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Chemical modification of cotton cellulose in supercritical carbon dioxide: Synthesis and characterization of cellulose carbamate

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Abstract

Chemical modification of cotton cellulose in supercritical carbon dioxide has been studied and cellulose carbamate has been successfully synthesized. Compared with the conventional carbamate process, the supercritical method had remarkably increased the nitrogen content of the modified cellulose. The effects of impregnating pressure, esterification temperature and esterification time on the nitrogen content of the products were discussed. The modified cellulose was characterized by Fourier transform infrared spectroscopy (FTIR), NMR spectrometer, X-ray diffraction (XRD), and thermogravimetry (TG). In addition, the surface morphology of modified cellulose fibers was investigated using scanning electron micrographs (SEM).

Keywords: Supercritical CO_2; Cellulose; Esterification; Cellulose carbamate; Nitrogen content

1. Introduction

Cellulose, a natural linear polysaccharide, is the most abundant and renewable biopolymer with outstanding properties and a variety of useful applications. However, chemical processing of cellulose is difficult in general because this natural polymer is not meltable and not soluble in common solvents due to its hydrogen bonds and partially crystalline structure (Fink, Weigel, Purz, & Ganster, 2001). Fortunately, the physical properties of cellulose can be significantly modified by derivatization (Edgar, Buchanan, Debenham, Rundquist, & Seiler, 2001). The modified properties of these cellulose derivatives have greatly expanded the applications of cellulose materials, such as modern coatings (Cook & Simm, 1999), controlled release of actives (Stithit, Chen, & Price, 1998; Dowler, Dailey, & Mullinix, 1999), plastics (with particular focus on biodegradable plastics) (Jandura, Kokta, & Riedl, 2000; Schauber, Vos, Huhn, Rieger, & Möller, 1999), composites and laminates (Glasser, Taib, Jain, & Kander, 1999; Muschio, 1996), optical films (Shimoda et al., 1997; Machell & Sand, 1993), liquid crystal displays (LCD) (Shuto & Taniguchi, 1999), as well as membranes and relevant separation media (Stamatialis, Dias, & Pinho, 2000; Okamoto & Kaida, 1994). For these reasons, converting cellulose to its derivatives (especially cellulose esters), experimentally and commercially, has been attracting considerable interests.

Considering their prominent properties and extensive applications, it is desirable to convert cellulose efficiently using an economic and environmentally friendly chemical process. The production of regenerated cellulose materials is based largely on the old viscose method in which fibers (viscose, rayon), films (cellophane) etc. are produced via a metastable soluble cellulose derivative (cellulose xanthogenate). However, this process is accompanied by environmental hazardous by-products including CS_2, H_2S, and heavy metals (Urbanowski, 1996). The cuprammonium

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process that converts cellulose to a soluble compound by combining it with copper and ammonia is another classical route for producing regenerated cellulose materials (Franks & Varga, 1980), but also faces environmental problems and therefore plays only a minor role in today's industry. So, new ways to avoid complicated processing routes and hazardous by-products have been presented continually long before. Among them, the NMMO-technology and the carbamate process are the two most successful methods in recent years. Johnson patented the solvent system on the basis of cyclic amine oxides, particularly *N*-methylmorpholine-*N*-oxide (NMMO), which can dissolve not only cellulose but other polymers as well (Johnson, 1969). A variety of regenerated cellulose materials, such as the well-known "Lyocell" fibers, have been produced by dissolving cellulose in the solvent NMMO (Johnson, 1969; Gannon, Graveson, & Mortimer, 1998).

Cellulose carbamate (CC) is the product of the carbamate process, an efficient alternative to the viscose process of producing fibers from cellulose. The carbamate process does not require any use of organic solvents and therefore avoids many difficulties brought by the viscose method (Calahorra, Cortazar, Eguiazabal, & Guzman, 1989; Ekman et al., 1983). Industrial tests have shown that cellulose carbamate can be processed feasibly on viscose spinning machines. Furthermore, cellulose carbamate and the regenerated fibers produced from it can biodegrade more easily than viscose fibers. However, these fibers became insoluble in alkali as the nitrogen content was reduced in spite of the progressive biodegradability (Woodings, 2001). So, there are abundant research activities around novel methods to improve their performance to exploit them in commercial applications.

