing relative humidity changing from 30 to 70%. That means, the humidity in the environment can affect the structure and performance of the membrane significantly. On contrast, the rejection of BSA changed slightly.

To further investigate the effect of the relative humidity on the structure of the membrane, the pore size distribution during different relative humidity and the pore radius corresponding to maximum pore size distribution for five membranes are illustrated in Fig. 5(b).

During exposure process of the casting solution, the evaporation of DMF proceeded more quickly at a

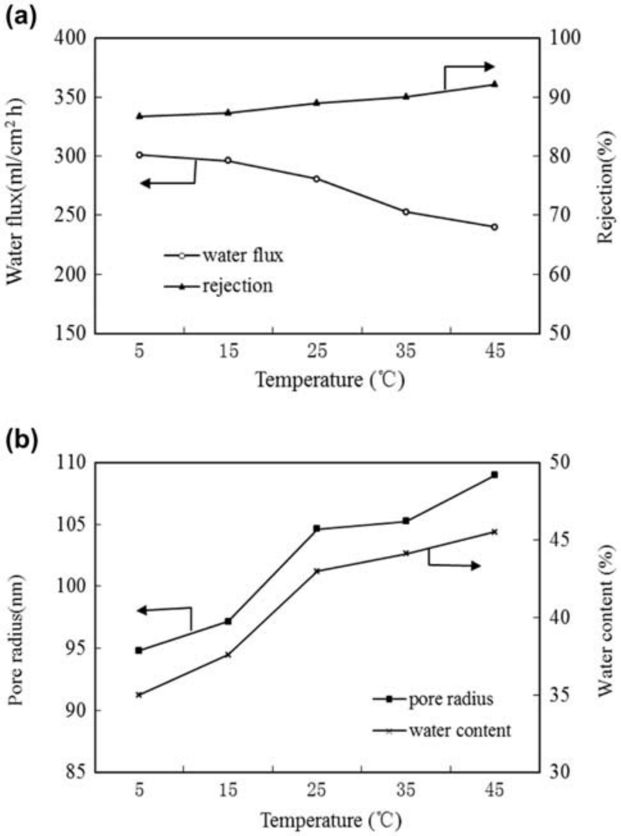

Fig. 4. Effect of temperature on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

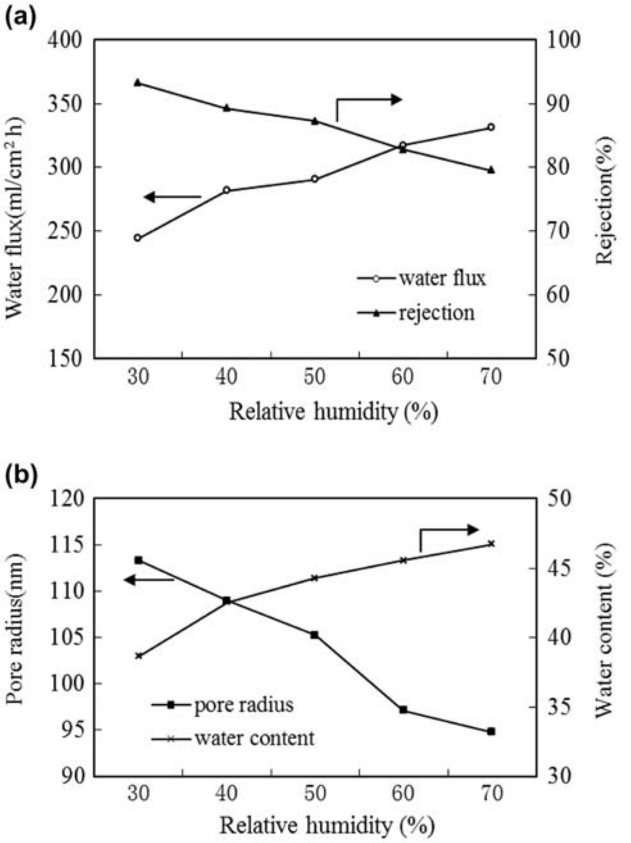

Fig. 5. Effect of relative humidity on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of the pore radius (×) and water content (■)

relatively low relative humidity, which would form a denser surface layer. Then smaller pores were obtained, contrarily, at high humidity, the evaporation rate of the solvent in casting solution is slow and loose membranes are formed. Conversely, a large hole can form, following which, the pure water flux will increase and retention decrease.

