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Enhancement of hydrophilicity and anti-fouling property of polysulfone membrane using amphiphilic nanocellulose as hydrophilic modifier

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Abstract. In the present work, we present a new effective hydrophilicity modifier for polysulfone (PSf) membrane. Firstly, amphiphilic nanocellulose (ANC) with different substitution degrees (SD) was synthesized by esterification reaction with nanocellulose (NC) and dodecyl succinic anhydride (DDSA). The SD and morphology of ANC were characterized by titration method and transmission electron microscopy (TEM). Then, the polysulfone (PSf)/ANC blend membranes were prepared via an immersion phase inversion method. The influence of SD on the morphology, structure and performances of PSf/ANC blend membrane were carefully investigated by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), mechanical property test, contact angle measuring instrument and filtration experiment. The results showed that the mechanical property, hydrophilicity and anti-fouling property of all the PSf/ANC blend membranes were higher than those of pure PSf membrane and PSf/NC membrane, and the membrane properties were increased with the increasing of SD values. As ANC-4 has the highest SD value, PSf/ANC-4 membrane exhibited the optimal membrane properties. In conclusion, the prepared ANC can be used as an additive to improve the hydrophilicity and anti-fouling properties of polysulfone (PSf) membrane.

Keywords: amphiphilic nanocellulose; Polysulfone (PSf) membrane; hydrophilic modification; anti-fouling; porous materials

1. Introduction

Polysulfone (PSf) is one of the most extensively used polymers for membrane separations, owing to its excellent properties, such as superior chemical stability, thermal stability, aging resistance, mechanical robustness and so on (Tran *et al*. 2012, Arash *et al*. 2015, Obaid *et al*. 2015). The excellent mechanical strength, good chemical and thermal stability of PSf membrane make it be widely applied in separation fields (Zhang *et al*. 2013; Ingole *et al*. 2016, Lu *et al*. 2017). However, due to the hydrophobic nature of PSf membrane, conventional PSf membranes often suffer from serious membrane fouling, resulting in the membrane having a low permeation flux, short lifetimes, and reduced self-cleaning effect during practical prolonged applications, which is considered as one of the serious problems for its application (Wu *et al*. 2017). Thus, it is very necessary to make a hydrophilic modification to improve the hydrophilicity and anti-fouling property of PSf membrane (Zhao *et al*. 2014a).

Various methods have been used to improve the hydrophilicity and anti-fouling property of PSf membrane (Zhao *et al*. 2014b). Among these methods, coating (Ohl *et al*. 2009), grafting (Higuchi *et al*. 2010, Mauter *et al*. 2011, Wang *et al*. 2014) and blending (Fan *et al*. 2008) are the most common methods. However, the coating and grafting methods are only limited to the surface modification, while the hydrophobicity of porous support layer is not improved very well. Blending metallic or non-metallic nanoparticles into the PSf matrices is deemed to be a simple and effective method to solve the above problem (Mahmoudi *et al*. 2015, Khosroyar *et al*. 2018). Many kinds of nanoparticles have been reported to effectively improve the hydrophilicity of PSf membrane, such as nano-sized Ag (Ng *et al*. 2013), SiO_2 (Habibi and Nematollahzadeh 2016), Al_2O_3 (Garcia-Ivars *et al*. 2014), TiO_2 (Pereira *et al*. 2014, Singh *et al*. 2018), Fe_2O_3 (Huang *et al*. 2010), ZnO (Ng *et al*. 2013), zeolite (Dong *et al*, 2015) and carbon nanotubes (Guo *et al*. 2015, Sianipar *et al*. 2016).

Nanocellulose (NC) is a kind of natural and biodegradable nanomaterial extracted from cellulose (Carpenter *et al*. 2015). As its large specific surface area, good biocompatibility and excellent hydrophilicity, NC can be used as the hydrophilic and anti-fouling modifier for PSf membrane (Yang *et al*. 2016). In our previous work, we found that the addition of NC can improve the hydrophilicity and anti-fouling property of PSf membrane. However, the excellent hydrophilicity of NC made it have poor compatibility with hydrophobic PSf matrix, which restricted its hydrophilic modification effect (Kaewtatip and Thongmee 2012, Sreenivasan *et al*. 2012). Amphiphilic cellulose (AC) is a kind of cellulose derivative containing both hydrophilic segments and hydrophobic segments (Cao and Li 2003). When AC is blending with non-polar polymers, the hydrophobic segments are anchored to the

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membrane skeleton by chain entanglement, while the hydrophilic ones are forced to segregate on the pore walls to form an anti-fouling layer during the phase inversion process (Wei *et al*. 2014). Therefore, it is necessary to prepare amphiphilic nanocellulose (ANC) to improve the compatibility of NC with PSf matrix (Wei *et al*. 2008, Wang *et al*. 2012).

Dodecyl succinic anhydride (DDSA) is a kind of safe functional polymer, and the polysaccharides modified by DDSA have amphiphilic property (Gibril *et al*. 2012). Despite the wide-spread use of DDSA in starch, as far as we know, there is no study on utilizing DDSA to prepare amphiphilic nanocellulose (ANC) and using ANC as a hydrophilic modifier for PSf membrane. The study on the hydrophilic modification of polysulfone membrane by amphiphilic nanocelluloses will be of great significance for better utilization both PSf membrane and NC. Therefore, in the present study, ANC was prepared for the first time by the esterification reaction between NC and DDSA with the N,N-dicyclohexyl carbodimide (DDC) and 4-dimethylamine pyridine (DMAP) used as coupling agent and catalyst in dimethyl sulfoxide (DMSO) solution. In order to fully research whether ANC can be used as an effective hydrophilic modifier for PSf membrane, the ANC with different SD was prepared and introduced to the PSf casting solution to prepare PSf/ANC membranes through the phase inversion process. In addition, the effects of SD on the morphology and performances of PSf/ANC blend membrane were carefully investigated. Bovine serum albumin (BSA) was used as a model protein to determine the solute rejection and anti-fouling performance of the prepared membranes.