In this study, we have presented a convenient method of remarkably increasing the nitrogen content of cellulose carbamate by using supercritical CO_2 as a solvent. Specific properties of supercritical fluids (SCFs), such as low viscosity, relatively high density, and no surface tension, allow easier mass transfer and have promoted scientific and industrial interests in polymer science, chemical separation, and porous materials, etc (Xu, Pang, Peng, Li, & Jiang, 2004; Wakayama, Itahara, Tatsuda, Inagaki, & Fukushima, 2001; Chang et al., 2004; Hebb, Senoo, Bhat, & Cooper, 2003; Xu et al., 2005). Thus, it is planned to take advantage of the environmentally benign green solvent (SC CO_2) to improve the carbamate process for producing the regenerated cellulose fibers.

2. Experimental

2.1. Materials

Cotton linter pulp from Henan Textile College was used as the starting cellulose. It contains about 93% α-cellulose, and the degree of polymerization (DP) of cellulose was about 520. The determination of the DP was based on the specific viscosity measurement of the sample dissolved in the cuprammonium solution. Urea (CH_4N_2O, AR) was purchased from Tianjin Kermel Chemical Reagent Development Center and was used as received. CO_2 with purity of 99.9% was obtained from Zhengzhou Sanfa Gas Co. All other chemicals were supplied by Tianjin Jinyu Chemical Plant and were used without further purification.

2.2. Preparation of the cellulose carbamate

In a typical experiment, ethanol (3 mL) was placed in a stainless steel autoclave of 50 mL capacity. Ethanol was used as the cosolvent to enhance the solubility of urea in the SC CO_2. Cotton pulp (1.5 g) and urea (1.9 g) were placed in a stainless cage fixed at the upper part of the autoclave without touching the ethanol at the bottom. Carbon dioxide was then introduced into the autoclave using a high-pressure syringe pump (Beijing Satellite Manufacturing Factory, China; DB-80) and the stirrer in the autoclave was started until vapor–liquid equilibrium was reached. In order to remove the air from the autoclave, it had been purged twice by gaseous CO_2 at condition ambient. Temperature of the autoclave was gradually increased and then maintained at 50 °C in a constant temperature circulator with an electrical heating-jacket (XTN-7000). The pressure in the autoclave was then increased to 18 MPa by charging with CO_2 again. Keeping the temperature (50 °C) and pressure, the reaction was allowed to last for 6 h in order to impregnate urea into the cellulose pulp adequately. Then $CO_2$was released and urea remained in the cellulose pulp. The autoclave was heated and maintained at the esterification temperature of cellulose and urea for 4 h. The autoclave was then cooled to room temperature and the samples were removed. The products were washed with hot water (80 °C) four times to remove redundant urea.

2.3. Characterization

Infrared spectroscopy (IR) experiments were performed using a Nicolet 460 FTIR under standard operating conditions. ^{13}C NMR spectra were obtained on a Bruker AV400 (100 MHz) NMR spectrometer in $CDCl_3$ at 20 °C. Thermogravimetric (TG) analysis was performed using a Netzsch TG209 instrument with a heating rate of 10 °C/min and a heating range from 35 to 550 °C under N_2 atmosphere. Wide-angle X-ray diffraction patterns were recorded by monitoring the diffraction angle 2θ from 5° to 50° on a Rigaku D/MAX-RB X-ray diffractometer (XRD) using Cu Kα radiation ($\lambda = 0.154$ nm). 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. The Kjeldahl method was used for analyzing the nitrogen contents of modified cellulose using a Kjeltec 2300 Analyzer Unit (FossTecator).

3. Results and discussion

In our method, urea was firstly impregnated into the cellulose pulp with the aid of SC CO_2, followed by esterification of cellulose. This scheme was shown in Fig. 1. Both the two steps had a significant influence for the preparation of cellulose carbamate. Therefore, effects of the impregnating conditions and the esterification conditions on the nitrogen content of modified cellulose were studied, respectively. The nitrogen content was used to determine the esterification number of modified cellulose.

