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Novel regenerated cellulose films prepared by coagulating with water: Structure and properties

Ran Li[a], Lina Zhang[a,*], Min Xu[b]

[a] Department of Chemistry, Wuhan University, Wuhan 430072, China
[b] Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

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ABSTRACT

Regenerated films were successfully prepared from cellulose/NaOH/urea solution by coagulating with water at temperature from 25 to 45 °C. The results of solid ^{13}C NMR, wide angle X-ray diffraction, scanning electron microscopy (SEM) and tensile testing revealed that the cellulose films possessed homogeneous structure and cellulose II crystalline, similar to that prepared previously by coagulating with 5 wt% H_2SO_4. By changing the coagulation temperature from 25 to 45 °C, tensile strength of the films was in the range of 85–139 MPa. Interestingly, the RC35 film coagulated at 35 °C exhibited the highest tensile strength (σ_b = 139 MPa). The inclusion complex associated with cellulose, NaOH and urea hydrates in the cellulose solution were broken by adding water (non-solvent), leading to the self-association of cellulose to regenerate through rearrangement of the hydrogen bonds. This work provided low-cost and “green” pathway to prepare cellulose films, which is important in industry.

1. Introduction

Cellulose is the most abundant renewable organic materials and it will become one of basic chemical materials in future. However, the utilization of cellulose is limited because it is insoluble in most solvents and also does not melt until thermal degradation because of the strong intra- and inter-molecular hydrogen bonding (Fengel & Wegener, 1989). The polluting viscose route for producing regenerated cellulose fibers and films still dominates the current processing of cellulose for more than 100 years. It is attracted the attention of industry to search for less polluting, simple, and less energy-consuming methods than the existing ones (Gavillon & Budtova, 2008). Several solvents have been used to dissolve cellulose, such as *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate (Biganska & Navard, 2005; Zhao et al., 2007), NaOH-additive-water solution (Cai et al., 2007; Mao, Zhou, Cai, & Zhang, 2006; Zhang, Li, Yu, & Hsieh, 2010), DMAc/LiCl solution (Ass, Belgacem, & Frollini, 2006), and Brönsted Acidic Ionic Liquids (Amarasekara & Owereh, 2009). To prepare cellulose products, the cellulose solution should be regenerated in certain coagulation agent. For cellulose–NMMO–water solution, polar liquids, such as water or alcohol, are used as coagulation agents, which are miscible with NMMO and cause its removal from cellulose solution (Broens, Altena, Smolders, & Koenhen, 1980; Frommer & Lancet, 1972; Koenhen, Mulder, & Smolders, 1977; Strathmann, Kock, Amar, & Baker, 1975). According to Shen's report (Shen & Cabasso, 1982), this kinetics is mainly controlled by the relative velocities of the diffusions of the solvent from the solution into the coagulation bath and the nonsolvent from the bath into the solution. The solvent power, the concentration of cellulose, and the strength of interaction between the solvent and the nonsolvent affect the precipitation kinetics. Laity, Glover, and Hay (2002) have studied the composition and phase changes during the regeneration of cellulose–NMMO–water solutions in water, indicating that the cross section of regenerated cellulose appears uniformly structure and porosity on the scale of a few nanometers. The regeneration of cellulose from NMMO solutions by coagulating with water is as a result of the phase separation (Fengel & Wegener, 1989).

In our laboratory, NaOH/urea aqueous solutions have been developed to dissolve cellulose. In NaOH/urea aqueous solution, NaOH “hydrates” can be more easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperatures, while the urea hydrates can possibly be self-assembled at the surface of the NaOH hydrogen-bonded cellulose to form an inclusion complex (IC), leading to the good dissolution (Cai et al., 2008). Moreover, it has been confirmed that a worm-like cellulose IC being surrounded with urea hydrates exists in the cellulose solution. The cellulose solution is relatively unstable and can be very sensitive to temperature, polymer concentration and storage time, leading to the aggregations (Cai et al., 2008). At either higher temperature (above 30 °C), or lower temperature (below

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* Corresponding author. Tel.: +86 27 87219274; fax: +86 27 68762005.
E-mail address: linazhangwhu@gmail.com (L. Zhang).

