Synthesis and Characterization of Cellulose Carbamate by Liquid-Solid Phase Method

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Abstract: An efficient and environmentally friendly method for the synthesis of cellulose carbamate from a mixture of cellulose pulp or the activated cellulose pulp and urea was presented in this paper. Cellulose carbamate with a nitrogen content of 1.21 % and 3.29 % were successfully synthesized via esterification reaction in the high-boiling aprotic and polar N-methyl-2-pyrrolidone solvents (hereinafter NMP). The structures of cellulose carbamate were characterized by Fourier transform infrared spectroscopy (FTIR), Kjeldahl analysis, thermo-gravimetric analysis, scanning electron microscopy (SEM), X-ray diffractometry (XRD), and ^{13}C-solid-state NMR. The results showed that some functional groups of the alkali cellulose were substituted by amino in the high-boiling aprotic and polar solvents, then the cellulose carbamate was prepared with the reduced crystallinity and thermal decomposition temperature. In addition, the product was prepared with uniform substitution and distribution of carbamate group in the cellulose chain, which guaranteed its good solubility in aqueous alkali as well as its spinnability to produce fiber.

Keywords: Liquid-solid method, Cellulose, High-boiling aprotic and polar solvents, Cellulose carbamate

Introduction

Cellulose as one of the most important skeletal component polymers in plants is an almost inexhaustible polymeric raw material with fascinating properties and a variety of useful applications [1-3]. The linear polysaccharide cellulose is converted by large scale industrial processing into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food castings, membranes, sponges, and so on) [4-9]. Nevertheless, the chemical processing of cellulose is difficult in general because it cannot be melted into a desired form or be dissolved in common solvents, which is attributed to its strong inter- and intramolecular hydrogen bonding and partially crystalline structure.

In cellulose-regenerated materials industries, the old viscose technology has occupied predominant status by which fibers (viscose, rayon), films (cellophane), and others are produced via a metastable soluble cellulose derivative (cellulose xanthogenate). However, the process accompanies environmental hazardous by-products including CS_2, H_2S, and heavy metals [10-15]. After years of researches, abundant original solvents of cellulose and innovative methods have been presented continually to avoid the complicated processing steps as well as to reduce hazardous byproducts [16,17]. Johnson [18] patented the solvent system on the basis of cyclic amine oxides, particularly N-methylmorpholine-N-oxide (NMMO), which can dissolve not only cellulose, but also other polymers.

Cellulose carbamate (CC) is the product of the CarbaCell process which is an efficient alternative method and a promising substitute for the conventional viscose process.

Compared with viscose process, the CarbaCell process has the advantage of better biodegradability, and most of the traditional devices for conventional viscose production can be used. To the best of our knowledge, converting cellulose to its derivatives, especially cellulose carbamate, has been attracting comprehensive interests [19-21]. In a previous study, our research group has already reported an efficient, solvent-free, and catalyst-free method for synthesis of cellulose carbamate by supercritical CO_2-assisted impregnation [22,23]. Unfortunately, high pressure and relatively complicated equipment make it hard to be applied in cellulose industry. Zhou *et al.* [24] disclosed a process for manufacturing cellulose carbamate using microwave heating. In spite of its obvious advantages and several known attempts, this method, however, has remained on the laboratory scale.

A convenient method to remarkably increase the nitrogen content of cellulose carbamate by using NMP as solvent was presented in this paper. Pyrrolidone ring in NMP is a favorable hydrogen-bonding acceptor which is apt to form hydrogen bond with hydroxyl group of cellulose macromolecule. Consequently, strong original inter- and intramolecular hydrogen bonding in cellulose was able to be destroyed. In accordance with the present liquid-solid phase method, an alkali-soluble cellulose carbamate was produced by the reaction of preliminarily activated cellulose with urea at elevated temperature. Treating the cellulose with urea dissolved in NMP solution, the NMP sufficiently penetrates into the cellulose carrying the dissolved urea. Then the cellulose containing the urea was heated to a temperature sufficiently high for reaction between the cellulose and the urea. The resulting cellulose carbamate was fairly readily soluble and the 9 wt% product can be dissolved in 9 wt% sodium hydroxide (NaOH) solution. Moreover, the solvent

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can be recycled, and the conventional equipment for a viscose production can be used, which would be economically sound and also convenient from the viewpoint of production of the cellulose carbamate fibers or films. This work provided a promising way to prepare cellulose carbamate and experimental basis of the preparation of environmental friendly fibers.

