

Hydrophilic modification of polytetrafluoroethylene flat membranes coated by acrylic acid water-absorbent resin

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ABSTRACT

To improve hydrophilicity and anti-fouling property of the polytetrafluoroethylene (PTFE) flat microfiltration (MF) membrane, a facile method was developed to modify the membrane via the post-cross-linking reaction of polyacrylic acid (PAA) and trimethylolpropane tris-(2-methyl-1-aziridinepropionate) (Sac-100) followed by soaking NaHCO₃ saturated solution. The surface chemical composition, surface morphology, hydrophilicity and filtration performance of the PTFE flat membrane were examined by XPS, ATR-FTIR, FESEM, water contact angle and pure water flux measurements, respectively. The results showed the hydrophilic groups such as carbonyl (C=O), hydroxyl (–OH) and carboxylic ion (–COO[–]) were observed on the surface of modified membrane, it can be seen as a water-absorbent resin system. After choosing this low-cost and simple modification method, the PTFE flat membrane was endowed with excellent hydrophilicity, high water permeation flux. Then, effects of surface modified conditions on membrane hydrophilicity were studied systematically. The anti-fouling tests were conducted using the modified PTFE flat membranes, results showed the modified PTFE flat membranes possess excellent bovine serum albumin (BSA) fouling resistance. Finally, the surface stability of the modified membrane was studied and the modified membranes showed stability under the acidic condition but weak to strong alkali. Therefore, this facile strategy holds attractive potential practical application in water environmental remediation, for example, treatment of medical wastewater.

Keywords: PTFE; Post-cross-linking reaction; Surface modification; Water-absorbent resin; Surface water contact angle; Anti-fouling property

1. Introduction

Polytetrafluoroethylene (PTFE) is known as the “King of Plastic” because of its excellent chemical resistance, superior thermal stability, anti-aging, outstanding nonstick, high mechanical strength, excellent lubricity and electrical insulating properties [1–4]. So it has been widely explored for many different kinds of applications, such as membranes bioreactor, water treatment equipment, medicine and other fields [5–8]. However, the PTFE are limited by the extremely symmetrical structure and low surface energy in their prac-

tical application, which were leads to superhydrophobic properties. Thus, it is necessary to make a few attempts to improve the properties of PTFE.

In recent years, in order to extend the application field of PTFE, the surface modification of PTFE membranes have been explored by different methods, such as “wet” chemical treatment modification [9,10], force chemical modification [11], radiation graft polymerization modification of surface [12–14], plasma treatment modification [15–17], laser modification [18,19], and dip coating method modified [20]. These modification methods can improve the hydrophilicity properties while decrease contact angle of

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the membranes. Their mechanism is basically the same, the hydrophilic group introduced into the membrane's surface, such as carboxy, amino, hydroxy, sulfonic acid group [21,22].

In these modified methods, radiation grafting, plasma irradiation and laser bursts are require complex technology and expensive equipment, which leads to industrial production severely restricted; For the "wet" chemical process, which is not only corrode the membranes surface but also produce severe toxic substances and the environmental pollution are more serious; For the dip coating method, polymer of containing hydroxy and amino have been selected as the substrate, monofunctional or difunctional compounds has been used as a cross-linker, the cross-linked product is a non-three dimensional network structure, which results in uneven coating layer and the coating be a poor fastness. So it is necessary to develop a new route.

In this work, a novel simple and environmental protection process of dip coating has been developed. A trifunctional compounds of trimethylolpropane tris-(2-methyl-1-aziridinepropionate) (Sac-100) has been used as cross-linker and poly (acrylic acid) (PAA) of the low degree of polymerization has been selected as a hydrophilic substrate. The fibril surface of PTFE flat membrane wrap a layer of poly acrylic acid water-absorbent resin layer via the post-cross-linking reaction of PAA and Sac-100 followed by soaking NaHCO_3 saturated solution. The surface element, chemical structure, morphology and wettability of the modified PTFE were investigated by Xray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), permeate water flux measuring equipment, contact angle goniometer. Meanwhile, the mechanism of improved hydrophilicity was analyzed and discussed.

2. Experimental

2.1. Materials

Polytetrafluoroethylene flat membrane (mean pore size $0.22 \mu\text{m}$, porosity 85%) was supplied by Zhejiang Kertice Hi-tech Fluor-material Co., Ltd.; Polyacrylic acid (PAA) (50 wt.% in H_2O , average molecular weight, $M_w = 3,000$) and Bovineserum albumin (BSA, $M_n = 68000$) were purchased from Aladdin (China); Trimethylolpropane tris(2-methyl-1-aziridinepropionate) was obtained form Shanghai UN Chemical Co., LTD and the chemical structure was shown in Fig. 1; Other reagents such as acetone, ethanol, $\text{NH}_3 \cdot \text{H}_2\text{O}$, HCl and NaHCO_3 were provided by Hangzhou Gaojing Fine Chemical Industry Co., Ltd, and used as received without further purification. All solutions were prepared using de-ionized water.

2.2. Membranes modifications by cross-linking poly(acrylic acid) and Sac-100

Flat membranes (area 45.53 cm^2) were first immersed in acetone for 1~1.5 h and subsequently cleaning with acetone to remove surface impurities and contamination. After that, they were dried in the vacuum oven at 40 for

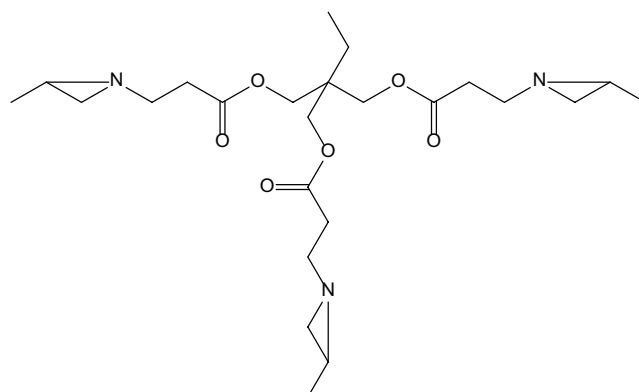


Fig. 1. Chemical structure of trimethylolpropane tris (2-methyl-1-aziridinepropionate).

a few minutes. PAA as hydrophilic reagent with different mass fraction were dissolved in de-ionized at 25. Following $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added into the pure PAA solution adjust to $\text{pH} = 7\sim 8$. The mixture was continuously stirred at room temperature, different mass fraction Sac-100 was added into the mixture solution. PTFE flat membrane samples were immersed in the freshly prepared solution after pre-wetting with ethanol, and shook at 50°C for 1~1.5 h. Then the pH of the mixed solution was adjusted to 5 using HCl ($0.2 \text{ mol} \cdot \text{L}^{-1}$) solution and the mixed solution was kept stirring for another 5~10 min (50), the modified flat membranes were took out and immersed in saturated NaHCO_3 solution for 0.5~1 h, at last the membranes were washed three times by de-ionized water, as shown in Fig. 2. Finally, the samples were dried in the vacuum oven at 40°C and kept in sealable bags.

