Direct Preparation of a Novel Membrane from Unsubstituted Cellulose in NaOH Complex Solution

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Received 12 November 2008; accepted 26 July 2009

ABSTRACT

An environmentally acceptable cellulose dissolution procedure was employed to prepare a membrane directly from an unsubstituted cellulose. The effects of coagulants and coagulation conditions on the structure and properties of regenerated cellulose membrane prepared from cellulose in a NaOH complex solution (8 wt% NaOH/6.5 wt% thiourea/8 wt% urea/77.5 wt% H₂O) are discussed. A series of cellulose membranes are prepared from cellulose solutions by coagulation with 5 wt% H₂SO₄, 5 wt% HCl, 5 wt% HAc, CH₃CH₂OH (abs.), 5 wt% H₂SO₄/5 wt% Na₂SO₄, 10 wt% Na₂SO₄, 10 wt% (NH₄)₂SO₄ and 10 wt% NH₄Cl, respectively. Moreover, the membrane coagulated at relatively low temperature possessed better mechanical properties compared to those coagulated at relatively high temperatures. The results indicated that in the coagulation bath of 7 wt% HAc aqueous solution, with coagulation temperature at 10°C for duration of 5 min, the tensile strength of novel cellulose membrane could reach 134 MPa, which was much higher than the commercial cellophane and those of the membranes prepared from NaOH/urea and NaOH/thiourea aqueous solutions. The CP/MAS ¹³C NMR, WAXD and FTIR spectra indicate that the regenerated membrane possesses a specific cellulosic crystal type. The novel cellulose membrane showed dense structure and the crystallinity which was higher than that of a viscose fiber, was an indication that it possessed much more stable structure. The coagulation mechanism can be described as a two-phase separation. Cellulose in the gel was precipitated and regenerated with the coagulation process to form a cellulose membrane. This work provides a potential promising way to prepare novel cellulose membrane with excellent physical properties by controlling the coagulation conditions.

INTRODUCTION

Cellulose as one of the richest natural polymers in the world is applied vastly by manufacturers to produce various useful products such as clothing, drug coating, packing materials, and membranes. In recent years, regenerated cellulose membranes have been widely used in membrane separation applications such as dialysis, ultrafiltration, and reverse osmosis for their natural and re-usable characteristics [1-3]. However, for their production it is exactly this virtue, which constitutes a considerable drawback due to the fact that the normal methods of membrane production require polymer solutions. For this reason industry goes a long way round by first...
transforming cellulose into a soluble derivative, which allows the preparation of membranes and subsequent regeneration of the original material. Such detours are also practiced in fibre industry, e.g., via the formation of xanthogenate (cellophane) [4] or by means of the creation of a copper complex (cuprammonium process, cuprophane) [5,6]. Owing to its high production costs and environmental pollution problems, it has been gradually replaced by polyolefin membrane which has advantages of simple production process and low cost [7]. However, many commercial membranes are still made of cellulose due to its unique hydrophilic characteristics, relatively high chemical stability, and remarkable environmental protecting capability. Thus, it has great significance to develop simple producing process for cellulose membrane [8].

Moreover, the properties of cellulose membrane are intimately related to their structure and morphology which are mainly controlled by conditions, nature, and mechanism of coagulation. Therefore, many attempts have been carried out by investigating the coagulation/regeneration process to design the desired morphology and properties of the cellulose membrane [9-11]. In recent years, the new and powerful organic solvent N-methylmorpholine N-oxide (NMMO) has been developed which dissolves cellulose straight away without any complex formation [8]. The cellulose fibres and membranes prepared from cellulose/NMMO/H2O solution exhibited excellent mechanical properties and permeation characteristics when the cellulose dope was coagulated in water at lower temperature by using the phase-inversion method [8,12-14]. Matsui investigated the structure and morphology of the cellulose films coagulated from cellulose in NaOH aqueous solution by using sulphuric acid as a coagulant at various concentrations [15]. The effect of coagulation conditions on the structure and properties of regenerated cellulose membrane prepared from cellulose in NaOH/urea and NaOH/thiourea aqueous solution has been examined by Zhang et al. [16-18]. The tensile strength of the prepared membrane was reported as 100 MPa.