3.1. Effects of impregnation conditions on the nitrogen content of modified cellulose

It is well known that supercritical CO_2 is highly compressible and its density and solvent properties (for example solvent strength) can be tuned over a wide range by varying pressure and temperature (Hebb et al., 2003). So, changing of the temperature and pressure of SC CO_2 certainly affects the impregnating process of urea. A series of products had been fabricated by changing the pressure of supercritical CO_2 in order to determine the effect of different impregnating conditions on the nitrogen content of modified cellulose. From Fig. 2 it can be seen that the nitrogen content of carbamated cellulose first increased from 2.21% to 8.61% with pressure and there was a maximum of the nitrogen content at the pressure of 18 MPa. Then the nitrogen content decrease with the increase of the impregnating pressure. According to our previous studies (Chang et al., 2004), there are usually many factors contributing to the impregnating process when SCF is used as a solvent and carrier, such as the solubility of urea in SC CO_2 and its cosolvent, the compatibility of urea with cotton cellulose pulp, and the swelling or plasticizing effect of CO_2 on cellulose substrate, etc. There also exist some

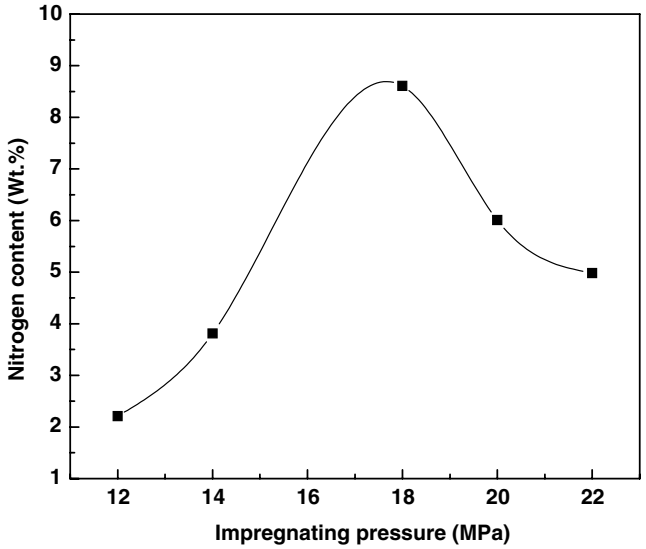

Fig. 2. The nitrogen content of modified cellulose as a function of impregnating pressure after being treated in SC CO_2 for 6 h at 50 °C.

complex interactions, such as competition among these factors. At low pressures, the solvent intensity of CO_2 was too poor to swell the cellulose substrate sufficiently to permit the rapid infusion of urea. At high pressures, CO_2 was a much better solvent for urea, and the partition of urea in the SC CO_2 fluid phase was also enhanced when it readily swelled cotton cellulose. So we suggested that the equilibrium partitioning of urea between SC CO_2 and cellulose can be achieved at about 18 MPa which favored the esterification of cotton cellulose.

3.2. Effects of esterification conditions on the nitrogen content of modified cellulose

Actually, the esterification temperature can influence the reactions in the carbamate process. Our results have

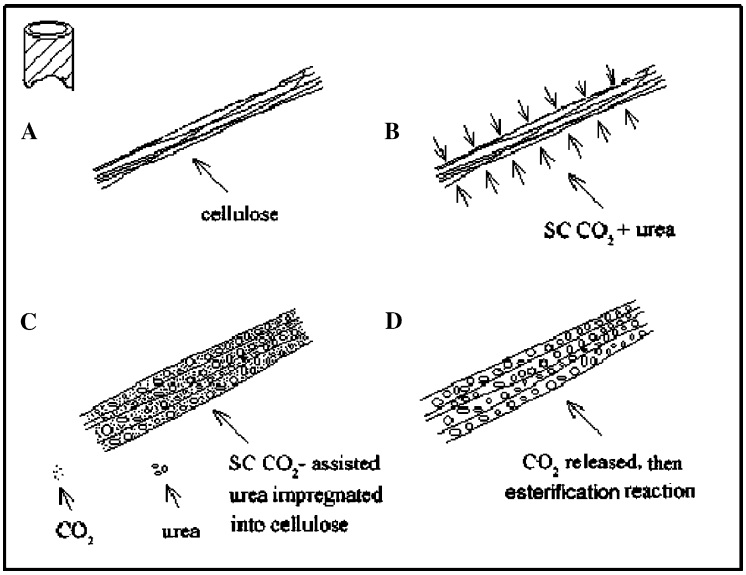

Fig. 1. Scheme of SC CO_2-assisted modification of cotton cellulose.