2.3. Membranes characterization

2.3.1. XPS

X-ray photoelectron spectroscopy (XPS, Kratos, XSAM800) was performed to characterize changes of chemical element on the surface of modified porous PTFE flat microfiltration membranes.

2.3.2. FTIR

Fourier transform infrared spectroscopy (FTIR, Nicolet5700 Thermo Electron, America) was performed to characterize changes of chemical groups on the surface of modified porous PTFE flat microfiltration membranes.

2.3.3. SEM and EDX

For providing the visual information of PTFE flat membranes, surface morphology and chemical element of original and modified PTFE flat membranes was observed by field emission scanning electron microscopy (FESEM, EVO MA 25, ZEISS), all the samples surface was gold sputtered before observation.

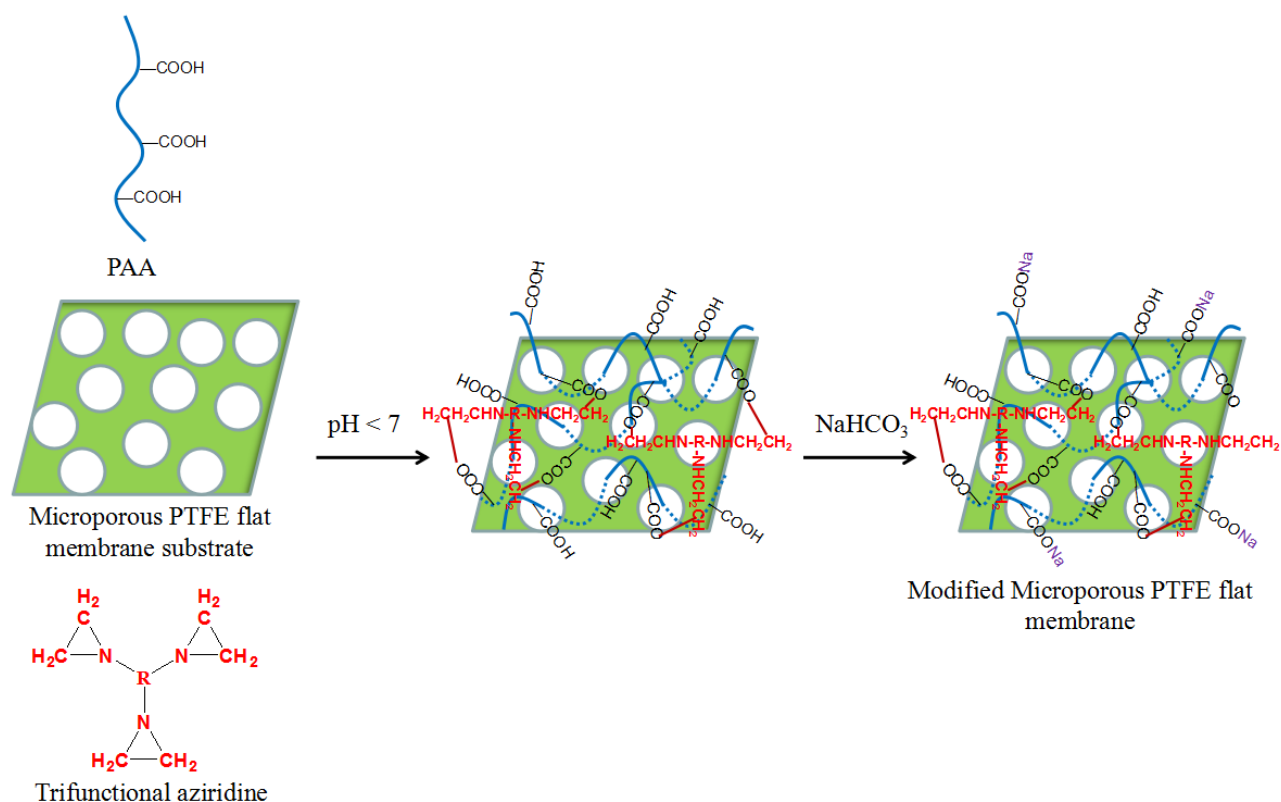


Fig. 2. Schematic representation of hydrophilic modification.

2.3.4. Permeate water flux

Permeate water flux test, of modified PTFE flat membranes by lab-made dead-end microfiltration apparatus as shown in Fig. 3, (test pressure of 0.1 MPa, flat membranes effective area is 13.85 cm²)

The permeate flux was calculated by the following equation of membranes (kg/m²·h):

$$J_w = \frac{M}{A \cdot t} \quad (1)$$

where J_w is the permeate flux (kg/m²·h), M is the mass of the permeate (kg), A is the effective surface area of the PTFE flat membranes (m²), t is the experimental running time (h).

2.3.5. Water contact angle

Water contact angles were measured on dried membranes by a contact angle goniometer (JY-82B, Chengde Dingsheng Testing Machine Co. Ltd. China) equipped with a video capture. A piece of membrane was attached on a glass slide and mounted on the goniometer. De-ionized water (30 μL) was dropped onto the membranes surface at room temperature for contact angle measurements and the contact angle was measured after 10 s. At last each reported reliable value was the average of five measurements, and the measurement error was ±1°.