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−3 °C) or for longer gelation time, the cellulose gels can form in the cellulose solutions, as a result of the strong self-association force of cellulose, because of the destruction of IC (Cai & Zhang, 2006). In our laboratory, H_2SO_4/Na_2SO_4 aqueous solution has been used as the coagulant to prepare regenerated cellulose membrane (Mao et al., 2006; Zhang, Mao, Zhou, & Cai, 2005b), fiber (Qi, Cai, Zhang, Nishiyama, & Rattaz, 2008), microsphere (Luo & Zhang, 2010) and hydrogel (Chang, Duan, Cai, & Zhang, 2010). It is worth noting that we have successfully spun regenerated cellulose fibers from custom-made equipments, which contains 1000 L dissolution tank, low-temperature-cycle cooling system, filter, vacuum defoamer, and spinning system (Li et al., 2010). So, we are interested in clarifying of the reason of the coagulation and regeneration of the cellulose solution by heating, adding H_2SO_4 or others. All the times we used H_2SO_4 as coagulant, and considered that the regeneration of cellulose was because of the neutralization of NaOH and H_2SO_4. The purpose of this work is to study on the water role as coagulant and mechanism of the regeneration. The cellulose solution was coagulated in water with different temperature to prepare regenerated films and their morphology, structure and properties were characterized to evaluate the potential applications in the industry. If we can use water as direct coagulant, this would lead to lower cost and less pollution, which is much useful in cellulose industry.

2. Experimental

2.1. Materials

The cellulose (cotton linter pulp) was provided by Hubei Chemical Fiber Group Ltd. (Xiangfan, China), and the α-cellulose content was more than 95%. The cellulose was used without further purification. The viscosity-average molecular weight (M_η) of cellulose in cadoxen was determined using an Ubbelohde viscometry at 25 °C to be 9.6×10^4 (degree of polymerization, DP = 600) according to Mark–Houwink equation $[\eta]\,(\mathrm{mL\,g^{-1}}) = 3.85 \times 10^{-2}\,(M_w)^{0.76}$ (Brown & Wikstrom, 1965). The cotton linter pulp sheets were shredded and dried for 8 h in a vacuum oven, stored in a desiccator until used. NaOH, urea, H_2SO_4 and Na_2SO_4 were bought from Sinophram Chemical Reagent Co., and were of analytical grade.

2.2. Films preparation

Cellulose solution was prepared according the previous method (Zhang, Cai, & Zhou, 2005a). Into a 250 mL beaker, a desired amount of NaOH, urea and distilled water (7:12:81 by weight) was added, and the resulting mixture aqueous solution was stored in a refrigerator. After the aqueous solution was precooled to −12.5 °C, cellulose was added immediately with stirring vigorously for 5 min at ambient temperature to obtain the transparent cellulose dope with concentration of 5 wt%. The cellulose dope was subjected to centrifugation at 120 Hz (7200 rpm) for 15 min at 5–10 °C in order to exclude the slightly remaining undissolved part, impurities, and bubbles. The transparent solution was immediately cast on a glass plate. Subsequently, the resulting gel sheets were immersed into water bath to coagulate and regenerate, then were washed in distilled water until pH 7, and at last were dried on PMMA sheet. The regenerated cellulose (RC) films prepared by coagulating with water at different temperature (25, 30, 35, 40, 45 °C) for 5 min were coded as RC25, RC30, RC35, RC40 and RC45, respectively. Films of different thickness (0.33 mm, 0.66 mm, 1.20 mm, 1.44 mm) were also prepared at 35 °C, which were coded as RC35-1, RC35-2, RC35-3, RC35-4. The film by coagulating with 5 wt% H_2SO_4 for 5 min was coded as RC0. Photographs of RC35 and RC0 are shown in Fig. 1.