2. Experimental

2.1 Materials

Nanocellulose (NC, average diameter 10.48 nm) extracted from corn husks by TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl) oxidation method was supplied by our own library (Yang *et al*.2016). Polysulfone (PSf, Udel P-1700 grade) purchased from Solvay Advanced Polymer Co., USA, was vacuum-dried prior to use. 12-ethylene succinic anhydride (DDSA, ≥99.9%), N,N-dicyclohexyl carbodimide (DDC, ≥95%), 4-dimethylamine pyridine (DMAP, ≥98%), N-methyl-2-pyrrolidone (NMP, ≥99.5%), polyvinylpyrrolidone (PVP, K30), acetone (CH3COCH3, ≥99.5%), p-toluene sulfonic acid ($C_7H_8O_3S$, ≥99%), ethanol (C_2H_5OH, ≥95%), acetic acid (CH_3COOH, ≥99.5%), hydrochloric acid (HCl, ≥36%), sodium hydroxide (NaOH, ≥96%) and silver nitrate ($AgNO_3$, ≥99.8%) were supplied by Sinopharm Chemical Co., Ltd,China. Dimethyl sulfoxide (DMSO, ≥99%) and bovine serum albumin (BSA, Mw~68KDa) were obtained from Aladdin chemical reagent Co., Ltd. All the chemicals were used as received without further purification.

2.2 Preparation of amphiphilic nanocellulose (ANC)

ANC was prepared as follows. 0.33g NC was dissolved in 10 mL DMSO solution, followed by constantly stirring at 60℃ for 30 min. Then, a certain amount of DDSA was slowly added dropwise to the above solution (mass ratio of DDSA to NC was 2:1, 4:1, 6:1, 8:1, 10:1 and 12:1, respectively). After 10 min constant stirring, 0.038 g DMAP and 0.34 g DCC were added to the solution. The above mixture reacted for 1 h at 80℃. Then the ANC was prepared after centrifuged washing at 5000 rpm for 10 min with acetone, ethanol, acetic and distilled water, repeatedly. The prepared ANC was named as ANC-2, ANC-4, ANC-6, ANC-8, ANC-10 and ANC-12, according to the mass ratio of DDSA to NC.

2.3 Preparation of PSf/ANC blend membranes

The PSf/ANC blend membranes were prepared by an immersion phase inversion process (Yang *et al*. 2016). 2 wt% ANC was homogeneously dispersed in NMP solvent at 15000 rpm for 10 min using a digital ultra-turrax. Afterwards, 20 wt% dried PSf and 6 wt% PVP were added to the mixture and stirred at 300 rpm for 12 h at 60℃. Then, the casting solution was coated uniformly on clean glass plates using a casting knife. After 20 s of exposure to air to evaporate the solvent, the wet films along with the glass plates were immersed in a coagulation bath consisted of deionized water. The prepared membranes were kept in deionized water for more than 12 h to remove residual solvent before test. The PSf/ANC blend membranes were noted PSf/ANC-2, PSf/ANC-4, PSf/ANC-6, PSf/ANC-8, PSf/ANC-10 and PSf/ANC-12, in corresponding with the kind of ANC used.

The control PSf and PSf/NC membranes were made by the same process as PSf/ANC blend membrane but without ANC or with the same content of NC in the casting solution.

2.4 Characterization of ANC

The substitution degree (SD) of ANC was determined using a titration method (Gibril *et al*. 2012). Firstly, the moisture content of each sample was exactly measured. Then, 1 g ANC sample and 10 ml 95 wt% ethanol solution were added to a 50 mL beaker followed by constant stirring for 10 min. After that, 10 mL 2.5 mol/L HCL-ethanol solution was added to the mixture. After 30 min stirring, the slurry was centrifuged at 5000 rpm for 10 min. Then, the supernatant was removed and centrifuged repeatedly with 95 wt% ethanol solution until no chlorine ion existed (detected by $AgNO_3$). Afterwards, the sample was moved to a 100 mL beaker and 70 mL distilled water was added to the beaker. After boiling for 30 min, 5 drops of phenolphthalein indicator were added to the above solution. Finally, the mixture was titrated with 0.1 mol/L standard sodium hydroxide solution. Meanwhile, the titrated experiment of NC was also tested as a blank sample. The SD of ANC was determined by Eq. (1)

$$\mathrm{SD} = \frac{162W}{100 \times 266 - (266 - 1)W} \quad (1)$$

where W is the mass fraction of DDSA; 266 is the

molecular weight of DDSA; 162 is the molecular weight of anhydrous glucose unit.

The mass fraction of DDSA (W) was calculated by the Eq. (2)

$$W = \left(\frac{V_2}{m_2} - \frac{V_1}{m_1} \right) \times c \times 10^{-3} \times 266 \times 100\% \quad (2)$$

where V_1 (mL) is the titrated volume of standard sodium hydroxide solution for NC; V_2 (mL) is the titrated volume of standard sodium hydroxide solution for ANC; m_1 (g) is the dry weight for NC; m_2 (g) is the dry weight for ANC; c (mol/L) is the concentration of standard sodium hydroxide solution.

The morphology of ANC was investigated by TEM using a JEM-2100 TEM (JEOL Ltd, Tokyo, Japan) device. One drop of 0.01 wt% ANC aqueous suspension was deposited onto a glow-discharged carbon-coated Cu grid. After the sample was dried at room temperature, the specimen was negatively stained with 2 wt% uranyl acetate solution and dried under ambient condition before the test.

2.5 Characterization of PSf/ANC blend membranes

The Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 8700 FTIR spectrometer (Thermo Fisher Scientific Co., Ltd, Waltham, MA, USA) in the range of 650-4000 cm^{-1} with a step of 0.5 cm^{-1} in the ATR mode.

The morphology and structure of the prepared membranes were examined using a scanning electron microscope (SEM) (TM300, HITACHI, Japan) with an accelerating voltage of 10 kV. The membrane samples were dried overnight in a vacuum over at 40℃ prior to analysis. To examine the cross sections, the membranes were frozen in liquid nitrogen and fractured. They were mounted on sample stages using double-side conductive tape and were sputter-coated with gold before the analysis.

The mechanical properties of prepared membranes were measured according to GB/T3923.1 by a multi-function fabric strength machine (HD026-510, Nantong Hongda Experiment Instruments Co., Ltd).

The contact angle of water on the membrane surface was measured to characterize the membrane hydrophilicity using a JY-82 contact angle measuring instrument at room temperature. For each membrane sample the contact angle was measured five times, and the reported data of the contact angle represent an average of the measurements.