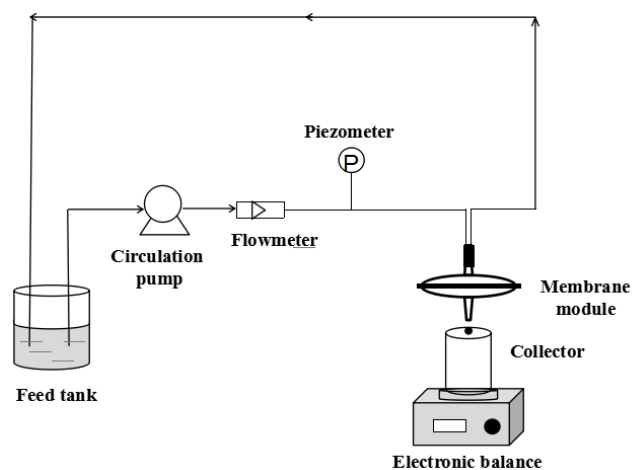


Fig. 3. The lab-made dead-end filtration system.

2.3.6. Performance evaluation

To investigate the stability of the modified PTFE membranes, the modified membranes were tested by soaking in a different solution, such as ethanol, 0.1 mol·L⁻¹ HCl solution, 0.1 mol·L⁻¹ NaOH solution, saturated NaHCO₃ solution, and measured 1~12 h after contact angle and pure water flux, respectively. The modified membranes were continuously washed by deionized water and then measured the water contact angle.

2.3.7. Membrane fouling

The anti-fouling tests of the modified PTFE flat membranes, the treated membrane was immersed into 100 mL of BSA solution (0.2 g/L, pH = 7.4) and shaken at 25°C for 24 h. The amount of adsorbed BSA was calculated from the concentrations of BSA in solution before and after BSA adsorption. After ultrasonic cleaning, the membrane continues to be remeasured.

The BSA adsorption was calculated by the following equation of membranes (g/m²):

$$\Gamma = \frac{(C_0 - C) \cdot V}{A} \quad (2)$$

where Γ is the BSA adsorption (g/m²), C_0 is initial concentration of the BSA solution (g/L), C is measured concentration of the BSA solution (g/L), and V is volume of the BSA solution (L), A is the effective surface area of the PTFE flat membranes (m²).

3. Results and discussion

3.1. Surface chemical elements analysis of modified membrane

The chemical elements of the membrane surfaces were also revealed by XPS spectroscopy. As shown in Fig. 4, the originated membrane only shows peaks of C1s and F1s at 284.75 meV and 689.29 meV, respectively. Peaks of O 1s and N 1s are observed after crosslinking of PAA and Sac-100. Besides, new peaks of Na 1s at 1079.48 eV were observed after soaking saturated NaHCO₃ solution. The Na element is derived from hydrolysis product of PAANA. These results show that the PTFE flat membranes are coated by acrylic acid water-absorbent resin successfully. Finally, elemental compositions of different PTFE flat membranes are shown in Table 1, which is consistent with the XPS spectra results above.

3.2. Surface chemical composition analysis of modified membrane

To understand whether the new chemical compound was coated on the surface of PTFE flat membranes, the

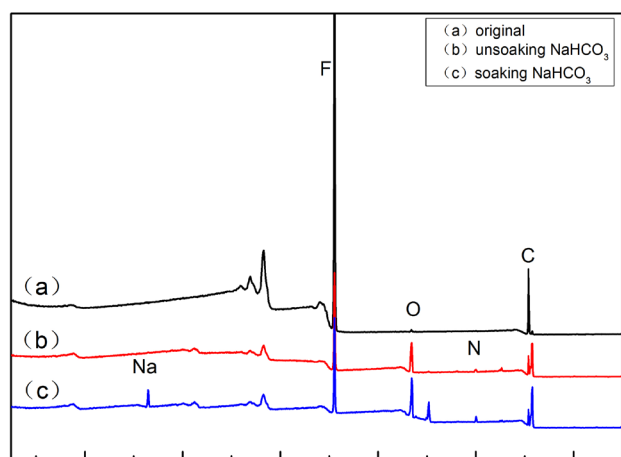


Fig. 4. XPS spectra of porous PTFE flat membrane (a) original; (b) unsoaking saturated NaHCO₃ solution modified membrane; (c) soaking saturated NaHCO₃ solution modified membrane.

chemical groups of organic materials, original and modified PTFE flat membranes from the ATR-FTIR analysis are shown in Fig. 5. The original and modified PTFE shows two characteristic peaks at 1149 cm⁻¹ and 1205 cm⁻¹, respectively, which are corresponding to the stretching vibration of -CF₂ groups [21,23]. The Sac-100, PAA and modified membranes have a similar sharp peaks at 1737 cm⁻¹, which correspond to the stretching vibration of C=O groups [24]. The PAA and modified membranes have a sharp peak at 1737 cm⁻¹ and wide peaks at 3291 cm⁻¹, which correspond to the stretching vibration of -COOH group [24]. It can be seen that the stretching vibration peak of -COOH group has decreased by soaking saturated NaHCO₃ solution, in addition, two fresh characteristic peaks can be discovered at 1571 cm⁻¹ and 1400 cm⁻¹ featuring the stretching vibration of -COO⁻ group [25], which indicates that the water-absorbent resin is successfully coated on the PTFE membranes surface, so the modified membranes was hydrophilic by blending cross-linking reaction.

Table 1
Elemental composition of different PTFE flat membrane as determined by XPS

Membrane	Composition(%)				
	C	F	O	N	Na
PTFE	33.17	66.83	/	/	/
Unsoaking NaHCO ₃ of modified membrane	55.72	25.97	15.18	2.71	/
Soaking NaHCO ₃ of modified membrane	52.94	22.9	17.53	3.57	3.06

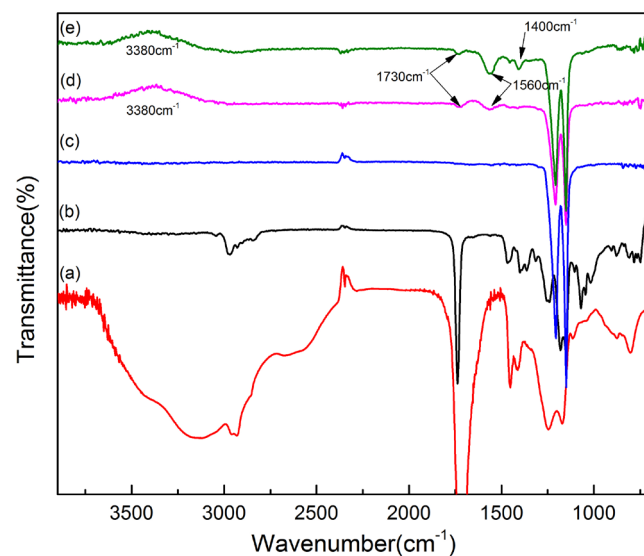


Fig. 5. FAIR-ATR spectra of porous PTFE flat membrane (a) pure PAA (b) pure aziridine Sac-100 (c) original (d) unsoaking saturated NaHCO₃ solution modified membrane (e) soaking saturated NaHCO₃ solution modified membrane.

