Improved Synthesis of Cellulose Carbamates with Minimum Urea Based on an Easy Scale-up Method

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S Supporting Information

ABSTRACT: Cellulose carbamates (CCs) were successfully prepared from cellulose/urea (CU) mixtures based on an easy scale-up method and minimum urea. Urea content and the reaction conditions on the nitrogen content of the reacted CU (RCU) mixtures and CCs were systematically investigated. RCU mixtures and CCs were characterized with elemental analysis, Fourier transform infrared spectroscopy, X-ray diffraction, NMR spectrometry and solubility testing. The result indicated that almost all of urea was involved in the derivatization reaction and cellulose was converted into CC with absence of byproducts. The nitrogen content of CCs increased with an increase of the urea content and the reaction temperature, as well as the reaction time. CCs retained the cellulose I crystalline, and the degree of polymerization hardly changed with the reaction conditions. CCs prepared from CU mixtures with the urea content of 3.4−4.6 wt % displayed good solubility in NaOH/ZnO aqueous solutions. Especially, RCU mixtures without washing could be also well dissolved in NaOH/ZnO solutions and its solubility could reach 97%. This work provided a simple, pollution-free and economic pathway for preparing CCs, which is expected to be useful for the CarbaCell process.

KEYWORDS: Cellulose carbamate, Urea, Conventional heating, Structure, Solubility

■ INTRODUCTION

Cellulose is the most abundant renewable biopolymer with outstanding properties and a variety of useful applications.[1,2] It is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β-(1→4)-linked glucose repeating units. There are numerous inter- and intramolecular hydrogen bonds, which result in poor solubility in water and common organic solvents.[3] To overcome these disadvantages, cellulose is always modified by derivatization so that it can be processed in common industrial processes, which greatly expands the applications of cellulosic materials.[4,5]

Throughout the years, there has been extensive research to design, synthesize and characterize carbamate derivatives of cellulose with various properties.[6−16] In these reports, the products were found to be applicable as regenerated cellulose fibers via the CarbaCell process, in which a new reaction variant employed urea to convert cellulose into cellulose carbamate (CC).[5,17] The CarbaCell process was advantageous in retaining the use of the viscose spinning technology while avoiding the use of hazardous sulfur-containing compounds (CS₂). CC was also advantageous due to its relatively high stability at room temperature, which allowed storage for over 1 year. Besides using in a rayon process, the carbamates were also employed in a variety uses such as in hygiene, healthcare and medical applications.[18−20] CCs could be prepared through various routes. In conventional processes, CCs with the nitrogen content (N%) of 1−2.5% were produced by reacting cellulose with urea above its melting point of 132.7 °C in an alkali medium and organic solvents such as xylene, toluene with or without the presence of catalyst.[21,22] An alternative path to obtain CC was through the mixing of cellulose with ammonia solution that containing urea.[23] In this case, ammonia brought the structural change in cellulose and facilitated its reaction with urea. Because of the rigorous condition and the consumption of the highly involved of chemicals (xylene, ammonia etc.), the above methods had limitations for technical application.[5,17] Recently, several methods for the synthesis of CCs including the isocyanate-pyridine procedure,[24] "pad-dry-cure" method,[25] supercritical carbon dioxide assisted impregnation[26−28] and electron radiation[29] were reported. In these methods, the weight ratio of urea and cellulose were high and mainly in the range of 1:1−4:1. All were aimed to obtain a homogeneous distribution of the substituent in cellulose pulp, which promoted its dissolution in alkali, and achieved the solution properties for fiber spinning. In our previous work, a novel method was presented for the synthesis of CCs through

microwave heating under catalyst-free and solvent-free conditions.[30−32] The process decreased the reaction time from hours to minutes, which was greatly significant for the commercialization of the carbamate process. However, the method holds some disadvantages, would benefit from further enhancement of easy workup procedure and reduced power consumption from urea recycling and washing water. There is still a challenge to find nontoxic, easily handled, economic and economically feasible method for the carbamation of cellulose.

In this work, CCs were prepared from cellulose with a small amount of urea through conventional heating. Additionally, the solubility of the as-obtained CCs in NaOH/ZnO aqueous solutions was systematically investigated. Compared with the traditional methods, it was an economic, pollution-free and easy scale-up method with absence of byproducts. This work provides a promising way to prepare CCs and to improve the CarbaCell process for the production of regenerated cellulose fibers.

■ EXPERIMENTAL SECTION

Materials. Cotton linter pulps with α-cellulose content of 93% were provided by Hubei Chemical Fiber Group Ltd. (Xiangyang, China), and the degree of polymerization (DP) was determined to be 620. Urea, ZnO and NaOH of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification.