Fig. 5(b) shows that the membrane was made with large diameter and low water content at low humidity. This indicates that a small number of the large pore structures were formed. On the contrary, when the humidity is high, considerable dense holes have taken shape. From the charts, we get that better membranes can be made at a humidity of 50%.

3.2.3. Evaporation time

To investigate the influence of evaporation time on membrane performances and morphologies, evaporation time of 10, 30, 60, 90, and 120 s were, respectively applied to prepare membrane at the relative humidity of 50%. The results of pure water flux and retention of BSA are presented in Fig. 6(a). It could be clearly seen that as the evaporation time increased, the pure water flux continuously decreased from an initial higher value of 336.4 ml·cm^{-2}·h^{-1} without exposure time to a relatively lower value of 235.4 mL cm^{-2} h^{-1} with evaporation time of 120 s. And, at the same time, the retention of BSA increased from 71.9 to 91.6%. The results indicates the exposure time of cast film in the air prolongs from 10 to 120 s, the solvent in the thin film evaporates more so that the top layer of membranes become denser leading to the decrease of pure water flux and an increase of retention of BSA. In addition, as shown in Fig. 6(b), when the solvent evaporated for 30 s, high-quality membrane with suitable pore density and pore size will be obtained.

3.2.4. Coagulation temperature

With the increasing coagulation temperature, the surface temperature of cast film is higher in membrane-making process, which is not conducive to the polymer molecule aggregation on the membrane surface rapidly, then, dense holes are formed easily; on the other hand, because the coagulation temperature increases, the exchange rate between solvent and the coagulation bath is accelerated, conducive to the formation of macropores on the membrane surface. It can be seen from Fig. 7(a), when the coagulation temperature is low, the former plays a major role, when the temperature is higher than 20℃, the latter plays a major role; as the temperature increases, the pure water flux rises principally, on the contrary, the retention of BSA decreases, and when the temperature is 20 and 25℃, the pure water flux and retention of BSA were both higher and very similar, in order to reduce the energy consumption, 20℃ is chosen as a better coagulation temperature. Moreover, it can be seen from Fig. 7(b) that when the coagulation temperature is 20℃, the membrane with higher pore density and suitable pore size will be prepared.

3.2.5. Coagulation time

Coagulation is the process of solvent being replaced constantly out of the bath, the longer the coagulation is conducted, the more the solvent is replaced so that membrane surface becomes more porous, the flux increases, and retention decreases. Within the first 30 min, the solvent concentration in the coagulation bath is low and then, the replacement is fast, hence the rate of change of the indicators is higher; over time, the solvent in the membrane decreases, the concentration in the coagulation bath increases, and the displacement gradually tends to balance resulting in the changes of the flux and other indicators' tendency to balance. From Fig. 8(a), it can be seen that a higher performance membrane can be obtained when coagulation time is 30 min.

