Morphology and Properties of Cellulose/Chitin Blends Membranes from NaOH/Thiourea Aqueous Solution

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ABSTRACT: Blend membranes of chitin/cellulose from 12 : 50 to 12 : 250 were successfully prepared from cotton linters in 1.5M NaOH/0.65M thirourea solution system. Two coagulation systems were used to compare with each other, one coagulating by 5 wt % H_2SO_4 (system H), and the other by 5 wt % $CaCl_2$ and then 5 wt % H_2SO_4 (system C). The morphology, crystallinity, thermal stabilities, and mechanical properties of the blend membranes were investigated by electron scanning microscopy, atomic absorption spectrophotometer, infrared spectroscope, elemental analysis, X-ray diffraction, different scanning calorimeter, and tensile tests. The cellulose/chitin blends exhibited a certain level of miscibility in the weight ratios tested. There were great differences between the two blends H coagulated with H_2SO_4 and C coagulated with $CaCl_2$ and H_2SO_4, respectively. The membranes H have a denser structure, higher thermal stability, tensile strength (σ_b), and crystallinity (χ_c), and values of σ_b (90 MPa for chitin/cellulose 12 : 150) were significantly superior to that of both chitin and regenerated cellulose membrane. However, the blend membranes C have much better breaking elongations (ϵ) than that of membranes H, and relatively large pore size ($2r_e = 210$ μm), owing to the removal of a water-soluble calcium complex of chitin as pore former from the membranes C. When the percentage content of chitin in the blends was from 5 to 7.5%, the values of breaking elongation for the blend membranes H and C all were higher than that of unblend membranes, respectively. The blends provide a promising way for application of chitin as a functional film or fiber in wet and dry states without derivates. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2025–2032, 2002

Key words: chitin; cellulose; blend membrane; coagulation conditions

INTRODUCTION

Recently, polymers from renewable resources have attracted much attention because of their biodegradability and potential to substitute for the petroleum resources in some fields.[1] Chitin, obtained from lobster, shrimp, and crab shell waste, is the second most abundant polysaccharide found in nature. It consists of a linear polymer of β (1 → 4) D-glucopyranose units backbone, and the 2-hydroxy is replaced by an acetamide group. It was reported that chitin and its derivatives are used in such areas as pharmaceutical and biomedical applications, paper production, textile finishes, photographic products, cements, heavy medical chelating agents, membranes, hollow fibers, and so on.[2–5] There were many studies especially of chitin as a biocompatible material, such as for artificial skin,[6–7] suture,[8] coating materials,[9] drug carrier,[10–12] and biomaterial.[13] Being a natural and biodegradable recourse, chitin has played an important role in dealing with pollution problems, as a environmental-friendly material.[14] Therefore, at the onset of the 21st century, chitin science and allied technologies face new opportunities to contribute the functional materials and environmental friendly materials to meet the diverse needs of today's society because of its nontoxic, biodegradable, biocompatible, antibacterial, and moisture retaining, and healing characteristics. However, poor solubility of chitin in many solvents and brittle properties limit its use. To solve the solubility problems of chitin, the modification of chitin, including glycol chitin,[15] O-alkyl chitin,[16] and carboxymethylated chitin,[17] discovers new solvents such as N,N-dimethylacetamide/LiCl.[18]

Generally, blending is a very simple process used for developing new materials. Miscibility among components has a marked influence on the mechanical properties of polymer blends, and hydrogen-bonding interaction in the blends is an important aspect of miscibility.[19] It was reported that the morphology and mechanical behaviors of polyamide 6/chitosan blends by casting their solution in formic acid,[20] an improvement for mechanical properties of β-chitin/poly(vinyl alcohol) blend films prepared in formic acid,[13] and
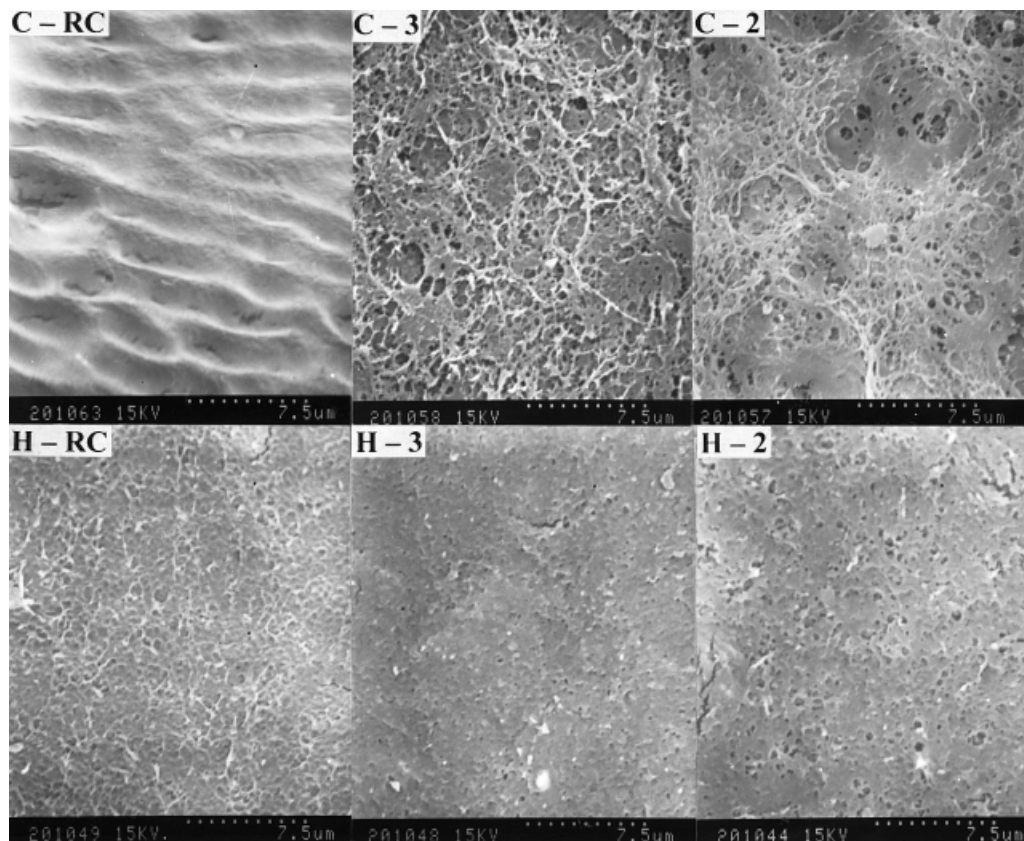
Figure 1 SEM of the free surface of the membranes.