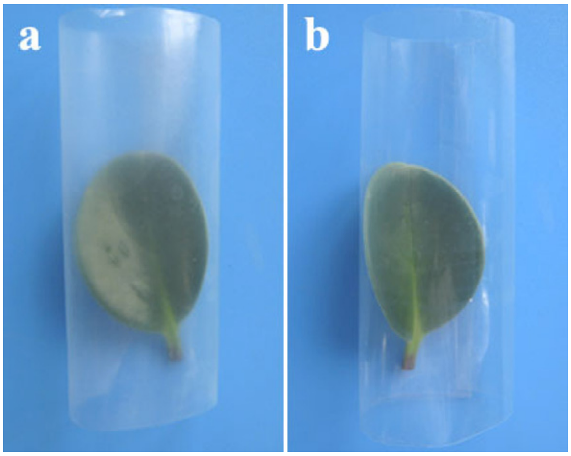


Fig. 1. Photographs of the regenerated cellulose films of RC35 (a) and RC0 (b).

2.3. Characterizations

The *N* contents in the cellulose films were measured with an elemental analyzer (Heraeus Co., Germany). Scanning electron micrographs (SEM) were taken on a Hitachi S-570 scanning electron microscope with 20 kV accelerating voltage and at magnification of 3000. The wet RC membranes were frozen in liquid nitrogen, immediately snapped and then vacuum-dried. The free surface (side in direct contact with the coagulant), the back surface (bottom side contact with the glass) and the fracture surface (cross-section) of the films were sputtered with gold, then were observed and photographed. Solid-state ^{13}C NMR spectra of the cellulose were recorded on a BRUKER spectrometer operated at a ^{13}C frequency of 100 MHz using the combined technique of proton dipolar decoupling, magic angle spinning (MAS) and cross-polarization (CP). The spinning speed was set at 12 MHz for all samples. The contact time was 2 ms, the acquisition time 30 ms and the recycle delay 4 s. A typical number of 7500 scans were acquired for each spectrum. X-ray diffraction (XRD) measurement was carried out on an XRD diffract meter (D8-Advance, Bruker). The patterns with CuKα radiation (λ = 0.15406 nm) at 40 kV and 30 mA were recorded in the region of 2θ from 5 to 45°. Samples were ground into powders and dried in a vacuum oven at 60 °C for 48 h. The crystallinity χ_c (%) of the cellulose fibers and composite fibers were estimated by Rabek's method, using the following relationship:

$$\chi_c = \left[\frac{S_c}{S_c + S_a}\right] \times 100$$

where S_c and S_a are the area of crystal and amorphous diffraction peaks of samples, respectively.

The tensile strength (σ_b) and elongation at break (ε_b) of the films in dry state were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) according to ISO 527-2, 1993 (E) at a speed of 5 and 10 mm $\mathrm{min^{-1}}$, respectively. The σ_b and ε_b values were the average of five measurements. Optical transmittance (T_r) of the films was measured with a UV–vis spectroscope (Shimadzu UV-160A, Japan) in the wavelength ranging from 400 to 800 nm.

3. Results and discussion

3.1. Structure of cellulose films

Fig. 1 shows the photographs of RC35 and RC0. The films prepared by coagulating with heated water were transparent, suggesting that good regeneration of the cellulose in the solution

