

Synthesis and Characterization of Cellulose Carbamate from Wood Pulp, Assisted by Supercritical Carbon Dioxide

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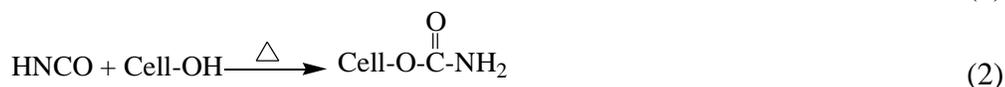
This paper considers the modification of wood-derived cellulose assisted by supercritical carbon dioxide (SC-CO₂). Cellulose carbamate derivatives were successfully prepared from softwood pulp at 150 °C and 3000 psi for 6 hours. Compared with conventional methods, SC-CO₂ was shown to be more efficient in the modification of wood-derived cellulose. The modified cellulose had a considerable increase in nitrogen content. During the characterization Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Thermogravimetry (TG), and Field Emission Scanning Electron Microscopy (FE-SEM) were employed to investigate the structural and morphological changes in modified cellulose from wood.

Keywords: Cellulose carbamate; Lignocellulose; Supercritical carbon dioxide; Wood pulp

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INTRODUCTION

Cellulose is known as the most abundant natural polymer material in the world, but the numerous and highly organized intra- and inter-molecular hydrogen bonds make it hard to dissolve in conventional solvents, which limits the development of its applications in many fields. Over the years, there have been efforts to find an ideal cellulose derivative to expand the range of utilization of cellulose in synthesis of materials (Fink *et al.* 2001). In recent years the viscose process has become unfavorably regarded due to environmental issues and recycling difficulties. As a result, cellulose carbamate, (CCs) as an emerging, green cellulose technology, is considered to be one of the most promising alternatives to viscose in the near future. In 1938, Hill had reported these cellulose derivatives (cellulose carbamate products), but it was not until 1983 that CCs first went into mass production at the Neste company (Finnish Patent: No 61033, 1983). In this process, urea is decomposed into isocyanates and ammonia in the first step. Isocyanates, as the intermediate, reacted with cellulose in the second step. These reactions can be displayed as follows:



Recently, new methods of CCs synthesis have emerged, such as a supercritical carbon dioxide method, a microwave heating assisted method, and an organic medium method (Yin *et al.* 2006, 2007; Guo *et al.* 2009, 2010; Klemm *et al.* 1988). Due to the limitations of the conventional synthesis method and the special inherent structure of wood-derived cellulose, most of the reports about CCs in recent years have been based on cotton pulps, and this has seriously restricted the innovation of CCs and its industrial development.

Compared with cotton cellulose, lignocellulose from wood has an inherently complex structure. Wood is predominantly composed of cellulose, hemicellulose, and lignin. The components of hemicellulose, which is a mixture of various polymerized short-chain sugar molecules, are characterized by a high degree of branching, a low degree of polymerization, and an amorphous ultra-structure. Lignin, acting as a binding agent to hold the cells together, is considered to be the reticular polymer, which was made of phenylpropane units connected by C-C covalent bonds (Yang 2000; Faulon and Gary 1994). Most of the hemicellulose and lignin are present in the primary walls and are difficult to completely remove (Nevell *et al.* 2000). Microfibrils can be considered a network of cellulose embedded in the matrix of hemicellulose and lignin. The existence of hemicellulose and lignin in the primary walls influences the reactivity of wood. In addition, most chemical pulps made today are produced by the kraft process (sulphate pulping). Compared with the NaOH process, sulphite pulp could hardly complete the hemicellulose hydrolysis, and Selin stated that pre-extraction is indispensable for the preparation of cellulose derivatives from sulfite (Franklin and Barton 1988; Sarkon 1987; Selin and Huttenen 1985). Therefore, the presence of hemicellulose not only strengthens the hydrogen bonds among the lignocellulosic polymers, but also reduces the reactivity of wood (Yang *et al.* 1991).

