

# Cellulose/Casein Blend Membranes from NaOH/Urea Solution

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**ABSTRACT:** Cellulose membranes and cellulose/casein blend membranes were successfully prepared from a new solvent system (6 wt % NaOH/4 wt % urea aqueous solution) by coagulation with a sulfuric acid aqueous solution. The structures and properties of the membranes were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy (SEM), wide-angle X-ray diffraction, differential scanning calorimetry, and a tensile test. The experimental results showed that the suitable coagulation condition was 5 wt %  $H_2SO_4$  for 5 min. When the casein content of the mixture was less than 15 wt %, the blend membranes were miscible because of the interactions between the hydroxyl groups of cellulose and the peptide bonds of casein. The blend membranes with 10 wt % casein had good miscibility, higher crystallinity, and the highest mechanical properties and thermal stability. In this case, the tensile strength and breaking elongation of the blend membranes were 109 MPa and 16%, respectively, and its pore size, obtained by SEM, was 290 nm, which suggests that the blend membranes provide a potential application for the field of separation technology. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3260–3267, 2001

**Key words:** blend; membrane; alkali soluble; cellulose; casein; miscibility

## INTRODUCTION

Cellulose is one of the most abundant renewable resources and biodegradable, environment-friendly materials because making use of cellulose to produce various products not only can protect the environment from pollution but can also save limited oil resources.<sup>1</sup> For the regenerated-cellulose industry, viscose and cuprammonium rayon processes still occupy a sole and exclusive position, despite

possible environmental hazards. Such circumstances have called for a renewed process and corresponding regenerated-cellulose products, based on scientific and industrial advances. Matsui et al.<sup>2</sup> prepared regenerated films from two types of cellulose, namely, Cell I, steam-exploded spruce pulp, and Cell II, regenerated cellulose from a cotton/cuprammonium solution in a NaOH aqueous solution system with aqueous sulfuric acid of various concentrations. This new process has the potential to overcome vital environmental problems. Recently, a novel solvent, 6 wt % NaOH/4 wt % urea, was discovered in our laboratory to have a strong power to dissolve linter (natural cellulose) and *Bemliese* (regenerated cellulose).<sup>3,4</sup>

Blending is a handy and important way to exploit new materials for polymers. The rich hydroxyl groups in cellulose facilitate the formation of intermolecular hydrogen bonds with other poly-

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mers and lead to good miscibility and novel functions and properties. Cellulose/synthetic polymer blends have been extensively studied in nonaqueous solvent systems, such as *N,N*-dimethylacetamide/lithium chloride<sup>5,6</sup> and dimethyl sulfoxide/paraformaldehyde.<sup>7</sup> We have studied blends of cellulose with other natural polymers such as casein<sup>8,9</sup> and alginate<sup>10,11</sup> from cuprammonium aqueous solutions to improve the mechanical properties or functions. For the cellulose/casein blend membranes from cuprammonium aqueous solutions, the tensile strength ( $\sigma_b$ ) is higher than that of the pure cellulose membrane. The blends are miscible when the casein content is less than 25 wt %. The blend membranes have the specific properties of cellulose, high performance and a low-cost manufacturing process, which offer the prospect of commercial interest.

In this study, we attempted to prepare cellulose-blend products (fibers or membranes) from NaOH/urea aqueous solution. The effects of the preparative condition and weight content of casein ( $w_{CA}$ ) on the structure and mechanical properties of the cellulose/casein blend membranes from 6 wt % NaOH/4 wt % urea were investigated and are discussed. Such materials may be not only biodegradable and recyclable but also low-cost, so they have the promise of application in medical foods, fibers for textile, hollow fibers for hemodialysis, membranes for separation, and so on.

