Preparation and Characterization of Composite Membranes of Polysulfone and Microcrystalline Cellulose

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ABSTRACT: Physical and chemical modifications of polymeric ultrafiltration membranes are necessary to improve their hydrophilic properties, strength, and other characteristics. Microcrystalline cellulose (MCC) was prepared from cellulose pulp by acid-catalyzed hydrolysis in the presence of ultrasonic radiation, and the properties of MCC were evaluated. Through the addition of MCC to a polysulfone (PS) membrane solution, a casting solution of a PS/MCC blend was obtained. Subsequently, the ultrafiltration membrane from the blend was further developed in a phase-inversion process comprising immersion and deposition. The capacity for ultrafiltration was better with increasing MCC content. When the ratio of MCC to PS was 0.3, the pure water flux of the composite membrane reached 234.2 L/m^2/h, and the retention of a bovine serum albumin solution (1 g/L) was as high as 93.4%. The membranes were also observed with scanning electron microscopy and atomic force microscopy to study their microstructures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 550–556, 2009

Key words: FT-IR; membranes; polysulfides

INTRODUCTION

Ultrafiltration is a filtration process driven by pressure. Because of the small pore size and chemical properties of the membrane surface, solvents and solutes with small molecular structures can pass through the membrane, whereas colloids and proteins with large molecular structures are retained and concentrated. Polysulfone (PS), poly(ether sulfone), poly-(vinylidene fluoride), and polyacrylonitrile are common membrane materials. To overcome the disadvantages of membrane materials, such as inferior hydrophilic properties, easy fouling, and low strength, a few physical and chemical modifications are needed. Recently, some scholars have studied modifications of membrane materials with the addition of Al_2O_3, SiO_2, TiO_2, or other inorganic nanoparticles. Composite membrane materials prepared through the filling of polymers with such inorganic nanoparticles perform excellently, displaying increased water flux and rejection ratios, good strength, and attractive antifouling properties.[1–3] Modified carbon nanofibers are suitable for uniform dispersal in elastomeric ethylene–propylene to yield nanocomposites, which in turn show abrupt changes in the critical gelation temperature, the stiffness of the gel, and the relaxation exponent. A change in the mechanism of physical gelation at a high concentration of carbon nanofibers occurs because of the formation of a bridge of polymer segments between two adjacent nanofillers in the concentrated nanocomposites.[4]

Cellulose is the most abundant biodegradable natural biopolymer in the world. Microcrystalline cellulose (MCC) is composed of microdimensional or nanodimensional cellulose crystals that have been isolated from their natural fibers. MCC has a lot of advantages, such as renewability and biodegradability, in addition to its low density, low cost, high strength, and high tensile modulus.[5,6] Therefore, it can be used as a reinforcement material or filling in environmentally friendly products as a substitute for fiberglass and other synthetic fibers. The whiskers/nanofibers of nanocrystal cellulose can be prepared either with chemical methods accompanied by ultrasonic treatment or with only ultrasonic treatment.[7–12] It not only has the same structure and function as cellulose but also has some characteristics peculiar to nanomaterials, such as huge surface areas, tremendous adsorption capacity, and increased reactivity.

The cellulose acetate/acetone/water system is one of the most studied of the various polymer/solvent/nonsolvent systems, and it can be manipulated to obtain asymmetric membranes with a wide variety of microstructural features. Alumina particles can change the microstructure of cellulose acetate membranes from one containing macrovoids to a structure with a uniform, small-pore network, and they are not agglomerated but are uniformly dispersed throughout

the cellulose acetate network.[13,14] The properties of compaction, pure water flux, water content, hydraulic resistance, and separation of dextran for a blend membrane of PS and cellulose acetate have been previously studied.[15] A metal oxide (Nb_2O_5) in the cellulose acetate matrix can improve the electrochemical properties of the membrane.[16] Cellulose nanocrystals have also been used to improve the performances of PS ultrafiltration membranes.[17] The addition of Aerosil fillers to a PS and N-methylpyrrolidone solution has been shown to have a big influence on the membrane-formation process.[18]

MCC was prepared in this study by acid-catalyzed hydrolysis aided by ultrasonic treatment, and a PS/MCC hybrid membrane was further developed with an immersion and deposition phase-inversion process to improve the performance of the PS membrane. MCC can be used to improve the antifouling properties, flux, and strength of a pure PS membrane because MCC has good hydrophilicity with many hydroxyl groups and superior strength. It can play an important role in the exploitation of natural, biodegradable, environmentally friendly materials and in the functional use of cellulosic materials.