2.6 Filtration performance of PSf/ANC blend membrane

The filtration performance of prepared membranes was measured by a dead-end filtration apparatus. The membrane area for filtration was 28.26 cm^2. Before filtration experiments, the membranes were first compacted with deionized water at 0.1 MPa for 300 min until a steady state of permeation was reached. Then the pure water flux was determined at 0.1 MPa for 1 h and calculated using Eq. (3) (Kebria *et al*. 2015)

$$J_w = \frac{Q}{A \times \Delta t} \quad (3)$$

where J_w (L/m^2h) is the pure water flux, Q (L) is the volume of the permeated solution, A (m^2) is the effective membrane area for filtration, and Δt (h) is the operation time.

In this study, the bovine serum albumin (BSA) was used as a model protein, and the separation performance of PSf/ANC membranes was tested with an initial feed concentration of 500 mg/L BSA solution using deionized water as solvent. The BSA rejection was a cumulated rejection rate, which were performed with each membrane under a transmembrane pressure of 0.1 MPa for 1 hour. Then, the permeate solution was collected and the BSA rejection was calculated by Eq. (4) (Kebria *et al*. 2015)

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (4)$$

where C_f and C_p represented the BSA concentrations in the initial feed and the permeate solutions after 1 hour of filtration, respectively. The BSA concentration in the solutions was determined with a UV-vis spectrophotometer (Lambda35, PerkinElmer, America) at a wavelength of 278 nm.

After protein ultrafiltration, the membrane was cleaned with deionized water for 10 min in an ultrasonic bath and then the pure water flux (J_{W2}) was measured again. To evaluate the anti-fouling property of the prepared membranes, the flux recovery ratio (FRR) was calculated using Eq. (5) (Yang *et al*. 2016; Eren *et al*. 2015)

$$FRR = \left(\frac{J_{w2}}{J_{w1}} \right) \times 100\% \quad (5)$$

where J_{W1} is the pure water flux of initial membrane and J_{W2} is the pure water flux of cleaned membrane after BSA rejection experiments.

3. Results and discussion

3.1 Substitution degrees (SD) and morphology of ANC

Amphiphilic nanocellulose (ANC) was synthesized by esterification in DMSO solution using DDSA, DDC, and DMAP as modifier, coupling agent, and catalyst, respectively. The synthesis mechanism schematic is exhibited in Fig.1. During the esterification process, the anhydride ring of DDSA was opened, which produced an ester group and a carboxyl group. The carboxyl group was combined with the hydroxyl group of NC, which formed a cellulose derivative, containing both hydrophilic segment and hydrophobic segment.

The relationship between SD and mass ratio of DDSA to NC is shown in Fig.2. At first, the SD increases from 0.0062 to 0.096 with the increasing of the mass ratio. However, when the mass ratio of DDSA to NC is more than 4:1, the SD begins to decrease and gradually become stable.

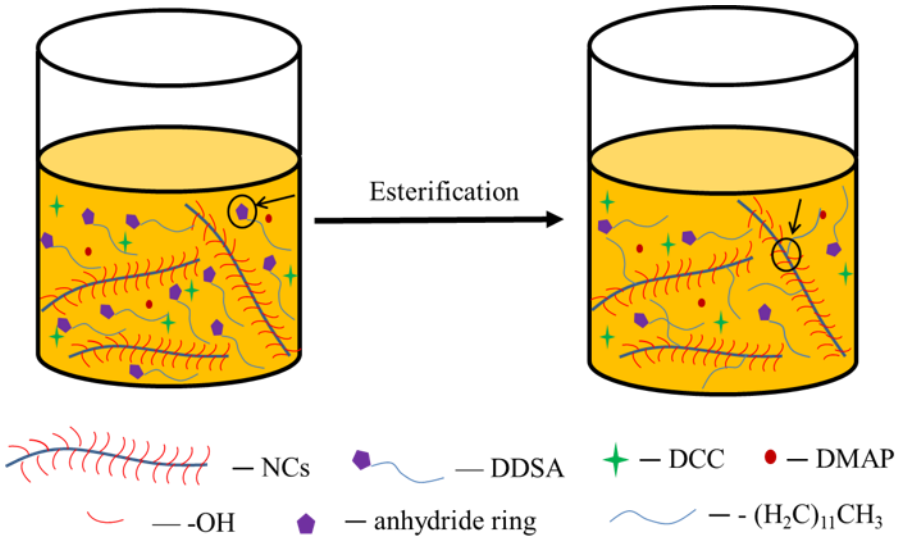

Fig. 1 Schematic diagram of ANC synthesis mechanism

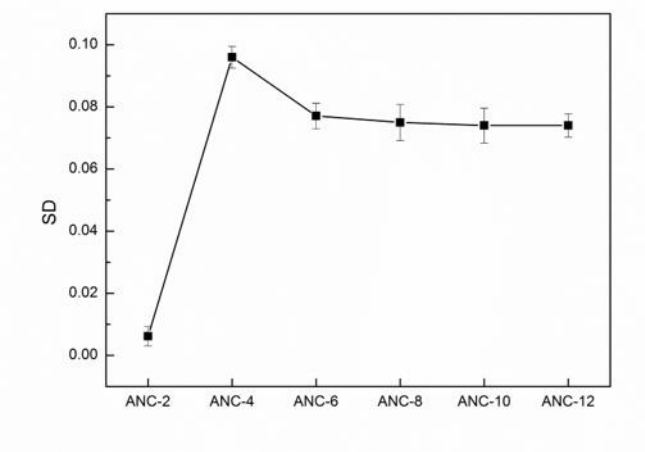

Fig. 2 Relationship between SD and mass ratio of DDSA to NC

This might be due to that, at lower dosages, DDSA has good solubility in DMSO solution, which facilitate its reaction with the active hydroxyl groups on the NC surface. However, at higher dosages, the large steric hindrance of DDSA reduces the number of opening rings, which affects the esterification efficiency between DDSA and NC, resulting in the decrease of SD.