## EXPERIMENTAL

### Preparation of Membranes

*Bemliese* (a regenerated cellulose), a nonwoven cloth made from cotton linters in cuprammonium, was a gift from Asahi Chemical Industry Co. Ltd. (Tokyo, Japan). Its viscosity-average molecular weight ( $M_\eta$ ) was determined to be  $11.4 \times 10^4$  from the intrinsic viscosity ( $[\eta]$ ) in a cadoxen solution at 25°C by  $[\eta] = 3.85 \times 10^{-2} M_w^{0.75}$  (where  $M_w$  is the weight-average molecular weight).<sup>12</sup> We prepared the 4 wt % cellulose solution by dissolving cellulose in a 6 wt % NaOH/4 wt % urea aqueous solution at 4°C according to our patent.<sup>3</sup> The cellulose solution was spread over a glass plate and then immediately immersed in H<sub>2</sub>SO<sub>4</sub> aqueous solutions [H<sub>2</sub>SO<sub>4</sub> concentration ( $C_{sa}$ ) = 2.5–50 wt %] for 1–9 min. The coagulation time ( $t_c = 5$  min) and the coagulation temperature ( $T_c \approx 8^\circ\text{C}$ ) were used for the investigation of  $C_{sa}$ . Similarly, the  $t_c$

dependence of the coagulation condition was examined at  $C_{sa} = 5$  wt % and  $T_c \approx 8^\circ\text{C}$ . The coagulated membranes were washed thoroughly with water for 1 day at 20°C and were then stuck on a polytetrafluoroethylene plate to dry in air.

The casein was dissolved in the 6 wt % NaOH/4 wt % urea solution to obtain a concentration of 23 wt %. The blend membranes of cellulose and casein were prepared by coagulating with 5 wt % H<sub>2</sub>SO<sub>4</sub> for 5 min. By changing the weight ratio of cellulose to casein to 100:0, 95:5, 90:10, 85:15, 80:20 and 0:100, a series of blend membranes coded RC, RCCA-1, RCCA-2, RCCA-3, RCCA-4 and CA were prepared, respectively.

### Characterization

IR spectra of the membranes were recorded with a Nicolet Fourier transform infrared (FTIR, USA) spectrometer after the samples were vacuum-dried for 2 days. The scanning range of the membranes was 400–4000 cm<sup>-1</sup>.

Scanning electron microscopy (SEM) micrographs were taken on a Hitachi S-570 microscope (Japan). The wet membranes were frozen in liquid nitrogen and then vacuum-dried. The surfaces of the membrane were coated with carbon and gold for SEM micrographs.

The X-ray diffraction (XRD) was measured with an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan) with Cu K $\alpha$  at 40 kV and 30 mA in the region of  $2\theta = 5\text{--}55^\circ$ . The degree of crystallinity ( $\chi_c$ ) was calculated with the usual method.<sup>13</sup> Apparent crystal size (ACS) was estimated through Scherrer's equation:<sup>14</sup>

$$\text{ACS} = k\lambda/\cos \theta \cdot \beta \quad (1)$$

$$\beta = (B^2 - b^2)^{1/2} \quad (2)$$

where  $k$  is the apparatus constant and is taken as 0.9 for cellulose,  $\lambda$  is the wavelength of the Cu K $\alpha$  line (1.542 Å),  $\theta$  is Bragg's angle,  $b$  is the instrumental constant (0.1°), and  $B$  is the half-width in radians of the diffraction angle of the (110), (1 $\bar{1}$ 0), and (200) planes.

Differential scanning calorimetry (DSC) was performed on a DSC-2C apparatus (Perkin-Elmer, USA) under a nitrogen atmosphere at a rate of 10°C/min from 50 to 400°C. The samples were preheated to 150°C to remove absorbed water from the membrane and then cooled for the measurement.