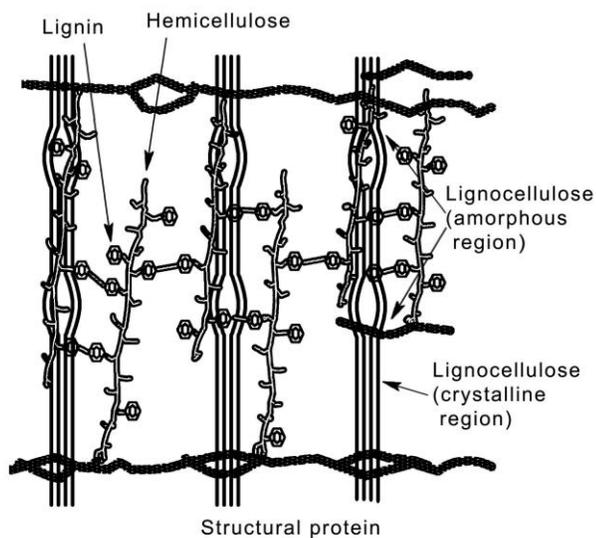


Fig. 1. The structure of lignocellulose from wood (based on concept by Kang *et al.* 2010).

As a new type of green solvent, supercritical carbon dioxide (SC-CO₂) has both the property of gas-like diffusivity and liquid-like density in a supercritical phase, making it widely applicable as processing solvents in polymer investigation (Nalawade *et al.* 2006). The high diffusivity of SC-CO₂ could promote the breathability of micro-fibers. Demessie and his partners found that SC-CO₂ extraction enhanced the permeability of

Douglas-fir (Kyoung and Hong 2001). Moreover, Kyoung investigated the supercritical carbon dioxide pretreatment of raw wood, discovering that SC-CO₂ pretreatment promoted the reactivity of lignocellulose and enhanced the sugar yields of moist wood to a significant extent (Demessie *et al.* 1995). A recent study demonstrated that SC-CO₂ promoted the dyeing of cellulosic fibers, especially when a plasticizing agent was present (Beltrame *et al.* 1998), which indicated that SC-CO₂ could activate the amorphous regions of cellulose.

In polymer modification, SC-CO₂ as the carrier of active chemical species has been shown to be a good solvent. Not only are some polymers soluble in it, but it is also quite soluble in many molten polymers (Ngo *et al.* 2003). It was reported that methyl acrylate and styrene were successfully grafted onto polypropylene in supercritical CO₂-assisted processes. Compared with the conventional melt modification, SC-CO₂ uses milder conditions, which reduces the degradation of polymer (Dong and Liu 2004; Liu *et al.* 2002). Moreover, the plasticizing action of SC-CO₂ makes it possible for manufacturers to control the modification process by changing the process conditions, namely pressure and temperature (Varma-Nair *et al.* 2003).

In this work, we present a SC-CO₂ assisted synthesis of CCs from wood without a catalyst. In order to scale up this synthetic method, we explored a new type of cellulose material and observed the morphological changes to the wood during SC-CO₂ treatment.

EXPERIMENTAL

Materials

Lignocellulosic pulps were obtained from Xinxiang Bailu Chemical Fiber Co., Ltd. (Xinxiang, Henan, China). This softwood pulp was derived from the kraft process, the concentration of α -cellulose was about 92%, and the degree of polymerization of the cellulose was 850. The purity of the liquid CO₂ was more than 99.999% from Tianjin Yingte Co., Ltd. The urea and ethanol used in this study were analytical grade and used without further purification.

Preparation of Cellulose Carbamate

An HPR-100 series high-pressure chemical reactor from Supercritical Fluid Technologies (SFT), Inc. (Newark, Delaware USA) was used in the process shown in Fig. 2. Ethanol was placed on the bottom of the autoclave as a co-solvent to enhance the solubility of urea in SC-CO₂ (the concentration of ethanol in reactor was 1 mol/L). Chemical pulp was placed around the outside of a stainless cage, and urea was placed within the cage such that the urea and chemical pulp did not contact. Then the cage was fixed at the upper cap with electromagnetic agitating mixer. In order to remove air from the autoclave, the reactor was purged with gaseous CO₂ at ambient pressure before heating. The temperature of the autoclave was set at 150 to 170°C. When the desired temperature was reached, CO₂ was introduced into the autoclave at a pressure of 2600 to 3200 psig. The reaction ran for 2 to 10 h; afterwards, the CO₂ over-pressurization was released from the autoclave. Finally, the samples were removed when the autoclave was cooled to room temperature. Samples were washed with an excess of warm water at 60°C in order to remove the un-reacted residual urea. This was continued until the wash water was neutral.