Experimental

Materials

Cotton linter pulp (CHTC Helon Co. Ltd., Shandong, China) had about 93 % α-cellulose and the degree of polymerization (DP) was determined to be 520. Urea (CH_4N_2O, AR) and NMP (C_5H_9NO AR) was purchased from Tianjin Kermel Chemical Reagent Development Center. Other reagents used in this study were of analytical grade and used without further purification.
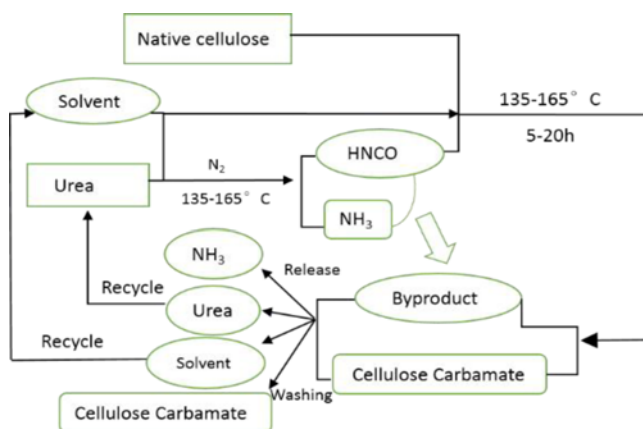
Preparation of Cellulose Carbamate

In a typical experiment, cotton linter pulps (10 g) were preliminarily activated by immersing in sodium hydroxide (mercerization). After the mercerization, the pulp, partly dried under vacuum and washed by distilled water, was treated with urea (30 g) dissolved in NMP solution (100 ml). The temperature of reactor was gradually increased and then maintained at 135-165 ^{o}C for 5-20 h (reaction can be written as in Scheme 1). Finally, the sample was washed with water and vacuum dried. Cellulose carbamate sample with 3.29 % nitrogen content was obtained. Especially, the NMP solution can be reused without any problems. By changing the reaction temperature and time, cellulose carbamates with different nitrogen contents could be prepared by this simple procedure. The whole procedure was displayed as seen in Figure 1.

Characterization

The Kjeldahl method was used for analyzing the nitrogen
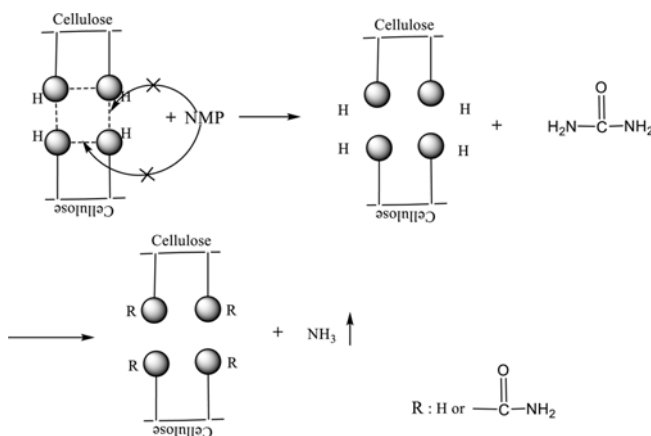
Figure 1. The preparation process of cellulose carbamate.

content of modified cellulose using a Kjeltec 2300 Analyzer Unit (FossTecator).

The FTIR-ATR spectra were performed using a Bruker FTIR spectrophotometer, model TENSOR37 at room temperature. The dried samples were made into potassium bromide (KBr) pellets and were scanned from 4500 cm^{-1} to 400 cm^{-1}.

Solid-state ^{13}C NMR spectra were obtained with Bruker AVANCE III 400 (^{13}C frequency=100 MHz) with a CP/MAS unit at ambient temperature.

Wide angle X-ray diffraction (WAXD) measurement was implemented on the instrument named Bruker AXS. XRD patterns with Cu K$_\alpha$ radiation (λ=1.54 Å) at 40 kV and 30 mA were recorded in the range of 2θ=5-40 ^{o}.