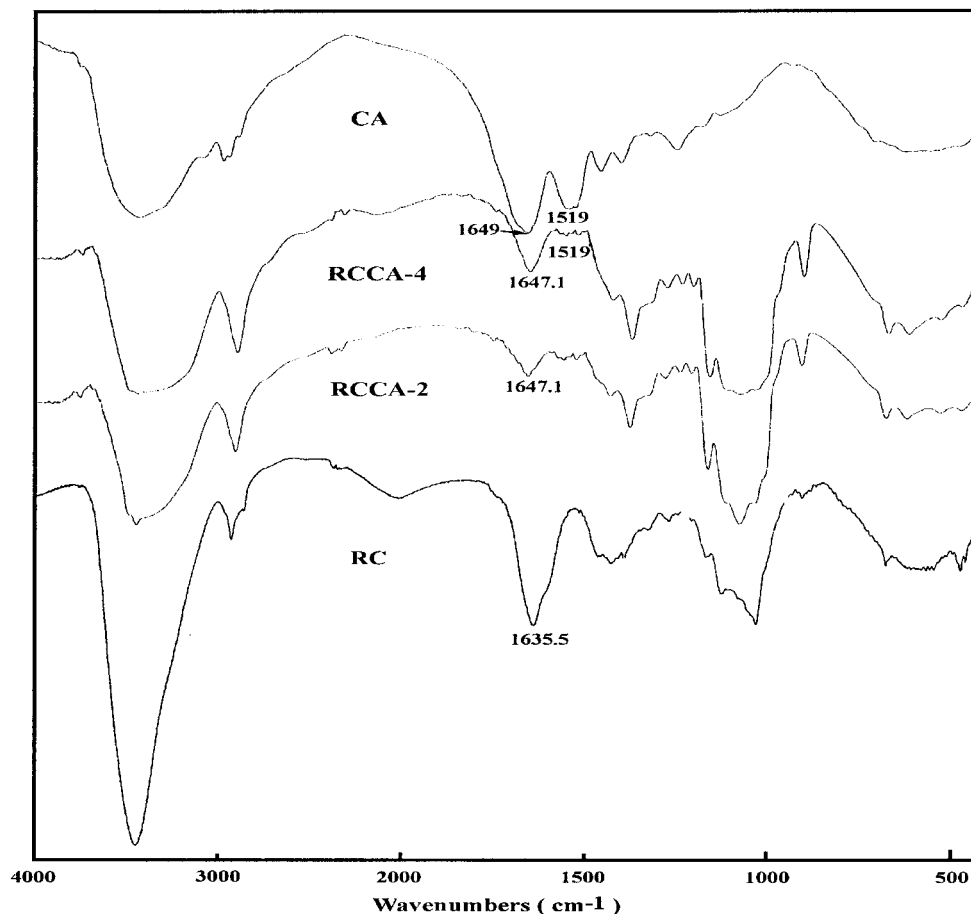


Figure 1 FTIR spectra of pure and blend membranes.

$\sigma_b$  and breaking elongation ( $\epsilon_b$ ) of the dry and wet membranes were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co., Ltd., China) under the following conditions: sample width = 10 mm, sample length = 100 mm (50 mm between the grips), tensile rate = 5 mm/min, humidity = 65%, and temperature = 20°C.