EXPERIMENTAL

Materials

Cellulose pulp was provided by Shandong Huatai Paper Mill (Shandong, China). H_2SO_4 (95–98%), HCl (36–38%), and N,N-dimethylacetamide were purchased from Beijing Chemical Plant (Beijing, China). PS (degree of polymerization = 1500) was purchased from Shanghai Shuguang Chemical Plant (Shanghai, China). Polyvinylpyrrolidone (K30; chemically pure, imported) and bovine serum albumin (BSA) were purchased from Beijing Chemical Reagent Co. (Beijing, China) and Beijing Aoboxing Biological Technology Co., Ltd. (Beijing, China), respectively. A cupriethylenediamine solution was made in our laboratory according to Chinese State Standard GB/T 1548-1989.

Preparation of MCC

Cellulose pulp (12.5 g; FA1004N electronic balance, Precision Science Instrument, Ltd., Shanghai, China) was immersed in 250 mL of an acid solution containing different concentrations of HCl and H_2SO_4 (1 : 2 v/v) and was allowed to react for a specific period by thorough mixing with an electric blender (Z89-1, Great Wall Industrial Foreign Trade, Ltd., Zhengzhou, China). The reaction temperature was 80°C, and ultrasonic radiation at 40 kHz was applied (KQ5200DB numerical control ultrasonic cleaner, Great Wall Industrial Foreign Trade). At the end of the reaction, the pH value of the solution was adjusted by washing

with deionized water until it was neutral. Subsequently, an MCC colloid solution was obtained. After sieving and drying, the solids were crushed with a ball mill (QM-ISP04, Nanjing University Instruments Co., Nanjing, China) to get MCC powder. To check the effects of different acid concentrations (v/v) and various reaction times on the degree of polymerization and crystallinity of the products, five acid concentrations (16, 18, 20, 22, and 24%) with a reaction time of 3 h and five tested reaction times (2, 2.5, 3, 3.5, and 4 h) with an acid concentration of 20% were tested.

Preparation of the composite ultrafiltration membranes

An Loeb-Sourirajan (L-S) phase-inversion method was used to prepare the composite ultrafiltration membrane. A specified quantity of PS (18 wt %) was dissolved in N,N-dimethylacetamide, and MCC powder (in different concentrations) and K30 (0.3 wt %) were added to it. To check the effect of the MCC concentration on the membrane performance, seven MCC concentrations (MCC/PS) were used: 0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 wt %. After it was swayed in the table concentrator for 48 h (constant-temperature table concentrator, SHK-99-II, Beijing North TZ-Biotech Develop. Co., Beijing, China), the casting solution was obtained. The casting solution was vacuumized to get rid of gas with a vacuum degree of 0.1 MPa. A small amount of the casting solution was dropped onto a clean glass board and scraped to a thin layer with a drawknife. The scraped layer was vaporized in air for 20 s and subsequently immersed in a coagulation water bath to gel. The gelled membrane was tested after soaking in distilled water for 24 h.

Yield ratio of MCC

The yield of MCC (W) was used to evaluate the yield ratio of MCC from cellulose pulp:

$$W = m_1/m_0 \times 100\% \qquad (1)$$

where m_1 and m_0 are the weights of MCC and the cellulose pulp (g), respectively.