Recently, we were able to dissolve cellulose rapidly in a NaOH complex solution (8 wt% NaOH/6.5 wt% thiourea /8 wt% urea/77.5 wt% H2O) at low temperature (-8ºC) to prepare a transparent cellulose solution [19,20]. The solvent system developed showed low toxicity and possessed higher solubility capacity for cellulose compared to NaOH, NaOH/thiourea, or NaOH/urea aqueous solutions [15-18]. It has been proved by 13C NMR spectra of the cellulose solution that this novel mixture is a direct solvent.

In this work, we attempted to prepare a series of cellulose membranes from cellulose in 8 wt% NaOH/6.5 wt% thiourea /8 wt% urea aqueous solution by coagulating with various coagulants such as 5 wt% H2SO4, 5 wt% HCl, 5 wt% HAc, CH3CH2OH (abs.), 5 wt% H2SO4/5 wt% Na2SO4, 10 wt% Na2SO4, 10 wt% (NH4)2SO4 and 10 wt% NH4Cl. As in the phase conversion process, the conditions of coagulation baths are key factors for adjusting and controlling the membrane morphology, which is decisive for the performance of membranes. Thus, the effects of coagulation conditions on the mechanical properties, structure, and morphology of the cellulose membranes were investigated by using CP/MAS 13CNMR, WAXD, FTIR, SEM and tensile testing.

NaOH/thiourea/urea aqueous solution was employed to prepare the membrane directly from unsubstituted cellulose for the first time. This work provides considerable potential for novel cellulose membrane production with respect to both environmental and economic issues. It has significant advantages including non-polluting, simple, and a safe dissolution procedure which can replace the viscose and cuprammonium processes. The coagulation mechanism of membrane in the coagulation bath is also analyzed in this paper as it is still a matter of vital research in the processing of polymer membrane.

**EXPERIMENTAL**

**Materials**

The cellulose (cotton linter pulp) was supplied by Shanghai Cellulose Pulp Factory, China. The viscosity-average molecular weight (Mη) of the cellulose was determined by viscometry in Cadoxen to be 8.56×10⁴. Cellulose samples were shredded into...
powder, and dried in a vacuum oven at 70°C for 24 h before use. All chemicals employed were of analytical grades and were purchased from commercial sources in China.

**Membrane Preparation**

Cellulose solution was prepared according to previously reported methods [19]. An amount of 23.3 g cellulose was dispersed in 400 g aqueous solution of 8 wt% NaOH/6.5 wt% thiourea/8 wt% urea, then pre-cooled to -8°C, followed by vigorous stirring for 3 min at room temperature. After 3 min, the temperature of the solution was controlled between -2 and 0°C using a salt-ice bath and the mixture was vigorously stirred for 17 min to obtain transparent cellulose dope containing 5.5 wt% cellulose. The cellulose dope was subjected to centrifugation at 10000 rpm for 20 min at 5-10°C in order to exclude the slightly remaining undissolved part and to carry out the degasification. The resulting transparent solution was immediately cast onto a glass plate at a thickness of 200 μm and then immersed into coagulants (2000 mL) for the desired time at the desired temperature. The resulting wet membranes were washed with running water and finally air-dried at ambient temperature. A series of aqueous solutions of 5 wt% H₂SO₄, 5 wt% HCl, 5 wt% HAc, 5 wt% H₂SO₄/5 wt% Na₂SO₄, 10 wt% Na₂SO₄, 10 wt% (NH₄)₂SO₄ and 10 wt% NH₄Cl and CH₃CH₂OH (abs.) were examined as coagulants.

**Characterization**

Cellulose membranes were pulverized and vacuum-dried overnight before the measurement of X-ray diffraction. The wide-angle X-ray diffraction (WAXD) was performed with an X-ray diffractometer (Rigaku/Dmax-B, Japan). X-ray diffraction patterns with Cu-Kα at 40 kV and 50 mA were recorded in a range of 20 from 5 to 40°. The degree of crystallinity (Xₗ) was calculated according to the peak separation method. Raw cellulose and the regenerated cellulose membrane obtained were characterized by solid-state ¹³C NMR (Bruker AV 400, Switzerland, magnetic field 9.4 T) using a CP/MAS unit at room temperature.

Fourier transform infrared spectroscopy (FTIR) of the regenerated cellulose membrane was performed between 4000-400 cm⁻¹ wavenumber on a Nicolet 410 spectrometer (USA) with a resolution of 4 cm⁻¹ and 64 scans per sample.

