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Effects of amphiphilic additive Pluronic F127 on performance of poly (ether sulfone) ultrafiltration membrane

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ABSTRACT

The amphiphilic additive Pluronic F127 can effectively improve the hydrophilic character of membranes. This article reported the effects of Pluronic F127 additive, Pluronic F127/oxalic acid, and Pluronic F127/polyethylene glycol 4000 blended additives on morphology, separation properties and hydrophilic of poly (ether sulfone) (PES) ultrafiltration membrane. The membrane was made by liquid/solid phase inversion method. The results showed that the Pluronic F127 can improve the water flux and retention of PES ultrafiltration membrane, increase pore size and porosity, and change the cross-section structure. The flux of PES membrane with F127 was lower than that with oxalic acid at the same concentration. As the concentration of F127 increased, the flux increased, the retention showed undulation, and the hydrophilic improved. Compared with only F127, the flux of the membrane with F127 blended additives slightly increased and the effect of F127 is the major in the blending system, and the blended additives changed the hydrophilic of membranes. The blended additives have a greater impact on the performance of F127 membrane. As the blended additives concentration increased, the membrane structure exhibited a skin layer, a porous layer, and a support layer. When blended additives were in high concentration, the morphology changed from finger-like to sponge-like macro-voids structure.

Keywords: PES; Ultrafiltration membrane; Pluronic F127; Oxalic acid; PEG4000

1. Introduction

With the application of a pressure-driven process to separate macromolecules from the small species improved, the ultrafiltration membranes have been widely used in water purification and treatment industries. Many polymer materials were used in the preparation of membranes. Among these materials, the poly (ether sulfone) (PES) as an engineering plastic with high mechanical strength has become an important material for ultrafiltration membranes [1–3]. In the membrane preparation process, the effects of additives on the performance of the membrane is very meaningful, and the additives that strongly affect the structure of casting solution and solvent evaporation rate are the significant factor in determining membrane properties. The additives generally contain

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organic and inorganic species, and different additives have different effects in the preparation of membranes. For instance, the Polyvinylpyrrolidone additive exerts a different influence on the structure of membranes, and the structure of skin layer strongly depended on the polymeric additives in the casting solution. And the acetic acid additive exerts an influence on the structure and filtration properties of membranes. Not only the surface morphology but also the structure of cross-section could be modulated by adding the acetic acid in the casting solution [4,5].

However, the blended additives have the better results and can reflect the advantages of different additives together. Thus, the development of ultrafiltration membrane with blended additives has become necessary. Wang et al. [6] utilized various molecular weight polyethylene glycols (PEG) and three kinds of inorganic salts LiCl, $ZnCl_2$, and $Mg(ClO_4)_2$ as the additives in terms of the different principle of organic and inorganic additives effects on making ultrafiltration membrane, it was shown that the use of blending additives to adjust pore diameter could get small pore diameter and high porosity hollow fiber ultrafiltration membrane. Yonglie et al. [7] prepared polyimide gas separation membranes by using metal-containing organic complex with big substituting group as additive, and the effects of organic ligand and metal complex on the permeability of polyimide homogenous membranes and asymmetric membranes for the separation of hydrogen and nitrogen were studied. It was shown that $MnCl_2$, $Co(NO_3)_2$ enhanced the separation coefficient and lowered the permeability of the membrane; organic additive enhanced the permeability and lowered separation coefficient; when metallorganic complex was used, the gas permeability was enhanced without decline of separation coefficient.

Among different additives, amphiphilic additives can effectively increase the hydrophilic of the membrane and improve the membrane-fouling resistance. Among them, Pluronic is the most investigated [8–13]. Pluronic is a commercialization of poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO–PPO–PEO) triblock amphiphilic copolymer. Among these series products, Pluronic F127, as a kind of the high hydrophilic material, has been used for the additives of membranes. Its molecular structure is shown in Fig. 1. In the membrane formation process, hydrophilic PEO chains of F127 block copolymer have the higher osmotic pressure, and spontaneously gathered on the membrane surface, while hydrophobic PPO chains give the role of anchoring to achieve low adsorption of proteins on the membrane surface [14].

Pluronic F127 can be used as porogen to increase the membrane pore and porosity to improve the performance of membrane separation and be used as surface modifier, and PEO chains can enhance the surface hydrophilic and improve the ability of inhibiting protein adsorption on the membrane surface. Wang et al. [15–19] utilized PES as membrane subject and Pluronic amphiphilic block copolymers as surface modifier to prepare the different types of surface segregation ultrafiltration membranes, and separation properties and fouling characteristics of PES–Pluronic surface segregation membrane were studied. It was shown that Pluronic can increase the membrane pore size and change pore structure, reduce the rate of protein retention. At the same time, PES–Pluronic membranes have excellent inhibition of protein adsorption and antifouling properties, the protein adsorption quantity can be reduced to 0, the flux recovery rate can reach up to 89%, higher than 62% of the blank membrane. In this work, Pluronic F127 was chosen as the additive because of its good hydrophilic and antifouling characteristics.