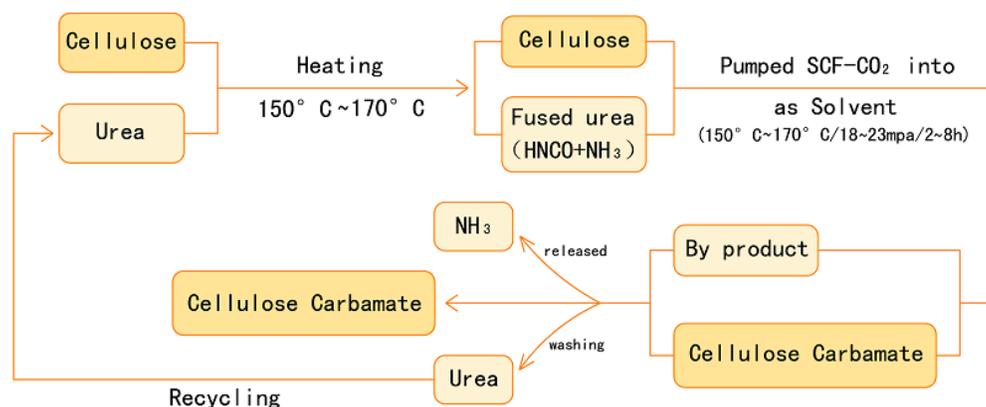


Fig. 2. The process of cellulose carbamate preparation

In this experiment, we prepared five kinds of CCs and focused on the effect of esterification time in the modification process. Table 1 lists the five kinds of CCs and their modification conditions.

Table 1. Modification Conditions of CCs

Number	Modification condition (Press/Temperature/Time)
WD	Chemical pulp
CC-1	3000 psig/150°C/2 h
CC-2	3000 psig/150°C/4 h
CC-3	3000 psig/150°C/6 h
CC-4	3000 psig/150°C/8 h
CC-5	3000 psig/150°C/10 h

Characterization

The nitrogen content of CCs was determined with the Kjeldahl Method, with use of a Foss -2300 Kjeltex Analyzer unit.

The FTIR spectra of the wood-derived pulp and its carbamate derivatives were recorded with a Fourier-transform infrared spectrophotometer (TENSOR37, BRUKER Co., Germany). The samples were obtained using a KBr technique.

Wide angle X-ray diffraction patterns were measured with an X-ray diffractometer (D8 DISCOVER with GADDS, Bruker AXS Co., Germany). The XRD patterns with Cu K α radiation ($\lambda = 1.5406 \times 10^{-10}$ m) at 40 KV and 30 mA were recorded in the range of $2\theta = 5^\circ$ to $2\theta = 40^\circ$.

Field Emission Scanning Electron Microscopy (S-4800 FE-SEM, HITACHI Co., Japan) images of the wood-derived pulp and its carbamate derivative were taken on the condition of 15 KV accelerating voltage. Fiber samples were cut with a blade and were spray-coated with gold subsequently.

Differential Thermal Analysis curves were measured with a thermal analyzer (STA 409, NETZSCH Co., Germany). All samples were dried for 24 h prior to analysis, and the heating rate was from 50°C to 450°C under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Determination of Nitrogen Content by Kjeldahl Method

Nitrogen content is one of the most important indexes in the characterization of CCs. The Kjeldahl Method was used to measure the nitrogen content of the samples, and could be calculated by Equation (3),

$$X = \frac{(V_1 - V_2) \times c \times 0.140}{m \times 10/100} \times 100 \quad (3)$$

where V_1 is the consumption of hydrochloric acid standard solution by sample, V_2 is the consumption of hydrochloric acid standard solution by reagent blank, C is the concentration of hydrochloric acid standard solution, and m is the weight of the sample.

