

Cellulose Acetate Membrane Synthesis from Biomass of Ramie

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ABSTRACT: A new route was developed for preparation of cellulose acetate (CA) membrane from ramie fiber, a sustainable biomass. Sulfuric acid catalyzed acetylation of ramie fiber was carried out in acetic anhydride. The optimum reaction conditions were determined as ramie fiber to acetic anhydride ratio 1 : 6 (w/w), temperature 353 K, and reaction time 0.5 h. To prepare CA membranes with improved properties, CA was modified with polyethylene glycol (PEG 600, $M_w = 600 \text{ g/mol}^{-1}$) and tributyl citrate (TBC). The effects of CA content and additive concentrations given by a mixture design of experiments on CA membrane compaction, morphology, water flux, water content, and mechanical properties were studied. The thermal stability and hydrophobicity/hydrophilicity of membranes pre-

pared with PEG 600 or TBC additives were also investigated. Addition of PEG 600 increased and addition of TBC decreased the thermal stability of CA membrane. The CA membranes prepared were used to separate dyes from their solutions. An inverse trend of the separation of solutions of Disperse Red S-R (DR) and Acid Scarlet 2G (AC) was observed for CA membranes modified with PEG 600 or TBC. The contact angle of CA membranes modified with PEG 600 or TBC decreased with increase in PEG 600 content, and increased with increase in TBC content. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 588–595, 2010

Key words: ramie fiber; cellulose acetate; membrane; hydrophobicity/hydrophilicity; thermal properties

INTRODUCTION

Cellulose, one of the most abundant materials in nature, is a cheap and regenerative amylose resource. The major superiority of cellulose lies in its efficient utilization:^{1,2} it is reproducible, biodegradable, biocompatible and can be derivatized. However, applications of natural cellulose have been far fewer than those of synthesized cellulose. Ramie (*Boehmeria nivea* (L.) Gaud. var. *nivea*), which is widely cultivated in southern areas of China, is one of the best plant fibers for textiles. Ramie is well known as "China grass" in Europe and America.³ The ramie resource is abundant in China, and the cellulose content of ramie is higher (65–75 wt %) than that of the other bast fibers such as hemp, flax, and jute. Most of the large reserves of ramie fibers are not used efficiently. It is important to rectify that situation and exploit applications of ramie in new technologies and materials.

Usage of natural cellulose has received increasing attention in recent years because of serious resource and environmental issues. The traditional methods for the preparation of chemical fibers produce residues that pollute the environment. Moreover, traditional methods are not economical because the preparation processes consume very large amounts of water and fuels.^{4,5}

The success of membrane technology has been impressively demonstrated for large scale industrial applications.⁶ Membrane separation technology, developed in the 1950s, has been widely used in several areas of industry since the 1970s. To apply high-tech membrane technology to natural cellulose products will provide this old material with a new potential development space. With the advent of membrane technology, separation, concentration, and purification have become industrially viable unit operations due to the high efficiency of separation. Furthermore, low energy of operation, simplicity of operation using modern compact modules, as well as recycling and re-use of chemicals and water have promoted membrane processing as a promising technique in separation processes. However, the manufacture of many membrane materials from fossil fuel materials has had negative impacts on the environment. Therefore, the production of industrial products from "green" plants is an urgent problem.

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Eco-friendly composites from plant-derived fiber and crop-derived polymers are novel materials for the 21st century and can be of great importance to the materials world, not only as a solution to growing environmental threats but also by helping to alleviate the uncertainty of the petroleum supply. There is a growing urgency to develop eco-friendly based polymers and composites and other innovative technologies that can reduce the widespread dependence on fossil fuels. The original cellulose acetate (CA) membrane, developed in the late 1950s by Loeb and Sourirajan, was made from cellulose diacetate polymer.^{7,8} The membrane is formed by casting a thin film of acetone-based solution of CA polymer with appropriate additives on a non-woven polyester fabric.^{9–11} The performance of CA can be improved by mixing it with appropriate additives to fulfill new requirements and impart associated membrane properties. Wettability is a very important property in materials, and is governed by both the surface chemical composition and geometric structure.^{12–24}

The ideal membrane requires tunable surface properties, i.e., hydrophobic or hydrophilic, large specific surface area, high porosity with desirable pore size and high density of reactive groups, in addition to the common requirements for good chemical and mechanical resistance.^{25–27} In the present work, we have developed a simple and inexpensive method for creating hydrophobic/hydrophilic surfaces on CA membranes. The hydrophobic/hydrophilic surfaces show long-term stability for pure water, and it is anticipated that this technique will make possible large scale production of hydrophobic/hydrophilic materials for industrial engineering.

