Preparation of hydrophilic polysulfone porous membrane by use of amphiphilic cellulose

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ABSTRACT: A cellulose-based amphiphilic co-polymer with grafted myristyl groups was synthesized and used as an additive to modify polysulfone (PSf) membranes. Fourier transform infrared (FTIR) spectroscopy and Solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C NMR) spectroscopy were used to characterize the structure of the synthesized amphiphilic cellulose. The good compatibility between amphiphilic co-polymer and PSf was confirmed by differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) was conducted to inspect morphology of the membrane. Furthermore, Thermal performance was indicated by thermogravimetric analysis (TGA). Contact angle, flux and retention behavior were also measured in this work. The structural similarity enhanced compatibility among components by introducing flexible alkyl groups. According to the findings obtained from characterization, better compatibility of cellulose with PSf was achieved after amphiphilic treatment. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41664.

INTRODUCTION

Polysulfone (PSf) is commonly applied as an engineering material in separation membranes due to its excellent properties, including the ability to easily form chemically stable membranes with excellent heat-resistant properties.[1–3] PSf membranes are widely applied in contemporary water treatment, hemodialysis, and desalination processes.[4–9]

However, PSf materials are limited by their intrinsic hydrophobicity, which makes them much more susceptible to fouling during practical applications. Membrane fouling is a serious problem for the practical applications. It is generally accepted that increasing the hydrophilicity can improve the antifouling property of the membranes.[10,11] Thus, it is important to improve the commercial applicability of PSf engineered membranes, and also the ability to adjust hydrophilicity modifications to produce PSf membranes more resistant to fouling and other degradation processes, including heat exposure.[7,12]

Contemporary strategies for hydrophilic modification of membranes have been achieved through blending, surface grafting, and surface coating.[13–15] Both surface coating and surface grafting suffer from the drawback that the internal pores cannot be modified. Blending hydrophilic materials is deemed to be a facile and effective method to solve this problem. However, applying design

and synthesis of amphiphilic co-polymers as membrane additives is a very recent addition to the array of available strategies for hydrophilicity modification of membrane materials.[16–19] Amphiphilic polymer consists of hydrophilic chain segments and hydrophobic chain segments. The hydrophobic chain segments can provide the persistent hydrophobic modification effect, because through the supramolecular non-covalent interactions, they can anchor to the membrane matrix. Hydrophilic chain segments can self-assembled at the membrane surface, and in the phase inversion process, the hydrophilic antifouling layer could be built.[20] Amphiphilic cellulose is a kind of cellulose derivatives, which can provide both hydrophilicity and hydrophobicity.[21,22] Through introducing a hydrophobic functional group into the hydrophilic cellulose skeleton and giving cellulose amphiphilicity. The hydrophilic chain segments were the backbone of cellulose, because it has a wealth of hydroxyl. The hydrophobic chain segments can be such as a long-chain alkyl, a long-chain ester groups, and a graft hydrophobic polymer chain.[23–25] Notably, facile manipulation and good modification efficiency are allowed simultaneously in this method, which is responsible for increased interest in this specialized field of research.[26,27]

Cellulose is one of the most widely available natural materials composed of poly-(1, 4)-D-glucose residues. The development of cellulose has aroused increasing interest over the past decade.[28,29]
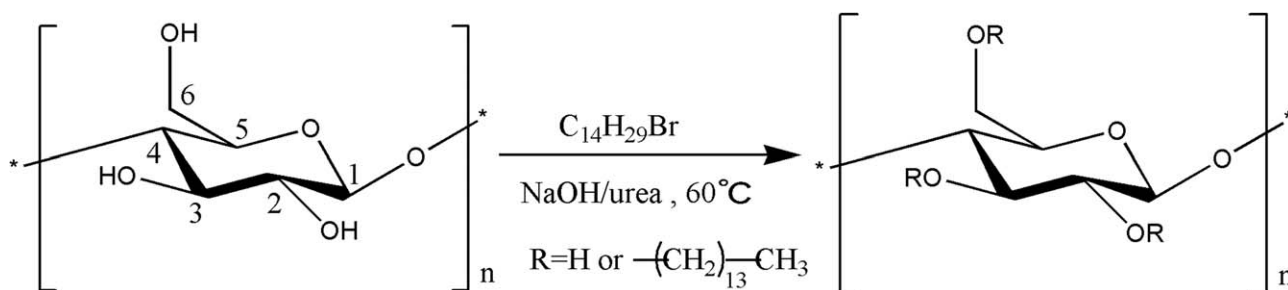
Figure 1. A chemical scheme for synthesis of amphiphilic cellulose.