Preparation of Cellulose Carbamates. Every 500 g of cotton linter pulp was immersed into 10 kg of urea solution with the concentration of 1, 2, 3, 5 and 10 wt %, respectively. The mixtures were then left at ambient temperature for 1 h, followed by filtration and oven drying. The corresponding cellulose/urea (CU) mixtures with urea content of 2.1, 3.4, 4.1, 4.6 and 9.8 wt % were obtained, and coded as CU1, CU2, CU3, CU5 and CU10, respectively. In a typical reaction procedure, the CU3 mixtures (40 g) were heated in a hot-air oven (DHG-9070A, Shanghai Suopu, China) at 180 °C for 50 min. Then, one-half of the reacted mixture was washed with distilled water, followed by vacuum-dry, and the corresponding CC coded as CC3-180-50 was obtained. The remaining reacted mixture without washing was coded as RCU3-180-50 for comparison. The N% of RCU3-180-50 and CC3-180-50 were determined to be 0.825% and 0.497%, respectively. By changing the urea content (2.1−9.8 wt %), the reaction temperature (140−180 °C) and time (0.5−2.5 h), the RCU mixtures and their corresponding CCs with different N% were obtained, and coded as RCUx-y-z and CCx-y-z, respectively, where x, y and z represent the concentration of urea solution for immersing, reaction temperature and time, respectively. The carbamation efficiency (E_c, %) of the CU mixtures during the synthesis process was calculated as the following equation:

$$E_c = \frac{N_1}{N_2} \times 100\% \tag{1}$$

where N_1 is the nitrogen content (%) of the obtained CC sample and N_2 is the nitrogen content (%) of the corresponding CU mixture.

Solubility Testing. In accordance with previous work,[33,34] an aqueous solution was prepared by directly mixing NaOH, ZnO and distilled water (7:1.6:81.4 in wt %). The solubility of RCU mixtures and CCs were examined through the dispersion of the samples in NaOH/ZnO solutions, followed by cooling to −12 °C. The dissolved and insoluble parts were separated through centrifugation at 7200 rpm and 25 °C for 15 min, followed precipitated with acetic acid (3 wt %) to obtain recovered cellulose. The recovered cellulose was washed with distilled water and then freeze-dried. The solubility (S_a) was calculated by

$$S_a = \frac{w_0 - w_1}{w_0} \tag{2}$$

where w_0 is the weight of the original sample (g) and w_1 is the weight of the insoluble part (g).

Characterizations. The intrinsic viscosity ($[\eta]$) of cellulose and CCs in cadoxen solution were measured with an Ubbelohde viscometer at 25 °C. The DP was calculated from $[\eta]$ by the following equation:[35]

$$[\eta] = 1.75 \times DP^{0.69} \ (\text{mL·g}^{-1}) \tag{3}$$

The nitrogen content (N%) of RCU mixtures and CCs was determined with an elemental analyzer (CHN-O-RAPID Heraeus Co., Germany), and the degree of substitution (DS) of CCs was calculated from their nitrogen content. Fourier transform infrared (FT-IR) spectra were obtained with a NICOLET 5700 FTIR spectrometer. The test specimens were prepared by KBr disk technique. X-ray diffraction (XRD) patterns were measured with an X-ray diffractometer (D8, BRUKERAXS GmbH, Karlsruhe, Germany). XRD patterns with Cu Kα radiation ($\lambda = 1.5406 \times 10^{-10}$ m) at 40 kV and 30 mA were recorded in the range of $2\theta = 6−40°$. The crystallinity index (CI, %) of the sample was calculated as the following equation:[36,37]

$$CI = 100 \times \frac{I_{020} - I_{am}}{I_{020}} \tag{4}$$

where I_{020} is the maximum intensity of the principal peak (020) lattice diffraction (at 22.7° of 2θ for cellulose I, and 21.7° of 2θ for cellulose II) and I_{am} is the intensity of diffraction attributed to amorphous cellulose (at 18° of 2θ for cellulose I and at 16° of 2θ for cellulose II).

Online thermal gravimetric mass spectrometry (TG-MS) analyses of the gases evolved from the CU10 mixture during the heating process were conducted on a Netzsch STA449F3 equipped with a Netzsch Q430C mass spectrometer. The TG experiment was operated from room temperature to 165 °C with a heating rate of 10 °C min^{-1}, and then kept at 165 °C for 1.0 h under a continuous flow of N$_2$ (100 mL min^{-1}). A transfer line, specially designed to connect a vacuum pump in order to optimize the amount of evolved gases, transferred from TG to MS. The signals for mass numbers of 17 (NH$_3$) and 43 (HNCO) were continuously detected.

Solid-state ^{13}C NMR spectra were recorded on a Bruker AVANCEIII spectrometer operated at a ^{13}C frequency of 75.15 MHz using the combined technique of magic angle spinning (MAS) and cross-polarization (CP). The spinning speed was set at 5 kHz, the contact time was 3 ms, the acquisition time was 50 ms, and the recycle delay was 3 s. The ^{13}C chemical shift was externally referenced to the high field resonance of hexamethylbenzene at 17.17 ppm. At least 5000 scans were accumulated for each spectrum. The liquid ^{13}C NMR measurements of RCU3-180-50 and CC3-180-50 in 7 wt % NaOH/ 1.6 wt % ZnO/D$_2$O were recorded on a Bruker Avance III 600 MHz NMR spectrometer (Bruker BioSpin, Rheinstetten, Germany) at 25 °C. The sample concentration was about 4.5 wt %.