There is no report on the synthesis of CA membrane from ramie fiber. Meanwhile, due to the richest reserves of the ramie fiber in China and the widely applications of CA membranes, in this article, the CA membranes have been prepared from ramie fiber, acetic anhydride and a variety of additives including PEG 600 and tributyl citrate (TBC), which were used as plasticizers incorporated in the CA membranes. Characterization of the CA membranes has also been investigated.

EXPERIMENTAL

Materials

The ramie fibers were supplied by the Hu'nan Yuanjiang Mingxing Co. (Yuanjiang, China). Acetic anhydride was purchased from the Chengdu Jinshan Chemical Co. (Jinshan, China). Acetic acid, acetone, and sulfuric acid were obtained from the Xi'an Chemicals Co. (Xi'an, China). PEG 600 was

purchased from the Tianjin Kermel Chemical Reagents Development Center (Tianjin, China). TBC was obtained from the Sinopharm Group Chemical Reagent Co. (Shanghai, China). The commercial dyes used in this study were obtained from the Xi'an Qinlong Co. (Xi'an, China). All chemicals were AR grade, used without further purification.

Measurements

Transmission Fourier transform infrared (FT-IR) spectra of membranes were collected using a Nicolet 870 spectrometer (Madison, WI); the spectra were recorded in the range 4000–400 cm^{-1} by accumulating 32 scans at 4 cm^{-1} resolution. The membranes were ground in a mortar cooled with liquid nitrogen and 1 mg of sample powder was dispersed in 150 mg potassium bromide. The membrane and KBr were carefully dried before disk preparation and were subjected to FT-IR analysis immediately after disk preparation. The transparency of membranes was examined using a UV-Vis-NIR spectrometer, model Lambda 950 (Perkin-Elmer Co., Waltham, MA).

Surfaces and cross-sections of the membranes were examined using a Philips-FEI Model Quanta 200 field emission scanning electron microscope (SEM) with acceleration voltage set to 20.0 kV (Eindhoven, The Netherlands). For preparation of the cross-sections, membranes were fractured in liquid nitrogen. The samples were gold coated by sputtering in a Bal-Tec SCD 005 instrument (BALZERS, Liechtenstein).

Differential scanning calorimeter (DSC) measurements were performed to determine the glass transition temperature of membranes, and thermogravimetric analysis (TGA) was carried out to verify their thermal stability. The glass transition temperature, T_g , was taken as the temperature corresponding to the intersection of tangents to the corresponding DSC curve. The DSC and TGA measurements were performed on a Thermoanalyzer System, model Q600SDT (TA Instruments, New Castle, DE). Samples of about 5 mg, placed in a DSC pan, were heated from 323 to 823 K at a scanning rate of 20 K min^{-1} , under a constant flow of dry nitrogen.

To determine the hydrophobicity/hydrophilicity of membranes, contact angles of water were measured with a JY-82 Tensiometer and Contact Angle Meter ($\pm 0.5^\circ$, Chengde Precision Testing Machinery Co., China). Membranes were cut to appropriate shape for dynamic mechanical analysis (Q800 DMA, TA Instruments, New Castle, DE) measurements in the single cantilever mode at 0.1 N min^{-1} elongation rate.

Procedures

Ramie fibers were swelled in acetic acid for 0.5 h at room temperature, and the swollen fibers (1.00 g) were reacted 353 K with 6 mL of acetic anhydride containing sulfuric acid as catalyst. The amount of catalyst was 0.3–0.8 wt % relative to the ramie fibers. After 30 min, a dark amber colored sol-gel of CA was obtained. Homogenous solutions of CA in acetone were prepared by adding the CA sol-gel to acetone at room temperature, with PEG 600 or TBC added. The solutions were cast on a support (culture dish) by spreading the solution via a syringe to control the thickness of the film. The membranes were cast using a doctor blade on the glass plate. The desired thickness was achieved by adjusting the height of the doctor blade. After evaporation times from 1 to 10 min to evaporate acetone, the film was immersed in a water bath (298 K) for at least 1 h to complete precipitation and formation of membranes. The membrane was removed from the water bath and washed thoroughly with distilled water to remove residual acetone and other compounds, then dried at room temperature for 24 h.