However, with more and more researches on Pluronic F127 additive, the large flux and pore structure of membranes became more important, especially the effects of blended additives containing Pluronic F127 on performance of membranes are not studied systematically.

The main objective of this work is to research the effects of Pluronic F127 additive, Pluronic F127/oxalic acid and Pluronic F127/PEG4000 blended additives on morphology, separation properties, and hydrophilic of PES ultrafiltration membranes. The effects of the polymer PES concentration and the additives concentrations are studied. In order to observe the cross-section structure of the membrane, the scanning electron microscopy (SEM) is used to evaluate the morphologies of membranes. And the contact angle analyzer is used to research the variation of the hydrophilic of membranes.

2. Methods

2.1. Materials

PES was purchased from Dalian Polymer New Material Co. Ltd., Liaoning, P.R. China and its chemical structure is shown in Fig. 2. N, N-Dimethylformamide (DMF) was used as solvent. Macromolecular polymer Pluronic F127 was chosen as the additive,

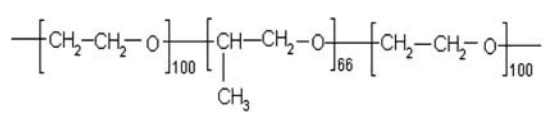

Fig. 1. Molecular structure of Pluronic F127.

which was purchased from Beijing Isomersyn Technology Co. Ltd., Beijing, P.R. China, and oxalic acid and PEG4000 (Mw 4000 ± 30 Da) were purchased from Beijing Yili Fine Chemicals Co. Ltd., Beijing, P.R. China.

The rejections of ultrafiltration membranes were measured by using bovine serum albumin (BSA, Mw 69,000 Da), and it was purchased from Sinopharm Chemical Reagent Beijing Co. Ltd., Beijing, P.R. China. All chemicals used in the experiments are analytical grade and without further purification.

2.2. PES ultrafiltration membrane preparation

The asymmetric ultrafiltration membranes were made by liquid/solid phase inversion method. Different amount of PES and additives, including Pluronic F127, oxalic acid, and PEG4000, were dissolved in DMF at constant temperature for 24 h with vigorous stirring until a homogenous polymer casting solution was formed. Then remove the casting solution, degassed for 12 h to prevent the prepared membrane generating pinholes and highlights. The standing solution was salivate on the flat glass and immediately precipitated in a coagulation bath filled with de-ionized water (DI water) until it was solidified. Each casting solution scraped at least six membranes. In order to remove all the residual solvent, the membrane was moved into another DI water bath at ambient conditions and kept for 12 h. In all experiments, the external and internal coagulations were DI water.

2.3. Ultrafiltration experiments

In this study, NDJ-1 rotational viscometer was used to measure the viscosity of the casting solutions. Select the appropriate rotor (1–4) and make sure that the height of casting solution is greater than the scale of the viscometer rotor line. After the casting solution stability, calculate the viscosity of different casting solutions.

The water permeation and solute retention tests were performed with a cross-flow filtration setup, and the feed solution was pumped into membrane module with a tube-side configuration. Then, at room temperature (20°C) and a transmembrane pressure of 0.1 MPa, the water flux of membrane was measured.

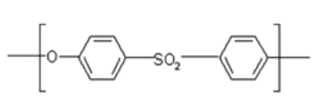

Fig. 2. Chemical structure of PES.

DI water was used to measure the pure water flux (J) that is calculated by Eq. (1):

$$J = Q/At \quad (1)$$

where Q is the total permeate volume in each experiment; A denotes the membrane area (m^2); t represents the filtration time (h).

A 2 L solution of BSA (500 mg/L) was used to measure the rejection of the membranes. The BSA concentration was determined by using a UV-spectrophotometer (UNICO-UV2102, China) at the wavelength of 280 nm. Rejection (R) is expressed by Eq. (2):

$$R = (1 - C_p/C_f) \times 100\% \quad (2)$$

where C_p and C_f are the concentrations of the permeation and the feed, respectively. The solute retention was also tested at 20°C and 0.1 MPa pressure. All results were the average value of three parallel tests. All the standard errors were in the acceptable range (less than 10% of the average value).