3.3. Morphology and cross section chemical element of original and modified membranes

In order to understand the surface changes on the structure of micropore PTFE flat membranes, the SEM was used to discover the surface morphology of original and modified membranes.

Fig. 6a shows the typical SEM picture of original PTFE flat membranes that it was composed of nodes and fibrils. It can be found that many micro-pores on the surface of the membranes. Because PTFE flat membranes were formed by biaxial stretching, they have a large number of cracks in the fibrils surface. The illustration shows the water droplets of superhydrophobic surface, the surface WCA value is $135 \pm 1^\circ$. Through being treated with post-cross-link coating under the conditions of 0.4 wt% aziridine Sac-100, 1.0 wt% PAA and pH = 5, a layer of cross-link products have been uniformly wrapped around the fibrils and the node and looked smooth, membrane pore size did not change much, but the membrane surface hydrophilicity was significantly increased, the surface WCA was reduced to $52 \pm 1^\circ$ (as shown in Fig. 6b), being attributed to hydrophilicity of carboxyl and tertiary amine group provided by post-cross-link products; After saturated sodium bicarbonate soaking of modified membrane by post-cross-linking reaction, surface WCA was decreased to $22 \pm 1^\circ$ as shown in Fig. 6c.

Cross-linking reaction at low concentration of PAA system or high concentration of aziridine Sac-100 system, due to the degree of cross-linking was too large, which leads to cross-link blend products have been precipitated and adhered to the surface of the membrane. It can be seen in the micro-pore of the PTFE flat membranes has been completely blocked, however, due to the increase of surface -COOH group, after saturated sodium bicarbonate soaking that the surface WCA reduced to $7 \pm 1^\circ$ as shown in Fig. 6d; Cross-linking reaction at high concentrations of PAA or low concentration of aziridine Sac-100 system, due to the degree of cross-linking was too small, and only some fibrils and nodes have been covered with cross-link blend products, after saturated sodium bicarbonate soaking that the surface WCA reduced to $59 \pm 1^\circ$ as shown in Fig. 6e.

The cross-link blend products can be destroyed when under the condition of strong acid (pH = 1), it can be found that part of the fibrils surface was still very rough and have been wrapped by the cross-link blend products, the surface WCA reduced to $76 \pm 1^\circ$ as shown in Fig. 6f. However, when the condition was slightly acidic (pH = 6), it can be seen that part of the node has been wrapped by the cross-link blend products, the surface WCA reduced to $59 \pm 1^\circ$ as shown in Fig. 6g.

In our case, too much or too little of the cross-link blend products was not conducive to the hydrophilicity of the PTFE flat membrane, and the reaction conditions must be strictly controlled.

The modified membrane cross-section SEM and EDX scan images is shown in Fig. 7. The whole membrane is well modified by PAA and Sac-100, the Na, N and O element are uniformly distributed in the inner pores of the modified membrane, which enhances the wettability, water permeation flux as well as anti-fouling performance of the membrane.

3.4. Effects of surface modification condition on the hydrophilicity of membrane

Figs. 8a,b show the water flux of the modified membranes were increased first and then decreased and the surface water contact angle (WCA) of the modified membranes were rapidly decreased first and then slowly increased with the increase of PAA concentration when the reaction conditions have been controlled under 0.4 wt% aziridine Sac-100 and pH = 5, the membrane surface WCA was decreased with the increase of the membrane surface hydrophilic content group. Due to the aziridine Sac-100 is a small molecule organics and water-soluble material, so the modified membranes have not hydrophilicity by aziridine Sac-100 solution soaking. Aziridine Sac-100 is a high performance cross-linker for the carboxyl group, the possible reaction mechanism of low concentration of PAA and aziridine Sac-100 was carried out as shown in Scheme 1a. The aziridine Sac-100 and the three carboxyl groups from the same PAA chain were reacted. In experiment, cross-linking reaction at low concentration of PAA system, due to the degree of cross-linking was too large, leading to cross-link blend products have been precipitated and adhered to the surface of the membrane and the micro-pore of the PTFE flat membranes has been completely blocked, so that the water flux and the surface WCA were changed too small. With the increase of the concentration of PAA, the possible reaction mechanism PAA and aziridine Sac-100 was carried out as shown as Scheme 1b. A cross-linker molecule can be reacted with three carboxyl groups from two different chains, and the ring structure of the products can be wrapped around the PTFE fiber, leading to the water flux was increased. With the increase of the carboxyl groups, a cross-linker molecule can be reacted with three carboxyl groups from three different chains, the possible reaction mechanism PAA and aziridine Sac-100 was carried out as shown in Scheme 1c. The products were not firmly wrapped on the fibril, and it has been separated from the water soaking and washing, which leads to the water flux reduced and the surface WCA increased.

Figs. 9a,b show the water flux of the modified membranes were rapidly increased first and then slowly decreased and the water WCA of the modified membranes were gradually with an increase of aziridine Sac-100 concentration when the reaction conditions have been controlled under 2.0 wt% PAA and pH = 5. Due to the PAA is a water-soluble material, so the modified membranes have not hydrophilicity by PAA solution soaking, and the water flux and the surface WCA were not changed. The blending cross-linking reaction was drove with the aziridine Sac-100 appeared, and the water flux and the surface WCA were changed, the mechanism is the same as above.