RESULTS AND DISCUSSION

A series of membranes, using combinations of CA and PEG 600 or TBC, were prepared based on the experimental design concept to improve membrane performance with respect to water flux, etc. The various combinations of CA and PEG 600 or TBC are shown in Table I.

FT-IR analysis

Figure 1 shows FT-IR spectra of the different membranes. Curves a, b, and c are spectra of the membranes of CA, CA/TBC and CA/PEG 600, respectively. After acetylation of cellulose, the spectrum of the acetylated sample (curve a) shows the expected acetyl group vibrations at 1752 cm^{-1} ($-\text{C}=\text{O}$) and 1375 cm^{-1} ($-\text{C}-\text{CH}_3$). The three spectra are similar except in the $3600\text{--}2800\text{ cm}^{-1}$ region where there are differences due to the additives.

TABLE I
Combinations of CA, Solvent, and Additive for the Preparation of Membranes

Membrane no.	CA (wt %)	Solvent (wt %)	Additive	Additive (wt %)
M _{P1}	15	80	PEG 600	5
M _{P2}	15	75	PEG 600	10
M _{P3}	15	70	PEG 600	15
M _{T1}	15	80	TBC	5
M _{T2}	15	75	TBC	10
M _{T3}	15	70	TBC	15

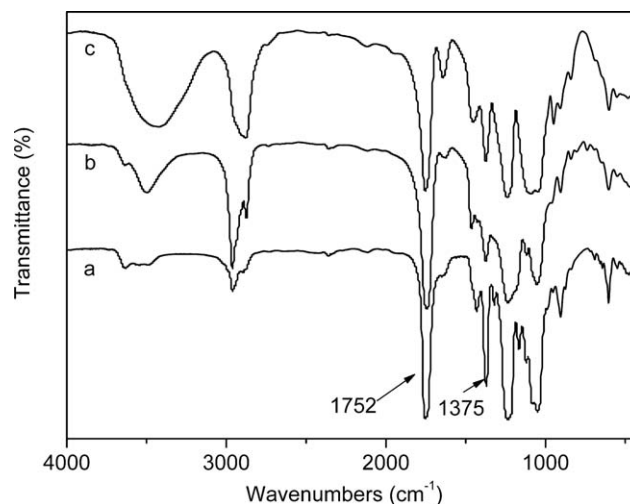


Figure 1 FT-IR spectra of different kinds of membranes. (a) CA membrane; (b) M_{T3} membrane; (c) M_{P3} membrane.

The most intense bands due to the $-\text{OH}$, $-\text{CH}$, and $-\text{C}=\text{O}$ stretching modes (ν_{OH} , ν_{CH} , and $\nu_{\text{C}=\text{O}}$) appear at $3500\text{--}3100$, 2944 and 2889 , and 1760 cm^{-1} , respectively, while the $\text{C}-\text{O}$ single bond stretching modes are located at 1228 and 1044 cm^{-1} . In the FT-IR spectra of CA, the $-\text{OH}$ stretching vibration appears as a broad band centered at 3500 cm^{-1} . The corresponding band in spectrum c (because of the OH groups in PEG 600) and in spectrum b (from TBC) strongly overlap the CA hydroxy band.

UV-Vis-NIR analysis

To compare the transparency of different membranes, UV-Vis reflectance spectra of membranes were measured with the results given in Figure 2. Curves a, b, and c are reflectance curves of CA, CA/PEG 600, and CA/TBC membranes, respectively. Figure 2 shows that the reflectance of the membranes increased when PEG 600 or TBC was added. The largest reflectance of the membranes was 37% at 255 nm , indicating that they had relatively high transparency.

TGA

TGA curves of the membranes are shown in Figure 3. Degradation of the CA membrane and the CA/PEG 600 blend membrane occurred in three stages. The first stage, from 323 to 603 K , is associated with volatilization of volatile compounds or evaporation of residual absorbed water. The second stage, starting at 603 K and ending at 673 K , is ascribed mainly to the thermal degradation of the CA chains. In the third stage, for which the onset temperature is higher than 673 K , carbonization of the degradation products to ash will occur. These three stages may