In spite of its beneficial properties such as biodegradability, recyclability, and sustainability, it's poor compatibility with non-polar polymers owing/due to high hydrophilicity capacity has restricted its usability as a modifier.[30–32] Cellulose can be dissolved in NaOH/urea solutions, which are particularly appealing because of their "green" environmental characteristics.[33] In particular, an aqueous solution of 7 wt % NaOH and 12 wt % urea rapidly pre-cooled to −12°C can be used to dissolve cellulose effectively. Moreover, some useful modifications are made to cellulose as a result of highly alkaline environment, as reported by Song et al., demonstrates a variety of cellulose derivatives attained by homogeneous quaternization of cellulose in aqueous NaOH/urea solutions.[33,34]

In present work, the amphiphilic cellulose was prepared by the partial etherification of cellulose with myristyl bromide using a NaOH/urea aqueous solution. The structure of amphiphilic cellulose was characterized. Amphiphilic cellulose, as a hydrophilic additive, was blended with PSf in the membrane preparation process. The effects of different concentrations of amphiphilic cellulose on hydrophilicity, morphology, and compatibility of PSf membranes were investigated.

EXPERIMENTAL

Materials
Microcrystalline cellulose (MCC) was purchased from the Sinopharm Chemical Reagent Co. (DP = 162.06; Beijing, China). Polysulfone (PSf) with a known degree of polymerization (1500; Shanghai Shuguang Chemical Plant, Shanghai, China), urea (Tianjin Beifangtianyi Chemical Reagent Factory, Tianjin, China), and bovine serum albumin (BSA; Beijing Aoboxing Biological Technology Co., Beijing, China) were purchased for current experiments. Additionally, chemically pure PEG (MW 600), NaOH, and N-dimethylacetamide (DMAC) were purchased from Beijing Chemical Plant (Beijing, China).

Preparation for Aqueous Cellulose Solutions
Cellulose solutions were prepared with NaOH/urea, as previously described.[33] Briefly, combining and agitating NaOH, urea, and distilled water (7 : 12 : 81) in a 1000 mL beaker; precooling the aqueous solution at −12°C, and then adding cellulose (2 wt %) by vigorous stirring for 20 mins.

Synthesis of Amphiphilic Cellulose
An adequate amount of myristyl bromide (molar ratio of myristyl bromide to anhydroglucose unit (AGU) of cellulose is 9 : 1) was added into the cellulose-NaOH/urea aqueous solution drop by drop and stirred for 3 hrs at constant 60°C. The synthesis process is shown in Figure 1. The reaction product was neutralized with aqueous HCl, precipitated, and washed with DMAC. In the modification process, the cellulose was partially modified by alkyl chains to obtain hydrophobic property, at the same time; the unmodified part of cellulose could help cellulose maintaining hydrophilic character to some extent.

Through the above steps, the dried amphiphilic cellulose samples were submerged into DMAC and homogenized with a high-pressure homogenizer (NS1001S2K, GEA Niro Soavi Co., Italy) to produce a colloidal suspension of amphiphilic cellulose-DMAC.

Preparation for Blend Membranes
Blend membranes were prepared by L-S phase-inversion.[10,20] PSf (18 wt %) and polyethylene glycol (PEG; 3 wt %) were dissolved in the prepared amphiphilic cellulose-DMAC colloidal suspension. This casting solution was then set at 50°C in a table concentrator for 24 hrs with a constant-temperature table concentrator apparatus (SHK-99-II, Beijing North TZ-Biotech Develop Co., China). Bubbles were purged from the solution by a vacuum degree of 0.1 MPa. The polymer solution was then poured onto a clean glass plate and scraped to form lamellar domains with a custom fabricated drawknife, vaporized in air for 10 s, and immersed into water for 5 mins. The resultant membranes were then soaked in distilled water for 24 hrs, and air-dried before characterization.