Thermogravimetric analysis (TGA) measurement was executed using a SEIKO TG/DTA6300 instrument under nitrogen atmosphere, 5 mg sample was gradually heated from 25 ^{o}C to 600 ^{o}C at the heating rate of 10 ^{o}C/min, and the residues were naturally cooled to normal temperature.

The fiber morphology was investigated using a JEOL JSM-5610LV scanning electron microscope (SEM). Fiber samples were cut with a blade and were subsequently sputter-coated with gold.
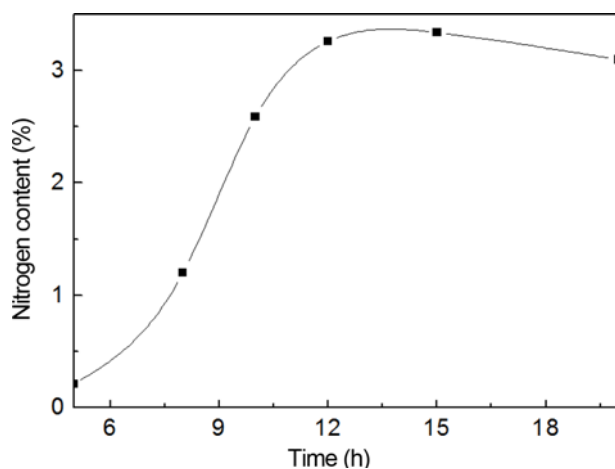
Results and Discussion

Effects of Esterification Temperature on the Nitrogen Content of Modified Cellulose

The influence of esterification temperature on the nitrogen content of carbamated cotton cellulose was investigated and the esterification time was 12 h. From Figure 2, it can be seen that the nitrogen content of carbamated cellulose firstly increased from 0.3 % to 3.29 % with the increasing reaction temperature and there was a maximum of the nitrogen content at the temperature of 150 ^{o}C. Then the nitrogen content decreased with temperature above 150 ^{o}C. The reason is that higher temperature intensifies thermal motion

Scheme 1. Liquid-solid method synthesis of cellulose carbamate.
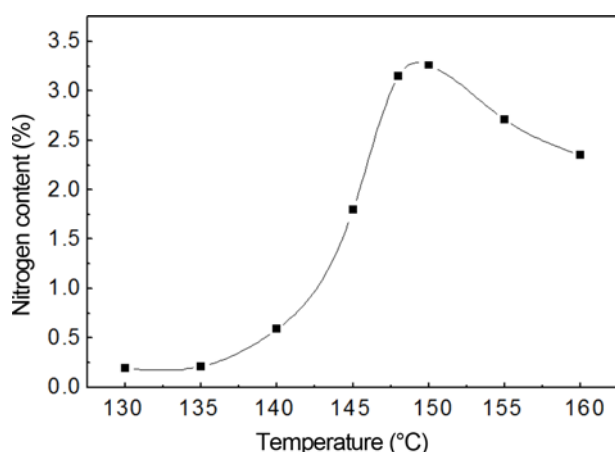
Figure 2. The relationship between temperature and the nitrogen content.

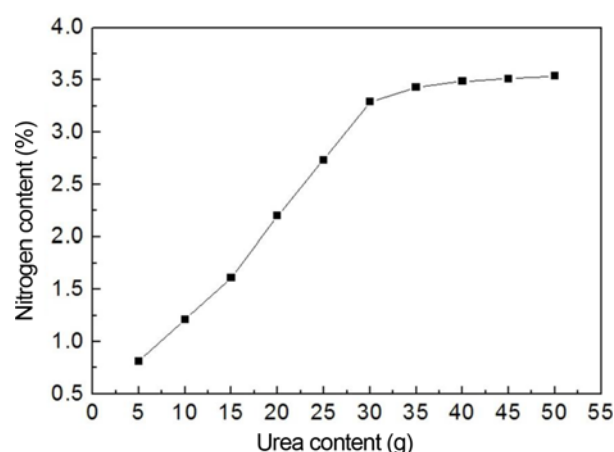**Figure 4.** The relationship between urea content and the nitrogen content.

Figure 3. The relationship between time and the nitrogen content.

of urea molecule and enhances the degree of esterification for cotton cellulose. With increasing activity of high-boiling aprotic and polar NMP solvent, the strong original inter- and intramolecular hydrogen bondings in cellulose are easier to be destroyed. However, higher temperature may result in the yellowing and thermal decomposition of cellulose and its derivative.