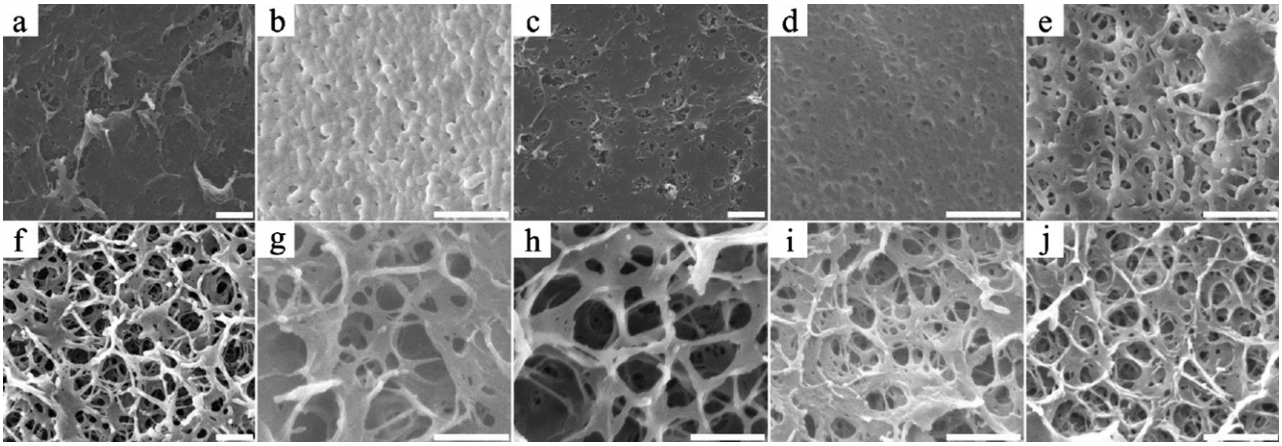


Fig. 2. SEM images of the surface of the films prepared from coagulation bath of water: up—the side contacted with a glass plate; down—the side contacted with the coagulant. (a, f) RC25; (b, g) RC30; (c, h) RC35; (d, i) RC40; (e, j) RC45. Scale bars stand for 2 μm.

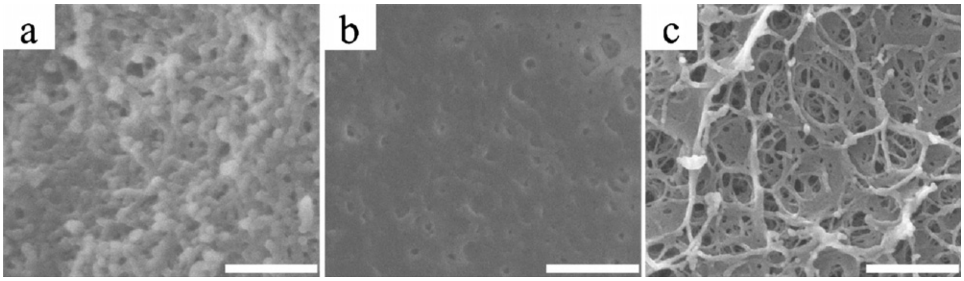


Fig. 3. SEM images of the cross section of the films prepared from coagulation bath of water. (a) RC25; (b) RC35; (c) RC45. Scale bars stand for 2 μm.

through the hydrogen-bonding rearrangement of the cellulose macromolecules. Fig. 2 shows the SEM images of the surface of the two sides: one is contacted with a glass plate (side A, bottom), and the other is contacted with the coagulant (side B, up). The films exhibited homogeneous porous structure, indicating a complete regeneration of cellulose. This was a physical regeneration during the coagulation. Interestingly, the pore size of the cellulose films at wet state was much larger in side B than that in side A. For example, the $2r_e$ (the average diameter of the pores from SEM image) in RC-35 was changed from 800 nm to 200 nm. This could be explained that the coagulant diffusing much faster in side B than that in side A. With an increase of the water temperature, the pore size of both surfaces of the cellulose films increased, as a result of the enhancement of the removal of the solvent from the cellulose solution, leading to the phase separation. The result of the elemental measurement indicated that there was no N in the films and the films were washed until pH 7, suggesting that NaOH and urea have been washed out. Fig. 3 shows the SEM images of the cross section of RC-25, RC-35 and RC-45. The $2r_e$ value increased from 100 nm to 350 nm with an increase of the temperature (Table 1). The cellulose solution was coagulated more slowly at low temperature than at relatively high temperature. However, high temperature (>50 °C) led to observable phase separation, resulting in the imperfect regeneration of cellulose.

Fig. 4 (left) shows the X-ray diffraction patterns of the cellulose films. The regenerated cellulose films exhibited three peaks at $2\theta = 12.4^\circ$, 20.2°, and 22.2°, assigned to the $(1\,\bar{1}\,0)$, $(1\,1\,0)$, and $(2\,0\,0)$ planes (Isogai, Usuda, Kato, Uryu, & Atalla, 1989; Kamide, Okajima, & Kowsaka, 1992). The regenerated cellulose films were quite different from that in the native cellulose (cotton linter pulp), in which the three peaks at $2\theta = 14.9^\circ$, 16.5°, 22.7°, assigned to the $(1\,1\,0)$, $(1\,\bar{1}\,0)$, and $(2\,0\,0)$ planes of cellulose I crystalline. This indicated that the original cellulose has transferred into cellulose II here. An obvious large peak appeared at 12° for $(1\,\bar{1}\,0)$, compared to the classic cellulose II crystal, suggesting the crystal state of conventional cellulose II in the films. The total crystallinity (χ_c, %) of the cellulose films decreased from 44.3% to 40.4% with an increase of the coagulation temperature as summarized in Table 2. Fig. 4 (right) shows CP/MAS ^{13}C NMR spectra of the native cellulose (a) and regenerated cellulose film (b). There were four main peaks at 105.8, 88.0, 73.2 (75.0, 72.5) ppm in the spectrum of