Characterization
Fourier transform infrared (FTIR) spectra of the native cellulose were obtained from dry powdered samples (Tensor 27, Bruker, Germany) in the range of 4000–400 cm^{-1}. Pellets were prepared from sample mixtures and KBr (1 : 100, by weight). A total of 32 scans were conducted at a resolution of 2 cm^{-1}. Solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C NMR) spectra were recorded using a Bruker Avance III 400 MHz spectrometer operating in the FT mode at room temperature (25°C) and 100.6 MHz.[35] 1 ms contact time, and 2 s dead time delay. DSC was determined with membrane weight of 5.0 mg and started heating from 50°C at the rate of 20°C/min. The thermal properties of samples with weights of 5–10 mg were examined by thermogravimetric analysis device (TGA; DTG-60, Shimadzu, Japan) in a temperature range from room temperature (25°C) to 600°C at the rate of 20°C/min under nitrogen flow. The cross-sectional morphologies of each membrane sample were also examined by scanning electron microscopy (SEM, S-3000n; Hitachi, Japan)
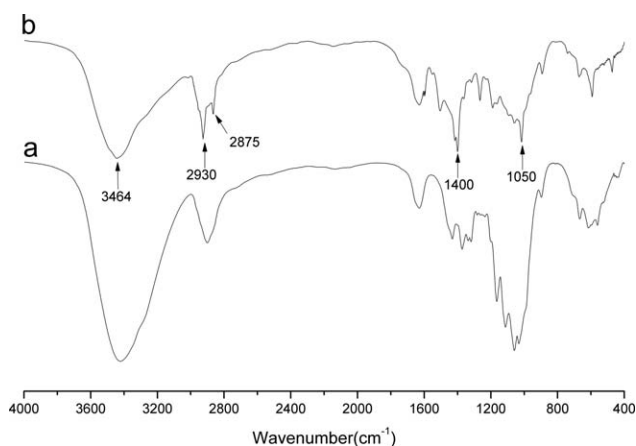
Figure 2. FT-IR of cellulose (a) and amphiphilic cellulose (b).

with an accelerating voltage of 5 kV. Prior to SEM examination, all surfaces were sputter-coated with gold. The contact angle between water and membrane was examined by a contact angle measuring instrument (360a, HAKE, China) to evaluate the hydrophilicity of membrane with different content of amphiphilic cellulose. Deionized water was used as the probe liquid in all measurements. The contact angle was measured at five random locations for each sample and then the average was reported to minimize the experimental error.[10]

Flux and Retention Evaluation
The flux of blend membrane were measured based on the previous works.[7] The pure water flux measured by a self-made ultra-filter. The initial water flux was taken about 30 min after the pressurization in the ultrafilter, at 0.15 MPa, and working at 0.1 MPa during the test. Pure water flux (J_w) was calculated over measured time intervals using the following equation:

$$J_w = Q/(A \times \Delta T)$$

Where Q is permeating of pure water (L); A is the effective membrane area (m^2), and ΔT (h) is the sampling time.

The retention coefficient (R) of membranes was measured by calculating the fluid retention capacity of BSA through membranes. Using the UV-spectrophotometer (UV-1801; BFRL, China) to measure the absorbance of the BSA solution (1 g/L) and the permeate solution at 280 nm. All tests were conducted at a working pressure of 0.1 MPa and room temperature. The retention coefficient (R) was calculated as follows:

$$R(\%) = (1 - \frac{A_1}{A_2}) \times 100\%$$

Where A_1 and A_2 are the absorbance of the filtrated and raw solution of BSA.

RESULTS AND DISSUSION

Structure of Amphiphilic Cellulose
Figure 2 showed the FTIR spectra of MCC [Figure (2a)] and amphiphilic cellulose [Figure (2b)]. Compared with that of MCC, the intensity of the wide peak at 3464 cm^{-1} corresponding to the stretching vibration of —OH group decreased in the spectra of amphiphilic cellulose, which indicated etherification occurred at the hydroxyl sites of cellulose. The characteristic

peaks at 2930, 2875 cm^{-1} were assigned to C—H stretching, and that at 1400 cm^{-1} was assigned to C—H bending, respectively, these peaks became stronger and sharper in the spectra of amphiphilic cellulose.[35] Besides that, the characteristic peak represents that the stretching vibration of C—O appeared at 1050 cm^{-1}. In research of amphiphilic cellulose, this finding has been previously reported to indicate the attachment of long chain alkyl groups to cellulose hydroxyl groups.[34]