semi-interpenetrating polymer networks (IPNs) of poly(N,N-dimethylacrylamide)/chitin in lithium chloride/N,N-dimethylacetamide,[20] etc. In our lab, we have exploited blends of two natural polymers in aqueous solution such as cellulose/alginate,[21] cellulose/silk fibroin,[22] carboxymethylated chitosan/alginate,[23] and so on. The mechanical properties of these blends as functional materials have been significantly improved compared to that of homopolymers.

It is well known that chitin is difficult to be processed as a solution because of the large amounts of strong interchain hydrogen bonds. Recently, we have developed a novel solvent (aqueous NaOH/thiourea) of cellulose,[24–25] which can dissolve cellulose and chitin to obtain a homogeneous solution and a blend membrane.[26] In this article, we attempted to prepare blends from in chitin and cellulose in 1.5M NaOH/0.65M thiourea aqueous solution. The blend miscibility and the effects of different coagulation condition on structure, mechanical properties, and transformation of crystal of the blends were investigated and discussed as functional materials.

EXPERIMENTAL

Materials

The cotton linters were supplied by Hubei Chemical Fiber Group, Ltd., and its viscosity-average molecular weight (M_η) was determined to be 10.3×10^4. All of the chemical reagents used in this work were of analytical grade and were purchased from commercial resources in China. Chitin was supplied by Zhejiang Yuhuan Co., Ltd., China, and its M_η was determined to be 1.31×10^6 and its degree of acetylation was 92.5%.

Preparation of membranes

The cellulose solution in 1.5M NaOH/0.65M thiourea aqueous solution was prepared according to a previous procedure (patent).[24] Ten grams of cellulose was dissolved in 1.5M NaOH/0.65M thiourea aqueous solution and was placed below 0°C for 8 h. Then, it was stirred vigorously for 1 h to obtain 5 wt % cellulose solution (I). Twenty grams of chitin was immersed in 16 mL 46 wt % NaOH in an ice bath for 6 h, and 103.8 g ice pieces was added to obtain 1.2 wt % chitin solution (II). A mixture of II and I was stirred, filtered, and degassed. The resulting mixture was cast on a glass plate to give a thickness of 0.2–0.3 mm and then immediately placed in a coagulation bath. There were two coagulation systems, one immersed in 5 wt % H$_2$SO$_4$ for 5 min, and subsequently 10 wt % glycerin for 10 min was coadded as H system. Another immersed in 5 wt % CaCl$_2$, and the following steps were the same as the H system coded as C system. The clear
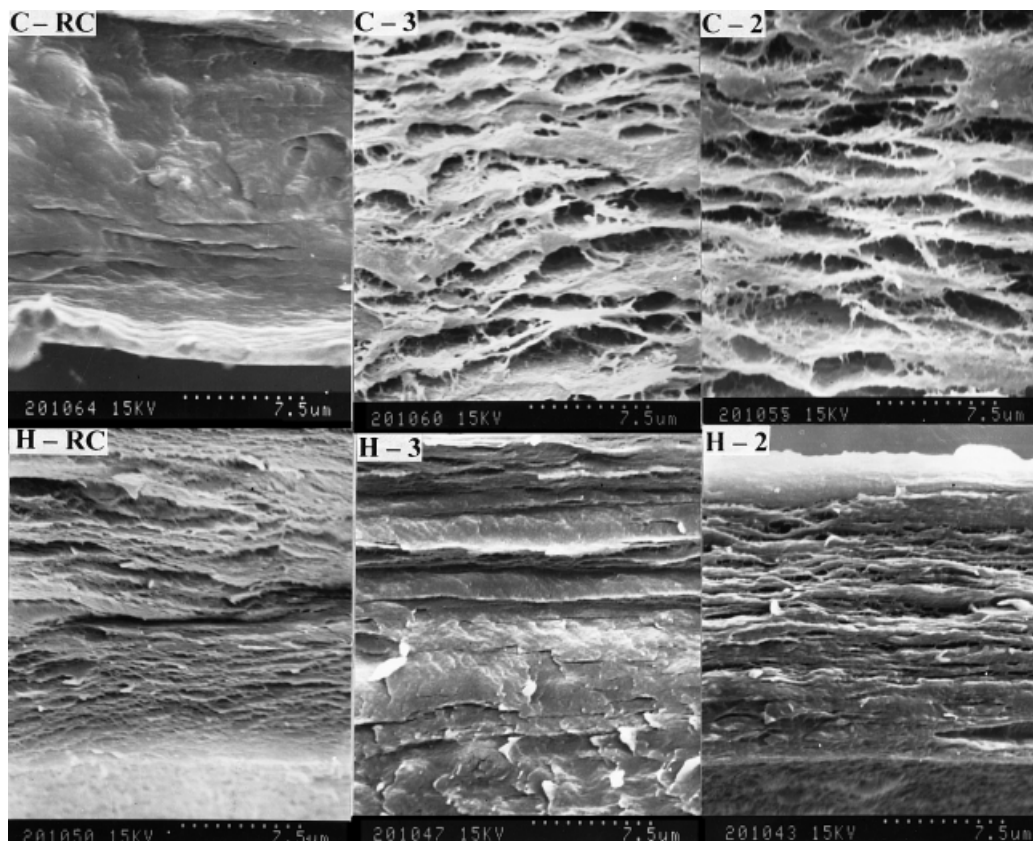
Figure 2 SEM of the fracture surface of the membranes.

