Fabrication and characterisation of cellulose nanocrystals from microcrystalline cellulose by esterification and ultrasound treatment

Longwei Jiang, Jingde Yang, Qian Wang, Lili Ren, Jiang Zhou

Key Laboratory of Bionic Engineering (Ministry of Education), College of Biological and Agricultural Engineering, Jilin University, Changchun 130022, People’s Republic of China
E-mail: jiang.zhou@jlu.edu.cn

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In the present work, needle-shaped cellulose nanocrystals (CNCs) were prepared from commercial microcrystalline cellulose (MCC) through esterification and ultrasound treatment. The prepared CNCs were characterised by using Fourier transform infrared, degree of substitution (DS), dynamic light scattering, scanning electron microscopy and X-ray diffraction. The results revealed that the ultrasound disintegration of MCC was significantly improved after the esterification with maleic anhydride and the ultrasound treatment did not affect DS of the CNCs. With increasing power of the ultrasound treatment, smaller CNCs with narrower size distribution could be obtained. Average diameter and length of the CNCs could reach ∼14 and ∼180 nm, respectively. Furthermore, the crystal structure of cellulose was not changed during the esterification and ultrasound treatment and crystallinity of the CNCs increased comparing with MCC.

1. Introduction: Cellulose is the most abundant renewable organic material that can be obtained from many sources [1, 2]. During biosynthesis, cellulose fibres occur as elemental fibres which pack into larger units called microfibrils that further in turn assembled into hierarchical structures [3, 4]. Among these cellulose fibres, there are the regions in which the cellulose chains arrange in a highly ordered (crystalline) structure and the regions that are disordered (amorphous-like) [5]. The crystalline regions contained in the cellulose microfibrils are extracted, resulting in cellulose nanocrystals (CNCs) [3]. CNCs are needle-like particles with a typical acicular structure measuring 4–25 nm in diameter and 100–1000 nm in length [5]. CNCs are interesting nanoscale building blocks due to their renewable nature, high strength and low cost [6, 7]. Previous studies show that CNCs have great potential applications in various fields, such as nanocomposites [8, 9], optics [10] and packaging [11].

A variety of methods have been applied to prepare CNCs. Acid hydrolysis was widely used for removing amorphous cellulose and getting CNCs [1]. CNCs have been obtained through acid hydrolysis from different resources, for instance, wood [4], cotton [12], wheat straw [13], bleached softwood pulps [14] and microcrystalline cellulose (MCC) [15]. However, there are several drawbacks in the use of acids, such as potential degradation of cellulose, corrosivity and environmental incompatibility [16]. Mechanical treatments, such as high-pressure homogenisation [17], ball milling [18], cryocrushing [19] and ultrasonic breaking [16], were also used to extract CNCs from cellulosic materials. However, due to the strong hydrogen bonding between the cellulose nanofibrils, huge energy is required to break down cellulose into CNCs by mechanical treatments alone, giving rise to high production cost. Therefore, developing simple and efficient disintegration process is necessary for commercial production and applications of CNCs.

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation had been used to fabricate wood cellulose nanofibres [20]. TEMPO-mediated oxidation selectively converts C6 primary hydroxyls on cellulose molecular chains to anionic carboxylate groups. Such modification makes it possible to loosen the adhesion between cellulose fibrils by preventing the formation of strong inter-fibril hydrogen bonds and strengthen the individualisation of the fibrils by mechanical treatment, such as ultrasound treatment. Effects of ultrasound are mainly from cavitation, which takes place at plenty of sites in the reactor simultaneously and causes high temperature and pressure, shock waves, intense shear forces and microjets [21]. In a previous study, lignocellulose nanofibres were prepared through esterification of wood flour with maleic anhydride and followed by the mechanical treatments with a disk mill and a high-pressure homogeniser [22]. Carboxylate groups were induced by the esterification of hydroxyl groups at the C2, C3 and C6 positions of cellulose. The energy consumption required to produce lignocellulose nanofibres was significantly reduced due to the presence of the carboxylate groups.

MCC, in which nanocrystals are bundled together with some amorphous parts, is a commercially available material obtained by acid degradation which removes part of the amorphous regions in cellulose [23]. It has been extensively investigated to produce CNCs via mechanical and chemical treatments in recent years [16, 24]. As far as our literature survey could ascertain, no work concerning the preparation of CNCs using MCC esterified with maleic anhydride and subsequent ultrasound treatment has been reported.