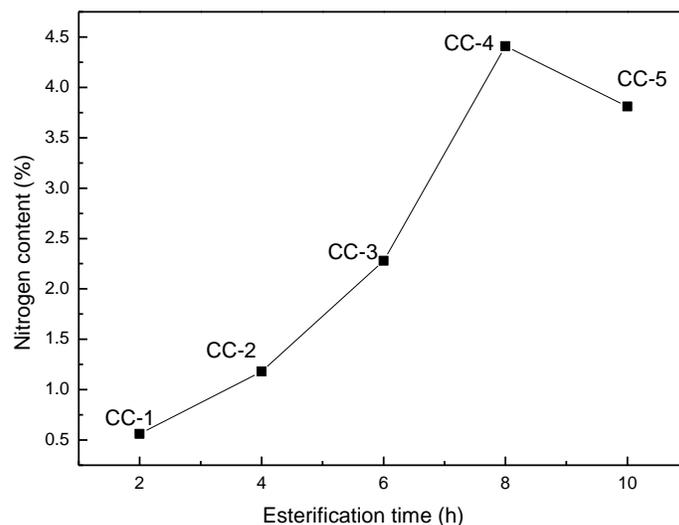


Fig. 3. Influence of the reaction time (Pressure = 3000psig; Temperature = 150 °C)

Figure 3 shows that the nitrogen content changed with the change of esterification reaction time. By increasing esterification time, especially from 4 to 8 h, it was found that the nitrogen content increased from 1.18% to 4.41%, and the maximum nitrogen content appeared when reacting time was about 8 h. In this process, the high reaction pressure allowed the urea to melt and to couple closely with cellulose. Besides, an adequate reaction time was of benefit for the urea to fully decompose and to impregnate into cellulose to facilitate cellulose esterification. When the reaction time was greater than 8 h, the reaction appeared to occur with crosslinking and carbonization, which resulted in the decline of nitrogen content of samples.

The results demonstrated the successful preparation of CCs, and the nitrogen content increased with the esterification time before 8 h, confirming the positive effect of SC-CO₂ on the reactivity of cellulose. The SC-CO₂ swelled the cellulose fibers and increased the accessibility of the cellulose towards esterification, which resulted in higher nitrogen content of the product. Compared with other conventional methods, the

superiority of the SC-CO₂-assisted process was reflected not only in the nitrogen content, but it also provided a new way to prepare CCs without poison and contamination.

FTIR Analysis

The FTIR spectrum of native cellulose and its cellulose carbamate derivatives with nitrogen contents of 1.18% and 4.41% are shown in Fig. 4. The spectra of CC-2 and CC-4 displayed a new absorption peak around 1713 cm⁻¹ (Nada and Hassan 2000). This new absorption peak was assigned to the stretching vibration of carbonyl in the base of the urethanes in the carbamate, which indicated that the urea had reacted with the lignocellulosic pulp to form CCs. In addition, the intensity of the new peak gradually increased with increasing nitrogen content of the carbamate. Furthermore, it is clear from Fig. 4 that the relative intensity of the OH group at 3420 cm⁻¹ and 1035 cm⁻¹ of the WD was higher than its carbamate derivatives CC-2 and CC-1. This may be attributed to the increase of reaction of urea with OH of cellulose chains (especially primary OH groups) and the decrease in hydrogen bonds. This also can be confirmed by the decrease of the crystallinity index in the next section (Laszkiewicz and Domasik 1989).

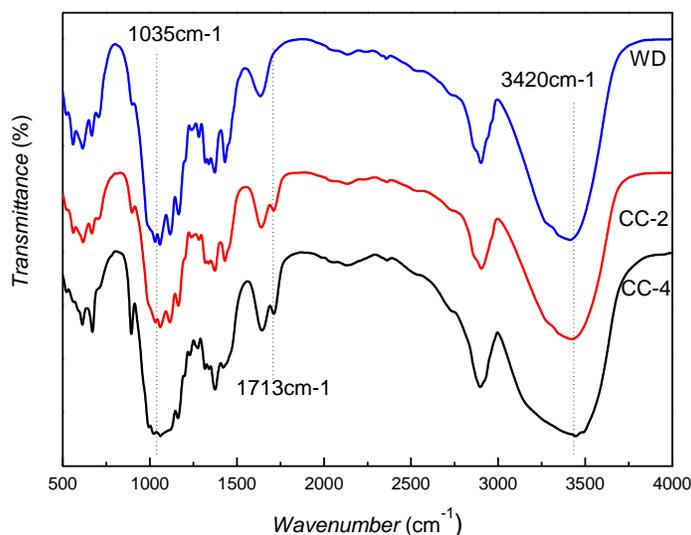


Fig. 4. FTIR spectrum of wood-derived cellulose and its carbamate derivative. (WD) cellulose pulp; (CC-2) cellulose carbamate with 1.18% nitrogen content; (CC-4) cellulose carbamate with 4.41% nitrogen content