Effects of Esterification Time on the Nitrogen Content of Modified Cellulose

The effect of the esterification time on the nitrogen content of carbamated cotton cellulose was investigated. As shown in Figure 3, the esterification temperature was 150 °C, the nitrogen content of the carbamated cellulose increased sharply with the increasing of esterification time. Furthermore, the maximum nitrogen content could be achieved to 3.29 % when the esterification time was extended to about 12 h. Meanwhile, the nitrogen content of products tended to decline with the esterification time beyond 14 h. It's because

of the by-products (for example biuret) which can result in excessive consumption of urea and disturb the esterification reaction between urea and cellulose. What's more, the longer time resulted in carbonization, thermal decomposition, and cross-linking of the cotton linter [23].

**Effects of Urea Content on the Nitrogen Content of Modified Cellulose**

The effect of the urea content on the nitrogen content of carbamated cotton cellulose was investigated. As shown in Figure 4, the esterification temperature was 150 °C and the esterification time was 12 h. It can be seen that the nitrogen content of cellulose carbamate increased from 0.81 % to 3.54 % with the increasing urea content. In addition, the maximum nitrogen content leveled off when the urea content was beyond 30 g (the cotton linter pulp was 10 g). It is suggested that the optimal urea content should be controlled among 30-40 g from the economic point of view.

FTIR and NMR Analysis

The obtained samples were confirmed as cellulose carbamate by means of FTIR and solid-state ^{13}C-NMR spectra. Figure 5 shows the FTIR spectra of native cellulose and cellulose carbamates with a nitrogen content of 1.21 % and 3.29 %. Through making a comparison with FTIR spectra of pristine cellulose, it can be obviously found the characteristic peak at 1715 cm^{-1} that can be attributed to the stretching vibrations of the ester carbonyl of the copolymer, which indicated that urea had reacted with cotton cellulose to form cellulose carbamate. As shown in Figure 5, the intensity of absorption band at 1713 cm^{-1} gradually increased with an increase in nitrogen content of the carbamated cellulose. On the basis of previous report [25], the relationship between absorption intensity ratio of the band at 1710 cm^{-1} to the band 1635 cm^{-1}, and the nitrogen content was approximately linear. Furthermore, the relative absorbance of hydroxyl groups at 3420 cm^{-1} and
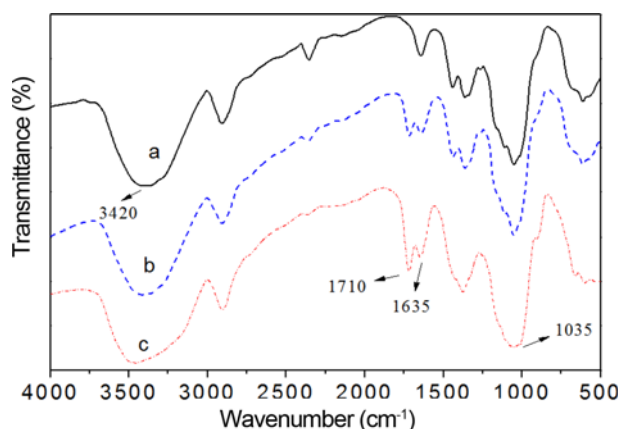
Figure 5. FTIR spectra of the pristine cellulose (a) and modified celluloses with different nitrogen contents: 1.21 % (b), and 3.29 % (c).
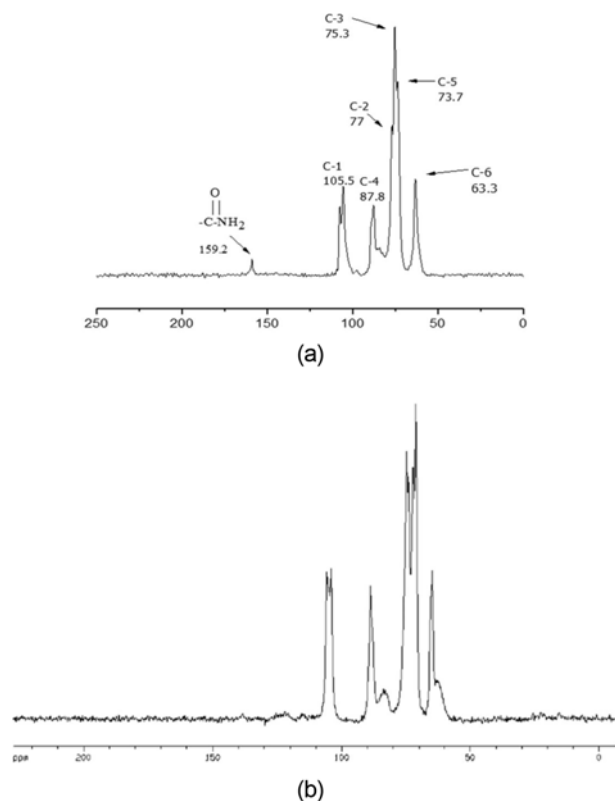
Figure 6. ^{13}C-CP/MAS solid-state NMR spectra of the native cellulose (b) and cellulose carbamates with nitrogen content of 3.29 % (a).