Scanning electron microscopy (SEM) was performed on a JSM-5600LV microscope (Japan). The membranes were frozen in liquid nitrogen, snapped immediately, and vacuum-dried. The free surface (side contacting the coagulant) and cross-section of the membranes were sputtered with gold for SEM measurements. SEM was obtained at 10 kV and 15 kV, which were considered to be a suitable condition because a too high energy level could burn the samples.

The tensile strength (σₚ) and elongation-at-break (εₚ) of the membranes were measured on a universal testing machine (YG-065H, Laizhou Test Machine Co. Ltd., Shandong, China) according to ISO 6239, 1986 (E) at speeds of 5 mm×min⁻¹. The σₚ and εₚ values are averages of 10 measurements.

**RESULTS AND DISCUSSION**

**Effect of Coagulant Components**

The results of the coagulation reagent dependence of coagulation rate for cellulose solution at 25°C are 5 wt% H₂SO₄, 5 wt% HCl for 3 min, 5 wt% H₂SO₄/5 wt% Na₂SO₄ for 5 min, 10 wt% Na₂SO₄, 10 wt% (NH₄)₂SO₄ and 10 wt% NH₄Cl and CH₃CH₂OH (abs.) were examined as coagulants.

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<tr>
<th>Anions/molecules in coagulant</th>
<th>Cations/molecules in coagulant</th>
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<tr>
<td>Ac⁻</td>
<td>H⁺</td>
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<td>SO₄²⁻</td>
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Cellulose that is dissolved by solvent-cellulose interaction and not as derivatives can be regenerated by neutralization or by the reduction of solvent concentration. The H⁺ is a key component to trigger the cellulose regeneration by causing the neutralization reaction in the membrane fabrication process. The cellulose can therefore be regenerated and precipitate from its dissolution state to form a membrane [17]. The addition of a strong electrolyte to H₂SO₄, e.g., Na₂SO₄ could reduce the H⁺ concentration in the coagulant, leading to a counter-diffusion rate and slower acid-alkali neutralization process than just H₂SO₄ itself. Thereby, the cellulose membrane coagulated with 5 wt% H₂SO₄/5 wt% Na₂SO₄ aqueous solution medium was moderate compared to that of the membrane coagulated from H₂SO₄. However, for a pure salt system such as Na₂SO₄, (NH₄)₂SO₄, and NH₄Cl aqueous solutions as coagulants, the former may involve a salt coagulation/water regeneration process because of the slower coagulation rate. Therefore, a longer coagulation time (about 15 min) is required to prepare membranes. For HAc aqueous solution as coagulant, because of its weak dissociation rate, the membrane has also exhibited good mechanical properties. In order to prepare cellulose membrane conveniently with moderate coagulation rate (membrane) and good properties, HAc aqueous solution was used as a coagulant for further tests.

**Effect of Coagulation Conditions**

Generally, in the membrane undergoing precipitation, the cellulose and HAc contents increase rapidly while the solvent (NaOH/thiourea/urea aqueous solution) level falls accordingly. Bath concentration, temperature, and coagulation time influence the properties of the membrane. The effect of these coagulation conditions on the tensile strength of regenerated cellulose membrane was investigated (Figure 1). With increase of coagulant concentration or coagulation time, the tensile strength increases at first, and then it decreases (Figures 1a and 1b).

The low concentration and short coagulation time could restrain the rate of the counter-diffusion between the coagulant and NaOH/thiourea/urea/H₂O solvent, leading to some difficulties in the cellulose regeneration process by coagulation method. The
increase in bath concentration leads to the increase in the rate of diffusion processes, and the stream of diffusing non-solvent gains more and more advantage over the stream of diffusing solvent from the spinning solution stream introduced into the bath.

It is accepted that HAc solution neutralized the membrane surface first and diffused into the membrane to perform the neutralization there until the whole neutralization of cellulose membrane was completed. This suggests that enough coagulation time is required for the membrane preparation. However, a too high concentration and/or a long coagulation time could not only be capable of facilitating degradation of cellulose but could be mainly responsible for an increase in the pore size of the membrane [21,24].

