ENHANCEMENT OF CELLULOSE REACTIVITY USING AN IONIC LIQUID PRETREATMENT STEP

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The pretreatment is one of the critical steps in influencing the reaction efficiency of cellulose. In this article, several pretreatment methods of microcrystalline cellulose (MCC) are presented: the ultrasonic, sodium hydroxide and 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) dissolution treatment, and the reactivity of cellulose to a TEMPO-NaClO-NaBr oxidation system is investigated. The treated cellulose is characterized by scanning electron microscopy, X-ray diffraction, and FTIR. Comparing the three pretreatment methods, the ionic liquid pretreatment does not destroy cellulose I and greatly reduces crystallinity, while enhancing the reactivity of cellulose.

Keywords: MCC, [C$_4$mim]Cl treatment, crystallinity, reactivity

INTRODUCTION

Cellulose is the most abundant natural biopolymer on earth. It represents the most obvious renewable resource for producing bio-composites. Its highly ordered structure is responsible for its desirable mechanical properties.[1,2] Therefore, chemical modification of cellulose into cellulose derivatives becomes an effective way to take advantage of cellulose material. Such cellulose derivatives with their unique structures allow the application of cellulose with a new way. Cellulose and cellulose derivatives offer value-added properties and considering the present emphasis on renewable materials, we will see a large increase in research efforts in this area. The ability to generate highly functional nanomaterials within areas such as nanocomposite polymer hydrogels,[3,4] pharmaceutical applications,[5] electronic materials[6,7] is clearly evident. The use of cellulose for biomedical applications has a great potential. Some work has been published on using ordered monolayers of cellulose nanowhiskers to direct tissue growth.[8,9] Oxidation modification is a proper approach to make cellulose derivations. A number of applications have been described for oxidized carbohydrates, relying on some of their specific properties, ranging from gelation, to complexation, anti-flocculation, adhesion, as well as a number of biological activities. The oxidation of primary alcohol groups in natural polysaccharides, catalyzed by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), has been recently proposed as a more selective, faster, and better-controlled method as opposed to the traditional procedure using nitrite/nitrate in concentrated phosphoric acid.[10,11,12]

In-situ NaOBr, generated from NaOCl and NaBr, is used to regenerate the catalyst. This method was first proposed for water-soluble polysaccharides,[11,12,13,14] such as cellulose, amylose and chitin. For oxidation of water-insoluble cellulose, a major obstacle that needs to be overcome is its low accessibility. In the case of native cellulose, Chang and Robyt[14] have observed a significant increase in the water-solubility of the oxidized product obtained from native cellulose (cellulose I). TEMPO-mediated oxidation of MCC at high temperature is synthesized and characterized[15] and the influence of temperature and oxidation procedure on oxidation yields of water-soluble products and crystal structures of water-insoluble residues are investigated.[16]

It has been shown that the cellulose decrystallization leads to a substantial increase in the polyglucuronic acid yield, but still minor quantities of water-insoluble material remain in all preparations.[17,18] It seems that cellulose can be oxidized to yield highly pure polyglucuronic acid only if regenerated cellulose samples are used.[19] So pretreatment can be the most effective process to promote the accessibility of cellulose. The pretreatment method for cellulose in liquid ammonia (L-NH$_3$) or in molecules, such as amines, diamines, or polyamines is a classical way to increase the accessibility of crystalline cellulose.[20] However, this method requires very harsh conditions and it is not cost-efficient.

From above, it can be seen that even though there are many researches focusing on the pretreatment and oxidation of cellulose, very little information is available on the comparison of different pretreatment methods (ultrasonic,[21,22] sodium hydroxide[23] and ionic liquid pretreatment[24]) on the effect of TEMPO-mediated oxidation activity of MCC. The aim of this study is to investigate the effect of different pretreatment methods on the oxidation accessibility of cellulose through comparative analyses among the three methods. Our main objective is to develop a simple and environmentally friendly pretreatment method of cellulose.

EXPERIMENTAL
Materials
Microcrystalline cellulose powder (DPv = 120) was obtained from Justness (China). TEMPO (2,2,6,6-tetramethyl piperidine-1-oxyl radical) was supplied by Wako Chemicals Co. Ltd. (Japan). Sodium hypochlorite solution (ca. 10% active chlorine) was supplied by Justness (Qingdao, China) and 1-butyl-3-methylimidazolium chloride by Cheng Jie Shanghai Reagent Company. All other chemicals were analytically pure (Shanghai Chemicals Co. Ltd., China) and were used without prior purification.