Fig. 10a,b. shows the water flux of the modified membranes were decreased first and then rapidly increased and the water WCA of the modified membranes were increased first and then rapidly decreased of pH when the reaction conditions have been controlled under 2.0 wt% PAA and 0.4 wt% aziridine Sac-100. Due to the selection of the aziridine Sac-100 nitrogen atoms not connected with the suction electronic groups, three membered ring above the high density of electron cloud, so it is a none activity aziridine, it can be known that the none activity of the aziridine has been opened the

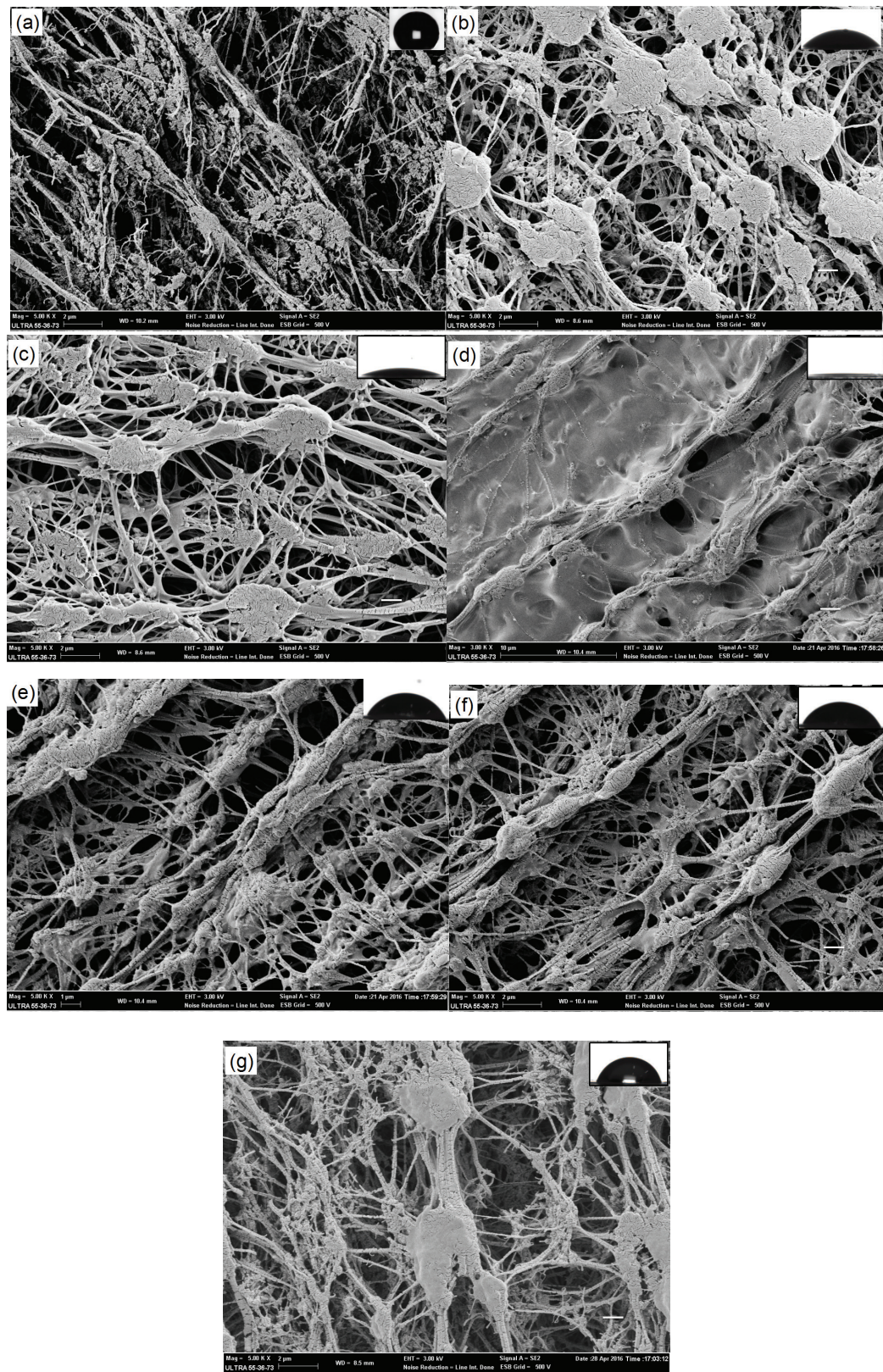


Fig. 6. SEM morphologies of porous PTFE flat membrane (a) original (b) unsoaking saturated NaHCO_3 solution modified membrane (c) soaking saturated NaHCO_3 solution modified membrane (d) the large degree of cross-linking (e) the small degree of cross-linking (f) strong acidic system and soaking saturated NaHCO_3 solution (0.4 wt% aziridine Sac-100, 2.0 wt% PAA and pH = 1) (g) weak acidic system and soaking saturated NaHCO_3 solution (0.4 wt% aziridine Sac-100, 2.0 wt% PAA and pH = 6).

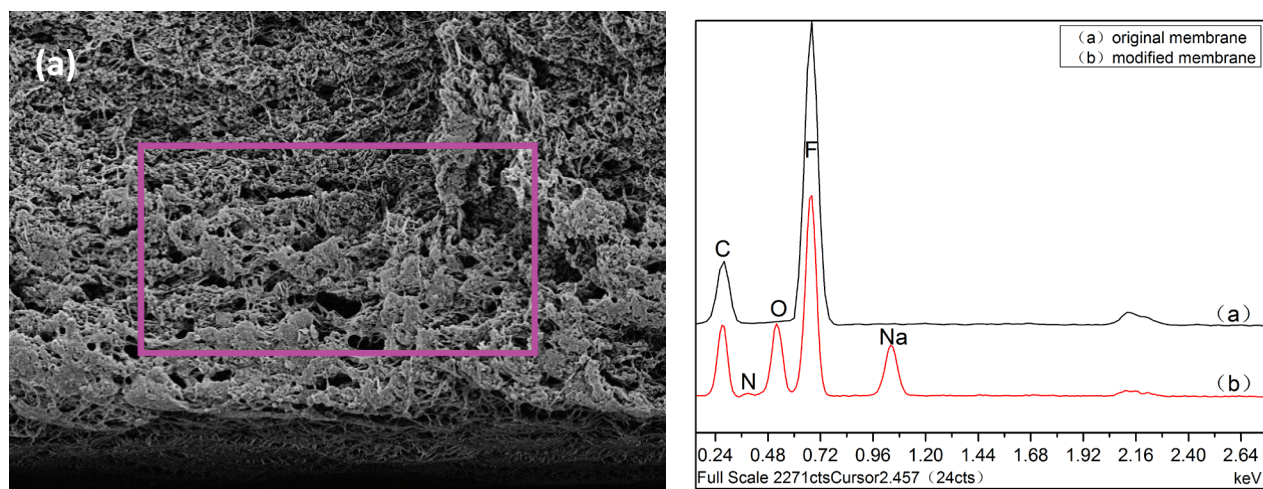


Fig. 7. (a) SEM, (b) EDX spectra of the cross section of modified PTFE flat membrane.