Polymerization degree and crystallinity of MCC

The polymerization degree of MCC was tested according to the procedure described in the study by Pan et al.[7] MCC was dissolved in a cupriethylenediamine solution, and the viscosity of the solution was obtained with a capillary viscometer (NDJ-1, Hengping Scientific Instrument, Ltd., Shanghai, China); the polymerization degree was calculated with the viscosity-average molecular weight method.

The crystallinity of MCC was tested with an X-ray diffraction instrument (XRD-6000, Shimadzu, Japan)

TABLE I
Effects of Different Acid Concentrations on MCC

Acid concentration (%)	Yield ratio (%)	Polymerization degree	Crystallinity (%)
16	82.6	96	65.8
18	78.6	82	66.7
20	76.0	73	69.5
22	73.4	69	72.9
24	72.1	66	75.4

with Cu Kα radiation, a nickel filter, a wavelength of 0.154 nm, a scan range of $2\theta = 6$–$40°$, and a scan step of $\Delta 2\theta = 0.1°/3$ s. The ratio of the areas under peaks at 22.5 and $18°$ was used to calculate the crystallinity.

Pure water flux and rejection ratio

The pure water flux was tested according to the method described by Li et al.[19] The volume of filtered water [V (m^3)] was obtained in some portions of the membrane with a working pressure of 0.1 MPa and a working time [t (h)]. Next, the pure water flux [J_w (L/m^2/h^1)] was calculated with the following equation:

$$J_w = V/(At) \qquad (2)$$

where A is the membrane area (m^2).

The rejection ratio of the BSA solution (1 g/L) was tested under a working pressure of 0.1 MPa, and the absorbance of the filtered solution was recorded at 280 nm with a UV-9100 ultraviolet–visible spectrophotometer (Third Analysis Apparatus Co., Shanghai, China).[19] The rejection ratio was calculated with eq. (3):

$$R = (1 - A_p/A_b) \times 100\% \qquad (3)$$

where R is the rejection ratio (%) and A_p and A_b are the absorbances of the filtered and raw solutions, respectively.

Porosity and mean pore size

The porosity and mean pore size of the membranes were tested according to the method provided earlier by Li et al.[19] The membranes were weighed when wet and were later dried in an oven. The porosity [P_r (%)] was calculated with the following equation:

$$P_r = (W_w - W_d)/(d_w A_m L_m) \qquad (4)$$

where W_w is the weight of the wet membrane (g); W_d is the weight of the dry membrane (g); d_w is the water density (g/cm^3); and A_m and L_m are the membrane area (cm^2) and thickness (cm), respectively.

The mean pore size [r (m)] was defined as follows:

$$r = [8 \times (2.9 - 1.75P_r) \cdot \eta LF/3600P_r \Delta P]^{1/2} \qquad (5)$$

where η is the viscosity of water (Pa s), L is the membrane thickness (m), F is the pure water flux (m^3/m^2·h), and ΔP is the working pressure (Pa).

Contact angle

The contact angle (θ) values of the composite membranes with different MCC contents were tested with a JGW-360a contact-angle-testing instrument (Chengde Testing Machines Ltd., Hebei, China). The surface energy (ω_A) was calculated with eq. (6) as follows:[20]

$$\omega_A = \gamma_W(1 + \cos \theta) \qquad (6)$$

where γ_W is the surface tension (7.28×10^{-2} N/m).

Fourier transform infrared (FTIR) of the composite PS membranes

The membranes were cut into pieces with areas less than 1 mm^2, blended with KBr, and ground into powders. The mixtures were then pressed into flakes before being tested with FTIR (Tensor 27, Bruker, Ettlingen, Germany).

Scanning electron microscopy (SEM)

The composite membrane and pure PS membrane were broken in nitrogen liquid, and the fractured cross sections were observed with SEM (S-3000n, Hitachi, Japan) after being sprayed with gold.[10]

Atomic force microscopy (AFM)

The membrane surfaces were scanned by AFM (XE-100, PSIA, Sungnam, Korea) under ambient conditions in a noncontact mode. A silicon cantilever with a nominal spring constant of 42 N/m and a resonance frequency of 330 KHz was used (PPP-NCH, Nanosensor, Neuchatel, Switzerland).