Ultrasonic pretreatment
A certain amount of MCC was added to a certain amount of water, processed with an ultrasonic generator for certain time. Then the cellulose dispersion was centrifuged for 5 min. Finally, the obtained solid was washed with distilled water for three times and dried in an oven.

Cellulose mercerization
The alkaline pretreatment was conducted by adjusting the pH of the sludge to 11.0 with 15% NaOH and maintained for 24 h, and then back to pH = 6.8 with the addition of 2 mol/L HCl. The mercerized product was air-dried and kept at 40 °C under vacuum, until constant weight.

Ionic liquid pretreatment of MCC
A desired amount of MCC powder was dissolved in 1-butyl-3-methylimidazolium chloride [C$_4$mim]Cl at 80 °C until a light yellow transparent cellulose solution was observed, followed by rapid precipitation with an anti-solvent, such as water. Then the precipitate was repeatedly washed until its colour turned to pure white. Finally, the precipitate was ground in a mortar and kept in a sealed bag.

TEMPO-NaBr-NaClO oxidation
The oxidation experiments were carried out under the following conditions. Pretreated microcrystalline cellulose (1.0 g, i.e 6 mmol of anhydroglucose units) was dispersed in Na$_2$CO$_3$/NaHCO$_3$ buffer solutions (75 ml) of pH = 10.83 for 2 min with an Ultra-Turrax homogeniser. TEMPO (30 mg, 0.2 mmol) and NaBr (0.32 g, 3.1 mmol) were added to the suspension, which was maintained at 15 °C operating temperature. The sodium hypochlorite solution (21%, 4.10 ml, 13.20 mmol) with the pH adjusted to 10 by addition of 0.5M aqueous HCl was added four times (each time after 30 min) to the suspension and mechanically stirred. When the reaction time reached 5 h, the reaction was stopped by adding 10 ml of methanol or/and a small amount of sodium borohydride. The reaction mixture was neutralized to pH = 3.0 with 0.5M HCl and centrifuged to remove the residual insoluble material. The oxidized cellulose sample in the supernatant liquid was precipitated by adding an excess of ethanol (2-3 volumes), followed by centrifugation. The precipitate was washed with ethanol/water (9/1), centrifuged several times and washed with acetone. Finally, the precipitate was dried at 40 °C in a vacuum oven. The oxidized product is called "cellouronic acids" in this work.

The oxidation yield of the oxidized product was calculated as follows:

$$Y = \frac{m}{m_0}$$

where m is the mass of the oxidation product; m$_0$ is the mass of pretreated microcrystalline cellulose before the oxidation reaction.

Characterization
Scanning electron microscopy (SEM) was carried out by a JSM-6700F electron microscope in order to study the phase structure and surface morphology of the pretreated MCC. Data of X-ray powder diffraction (XRD) were collected on a D/MAX-1200 (WQF-410 X-ray diffraction) powder diffractometer (Rigakav, Japan) with CuKα radiation of 1.54051 Å at 40 kV, 20 mA; Ni lisp filtering wave, λ = 0.154 nm, scanning scope: 2θ = 0∼80°, stepping scanning: 2θ = 0.1°/3s. FTIR experiments were carried out on an RFX-65A Fourier transform infrared spectrophotometer

purchased from American Analect Company at wave numbers from 400 cm^{-1} to 4000 cm^{-1}.

RESULTS AND DISCUSSION
Morphology of pretreated MCCs

The scanning electron micrographs of virgin MCC and pretreated MCC using ultrasonic pretreatment, mercerized pretreatment and pretreatment with ionic liquid methods are shown in Fig.1. The surface of untreated MCC is smooth and the arrangement of the fibers is regular. The surface of pretreated MCC (Fig. 1b-d) is coarser compared to that of untreated MCC (Fig. 1a), and the fiber bundles are loosened and move randomly inside the matrix. The SEM pictograph of the sample mercerized in NaOH (Fig. 1c) shows that the surface appears to peel, fibrils are irregular and rough, similar to a sponge-like bulk. The SEM micrograph of the sample pretreated with ionic liquid (Fig.1d) indicates that the ionic liquid-treated sample lost the fibrillar morphology and became a coagulated mass with a bumpy surface. If one compares the sample mercerized in 15% NaOH with the sample pretreated in ionic liquid, it can be observed that the ionic liquid treatment promoted an additional separation of the fiber bundles.