■ RESULTS AND DISCUSSION

Effects of Reaction Temperature. Scheme 1 illustrates the improved synthesis of CCs based on an easy scale-up method and minimum urea. Cotton linter pulp was first immersed in a dilute urea solution (1−10 wt %). Urea could be effectively absorbed on the cotton linter pulp to form

Scheme 1. Improved Synthesis of Cellulose Carbamate Based on an Easy Scale-up Method and Minimum Urea
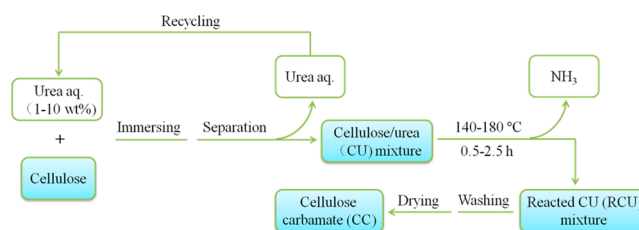
homogeneous mixtures because of the good absorption ability of cellulose fibers. The excessive urea solution was recycled after filtration, and the recovery percent was in the range of 85−95%. And then, the dried CU mixtures with the urea content of 2.1−9.8 wt % was heated in a conventional oven at 140−180 °C for 0.5−2.5 h. The RCU mixtures with little byproducts were obtained finally. After water-washed and oven-dried, the white or slight yellow CCs could be obtained. Previously, cellulose was usually modified with a large amount of urea to achieve abundant carbamate groups on the cellulose backbone, along with producing plenty of hazardous by-products such as isocyanate, biuret etc.[12] Moreover, washing of the byproducts and recycle of the excessive urea prolong the processing procedures and resulted in a high cost. Compared with previous methods, the urea content of CU mixtures was decreased from 10−80 wt % to 2.1−9.8 wt %, while avoiding the release of excess NH_3 during the synthesis process. Therefore, preparation of CCs from cellulose with small amount of urea under conventional heating was green, economic and easy to scale up.

Figure 1a shows the dependence of the N% of the RCU mixtures on the reaction temperature for 50 min. As the

of RCU10 mixtures decreased from 2.902 to 1.547%. That is to say, the urea decomposed into isocyanic acid and NH_3 and escaped from the mixtures.[15,21] Figure 1b displays the dependence of the N% of CCs on the reaction temperature for 50 min. The result indicated that the N% of CCs was relative low when the reaction temperature was lower than 150 °C and ranged from 0.091 to 0.215% (DS, 0.011 to 0.025). As the temperature increased from 150 to 180 °C, the N% of the CCs increased gradually and reached 0.095−0.847% (DS, 0.011−0.101). The reason was that the higher temperature favored the esterification and enhanced the degree of esterification for cellulose. However, higher temperature might result in yellowing and cross-linking of cellulose.[12,24,38]

Effects of Reaction Time. Figure 2a displays the dependence of the N% of the RCU mixtures on the reaction

Figure 2. Effect of the reaction time on the nitrogen content of (a) RCU mixtures and (b) CCs obtained from CU mixtures with different urea content. (Reaction temperature is 165 °C).
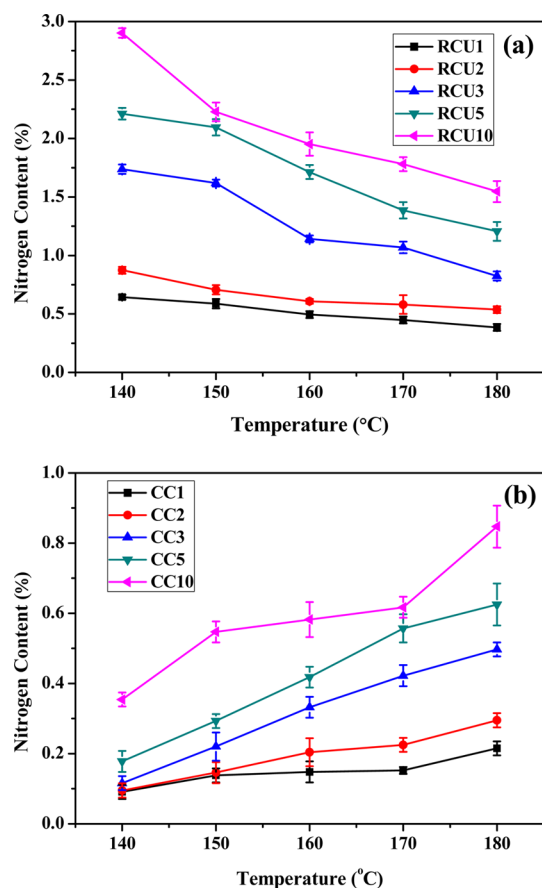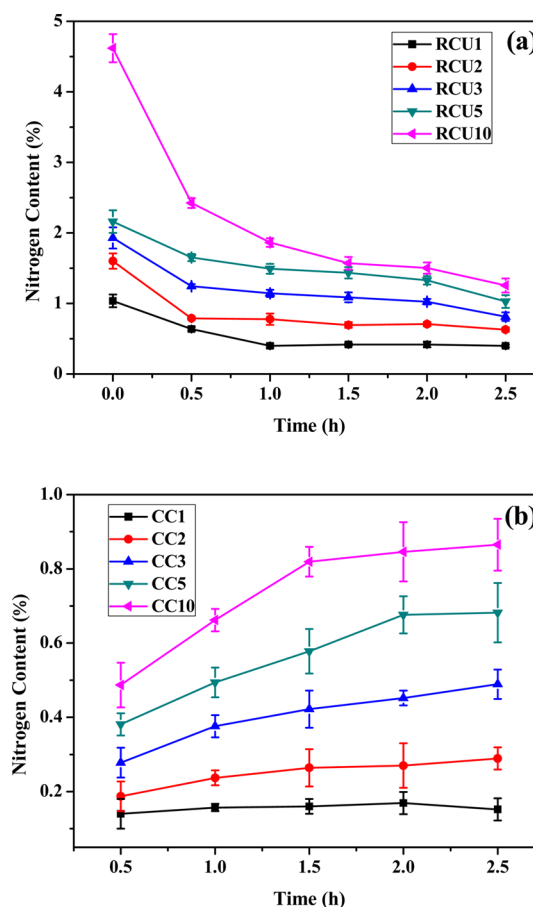