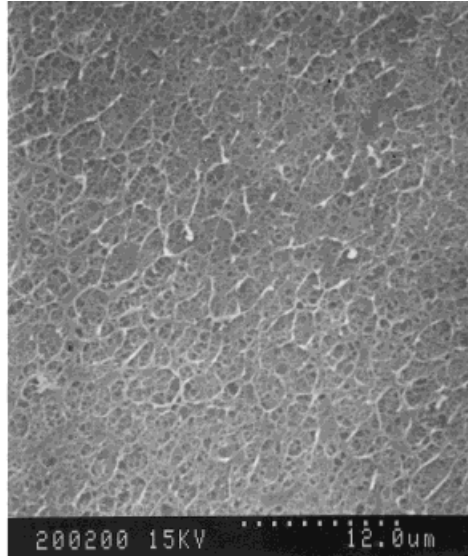
## RESULTS AND DISCUSSION

### Intermolecular Interaction and Miscibility

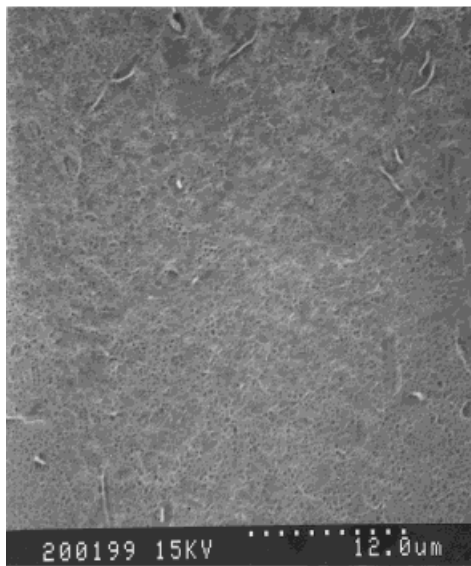
Figure 1 shows the IR spectra of the membranes. The —OH stretching vibration bands around  $3400\text{ cm}^{-1}$  for the RCCA-2 and RCCA-4 blends broadened and shifted to a lower wavenumber compared with RC and casein (CA). This reflected a reasonably wide distribution of hydrogen-bond distances and geometries because of the new intermolecular interactions. Moreover, the absorp-

tion band at  $1649\text{ cm}^{-1}$  for CA assigned to C=O of the casein shifted to a lower wavenumber for the blend membranes; such shifts are widely considered to be the “acid test.” This further proved the formation of hydrogen bonds between the hydroxyl groups of cellulose and the carboxylate groups of the casein in the blends. In addition, the bands for CA around  $1530\text{--}1550\text{ cm}^{-1}$  were attributed to the bending vibration and stretching vibration of N—H and C—H of the peptide bonds in the casein. The IR spectra of both RCCA-2 and RCCA-4 indicated that the blend membranes consisted of cellulose and casein.

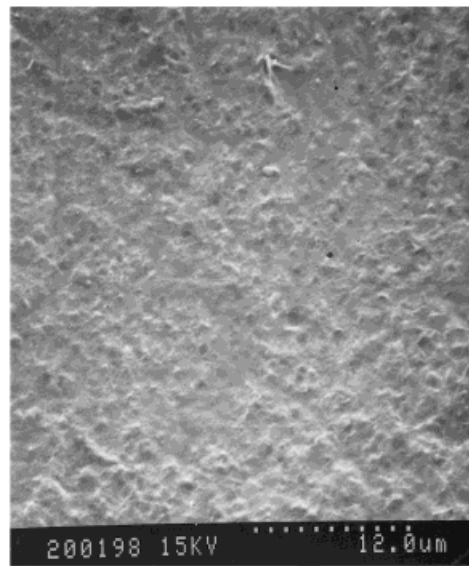
Figure 2 shows SEM micrographs of the membranes. The membranes of RC and RCCA-2 displayed smooth surfaces with homogeneous pores, similar to the RC-S3 blend membrane of cellulose/casein prepared from a cuoxam solution system,<sup>8</sup> which suggests that the RCCA-2 blend was miscible. In contrast, the RCCA-4 membrane showed a rough surface with smaller globules because of



RC



RCCA-2



RCCA-4

**Figure 2** SEM micrographs of blends of regenerated cellulose and casein: RC, RCCA-2, and RCCA-4.

the decrease in the degree of miscibility. Moreover, the mean pore size of the RCCA-2 membrane was 290 nm from SEM. These membranes have promise as applications for separate and medical function materials.

