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Modified PVA-CA blend ultrafiltration membrane by alkali metal chloride①

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Abstract: The modified PVA-CA blend ultrafiltration membranes were prepared by phase inversion from the casting solutions consisting of polyvinyl alcohol(PVA), cellulose acetate(CA), acetic acid, alkali metal chloride and water. The effects of different concentration of alkali metal chloride on the properties of membranes were investigated. The results show that when the mass fraction of the salt in the casting solution is not greater than 1%, the property of rejection of the alkali metal salt modified ultrafiltration PVA-CA blend membrane has little change compared with that of the unmodified PVA-CA blend membrane, but the permeation flux is much greater than that of the unmodified membrane under the same operation condition. When the mass fraction of the salt is greater than 1.5%, the permeate flux increases much greater than that of the unmodified membrane, but the property of rejection of the modified ultrafiltration membrane decreases greatly. The results also show that the contact angle of the salt modified PVA-CA blend UF membrane decreases but the swelling in water increases with the increment of the mass fraction of alkali metal salts. Furthermore, the NaCl modified PVA-CA blend membrane has a slightly lower swelling and a little smaller contact angle of water than the KCl modified PVA-CA blend membrane does when the mass fraction of salts is the same.

Key words: polyvinyl alcohol; cellulose acetate; blend; phase inversion; ultrafiltration; modification

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1 INTRODUCTION

Ultrafiltration(UF) is a membrane separation process which has found wide applications in such fields as petroleum, textile, bioseparation, pharmacy, food, wastewater treatment, preparation of drinking water[1-3]. Many researchers have devoted themselves to improving the permeation flux of the UF membrane under the same rejection, and preventing the formation of a fouling layer on the surface of UF membrane. Many novel membrane materials and various modification technologies have been developed, some modification methods, such as co-polymerization, blend, modification of the surface, are used in the preparation of membranes, among which blend is widely used in the modification of the membrane as it is simple and feasible[4-6].

Polyvinyl alcohol(PVA) polymer seems attractive for the preparation of membranes, because of its high hydrophilicity and good film forming properties. It has also been known that polyvinyl alcohol is little affected by greases, hydrocarbons, and chemical stability against organic solvents. But PVA is readily swelling and soluble in water, thus the modification of PVA is necessary for the industrial application. Heat-treatment, cross-linking, acetalization, blend etc are the usual methods of modification[7-12]. We have ever investigated the preparation and the properties of the PVA-CA blend UF membrane[12]. In this paper, we are further studying the modification of PVA-CA blend UF membrane by alkali metal chloride.

2 EXPERIMENTAL

2.1 Reagents

Polyvinyl alcohol (PVA), with a degree of polymerization 1 750, and a degree of hydrolysis 99.8% - 100%; cellulose acetate(CA), with a combo acetic acid of 54.5% - 56%; acetic acid, Tween-20, sodium chloride, potassium chloride, are all analytical pure grade.

2.2 Preparation of blend UF membranes

PVA-CA blend ultrafiltration membrane was prepared by phase inversion from the casting solutions consisting of polyvinyl alcohol(PVA), cellulose acetate(CA), acetic acid and water, the casting solution of which consists of 10% (mass fraction) of polymer, among which the mass fraction of CA is 8%, acetic acid 50%, and water[12]. The alkali metal chloride modified PVA-CA blend ultrafiltration mem-

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branes were prepared by adding different concentrations of alkali metal chloride to the casting solution, and the method of preparation is the same.

3 PROPERTIES OF BLEND UF MEMBRANES

3.1 Flux of permeation

Flux of permeation is the permeation volume through unit area within unit time under a certain operation pressure, expressed with the sign F, which is one of the main factors for evaluating properties of membrane.

3.2 Rejection

The oil/water emulsion was prepared by adding 1 000 mg kerosene and a certain mass of Tween-20 to 1 000 mL distilled water, then stirring at the rate of 10 000 round per minute for 2 min by JRJ-300-I type high-speed cutting emulsifier.