2.4. Contact angle experiments

JC-2000C1 contact angle analyzer was used to measure the contact angle of the ultrafiltration membranes. The freeze-dried sample was tiled on the loading platform, and flattened, then drop 5 μL of DI water in the membrane surface. Through the software of the instrument, the contact angle data was calculated. Each sample was measured at least five times and averaged. Finally, the contact angle data was used to analysis the hydrophilic of the F127 membranes.

2.5. Morphology of PES ultrafiltration membrane

SEM was used to observe the morphology of membrane cross-section. To avoid destroying the structure of the ultrafiltration membrane, the membrane samples for SEM imaging were firstly cryogenically immersed in liquid nitrogen, fractured, and then sputtered with metallic gold to get an adequate contrast of the membrane fracture. A JSM-6301 field emission scanning electron microscope (JEOL Ltd.) was used to observe the membrane morphology.

3. Results and discussion

3.1. Effects of PES concentration

From Fig. 3, it is observed that the viscosity of the casting solution increased while the PES concentration increased from 10 to 20 wt.% and compared with the

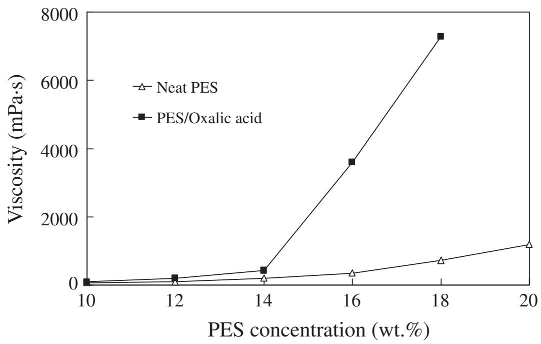

Fig. 3. Effects of PES concentrations on viscosity of different casting solutions (15℃).

neat PES, the viscosity of PES solution with oxalic acid additive was higher, especially from 14 wt.%. As the PES concentration increased, the density of the polymer chain segments in the casting solution system increased, the distribution of the PES molecular chain segments was more uniform, nonsolvent spread into the casting solution more difficult, and the phase separation time became longer so that polymer chain segments had more time to come together, finally formed a more dense membrane. When oxalic acid added into the casting solution, because oxalic acid has strong affinity with water and can be solved in the water, phase inversion trend is improved, the hydrogen atom of the oxalic acid molecule bonded with the carbonyl oxygen atom of the PES molecule, and it changed the solubility of PES solution, greatly improved the viscosity of the casting solution.

It suggested in Fig. 4 that *J* decreased and *R* of neat membrane increased while increasing the PES concentration. When the PES concentration was 16 wt. %, *J* approached to 0 and *R* was 99%. When the polymer concentration is at high, the casting solution is easy to form the aperture smaller dense membrane, and it resulted in the low water flux and high retention. When the polymer concentration is low, the large pore structure forms. With the increasein PES concentration, the polymer concentration at the exchanged interface in phase was higher, resulting in the polymer volume fraction increased, the porosity decreased, so the concentration of polymer in the casting solution is an important factor affecting the membrane performance. As the PES concentration increased, the number of the finger-like holes in the sublayer region of the skin layer was reduced, and the pore size and the number of the finger-like holes in the support layer decreased, the sponge-like structure connecting with the finger-like gradually appeared.

Compared with the neat PES membrane, it is observed in Fig. 5 that the water flux of membranes with oxalic acid was significantly higher, and it ranged from 800 to 1,000 $L/m^2 h$, the retention was broken-line shape. As the PES concentration increased, *J* and *R* showed a downward trend, but when PES concentration is 16 wt.%, *J* was not close to zero and *R* was 60%. Oxalic acid can obviously affect the membrane structure. On the one hand, because the hydrogen bonds combination of the hydrogen atom of oxalic acid and the oxygen atom on the carbonyl, a highly hydrophilic compounds is formed, and it has an impact on the phase inversion process; On the other hand, the hydrogen atom of oxalic acid can also combine with the carbonyl and sulfonyl of the oxygen atom, and form hydrogen bond compounds. Due to the steric effect, the sensibility of the PES polymer chain enhanced, and the time required for the molecular chain rearrangement and the phase separation time becomes shorter. While oxalic acid additive added, the membrane morphology was affected by the PES concentration. The dense finger-like holes of the cross-section membrane decreased, and the pore size became larger, the sponge-like holes gradually increased (Fig. 7).