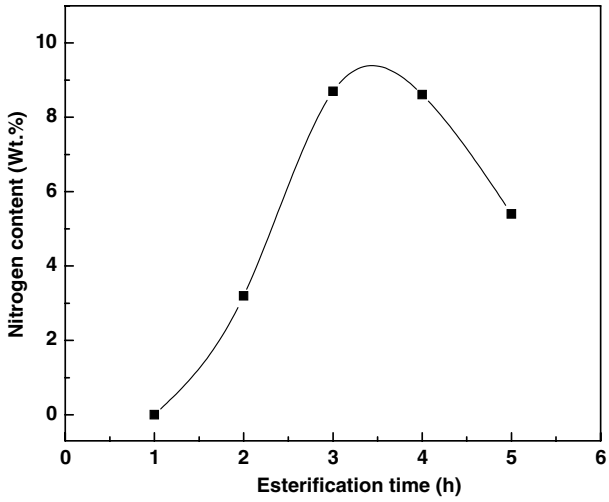

Fig. 3. The nitrogen content of modified cellulose as a function of esterification time at 140 °C. (Impregnation conditions in SC CO_2: 50 °C, 18 MPa, 6 h).

indicated that the esterification number of cellulose was quite low when the esterification temperature was below 120 °C. The temperature increasing from 130 to 150 °C leads to higher nitrogen content of modified cellulose. The reason is that the higher temperature favors the esterification reaction and enhances the degree of esterification for cotton cellulose. However, higher temperature may result in the yellowing and pyrolysis of cellulose and its derivatives. So, we chose a temperature of 140 °C as the practical esterification temperature.

In addition, the effect of the esterification time on the nitrogen content of carbamated cotton cellulose was investigated. As shown in Fig. 3, the nitrogen content of the carbamated cellulose ascends sharply with the increasing of esterification time. The maximum nitrogen content can be achieved when the esterification time was increased to about 3.5 h. Furthermore, the nitrogen content of modified cellulose is a maximum when the reaction time is about 3.5 h. This can be attributed to the increase of by-products (for example biuret) which can result in excessive consumption of urea and disturb the esterification reaction between urea and cellulose when the reaction time is too long. Meanwhile, the pyrolysis of partial cellulose and its derivatives also might result in the decline in the nitrogen content of modified cellulose.

3.3. FTIR and NMR analysis

The dried products of modified cellulose were made into KBr pellets and analyzed with the FTIR spectrometer. A blank sample from pristine cellulose pulp was also analyzed in the same way.

Fig. 4 shows the FTIR spectra of pristine cellulose and modified cellulose with the nitrogen content of 4.98% and 6.01%, respectively. Compared with pristine cellulose, we can see that the modified cellulose has an obvious new absorption peak at 1713 cm^{-1}, which was assigned to the stretching vibration of the carbonyl (C═O) in the base of urethane. This indicated that urea had reacted with cotton cellulose to form cellulose carbamate. Furthermore, the absorption band at 1713 cm^{-1} gradually rose with the increasing nitrogen content of the carbamated cellulose. According to a previous report (Nada, Kamel, & El-Sakhawy, 2000), there was an approximately linear relationship between the intensity ratio of the band at 1713 cm^{-1} to the band at 1645 cm^{-1} and the nitrogen content. The absorption peak at 1645 cm^{-1} appears in cellulose itself and did not vary in intensity in the esterification process. This was in agreement with our experimental data. In addition, the relative absorbance of hydroxyl bands at 3420 and 1035 cm^{-1} (primary —OH) decreases with increasing nitrogen content of the carbamated cellulose. These can be attributed to the increase of reaction of urea with hydroxyl groups on the cellulose chains. The indensity of the band at 1425 cm^{-1}(C—H rocking of the ring) results in an obvious increase after the esterification of cellulose, which corresponds to the decrease in the hydrogen bonds.

NMR technical data for cellulose derivatives have been proved to be a convenient and reliable method for elucidating the chemical structures of modified cellulose. Fig. 5 shows the ^{13}C NMR spectra of pristine cellulose and modified cellulose sample with 6.01% of nitrogen content, and the possible assignments of the peaks are also shown according to the references. It can be seen that the spectrum of modified cellulose contains a remarkable signal at 159 ppm typical for the carbonyl carbon of the carbamate function. Consequently, the chemical structure of synthetical cellulose carbamate can be confirmed once again.