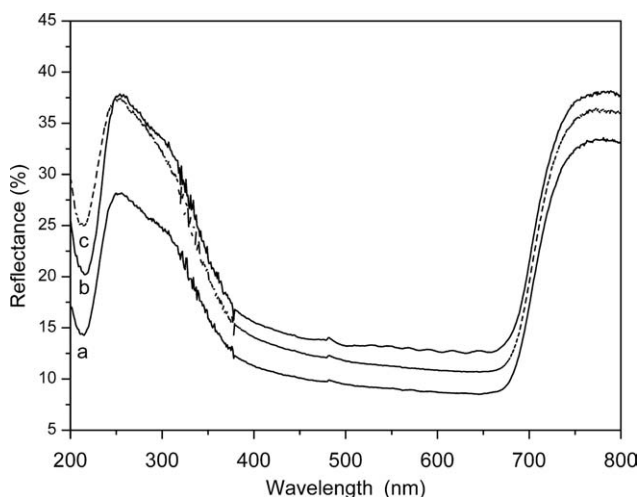


Figure 2 UV-Vis-NIR spectra of different kinds of CA membranes. (a) CA membrane; (b) M_{P3} membrane; (c) M_{T3} membrane.

be the common characteristic processes for thermal degradation of cellulose based materials. Although the thermal stability of CA is only slightly modified by the presence of PEG 600, the degradation of the CA/TBC blend membrane occurs in four stages.

The additional stage in the temperature range 473–563 K can be attributed mainly to thermal degradation of TBC. From the above results, it is noteworthy that combination of CA and PEG 600 resulted in increased thermal stability, while the addition of TBC decreased the thermal stability of CA membranes.

DSC

The glass transition temperature (T_g) is generally used to interpret membrane structure. DSC scans of CA, CA/PEG 600, and CA/TBC membranes are

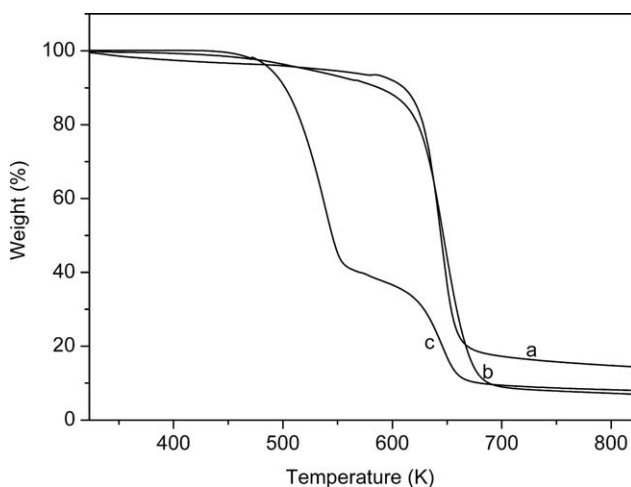


Figure 3 TGA curves of CA membranes with PEG 600 or TBC. (a) CA membrane; (b) M_{P3} membrane; (c) M_{T3} membrane.

shown in Figure 4. It is a common fact that a lower T_g implies more free volume and consequently a looser structure, and vice versa. It is interesting to note that the glass transition temperature shifts to lower temperatures with addition of PEG 600 or TBC. For CA, CA/PEG 600, and CA/TBC membranes typical values of T_g were 583, 569, and 543 K, respectively.

When the thermal flow of the samples is considered, in general all the membranes show endothermic peaks. The differences in the endothermic heat flows could be due to the differences in the PEG 600 or TBC contents as well as the packing density in the different membranes.

Morphology

Figure 5 illustrates the morphology of different CA membranes. By adding a small amount of PEG 600 or TBC to CA, the structure of the CA membrane can be changed. Figure 5 shows typical cross-section morphologies of CA/PEG 600 and CA/TBC membranes. CA/PEG 600 membrane displayed the rough cross-section and there are some pores in CA membrane, which was shown in Figure 5(b). This was caused by the solubility of PEG 600 in water, when the PEG 600 went into the water it leave the hole in the CA membrane.