Figure 3 showed the solid-state CP/MAS ^{13}C NMR spectra of cellulose (Figure a) and amphiphilic cellulose (Figure b). In chemical shift, cellulose at around 60–70 ppm of the peaks was primary hydroxyl in C-6 signal displacement. Those at around 70–80 ppm were the signals of displacement of no-glycosidic linking bond ring carbon C-2, C-3, and C-5. Total of 80–93 ppm appears to be the signal of the displacement of C-4, and 100–110 ppm was the signal of the displacement of C-1. It could be found from the comparison of Figure a and Figure b that all above positions were corresponded to the displacement of signals, but peak types that represent resolution tend to be different; the resolution of modified amphiphilic cellulose became lower. High resolution means more complete crystal structure. Lower resolution means that in the process of cellulose dissolving, crystalline region of cellulose has also been affected. In the process of recrystallization in later reaction,
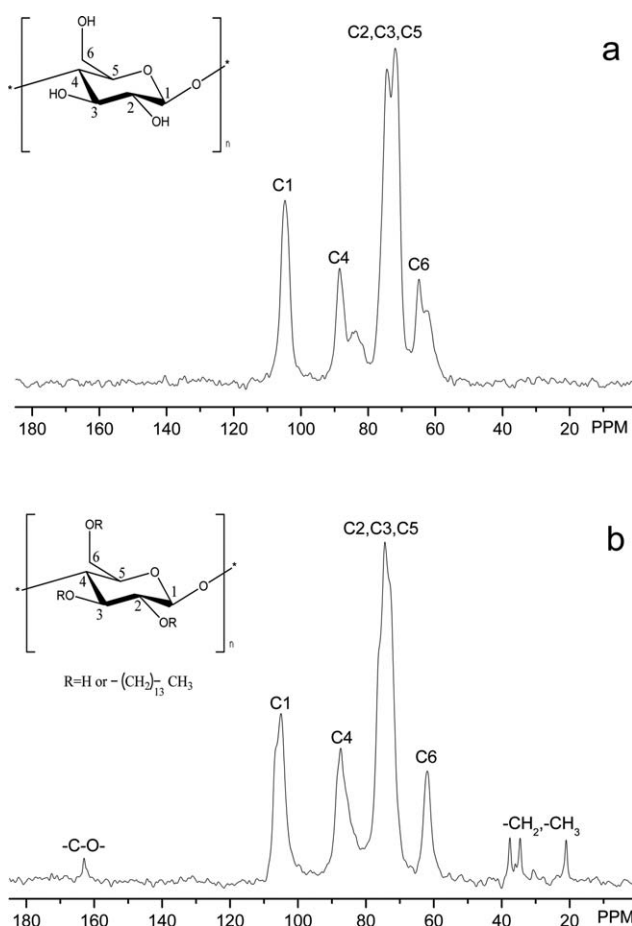

Figure 3. Solid-state CP/MAS ^{13}C NMR of cellulose (a) and amphiphilic cellulose (b).
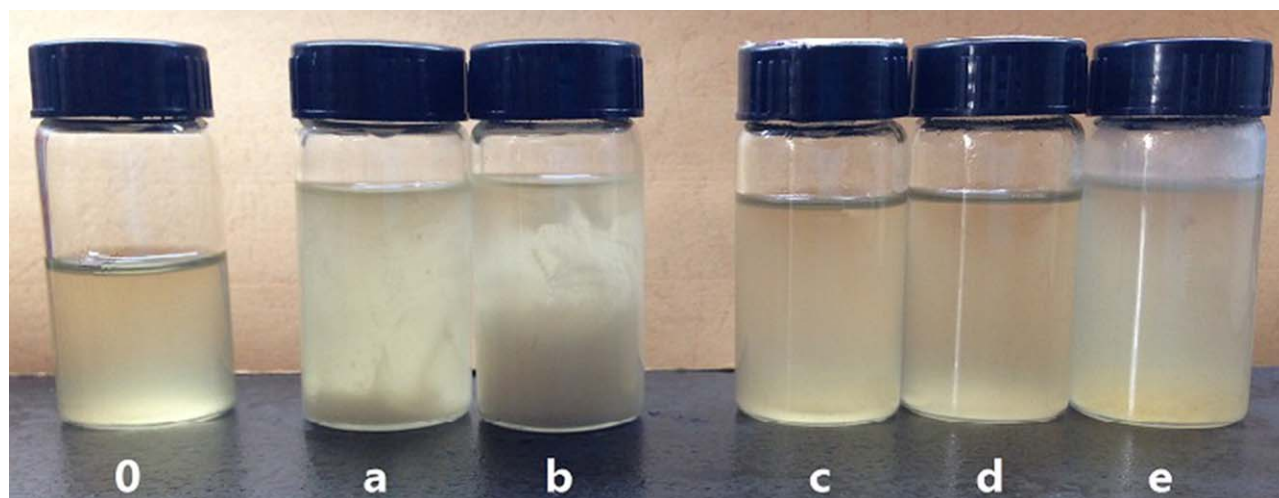
Figure 4. Photograph of membrane casting solutions.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dilute hydrochloric acid and solvent quickly separate amphiphilic cellulose out. Also, the changes of the group caused by chemical modification and regularity impact the crystalline structure of cellulose.