TABLE II
Effects of Different Reaction Times on MCC

Reaction time (h)	Yield ratio (%)	Polymerization degree	Crystallinity (%)
2.0	80.60	85	66.10
2.5	77.90	78	68.40
3.0	76.00	73	69.50
3.5	74.20	69	70.60
4.0	73.10	68	72.20
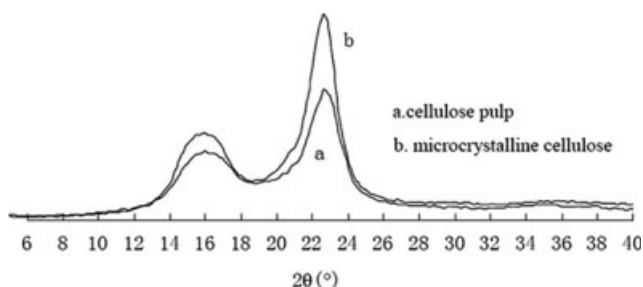
Figure 1 X-ray diffraction of the MCC and raw material.

TABLE III
Comparison of the Crystallinity and Crystal Dimensions Between MCC and the Raw Material

Sample	Crystallinity (%)	Dimensions of the crystal lattice (nm)		
		002	101	10$\bar{1}$
Cellulose pulp	54.2	5.2	4.2	4.7
MCC	75.4	5.6	4.7	5.3

RESULTS AND DISCUSSION

Preparation of MCC

The acid concentration and reaction time were important factors that affected the polymerization degree and crystallinity of the products. The yield ratio and polymerization degree decreased whereas the crystallinity increased as the acid concentration increased (Table I). The polymerization degree of the raw material (cellulose pulp) was about 750, but that of MCC was reduced remarkably to only about 50–90. The long chains of the cellulose pulp were ruptured in the hydrolysis reaction. The increase in the acid concentration increased the acid catalysis, so the hydrolysis reaction could be completed thoroughly.[21] An increasing number of noncrystal structures of cellulose became glucides, and the yield ratio decreased, whereas the crystallinity increased.[7] The crystal and noncrystal structures crisscrossed in the cellulose, and the cellulose molecules passed through both of them. Some noncrystal structures might have been enclosed within crystal structures, and these combination structures could be sufficiently taut to prevent the acid solution from entering inside and reacting with the noncrystal portions. This was one reason for the crystallinity of the product not reaching 100%.[8,9] Noncrystalline cellulose

was present in the final product. The hydrolysis reaction occurred not only in the noncrystalline section but also in the crystalline section, which had a defective structure. The defective crystal could crack, and the particles thus obtained had an intact crystal structure and increased regularity, which resulted in increased crystallinity.

The yield ratio and polymerization degree decreased whereas the crystallinity increased as the reaction time was extended (Table II). In the first 2 h of the experiments, the polymerization degree decreased sharply from 750 to less than 100. This indicates that in the 2-h reaction time, the noncrystal structures that the acid solution could reach easily were degraded, after which the degradation velocity decreased. After 2 h, the polymerization degree decreased slowly. This was probably due to the cracking of the defective crystalline cellulose, and the noncrystal structure was exposed after the degradation of the large chains; this led to a small increase in the crystallinity.