XRD Analysis

XRD technology has been one of the most important methods for the investigation of cellulose crystallization. The patterns of diffraction peaks in an XRD spectrum represent the crystalline state of samples. Among all of the crystalline forms of cellulose, the C-I form is known to correspond to diffraction peaks at 16.4°, 22.5°, and 34.4° (Kolpak and Blackwell 1967). The C-II form corresponds to diffraction peaks at 12.1°, 20.0°, and 21.7° (Fink *et al.* 1995).

The XRD patterns of WD and its carbamate derivatives with nitrogen contents of 1.18% and 4.41% are shown in Fig. 5. From the figure it is evident that the patterns of WD and CC-2 contained cellulose of the C-I crystalline form, especially the WD, which was comparable to reports by Nishiyama *et al.* (2002). Meanwhile, some new diffraction

peaks were observed in the curves of CCs, and the increase of nitrogen content brought about increasing intensities of the new peaks. Furthermore, the diffraction peak of CC-4 appeared at 12.6° , which was derived from C-II formation. This indicates that the interplanar spacing of the crystalline cellulose increased with the increase of nitrogen content. Compared with WD, the new peaks appeared at $2\theta = 12.6^\circ$ and $2\theta = 24.9^\circ$, and it was judged that the crystalline formation of this new derivative more closely resembles C-II formation (Mansikkamaki *et al.* 2005).

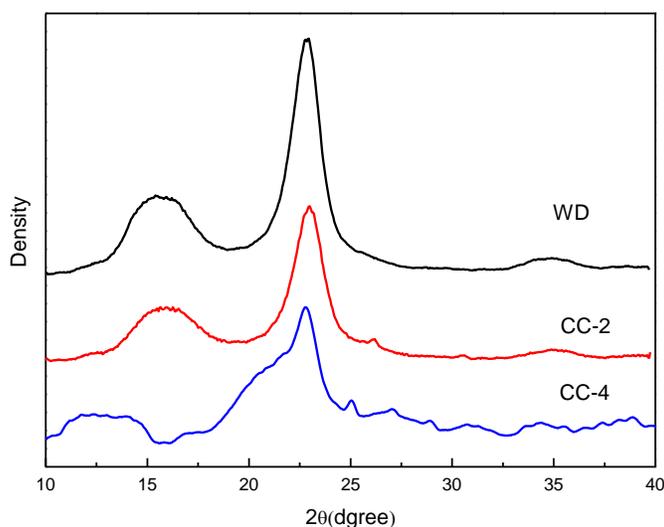


Fig. 5. The XRD patterns of wood-derived cellulose and its carbamate derivative. (WD) cellulose pulp; (CC-2) cellulose carbamate with 1.18% nitrogen content; (CC-4) cellulose carbamate with 4.41% nitrogen content

According to Equation (4), the crystallinity degrees of the cellulose and its derivative were determined by using the Jade curves fitting software toolbox of the Burker XRD instrument (Segal *et al.* 1959). The result shows that when the nitrogen content was increased from 1.18% to 4.41%, the crystallinity degree of the samples decreased from 63.5 to 51.9. This result confirmed the analysis that the gas-like SC-CO₂ could have affected the crystalline structure of the cellulose.

$$Cr(\%) = \frac{Sc}{Sc + Sa} \times 100\% \quad (4)$$

In Eq. 4, Cr is the crystallinity degree, Sc is the area of crystal peak, and Sa is the area of non-crystal peak.