Crystalline structure of pretreated MCCs

XRD patterns of ultrasonic pretreated, mercerized, ionic liquid pretreated and untreated MCC samples are shown in Fig. 2. Untreated MCC corresponds to cellulose I crystal form characterized by 2θ ($\overline{110}$) = 14.7°, $2\theta(110)$ = 16.5°, $2\theta(200)$ = 22.7° and shows almost no changes when the material is treated by ultrasound, characterized by $2\theta(\overline{110})$ = 14.7°, $2\theta(110)$ = 16.5°, $2\theta(200)$ = 22.7°. The conversion of partial cellulose I crystal form into the cellulose II crystal form for the mercerized sample has been observed by X-ray diffraction, as shown in Fig. 2. During mercerization, the alkali penetrates the cellulose fiber and causes a rearrangement of the crystal packing of the chains from native cellulose I crystal form (chains aligned in parallel) to cellulose II crystal form (anti-parallel). This change is irreversible and normally accompanied by a decrease in the crystallinity. As shown in Fig. 2, XRD results suggest that during pretreatment with [C$_4$mim]Cl at relatively low temperature, MCC crystallinity is disrupted.
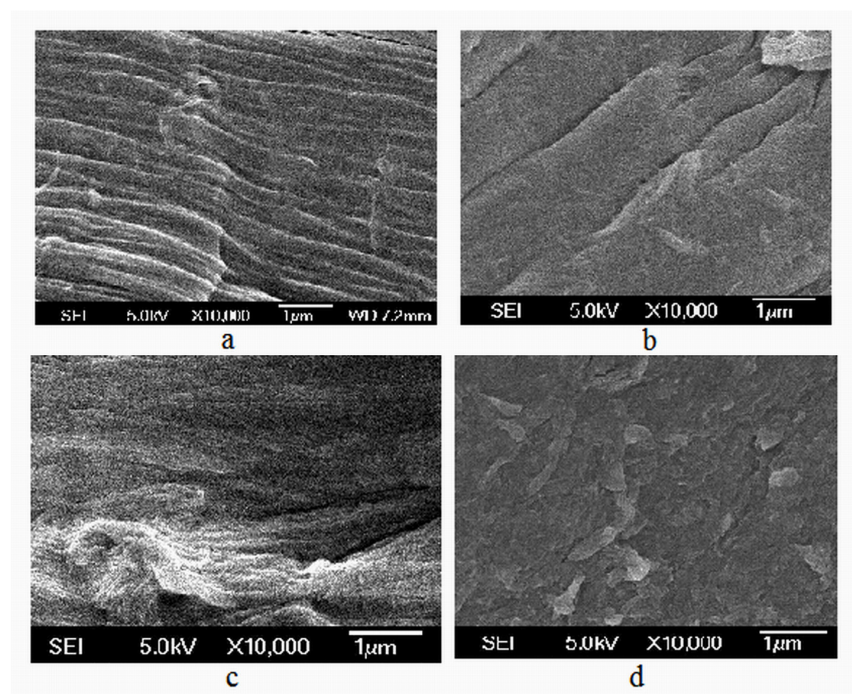

Figure 1: SEM micrographs of untreated and pretreated microcrystalline cellulose (a: untreated MCC; b: ultrasonic pretreated MCC; c: mercerized MCC; d: MCC pretreated with ionic liquid)
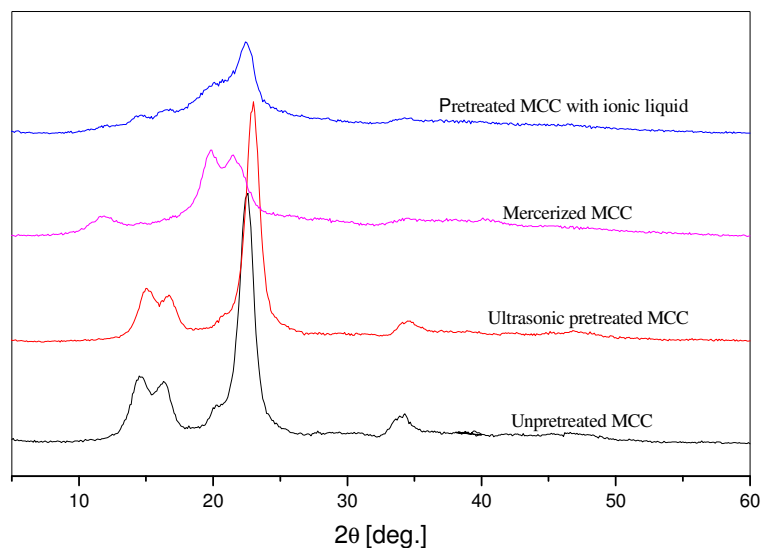
Figure 2: X-ray powder diffraction patterns for pretreated and untreated MCC
(the spectra are shifted vertically for clarity)