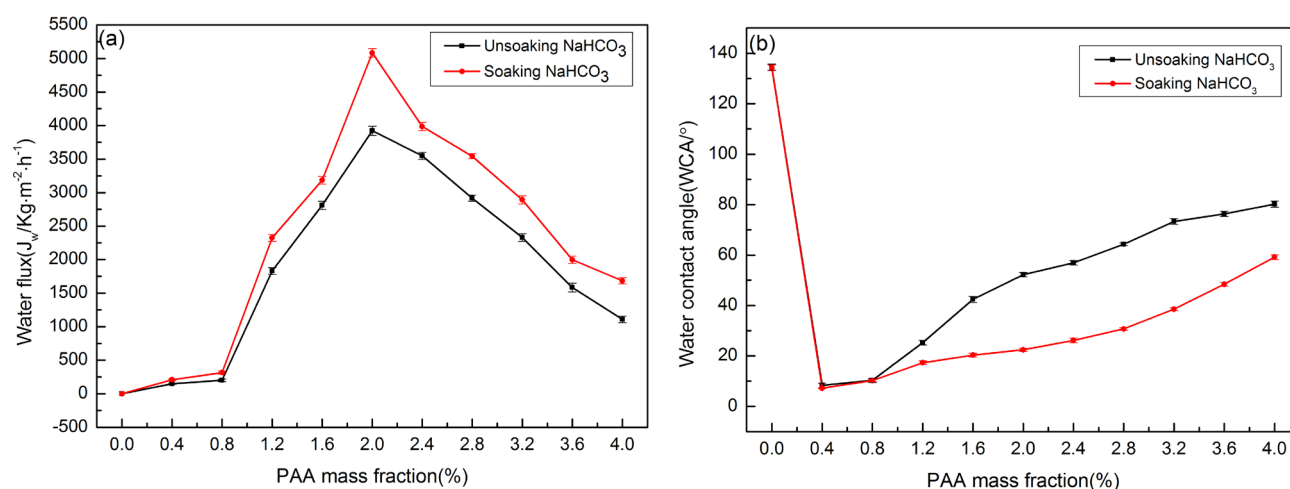


Fig. 8. Relationship between membrane hydrophilicity and concentration of PAA (pH = 5, 0.4 wt% aziridine Sac-100) (a) the water flux (b) the surface water contact angle.

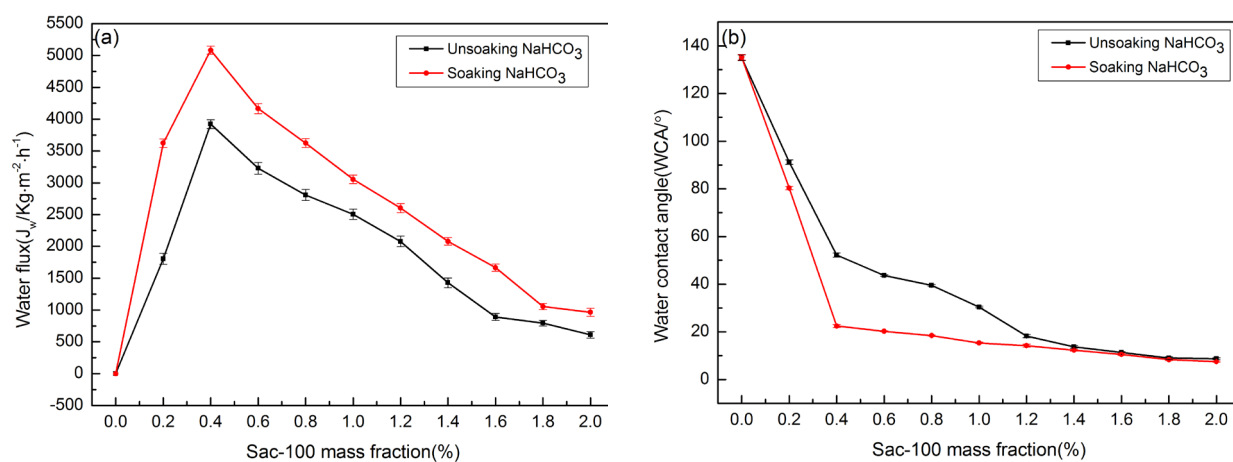


Fig. 9. Relationship between membrane hydrophilicity and concentration of Sac-100 (pH = 5, 2.0 wt% PAA) (a) the water flux (b) the surface water contact angle.

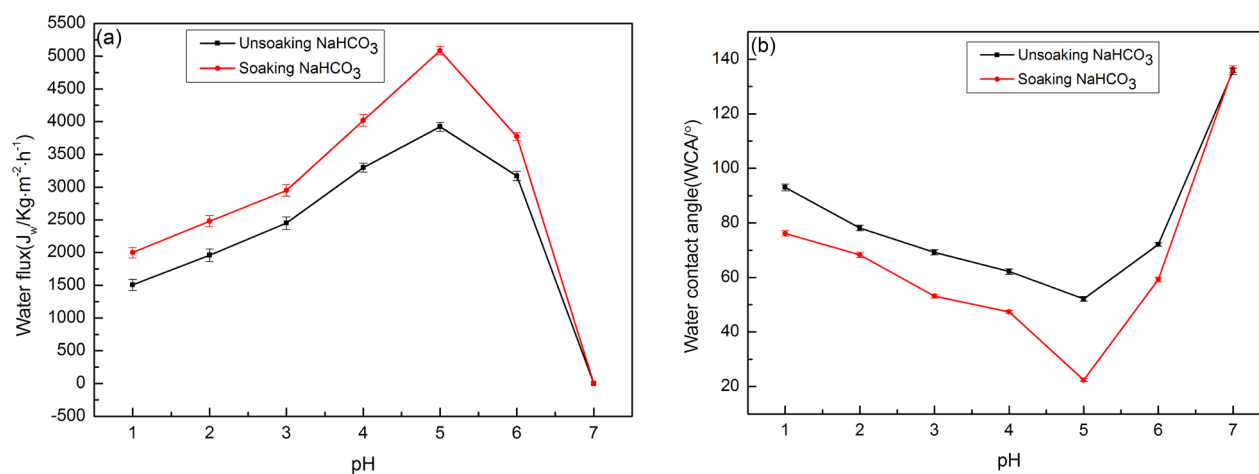


Fig. 10. Relationship between membrane hydrophilicity and concentration of pH (2.0 wt% PAA, 0.4 wt% aziridine Sac-100) (a) the water flux (b) the surface water contact angle.