The results also indicate that a membrane prepared at relatively low temperature possesses better mechanical properties compared to the membrane coagulated at relatively high temperatures (Figure 1c), which can be explained by the notion that the diffusion velocity between solvent and non-solvent increases with the elevation of temperature and increased coagulation rate. As it is known, the regenerated fibre prepared by slower solidification process is better than the one prepared by rapid solidification process. The rapid solidification process gives the cellulose chains less time to be packed into an ordered structure and form a crystalline structure. Moreover, at high temperature, cellulose chains in acidic conditions will be easily subjected to more degradation, resulting in a drop in mechanical properties [17, 21-24]. As shown in Figures 1a-1c, the optimal coagulation conditions for the cellulose membranes are 7 wt % HAc and 5 min at 10°C, in which the $\sigma_b$ value of the membrane is 134 MPa.

Properties of Cellulose Membranes

Figure 2 shows the WAXD spectra of novel regenerated cellulose membranes under two different coagulant conditions (HAc solution), respectively. The characteristic diffractions of the membranes at 11.9, 20.0, and 21.8 corresponding to the 110, 110, and 200 planes are assigned to the typical cellulose II crystal [25]. Although the intensity of peak for 110 and 200 planes of regenerated cellulose membrane in two kinds of coagulations exhibits no significant differences, the intensity for 110 plane of Figure 2a is greatly smaller than that of Figure 2b.

Commonly, the 110 and 200 planes reflect the intra-molecular hydrogen bondings of cellulose II [26]. The 110 plane is formed by hydrophobic interaction with the piling up of glucopyranose rings [27]. The intermolecular hydrogen bonding of 110 plane mainly takes place at C-6 site of cellulose [28]. This indicates that the optimal coagulation conditions efficiently facilitate cellulose chains from ordered rearrangement and become more stable during the
The degree of crystallinity ($X_c$) of the novel cellulose membrane was calculated to be 52-68% according to the peak separation method, which is higher than that of cellophane and cuprophane (40-50%) [8]. This can be attributed to the better lateral supermolecular structure formed in the direct dissolution and regeneration process.

The structure of raw cellulose and regenerated cellulose membranes was investigated by solid-state $^{13}$C NMR spectroscopy (Figure 3). Considerable differences are evident in the $^{13}$C NMR spectra. The C4 resonance shows a sharp peak that can be assigned to crystalline and amorphous regions, respectively [29]. The sharp peak becomes broader and less intense in the membranes, which indicates the destruction of hydrogen bonds. In addition, the C6 main peak (64.9 ppm for raw cellulose) shifts to a higher magnetic field (62.5 ppm for membrane), which suggests that the t-g conformation of CH$_2$OH shifts to a g-t conformation, and intermolecular O6-H-O2' hydrogen bonds are being formed [30]. The NMR spectrum indicates that the conformation of most of the cellulose has changed from cellulose I (raw cellulose) to cellulose II (cellulose membrane).

Figure 4 shows FTIR spectra of the raw cellulose and the cellulose membrane. The FTIR spectra of raw cellulose shows two absorption bands at 3338 cm$^{-1}$ and 3270 cm$^{-1}$ which are assigned to intra-molecular hydrogen bonds O3-H...O5' and hydrogen bonds O2-H...O6' of cellulose I$\beta$, respectively [31]. However, in the FTIR spectrum of cellulose membrane two significant absorption bands appear at 3482 cm$^{-1}$ and 3446 cm$^{-1}$, which reflect hydrogen bonds' stretching of cellulose II [32]. These shifts reflect the membrane's weaker inter- and intra-chain H-bonds. Moreover, in the case of the membrane spectrum, the O-H stretching region appears broader which suggests the existence of little order in the membrane.

It is worth noting that, the spectrum of the membrane has two sharp absorption peaks at 2850 cm$^{-1}$ and 2920 cm$^{-1}$, respectively, which are assigned to C-H and CH$_2$ stretching motions. The sharp peaks indicate that there are few interactions between C-H, CH$_2$, and other chemical groups. This also means that the molecular chain arrangement in membrane is not as much compact as the raw cellulose and the crystallinity has been partly destroyed during the regenerating process.

Absorption bands at 1421 cm$^{-1}$ for the cellulose membrane, which is assigned to CH$_2$ scissoring motion is weakened and it is shifted to lower wavenumber compared to 1432 cm$^{-1}$ peak for the cotton linters. This observation indicates that the structural changes in the intra-chain H-bonds involve O6 [33]. A new shoulder at 990 cm$^{-1}$ belonging to the CO stretching vibration in the amorphous region emerges in the cellulose membrane but not in the cellulose I crystallites [34].