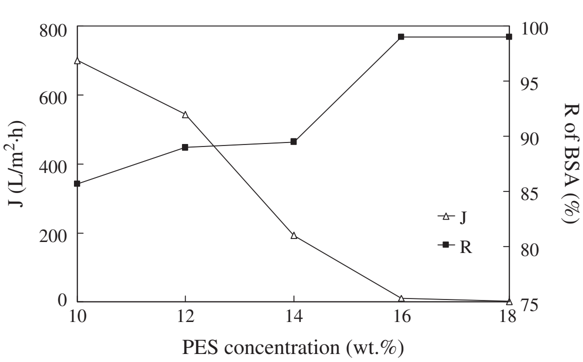

Fig. 4. Effects of PES concentrations on *J* and *R* of the neat PES ultrafiltration membrane.

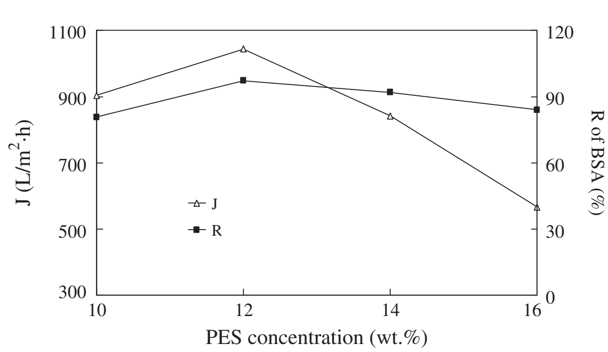

Fig. 5. Effects of PES concentrations on *J* and *R* of the PES/5 wt.% oxalic acid ultrafiltration membranes.

3.2. Effects of additives

3.2.1. Pluronic F127

The additives have great effects on the microstructure of the casting solution and the properties of the membrane. Therefore, it is very important to add one or more additives into the casting solution. In fact, through adjusting the proportion of additives, solvents, and polymers, casting solution viscosity, phase separation speed can be adjusted to achieve the purpose of the control of membrane structure and properties of the membrane, the quantity and type of additives affect the structure of the polymer solution and the size of the macromolecular polymer.

The different additives have different effects on the water flux and rejection of the membrane. Pluronic F127, as a kind of the high hydrophilic material, has been used for the additives of membranes. In this study, 14 wt.% PES and DMF solvent were used. From Fig. 6, it suggested that *J* increased and *R* decreased when increasing the Pluronic F127 concentration from 1 to 9 wt.%, and when the Pluronic F127 concentration is 11 wt.%, the flux decreased, and *R* increased as well. Compared with the 14 wt.% PES membrane with oxalic acid, the water flux of membrane with Pluronic F127 was lower. The SEM micrographs are shown in Fig. 7. It is observed that the membrane morphology was affected by the concentration of Pluronic F127.

Because of these two properties of Pluronic F127, the hydrophilic and structure of membrane changes, the water flux gradually increases while the concentration increases. However, the effects of oxalic acid on the structure of membrane are greater than F127, the pore size and density of the membrane with F127 are less than membrane with oxalic acid. So the flux of membrane with F127 was lower than oxalic acid. Because BSA molecular is large, the PES/Pluronic F127 membrane of BSA retention rates are not low. With the increase of Pluronic F127 addition, the BSA rejection rate decreased slightly. It suggested that PES membrane with Pluronic F127 can be effectively retain spherical molecule of molecular weight cutoff at 67 kDa. Compared with the retention of 14 wt.% PES membrane with oxalic acid, the average retention of F127 is greater than oxalic acid, because the membrane with oxalic acid has a larger pore size and higher porosity, resulting in the lower retention.

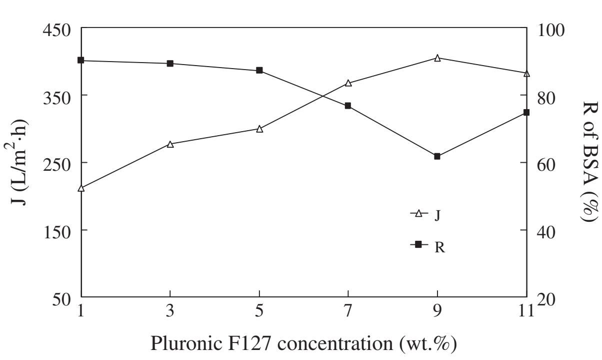

Fig. 6. Effects of Pluronic F127 concentrations on *J* and *R* of PES/ Pluronic F127 ultrafiltration membranes.