XRD of MCC

MCC had the same crystal structure as cellulose I, and the crystallinity was increased in comparison with the raw material (Fig. 1). The crystallinity of the regenerated cellulose was also increased after mechanical treatment.[10] The dimensions of the
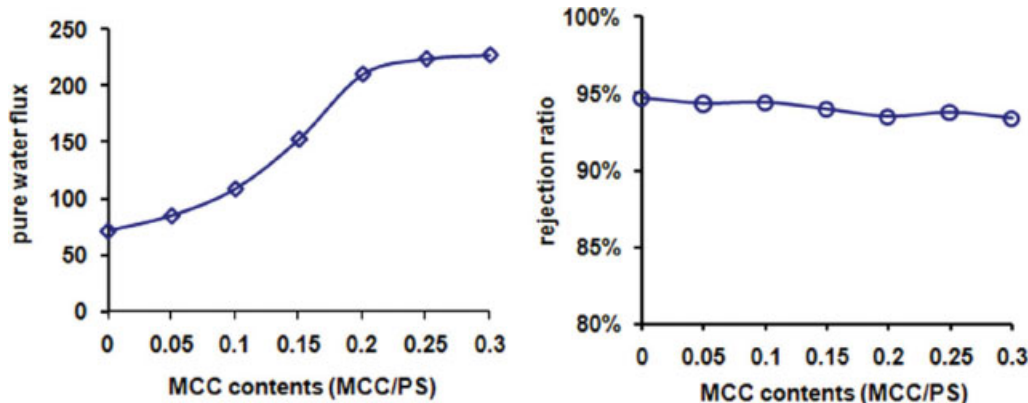

Figure 2 Effects of the MCC content on the (left) pure water flux and (right) rejection ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
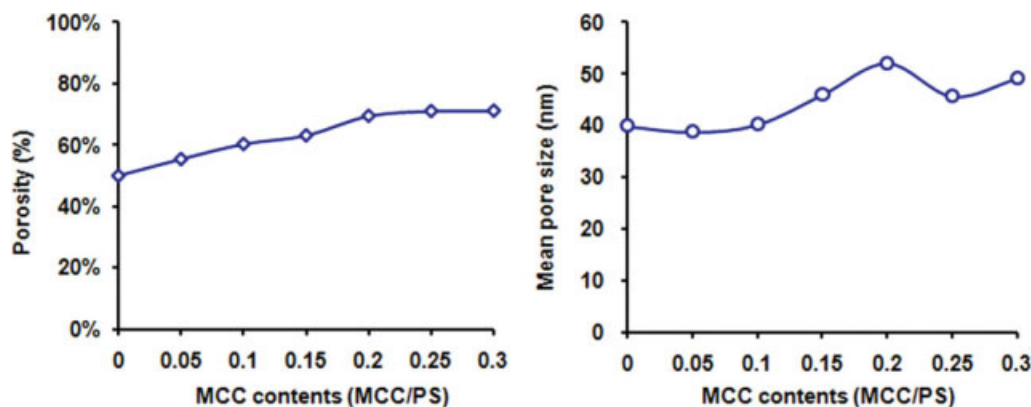
Figure 3 Effects of the MCC content on the (left) porosity and (right) mean pore size. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crystal lattice were obtained with the Scherrer formula (Scherrer constant $K = 0.94$).[3] Table III shows the crystallinity and crystal dimensions of the cellulose pulp and MCC. The mean dimensions of the MCC crystal lattice were bigger than those of the pulp because the crystal structure was defective in the raw material. After several defective crystal structures were destroyed in the hydrolysis, the mean dimensions increased a little. It is a common notion that the dimensions of the crystal lattice in a completely crystalline structure do not change during the hydrolysis reaction.[3,7]

Effect of the MCC content on the membrane performance

The pure water flux increased with an increase in the MCC content (Fig. 2). The pure water flux of the composite membrane (MCC/PS = 0.3) reached 234.16 L/m^2/h in comparison with 71.27 L/m^2/h for the pure PS membrane, whereas the rejection ratio was maintained at a high level of 93–95%. There are many hydroxide radicals in cellulose molecules,

so strong hydrogen bonds can be formed both within the molecule and between various molecules. MCC is a material with small dimensions, so it has a huge surface area and exposed hydroxide radicals. It has good moisture-absorption capability, adsorbing a substantial amount of water to form a colloidal solution. Therefore, it can accelerate the velocity of diffusion of water into a casting solution and accelerate the phase-inversion process. Because the membranes had a porous and loosened structure, the porosity and pure water flux increased.