#### Structure of Blends

The XRD patterns of the membranes are shown in Figure 3. The measurements were recorded by

the irradiation of the perpendicular to the front surface of the membranes. The diffraction peaks were observed at  $2\theta = 12, 20, 22, 28,$  and  $41^\circ$  for the membranes RC, RCCA-2, and RCCA-4 and  $2\theta = 9$  and  $20^\circ$  for CA. The peak intensities of (110) for the RC and blend membranes were higher than those of the (200) plane, which suggests that the (110) plane was perpendicular orientation and the (200) plane was bias orientation to the

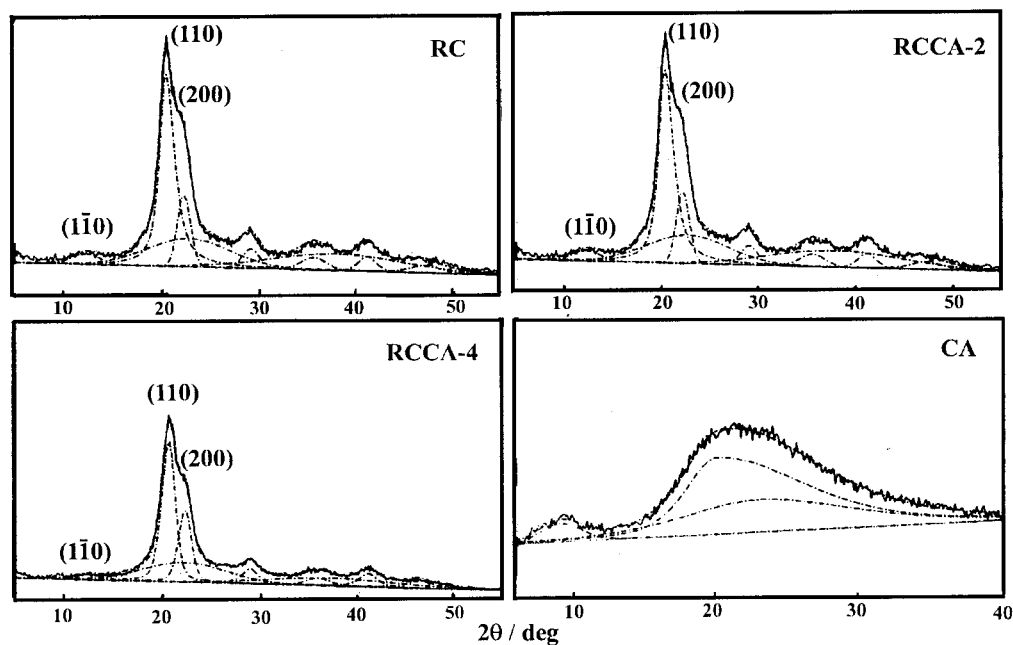


Figure 3 XRD patterns of the membranes.

surface of the membrane. These orientation phenomenon of  $(\bar{1}\bar{1}0)$ ,  $(110)$ , and  $(200)$  planes are classified as selective uniplanar orientation.

$\chi_c$  and ACS of the  $(\bar{1}\bar{1}0)$ ,  $(110)$ , and  $(200)$  planes are summarized in Table I.  $\chi_c$  values of RCCA-2 and RCCA-4 were higher than those of RC, and ACS  $(\bar{1}\bar{1}0)$  and ACS  $(200)$  for RCCA-2 were the largest among these membranes. This means that casein facilitated the crystallization of cellulose, and an appropriate amount of casein also acted as an innerplanar bridge in  $(\bar{1}\bar{1}0)$  planes and a promoter of interplanar hydrogen bonding between  $(\bar{1}\bar{1}0)$  planes, which suggests that casein promoted the arrangement of hydrogen bonding in the cellulose [mainly for intramolecular hydrogen bonding in  $(110)$  planes]. In contrast,  $\chi_c$  values for cellulose/casein blend membranes from cuoxam

increased, whereas ACS  $(200)$  and ACS  $(110)$  decreased with an increase in  $w_{CA}$ , which indicates that the number of crystalline nuclei increased with the addition of casein to the system.<sup>9</sup>

### Thermal Properties

The DSC thermograms of the membranes are described in Figure 4. There was an endothermic peak of thermal decomposition for cellulose at 359°C and a melting endotherm for casein at 275°C. The endothermic peaks of blends tended to shift to the lower temperature, and a shoulder peak appeared. The thermal degradation peak of cellulose in RCCA-2 shifted to a higher temperature, and the melting peaking of casein did not seem obvious because of the peak overlapping with those peaks for cellulose.