However, the cross-section of CA/TBC membrane was smooth as shown in Figure 5(d). The cross-sections show highly interconnected pores, which would provide high internal surface areas for the membranes. This may be due to the lower ability of TBC to dissolve in water than that of PEG 600. When PEG 600 is leached by water from CA/PEG 600 membrane, it will leave pores in the membrane. On the other hand, TBC is hydrophobic and not

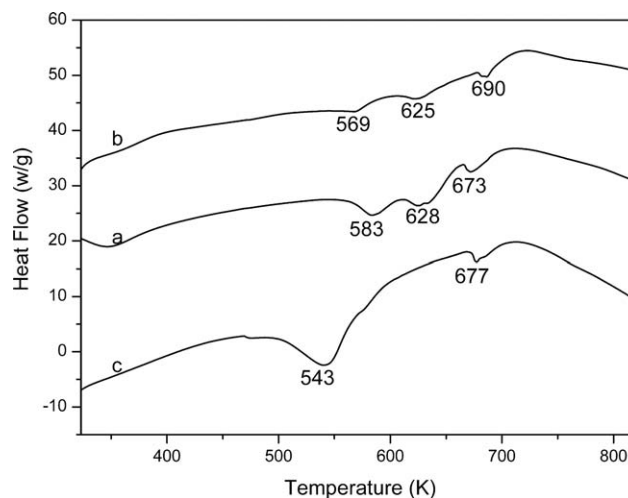


Figure 4 DSC curves of CA membranes with PEG 600 and TBC. (a) CA membrane; (b) M_{P3} membrane; (c) M_{T3} membrane.

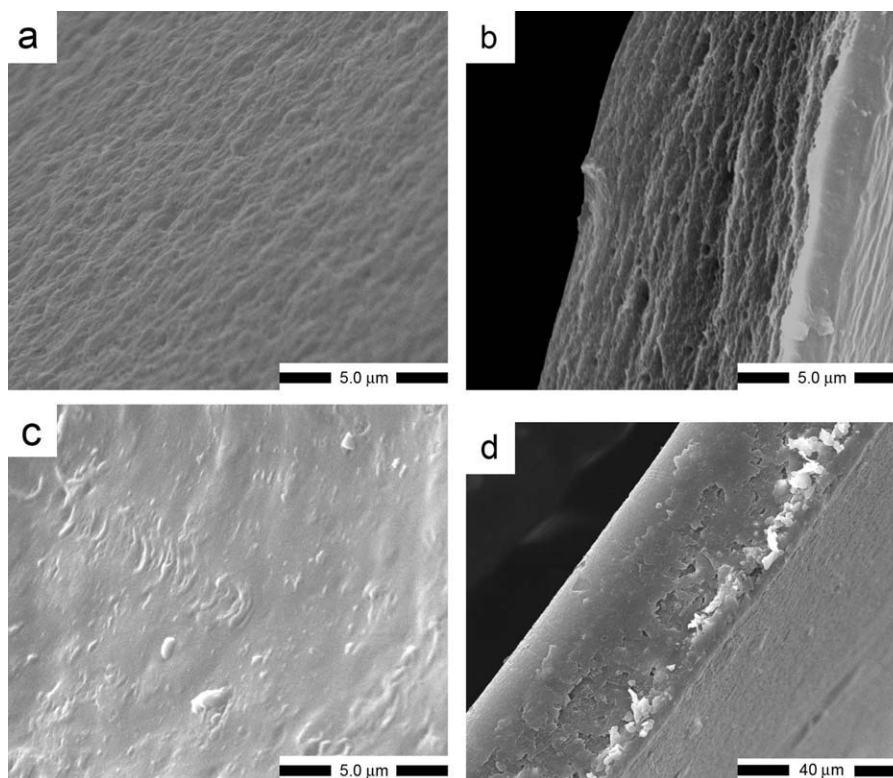


Figure 5 SEM micrographs of membranes. CA/PEG 600 blend, surface (a), cross-section (b); and CA/TBC blend, surface (c), cross-section (d).

water soluble, so that when CA/TBC membrane was immersed in water TBC would not have been leached out of the membrane. Thus, the cross-section of the CA/TBC membrane is much smoother than that of the CA/PEG 600 membrane. This factor also led to the different surface morphology of the CA/PEG 600 and CA/TBC membranes [Fig. 5 (a,c)].

Water flux

Membranes were subjected to water flux determination at a trans-membrane pressure of 0.1 MPa at 20°C for 5 h. The prepared membranes were cut into desired size needed for fixing it up in the filtration equipment of 5 cm². The flux of dye solution was tested at the same conditions above. The permeability was measured under steady state flow, and the water flux was determined using eq. (1).²⁸

$$J_w = \frac{Q}{A \times \Delta T} \quad (1)$$

where J_w is the water flux (l m⁻² h⁻¹), Q is the quantity of permeate (l), A is the membrane area (m²), and ΔT is the sampling time (h).