Figure 3 shows the effects of the MCC content on the porosity and mean pore size. The porosity increased with increasing MCC content. It reached 70% versus 50% in the pure PS membrane, whereas the mean pore size increased a little, with a distribution around 40–50 nm. The liquid–liquid phase separation was increased and the phase-inversion process was altered because of the presence of MCC. It helped the generation of the inferior polymer phase and the formation of finger-shaped and column-shaped porous structures. Thus, the porosity of the membrane was increased.
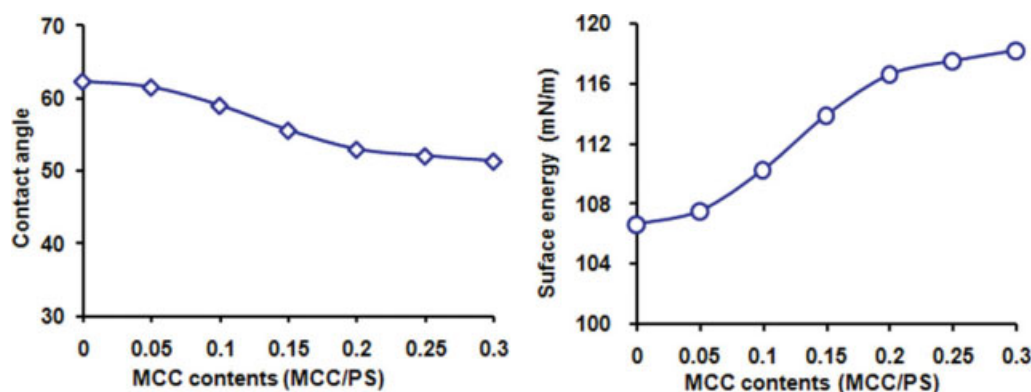

Figure 4 Effects of the MCC content on the (left) contact angle and (right) surface energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
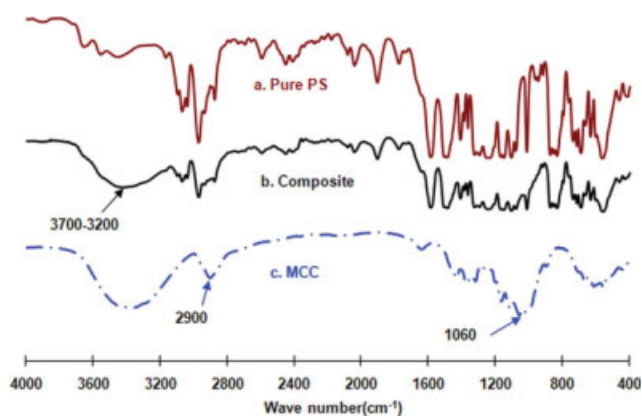
Figure 5 FTIR of the (a) pure PS membrane, (b) composite membrane, and (c) MCC. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

The contact angle between the membrane surface and water can express the hydrophilic character of the membrane. A lower contact angle implies that the membrane has excellent hydrophilic and antifouling characteristics. Figure 4 shows that the contact angle decreased with an increase in the MCC content. Therefore, the addition of MCC improved the hydrophilic nature of the PS membrane.

FTIR of the composite membranes

Figure 5 shows the FTIR spectra of pure PS, a composite membrane (MCC/PS = 0.2), and MCC. MCC retained the FTIR characteristics of pure cellulose. The peaks at 3700–3200, 2900, and 1060 cm^{-1} were attributed to the flex vibrations of O—H of cellulose hydroxide radicals, C—H of cellulose, and C—O of the ether bond in cellulose molecules, respectively. Comparing Figure 5(a,b), we find that the composite membrane had the same absorption spectrum as the pure PS membrane, but the adsorption intensity

decreased. This was because the adsorptions of PS and MCC were superimposed at the same wave numbers; however, the composite membrane had an obvious adsorption peak at 3700–3200 cm^{-1}, which was different from that of the pure PS membrane. This indicated that MCC and PS were mixed favorably and MCC was well distributed in the composite membrane.