3.4. TG analysis

Thermogravimetric curves for pristine cellulose and modified celluloses with different nitrogen content are shown in Fig. 6. After initial loss of moisture and desorption of gases at about 100–120 °C, a major decomposition proceeded from 338 to 378 °C for pristine cellulose and its maximum decomposition temperature appeared at 363 °C. For modified cellulose, there was an additional loss of weight at 150–225 °C which was attributed to the actual pyrolysis brought by the minor decomposition reaction. The major decomposition temperature for modified celluloses is lower than that of unmodified ones. Furthermore, it is found that the minor and maximum decomposition temperatures of modified cellulose shift towards lower temperatures with the increase of the nitrogen content. It has been noted that thermal stability of cellulose and modified cellulose depends mainly on its crystallinity (Calahorra et al., 1989; Nada et al., 2000). Therefore, the shifts of decomposition temperatures can be attributed to the increase in the amorphous or disordered region which is decomposed by thermal treatment faster than the crystalline part in the cotton cellulose pulp.

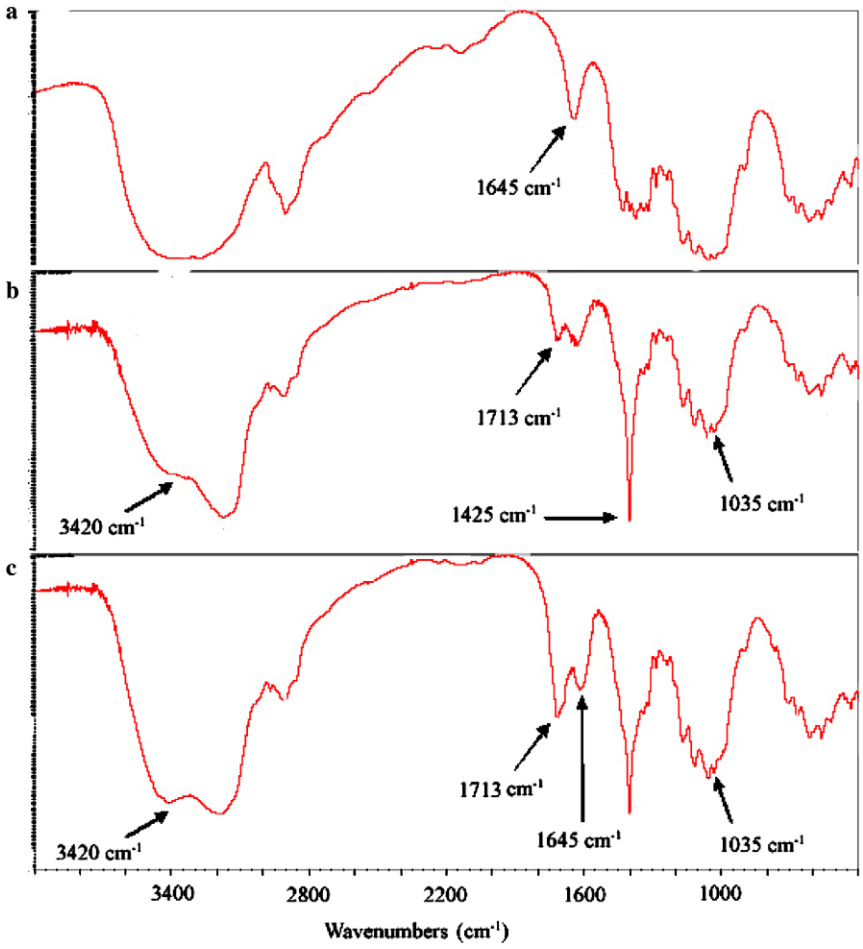

Fig. 4. FTIR spectra of the pristine cellulose (a) and modified celluloses with different nitrogen contents: 4.98% (b); 6.01% (c).

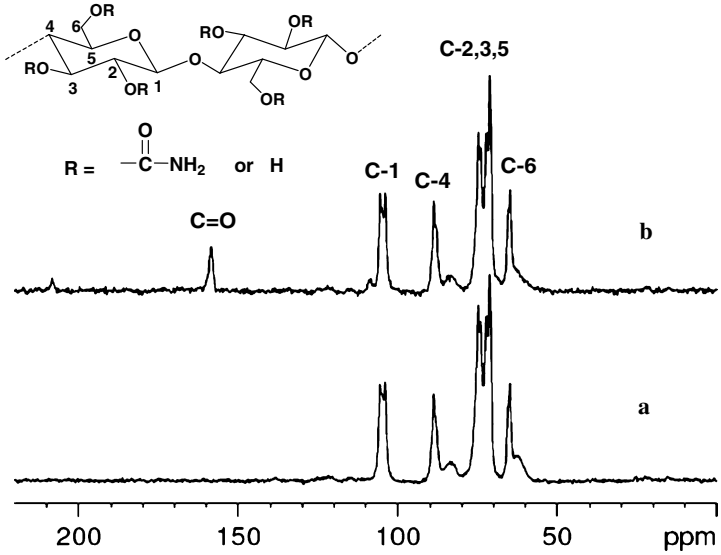

Fig. 5. ^{13}C NMR spectra of pristine cellulose and modified cellulose sample with nitrogen content of 6.01%.