The morphology changes of NC and ANC were investigated by TEM. Fig.3 shows the TEM images of NC, ANC-2 and ANC-4. The three samples exhibit interconnected webs with slender nanofibrils. After grafted the flexible DDSA long-chain groups on the surface, the boundary of ANC becomes blurred. The boundary of ANC-4 is more obscure than that of ANC-2, as it has a higher SD. In addition, the average diameters of the samples were determined from a minimum of 100 measurements by TEM software. According to the measurements data, the average diameter of NC, ANC-2, and ANC-4 are 22.53±1.64 nm, 40.87±3.75 nm, and 51.98±5.31 nm, respectively. Compared with NC, the average diameters of ANC-2 and ANC-4 are increased obviously, due to the grafting of DDSA long-chain groups and DMSO swelling. Moreover, because of the higher SD, the average diameter of ANC-4 is larger than that of ANC-2.

3.2 Characterization of PSf/ANC blend membranes

FTIR spectra of the prepared membranes are plotted in Fig.4. The presence of the absorption peaks at 1292 cm^{-1} and 1150 cm^{-1} corresponding to the symmetric stretching vibration of O=S=O group in the three samples (Eren *et al*. 2015), indicate that the main structure of polysulfone is not changed. The intensity of the wide peak at 3419 cm^{-1} corresponding to the stretching vibration of -OH group (Sun *et al* .2005), appears in the spectra of PSf/NC membrane and PSf/ANC membrane, which doesn't appear in pure PSf membrane, exhibiting that NC and ANC are added to the blend membranes. In addition, compared with pure PSf membrane, the peaks at 1505 cm^{-1} and 1586 cm^{-1} originating from the stretching vibration of -C=C- and -C-C- become stronger and sharper (Zhao *et al*. 2011). This is caused by the superposition of C=C and C-C bonds in both cellulose and polysulfone, which also proved the existence of NC and ANC in the PSf blend membranes. The above two bonds also exist in the molecular structure of DDSA. However, due to the low SD of ANC, the number of DDSA grafted on the surface of ANC is very small. Therefore, there are no obvious differences in the intensity of the corresponding absorption peaks between the spectra of PSf/NC and PSf/ANC blend membranes. The small absorption peak appears at 1700 cm^{-1} associated with the carbonyl stretching vibration in the spectrum of PSf/NC blend membrane, which attributes to the fact that NC used in this experiment was obtained by TEMPO oxidation method, and part of hydroxyl group on the surface of NC was oxidized to carboxyl group during the TEMPO oxidation process. However, the carbonyl absorption peak shifts to 1724 cm^{-1} and becomes sharper in the spectrum of PSf/ANC blend membrane, mainly due to the overlapping of the carboxyl group vibration peak formed by TEMPO

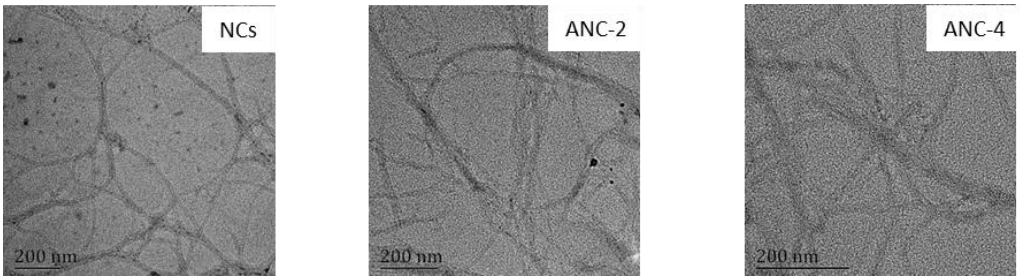

Fig. 3 TEM images of NC, ANC-2(SD=0.0062), and ANC-4(SD=0.096)

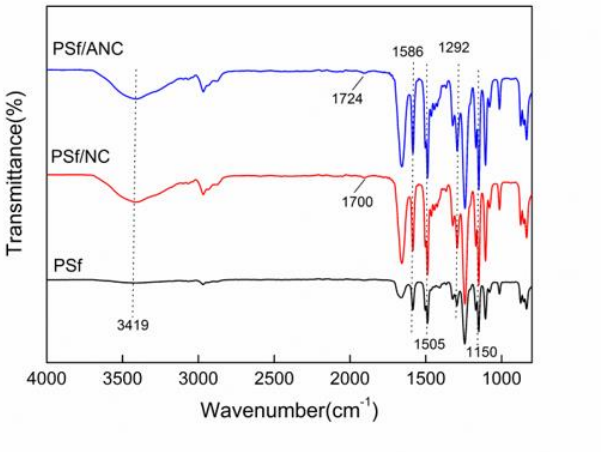

Fig. 4 FTIR spectra of PSf membrane, PSf/NC membrane and PSf/ANC membrane

Table 1 Mechanical properties of PSf, PSf/NC and PSf/ANC membranes

Membranes	Break strength (MPa)	Enlongation at break (%)	Young's modulus (MPa)
PSf	1.75±0.02	7.71.±0.21	23.16±0.26
PSf/NC	1.82±0.01	8.97±0.32	20.34±0.22
PSf/ANC-2	1.97±0.02	13.05±0.34	15.13±0.30
PSf/ANC-4	2.27±0.03	14.21±0.26	14.60±0.19
PSf/ANC-6	2.04±0.02	14.05±0.39	15.91±0.37
PSf/ANC-8	1.98±0.01	10.97±0.41	18.29±0.24
PSf/ANC-10	1.97±0.03	10.45±0.22	18.90±0.27
PSf/ANC-12	1.97±0.02	10.27±0.36	19.20±0.35

oxidation process and the ester group vibration peak formed by the esterification reaction of DDSA and NC, which confirms the presence of ANC in the PSf/ANC blend membrane.

The cross-section morphology of PSf/ANC blend membranes was investigated by SEM, as shown in Fig.5. All the prepared membranes have a dense top layer and a porous sub-layer. Pure PSf membrane has many obvious macro-voids in the porous sub-layer, while the macro-voids are suppressed and the finger-like pores traverse the cross-sectional structure in the PSf/NC and PSf/ANC blend membranes, exhibiting that the addition of NC and ANC promotes the formation of longer finger-like pores in the sub-layer. Compared with PSf/NC blend membrane, the finger-like pores become more homogeneous, and the structure of porous support layers become denser in PSf/ANC blend membranes. This is attributed to the presence of hydrophobic group making ANC have a good compatibility with PSf matrix. ANC can disperse more evenly in the casing solution, which results in the structure of pores more uniform. As the SD of the prepared ANC is very low, the cross-section morphology of the prepared PSf/ANC blend membranes has no obvious differences.