Table 1
Experimental results of mean pore size ($2r$) and standard deviation (σ) for various regenerated cellulose films analyzed from SEM.

Samples	From SEM images					
	Free surface		Cross section		Bake surface	
	$2r_e$	σ_e	$2r_e$	σ_e	$2r_e$	σ_e
RC-25	342	118	140	26	159	43
RC-30	411	87	–	–	197	52
RC-35	547	73	280	40	223	35
RC-40	675	103	–	–	256	33
RC-45	809	76	343	58	277	39
RC-0	265	60	211	36	202	42

Table 2
Total crystallinity (χ_c) and physical properties for various regenerated cellulose films.

Samples	χ_c (%)	σ_b (MPa)	ε_b (%)	T_r (at 800 nm)
RC-25	44.3	90 ± 5	1.85	71
RC-30	43.7	97 ± 3	3.53	68
RC-35	43.4	129 ± 10	4.44	69
RC-40	41.5	100 ± 5	2.96	67
RC-45	40.4	89 ± 4	3.27	57
RC-0	45.7	105 ± 6	8.14	87

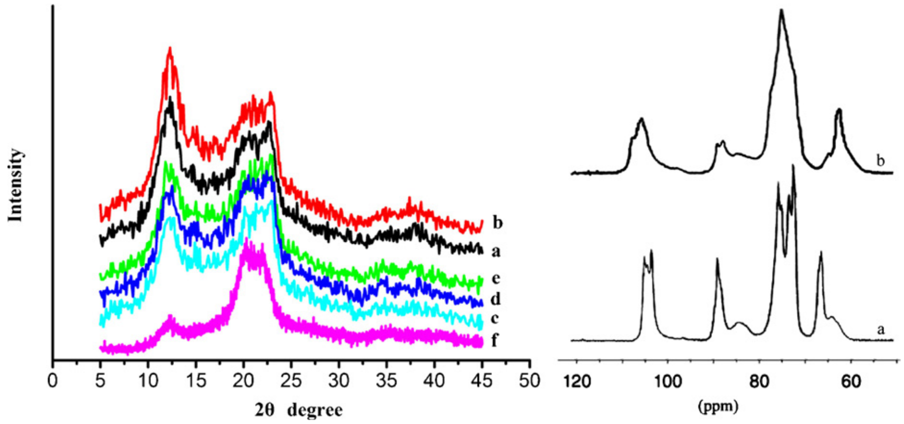


Fig. 4. Left: X-ray diffraction patterns of the films prepared from coagulation bath of water. (a) RC25; (b) RC30; (c) RC35; (d) RC40; (e) RC45; (f) RC0. Right: CP/MAS ^{13}C NMR spectrum of cellulose I (cotton linter pulp) (a), the regenerated cellulose film (b).