blend membranes obtained were washed in running water for 5 min, followed by drying in air. By changing the weight ratio of cellulose to chitin such as 50 : 12, 100 : 12, 150 : 12, 200 : 12, and 250 : 12, two series of regenerated cellulose/chitin blend membranes were prepared, coded as H-1, H-2, H-3, H-4, and H-5 and as C-1, C-2, C-3, C-4, and C-5, respectively. The membranes H-RC and C-RC were prepared from pure cellulose in 1.5M NaOH/0.65M thiourea aqueous solution, and pure chitin as a precipitant cannot form membranes.

Characterizations

IR spectra of the membranes were recorded with a Spectrum One FTIR Spectrometer (Perkin–Elmer Instruments, USA). Scanning electron micrographs (SEM) were taken with a Hitachi X-650 SEM. The wet membranes were frozen in liquid nitrogen and snapped immediately, and then were vacuum dried. The free surface (side directly in contact with coagulant) and fracture surface were coated with carbon and gold and observed and photographed.

The X-ray diffraction was measured with an X-ray diffractometer (D/MAX 1200, Rigaku Denki, Japan). The X-ray diffraction patterns with CuKα radiation (λ = 1.5406 $\times$ 10^{-10}M) at 40 kV and 30 mA were recorded in the range of 2θ = 6–40°. The degree of crystallinity (χ_c) was calculated according to the usual method.[27]

The elemental contents of nitrogen in the blend membranes were determined by an elemental analyzer (CHN-O-RAPID Heraeus Co., Germany). The constant of calcium and sodium in the dried membranes was determined with a Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrophotometer (AAS). The membranes were treated as follows: 20 mg of membrane, 4 mL concentrated HNO$_3$, and 2 mL 30% H$_2$O$_2$ were heated at 100°C, keeping the solution slightly boiling. Two milliliters of concentrated HNO$_3$ was added after cooling and then heated at 100°C until the solution concentrated to $\sim$ 0.5 mL. After cooling, the residual solution was diverted into a container of 50 mL and diluted by distilled water to use for AAS determination.

The different scanning calorimeter (DSC) analysis for the membranes was performed on a thermal analyzer (DTA 1700, Perkin–Elmer) under air atmosphere at a heating rate of 20°C min^{-1} from room temperature to 400°C.

The tensile strength (σ_b) and breaking elongation (ϵ_b) of the membranes in dry and wet states were measured on a universal testing machine (CMT 6503, Shenzhen SANS Test Machine Co., Ltd.) according to
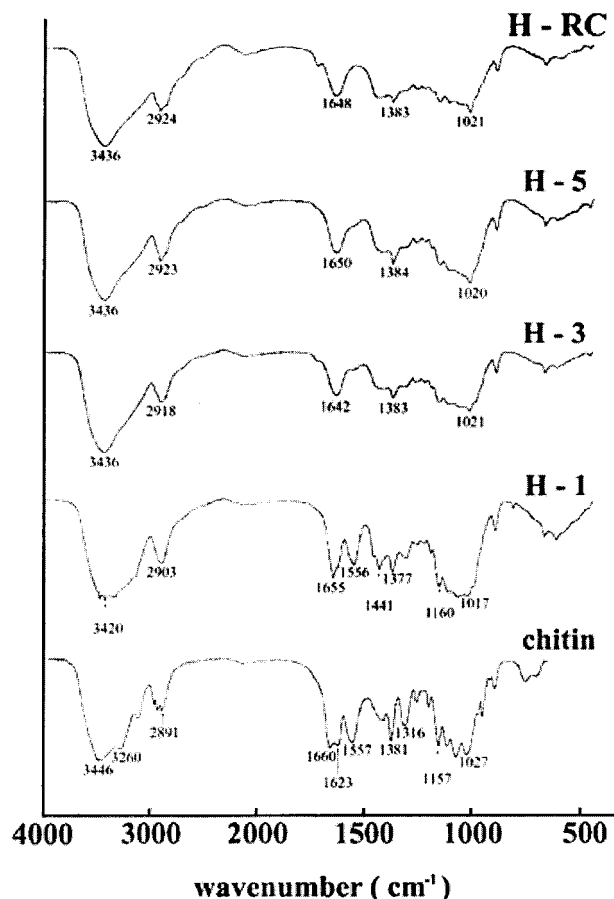
Figure 3 IR spectra of the membranes H coagulated with 5 wt % H_2SO_4.

Figure 4 IR spectra of the membranes C coagulated with 5 wt % $CaCl_2$ and then 5 wt % H_2SO_4.

ISO 6239-1986 (E) under the following conditions: sample width, 10 mm; length, 70 mm (50 mm between the grips); stretch rate, 5 mm min^{-1}. The wet state membranes were measured immediately after soaking in water for 1 h.