R is retention defined as follows:

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

where C_f and C_p are the oil concentrations of the feed and permeation, respectively.

4 RESULTS AND DISCUSSION

4.1 Effects of alkali metal chloride on properties of blend membranes

The properties and structure of membrane are affected by the addition of alkali metal chloride to the casting solution. In order to investigate the effects of alkali metal chloride on properties of blend membrane, we prepared a series of different concentrations of salts in the casting solution, and a series of blend membrane were prepared under the same condition. The properties, including the permeation flux and retention, were tested under the operation pressure of 0.30 MPa, and the results are shown in Fig. 1 and Fig. 2, where ω is the mass fraction in the blend membrane.

Fig. 1 and Fig. 2 illustrate that the permeation flux of the blend membranes increases but the rejection decreases with the increase of the concentration of salts under the operation pressure 0.30 MPa. The salt modified blend membrane has a little higher permeation flux but the rejection has little change when ω is not greater than 1%. The permeation flux of modified blend membrane is much greater than that of unmodified blend membrane but the retention is a little lower than that of unmodified membrane when the mass fraction of salt is greater than 1.5%.

Thus, the better properties of modified PVA-CA UF membrane can be obtained when the mass fraction of salt is within 1%.

Fig. 3 shows the SEM photograph of sodium chloride modified PVA-CA UF membrane. Fig. 3 (a) shows that the surface of the membrane is uniform, salt is dispersed evenly in the blend membrane when the concentration of salt is small. When the membrane is immersed in water, a part of salt will dissolve, and diffuse into water, so the micro-void is formed. Thus, it is clear that the permeation flux of UF membrane increases without decrease of rejection. Sodium chloride crystal can be seen on the surface of the membrane in Fig. 3(b) which indicates that the sodium chloride crystal can be produced in the process of forming membrane. When the membrane is immersed in water, sodium chloride crystal will dissolve, and diffuse into water, and macro-void is formed. Thus, the permeation flux of UF membrane increases greatly and the rejection decreases a lot.

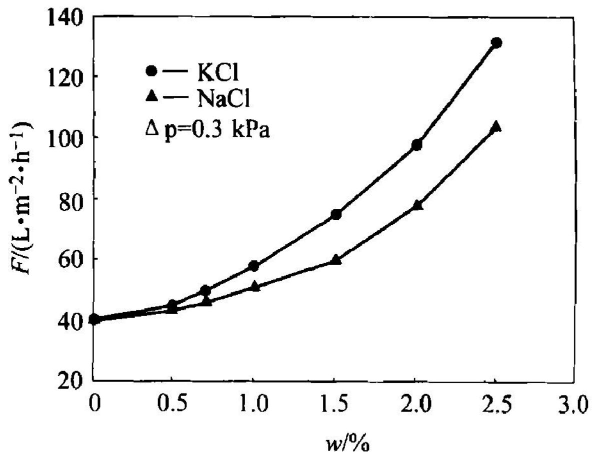

Fig. 1 Mass fraction of salts vs permeate flux

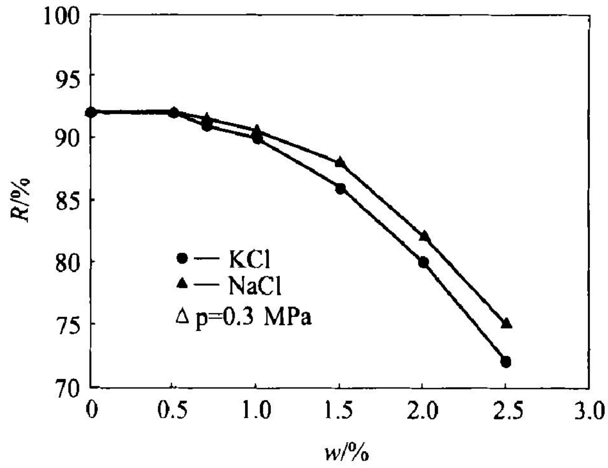

Fig. 2 Mass fraction of salts vs rejection

The properties and structure of membrane can be changed by the addition of alkali metal chloride. Fig. 4 illustrates that the addition of alkali metal chlorides NaCl and KCl can make the swelling of blend membranes increase, and the swelling of membranes increases with the augment of alkali metal salt. It is also shown that KCl modified UF membrane has a slightly greater swelling than that of NaCl modified