Figure 1. Effect of the reaction temperature on the nitrogen content of (a) RCU mixtures and (b) CCs obtained from CU mixtures with different urea content. (Reaction time is 50 min).

temperature increased from 140 to 180 °C, the N% of RCU1 and RCU2 mixtures decreased slightly and varied in the range of 0.644−0.385% and 0.874−0.573%, respectively. However, the N% of RCU3, RCU5 and RCU10 mixtures decreased significantly with increasing temperature. For example, the N%

time at 165 °C. Within the first 0.5 h, the N% of RCU mixtures decreased linearly. Especially, the N% of RCU10 decreased sharply and varied from 4.618 to 1.255%. With an increase of the reaction time from 0.5 to 2.5 h, the N% of all RCU mixtures decreased slightly. Figure 2b shows the dependence of the N% of CCs on the reaction time at 165 °C. By increasing the reaction time from 0.5 to 2.0 h, the N% of CCs increased linearly, and the maximum N% value appeared when the time was 2.5 h. For example, the N% of CCs obtained from RCU3 increased from 0.381 to 0.676% in the first 2.0 h, and almost constant (0.682%) with further increase of the reaction time. The lower reaction rate after 2.0 h might be attributed to the

sharp decrease of the urea content in the RCU mixture and some side reactions.

Figure 3 presents the online TG-MS profile of the CU10 mixture. As the temperature reached 80−100 °C, CU10
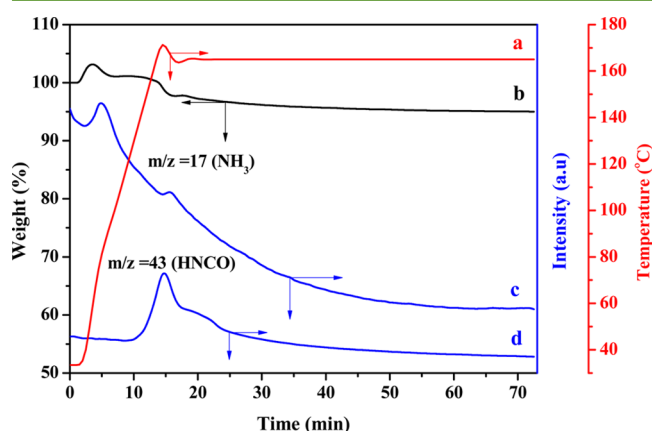

Figure 3. Analysis of the outlet gases from the reacted CU10 mixture during the heating process by online TG-MS under a nitrogen atmosphere: (a) temperature, (b) TG and (c, d) evolved gases curves.

mixture showed the first weight loss, which was mainly attributed to the release of moisture. At the same time, the first peak in the curve assigned to NH_3 ($m/z = 17$) emerged, which should be caused by the hydrolytic reaction of urea.[39] As the temperature increased to 165−170 °C, the second weight loss peak of CU10 mixture occurred. Meanwhile, both the curves of NH_3 and isocyanic acid (HNCO, $m/z = 43$) displayed an obvious peak. This demonstrated that the decomposition of urea into NH_3 and HNCO during the heating process. Figure 4
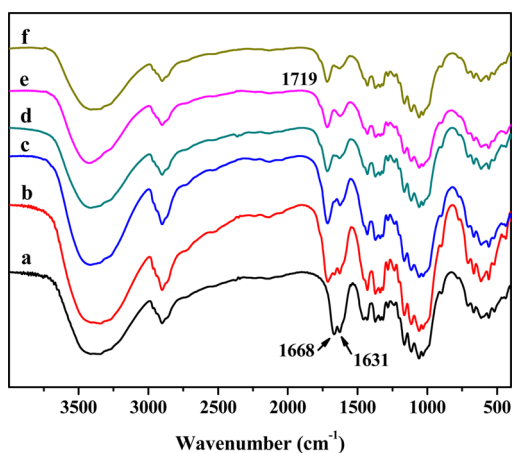

Figure 4. FT-IR spectra of (a) CU10, (b) RCU10-165-0.5, (c) RCU10-165-1.0, (d) RCU10-165-1.5, (e) RCU10-165-2.0 and (f) RCU10-165-2.5.

shows the FT-IR spectra of CU10 and its reacted products at 165 °C with different time. The peak at 1668 cm^{-1} in CU10 mixture assigned to the stretching vibration of the carbonyl (C=O) in the base of urea almost disappeared in the first 0.5 h.[40] There was a new absorption immerged at 1719 cm^{-1} in all of the reacted mixtures, corresponding to the stretching vibration of carbonyl in the base of the urethanes in the carbamates, which increased with an increase of the reaction time.[41] The results illustrated that carbamate ester groups

gradually introduced into the cellulose chain by reaction of hydroxyl groups with HNCO formed as an active intermediate on the decomposition of urea.