The test results of mechanical properties including breaking strength, elongation at break and Young's modulus are shown in Table 1. It can be seen that the break strength and elongation at break of PSf/ANC blend membranes are higher than those of pure PSf membrane and PSf/NC blend membrane, showing that ANC is more effective in improving the mechanical property of PSf membrane. This is because that the long-chain DDSA groups on the surface of ANC form many brush-like structures, which can embed into the PSf matrix easily. The cross-link network of hydrogen bonds between PSf and ANC lead to a good interfacial combination. The tensile force can transfer from matrix to ANC more effectively, thus improving the mechanical properties of PSf/ANC blend membranes (Baheti *et al*. 2013). Moreover, both the break strength and the elongation at break of PSf/ANC blend membranes show an escalating trend along with the increase in the SD value. Due to the highest SD value of ANC-4, the break strength and elongation at break of PSf/ANC-4 reaches maximum values, which are 1.30, and 1.84 times larger than those of pure PSf membrane. This might be ascribed to the fact that the number of flexible long-chains DDSA groups on the surface of ANC increases with the increasing of SD values, which results in a better interfacial combination between PSf matrix and ANC. As shown in Table 1, the Young's modulus of PSf/ANC blend membranes decreases with the improvement of SD value of ANC. The reason is the enhancement of the cross-link network of hydrogen bonds between PSf and ANC according to the increase of SD. This reduces the brittleness of PSf membrane and improves its deformation resistance property, which leads to the decrease of the Young's modulus of the blend membranes. The PSf/ANC-4 membrane has the lowest Young's modulus, indicating that it has the lowest stiffness and the best deformation property.

The surface hydrophilicity changes of PSf/ANC blend membranes are revealed by surface contact angle, which is

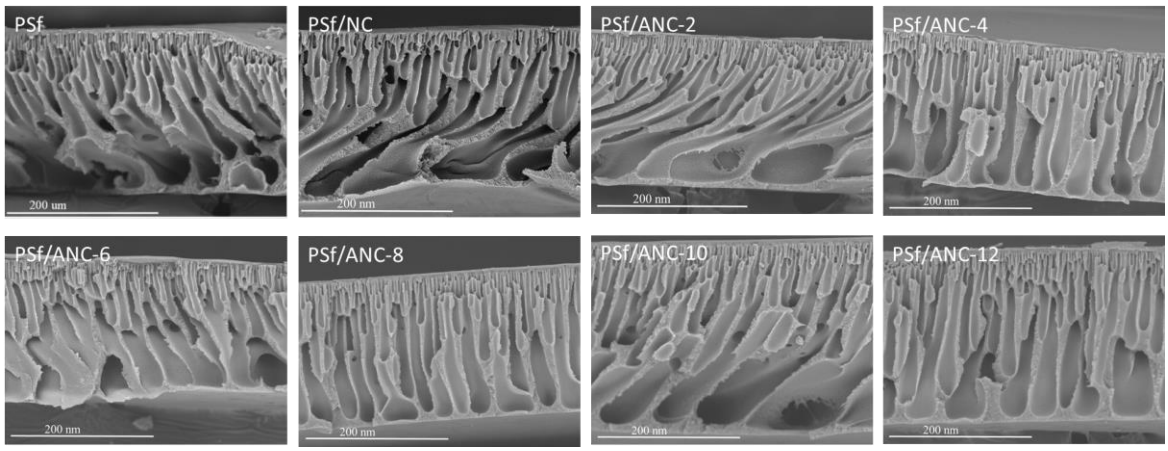

Fig. 5 Cross-section SEM images of the prepared PSf membranes

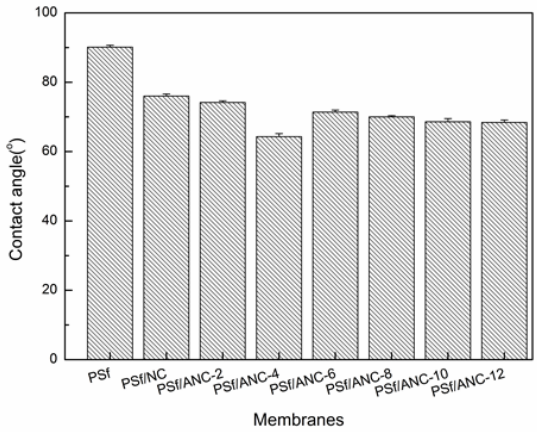

Fig. 6 Contact angles of pure PSf membrane, PSf/NC membrane and PSf/ANC blend membranes

shown in Fig.6. The PSf membrane has the highest surface contact angle, exhibiting the worst hydrophilicity of PSf membrane. By adding ANC to the membrane casting solution, the water contact angle on the membrane surface decreases from 90.1° to 64.3°. This exhibits the improvement of hydrophilicity of PSf membrane by the incorporation of ANC. It may be mentioned that contrast with PSf/NC membrane, PSf/ANC membranes have lower contact angles, which exhibits that ANC has a better ability in hydrophilic modification of PSf membrane, due to the better dispersion between ANC and PSf matrix. In addition, the surface hydrophilicity of PSf/ANC blend membranes is improved gradually with the increasing of SD values. This might be ascribed to the better dispersion in PSf matrix for the higher SD value of ANC.

3.3 Separating property of PSf/ANC blend membranes

The permeability and separating property of the prepared membranes are measured by filtration experiment. Fig.7 shows that compared with the pure PSf membrane, the steady water fluxes increase at the rate of 116.87%, 260.90%, 460.83%, 366.06%, 338.08%, 294.27% and 303.04% for PSf/NC, PSf/ANC-2, PSf/ANC-4, PSf/ANC-6, PSf/ANC-8, PSf/ANC-10 and PSf/ANC-12 membranes, respectively, which exhibits the membrane permeability increases with the increase of SD values. The pure water flux of PSf/ANC-4 membrane reaches a peak value, due to the highest SD value of ANC-4. This can be ascribed to the improvement of hydrophilicity and porous structure uniformity with the increase of SD values as discussed in the preceding sections, which are beneficial to weaken the resistance of water permeation and increase membrane permeability.