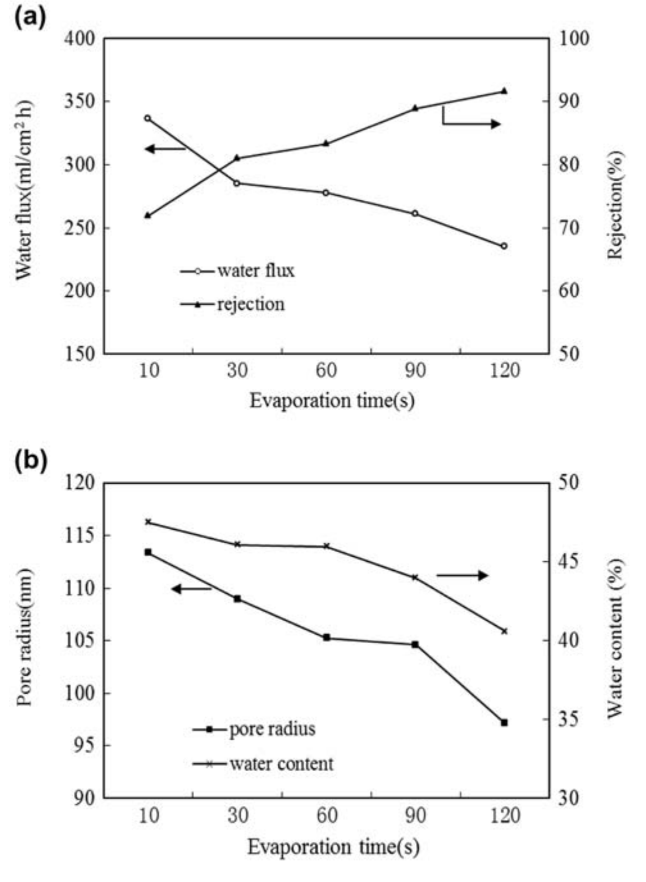

Fig. 6. Effect of the evaporation time on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

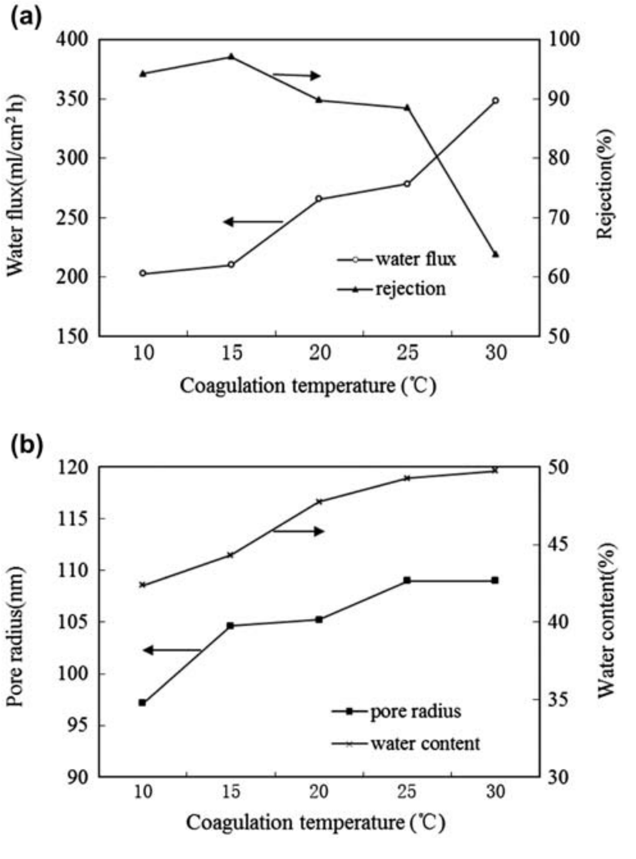

Fig. 7. Effect of coagulation temperature on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

3.3. The control of pore sizes of membranes using chemical methods

As reported by Liang et al. [12], the membrane pore size distribution is more uniform due to the presence of chemical reaction between carbonates or bicarbonates in the coagulation bath and glacial acetic acid in membrane casting solution. So, the chemical reaction was studied in present work and the optimum conditions were selected. Glacial acetic acid, selected in the experiment, was added to the casting solution of 10 wt.%, reviewing impact of carbonates and bicarbonates with different concentrations in the coagulation bath.

The working solution with different salt concentrations in coagulation bath was prepared by dissolving different weighed amounts of salt according to the stoichiometric reaction equation in Section 2.3, and the working solution in coagulation bath is showed in Table 1. The experimental results are shown in Fig. 9 and Fig. 10, respectively.