In addition, in Figure b, there appeared signal displacement peak that represented the alkyl chain in the range of 20–40 ppm; there appeared signal displacement of C—O at 165 ppm. These data further confirmed the formation of amphiphilic cellulose in Figure 1.

Dispersing Performance of Amphiphilic Cellulose
The photograph of membrane casting solutions was shown in Figure 4, and the constitutions of the casting solutions were listed in Table I. It is observed that cellulose in the casting solution displayed an obvious stratification. Although it could be better dispersed after high speed mixing, the non-uniform solutions of these two samples would rarely result in a continuous and uniform ultrafiltration membrane. Compared with cellulose, amphiphilic cellulose in the casting solution presented a better dispersion. A transparent and uniform casting solution was obtained as the content of amphiphilic cellulose increased from 5 to 10 wt %, while slight non-uniform was observed when the content of amphiphilic cellulose increased to 15 wt %. The result indicated the amphiphilic cellulose was feasible to be used in modifying polysulfone (PSf) membranes. Actually, the good compatibility of the PSf and amphiphilic cel-

lulose blending system was suggested when they were blended in solutions. Compared to microcrystalline cellulose, amphiphilic cellulose showed dispersibility. Sample c and d were two manifestations of homogeneous casting solution; casting solution e was only slightly turbid. These demonstrated that after modification, on the one hand, the introduction of a hydrophobic alkyl chain made cellulose macromolecules skeleton obtain an ideal hydrophobic segment; on the other hand, the crystallinity of amphiphilic cellulose was greatly reduced in the dissolution—reproduction process, and it greatly strengthened the accessibility and activity of amphiphilic cellulose. Therefore, the compatibility between amphiphilic cellulose and PSf enhanced greatly. During the preparation of the casting solution, intermolecular forces were produced between PSf and amphiphilic cellulose, and casting solution formed a stable homogeneous system.

Chemical Compatibility Analysis
The DSC spectra for the PSf membrane (a), amphiphilic cellulose (c), and the membrane with amphiphilic cellulose additives (b) are shown in Figure 5. The spectrum demonstrated that a characteristic glass transition (T_g) was exhibited in the spectrum of pure PSf membranes and amphiphilic cellulose at approximately 172 and 198°C, respectively. Whereas, a compound peak was observed in the spectra of the blend membranes with amphiphilic cellulose. As shown in Figure 4, amphiphilic cellulose exhibited a T_g similar to that observed in PSf. These similar transition points indicated that amphiphilic cellulose was highly compatible with PSf as an additive in casting solutions. The spectrum of the blended co-polymer membranes was consistent with the result of current analysis.

As summarized from both Figures 4 and 5, the performance of casting solutions was highly consistent with the finding of our analysis as well as the DSC determination. The good interaction between amphiphilic cellulose and PSf was considered to be helpful for stabilization of the amphiphilic component and the PSf. It was worth noting that the good compatibility of PSf and amphiphilic additives was necessary for the membrane-forming.

Table I. Compositions of Casting Solution for Membranes

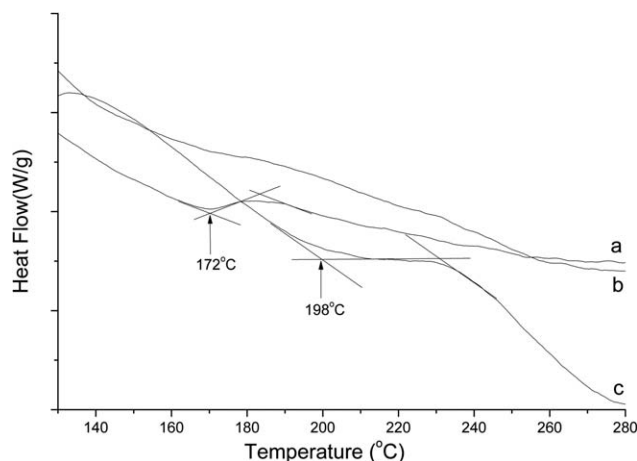| ID	PSf (g)	Cellulose (g)	Amphiphilic cellulose (g)	PEG (g)	DMAc (g)
0	3.6	0	0	0.6	16.4
a	3.6	0.19	0	0.6	16.4
b	3.6	0.63	0	0.6	16.4
c	3.6	0	0.19	0.6	16.4
d	3.6	0	0.40	0.6	16.4
e	3.6	0	0.63	0.6	16.4

Figure 5. DSC spectrum of (a) the pure PSf membrane, (b) the co-polymer blend membrane, and (c) amphiphilic cellulose.