3.5. XRD analysis

X-ray diffraction results show some important information about the esterification reaction and crystallinity of cellulose. Actually, the degree of crystallinity of cellulose and the dimensions of the crystallites have been subjects of extensive investigations for many years, some results of X-ray diffraction measurements of native celluloses have

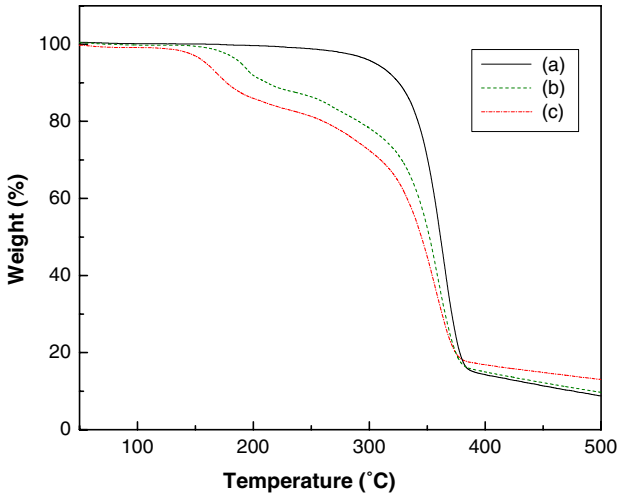

Fig. 6. TG curves of the pristine cellulose (a) and modified celluloses with different nitrogen contents: 4.98% (b); 6.01% (c).

been accomplished (Klemm, Heublein, Fink, & Bohn, 2005). In our results, the XRD patterns of the pristine cellulose and the modified celluloses with different nitrogen content are shown in Fig. 7. It can be seen that the pristine cellulose has 2θ diffraction peaks at 14.8°, 16.4°, 22.6°, and 34.5° which are typical cellulose I crystalline form, in good agreement with previous report (Klemm et al., 2005). These characteristic peaks also appear at the XRD patterns of modified celluloses, which reveal that the esterification reaction does not change the main crystalline form of cellulose. Meanwhile, the degree of crystallinity of modified cellulose has declined markedly when the abundant —OH group in the texture of cellulose was substituted by urea. As a result of the supramolecular structure and interaction of hydrogen bonds, cellulose is represented by high crystallinity and insolubility. The degree of crystallinity of cotton linters cellulose is about 56–65% (Klemm et al., 2005). The substitution of hydroxyl group has reduced the density of hydrogen bonds and then partially destroyed the crystalline structure of cellulose. So, the solubility of modified cellulose in alkali is evidently improved with increasing nitrogen content. Furthermore with the increase of nitrogen content, XRD patterns of modified celluloses display some new peaks at $2\theta = 10.3°$, 12°, 18.9°, 26.5°, and 28°. The formation of new crystal planes shows the possibility of the transition of cellulose crystalline form (from I to II). And we can find that the intensities of new peaks rise with increasing nitrogen content. This testifies the effect of the substitution reaction on the crystalline dimensions of modified