SEM observations of the pure PS and composite membranes

SEM images showed that the pore size of the support layer of the composite membrane was larger than that of the pure PS membrane (Fig. 6). This was because MCC accelerated the velocity of the diffusion of water into the casting solution. The surface layer that formed thereafter prevented the solvent from entering the water bath and provided appropriate growing conditions for the phase with a low polymer content. The liquid phase with a low polymer content could grow favorably and form large-pore structures. The pores had good connectivity, and the porosity increased. The pure PS membrane was different and had a closed surface layer with a small pore size. Because of an increase in the number of low-polymer-phase molecules formed, rather than growing favorably, the pure PS membrane had an obvious fingerlike structure.

AFM analysis of the composite membranes

The surface of the composite membrane was dotted with bumps, and many pores of different sizes were found on it (Fig. 7). The surface layer was packed with pores of small sizes, and the support layer was loose with pores of bigger sizes. After a statistical analysis of the AFM images with XEI software, the pore size distributions on the surface and support layers were obtained. The mean pore size of the
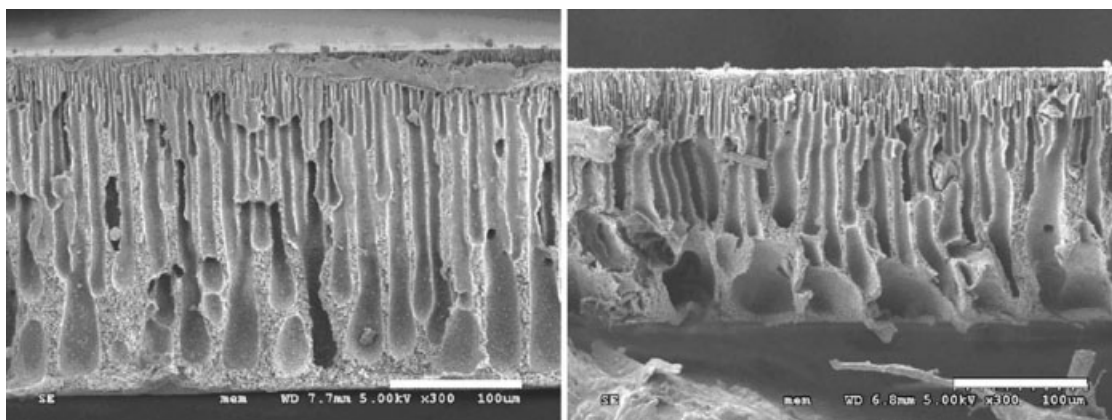

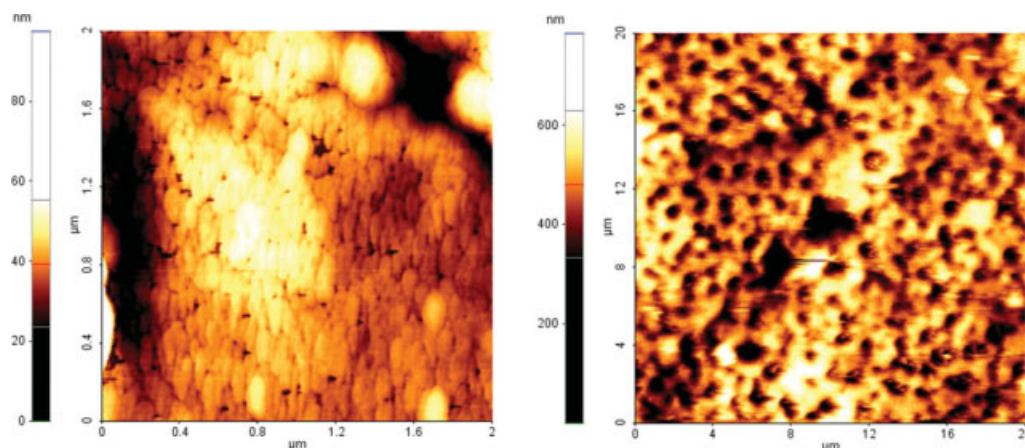**Figure 6** SEM images of the (left) pure PS and (right) composite membranes.