Table I Structural and Mechanical Parameters of the Blend Membranes

Membrane Number	$\chi_c$ (%)	ASC (Å)			$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	DSC $T$ (°C)
		$(\bar{1}\bar{1}0)$	$(110)$	$(200)$			
RC	58	24.6	45.3	50.4	99	13	359
RCCA-2	63	26.4	45.8	57.9	109	16	361
RCCA-4	63	24.1	49.3	52.1	66	9	356
CA	65						275 <sup>a</sup>

<sup>a</sup>Melting endotherm.

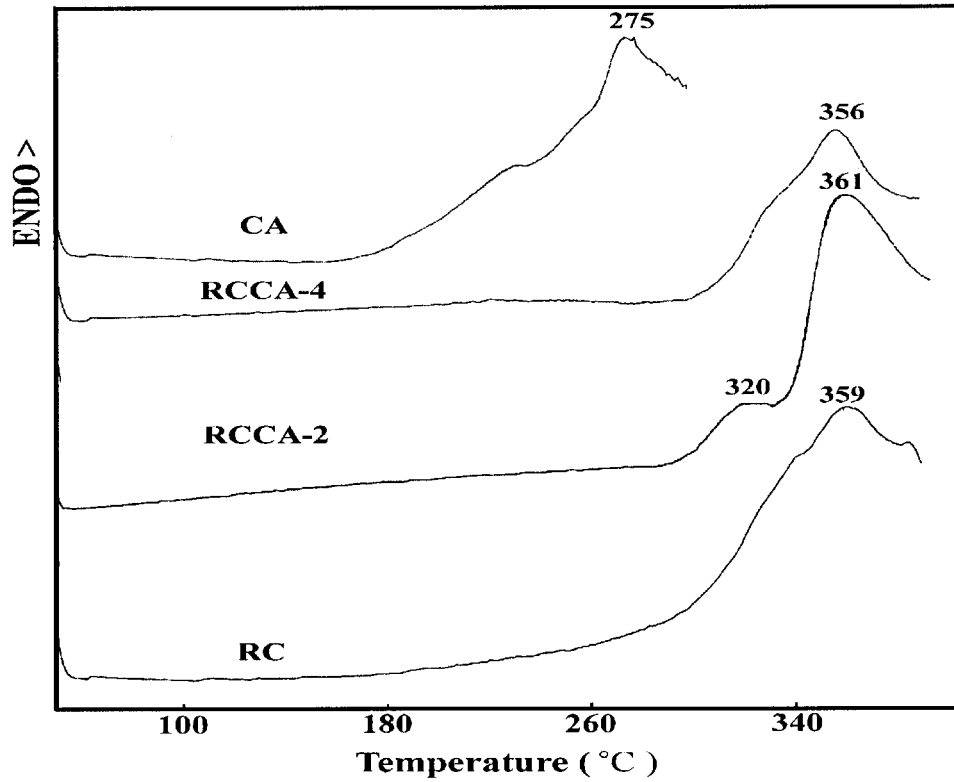


Figure 4 DSC of blend membranes of regenerated cellulose and casein.

The upward shift of the degradation peak of cellulose and the melting peak of casein suggest that the blends exhibited a good miscibility and contributed to the interaction, based on the hydrogen bonding,

between cellulose and casein. Nishioka et al.<sup>15</sup> reported that the difference in thermal decomposition behavior was correlated with the difference in miscibility.