Pluronic F127 has a kind of amphiphilic additive, and it can be used as porogen to increase the membrane pore and porosity to improve the performance of membrane separation, and PEO chains can enhance the surface hydrophilic and improve the ability of inhibiting protein adsorption on the membrane surface. When Pluronic F127 is added into the casting solution, the viscosity greatly increases and the movement of macromolecule is suppressed. When amphiphilic material is added into the casting solution, the system will appear the phenomenon of micellization, and the stability of the system is enhanced. So F127 is an important factor affecting the casting solution micelle structure. The pore size and density of the membrane are related to the volume and density of the micelles in the casting solution. Therefore, the amount of F127 has effects on the flux and rejection of membranes. When increasing the F127 additive, the size and density of micelle increase, the membranes consisted of a dense skin layer, the porous sublayer, and the macroporous support layer. The sublayer gradually thickened into a dense sponge-like structure, the finger-like holes of support layer became larger and gradually extended to the bottom of the membrane (Fig. 7).

The hydrophilic membrane surface can form hydrogen bonds with water, when the hydrophobic solutes close to the membrane surface, the hydrogen bonds must be destroyed, and this process requires energy and is not easy to happen, and thus the membrane is not easy to be contaminated. Instead, because the hydrophobic membrane has no hydrogen bonds, the membrane surface easily adsorbed solute and can be contaminated. Therefore, the membrane with more hydrophilic has the higher antipollution capability. The hydrophilic of the membrane was determined by measuring the static water contact angle method. The smaller the contact angle is, the stronger hydrophilic the membrane has. As the F127 concentration increased, the contact angle gradually decreased, when the F127 concentration was 9 wt.%, the contact angle decreased to 67.7° (Table 1). And the contact angle of the neat PES membrane was 82°, so because the F127 added, the density of PEO chains of the membrane surface increased, and the hydrophilic of the membrane surface improved.

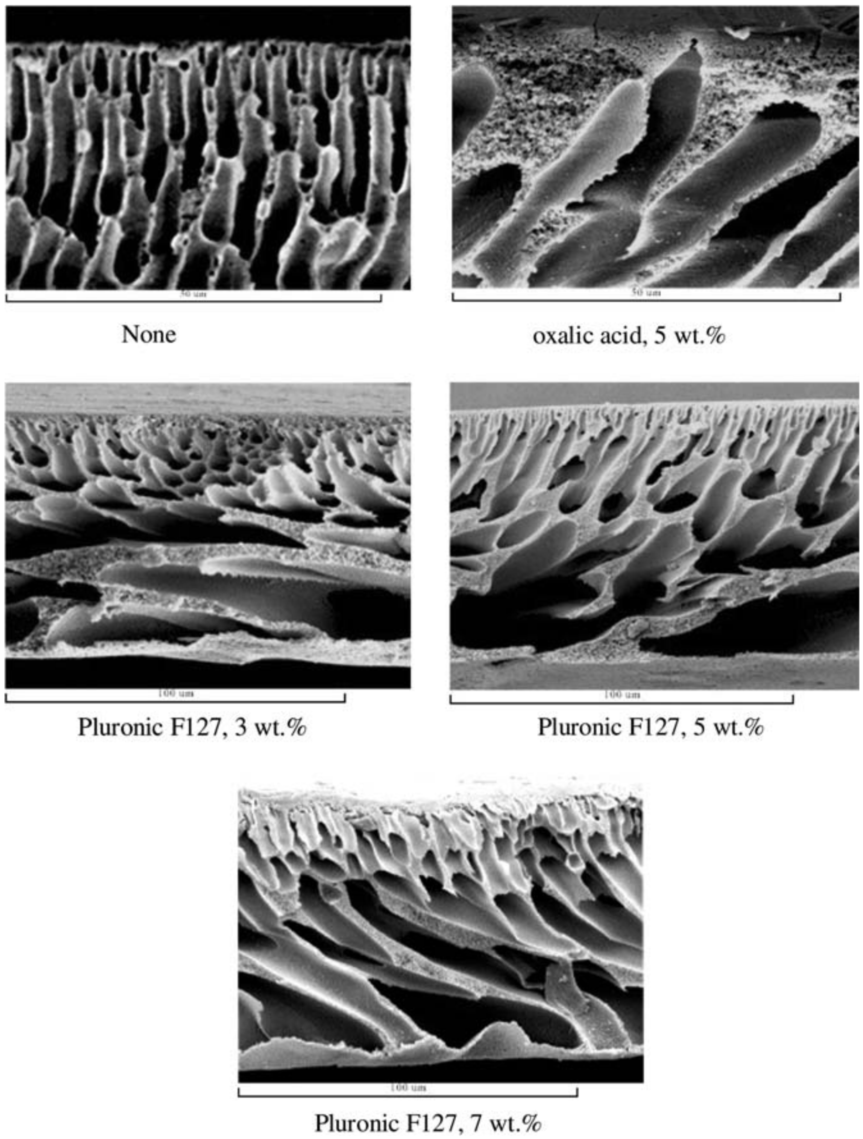

Fig. 7. Cross-section SEM micrographs of PES ultrafiltration membranes for different additives.