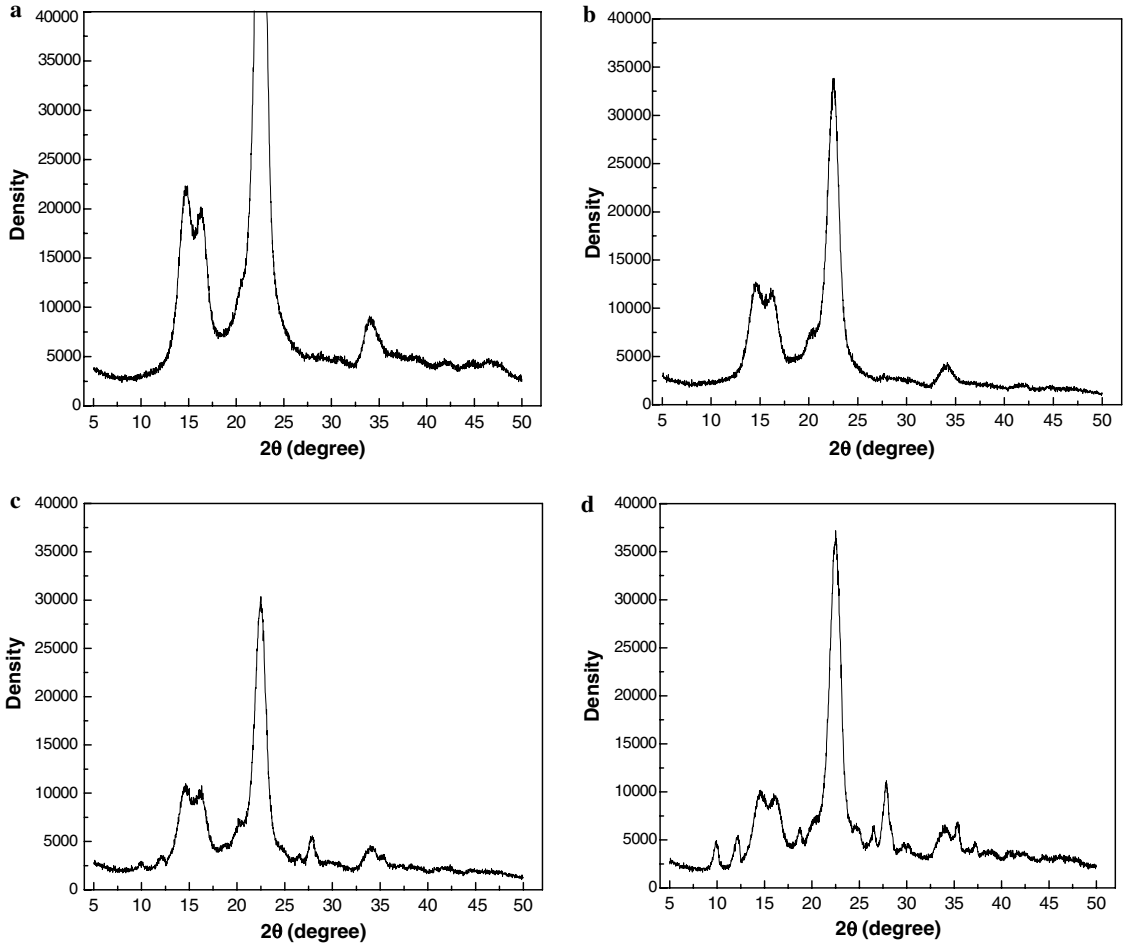

Fig. 7. X-ray wide-angle scattering curves of the pristine cellulose (a) and modified celluloses with different nitrogen contents: 1.78% (b); 3.81% (c); 8.61% (d).

cellulose. The interplanar distances of some new crystal planes (10.3° and 12°) are wider than cellulose I crystalline form, which is considerably advantageous for the accessibility in chemical reactions and alkali-solubility.

3.6. Morphology

The numerous applications of cellulose are based on its distinct fiber morphology. Thus, there may be a relation between the surface feature and the properties of modified celluloses. In order to attain a better understanding of the effect of SC CO_2 treatment and the substitution reaction on the properties of modified celluloses, a microscopic study was carried out using scanning electron microscopy (SEM). Fig. 8a shows SEM photograph of pristine cellulose of cotton linter pulp. The cellulose fibers of cotton pulp have a smooth and compact surface and show no sign of external fibrillation or formation of fibrils.

In contrast, SEM photographs of modified celluloses of cotton linter pulp are shown in Fig. 8. From the appearance of modified cellulose, we can see that the change in the structure of fibers' surface is comparatively notable. After the treatment of SC CO_2 and chemical modification, the surface of cellulose fibers become rough, loose and striated. The external fibrillation of modified cellulose fibers was also exfoliated partially (Fig. 8c). In addition, an unexpected sight has aroused our curiosity. The surface of cellulose fibers shows some helical ditches orientated along the direction of microfibrillar bands (Fig. 8d–f). The helical ditches in the cellulose fibers keep uniform spacing interval and are filled with microfibrils, which indicates morphological hierarchy of typical cellulose fiber morphology. These