The water resistivity (R) of the membranes was evaluated from σ_b (dry) value in dry state and σ_b (wet) in wet state by the equation

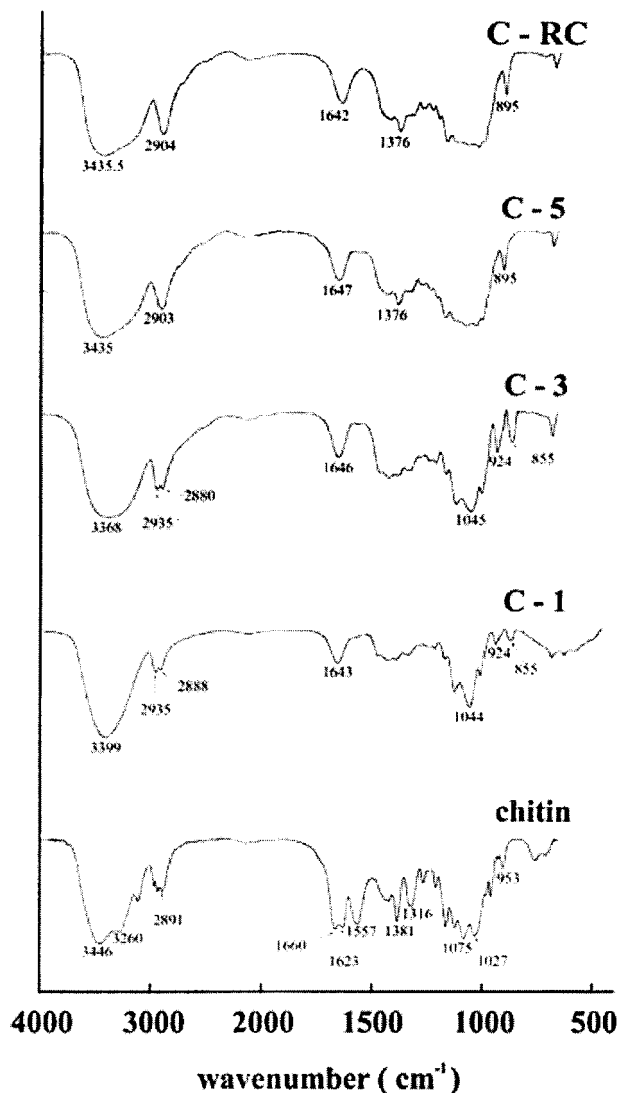$$R_b = [\sigma_b(\text{wet})/\sigma_b(\text{dry})] \times 100\%$$

RESULTS AND DISCUSSION

Table I shows the content of elements N, Ca, and Na in the membranes. The Ca and Na contents in the membranes (Table I) did not exceed 0.1%, indicating that

TABLE I
The Contents of Nitrogen, Calcium and Sodium, Crystallinity (χ_c), and Mechanical Properties of the Membranes

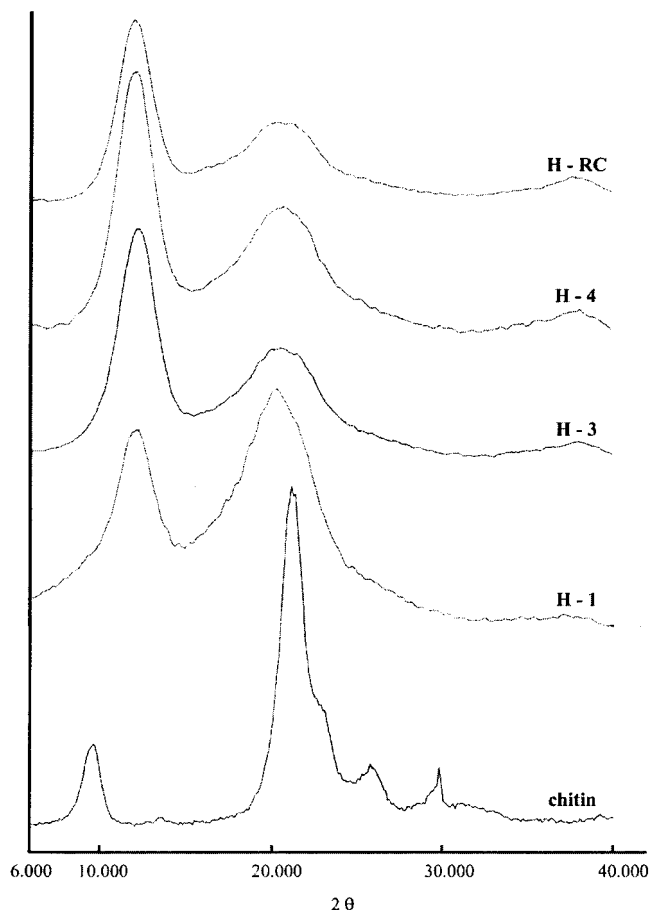| Samples | N (%) | | Ca^{2+} | Na^+ | χ_c | Intensity | | σ_b (MPa) | | R_b | ε (%) | |
	Calculated	Tested	(%)	(%)	(%)	I_{110}/I_{IT0}	I_{200}/I_{IT0}	Dry	Wet	(%)	Dry	Wet
H-1	1.22	1.08	—	—	60	0.89	0.59	64	4	6	3	9
H-3	0.47	0.37	—	—	65	0.26	0.17	90	17	19	5	17
H-4	0.40	0.39	—	—	69	0.22	0.23	73	13	18	5	18
H-RC	—	—	—	—	67	0.20	0.17	53	20	38	11	28
C-1	1.22	0.61	0.063	0.081	54	1.82	1.08	4	1	31	21	12
C-2	0.69	0.38	0.022	0.062	48	1.80	2.00	11	4	39	24	22
C-3	0.47	0.24	0.044	0.053	53	1.34	1.08	9	5	55	20	30
C-RC	—	—	—	—	66	0.05	0.09	62	19	31	7	14

Figure 5 X-ray diffraction spectra of the membranes H coagulated with 5 wt % H_2SO_4.

blend membranes H and C consist of cellulose and chitin, and Ca and Na from solvents and coagulants were removed during the process. The N content in membrane H is almost the same with the theory-calculated values, whereas half of the N content was lost in membrane C. It can be explained that the calcium ions can be chelated by chitin during the coagulating process to form a calcium complex, which was washed away.