The effect of the additives on the water flux of CA membranes is listed in Table II. It is apparent that the water flux of CA blends with PEG 600 is much larger than that of CA/TBC blends. Increasing in

PEG 600 concentration increases the water flux because a greater number of pores were formed. It was observed that the CA/PEG 600 membranes designated as M_{P1} , M_{P2} , and M_{P3} , prepared from CA with 5, 10, and 15% PEG 600, showed a steady state water flux. However, the CA/TBC membranes M_{T1} , M_{T2} , and M_{T3} , prepared from CA with 5, 10, and 15% TBC, showed small water flux. It is also seen from Table II that the permeate flux of all dyes increased when higher content of PEG 600 in CA. This may be due to the presence of PEG 600 in the casting solution forming larger pores on the surface layer. However, when the wt % of TBC increased from 5% to 15%, the permeate flux of all dyes decreased. This may be due to the hydrophobic character of TBC. By contrast, PEG 600

TABLE II
Effect of Additives on Water Flux of Membranes^a

Membrane no.	Water flux (l m ⁻² h ⁻¹)	Flux for DR (l m ⁻² h ⁻¹)	Flux for AC (l m ⁻² h ⁻¹)
M_{P1}	9.80	9.34	9.22
M_{P2}	10.70	9.67	9.36
M_{P3}	25.71	24.29	23.64
M_{T1}	1.38	0.96	0.65
M_{T2}	0.92	0.44	0.37
M_{T3}	0.73	0.37	0.28

^a Conditions: 0.1 MPa, 20°C, 5 h.

TABLE III
Water Content of the Membranes

Membranes no.	Water content (%)
M _{P1}	60.22
M _{P2}	55.56
M _{P3}	53.25
M _{T1}	38.42
M _{T2}	23.35
M _{T3}	20.12

is much more hydrophilic than that of TBC, and led to a much higher porosity membrane structure after extraction of PEG 600 by water from CA/PEG 600 membranes.

Saturation water content

The water content of membranes was obtained as follows. The membranes were soaked in water for 24 h and weighed after mopping with blotting paper. The wet membranes were dried in a vacuum oven at 333 K for 48 h and the dry weights determined. The percent water content was evaluated from eq. (2).²⁹

$$\% \text{Water content} = \frac{\text{Wet sample weight} - \text{Dry sample weight}}{\text{Wet sample weight}} \times 100 \quad (2)$$

The water contents of the membranes with different additives in the casting solution are listed in Table III. The addition of PEG 600 to a casting solution of pure CA enhanced the water content of the membranes. This is clearly apparent from the values obtained for the M_{P1} to M_{P3} membranes, with PEG concentration increasing from 5% to 15% and corresponding increases in the water content.

A similar (but converse) trend was also found for membranes M_{T1} to M_{T3}, where the water content decreased with increase in the proportion of TBC. The variation of water content in the membranes can be explained on the basis of hydrophilic/hydrophobic properties of the additives. The greater the hydrophilicity of the additive, the more pores that are formed by dissolution of the additive. Thus, the hydrophilic/hydrophobic properties of the membrane can be regulated and controlled over a wide range by changing additives and their concentrations. The thickness of wet membranes was obtained by soaking the membranes in water for 24 h and measured after mopping with blotting paper. The thicknesses of wet and dry membranes were about 20 to 30 μm, which were not quite dif-

TABLE IV
Water Contact Angle of Membranes

Membranes no.	Contact angle (°)
M _{P1}	61.30
M _{P2}	60.20
M _{P3}	58.40
M _{T1}	73.20
M _{T2}	78.50
M _{T3}	81.30

ferent. This may be caused by the low content of additives.

Assessment of the hydrophobicity/hydrophilicity of membranes

The water contact angles of the membranes are shown in Table IV. The changes of the contact angle reflect the hydrophobicity of membranes. Thus, the contact angle of membranes decreased with increase in the concentration of hydrophilic PEG 600, and increased on increase in the concentration of hydrophobic TBC.

Mechanical properties

Mechanical properties for the membranes are listed in Table V, and reveal that the stress increased with increase in the concentration of additive. The increase in additive concentration increases the stress because more hydrogen bonds are formed between the hydroxyls and the CA molecules. Because there are more hydroxyls in PEG 600 than in TBC, the stresses of membranes M_{P1} to M_{P3} are nearly twice those of M_{T1} to M_{T3}. The changes of strain of the membranes are also related to the content of hydroxyl group reacted with additive. Proper amount of hydroxyl group increased the strain of membranes, however, too much hydroxyl leads to increased crystallization of the membranes, thus the strain decreased.