1035 cm^{-1} (primary -OH) decreased with increasing nitrogen content of the carbamated cellulose, since the esterification reaction between urea and hydroxyl groups on the cellulose chain was stronger.

NMR spectroscopy was an efficient and reliable method to demonstrate the chemical structure of cellulose carbamate.

Figure 6 represented the ^{13}C-CP/MAS solid state NMR spectra of the native cellulose and cellulose carbamates with 3.29 % nitrogen content. The cotton linter and the cellulose carbamate samples revealed a characteristic cellulose I crystal form, and the chemical shifts of carbon could be assigned to 105.5 ppm for C-1, 77 ppm for C-2, 75.3 ppm for C-3, 87.8 ppm for C-4, 73.7 ppm for C-5, and 63.0 ppm for C-6 [26]. In comparison with original cellulose, the cellulose carbamate samples displayed a remarkable signal at 159.2 ppm which was typical carbonyl carbon of carbamate function group. That is to say, cellulose carbamate has been successfully synthesized via liquid-solid phase method.

Thermal Analysis

Figure 7 displayed thermogravimetric curves of pristine cellulose and cellulose carbamate with a nitrogen content of 1.21 % and 3.29 %. For all curves it was obvious to find that native cellulose and cellulose carbamate have two temperatures, pyrolysis and decomposition temperatures, and major decomposition was proceeded at 310 °C to 380 °C for these samples. The decomposition and charring temperatures of the carbamated cotton linters were lower than those of cotton linters. The initial decomposition and charring temperatures decreased with increasing the nitrogen content in the carbamated cotton linters, since the degradation of cotton linters during the carbamation process of the cotton linters. In order to obtain further thermal characteristic of cotton linters and cellulose carbamate, the DTG measurement of these samples was carried out. Figure 8 showed that as the nitrogen content increased the maximum decomposition temperature of cellulose carbamate shifted toward lower temperature as compared with the temperature of maximum decomposition of cotton linters. The decomposition temperature of native cellulose and cellulose carbamate with 1.21 % and 3.29 % were 357.07 °C, 344.67 °C, and 342.93 °C, respectively.
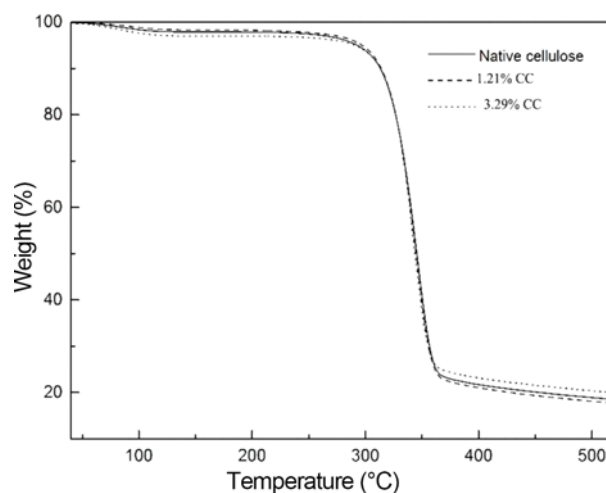
Figure 7. TG curves of the native cellulose and cellulose carbamates with nitrogen content of 1.21 % and 3.29 %.
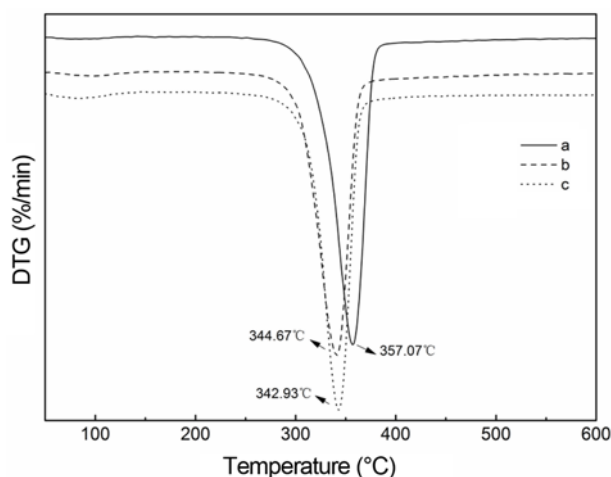
Figure 8. DTG curves of the native cellulose (a) and cellulose carbamates with nitrogen content of 1.21 % (b), and 3.29 % (c).
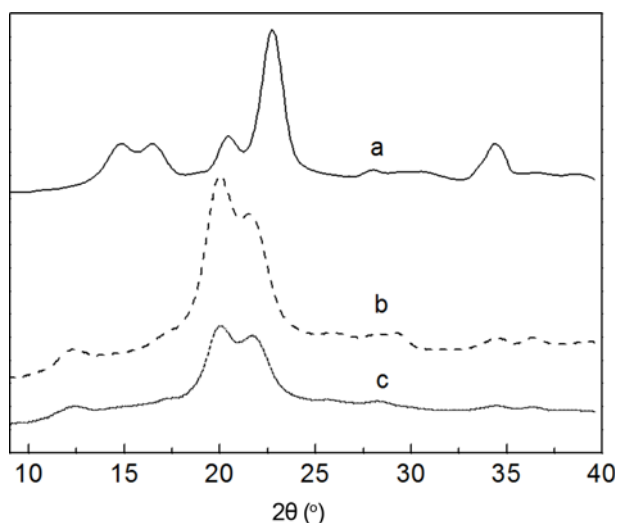
Figure 9. X-ray diffraction patterns of the native cellulose (a) and cellulose carbamates with nitrogen content of 1.21 % (b), and 3.29 % (c).