Effects of Urea Content. During the carbamation process, urea was first decomposed into isocyanic acid, which then reacted with cellulose to form CCs. Thus, the urea content in the CU mixtures plays an important role in the esterification of cellulose. As shown in Figures 1a and 2a, the N% of RCU mixtures decreased markedly as the urea content of CU mixtures was high (4.1−9.8 wt %). Meanwhile, the N% of CCs increased gradually. For example, as heated the CU mixtures with the urea content of 2.1, 3.4, 4.1, 4.6 and 9.8 wt % at 180 °C for 50 min, the N% values of the obtained CCs were 0.215, 0.295, 0.497, 0.625 and 0.847% (DS, 0.025, 0.034, 0.058, 0.074 and 0.101), respectively.

Figure 5 shows the FT-IR spectra of the cellulose and CCs. In comparison with the native cellulose, CCs showed an
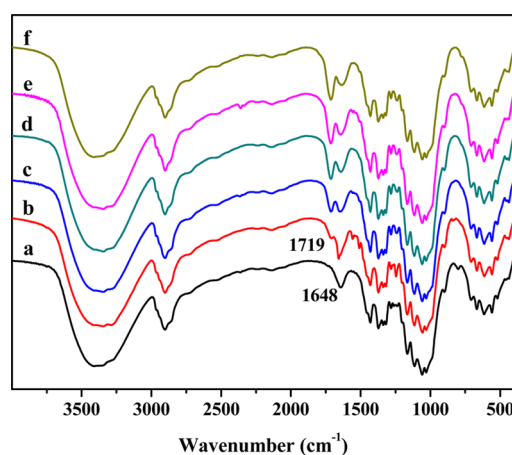

Figure 5. FT-IR spectra of (a) cellulose pulp, (b) CC1-180-50 (N% = 0.215, DS = 0.025), (c) CC2-180-50 (N% = 0.295, DS = 0.034), (d) CC3-180-50 (N% = 0.497, DS = 0.058), (e) CC5-180-50 (N% = 0.625, DS = 0.074) and (f) CC10-180-50 (N% = 0.847, DS = 0.101).

obvious new absorption peak at 1719 cm^{-1}. The peak was assigned to the stretching vibration of the carbonyl (C=O) in the base of urethane and it gradually increased from CC1-180-50 to CC10-180-50, with an increase of the urea content. This also agreed well with the result of elementary analysis. Moreover, the relative absorbance of hydroxyl groups at 3200−3500 cm^{-1} decreased with an increase of the N% of CCs, indicating a decrease in the hydrogen bonding of cellulose upon chemical modification.[30] Figure 6 shows the solid-state ^{13}C CP/MAS NMR spectra of cellulose and CCs. The chemical shifts of carbon in the spectra could be assigned to 106.1 ppm for C1, 89.0 ppm for C4, 74.8 ppm for C2, C3, C5 and 65.3 ppm for C6.[42] Except for the chemical shifts of cellulose, CCs displayed a remarkable signal at 158.9 ppm typical of the carbonyl carbon. The signal was obviously different from the carbon chemical shifts of C=O for urea at 163.4 ppm.[30] Moreover, the peak intensity of 158.9 ppm increased slightly with increasing urea content of the CU mixtures.

Figure 7 shows the XRD patterns of CCs prepared from the CU mixtures with different urea content at 180 °C for 50 min. All of the samples displayed distinct peaks at 2θ of 15.0°, 16.7° and 22.9°, which correspond to the ($1\bar{1}0$), (110) and (020) planes of the cellulose I crystalline form. It has been reported that the transformation of supercritical CO_2-assisted impreg-
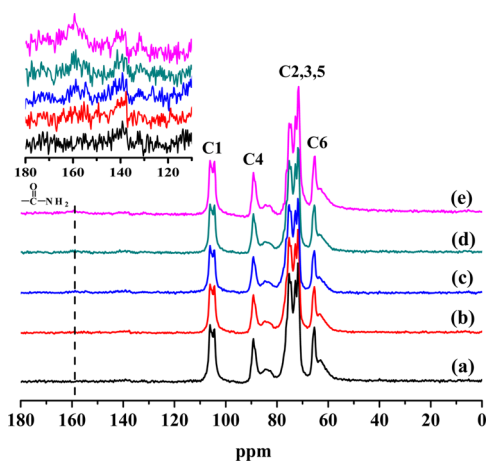
Figure 6. Solid-state ^{13}C CP/MAS NMR spectra of (a) cellulose pulp, (b) CC1-180-50, (c) CC3-180-50, (d) CC5-180-50 and (e) CC10-180-50.
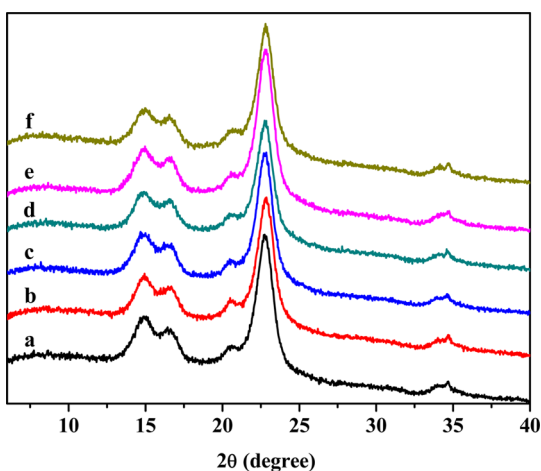