The BSA rejection values for PSf/NC, PSf/ANC-2, PSf/ANC-4, PSf/ANC-6, PSf/ANC-8, PSf/ANC-10 and PSf/ANC-12 membranes were calculated as 53.71%, 65.34%, 73.18%, 71.39%, 70.41%, and 68.82%, respectively. It should be noted that compared with the 62.42% of pure PSf membrane, the BSA rejection of PSf/NC blend membrane decreases slightly, due to its large pore size. However, the BSA rejection of PSf/ANC membranes is enhanced, and improved with the increase of SD. This can be explained by the increase of homogeneous pore numbers and the improved hydrophilicity with the enhancement of SD values. The dense and homogeneous structure prevents BSA passing through the PSf/ANC blend membrane, leading to the increase of the BSA rejection. In conclusion, the filtration experiment results show that PSf/ANC blend membranes possess superior permeability and improved BSA retention.

3.4 Anti-fouling property of PSf/ANC blend membranes

In this study, flux recovery ratio (FRR) is used to evaluate the anti-fouling performance of the prepared membranes, which is calculated by Eq. (5). A higher FRR value indicates a better anti-fouling property. It can be seen from Fig.8 that all the FRR values of PSf/ANC blend membranes are above 90%, which is much higher than 57.14% of pure PSf membrane and 73.34% of PSf/NC blend membrane. This result exhibits that ANC has more pronounced effect on improving the anti-fouling properties of PSf membrane than NC. In addition, the FRR value of PSf/ANC blend membrane is enhanced with the

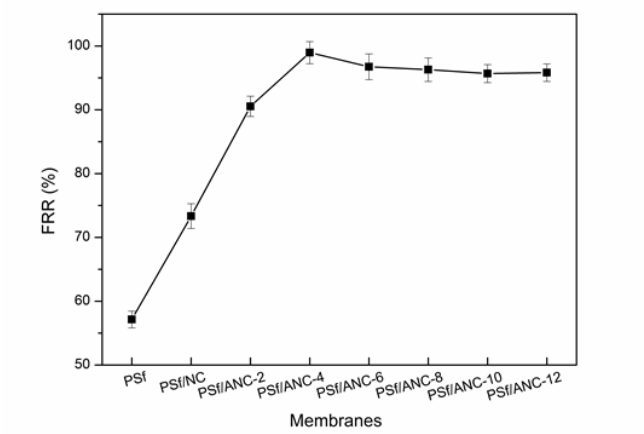

Fig. 6 Flux recovery ratio (FRR) of pure PSf membrane, PSf/NC membrane, PSf/ANC membranes

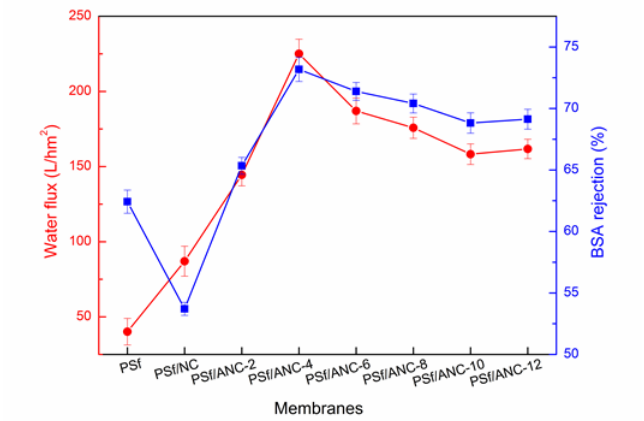

Fig. 7 Pure water flux and BSA rejection of pure PSf membrane, PSf/NC and PSf/ANC membrane

improvement of SD, which indicates that the PSf/ANC-4membrane is easier to clean than the others. This is probably related to the improved hydrophilicity of PSf/ANC blend membranes with the increase of SD. Previous studies have suggested that hydrophilic surfaces have the ability to resist protein adsorption, which is often a prerequisite for a membrane surface to resist the adhesion or attachment of most bio-foulants in water treatment (Zhang *et al*. 2013; Xu *et al*. 2013). Therefore, higher hydrophilicity of the membrane surface makes the protein molecules deposit and absorb on the surface more difficultly, leading to a better anti-fouling property of PSf/ANC membrane. In addition, the dense and homogeneous structure of PSf/ANC membranes prevents BSA passing through the membrane, leading to less BSA solute remained in the membrane pores. Due to the hydrophilicity of PSf/ANC membrane surface, BSA solute trapped on the membrane surface can be easily cleaned, thus increasing the anti-fouling property of the membrane.

4. Conclusions

In this study, amphiphilic nanocellulose (ANC) with different substitution degree (SD) was synthesized by esterification with nanocellulose (NC) and 12-ethylene succinic anhydride (DDSA). The obtained ANC was used as a hydrophilic anti-fouling agent for pure PSf membrane. With the increase of mass ratio of DDSA to NC, the SD of ANC was increases first, and then began to decrease. When the mass ratio of DDSA to NC was 4:1, the SD reached a peak value. Compared to NC, the morphology of ANC did not change obviously. However, as the grafted of long-chain DDSA on the surface of ANC, the boundaries of ANC became progressively blurred. The average diameter of ANC is increased obviously, due to the grafting of DDSA long-chain groups and DMSO swelling. PSf/ANC blend membranes were successfully prepared by immersion phase-inversion method. Mechanical property, hydrophilicity, permeation property and anti-fouling property of PSf membrane were improved by adding ANC in the membrane casting solution. In addition, the performances of the blend membranes were increased with the increase of SD values. Meanwhile, the BSA rejection of PSf/ANC membranes was also improved slightly. Due to the highest SD of ANC-4, the PSf/ANC-4 membrane exhibited the most excellent properties in multiple aspects, which were 1.30, 1.84, 1.21, 4.61, 1.73, and 1.17 times in break strength, elongation at break, hydrophilicity, pure water flux, FRR values, BSA rejection, respectively, as compared to pure PSf membrane. In summary, all the experimental implied that ANC has a better effect than NC on the hydrophilic modification of PSf membrane. And it is promising in the preparation of PSf membrane with high flux and low fouling.