The SEM of the membranes is shown in Figures 1 and 2. This shows a homogeneous structure in free surface and fracture surface, indicating a certain level of miscibility of the blend membranes. However, there are apparent differences between the two blend membranes coagulated with 5 wt % H_2SO_4 and 5 wt % $CaCl_2$, then 5 wt % H_2SO_4. In Figure 1, the membranes H have smoother surfaces, denser structure, and relatively smaller porosity than the membranes C. The surfaces of blend membranes C-2 and C-3 have relatively large porosity, whereas the membrane C-RC has a dense and nonporous structure. The membrane C-3 especially exhibited a mess structure which was not found for membranes H. The mesh structure of the membranes C may be caused by coagulation with

$CaCl_2$ aqueous solution, and a same result was obtained for the cellulose membranes and its blends with alginate in 6 wt % NaOH/4 wt % urea aqueous solution.[28] In Figure 2, the fracture surface of the blend membranes showed a layerlike structure and from the membrane H-RC to H-3 the layers became thinner with an increase in chitin content. However, the membranes C had an apparent channellike porous structure and even channellike structures, in which the pore size ($2r_e$ = 210 μm) was relatively large. The result supported the finding that the intermolecular hydrogen bonds between the cellulose and chitin in the blends can be broken into 5 wt % $CaCl_2$ aqueous solution, and a water-soluble calcium complex part of chitin as a pore former was removed.

IR spectroscopy is useful to study the hydrogen bonding and other interactions as well as the miscibility. Figures 3 and 4 show the IR spectra of the blend membranes C and H. The major peaks for the regenerated cellulose membranes C-RC and H-RC (cellulose-II)[29] are located at 3436 cm^{-1} for —OH stretching vibration, 1642 cm^{-1} for C, and 1648 cm^{-1} for H of trace water. Usually, IR spectrum of α-chitin exhibited major peaks at 3446 cm^{-1} for —OH stretching vibra-
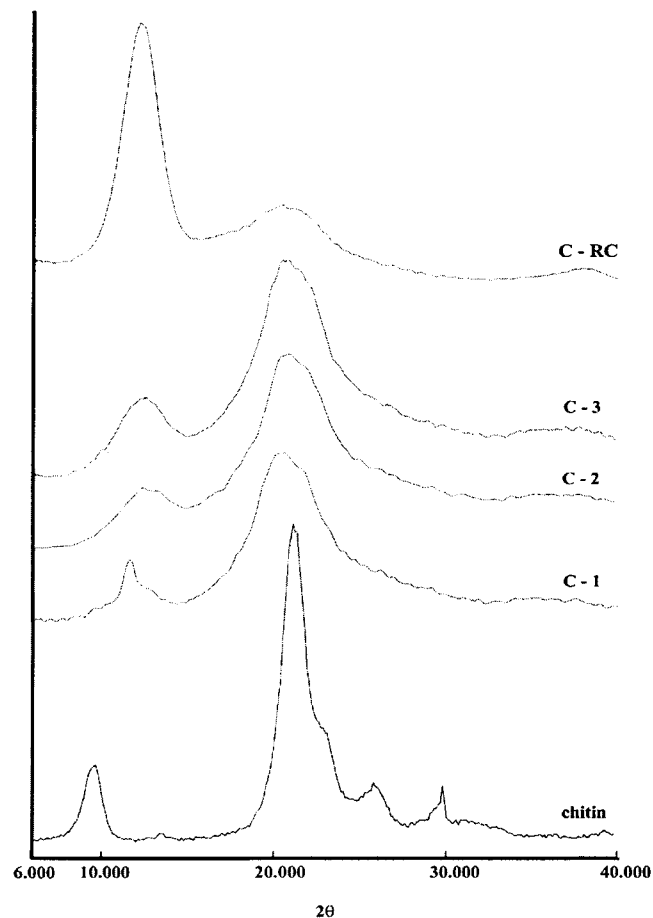

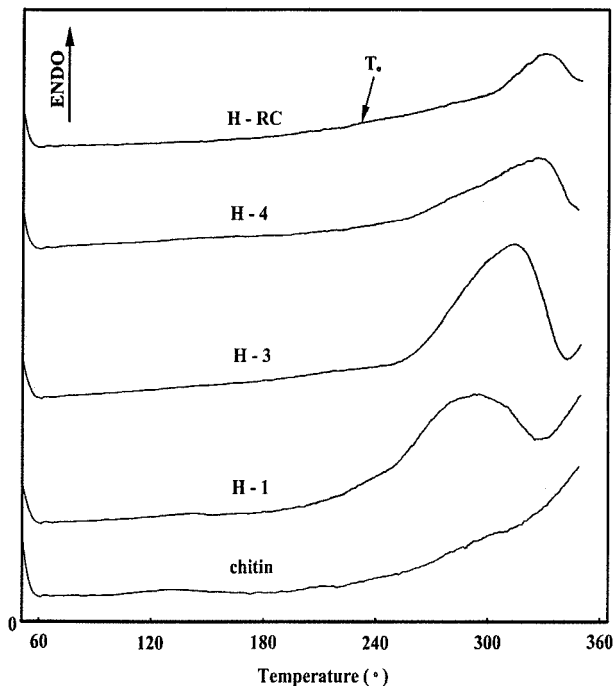**Figure 6** X-ray diffraction spectra of the membranes C coagulated with 5 wt % $CaCl_2$ and then 5 wt % H_2SO_4.