the regenerated cellulose film, assigned to the C1, C4, C5 (C3, C2), and C6 peak at 63.3 ppm. Compared with native cellulose sample, the C6 signal of the regenerated cellulose film obviously shifted from 65.6 to 63.3 ppm as a single peak, suggesting that the "t–g" conformation (ca. 66 ppm for C6) of the C6–OH group for the crystalline parts of cellulose I had changed into a "g–t" conformation (ca. 61–63 ppm for C6) of cellulose II (Kamide, Okajima, & Kowsaka, 1992). The results strongly confirmed that the cellulose could be regenerated completely by coagulating with water and the cellulose solution did transform into regenerated cellulose II. The C4 signal at around 88 ppm and its shoulder peak at 84.0 ppm depended on the status of carbons located in either the crystalline or amorphous regions, respectively (Clark, Fowler, & Stephenson, 1983). For the regenerated cellulose film, the C4 peaks located at 88.0 ppm shifted to higher magnetic fields than that of the native cellulose (89.3 ppm), and the intensity was significantly lower, suggesting a decrease in crystallinity. It was demonstrated further that the cellulose solution was regenerated completely in the water coagulant to form regenerated cellulose films. Therefore, water was used successfully for the coagulation of the cellulose solution to prepare regenerated cellulose films through the hydrogen bonding rearrangement. Compared with H_2SO_4 aqueous solution as coagulant, this coagulation with water is "green" process, and it is quite useful in the industry for the packaging materials.

3.2. *Properties of cellulose films*

Fig. 5 (left) shows the stress–strain curves of the cellulose films. The tensile strength (σ_b) and elongation at break (ε_b) of the films prepared from the water coagulant at various temperatures are listed in Table 2. The RC35 film coagulated at 35 °C exhibited the better mechanical properties and the σ_b values achieved to 139 MPa, much larger than that of the RC0 cellulose film coagulated with the acidic. The other cellulose films of RC25, RC30, RC40, and RC45 displayed tensile strength similar to RC0. Usually, optical transmittance (T_r) reflects the homogeneity, and is related to the structure of the materials. The T_r values at 800 nm of the RC films are summarized in Table 2. The regenerated cellulose films exhibited a good optical transmittance at 800 nm on the whole, indicating a homogeneous structure. Obviously the T_r values of the films (RC25–RC45) were lower than that coagulated with the sulfuric acid. This could be explained that there were many bigger holes in and on the surface of the films coagulated in water, compared with that in acid. These holes made the light to lose, leading to the reducing of the T_r value. In addition, the film was contracted more easily in the sulfuric acid aqueous system, leading to the relatively smaller pore size of the RC0 film. However, if the drawing orientation was performed, the porosity would be reduced, leading to the improvements of the transmittance and the mechanical properties of the films.

The mechanical properties of the cellulose films with different thickness are shown in Fig. 5 (right). It was indicated that with a decrease of the thickness of the cellulose films, the tensile strength increased on the whole. This further proved that the coagulation and regeneration were mainly influenced by the diffusion speed of the nonsolvent. Thinner film was regenerated more completely, leading to higher tensile strength. Water is low-cost and nonpolluted coagulant, where no other chemical agents were brought to the system. So the waste water from the producing of the regenerated cellulose films is easy to be recycled. Therefore, this coagulant is "green", and it is very important in the industry of novel cellulose materials.

3.3. *Regeneration process of cellulose in water*

From the above results, the regeneration of cellulose depended on the rate of coagulation, namely the rate of solvent diffusing out of, and the rate of non-solvent diffusing into the cellulose solution. As shown in SEM images of Figs. 2 and 3, relatively large pore size of the films displayed at higher temperature. Namely, the non-solvent (water) entering into cellulose solution and the solvent (NaOH and urea) diffusing out were faster at higher temperature than at lower temperature. Cellulose inclusion complex (IC) was destroyed by heating, resulting in the cellulose gelation through the formation of new hydrogen bonding networks (Cai & Zhang, 2006). Actually, by raising temperature, the inclusion complex (IC) associated with NaOH and urea hydrates bound on the cellulose chains were perturbed, and water was the non-solvent, so the junction between cellulose molecules occurred as a result of the strong self-association force of cellulose, which supported the viewpoint above.