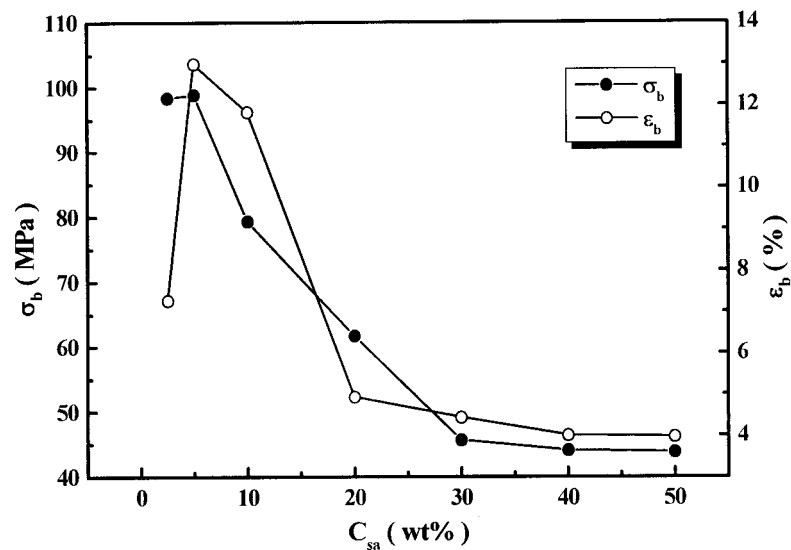
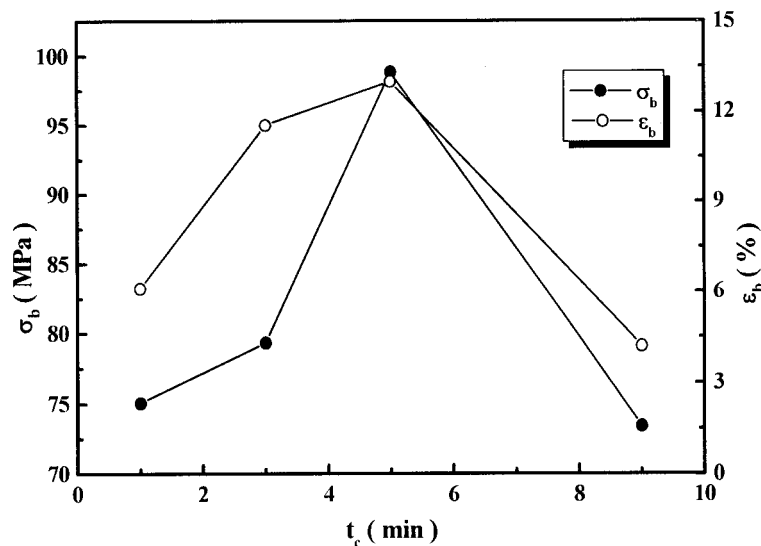


Figure 5 Effect of  $\sigma_b$  and  $\epsilon_b$  of the regenerated cellulose membrane on  $C_{sa}$  ( $t_c = 5$  min,  $T_c = 8^\circ\text{C}$ ).