Figure 3. Solid-state $^{13}$C NMR spectra of: (a) raw cellulose and (b) novel regenerated cellulose membrane.
Figure 4. FTIR spectra of (a) raw cellulose and regenerated cellulose membrane; (b) spectra in the 2200-3800 cm\(^{-1}\) region; (c) spectra in the 800-1800 cm\(^{-1}\) region.

Figure 5. SEM images of regenerated cellulose membrane coagulated at optimal conditions: (a) free surface and (b) cross-section.

Figures 5a and 5b show the SEM images of the free surface and cross-section of the membrane prepared under optimal coagulation conditions (C = 7%, t = 5 min, T = 10°C), membrane with homogeneous dense structure can be observed even at high-magnified images. This is quite different from membranes prepared in NaOH/H\(_2\)O [15], NaOH/urea/H\(_2\)O [17,18] and NaOH/thiourea/H\(_2\)O [16] which displays porous structures with mesh networks in the free surface and microporous structures in their cross-sections.

In view of these results, it can be deduced that dense structure is a guaranty of better mechanical properties (from 112 MPa to 134 MPa in Table 2). The elongation-at-break was found to be 7-12.4% for the prepared membranes compared to 17-21% for the
Cellophane. The difference might be caused by the varied degree of membrane crystallinity, or by the simple addition of softeners or plasticizers in the commercial cellophane membrane. Experimental results have shown that the elongation-at-break value of this novel membrane prepared from NaOH complex solution increases more than twice after treating with 8% glycerol solutions (glycerol in methanol) and drying in an oven.

Coagulation Mechanism
The coagulation rate always refers to the counter-diffusion rate between casting solution and coagulant which mainly determines the inherent mechanical properties of the membrane. It also suggests that the coagulation process by this solvent is a two phase separation. Similar to that of NH₃/NH₄SCN and NMMO/H₂O systems which are just diffusion-controlled processes [8,35,36].

As the cellulose solution contacts the coagulation bath, a solvent exchange occurs, resulting in the changing of ratio of polymer, solvent, and non-solvent in the membrane formation region. The exchange of solvent with non-solvent leads to a desolvation of the cellulose molecules and to a reformation of the intra- and inter-molecular hydrogen bonds. Once the ratio enters the heterogeneous region of the phase diagram, a polymer-rich dense phase and a lean phase almost without polymers are generated. The dense phase will eventually cure to become a membrane [36].

CONCLUSION
Cellulose was dissolved directly in a NaOH complex solution (8 wt% NaOH/6.5 wt% thiourea/8 wt% urea/77.5 wt% H₂O) to obtain a transparent solution. A series of cellulose membranes were prepared from this cellulose solution by coagulating with CH₃CH₂OH (abs.) and aqueous solutions of 5 wt% H₂SO₄, 5 wt% HCl, 5 wt% HAc, 5 wt% H₂SO₄/5 wt% Na₂SO₄, 10 wt% Na₂SO₄, 10 wt% (NH₄)₂SO₄ and 10 wt% NH₄Cl, respectively. Moreover, the membrane coagulated at relatively low temperature possessed better mechanical properties as compared to those of the prepared membranes at relatively high temperatures. The best coagulant conditions of the novel cellulose membranes is 7 wt% HAC for 5 min at 10°C. This was resulted in a membrane possessing more homogeneous dense structure as has been observed by SEM and better mechanical properties. The values of σ₀ (134 MPa) of the cellulose membranes are better than those of commercially available cellophane and membranes prepared from NaOH/thiourea and NaOH/urea solutions. From CP/MAS ¹³CNMR, WAXD and FTIR spectra, the novel cellulose membrane was found to be special cellulose II crystal type. The result from WAXD also indicates that the optimal coagulation conditions efficiently facilitate cellulose chains rearrangement and make them more stable during regeneration process. The coagulation mechanism can be described as a two phase separation, namely a cellulose-rich phase in the gel and a cellulose-poor phase in solution. Cellulose in the gel phase is precipitated and regenerated during the coagulation process to form a cellulose membrane.

REFERENCES
1. Yang G, Zhang L, Regenerated cellulose microporous membranes by mixing cellulose