In view of these results, a model describing the regeneration process of the cellulose in NaOH/urea aqueous solution is proposed in Scheme 1. The cellulose inclusion complex hosted by urea existed in NaOH/urea aqueous solution to form homogeneous cellulose solution, as shown in Scheme 1a. By adding water (non-solvent), the IC consisted of NaOH and urea, which was bound on the cellulose molecules, were broken. Thus, the cellulose aggregates occurred, as a result of the self-association of cellulose chains. In this case, NaOH and urea molecules bonded on the –OH groups of cellulose were removed out in water, and the new –OH groups of cellulose were regenerated through the exchanging with water to form regenerated cellulose gel sheets, as shown in Scheme 1b. The

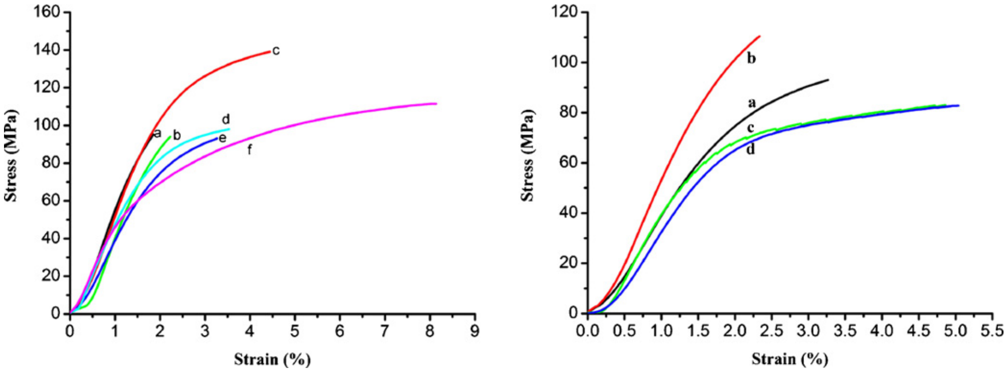
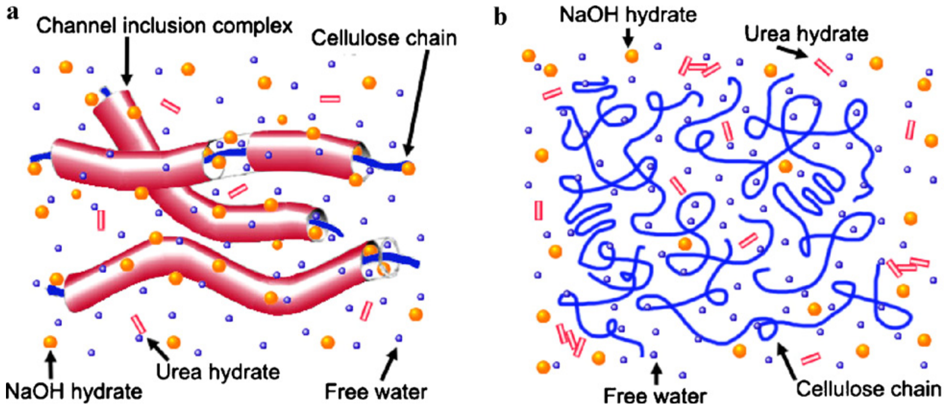


Fig. 5. Left: stress–strain curves of the films prepared from coagulation bath of water. (a) RC25; (b) RC30; (c) RC35; (d) RC40; (e) RC45; (f) RC0. Right: stress–strain curves of the films at different thickness prepared from coagulation bath of water. (a) RC35-1; (b) RC35-2; (c) RC35-3; (d) RC35-4.



Scheme 1. The schematic diagram of the regeneration mechanism.

rearrangement of the hydrogen bonds of cellulose occurred here, leading to the regeneration. There were many pores in the cellulose gel sheets, as a result of the phase separation between solvent and non-solvent.

4. Conclusion

The cellulose solution was successfully coagulated in water at various temperatures to prepare regenerated cellulose films. Their structure and properties were similar to the films which were regenerated in the sulfuric acid. These films have homogeneous structure and cellulose II crystal, confirming that the cellulose in the solution has been regenerated completely by coagulating with water. The regeneration mechanism was proposed that the inclusion complex associated with cellulose, NaOH and urea hydrates were broken by adding water (non-solvent), leading to the self-association of cellulose to form the gel sheets. Thus the regenerated cellulose film was formed through rearrangement of the hydrogen bonds. With an increase of the temperature from 25 to 45 °C, the diffusion was faster, leading to the increased pore size. In our findings, 35 °C was the better coagulation temperature. As a coagulant, water is low cost and “green”, and it is useful for the recycle of cellulose solvent. This technology would bring wide application prospect in the cellulose industry.

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