Based on the previous works and starting from commercial MCC, this study aims to individualise CNCs from MCC by modification with maleic anhydride combined with subsequent mechanical disintegration via ultrasound treatment. The esterification reaction between maleic anhydride and MCC was characterised using Fourier transform infrared (FTIR). The extent of esterification of cellulose with the anhydride was evaluated by weight increase. Through examining size, morphology and structure of the obtained CNCs, effects of ultrasonic treatment on morphological and structural characteristics of CNCs were investigated. The results of this study not only provide technical parameters for fabrication of CNCs from MCC but also the data to compare the characteristics of CNCs obtained with different methods.

2. Experimental

2.1. Materials: MCC and maleic anhydride were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Absolute ethanol and sodium hydroxide (NaOH) were purchased from Beijing Chemical Works (Beijing, China). All chemicals were used as received.

2.2. Esterification of MCC: The esterification of MCC with maleic anhydride was carried out following the method for esterifying...
wood [22] with slight modification. MCC (5 g) and maleic anhydride (25 g) were mixed at room temperature and then kept at 120°C for 3.5 h. The esterification reaction did not require solvents and stirring, possessing the benefit of low cost, easy to purify and environment-friendly. Absolute ethanol was used to wash the reactants after the esterification reaction, and then purified water was used until the filtrate became neutral. NaOH aqueous solution (1.0 M) was added into the esterified MCC (E-MCC) suspension until the pH of 11 is reached, the introduced carboxyl –COOH was changed into carboxylate salt (−COO−Na+). In order to remove the excess NaOH, the suspension was washed with purified water until the pH became 7.8. Finally, the E-MCC suspension was diluted by adding purified water until the concentration was 0.5 wt%.

2.3 Ultrasound treatment: A 22 kHz ultrasound generator (HN-1000Y, Shanghai Hanuo Instrument Corp., China), equipped with a tapered horn tip (10 mm end diameter), was used for the ultrasonic treatment of the 0.5 wt% E-MCC suspension (30 g in a plastic beaker of 50 ml). The output power of the ultrasound treatments was set at 200, 400 and 600 W, respectively. The ultrasonic treatment was carried out in an ice/water bath and pulses of 1 s on and 1 s off were applied. The treating time was 30 min. Fig. 1 shows the preparation scheme of the esterified CNCs.

Table 1 Mean equivalent size, PDI and zeta potential of E-MCC, MCC after 600 W ultrasound treatment for 30 min

| Samples    | Mean size, nm | PDI    | Zeta potential, mV |
|------------|---------------|--------|-------------------|
| E-MCC      | 2880 ± 314.1  | 0.73 ± 0.02 | −23.7 ± 0.4        |
| MCC600     | 1651 ± 92.5   | 0.89 ± 0.12 | —                 |
| E-MCC200   | 528.2 ± 42.5  | 0.41 ± 0.01 | −33.1 ± 0.2        |
| E-MCC400   | 419.2 ± 4.7   | 0.35 ± 0.02 | −35.5 ± 0.7        |
| E-MCC600   | 330.3 ± 6.4   | 0.27 ± 0.03 | −36.7 ± 0.4        |

was calculated based on the ratio of the areas of the diffraction peaks to the area of the total diffraction pattern from 2θ of 10° to 30° subtracted amorphous background.

3. Results and discussion

3.1 FTIR and DS analysis: FTIR spectroscopy is an appropriate technique that has been extensively used to obtain information of chemical structure. Fig. 2 shows FTIR spectra of the MCC, E-MCC and the E-MCCs with 200, 400 and 600 W ultrasound treatments for 30 min (E-MCC200, E-MCC400 and E-MCC600). Comparing with the spectrum of MCC, a new peak at 1720 cm−1 attributable to C=O stretching of the maleate moiety was observed in the E-MCC, E-MCC200, E-MCC400 and E-MCC600, indicating a successful introduction of the maleate groups onto the MCC [27]. The peak at 2900 cm−1 is attributable to the C–H stretching in cellulose [28]. The intensities of the C=O stretching at 1720 cm−1 (A1720) relative to the C–H stretching at 2900 cm−1 (A2900) are related to DS of the samples [29]. For the ultrasound treated EMCC, the value of A1720/A2900 was almost unchangeable, suggesting that the ultrasound treatments have no considerable effect on the DS of E-MCC. DS of the maleate group introduced onto cellulose molecular chains was calculated by weight gain. The values of DS for E-MCC, E-MCC200, E-MCC400 and E-MCC600 were 0.39, 0.38, 0.38 and 0.38, respectively, indicating that the maleate groups were still on cellulose molecules after the ultrasound treatments.