Heat Stability Analysis

The thermogravimetric curves were shown in Figure 6. In the amphiphilic cellulose curve, the amphiphilic cellulose started decomposing at around 275°C, then it persisted until 395°C and showed a solid residual at 600°C. In the curves of the pure PSf and blending co-polymer membranes, two decomposition stages were observed in the ranges of 425–475°C and 500–600°C. The first stage exhibited only a slight weight loss process; however, the weight loss was much more significant in the second stage. Compared with the pure PSf membrane (Figure c), the thermal stability of the blend membrane was slightly improved when the incorporation of amphiphilic cellulose (Figure d). These results demonstrated that there were interactions between amphiphilic cellulose and PSf materials.[36] Based on the molecular structural characteristics, bending and entangling could occur between hydrophobic groups of amphiphilic cellulose and PSf molecular chain. Moreover, hydrogen bonds were formed between hydroxyl groups of amphiphilic cellulose and function groups of PSf. The thermogravimetric curves further confirmed the good compatibility between PSf and amphiphilic cellulose.

Morphological Studies

The cross-sectional morphologies of the pure PSf membrane and the blend membranes were revealed by SEM, which was showed in Figure 7. Compared with the pure membrane, more porous cross-sections were observed in the blend membranes. The quantity of the introduction of the amphiphilic cellulose played an important role on the membrane materials forming. Blend membrane cortex became more porous and loose. While the finger holes became large and penetrated the cross section of membrane. Especially, the sponge layer between the finger holes, with the increase of amphiphilic cellulose sponge pore expanding trend obviously, enhanced connectivity between film hole. This variation in pore size can be attributed to the strong pore-forming effect of the amphiphilic modifier. Increasing the amount of amphiphilic cellulose can greatly improve the hydrophilicity of casting solution, so it makes coagulation bath deliver fast in casting solution during the phase inversion process. At the same time, good compatibility between amphiphilic cellu-

lose and PSf increased the migration of amphiphilic cellulose in casting solution. These two factors limited the total amount of coagulation bath into casting solution system, and also affected the pore forming ability of finger holes, so the hole wall thickened. During the phase inversion process, because the content of amphiphilic cellulose was improved, the hydrophilicity of casting solution was also improved. Therefore, with the increase of the amphiphilic cellulose, the width of finger hole tend to increase; however, layers between the holes became thicker, and the micropore diameter of hole wall was increased.

Contact Angle

Contact angles were measured to evaluate the changes in the hydrophilicity and surface properties of porous PSf membranes after blending with amphiphilic cellulose. Figure 8 showed the effect of different content of amphiphilic cellulose on contact angle. The highest contact angle for PSf membrane was obtained when there was no addition of amphiphilic cellulose, which showed the worst hydrophilicity. As amphiphilic cellulose content increased, the contact angle of the blend membrane was gradually decreased. It proved that within a certain range, the increasing content of amphiphilic cellulose can improve the hydrophilicity of blend membranes. During this process, there are some hydrophilicity differences of the casting solutions because the amphiphilic cellulose has different content in the membrane casting solutions. However, it could be observed that the hydrophilicity did not vary linearly. On the one hand, this may be due to the increasing concentration of amphiphilic cellulose, and with the increase of the total content, the cellulose content in the system was also increased, so total amount of cellulose affected the film surface. On the other hand, anchoring effect was produced because the hydrophobic segment of the amphiphilic cellulose wrapped the long-chain part of the PSf, but hydrophobic segment became a little bit shorter by this kind of preparation, so the intermolecular forces were not firm between amphiphilic cellulose and PSf. Therefore, when casting solution contained high concentrations of amphiphilic cellulose, some amphiphilic cellulose would be washed off during the phase inversion process. Thus, it limited the materials to further improve the hydrophilicity of the membrane.
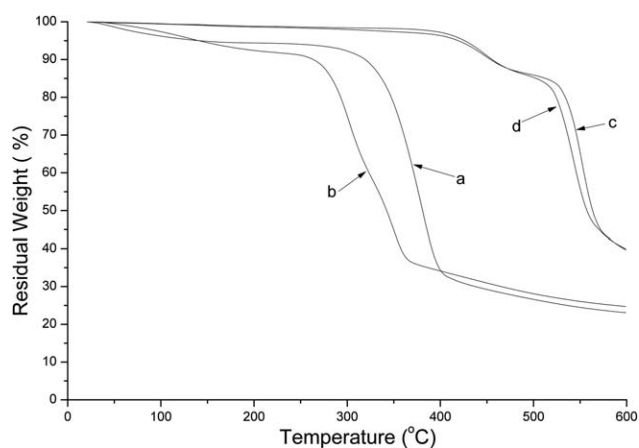