It can be seen from Fig. 9 and Fig. 10 that both kinds of coagulation bath and the composition of

Table 1
The concentration of coagulation bath as different chemical reaction ratio

Ration of salt to glacial acetic acid	Na_2CO_3 (wt.%)	$NaHCO_3$ (wt.%)
$0^{\#}$	Without glacial acetic acid	
$1^{\#}$	0:1	0:1
$2^{\#}$	0.25:1	0.5:1
$3^{\#}$	0.5:1	1:1
$4^{\#}$	1:1	2:1
$5^{\#}$	5:1	10:1

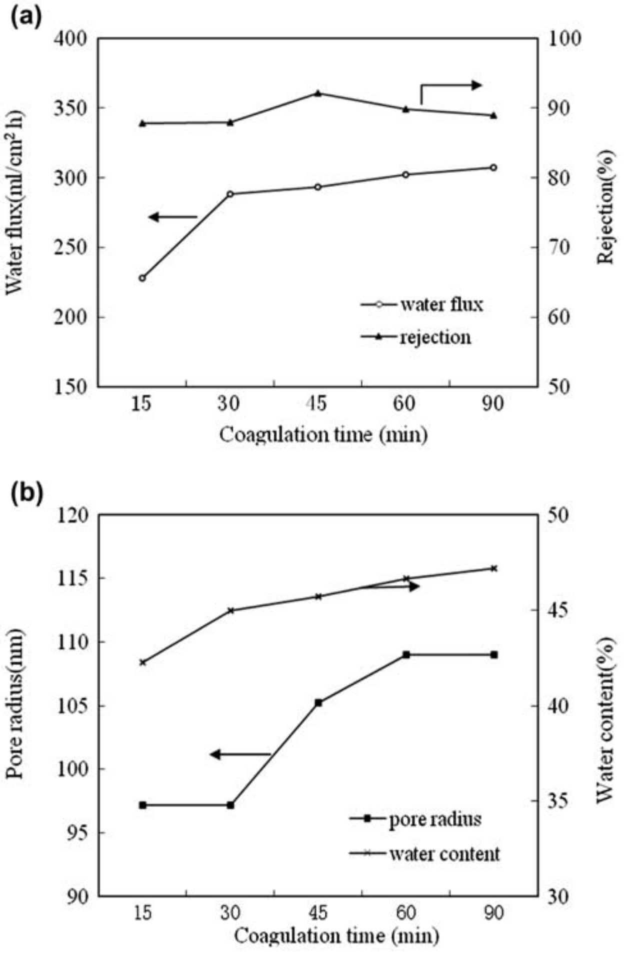

Fig. 8. Effect of coagulation time on membrane properties. (a) Pure water flux (○) and retention of BSA (▲) of the prepared membrane at 0.2 MPa. (b) Values of pore radius (×) and water content (■).

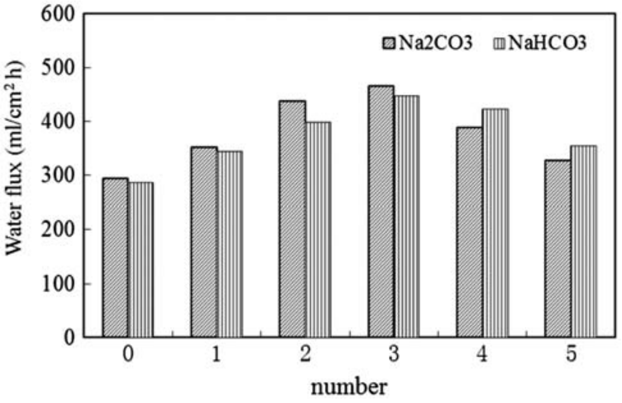

Fig. 9. Comparison of pure water flux at Na_2CO_3 and $NaHCO_3$ used as coagulation bath.