Table 1
Degree of crystallinity and oxidation yield of different pretreatment MCC

Samples	Untreated MCC	Ultrasonic treated MCC	Mercerized MCC	[C$_4$mim]Cl treated MCC
Crystallinity	78.44%	70.99%	42.23%	36.97%
Oxidation yield	6.80%	8.96%	77.1%	84.7%

The crystallinity of MCC pretreated by different methods is shown in Table 1. It is seen that the crystallinity of MCC decreases drastically with the use of ionic liquid pretreatment, compared to the ultrasonic and NaOH pretreatments. Rapid precipitation with anti-solvent may prevent the restructuring of some part of the dissolved cellulose into its crystalline form. Cellulose I crystal form has partly transformed into cellulose II crystal form, characterized by $2\theta(\overline{110}) = 11.8°$, $2\theta (110) = 19.8°$, $2\theta(200) = 21.7°$. The samples treated with [C$_4$mim]Cl at relatively low temperature present features from both cellulose I crystal form and cellulose II crystal form. Comparing the three pretreatment methods, the ionic liquid pretreatment method can partly keep cellulose I crystal form, while greatly reducing crystallinity and enhancing the reactivity of cellulose.

Chemical structure of pretreated MCCs

In Fig. 3, the FTIR spectrum shows that before and after MCC pretreatment basically the infrared absorption bands of the samples are similar in shape, but the absorption intensity is different, indicating that these three pretreatment methods can change the morphology of cellulose without destroying its chemical structure. Each structural unit of cellulose molecules contains three hydroxyls, so cellulose chains easily form hydrogen bonds. It has been observed that the absorption peak at 3420 cm^{-1} is associated to the intramolecular O-H stretching vibration. The hydrogen bonds lead to the low availability of cellulose to chemical agents, thus the chemical reactive modification of cellulose has poor performance. The ultrasonic, sodium hydroxide and ionic liquid pretreatments enhance the band, indicating that these three kinds of pretreatment methods can damage part of the hydrogen bonds. The absorption peak at 897 cm^{-1} corresponding to the β-D-glucoside peak has shifted a little, indicating that the structure of the cellulose has been changed slightly by these three pretreatment methods.

TEMPO-NaBr-NaClO oxidation of pretreated MCCs

The selectivity of TEMPO-NaBr-NaClO oxidation reaction towards primary alcohol groups is easily observed by FT-IR spectroscopy. The infrared spectra of initial MCC and cellouronic acids obtained by the different pretreatment methods are shown in Fig. 4. Comparing the cellouronic acids with initial MCC, the FT-IR peak shape and the peak positions are not basically changed. The bands at around 3400 cm^{-1} are assigned to the O-H stretching vibrations, the bands at around 2900 cm^{-1} are related to CH$_2$ stretching vibrations and those at 1160 cm^{-1}, 1058 cm^{-1} are associated to C-O-C vibrations, while C-O vibrations linking with hydroxyl groups in turn are hardly changed. Thus, the TEMPO-NaBr-NaClO oxidation reaction does not destroy the chemical structure of cellulose.

Cellouronic acids with different pretreatment methods display vas(COONa) at 1612 cm^{-1} and vs(COONa) at 1430 cm^{-1}. The spectra of cellouronic acids present C=O stretching vibrations at 1740 cm^{-1} (COOH), which is the direct proof of the carboxylation reaction taking place on the primary hydroxyl groups during the TEMPO-NaBr-NaClO oxidation process, thus confirming the character of cellouronic acids in FT-IR spectroscopy.[25] FT-IR spectroscopy proves the selectivity of TEMPO-NaBr-NaClO, no minor signals correspond to oxidation at the OH-2 or OH-3 positions. Any oxidation at secondary hydroxyl groups (OH-2 or OH-3 positions) would give keto groups, which could induce β-elimination reaction, leading to the cleavage of glycosidic bonds under alkaline synthesis conditions.[26,27]