ring must require proton acid or Lewis acid. Under acidic condition, the nitrogen atom was charged partial positive by the nitrogen atom of aziridine combined with proton acid or Lewis acid, and the electron density of three membered ring was reduced [26]. So that it can be easier to carry out a nucleophilic reaction, and the reaction was controlled by pH. Under $\text{pH} \geq 7$, the blending cross-linking reaction can not be carried out, under $\text{pH} < 7$, it can be easily cross-linked of aziridine Sac-100 and PAA. In order to control the reaction, the PAA solution was neutralized by adding ammonia. A large number of ester groups were observed from the structure of reaction products, it was reversible hydrolysis reaction under strong acidic condition. But it can be seen that a large amount of tertiary amine were contained from the product structure, due to the part of hydrogen ion and nitrogen combined to form ammonium under acidic condition, so the hydrolysis rate of the ester was reduced, and the hydrophilic of the modified membrane was saved.

The membrane was modified by blending cross-linking reaction, and then it was soaked in saturated sodium bicarbonate. It can be found that the water flux has been increased, and the surface WCA has been decreased, as shown in Figs. 8–10. The reason is that the low molecular weight of PAA was used, and the carboxyl groups can be transformed into carboxyl ions under weak base condition. Due to the electronic effect of neighbouring groups, it only can be transformed some carboxyl groups into carboxylic ions, which the modified membrane contained carboxyl groups and carboxylic ions, a single system of polyacrylic acid was converted into a water-absorbent resin system of polyacrylic acid. So the modified membrane surface WCA was decreased and the water flux was increased.

3.5. Stability evaluation of modified membranes

Stability of hydrophilicity, it is an important role in the separation performance, which is studied by measuring the WCA and water flux variation after the treating process. Fig. 11a shows the water flux of the modified membranes was decreased with an increase of time when soaked in 0.1 mol·L⁻¹ NaOH solution, and it can be found that the sur-

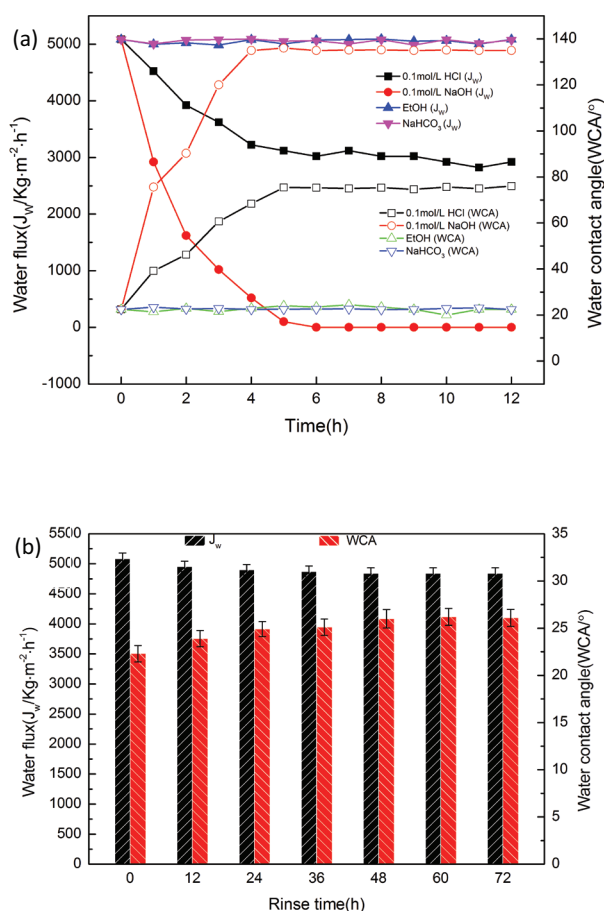


Fig. 11. The stability of modified membrane with different solution treatment (a) chemical stability, (b) physical stability.

face of WCA has been gradually increased, finally, the water flux and the surface WCA was no different compared with the original membrane. The reason is that the ester groups ($-\text{COO}-$) of cross-link blend products have been irreversible hydrolysis reaction under strong base condition, lead-

ing to the hydrophilic material fell off from the surface of the membrane, therefore the hydrophilicity of modified membranes were reduced. For the modified membrane was soaked in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl solution, it can be observed that the water flux has been decreased and the surface WCA has been increased with an increase time, but the hydrophilicity of modified membranes were not completely lost. Because of the $-\text{COO}^-$ groups have been reversible hydrolysis reaction under slightly acidic condition, so some hydrophilic material still was wrapped in the fibrils surface, and has hydrophilic. When the modified membranes were soaked in saturated NaHCO_3 solution or ethanol, it can be seen the flux and the surface WCA that has not changed, due to the $-\text{COO}^-$ groups were unable destroyed under weak alkali solution, and the products were not dissolved. Hence, the modified membranes can be applied to none strong base wastewater processing system.

Mechanical stability of the acrylic acid water-absorbent resin layer on the PTFE flat membranes is also important. In order to identify the mechanical stability of the layer materials, the durability of surface hydrophilic layer has been studied by pure water filtration process for 72 h under the pressure of 0.1 MPa. The results are shown in Fig. 11b. The contact angle of modified membranes increases with the increase of wash time first and tends to be stable after washing for 48 h. The water flux of modified membranes decreases with the increase of wash time first and tends to be stable after washing for 48 h. These results indicate that the hydrophilic layer materials on the membrane show superior stability.