3.2 Size, PDI and zeta potential analysis: DLS analysis has been developed for measuring the dimensions of spherical particles, so that the measurement of fibrils will result only in approximate values [30]. The size of the fibrils will depend on their orientation in the fluid. The Malvern system assesses the equivalent size of fibrils by measuring the Brownian motion of the fibrils, and the established theory can be used to determine the size of the fibrils. The non-dimensional PDI defines the size distribution obtained from DLS.

Fig. 1 Preparation scheme of CNCs by esterification and ultrasound treatment
(MCC600), E-MCC200, E-MCC400 and E-MCC600. The sizes of the E-MCC and MCC600 were micrometre scale and the values of PDI were bigger than 0.7. These results indicated that large size fibrils exist in the samples and the size distribution was very broad. However, for the ultrasound treated E-MCCs, the size was significantly smaller than that of the ultrasound treated MCC (without the esterification modification), and the size decreased with increase in ultrasound power. Since PDI smaller than 0.5 means the colloidal suspensions has a good quality, the lower values of PDI for the ultrasound treated E-MCCs suggested that the esterification improved ultrasound disintegration of cellulose fibrils and increased dispersibility of the suspension so that the obtained cellulose fibrils could be homogeneously dispersed in water and form a stable and uniform aqueous suspension.

Fig. 3 presents the typical size distribution of the E-MCC, ultrasound treated MCC and ultrasound treated E-MCCs with different conditions. As seen from Fig. 3, there was only one peak in the size distribution pattern of the E-MCC. The peak located at around 955 nm and the equivalent size of the cellulose fibrils ranged from hundreds of nanometres to several micrometres, suggesting there were large size cellulose fibrils. For the ultrasound treated E-MCCs, there are two peaks in the size distribution patterns. The main peak shifted to small size ranging from about 459 to 295 nm and the width of the peak became narrow when power of ultrasound treatment increased, suggesting the size of cellulose fibrils was smaller and more uniform. The decrease in PDI also indicated that the cellulose fibrils become more uniform when ultrasound with higher power was used. For the ultrasound treated MCC without esterification, there were also two peaks in the size distribution pattern. The small peak was at about 142 nm, but the main peak ranged from nanometre (∼400 nm) to micron scale, indicating that the MCC was not completely nanofibrillated and the range of the size was very broad.

Zeta potential refers to the potential difference between the stationary layer of fluid attached to the dispersed particle and the dispersion medium. Whether the particles within a liquid will flocculate is largely dependent on zeta potential of the sample [31]. For electrostatic stabilised systems, a zeta potential of at least −30 mV is desired to obtain a physically stable suspension [32]. The zeta potentials of the suspensions of E-MCC and ultrasound treated E-MCCs are given in Table 1. All the values were negative because of the presence of carboxyl anion (−COO−) groups introduced by maleic anhydride esterification. It was noted that the zeta potentials of the suspensions of ultrasound treated E-MCCs were lower than −30 mV, indicating the suspensions could remain stable.

3.3. Transmittance and visual examination analysis: Fig. 4 shows the UV–Vis spectra of the suspensions (0.5 wt%) of MCC600, E-MCC, E-MCC200, E-MCC400 and E-MCC600. The light transmittance of E-MCC and MCC600 suspensions at the wavelength of 800 nm was 0.14 and 0.03%, respectively, indicating that the size of the cellulose fibrils in these suspensions was large enough to scatter the incident light so that it cannot pass through the suspensions. However, the transmittance of the suspensions containing the ultrasound treated E-MCCs increased with increase in the ultrasound treatment power. This is understandable because transmittance of the suspension is influenced by light scattering which depends on the size of cellulose fibrils. Light scattering by particles is the process by which small particles cause optical phenomena. According to recent research, Rayleigh and Mie scattering could not be negligible in the visible region when the size of the particles is larger than 100 nm [33, 34]. When the particle size is larger than the wavelength, Mie scattering is dominant and the light scattering becomes much serious as the particle size increases [34]. For the medium containing nanofibrils in this study, the scattering is isotropic when diameter of the fibres is much smaller than the wavelength of incident light and light transmittance increases with decreasing of fibre diameter [35]. The results of transmittance test suggested that the esterification improved disintegration of MCC into nanofibrils during the ultrasound treatment, and these results were consistent with that of DSL measurements shown in Table 1; the size of cellulose fibrils decreased with increase in the ultrasound power applied.