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References

Arash, Y., Ahmad, A. and Hosna, S. (2015), "Preparation of novel NF membrane via interfacial cross-linking polymerization", *Membr. Water Treat.*, **6**(3), 173-187. https://doi.org/10.12989/mwt.2015.6.3.173.

Baheti, V., Militky, J. and Marsalkova, M. (2013), "Mechanical properties of poly lactic acid composite films reinforced with wet milled jute nanofibers", *Polym. Composite.*, **34**, 2133-2141. https://doi.org/10.1002/pc.22622.

Cao, Y. and Li, H. (2003), "Micellar solutio.ns of amphipathic copolymers based on carboxymethyl cellulose", *Polym. Int.*, **52**, 869-875. https://doi.org/10.1002/pi.989.

Carpenter, A.W., De Lannoy, C.F. and Wiesner, M.R. (2015), "Cellulose Nanomaterials in Water Treatment Technologies", *Environ. Sci. Technol.*, **49**(9), 5277-5287. https://doi.org/10.1021/es506351r.

Dong, L., Yang, H., Liu, S.,Wang, X., Xie, F. (2015), "Fabrication and anti-biofouling properties of alumina and zeolite nanoparticle embedded ultrafiltration membranes", Desalination, **365**, 70-78. https://doi.org/10.1016/j.desal.2015.02.023.

Eren, E., Sarihan, A., Eren, B., Gumus, H. and Kocak, F.O. (2015),

"Preparation, characterization and performance enhancement of polysulfone ultrafiltration membrane using PBI as hydrophilic modifier", *J. Membrane Sci*., **475**, 1-8. https://doi.org/10.1016/j.memsci.2014.10.010.

Fan, Z., Wang, Z., Sun, N., Wang, J. and Wang, S. (2008), "Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers", *J. Membrane Sci.*, **320**, 363-371. https://doi.org/10.1016/j.memsci.2008.04.019.

García-Ivars, J., Alcaina-Miranda, M.I., Iborra-Clar, M.I., Mendoza-Roca, J.A. and Pastor-Alcañiz, L. (2014), "Enhancement in hydrophilicity of different polymer phase-inversion ultrafiltration membranes by introducing PEG/Al_2O_3 nanoparticles", *Sep. Purif. Technol.*, **128**, 45-57. https://doi.org/10.1016/j.seppur.2014.03.012.

Gibril, M.E., Li, X.D., Li, H., Li, H.F., Zhang, Y., Zhong, X. and Yu, M.H. (2012), "Reactive extrusion for in-situ chemical modification of cellulose with De-Octenyl succinic anhydride (DDSA) in presence of ionic liquid", *Int. J. Eng. Sci. Technol.*, **4**, 3572-3583.

Guo, J., Liu, J., Wang, L. and Liu, H. (2014), "Modification of ultrafiltration membranes with carbon nanotube buckypaper for fouling alleviation", *Membr. Water Treat.*, **6**, 1-14. https://doi.org/10.12989/mwt.2015.6.1.001.

Habibi, S. and Nematollahzadeh, A. (2016), "Enhanced water flux through ultrafiltration polysulfone membrane via addition-removal of silica nano-particles: Synthesis and characterization", *J. Appl. Polym. Sci.*, **133**(25), 1-9. https://doi.org/10.1002/APP.43556.

Higuchi, A., Tamai, M., Tagawa, Y., Chang, Y. and Ling, Q. (2010), "Surface modification of polymeric membranes for low protein binding", *Membr. Water Treat.*, **1**(2), 103-120. https://doi.org/10.12989/mwt.2010.1.2.103.

Huang, Z.Q., Chen, L., Chen, K., Zhang, Z. and Xu, H. (2010), "A novel method for controlling the sublayer microstructure of an ultrafiltration membrane: The preparation of the PSF-Fe_3O_4 ultrafiltration membrane in a parallel magnetic field", *J. Appl. Polym. Sci.*, **117**(4), 1960-1968. https://doi.org/10.1002/app.32191.

Ingole, P.G., Sawant, S.Y., Ingole, N.P., Pawar, R.R., Bajaj, H.C., Singh, K., Cho, M.H. and Lee, H.K. (2016), "Preparation of activated carbon incorporated polysulfone membranes for dye separation", *Membr. Water Treat.*, **7**(6), 477-493. https://doi.org/10.12989/mwt.2016.7.6.477.

Kaewtatip, K. and Thongmee, J. (2012), "Studies on the structure and properties of thermoplastic starch/luffa fiber composites", *Mater. Design*, **40**, 314-318. https://doi.org/10.1016/j.matdes.2012.03.053.

Kebria, M.R.S., Jahanshahi, M. and Rahimpour, A. (2015), "SiO_2 modified polyethyleneimine-based nanofiltration membranes for dye removal from aqueous and organic solutions", *Desalination*, **367**, 255-264. https://doi.org/10.1016/j.desal.2015.04.017.

Khosroyar, S. and Arastehnodeh, A. (2018), "Improving hydrophilic and antimicrobial properties of membrane by adding nanoparticles of titanium dioxide and copper oxide", Membr. Water Treat., 9(6), 481-497. https://doi.org/10.12989/mwt.2018.9.6.481.

Liu, Z., Cui, Z., Zhang, Y., Qin, S., Yan, F. and Li, J. (2017). "Fabrication of polysulfone membrane via thermally induced phase separation process", *Mater. Lett.*, **195**, 190-193. https://doi.org/10.1016/j.matlet.2017.02.070.

Mahmoudi, E., Ng, L.Y., Ba-Abbad, M.M. and Mohammad, A.W., (2015), "Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanoplates", *Chem. Eng. J.*, **277**, 1-10. https://doi.org/10.1016/j.cej.2015.04.107.

Mauter, M.S., Wang, Y., Okemgbo, K.C., Gianelis, E.P. and Elimelech, M. (2011), "Antifouling Ultrafiltration Membranes via Post-Fabrication Grafting of Biocidal Nanomaterials", *Acs Appl Mater Interfaces*, **3**(8), 2861-2868. https://doi.org/10.1021/am200522v.

Ng, L.Y., Mohammad, A.W, Leo, C.P. and Hilal, N. (2013), "Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review", *Desalination*, **308**(1), 15-33. https://doi.org/10.1016/j.desal.2010.11.033.