3.2.2. Pluronic F127/oxalic acid

Different types of additives have different effects on performance of membranes, and inorganic and organic additives have their advantages and disadvantages. Oxalic acid, as a small molecule inorganic additive, has strong affinity with water, phase inversion trend is improved, the hydrogen atom of the oxalic acid molecule bonded with polymer solution, the viscosity of the casting solution improved as well. As a result, the porosity of the membrane improved. Pluronic F127 is a kind of macromolecular organic additives, it can regulate the high molecular state of casting solution, which affects the membrane structure. If blended these additives, their respective advantages are used, so that the casting solution can show the effect of homogenization, finally prepare the higher flux of membranes.

Table 1
Effects of Pluronic F127 concentrations on water contact angles of different PES ultrafiltration membranes

Additives	Water contact angles of PES ultrafiltration membranes (°) wt.%				
	1	3	5	7	9
Pluronic F127	77.0	72.8	71.2	68.2	67.7
Pluronic F127/oxalic acid	71.3	68.5	70.0	69.0	65.7
Pluronic F127/PEG4000	73.5	73.3	71.3	70.8	69.4

It was shown in Fig. 8 that when PES concentration was 14 wt.% and F127 was 3 wt.%, *J* slowly rose, while the oxalic acid concentration increased from 0.5 to 5 wt.%. *R* was basically maintained at between 75 and 90%. Compared with only F127 additive, the water flux of F127/oxalic acid did not change significantly as oxalic acid concentration increased. Though the best result of oxalic acid concentration was 3 wt.%, it unstably changed. And the effect of F127 was stronger than oxalic acid. Thus, 1 wt.% oxalic acid was chosen to prepare the membranes. From Fig. 9, it suggested that the flux of membrane with F127/1 wt.% oxalic acid gradually increased as the F127 concentration increased from 1 to 9 wt.%, when the concentration was 5wt.%, the flux tended to smooth. The highest retention was 90%, and others remained at around 79%. Compared with only F127 additive, the flux slightly increased and the effect of oxalic acid was not obvious. So F127 has the main effects on performance of membranes with F127/oxalic acid blended additives.

For the organic macromolecular additives, the solvent in the casting solution is also a good solvent, resulting in the additives and polymer solute compete solvent for each other. This is equivalent to the increase in polymer concentration. A variety of polymer chain segments are entangled and curly, and the polymer dispersions become uneven. If oxalic acid is a small molecule additive, when oxalic acid contacts with the air having water vapors, oxalic acid could absorb nonsolvent water into the casting solution by hydrogen bonds. Thus, the viscosity of casting solution increased, and the phase inversion velocity became quicker and *J* increased. When oxalic acid adds in the casting solution, the water flux slightly increases. As the oxalic acid concentration increases, the flux gradually increases at the same conditions, but if the oxalic acid concentration is too large, more

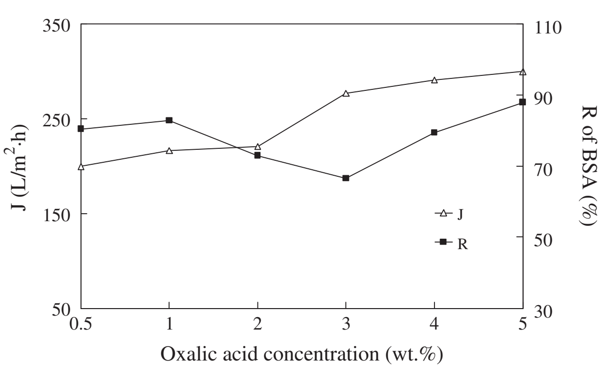

Fig. 8. Effects of oxalic acid concentrations on *J* and *R* of PES/3 wt.% Pluronic F127/oxalic acid ultrafiltration membranes.

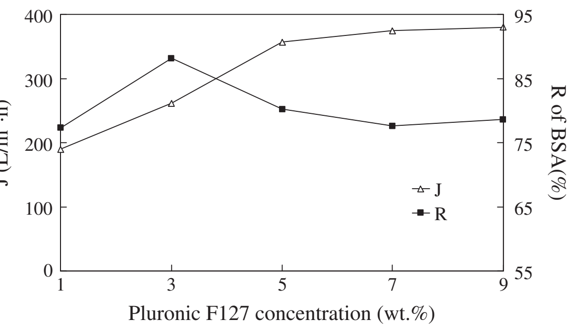

Fig. 9. Effects of Pluronic F127 concentrations on *J* and *R* of PES/Pluronic F127/1 wt.% oxalic acid ultrafiltration membranes.

than 5%, the casting solution conditions would be declined, and membrane products are ineffective. Therefore, oxalic acid addition should not be too large. When adding 1 wt.% oxalic acid addition, the flux increased while the F127 concentration gradually increased, but compared with only F127 adding, there is a little variation. The effect of hydrophobic block of F127 additive is suppressed, and the flux and rejection do not change significantly. Therefore, when F127 and oxalic acid blend together, the effect of F127 additive is the major.