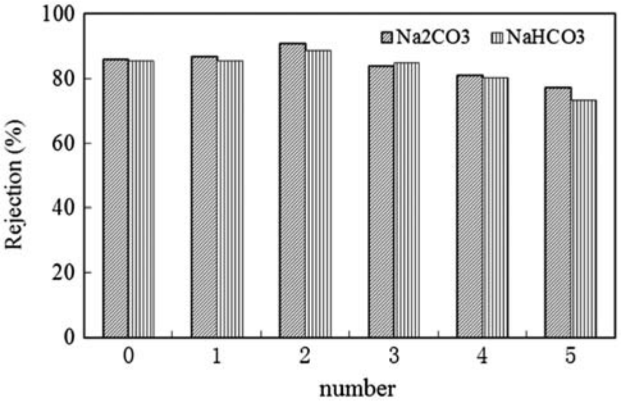

Fig. 10. Comparison of retention of BSA at Na_2CO_3 and $NaHCO_3$ used as coagulation bath.

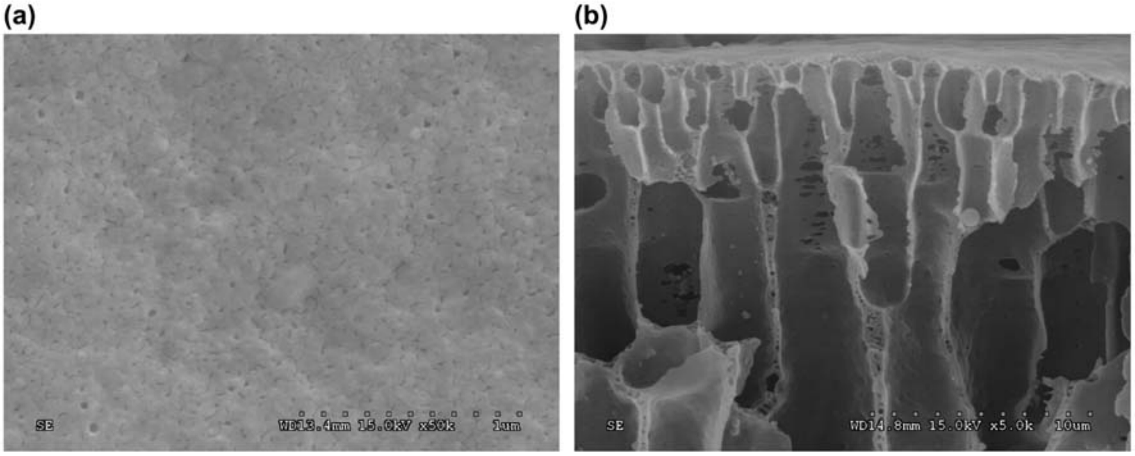

Fig. 11. SEM images of top surface and cross-section for the VC-co-VAc-OH membrane prepared with reaction under the best conditions.

coagulation bath are important factors influencing the chemical-introduced phase inversion process for preparation of the VC-co-VAc-OH membrane. When carbonates or bicarbonates concentration of the coagulation bath increases from 0% to saturation, the pure water flux of the membrane increases initially and then decreases. At the same time, it was observed that retention slightly decreased, but this change is not obvious. This is consistent with others' report [12]. The pure water flux would be larger when the content of carbonates or bicarbonates in the coagulation bath was controlled at the stoichiometric ratio. Moreover, as presented in Fig. 11, the surface of the membrane prepared by the chemical-introduced phase inversion process is looser and the membrane pore size distribution is more uniform, which is a benefit for the flux improvement.

4. Conclusions

(1) The VC-VAc-OH material coated on pretreated nonwoven to prepare flat-sheet membrane by phase inversion method showed excellent performance which proves that this membrane material can be applied during industrial production.

(2) Experiments show that the membrane pretreated on the nonwoven would make pure water flux to decrease and the retention of BSA to increase, but the change is slightly lesser than that when scratched on the glass.