The degree of oxidation for the different pretreatment methods for cellulose is shown in Table 1. The oxidation of untreated MCC only yields 8-10% of the product. Meanwhile, for the MCC pretreated with sodium hydroxide and [C$_4$mim]Cl ionic liquid, the yields reach 77.1% and 84.7%, respectively. In all the cases, the oxidation yields of mercerized and [C$_4$mim]Cl treated MCC samples are much higher than those of the ultrasonic treated MCC and untreated MCC samples. The data analysis clearly indicates that the sodium hydroxide mercerized and [C$_4$mim]Cl treated MCC samples are more reactive than untreated MCC. Moreover, a higher reactivity is observed for the samples treated by [C$_4$mim]Cl, when compared to that of the sodium hydroxide mercerized treated sample. It indicates that the bonding within the fiber bundles of MCC has been loosened due to the NaOH mercerization and ionic liquid pretreatment, causing the fibers to move apart and allowing the oxidation agents to penetrate farther and reach the interior crystalline zones, and thus it leads to the observed high oxidation yield. Also, the ionic liquid pretreatment can play the strongest role in the decrystallization of cellulose.
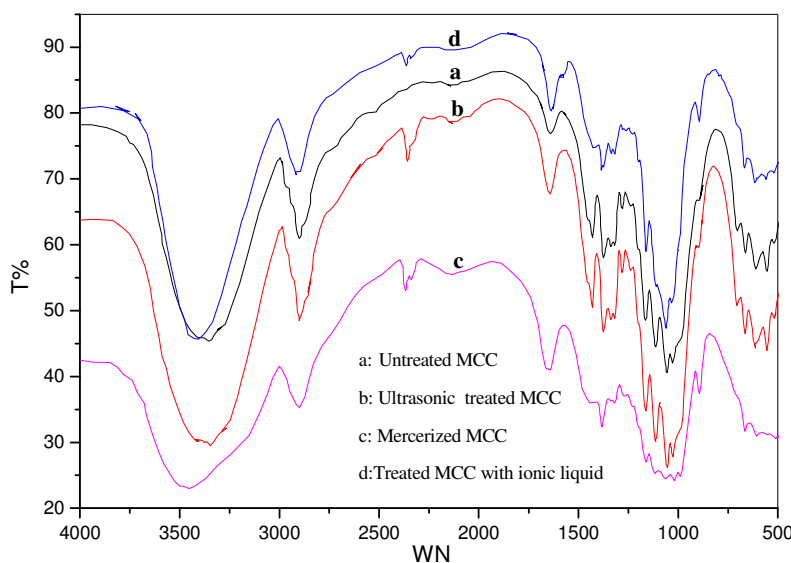

Figure 3: FT-IR spectra of pretreated and untreated MCC (the spectra are shifted vertically for clarity)
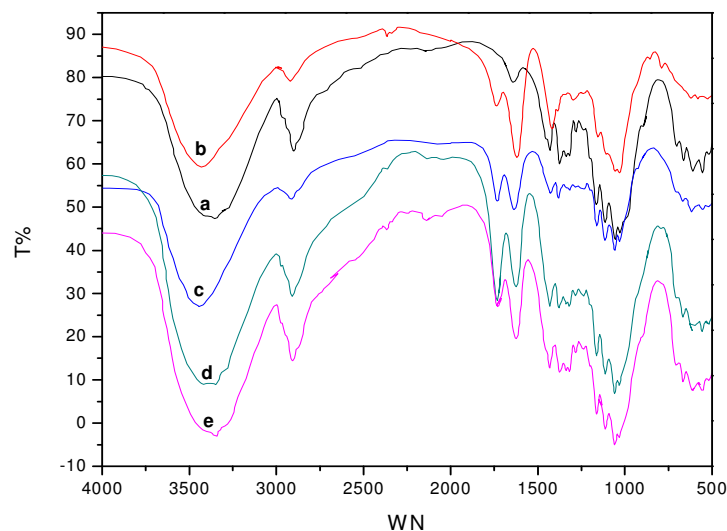
Figure 4: FTIR spectra of original MCC and cellouronic acids obtained by different pretreatment methods (a: original MCC, b: untreated MCC; c: ultrasonic pretreated MCC, d: mercerized MCC, e: MCC pretreated with ionic liquid). The spectra are shifted vertically for clarity

The highest oxidation yield can be obtained from MCC pretreated with ionic liquid. Considering that ionic liquids have such attractive properties as chemical and thermal stability, non-flammability, immeasurably low vapor pressure,[28] as well as recyclability, due to which they are known as green solvents, it may be concluded that ionic liquid pretreatment is an eco-friendly method for enhancing cellulose reactivity.

CONCLUSION

Based on the results obtained in the present study, it may be concluded that TEMPO-mediated oxidation of microcrystalline cellulose can be enhanced by several pretreatment methods. The highest oxidation production yield was achieved by the ionic liquid pretreatment, the oxidation yield efficiency followed the order: ionic liquid pretreatment > NaOH mercerization pretreatment > ultrasonic pretreatment. Based on the comparison of the results, the ionic liquid pretreatment method is recommended as it hardly changed the basic chemical structure of MCC, greatly reduced the crystallinity and enhanced the reactivity of cellulose, as well as due to the excellent recycling ability of ionic liquids.

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