As the F127/oxalic acid blended additives of different concentrations added, the membranes exhibited a dense skin layer at the outer region, a porous layer and a support layer (Fig. 10). The structure is similar with the only F127 membrane, the membrane morphology gradually changed from finger-like to sponge-like macro-voids structure while the concentration increased. It was given in Table 1 that the contact angle of F127/oxalic acid blended additives membranes slightly decreased while the F127 concentration increased and the hydrophilic did not largely decrease. Therefore, Pluronic F127/oxalic acid blended additive has certain effects on the hydrophilic of the PES ultrafiltration membranes.

3.2.3. Pluronic F127/PEG4000

PEG4000, as a kind of water solubility organic surfactant, has two effects on the casting solution. On the one hand, it can improve the affinity activity with the solvent. The hydrogen bonds can be formed between them in order to decrease their thermodynamics stability, the phase separation process could be accelerated as well. Finally, the pore size increases and the membrane separation performance changes. On the other hand, PEG4000 can increase the viscosity of casting solution, which leads to the longer phase separation time. Therefore, the smaller pore in the

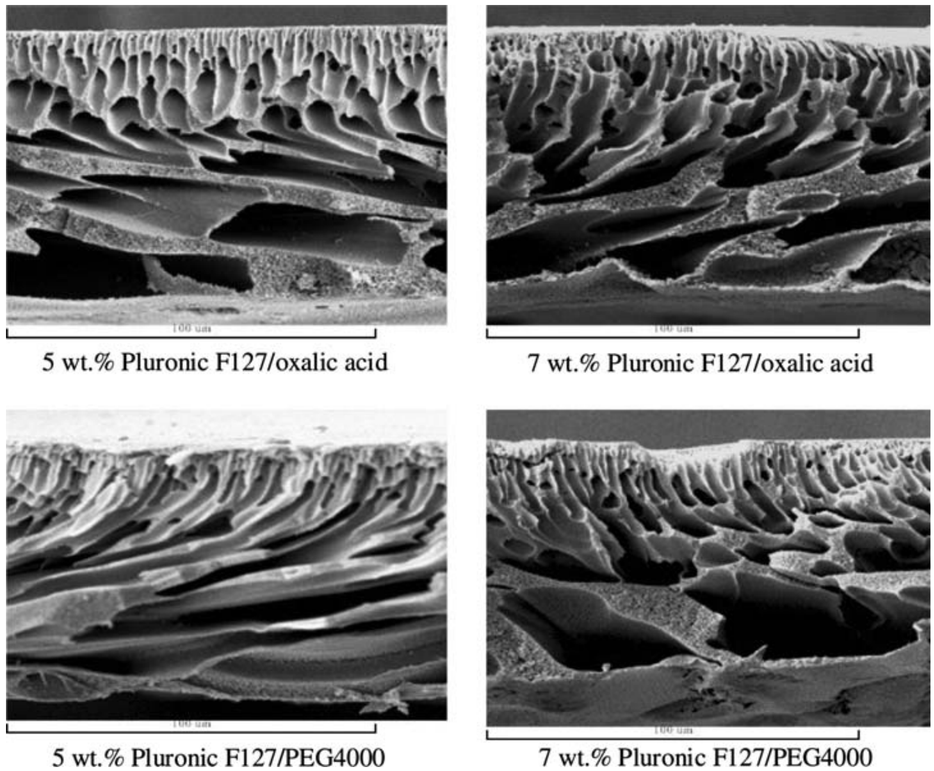

Fig. 10. Cross-section SEM micrographs of PES ultrafiltration membranes for different Pluronic F127 blended additives.

membranes could be formed. If blended Pluronic F127 and PEG4000, the viscosity of casting solution increases, the behavior of phase inversion process could be affected, the membrane separation performance changes.