Dye rejection studies

The rejection capacity of CA membranes was determined by measuring changes of absorbency of a dye

TABLE V
The Stress and Strain of Different Kinds of Membranes

Membrane no.	Stress (MPa)	Strain (%)
M _{P1}	25.65	3.96
M _{P2}	28.97	5.97
M _{P3}	30.05	4.55
M _{T1}	18.29	1.86
M _{T2}	20.34	2.08
M _{T3}	21.62	1.73

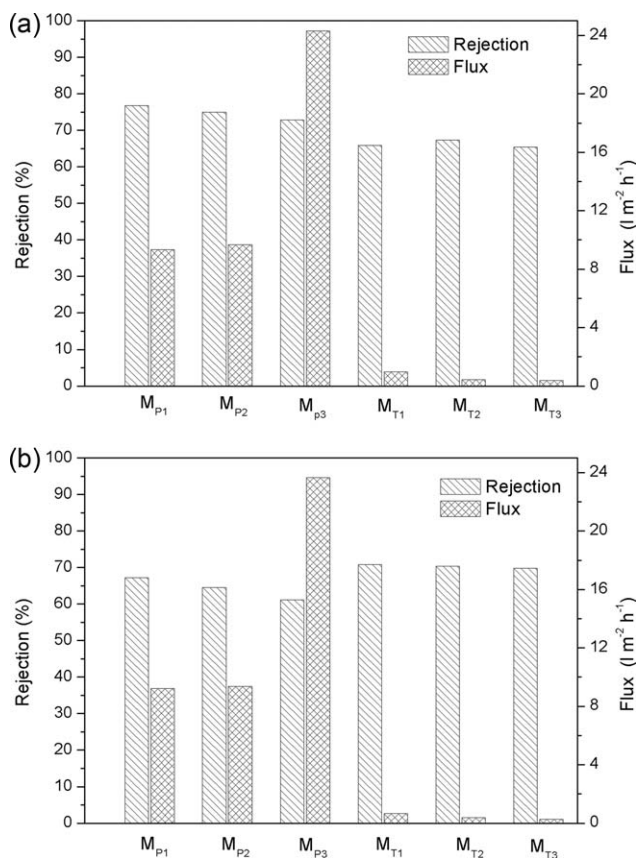


Figure 6 (a) Percentage rejection and water flux of DR separated by membranes. (b) Percentage rejection and water flux of AC separated by membranes.

solution after rejection by CA membranes. The dyes used were Disperse Red S-R (DR, $C_{22}H_{25}N_5O_7$, $M_W = 471$ g/mol), and Acid Scarlet 2G (AC, $C_{23}H_{18}N_3O_6S_2Na$, $M_W = 520$ g/mol), which were purified in acetone before use. The rejection behavior of the membranes was studied at 20°C by passing the dye solutions ($1,000 \mu\text{g l}^{-1}$) through the prepared membranes at 0.1 MPa pressure.

In relation to the percentage rejection during separation of different solutions, an inverse trend was observed as shown in Figure 6. Higher content of PEG 600 gave lower rejection of DR in the range 76.78–72.88% and AC in the range 67.26–61.14%. Membranes prepared using higher proportions of PEG 600 showed decreased percent rejection of both dyes. Higher TBC content did not significantly change rejection of the dyes. This may be due to the different membrane structures of the two kinds of membranes. CA membrane is a lipophilic material, and the more paraffin in the dye molecule, the more dye will be rejected. There are more alkyl groups in the DR structure than in AC, thus, the rejection capacity for DR is larger than for AC.

It is also seen from the Figure 6(a,b) that the permeate flux of all the dyes is increased when higher content of PEG 600 and it was decreased with the

wt % of TBC is increased. This may be due the different character of PEG 600 and TBC, and this was also demonstrated in Table II.

CONCLUSIONS

A new route was developed for preparation of CA from ramie fiber, a sustainable biomass. The new route for preparing CA porous membrane from biomass of ramie fiber will contribute to protection of the environment.

Acetylation of ramie fiber is effected in a medium (acetic anhydride) that is both acetylating reactant and the solvent for the catalyst and soluble reaction products. This strategy is adopted to minimize the chemicals used. The optimum reaction conditions for preparation of CA by reacting ramie fiber with acetic anhydride under acidic condition were determined, namely ramie fiber to acetic anhydride ratio 1 : 6 (w/w), at 353 K for 0.5 h. CA membrane was prepared by solution casting the synthesized CA.