The inset of Fig. 4 shows photographs of the suspensions (0.5 wt %) of MCC600, E-MCC, E-MCC200, E-MCC400 and E-MCC600 at condition of rest for 24 h. The MCC600 fully settled down to the bottom of the vial (a) due to large size. For the E-MCC, only part of E-MCC settled at bottom of the vial after 24 h (b). However, when the ultrasound treatment was applied, no observable sedimentation happened in the suspensions (vials c–e), which was consistent with the results of zeta potential analysis.

3.4. SEM analysis: Fig. 5 shows the SEM images of MCC, E-MCC, MCC600, E-MCC200, E-MCC400 and E-MCC600, respectively. It was observed that the morphological features of MCC and E-MCC were quite different (Figs. 5a and b). The surface of MCC was smooth, while the surface of E-MCC showed a certain degree fibrillation. The reason is attributable to the carboxyl anion (−COO−) groups introduced by maleic anhydride esterification. The anionic charges on cellulose fibrils resulted in electrostatic repulsion among the microfibrils which are bonded to each other mainly by hydrogen bonds. As shown
In Fig. 5d, after 30 min ultrasound treatment with an output power of 200 W, the E-MCC was disintegrated into nanofibril network structure. When the ultrasound treatment was conducted at 400 W, the high power of ultrasound treatment destroyed the web-like network structure, yielding needle-shaped cellulose nanofibrils (Fig. 5e). When the E-MCC was subjected to 600 W ultrasound treatment, the width and length of the needle-shaped cellulose nanofibrils further decreased and the obtained cellulose nanofibrils become more uniform (Fig. 5f). However, as shown in Fig. 5c, the MCC without esterification was not completely fibrillated even after 600 W ultrasound treatment.

In order to further analyse the effect of ultrasound treatment on E-MCC, distributions of diameter and length for E-MCC400 and E-MCC600 were determined, and the results are presented in Fig. 6. It was quite obvious that, with increases in power of the ultrasound treatment, the prepared cellulose nanofibrils were thinner and shorter. The mean diameter and length of the obtained cellulose nanofibrils decreased from 28.53 and 301.53 nm to 14.06 and 180.4 nm, respectively, when the power of the ultrasound treatment increased from 400 to 600 W.

It is known that when sufficiently high amplitude acoustic waves pass through a liquid medium, bubbles or cavities would form [36]. The mechanical action arising from cavitation bubbles can generate high strain rates in the surrounding liquid upon implosion [37]. At the MCC/liquid interface, the generated shock waves due to the collapse of bubbles can loosen the surface of MCC and lead to bond breakages, causing erosion of the surface of fibrils to split along the axis [16, 31]. Thus, with the increase of ultrasound power, micron-sized MCC fibrils will be gradually disintegrated into nanofibrils.

3.5. XRD analysis: The crystallinity of cellulose nanofibrils is a key factor to determine their mechanical and thermal properties. Fig. 7 gives the XRD patterns of MCC, E-MCC, MCC600, E-MCC200,
results of DLS, SEM and XRD, it could be concluded that the needle-shaped cellulose nanofibrils obtained from MCC by esterification and ultrasound treatment are CNCs.

4. Conclusion: Needle-shaped CNCs with a diameter of ~14 nm and length of ~180 nm were prepared from MCC through esterification and ultrasound treatment. FTIR analysis confirmed that the esterification modification was successful and ultrasound treatment did not detach the maleate groups. The esterification significantly facilitated the ultrasound disintegration due to the strong electrostatic force. The mean size of the CNCs decreased with increase in the ultrasound power applied. Zeta potential of the obtained CNCs suspension could be up to ~36.7 ± 0.4 mV at pH 7.8, which maintained the suspension stable. The esterification modification of MCC with maleic anhydride and subsequent ultrasound disintegration did not change crystalline structure of cellulose fibrils and the crystallinity of prepared CNCs reached 82.86%. This study provides a simple and efficient approach to produce CNCs that can be used in a variety of applications.

5 References

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