Figure 7 DSC curves of the membranes H oagulated with 5 wt % H_2SO_4.

tion and 3260 cm^{-1} for —NH stretching vibration, and the C=O region consists of three sharp bands at 1660 cm^{-1} (amide I band for amorphous or irregular regions in the vicinity of missing acetyl groups), 1623
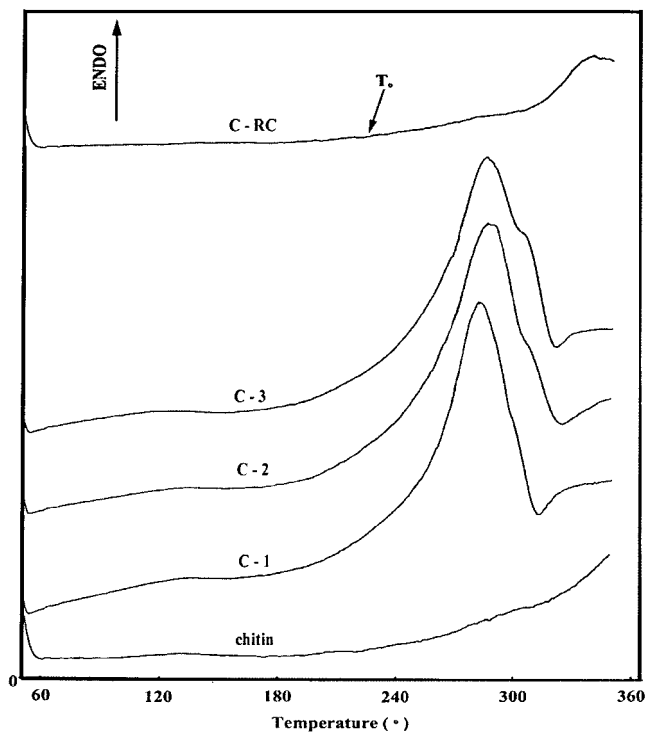

Figure 8 DSC curves of the C membranes coagulated with 5 wt % $CaCl_2$ and then 5 wt % H_2SO_4.
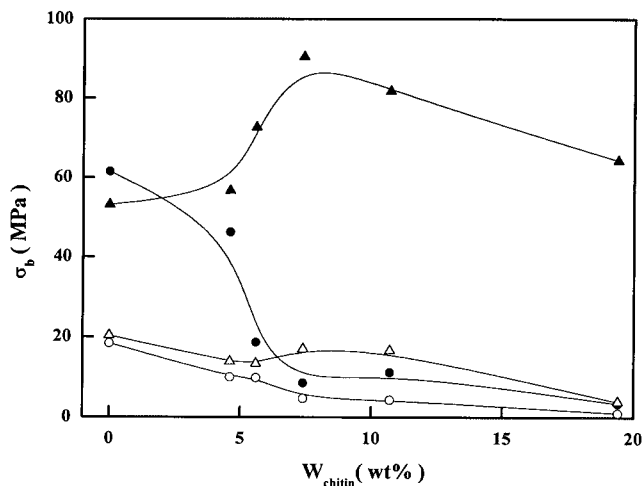

Figure 9 Dependence of tensile strength (σ_b) on the content of chitin (W_{chitin}) of membrane H in dry (▲) and in wet (△) states, and membrane C in dry (●) and in wet (○) states.

cm^{-1}, and 1557 cm^{-1} (amide II).[30] As shown in Figure 3, from H-1 to H-RC, the bands at 1557 cm^{-1} for amide decreased and even disappeared with a decrease of chitin content. The —NH stretching band of chitin disappeared in blend membranes, and the —OH stretching band broadened, implying a strong interaction between cellulose and chitin and contributed mostly to intermolecular hydrogen bonding, because a large amount of chitin still exists in the blend membranes, as shown in Table I. The —OH groups of cellulose and the —NHCOCH$_3$ groups of chitin interacted with each other, which makes the C=O stretching bands shift to a lower frequency and results in the vanishing of —NH-absorbed band. This strong intermolecular hydrogen bonding reflects a good miscibility of the blends. The results are in good agreement with the conclusion from SEM of the blends.