Thermogravimetric (TG) Analysis

The TG curves of the WD and its carbamate derivatives with nitrogen contents of 1.18% and 4.41% are shown in Fig. 6. The TG curves were separated into three sections. At first, the weight loss in the temperature range of 100°C to 150°C could be assigned to the evaporation of water and absorbed gas by cellulose. In the range of 150°C to 250°C there appeared a minor thermal decomposition of residues. In the TG curves of each sample it has been found that all the major decompositions are located in the range of

300°C to 385°C (Calahorra *et al.* 1989). Furthermore, when comparing each of the samples, it was discovered that the major decomposition temperature of the lignocellulose pulp was higher than its carbamate derivatives, and the major decomposition temperature decreased with the increasing of nitrogen content. According to the previous report, the thermostability of cellulose is mainly attributable to its crystallinity degree; therefore, the major decomposition temperature of derivatives shifting to a low temperature indicated that the crystal region was partly destroyed (Nada *et al.* 2000). This inference also supports the discussion in the FTIR section that esterification diminished the intensity of hydrogen bonding, thus improving the accessibility of the cellulose towards esterification.

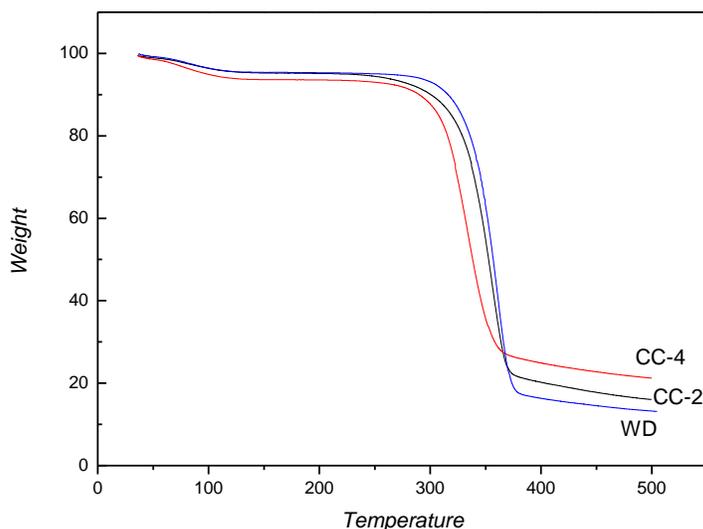


Fig. 6. TG curves of cellulose and its carbamate derivatives. (WD) cellulose pulp; (CC-2) cellulose carbamate with 1.18% N content; (CC-4) cellulose carbamate with 4.41% N content

Morphology Analysis

In previous works it was found that after the treatment of SC-CO₂, the surface of cellulose fibers become loose and rough, and a sight of helical ditch appeared along the direction of microfibrillar angle for 30° (Yin *et al.* 2006, 2007). After analysis this phenomenon was attributed to the typical cotton fibril arrangement and the high permeability of SC-CO₂. In cotton fibers, the fibrils are arranged as parallel spiral forms and there is a large angle between the fibrils and the cotton fiber axis.

Figure 7 compares the FE-SEM photos of the cellulosic pulp and its carbamate derivatives. Based on Figs. 7a and 7b. The fibers exhibited smooth surface features and showed no signs of breakage on the surface. However, the derivatives in Figs. 7c to 7f showed a roughly corrosion change and even some unexpected features on its surface. For instance, Figs. 7c, 7d, and 7f illustrate, as the result of internal pressure, that there emerged a bursting ditch on the surface of CCs fibers, which was oriented along the microfibrillar direction. In addition, as Fig. 7e shows, a scaly fragment was shed off from the fibers, and this was just along the fiber axis. These phenomena corresponded to the description of wood fibers, for which the angle between fibril and fiber axis is small. Therefore, it was concluded that the gas-like SC-CO₂ could efficiently affect the compact structure of the wood fibers, thereby enhancing the reactivity of the cellulose.