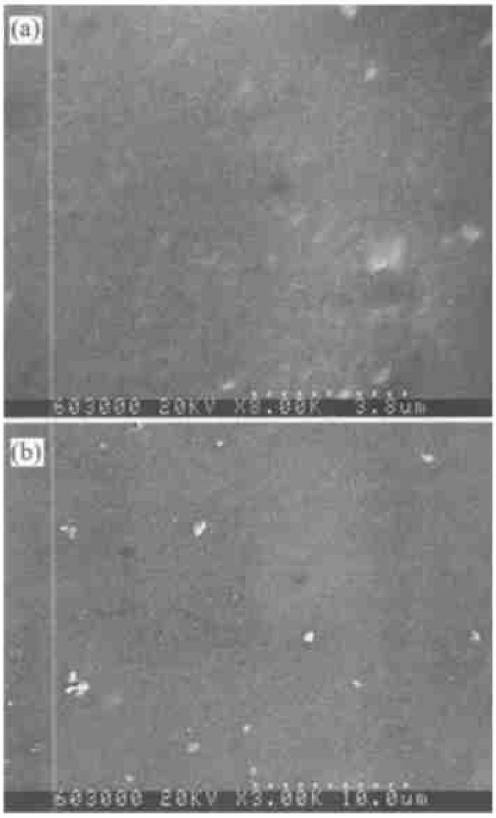

Fig. 3 SEM of NaCl modified PVA-CA membrane
(a) —ω(NaCl) = 1%; (b) —ω(NaCl) = 2.5%

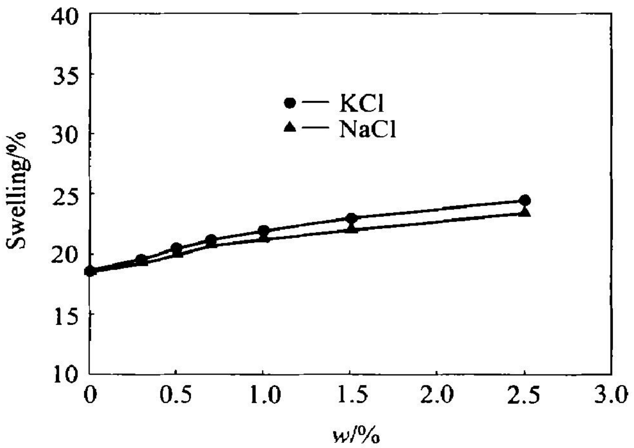

Fig. 4 Mass fraction of salts vs swelling of membranes

UF membrane when the mass fraction of salts is the same. Because the addition of salts can increase the hydrophilicity of the membrane, and the formation of micro-void can increase the containing water of the membrane, when the mass fraction of salt increases, the crystalline salts will dissolve in water and the macro-void can be formed, so the swelling of the membrane increases with the salts which it contains.

Not only the process of forming membrane but also the properties of the surface and the hydrophilicity of membrane are affected by the addition of alkali metal salts. Fig. 5 shows that the addition of both NaCl and KCl can decrease the contact angle of water on the surface of blend membranes. Furthermore, the contact angle decrease with the increase of salts, and NaCl modified UF membrane has a slight lower contact angle of water than that of KCl modified UF membrane when the mass fraction of salts is the same.