Table 1. X-ray diffraction peaks of crystalline cellulose

Indices of crystal face (*hkl*)	110	1$\bar{1}$0	020	021	020	040
Cellulose I, 2θ (°)	14.8	16.3	22.6	20.6	17.2	34.9
Cellulose II, 2θ (°)	12.1	19.8	22.0	20.4	17.2	34.9
Cellulose III, 2θ (°)	11.8	20.7	20.7			

This can be attributed to the increase in the amorphous or disordered region, which was decomposed by thermal treatment faster than the crystalline part in the cotton cellulose pulp.

XRD Analysis

The XRD patterns of the native cellulose and cellulose carbamates with different nitrogen contents were shown in Figure 9 and Table 1. It can be seen that the pristine cellulose displayed distinct 2θ diffraction peaks at 14.8 °, 16.3 °, 22.6 °, and 34.9 ° which were corresponding to the (110), (1$\bar{1}$0), (020), and (040) planes of the cellulose I crystalline form, respectively [1]. Compared with native cellulose, XRD patterns of modified celluloses displayed some new peaks at 2θ=11.7 ° and 20.7 °, since the degree of crystallinity of modified cellulose has declined markedly when the abundant -OH group was substituted by urea. In previous report, it has been told that the transformation of the alkalized cellulose with urea led to structures that were similar to the cellulose modification II and III, depending on the derivatization procedure [24]. This is to say, the alkalization and esterification have partially destroyed the crystalline structure and supramolecular structure of cellulose and reduced the density of hydrogen bonds, leading to the increase of amorphous region. Those phenomena were considerably advantageous for the accessibility in chemical reactions and alkali-solubility.

Morphology Analysis

In order to better understand the influence of NMP treatment and the esterification reaction on the surface feature of cellulose carbamates, morphological study was carried out using a scanning electron microscopy (SEM). Figure 10 showed SEM photographs of native cellulose, alkali cellulose, and esterified cellulose of cotton linter pulp. The surface feature of pristine was smooth, mellow, and plump, and no sign of external fibrillation or formation of fibrils can be found (Figure 10(a), (b)) as well as the alkali cellulose (Figure 10(c), (d)).