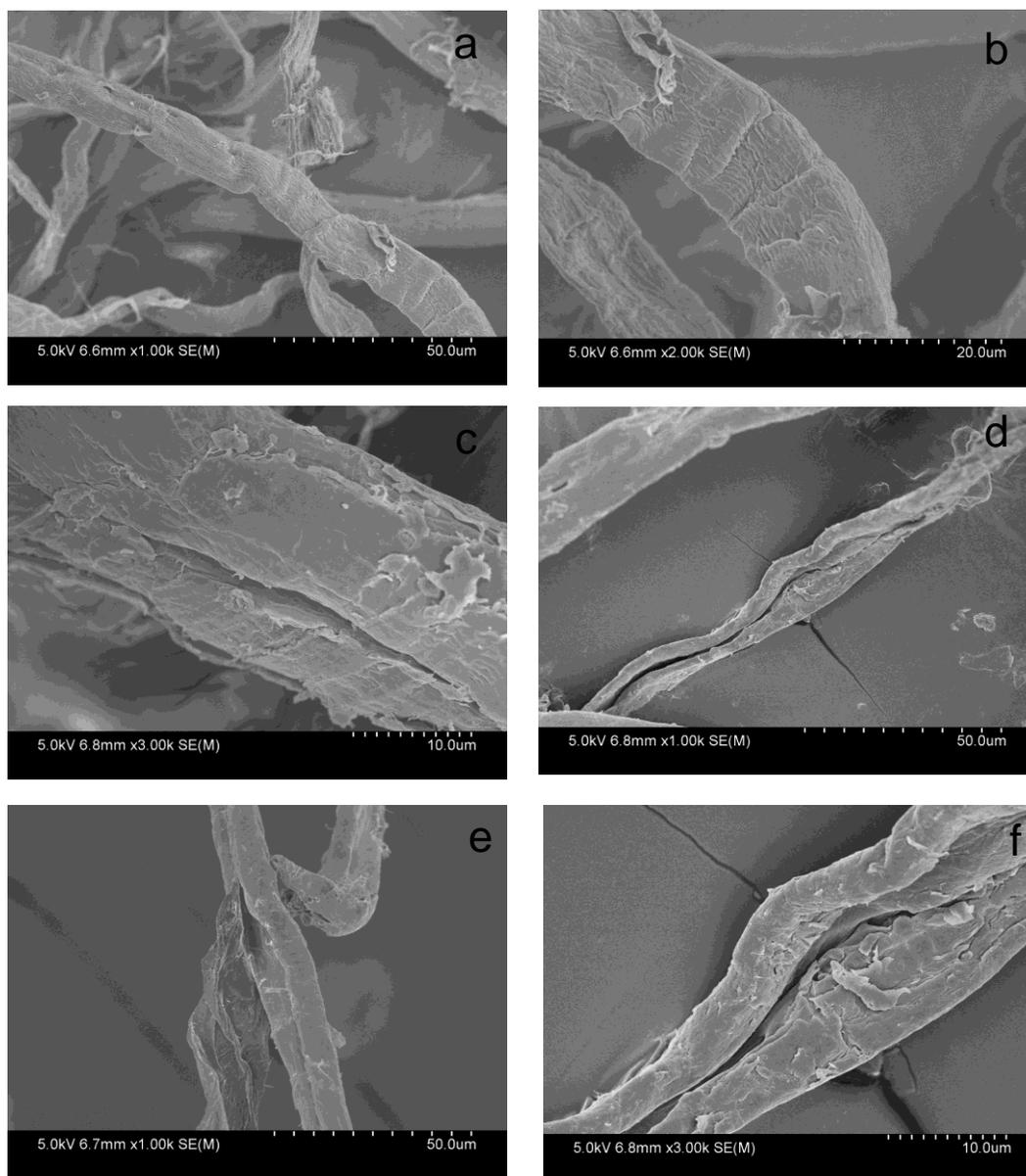


Fig. 7. The FE-SEM photos of wood-derived cellulose and its carbamate derivatives. (a-b) cellulose; (c-f) carbamate

CONCLUSIONS

In this work cellulose carbamate was successfully prepared from lignocellulosic pulp. Samples with nitrogen content as high as 4.41% were obtained. The carbamate still maintained a crystalline form of C-I, but it contained some C-II crystallinity. At the same time, the crystallinity degree decreased with an increase of nitrogen content. In addition, a typical bursting ditch orientated along the microfibrillar direction was observed in the morphology analysis. Compared with the conventional method, the SC-CO₂ method offers a new environmentally compatible way to prepare CCs. The higher nitrogen content of CCs demonstrated that the SC-CO₂ method provided a convenient way for

commercial production, helping to avoid troubles associated with pre-treatment and radio-activation of cellulose from lignocellulosic fibers.

ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (863 Program, 2012AA03A6022010) and the Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin, China.

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Article submitted: December 7, 2012; Peer review completed: January 17, 2013; Revised version received and accepted: January 21, 2013; Published: January 29, 2013.