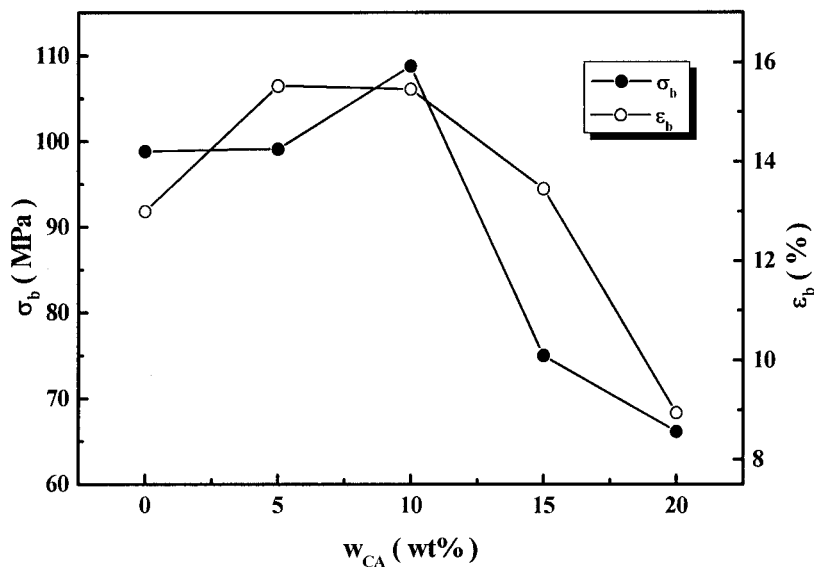
**Figure 6** Effect of  $\sigma_b$  and  $\epsilon_b$  of the regenerated cellulose membrane on  $t_c$  ( $C_{sa} = 5$  wt %,  $T_c = 8^\circ\text{C}$ ).

### Mechanical Properties

The effect of the coagulation conditions ( $C_{sa}$  and  $t_c$ ) on the mechanical properties of the CA membranes is plotted in Figures 5 and 6.  $\sigma_b$  and  $\epsilon_b$  increased, then abruptly decreased at  $C_{sa} \leq 30$  wt %, and finally became almost constant with the increase of  $C_{sa}$ . Therefore, a suitable  $C_{sa}$  was 5 wt %. The values of  $\sigma_b$  and  $\epsilon_b$  exhibited maxima at  $t_c = 5$  min, so the best  $t_c$  in this system was 5 min. The coagulation conditions played an important

role in improving the structure and properties of the membranes.  $\text{H}_2\text{SO}_4$  aqueous solutions with higher  $C_{sa}$  had higher dehydration power, neutralization rates, and solubility against cellulose, which led to a faster coagulation rate and the restriction of crystallization and arrangement in order for cellulose molecules.

The effects of  $w_{CA}$  on  $\sigma_b$  and  $\epsilon_b$  of the blend membranes are shown in Figure 7. The values of  $\sigma_b$  and  $\epsilon_b$  exhibited maxima at  $w_{CA} = 10$  wt %, and



**Figure 7** Effect of  $\sigma_b$  and  $\epsilon_b$  of the blend membranes on  $w_{CA}$  ( $t_c = 5$  min,  $C_{sa} = 5$  wt %,  $T_c = 8^\circ\text{C}$ ).

followed by a decrease that corresponded well with the results from SEM,  $\chi$ , and ACS (110). When  $w_{CA}$  increased from 10 to 20 wt %,  $\sigma_b$  abruptly decreased; the depression of  $\sigma_b$  indicated a decrease in the degree of miscibility. When  $w_{CA}$  was smaller than 15 wt %, the cellulose/casein blend membranes obtained from NaOH/urea aqueous solution were miscible.

## CONCLUSIONS

Blend membranes of cellulose/casein were successfully prepared from a new solvent system, 6 wt % NaOH/4 wt % urea aqueous solution, by coagulating in a sulfuric acid aqueous solution. The suitable coagulation conditions for the cellulose from NaOH/urea solution was the concentration of sulfuric acid as coagulate  $C_{sa} = 5$  wt % and  $t_c = 5$  min. When the casein content in the mixture was less than 15 wt %, the blend membranes were miscible because of the interactions between the hydroxyl groups of cellulose and the peptide bonds of casein in the blends. The blend membranes with 10 wt % casein had excellent mechanical properties and thermal stability.  $\sigma_b$  and  $\epsilon_b$  of the RCCA-2 blend membrane were 109 MPa and 16%, respectively, and the pore size of the RCCA-2 blend membrane was obtained from SEM as 290 nm, which is much larger than that of cellulose/casein from a cuoxam solution.

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