CA membranes incorporating additives were prepared using the mixture design of experiments concept, for modified CA membrane characteristics such as water flux, dye rejection, water content, and membrane hydrophilicity/hydrophobicity. To prepare membranes with improved properties, CA was modified with PEG 600 and TBC. The permeation properties of a series of CA membranes, presenting a wide range of characteristics, were determined and correlated with the pore structure, the polymer hydrophilicity/hydrophobicity, and the morphology of the surface of the active layer. The process of dye wastewater treatment through nanofiltration membrane was studied. The membrane shows higher rejection for dye solutions. PEG 600 and TBC also have a significant role in altering the thermal properties, especially thermal stability, of the membranes.

References

1. Yang, K.; Wang, Y. J.; Kuo, M. I. *Biotechnol Prog* 2004, 20, 1053.
2. Yang, K.; Wang, Y. J. *Biotechnol Prog* 2003, 19, 1664.
3. Liu, F. H.; Li, Z. J.; Liu, Q. Y.; He, H.; Liang, X. N.; Lai, Z. J. *Genet Resour Crop Evol* 2003, 50, 793.
4. Qu, Z. L.; Jiang, H. W. *Synth Fiber Ind* 1995, 18, 33.
5. Zhang, X. S.; Zhu, J. L. *Chem Ind Times* 2004, 18, 1.
6. Rosberg, P. *Desalination* 1997, 110, 107.
7. Li, D. F.; Chung, T.-S.; Ren, J. Z.; Wang, R. *Ind Eng Chem Res* 2004, 43, 1553.
8. Altena, F. W.; Smolders, C. A. *Macromolecules* 1982, 15, 1491.
9. Khan, S.; Ghosh, A. K.; Ramachandran, V.; Bellare, J.; Hanra, M. S.; Trivedi, M. K.; Misra, B. M. *Desalination* 2000, 128, 57.
10. Zeman, L.; Fraser, T. *J Membr Sci* 1994, 87, 267.
11. Altena, F.; Smid, J.; Van Den Berg, J. W. A.; Wijmans, J. G.; Smolders, C. A. *Polymer* 1985, 26, 1531.
12. Shibuichi, T. S.; Onda, T.; Satoh, N.; Tsuji, K. *J Phys Chem* 1996, 100, 19512.

13. Chen, Y.; He, B.; Patankar, N. A. *J Colloid Interface Sci* 2005, 281, 458.
14. Miwa, M.; Nakajima, A.; Hashimoto, K. *Langmuir* 2000, 16, 5754.
15. Nakajima, A.; Hashimoto, K.; Watanabe, T. *Langmuir* 2000, 16, 7044.
16. Nakajima, A.; Fujishima, A. *Adv Mater* 1999, 16, 1365.
17. Youngblood, J. P.; Mccarthy, T. J. *Macromolecules* 1999, 32, 6800.
18. Bico, J.; Queed, M. *Europhys Lett* 1999, 47, 220.
19. Ma, M.; Hill, R. M.; Lowery, J. L. *Langmuir* 2005, 21, 5549.
20. Feng, L.; Li, S.; Li, Y.; Zhang, J.; Jiang, L.; Zhu, D. *Adv Mater* 2002, 14, 1857.
21. Ren, S.; Yang, S.; Zhao, Y.; Yu, T.; Xiao, X. *Surf Sci* 2003, 546, 64.
22. Feng, L.; Song, S.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2003, 42, 800.
23. Herminghaus, S. *Europhys Lett* 2000, 52, 165.
24. Shang, H.; Wang, Y.; Limmer, L. S. *Thin Solid Films* 2005, 472, 37.
25. Xia, B.; Zhang, G.; Zhang, F. *J Membr Sci* 2003, 226, 9.
26. Suen, S.-Y.; Liu, Y.-C.; Chang, C.-S. *J Chromatogr B* 2003, 797, 305.
27. Karakoc, V.; Yavuz, H.; Denizli, A. *Colloids Surf A* 2004, 240, 93.
28. Liu, C. X.; Bai, R. B. *J Membr Sci* 2005, 267, 68.
29. Arthanareeswaran, G.; Srinivasan, K.; Mahendran, R.; Mohan, D.; Rajendran, M.; Mohan, V. *Eur Polym J* 2004, 40, 751.