3.6. Zeta potential and fouling of original and modified membranes

Zeta potentials and BSA adsorption of the different PTFE flat membranes were measured at 25°C . As revealed in Fig. 12a, in the acidic medium, the modified membrane is easy to adsorb hydrogen ions, so that the Zeta potential of the modified membrane is lower than that of the original membrane. In the alkaline medium, the membrane surface contains a large amount of carboxyl anion, due to the common ion effect, the membrane is not easy to adsorb the hydroxide ions, and then the Zeta potential of the modified membrane is higher than that of the original membrane. Fig. 12b shows the results of static BSA adsorption on the membrane surface at different of time under $\text{pH} = 7.4$. It can be found that the original membrane had a higher amount of BSA adsorption than the modified membrane. Due to the hydrophobic surface of the PTFE membrane has a large number of adsorption sites, which leads to greater amount of BSA adsorption, and the surface of modified membrane was coated with hydrophilic substance, thus the BSA molecules contact with the membrane was hindered, which leads to smaller amount of BSA adsorption; with the adsorption of the membrane surface adsorption sites less until disappeared, the BSA molecules were not easily adsorbed, which leads to the adsorption amount tends to be stable. The membrane of adsorbed BSA has been treated by ultrasonic cleaning, and then immersing in new BSA solution. It can be found that the BSA molecule deposited on the surface with hydrophilic groups is eas-

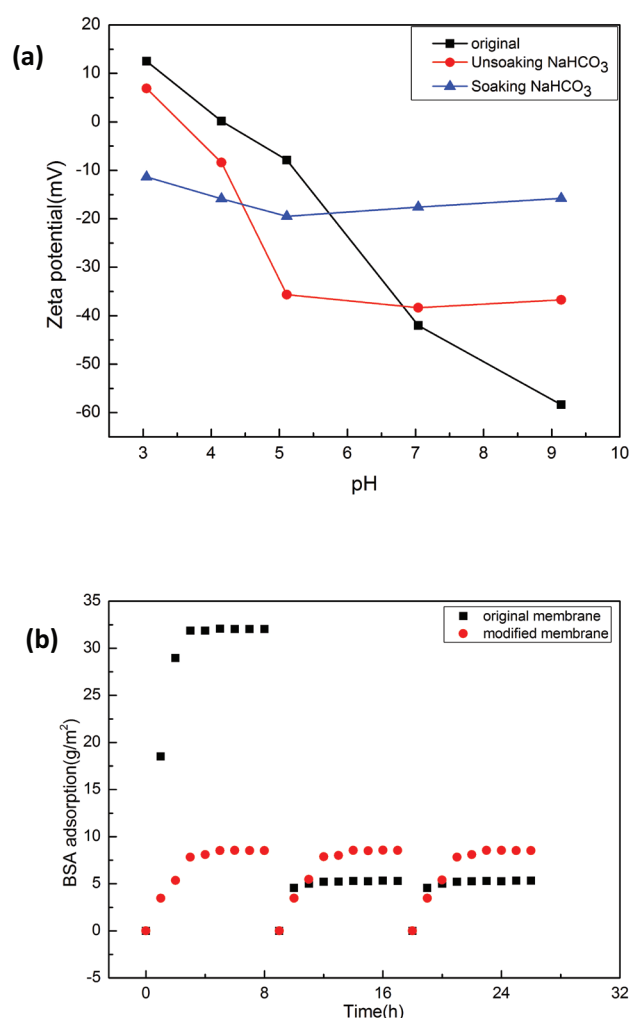


Fig. 12. (a) Zeta potentials of original and modified flat membranes as function of pH value (b) The BSA adsorption of PTFE membrane ($\text{pH} = 7.4$; BSA concentration: $1 \text{ g}/\text{L}$).

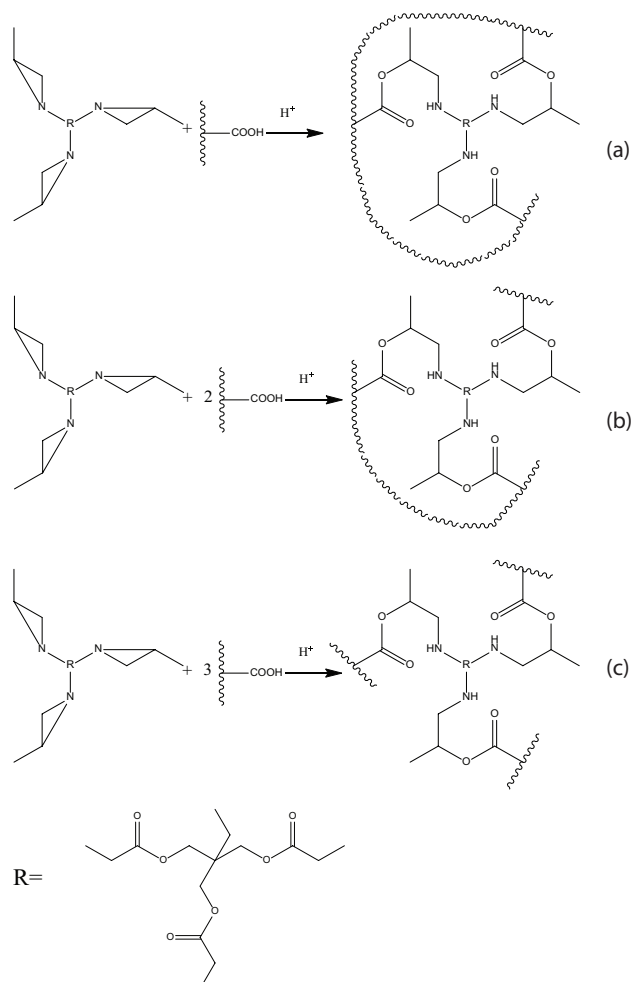
ier to be removed owing to the faintish interaction [27]. In summary, the hydrophilicity of the composite membrane fouling is better than PTFE flat membrane.

4. Conclusion

The porous hydrophobic PTFE flat membranes surface was modified by blending cross-linking reaction, and the different factors of the modification on the hydrophilicity of PTFE flat membrane were explored. The following conclusions were obtained from the experimental results:

The contact angle of PTFE decreased from the untreated $135 \pm 1.32^\circ$ to $22.4 \pm 1.22^\circ$ treated byrylic acid water-absorbent resin, the modified membranes can have a good hydrophilicity.

The hydrophilic groups such as $-\text{COOH}$ group and $-\text{COO}^-$ group were introduced as demonstrated by FTIR spectra, which leads to the membrane had a good anti-fouling properties.



Scheme 1. The possible reaction mechanism of PAA and aziridine Sac-100.

According to the XPS result, peaks of O 1s and N 1s are observed after crosslinking of PAA and Sac-100, besides, new peaks of Na1s at 1079.48 eV were observed after soaking saturated NaHCO_3 solution.

The XPS, FIRT, SEM and EDX results suggested that the acrylic acid water-absorbent resins were distributed the inner and outer surfaces of PTFE flat membrane, so they have a high water flux.

Acknowledgments

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