Figure 7 AFM images of the (left) surface and (right) support layers of the composite membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface layer was about 35 nm, which was smaller than that calculated previously. The pore sizes of the support layer were chiefly smaller than 1000 nm, and the mean pore size was about 405 nm. Therefore, the composite membrane had a typical asymmetrical membrane structure.

CONCLUSIONS

MCC was successfully prepared from cellulose pulp by acid-catalyzed hydrolysis in the presence of ultrasonic radiation. It had a high degree of crystallinity, and its polymerization degree was greatly decreased. According to XRD observations, MCC retained the crystal structure of cellulose I, which has a relatively integrated crystal structure. A composite membrane composed of PS and MCC was prepared by a phase-inversion method. When the MCC content was 30% of the PS content, the pure water flux of the composite membrane reached 234.2 L/m^2/h, and the retention of a BSA solution (1 g/L) was as high as 93.4%. The porosity of the membrane reached 70% from 50%, whereas the mean pore size increased fractionally, with a distribution around 40–50 nm. The contact angle decreased and the surface energy increased with the MCC content increasing. MCC improved the hydrophilic ability of the PS membrane. According to observations of SEM and AFM images, the membrane had an obviously asymmetrical structure. MCC changed the structure of the membrane and thereby changed its properties. The

mean pore sizes of the surface and support layers were about 35 and 405 nm, respectively.

References

1. Zhang, Y.; Ding, J.; Wang, R. J Tianjin Inst Technol 1999, 89, 15.
2. Jiang, Y.; Wang, R. Chem Eng 2003, 38, 31.
3. Peng, Y.; Liu, Y.; Qian, Y. Membr Sci Technol 2006, 31, 26.
4. Antonis Kelarakis, A.; Yoon, K.; Somani, R. H.; Chen, X.; Hsiao, B. S.; Chu, B. Polymer 2005, 46, 11591.
5. George, J.; Sreekala, M. S.; Thomas, S. Polym Eng Sci 2001, 1471, 41.
6. Nakagaito, A. N.; Yano, H. Appl Phys A 2005, 155, 80.
7. Pan, S.; Tang, L.; Wang, Z.; Zhu, Y.; Wang, Z. J Cell Sci Technol 1994, 1, 1.
8. Li, G.; Ding, E.; Li, X.; Jiang, Y. J Cell Sci Technol 2002, 12, 10.
9. Li, X.; Ding, E.; Li, G. J Cell Sci Technol 2001, 29, 9.
10. Cheng, Q.; Wang, S.; Rials, T. G.; Lee, S. H. Cellulose 2007, 14, 593.
11. Wang, S.; Cheng, Q. J Appl Polym Sci, to appear.
12. Cheng, Q.; Wang, S.; Han, Q. J Appl Polym Sci, to appear.
13. Wara, N. M.; Francis, L. F.; Bhaskar, V.; Velamakanni, B. J Membr Sci 1995, 104, 43.
14. Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M. J Membr Sci 1992, 73, 259.
15. Sivakumar, M.; Susithra, L.; Mohan, D. R.; Rangarajan, R. J Macromol Sci A 2006, 43, 1541.
16. Campos, E. A.; Gushikem, Y. J Colloid Interface Sci 1997, 193, 121.
17. Noorani, S.; Simonsen, J.; Atre, S. Cellulose 2007, 14, 577.
18. Aerts, P.; Van Hoof, E.; Leysen, R.; Vankelecom, I. F. J.; Jacobs, P. A. J Membr Sci 2000, 176, 63.
19. Li, J.; Dong, S.; Zeng, Z.; Li, X. J Funct Polym 2005, 42, 18.
20. Ke, L.; Wu, G.; Xu, S. Membr Sci Technol 2005, 25, 5.
21. Lai, Y.-Z. In Wood and Cellulosic Chemistry; Hon, D. N.-S.; Shiraishi, N., Eds.; Marcel Dekker: New York, 2000; p 450.