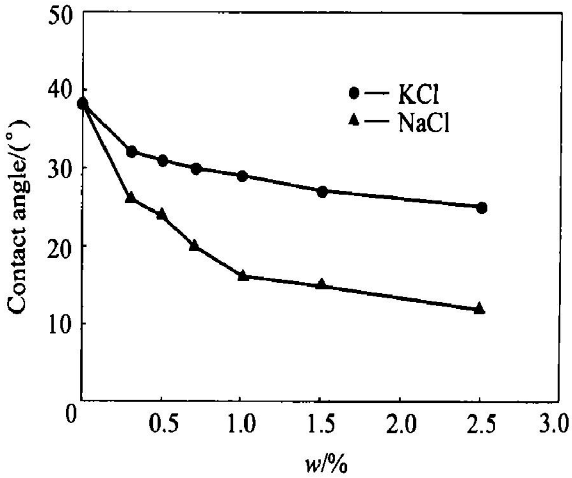

Fig. 5 Mass fraction of salts vs contact angle of membranes

4.2 Effects of operation pressure on properties of blend membranes

To further compare the properties of the alkali metal salt modified blend membrane with unmodified blend membrane, the permeation flux and rejection of oil were tested under different operation pressure, the results are shown in Fig. 6 and Fig. 7. They can be shown that the permeation flux of membranes increases with the operation pressure, but the permeation flux is not proportional to the operation pressure in the range of 0.2 – 0.5 MPa, especially when the operation pressure is greater than 0.4 MPa. Fig. 7 shows that the oil rejection decreases with the increase of operation pressure. The possible reason is that when the trans-membrane pressure increase, the asymmetric layer

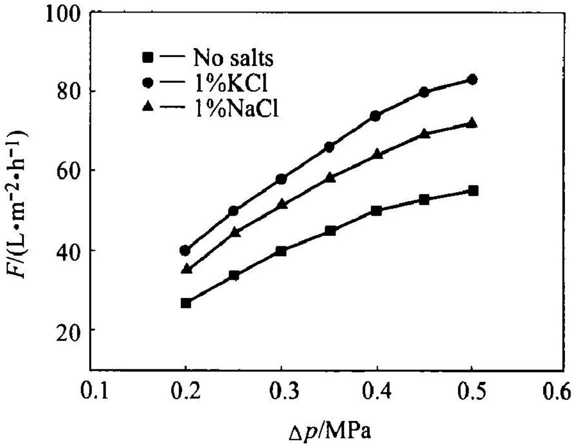

Fig. 6 Trans-membrane pressure vs permeate flux

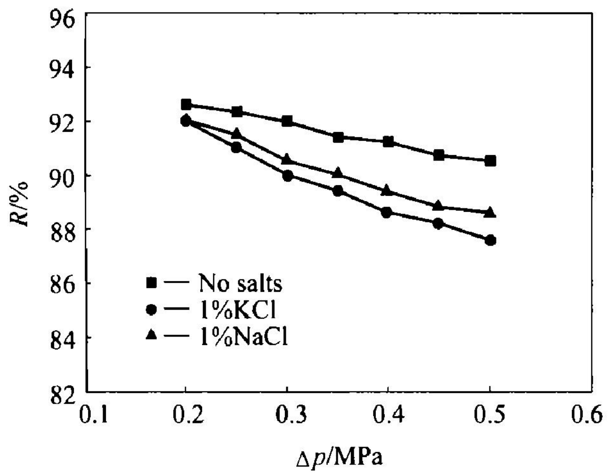

Fig. 7 Trans-membrane pressure vs retention

may be compressed and the void fraction decreases, so the resistance against the flow of permeation increases. Thus, the increment of water flux is relatively small when the trans-membrane pressure is greater than 0.4 MPa. In addition, the concentration polarization on the surface of the membrane will be strengthened when the permeation flux increases, so the oil concentration in the permeation will increase a little, and the apparent oil retention seems to decrease.