The effect of PEG4000 concentration on the membranes is shown in Fig. 11. The PES concentration was 14 wt.% and F127 was 3 wt.%. When PEG4000 concentration increased from 1 to 5 wt.%, J maintained between 200 and 300 $L/m^2 h$, R was not large. Compared with only F127 at the same concentration, the PEG4000 did not significantly increase the water flux and R was obviously decreased. The effect of PEG4000 was small and the 4 wt.% PEG4000 was chosen to prepare the membrane with F127/PEG40000 blended additives. It observed from Fig. 12 that while the F127 concentration increased from 1 to 9 wt.%, the water flux gradually increased. When F127 concentration was 7 wt.%, the flux reached the maximum of 434 $L/m^2 h$ and it was higher than the flux of membrane with only F127. The retention was not large and showed undulation. Compared with F127/oxalic acid blended additives, the flux of different membranes was similar and the PEG4000 concentration had little effect too. The retention of membranes with F127/PEG4000 became small. But when the PEG4000 was 4 wt.% in the blended system, the flux increased little (Figs. 6 and 12) and the retention decreased. Thus, F127 plays the major in the F127/PEG4000 blended additives system.

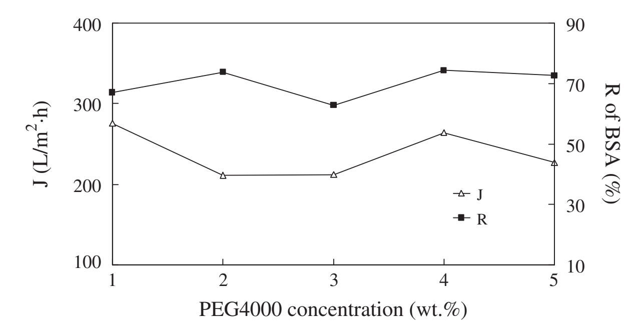

Fig. 11. Effects of PEG4000 concentrations on J and R of PES/3 wt.% Pluronic F127/PEG4000 ultrafiltration membranes.

The structure of the F127/PEG4000 membrane also exhibited a dense skin layer, a porous layer, and a support layer (Fig. 10). The finger-like holes became larger and extended to bottom of the membrane. The sponge-like macro-voids structure gradually formed. Compared with F127/oxalic acid, the F127/PEG4000 membrane had more sponge-like holes in the support

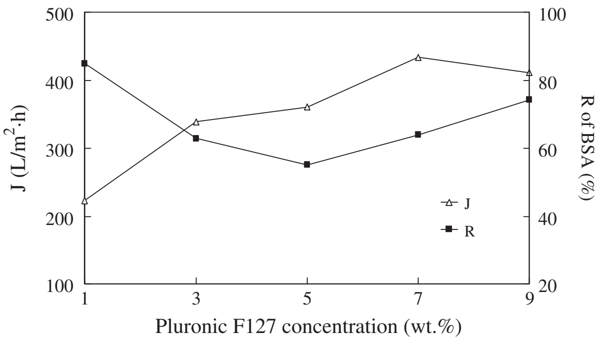

Fig. 12. Effects of Pluronic F127 concentrations on *J* and *R* of PES/Pluronic F127/4 wt.% PEG4000 ultrafiltration membranes.

layer, and the pore size is larger. Compared with only F127 membranes, the contact angle of F127/PEG4000 membranes became larger (Table 1), so F127/PEG4000 blended additives do not help to improve the hydrophilic of the membrane.

4. Conclusions

The additives can effectively improve the water flux and retention of PES ultrafiltration membrane, increase pore size and porosity of the PES membrane, and change the cross-section structure. Because of additives, the viscosity of the casting solution improved significantly. The phase inversion trend was improved, and the solubility of PES solution was changed. With the rise of PES concentration, the water flux of the membrane with additives was higher than the neat membrane, and the oxalic acid additive could change membrane morphology from finger-like to sponge-like structure. The flux of PES membrane with Pluronic F127 was lower than that with oxalic acid at the same concentration. As the concentration of Pluronic F127 increased, the flux of the membrane gradually increased, the retention of the membrane showed undulation, the hydrophilic of the membrane gradually improved. Compared with only Pluronic F127, F127/oxalic acid blended additives had different effects on performance of PES ultrafiltration membrane. The flux slightly increased and the effect of F127 was stronger than oxalic acid, the effect of F127 was the major in the blending system. The same situation happened in Pluronic F127/PEG4000 blended additives, but the F127/PEG4000 membranes had a larger flux and small retention. So the different blended additives have the different impact on the performance of F127 membrane. Because of blended additives, the contact angle changed, and the hydrophilic changed accordingly. As the blended additives concentration increased, the membrane structure exhibited a skin layer, a porous layer and a support layer. When blended additives were in high concentration, the membrane morphology changed from finger-like to sponge-like macro-voids structure.

Acknowledgments

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