By contrast, the surface feature of cellulose using NMP treatment was irregular, rough, and wizened (Figure 10(e), (f)). Especially, remarkable cracks can be seen in modified cellulose, which might be attributed to alkalization and the strong polar of NMP solvent. These cracks made it possible for urea to substitute and distribute uniformly in the cellulose chain, which guaranteed its good solubility in aqueous alkali as well as its spinnability to produce fiber.

Conclusion

An innovative liquid-solid phase method for the synthesis of cellulose carbamate a mixture of cellulose pulp or the activated cellulose pulp and urea was presented. Cellulose carbamates with a nitrogen content of 1.21 % to 3.29 % were successfully obtained by this method. In this manner, the NMP solvent has sufficiently penetrated into the cellulose carrying the dissolved urea, therefore, the product was prepared with uniform substitution and distribution of
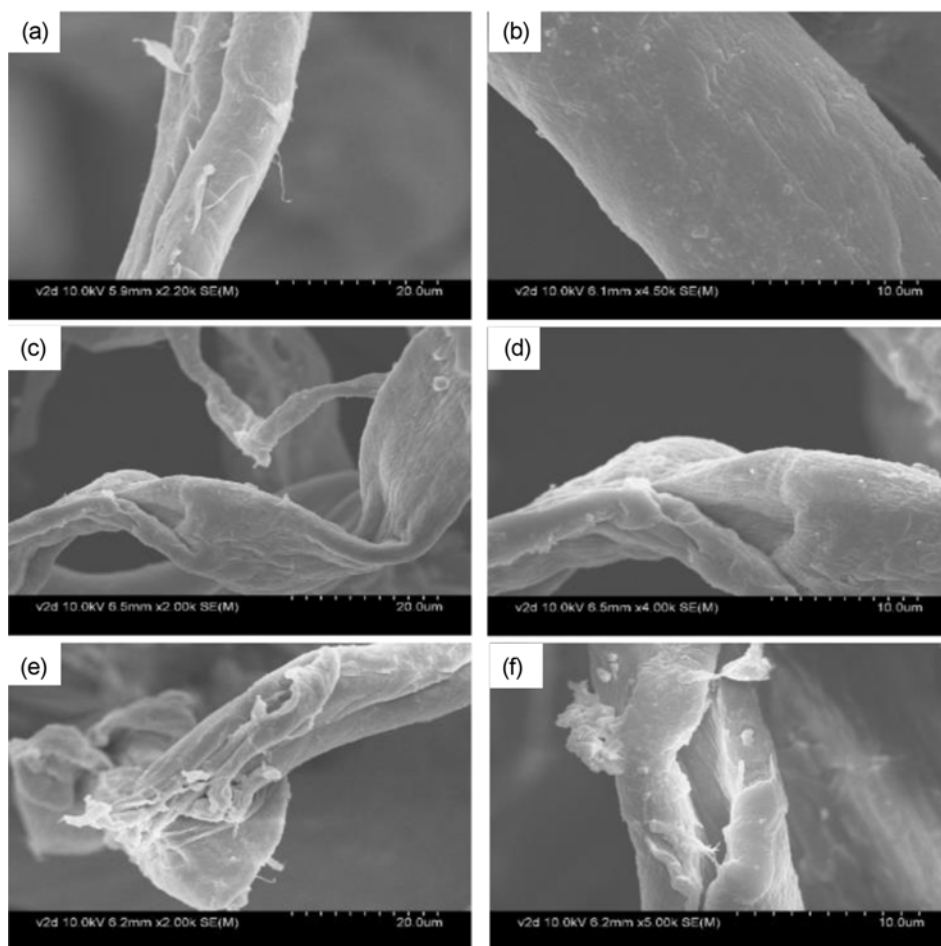
Figure 10. SEM photographs of native cellulose (a, b), alkali cellulose (c, d), and esterified cellulose (e, f).

carbamate group in the cellulose chain, which guaranteed its good solubility in aqueous alkali as well as its spinnability to produce fiber. The resulting cellulose carbamate was fairly readily soluble. Moreover, the nitrogen content of cellulose carbamate can be adjusted by the esterification temperature and esterification time.

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