Figure 6. TGA curves of (a) cellulose, (b) amphiphilic cellulose, (c) the pure PSf membrane, and (d) the composite membrane.
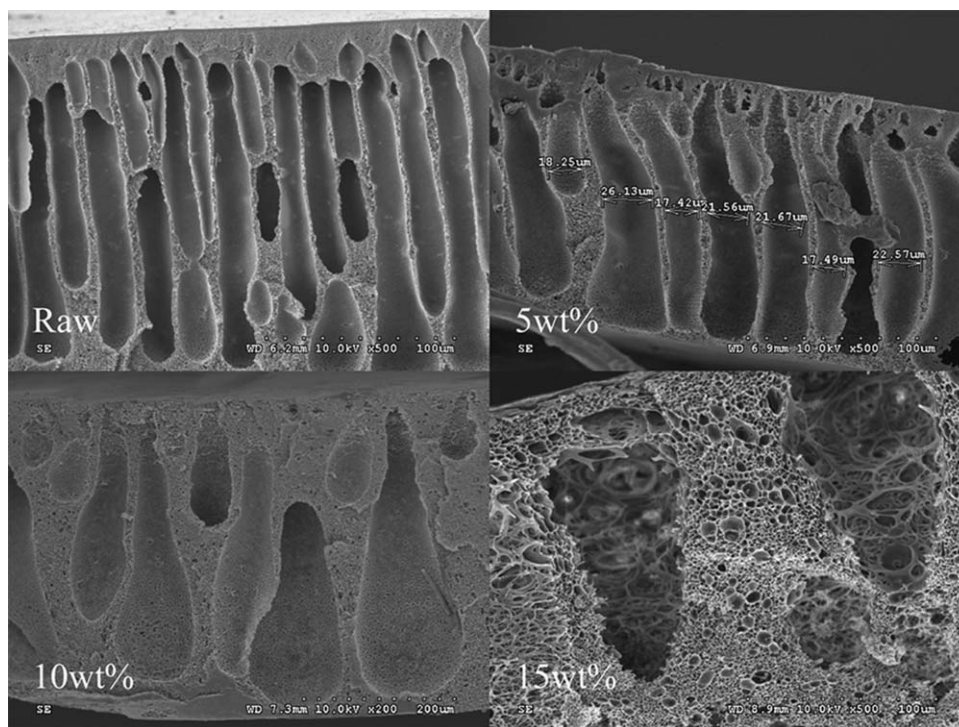
Figure 7. SEM morphologies of the PSf membrane and the amphiphilic cellulose co-polymer blend membrane with a constant additive rate of 5, 10, and 15 wt %.

Membrane Ultrafiltration Performance

Figure 9 showed the pure water flux and antifouling properties of blend membrane with different content of amphiphilic cellulose to different solution. With the increase of the amphiphilic cellulose content in PSf membrane, It can be seen from the figure that pure water flux of the blend membrane has been significantly improved compared to the pure polysulfone membrane. And compared to pure water flux, JB which represents the flux of BSA solution showed more significant improvement. On one hand, JB improved faster than J_w1; On the other hand, with the increase of the amphiphilic cellulose

content in PSf membrane, the BSA solution through the membrane material flux decline becomes smaller. The anti-fouling properties of blend membrane were more pronounced in J_w2. Contrast J_w1 and J_w2, you can clearly see that with the increase of the added amount of amphiphilic cellulose, and anti-fouling properties of blend membrane has been significantly enhanced.