Figure 7. XRD patterns of (a) cellulose pulp, (b) CC1-180-50, (c) CC2-180-50, (d) CC3-180-50, (e) CC5-180-50 and (f) CC10-180-50.

nation method and the alkalized cellulose with urea leaded to the cellulose modification II.[5,28] Obviously, there was no new diffraction peaks found in the XRD patterns of CCs in this work, which revealed that the modification did not change the crystalline form of cellulose. The CI values of the native cellulose and CCs with the N% of 0.215, 0.295, 0.491, 0.625 and 0.847% were determined to be 65, 63, 66, 62 and 65%, respectively, which hardly changed with regard to the nitrogen content. The reason might be attributed to the derivative reaction was mainly occurred in the amorphous region and surface of the crystal region.[43] Moreover, the DP of the CCs hardly changed with the various of reaction condition and urea content, and in the range of 540−620 (Figure S1 of the Supporting Information).

In view of the above results, we could conclude that the extent of the carbamation of cellulose increased with an increase of the urea content. However, as shown in Figure S2 of the Supporting Information, the carbamation efficiency increased with increasing the urea content and then decreased at higher urea content. The highest carbamation efficiency obtained was 31.6% by heating CU5 at 165 °C for 2.0 h, instead of CU10 with the highest urea content. This could be attributed to excessive consumption of urea which caused the increase of

byproducts (for example, biuret and isocyanate, etc.). The byproducts would disturb the esterification between urea and cellulose. This phenomenon was in accordance with several observations in the etherification and esterification of starch.[38,44]

Dissolution of CCs. It is well-known that the introduction of carbamate groups on the cellulose backbones leads to the increase of its solubility. The previous reports revealed that high degree of substitution (DS ≥ 0.25, N% ≥ 2%) was beneficial for the dissolution of CCs in NaOH solution. However, according to our recent studies, it was found that CCs with the N% as low as 0.5% could be well dissolved in the NaOH solution by adding a small amount of ZnO (0.4−2.0 wt %).[33] This could be attributed to the formation of hydrogen bonds between CCs and ZnO.[45,46] Effect of the reaction conditions and urea content on the solubility of CCs in NaOH/ZnO solutions are shown in Figure 8. With an increase of the reaction
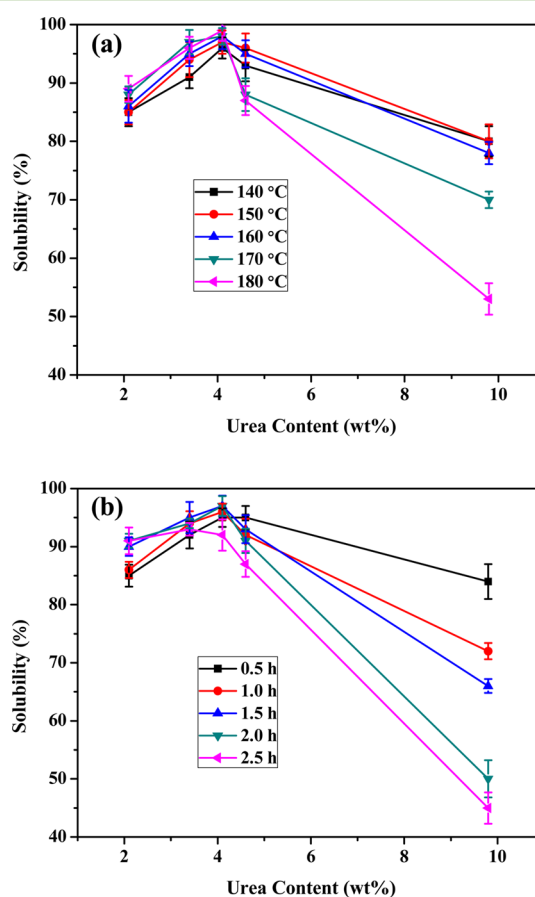

Figure 8. Effects of (a) the reaction temperature (reaction time is 50 min) and (b) time (reaction temperature is 165 °C) on the solubility of CCs prepared from CU mixtures with different urea content.

temperature, the solubility of CCs obtained from CU1, CU2 and CU3 mixtures increased significantly. For example, the solubility of CC1-180-50 was 89%, which was much higher than that of cellulose pulp (74%). Especially, CCs obtained from CU3 mixtures at 160−180 °C could be completely dissolved in the NaOH/ZnO solution. As the reaction time varied from 0.5 to 2.5 h, the solubility of CCs displayed a similar trend and the optimal reaction time was 1.0−2.0 h. The urea content of the CU mixtures also had significant influence on the solubility of CC products. As shown in Figure 8, the solubility of CCs

initially increased as the urea content lower than 4.1 wt %, and then decreased with increasing urea content. Therefore, to prepare CC dope with a high concentration, the CCs should be obtained from CU mixtures with the urea content of 3.4−4.6 wt % at 150−170 °C for 1.0−2.0 h.