The X-ray diffraction patterns of the membranes are shown in Figures 5 and 6, and the crystallinity (χ_c) and intensity are summarized in Table I. The peaks at 2θ = 12, 20, and 22° in regenerated cellulose membrane, corresponding the (1 $\bar{1}$ 0), (1 1 0), and (2 0 0) planes are assigned to typical cellulose II crystalline form.[31] As shown in Table I, the peak's intensity at 20° and 22° of the H blend membranes increased, and that at 12° decreased with an increase of chitin content. The (1 $\bar{1}$ 0) plane is formed with hydrophobic interaction by piling up of glucopyranose rings,[32] and the intermolecular hydrogen bonding of (1 $\bar{1}$ 0) plane mainly sited on C-6 cellulose.[33] The (1 1 0) and (2 0 0) planes reflect the intramolecular hydrogen bonding of cellulose II.[34] This indicated that with an increase of chitin content in the blends, the peak at 12° decreased, suggesting that intermolecular hydrogen bonding of cellulose was destroyed. The same order was observed in the C membranes, but interestingly, the intensity at 20° and 22° of the blend membranes was much higher

TABLE II
The Results of DSC of Blend Membranes

Sample	T_o (°C)	T_{max} (°C)	Sample	T_o (°C)	T_{max} (°C)
H-1	248.2	285.9	C-1	254.5	281.3
H-3	262.1	313.3	C-2	254.0	286.2
H-4	265.5	325.9	C-3	257.0	285.5
H-C	307.0	328.7	C-C	—	—

than that at 12°. All the intensity of blend membranes at 20° and 22° was higher than that of cellulose. The χ_c of the blend membranes C was lower than that of cellulose and also the corresponding H membranes, suggesting that the cellulose crystalline in blends C was more easily destroyed because of the effect of interaction between chitin and $CaCl_2$ in aqueous solution.

DSC thermograms for the blend membranes are shown in Figures 7 and 8. The onset temperatures (T_o) of decomposition and peak temperature (T_{max}) are summarized in Table II. The cellulose reveals a distinct endothermic peak in the temperature interval between 303 and 345°C,[35] and some pointed to that between 300 and 480°C, meaning decomposition takes places.[36] The decomposition peak of the H-RC membrane was around 320°C, while there was no apparent peak for chitin. Compared with cellulose, the decomposition peaks of all blend membranes have shifted to a lower temperature. The T_o shifted from 248 to 266°C and peak temperature (T_{max}) shifted from 285 to 325°C with the increase of cellulose, indicating that the thermal stabilities of the blend membranes were lower than cellulose. One peak for decomposition shows the good miscibility of blends. As shown in Figure 8, the peaks for decomposition of the blend membranes C also shifted to a lower temperature, and the peak of cellulose occurred at higher temperatures than 400°C, according to previous work.[36] Comparing the spectra of two blends, the membranes C have lower decomposition temperature than membranes H. The results are in accord with the loose structure and low chitin content of the membranes C, suggesting the that the interaction between chitin and cellulose favor to improve the thermal stability and strength of the blend membranes.

Figures 9 and 10 show the dependence of tensile strength (σ_b) and breaking elongation (ϵ) on chitin content. The tensile strength (σ_b) of the membranes H in both states (wet and dry) increased with an increase of percentage content of chitin (W_{chitin}) until $W_{chitin} = 7.5$ wt % in the blends. The σ_b values of the blend membranes C were lower than that of the blend membranes H. However, the ϵ values of the membranes C were much higher, especially in the wet state, than that of blends H. All the membranes have the same tendency to change the mechanical properties. These

results conform to the blend membranes C exhibiting lower tensile strength and higher breaking elongation, owing to a relatively weak interaction between cellulose and chitin caused by an addition of chitin and a porous structure. The blend membranes H have relatively higher tensile strength and thermal stability, suggesting that a strong interaction exists between cellulose and chitin in the H blends. Interestingly, the values of breaking elongation (ϵ_b) of both membranes C and H containing chitin from 5 to 7.5 wt % were higher than unblended cellulose membranes H-RC and C-RC, respectively, suggesting an enhancement of toughness. In this case, chitin plays an important role in the improvement of mechanical properties of cellulose or chitin. Therefore, the blends provide a new way for promising functional materials developed from chitin.

CONCLUSION

A mixture of cellulose and chitin can dissolve in the new solution system, $1.5M$ NaOH/$0.65M$ thiourea. The blend membranes of cellulose and chitin were successfully prepared from the mixture solution by coagulating with 5 wt % H_2SO_4 or 5 wt % $CaCl_2$ and then 5 wt % H_2SO_4. There were great differences in structure and properties between the blend membranes C and H. The blend membranes H coagulated with H_2SO_4 have relatively dense structure, high crystallinity, and strong intermolecular hydrogen bonding between cellulose and chitin, leading to higher mechanical properties and thermal stability. When the chitin content was 7.5 wt %, the σ_b of the blend membrane H-3 was 90.4 MPa and even higher than that of the unblended membrane H-RC, and the values of ϵ_b for the blend membranes H and C were all higher than
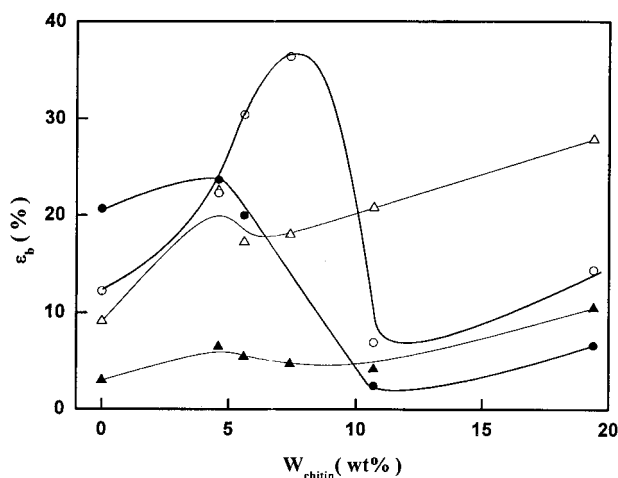

Figure 10 Dependence of breaking elongation (ϵ_b) on the content of chitin (W_{chitin}) of the membranes H in dry (▲) and in wet (△) states, and the membranes C in dry (●) and in wet (○) states.

unblended membranes H-RC and C-RC, respectively. This provides promising application in pharmaceutical and biomedical fields of chitin as the functional materials keeping its characteristics. The blend membranes C have a mess structure and relatively large pores ($2r_e = 210 \ \mu$m) due to a loss of chitin in the process, resulting in lower σ_b and higher ϵ_b. The intermolecular hydrogen bonds between the cellulose and the chitin in the blends can be broken in 5 wt % $CaCl_2$ aqueous solution, in which a water-soluble calcium complex of chitin as pore former was removed from membranes.