5 CONCLUSIONS

1) The modified PVA-CA blend ultrafiltration membranes were prepared by phase inversion from the casting solutions consisting of polyvinyl alcohol (PVA), cellulose acetate (CA), acetic acid, alkali metal chloride and water, and the effects on the properties of membranes of different concentration of alkali metal chlorides were investigated.

2) When the mass fraction of the alkali metal salt in the casting solution is not greater than 1%, the property of rejection of the salt modified ultrafiltration PVA-CA blend membrane has little change compared with the unmodified PVA-CA blend membrane, but the permeation flux is much greater than that of the unmodified membrane under the same operation condition. When the mass fraction of the salt is greater than 1.5%, the permeation flux increases much greater than that of the unmodified blend membrane, but the property of rejection of the modified blend ultrafiltration membrane decreases greatly.

3) For alkali metal salt modified PVA-CA blend UF membrane, the contact angle of which decreases but the swelling increases with the increment of the mass fraction of alkali metal salts. Furthermore, the NaCl modified PVA-CA blend membrane has a slightly lower swelling and a little smaller contact angle of water than the KCl modified PVA-CA blend membrane does when the mass fraction of salts is the same.

REFERENCES

[1] Ciardelli G, Corsi L, Marcucci M. Membrane separation for wastewater reuse in the textile industry [J]. Resources, Conservation and Recycling, 2001, 31(2): 189 - 197.

[2] Tavares C R, Bergamasco R, Petrus J C C. Application of ultrafiltration-complexation process for metal removal from pulp and paper industry wastewater [J]. J Membr Sci, 2001, 194(2): 273 - 276.

[3] Nakatsuka S, Ase T, Miyano T. High flux ultrafiltration membrane for drinking water production [J]. Water Science and Technology: Water Supply, 2001, 1 (5 - 6): 177 - 184.

[4] Gu A. Study of ultrafiltration membrane made from polyvinyl chloride/polyacrylonitrile blend [J]. Polymer-Plastics Technology and Engineering, 2001, 40 (5) : 615 - 625.

[5] Schauer J, Albrecht W, Weigel T. Microporous membranes prepared from blends of polysulfone and sulfonated poly(2, 6-dimethyl-1, 4-phenylene oxide) [J]. J Appl Polym Sci, 2001, 81(1): 134 - 142.

[6] Bowen W, Richard D, Teodora A, et al. Polysulfone-sulfonated poly (ether ether) ketone blend membranes: Systematic synthesis and characterization [J]. J Membr Sci, 2001, 181(2): 253 - 263.

[7] LI Na, LIU Zhong-zhou, XU Shi-guang. Review on studies of anti-fouling poly(vinyl alcohol) membranes [J]. Membr Sci & Tech, 1999, 19(3): 1 - 7. (in Chinese)

[8] Katz M G, Wydeven T. Selective permeability of PVA membranes. II. Heat treated membranes [J]. J Appl Polym Sci, 1982, 27(1): 79 - 87.

[9] QIU Yun-ren, ZHANG Qi-xiu, WU Zheng-dong. Preparation and properties of modified polyvinyl alcohol ultrafiltration membranes [J]. Membr Sci & Tech, 2001, 21(5): 25 - 28. (in Chinese)

[10] Jegal J, Lee K H. Pervaporation separation of water-ethanol mixtures through PVA-sodium alginate blend membranes [J]. J Appl Polym Sci, 1996, 61(2): 389 - 392.

[11] Matsuyama H, Terada A, Nakagawara T, et al. Facilitate transport of CO through polylenimine / poly (vinyl alcohol) blend membrane [J]. J Membr Sci, 1999, 163 (2): 221 - 227.

[12] QIU Yun-ren, ZHANG Qi-xiu. Preparation of PVA-CA blend ultrafiltration membrane and its properties [J]. Modern Chemical Industry, 2001, 21(10): 28 - 31. (in Chinese)

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