To analyze the reason that causes the poor solubility of CCs under the condition of excess urea, high reaction temperature or long reaction time, the dissolved and insoluble part of CC10-180-50 were studied with XRD and NMR measurements. As shown in Figure 9, compared with the CCs with cellulose I
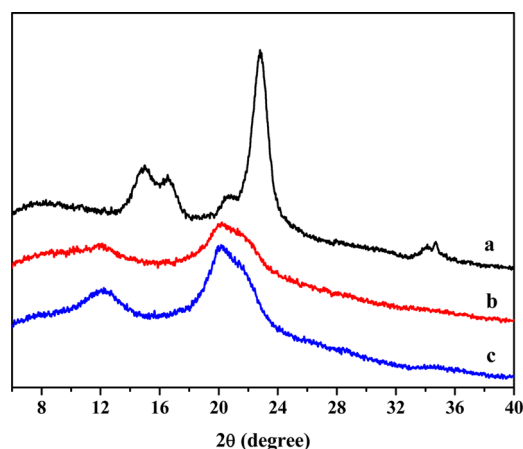
Figure 9. XRD patterns of (a) CC10-180-50, and its (b) insoluble and (c) dissolved parts in NaOH/ZnO aqueous solution.

crystalline, both the patterns of the dissolved and insoluble parts appeared to be form cellulose II. The crystal transformation for insoluble parts might be caused by mercerization. The CI value of the insoluble parts (21%) was much lower than that of the dissolved part (32%). As illustrated in Figure 10, the
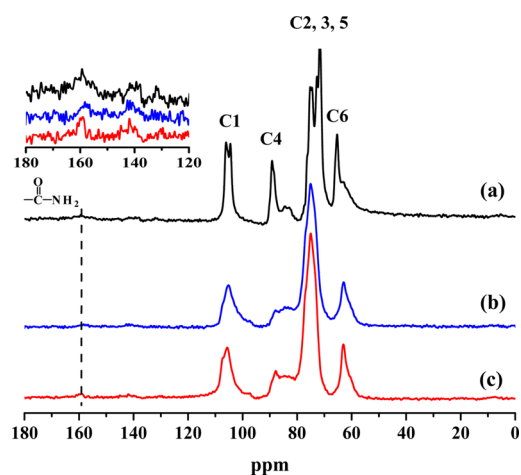
Figure 10. Solid-state ^{13}C CP/MAS NMR spectra of (a) CC10-180-50, and its (b) insoluble and (c) dissolved parts in NaOH/ZnO aqueous solutions.

chemical shifts of C1 (105.2 ppm), C4 (87.8) ppm, C5 (75.0 ppm) and C6 (62.8 ppm) for the both parts are almost the same as those for regenerated cellulose fibers from CC-NaOH/ZnO solution.[33,34] In a comparison of the dissolved part, the C4 peak of the insoluble was relatively weak. The previous studies revealed thermal treatment of cellulose would lead to decrease of bands associated with hydroxyl and glycosidic

groups, especially in the C4 signal.[47,48] Moreover, the chemical shift of the carbonyl carbon at 158.9 ppm in the insoluble part is relative weaker than those of the original CC and the dissolved part. Therefore, the different structure between the dissolved and insoluble parts was mainly attributed to the cross-linking and carbonization of cellulose, which caused poor solubility of the resulted CCs. In addition, the DP values of CC-180-50, its dissolved and insoluble parts were determined to be 556, 501 and 620. The result indicated that only slight degradation occurred during the dissolving process and cross-linked cellulose had been formed in the synthesis stage.

Dissolution of RCU Mixtures. In the previous methods, there was always a large amount of urea in the CU mixtures, and the resulted RCU mixtures without washing could not be directly dissolved for wet spinning. However, the urea content as low as 2.1−4.1 wt % was used in the present work and it motivated us to investigate the solubility of the obtained RCU mixtures. Liquid ^{13}C NMR spectra of the RCU3-180-50 mixture compared with CC3-180-50 are shown in Figure 11.
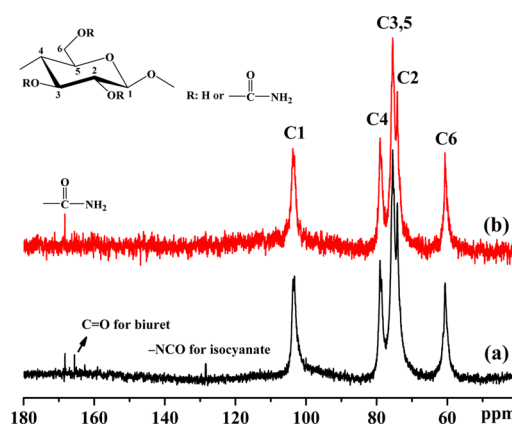
Figure 11. Liquid ^{13}C NMR spectra of (a) RCU3-180-50 and (b) CC3-180-50 in NaOH/ZnO/D$_2$O solutions.