(3) The optimum conditions for the VC-VAc-OH membrane were as follows: solid content was 16 wt.%; solvent species was DMF, additive species was PEG 2000 with 4 wt.%, the temperature of the membrane was 20℃, relative humidity was 40%, evaporation time was 30 s, coagulation temperature was 20℃, coagulation time was 30 min, and the nonwoven bathed in solvent was 0.5 h, then evaporated for 2 min, the average pure water flux was about $287.9\,\mathrm{mL\,cm^{-2}\,h^{-1}}$; the retention of BSA was about 87.4%,and the pore size was about 0.10 μm.

(4) The method that produced CO_2 by the chemical reaction between organic acids in the casting solution and coagulation medium with carbonate solution can make the pore size distribution of the membranes more uniform.

Acknowledgement

Support for this work was provided by the Beijing Natural Science Foundation (Project No. 2122009) and the Beijing Municipal Commission of Education (KM200911417008).

References

[1] A.N. Cherkasov, S.V. Tsareva, A.E. Polotsky, Selective properties of ultrafiltration membranes from the standpoint of concentration polarization and adsorption phenomena, J. Membr. Sci. 104 (1995) 157–164.

[2] X. Zhang, Y. Chen, A.H. Konsowa, Evaluation of an innovative polyvinyl chloride (PVC) ultrafiltration membrane for wastewater treatment, Sep. Purif. Technol. 70 (2009) 71–78.

[3] K. Bierbrauer, L.G. Mar, E. Riande, Gas transport in fluorothiophenyl modified PVC membranes, J. Membr. Sci. 362 (2010) 164–171.

[4] S. Mei, C. Xiao, X. Hu, Hydrolysis modification of PVC/PAN/SiO_2 composite hollow fiber membrane, Desalination 280 (2011) 378–383.

[5] C.J. Chen, I.H. Tseng, H.T. Lu, Thermal and tensile properties of HTPB-based PU with PVC blends, Mater. Sci. Eng. A 528 (2011) 4917–4923.

[6] S.M. Hosseini, S.S. Madaeni, A.R. Khodabakhshi, Preparation and surface modification of PVC/SBR heterogeneous cation exchange membrane with silver nanoparticles by plasma treatment, J. Membr. Sci. 365 (2010) 438–446.

[7] 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.

[8] S. Yang, Z. Liu, Preparation and characterization of polyacrylonitrile ultrafiltration membranes, J. Membr. Sci. 222 (2003) 87–98.

[9] S. Yang, Z. Liu, H. Chen, A gas–liquid chemical reaction treatment and phase inversion technique for formation of high permeability PAN UF membranes, J. Membr. Sci. 246 (2005) 7–12.

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

[11] C. Zhou, Z. Wang, Y. Liang, J. Yao, Study on the control of pore sizes of membranes using chemical methods Part II. Optimization factors for preparation of membranes, Desalination 225 (2008) 123–138.

[12] Y. Liang, Z. Wang, X. Ye, W. Li, X. Xi, L. Yang, X. Wang, J. Zhang, Y. Liu, Z. Cai, Study on the control of pore sizes of membranes using chemical methods Part III. The performance of carbonates and bicarbonates in the membrane-making process by the chemical reaction, Desalination 267 (2010) 42–48.

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

[14] L. Yang, Z. Wang, Y. Sun, Z. Hu, S. Zhao, X. Wang, W. Li, X. Xi, J. Zhang, Z. Pei, Influence of various operating conditions on cleaning efficiency in sequencing batch reactor (SBR) activated sludge process—backwash and water rinsing introduced membrane filtration process, Desalination 272 (2011) 76–84.

[15] 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.

[16] M. Sivakumar, R. Malaisamy, C.J. Sajitha, Ultrafiltration application of CA-PU blends membranes, Eur. Polym. J. 35 (1999) 1647–1651.

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