Obaid, M., Barakat, N.A.M., Fadali, O.A., Al-Meer, S., Elsaid, K. and Khalil, K.A. (2015), "Stable and effective super-hydrophilic polysulfone nanofiber mats for oil/water separation", *Polym.*, **72**, 125-133. https://doi.org/10.1016/j.polymer.2015.07.006.

Ohl, A., Besch, W., Steffen, H., Foest, R., Arens, M. and Wandel, K. (2009), "Surface coating by repeated plasma-assisted grafting and cross-linking of molecular precursors, plasma process". *Polym.*, **6**, 425-433. https://doi.org/10.1002/ppap.200930006.

Pereira, V.R., Isloor, A.M., Ahmed, A.A. and Ismail, A.F. (2014), "Preparation, characterization and the effect of PANI coated TiO2 nanocomposites on the performance of polysulfone ultrafiltration membranes", New J. Chem., 39(1), 703-712. https://doi.org/10.1039/C4NJ01594K.

Sianipar, M., Kim, S.H., Min, C., Tijing, L.D. and Shon, H.K. (2016), "Potential and performance of a polydopamine-coated multiwalled carbon nanotube/polysulfone nanocomposite membrane for ultrafiltration application", *J. Ind. Eng. Chem*., **34**, 364-373. https://doi.org/10.1016/j.jiec.2015.11.025.

Singh, S., Karwa, V. and Marathe, K.V. (2018), "UV-assisted surface modification of polyethersulfone (PES) membrane using TiO2 nanoparticles", *Membr. Water Treat.*, **9**(6), 393-403. https://doi.org/10.12989/mwt.2018.9.6.393.

Sreenivasan, V.S., Ravindran, D., Manikandan, V. and Narayanasamy, R. (2012), "Influence of fibre treatments on mechanical properties of short Sansevieria cylindrica/polyester composites", *Mater. Design*, **37**, 111-121. https://doi.org/10.1016/j.matdes.2012.01.004.

Sun, X.F., Xu, F., Sun, R.C., Geng, Z.C., Fowler, P. and Baird, M.S. (2005), "Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw", *Carbohyd. Polym*., **60**, 15-26. https://doi.org/10.1016/j.carbpol.2004.11.012.

Tran, A.T.T., Patterson, D.A. and James, B.J. (2012), "Investigating the feasibility of using polysulfone-montmorillonite composite membranes for protein adsorption", *J. Food Eng.*, **112**, 38-49. https://doi.org/10.1016/j.jfoodeng.2012.03.031.

Wang J., Sun, H., Gao, X. and Gao, C. (2014). "Enhancing antibiofouling performance of Polysulfone (PSf) membrane by photo-grafting of capsaicin derivative and acrylic acid", *Appl. Surf. Sci.*, **317**, 210-19. https://doi.org/10.1016/j.apsusc.2014.08.102.

Wang, X., Guo, Y., Li, D., Chen, H. and Sun, R.C. (2012), "Fluorescent amphiphilic cellulose nanoaggregates for sensing trace explosives in aqueous solution", *Chem. Commun.*, **48**(45), 5569-5571. https://doi.org/10.1039/c2cc30208j.

Wei, X., Li, G., Nie, J., Xiang, H. and Chen. J. (2014), "Preparation and improvement anti-fouling property and biocompatibility of polyethersulfone membrane by blending comb-like amphiphilic copolymer", *J. Porous Mat.*, **21**, 589-599. https://doi.org/10.1007/s10934-014-9805-8.

Wei, Y., Cheng, F., Hou, G. and Sun, S. (2008), "Amphiphilic cellulose: Surface activity and aqueous self-assembly into nano-sized polymeric micelles", *React. Funct. Polym.*, **68**, 981-989. https://doi.org/10.1016/j.reactfunctpolym.2008.02.004.

Wu, H., Liu, Y., Mao, L., Jiang, C. and Lu, X. (2017). "Doping polysulfone ultrafiltration membrane with TiO2-PDA nanohybrid for simultaneous self-cleaning and self-protection", *J. Membrane Sci.*, **532**, 20-29. https://doi.org/10.1016/j.memsci.2017.03.010.

Xu, J., Feng, X., Hou, J., Wang, X., Shan, B., Yu, L. and Cao, C. (2013), "Preparation and characterization of a novel polysulfone UF membrane using a copolymer with capsaicin-mimic moieties for improved anti-fouling properties", *J. Membrane Sci.*, **446**, 171-180. https://doi.org/10.1016/j.memsci.2013.06.041.

Yang, X., Liu, H., Zhao, Y. and Liu, L. (2016), "Preparation and Characterization of Polysulfone Membrane Incorporating Cellulose Nanocrystals Extracted from Corn Husks", *Fiber. Polym.*, **17**, 1820-1828. https://doi.org/10.1007/s12221-016-6762-7.

Zhang, G., Lu, S., Zhang, L., Meng, Q., Shen, C. and Zhang, J. (2013), "Novel polysulfone hybrid ultrafiltration membrane prepared with TiO_2 -g-HEMA and its antifouling characteristics", *J. Membrane Sci.*, **436**, 163-173. https://doi.org/10.1016/j.memsci.2013.02.009.

Zhang R, Li J, Liu C, Shen, J., Sun, X., Han, W. and Wang, L. (2013), "Reduction of nitrobenzene using nanoscale zero-valent iron confined in channels of ordered mesoporous silica", *Colloid Surface A*, **425**,108-114. https://doi.org/10.1016/j.colsurfa.2013.02.040.

Zhao, S., Wang, Z., Wei, X., Zhao, B., Wang, J.X., Yang, S.B. and Wang, S.C. (2011), "Performance improvement of polysulfone ultrafiltration membrane using PANiEB as both pore forming agent and hydrophilic modifier", *J. Membr. Sci.*, **385**, 251-262. https://doi.org/10.1016/j.memsci.2011.10.006.

Zhao, X., Su, Y., Li, Y., Zhang, R., Zhao, J. and Jiang, Z. (2014), "Engineering amphiphilic membrane surfaces based on PEO and PDMS segments for improved antifouling performances", *J. Membrane Sci.*, **450**, 111-123. https://doi.org/10.1016/j.memsci.2013.08.044.

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