Figure 10 showed the retention capacity of blend membrane by adding different content of amphiphilic cellulose into BSA solution. It can be seen from the figure that a small amount of amphiphilic cellulose improved the retention capacity of membrane material, and the introduction of such amphiphilic cellulose
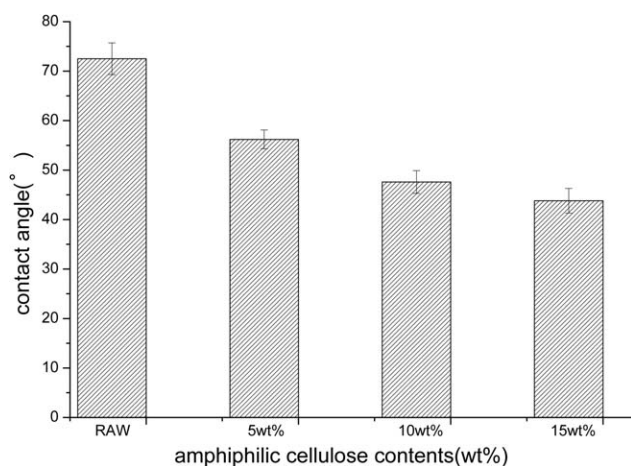

Figure 8. Effects of the amphiphilic cellulose contents on contact angle of composite membranes.
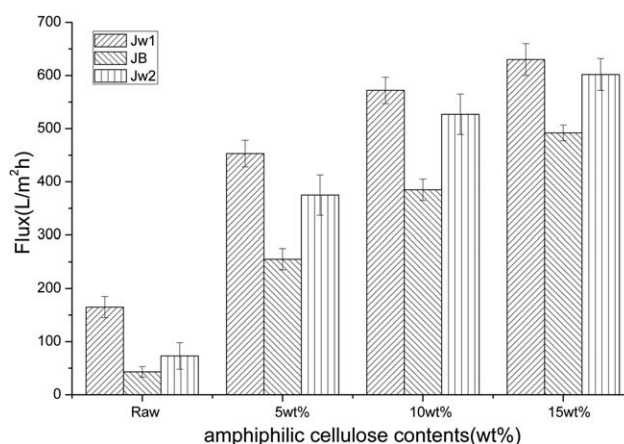

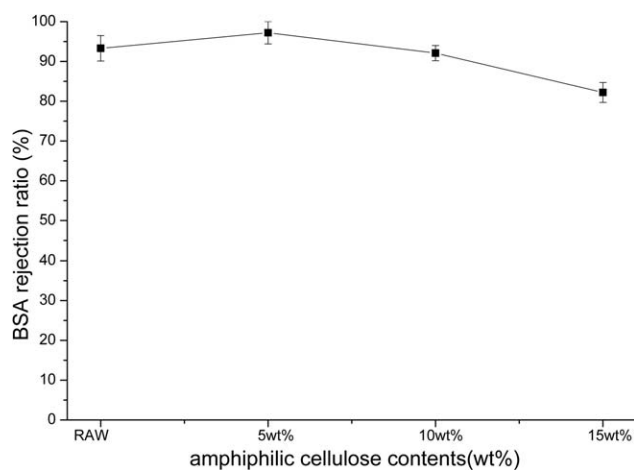**Figure 9.** Effects of the amphiphilic cellulose contents on the fluxes of composite membranes.

Figure 10. Effects of the amphiphilic cellulose contents on the BSA retention coefficient of composite membranes.

allowed membrane to produce repulsive force to BSA molecules. However, the retention coefficient of blend membrane decreased with continued adding amphiphilic cellulose, which was related to the structure of the blend membrane. PSf was the substrate material of membrane when there was no additive in it. The surface structures tended to be small with almost no holes. However, after adding amphiphilic cellulose, the changes in membrane surface pore solution not only improved the infiltration capacity of the blend membrane, but also reduced the interception capability trend of BSA molecules. Therefore, when adding the superfluous amphiphilic cellulose into blend membrane, the retention capacity of BSA molecules was reduced to 90% or less.

CONCLUSIONS

Amphiphilic cellulose was successfully synthesized by introducing hydrophobic myristyl groups, and producing cellulose with structurally modified hydrophilicity. The produced amphiphilic cellulose with structurally modified hydrophilicity was then applied as an additive for extension of hydrophilicity in PSf membranes. It was found that:

1. The good compatibility of amphiphilic cellulose and PSf was confirmed by differential scanning calorimetry (DSC).
2. Good interaction between amphiphilic cellulose and PSf was helpful for stabilization of the amphiphilic component and PSf.
3. Adding a certain amount of amphiphilic cellulose can improve the hydrophilicity and retention capacity of the membrane.

It is accordingly concluded that amphiphilic cellulose can be effectively used as an additive for modification of PSf membranes.

ACKNOWLEDGMENTS

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