References

1. Zhang, L.; Yang, G.; Liu, H.; Cellul Commun 1999, 6, 89.
2. Rathke, J. D.; Hudson S. M. J Macromol Sci: Rev Macromol Chem Phys 1994, C34, 375.
3. Muzzarelli, R. A. A. Chitin in Naturally Chelating Polymers; Pergamon Press: New York, 1977.
4. Muzzarelli, R. A. A. Chitin; Pergamon Press: New York, 1977.
5. Zikakis J. P., Ed. Chtin, Chitosan and Related Enzymes; Academic Press: Orlando, FL, 1984.
6. Kim, S. S.; Lee, Y. M.;. J Polym Sci, Polym Chem Ed 1995, 33, 2285.
7. Kim, S. S.; Lee, Y. M.; Cho, C. S. Polymer 1995, 36, 4497.
8. Nakajima, M.; Atsumi, K.; Kifune, K.; Advances in Chitin and Chitosan; Brine, C. J.; Sanford, P. A.;Zikakis, J. P., Eds.; Elsevier Applied Science: London, 1993; p 407.
9. Komai, T.; Kaifu, K.; Matsushita, M.; Koshino, I.; Kon, T. Chitin in Nature and Technology; Proceedings from the 3rd International Conference on Chitin and Chitosan; Plenum Press: New York, 1986; p 497.
10. Ouchi, T.; Inosaka, K.; Banba, T.; Ohya, Y.; Advances in Chitin and Chitosan; Brine, C. J.; Sanford, P. A.; Zikakis, J. P., Eds.; Elsevier Applied Science: London, 1992; p 106.
11. Miura, Y.; Kaneda, Y.; Uraki, Y.; Tokura, S. Advances in Chitin and Chitosan; Brine, C. J.; Sanford, P. A.; Zikakis, J. P., Eds.; Elsevier Applied Science: London, 1992; p 116.
12. Baba, S.; Uraki, Y.; Miura, Y.; Tokura, S.; Chitin and Chitosan; Proceedings from the 4th International Conference on Chitin and Chitosan; Plenum Press: New York, 1988; p 703.
13. Lee, Y. M.; Kim, S. H.; Kim, S. J. Polymer 1996, 37, 5897.
14. Marting, G. P. J Macromol Sci: Pure Appl Chem 1995, A32, 629–640.
15. Yamada, H.; Imoto, T. Carbohydr Res 1981, 92, 160.
16. Tokura, S.; Yoshida, J.; Nishi, N.; Hiraoki, T. Polym J 1982, 14, 257.
17. Riccardo, A. A. M. Carbohydr Polym 1988, 8, 1.
18. Andre, M. S. Carbohydr Polym 1997, 34, 267.
19. Williamson, S. L.; Armentrout, R. S.; Porter, R. S.; McCormick, C. L. Macromolecules 1998, 31, 8134.
20. Dufresne, A.; Caraille, J. Y.; Dupeyre, D.; Ramirez, M. G.; Romero, J. Polymer 1999, 40, 1657.
21. Zhang, L.; Zhou, J.; Zhou, D.; Tang Y. J Membr Sci 1999, 162, 103.
22. Yang, G.; Zhang, L.; Liu, Y. J Membr Sci 2000, 177, 153.
23. Zhang, L.; Guo, J.; Zhou, J.; Yang, G.; Du, Y. J Appl Polym Sci 2000, 77, 610.
24. Zhang, L.; Ruan, D.; Gao, S. Pat. Appl. CN 00128162.3, December 2000.
25. Zhang, L.; Ruan, D.; Gao, S. J Polym Sci, Part B: Polym Phys to appear.
26. Zhang, L.; Guo, J. Pat. Appl. CN 00134782.3, March 2001.
27. Rabek, J. F. Experimental Methods in Polymer Chemistry: Applications of Wide-Angle X-ray Diffraction (WAXS) to the Study of the Structure of Polymers; Wiley Interscience: Chichester, 1980; p 505.
28. Zhou, J.; Zhang, L. J Polym Sci, Part B: Polym Phys 2001, 39, 451.
29. Otto, E.; Spurlin, M., Eds., Cellulose and Cellulose Derivatives, 2nd ed.; Vol. II, Interscience: New York, 1954.
30. Gow, N. A. R.; Gooday, G. W.; Russel, J. D.; Wilson, M. J. Carbohydr Res 1987, 165, 105.
31. Otto, E.; Spurlin, M., Eds., Cellulose and Cellulose Derivatives, 2nd ed.; Vol. II, Interscience: New York, 1954.
32. Yamane, C.; Mori, M.; Saito, M.; Okajima, K. Polym J 1996, 28, 1039.
33. Yang, G.; Zhang, L.; Feng, H. J Membr Sci 1999, 161, 31.
34. Kolpak, F. J.; Blackwell, J. Macromolecules 1976, 9, 273.
35. Wielage, B.; Lampke, Th.; Marx, G.; Nestler, K.; Starke, D. Thermochim Acta 1999, 337, 169.
36. Urea, N. Y.; Pineda, E. A. G.; Hechenleitner, A. A. W. Int J Pharm 2000, 206, 85.