Five major peaks at around 60 to 105 ppm in the spectra are readily identified: C1 (103.5 ppm), C4 (79.1 ppm), C3,5 (75.5 ppm), C2 (74.3 ppm) and C6 (60.6 ppm). The peaks were almost the same as those for cellulose in alkali solutions.[49] Except for the chemical shifts of the native cellulose, both the RCU and CC mixtures displayed a remarkable signal at 168.6 ppm, which was typical for the carbonyl carbon of carbamate.[30] Moreover, it was noted that the carbon chemical shifts of C═O for urea mainly at 162.7 ppm was not obvious in the spectrum of RCU3-180-50 mixture.[50] Instead, there were two small peaks at 165.6 and 128.3 ppm for RCU3-180-50. The peaks could be assigned to the chemical shifts of the carbonyl carbon for biuret and isocyanate group (−NCO) for isocyanate, respectively. The result proved that most of urea had reacted with cellulose, and the RCU mixtures with little by products, as same as CCs, could be well dissolved in NaOH/ZnO solution.

Figure 12 shows the dependence of the solubility of RCU mixtures on the reaction temperature and time. For the RCU1 and RCU2 mixtures, with the increase of the reaction temperature and time, solubility of the mixtures increased continuously. The solubility of the RCU mixtures could also be enhanced by increasing the urea content to 4.1 wt %. Especially, the solubility of RCU mixtures obtained by heating CU3 at 160−170 °C for 1.0−1.5 h could reach 97%. However, the high reaction temperature (180 °C) or long reaction time (2.5 h)
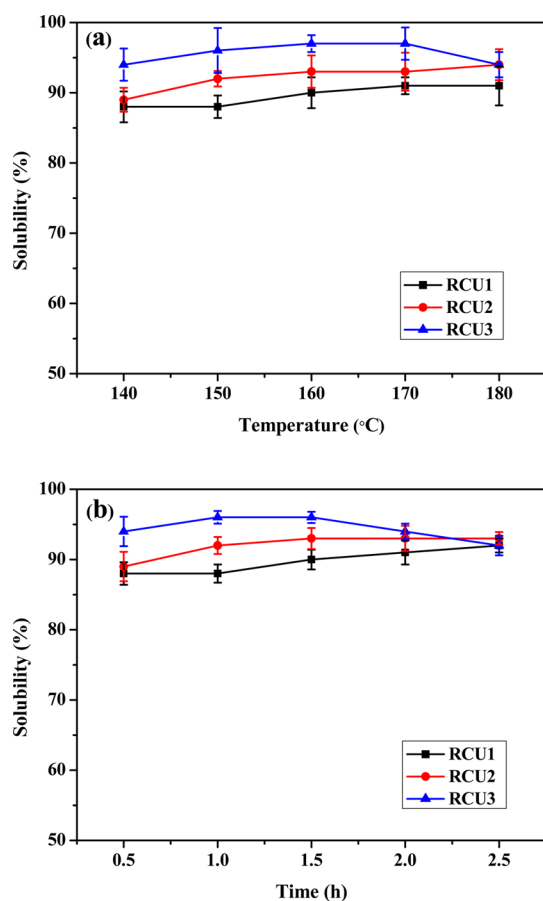
Figure 12. Effects of (a) the reaction temperature (reaction time is 50 min) and (b) time (reaction temperature is 165 °C) on the solubility of RCU mixtures.

might induce the decrease of solubility, as the case for CCs in Figure 8. Furthermore, it had been proved that the concentration of RCU mixtures in NaOH/ZnO(aq) could be reached to 8−9 wt % as the DP of the primary cellulose was about 400, and the spinning dope could be performed on a pilot-scale spinning matching smoothly. Compared to the conventional method, the washing process could be avoided completely in our method and there would be less wastewater discharge. Thus, the present synthesis method was green, economic and could be easily applied to industrial production on a large scale.

CONCLUSIONS

Cellulose carbamates were successfully prepared from the cellulose/urea mixtures with low content of urea through conventional heating. Urea content in the mixture, reaction temperature and time play important roles in the carbamation of cellulose. The urea content of the mixture was optimized between 3.4 and 4.6 wt % for enhancing the solubility of CCs and saving the cost of materials. The reaction temperature and time were set a maximum of 170 °C and 2.0 h to avoid the carbonization and cross-linking of cellulose. CCs retained the cellulose I crystalline form and the CI values hardly changed with the incorporation of carbamates. Furthermore, both the reacted CU mixtures and CCs prepared under optimized conditions could be well dissolved in NaOH/ZnO solution and the washing process could be abandoned completely. Because of the low consumption of urea and no wastewater discharge,

the economic and green process reported here would be particularly beneficial for industrialization.

ASSOCIATED CONTENT

Supporting Information

Effects of the reaction temperature and time on the carbamation efficiency of cellulose; and the effects of the reaction temperature and time on the degree of polymerization of CCs. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00219.

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Notes

The authors declare no competing financial interest.

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