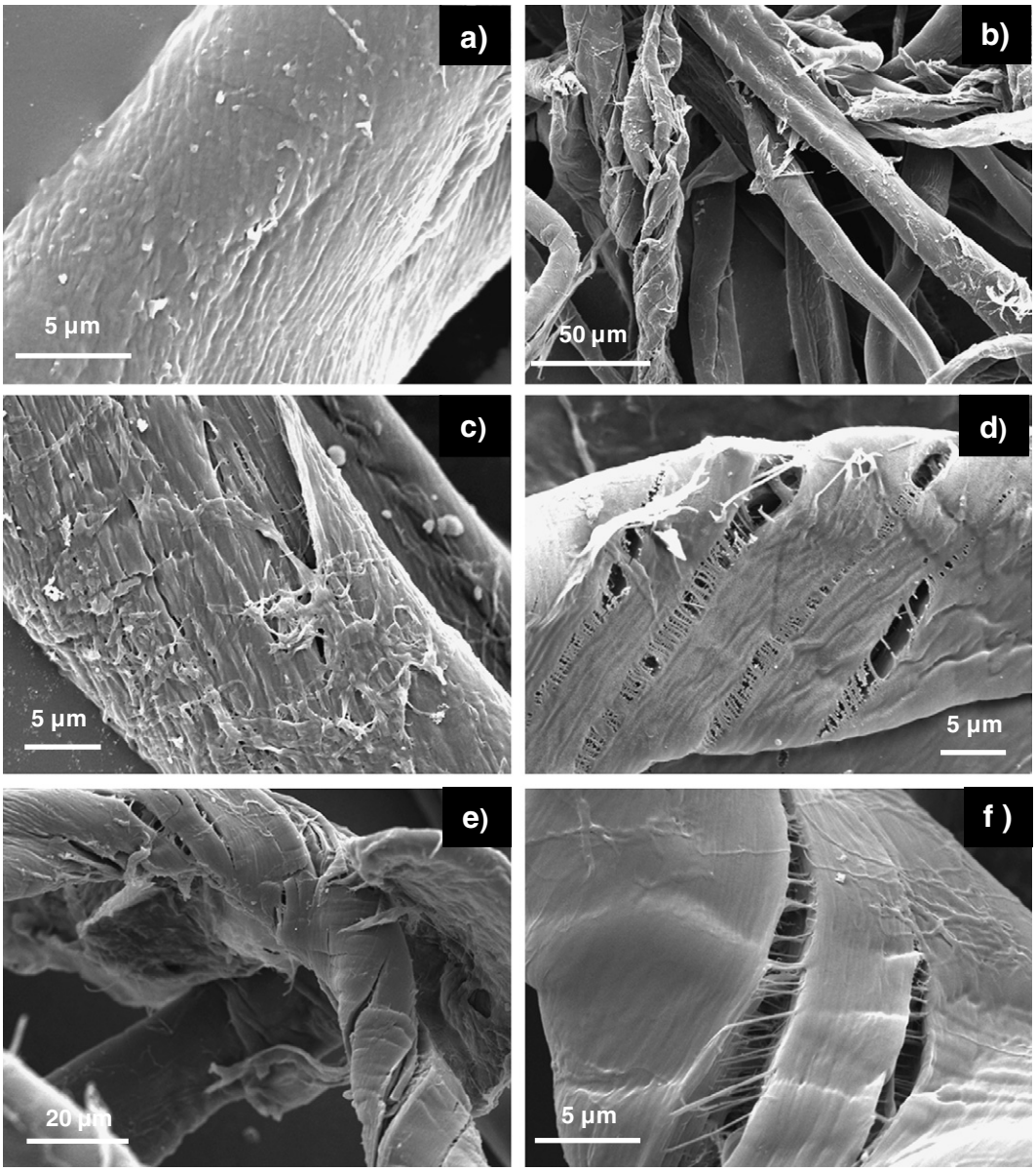

Fig. 8. SEM photographs of pristine cellulose (a) and modified celluloses (b–f) of cotton linter pulp.

changes in the structure of cellulose fibers might be attributed to the excellent properties, high diffusion and good swelling to polymer, of SC CO_2. They are considerably important for the accessibility in chemical reactions, solubility and spinnability of modified cellulose.

4. Conclusions

Chemical modification of cotton cellulose with the aid of supercritical carbon dioxide has been studied. In this method, urea was first impregnated into the cellulose pulp using SC CO_2 as a solvent and carrier, followed by the esterification of cellulose at a suitable temperature, resulting in cellulose carbamate. The yielded cellulose carbamate is endowed with high nitrogen content and good solubility in alkali. And the nitrogen content of modified cellulose can be adjusted by the impregnating pressure, esterification temperature, and esterification time. Moreover, typical surface structure of helical ditches orientated along the direction of microfibrillar bands was found in the modified cellulose fibers.

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