

Preparation and Characterization of Dialdehyde Nanocellulose

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Abstract. Dialdehyde nanocellulose (DANC) was prepared by periodate selective oxidation of secondary hydroxyl group of nanocrystalline cellulose (NCC). NCC and DANC samples were characterized by FT-IR, XRD and conductimetric titration. Aldehyde groups were introduced during the process of sodium periodate oxidation, which was confirmed by the FT-IR spectra. The aldehyde group content increased with the increase of sodium periodate. The crystallinity index (CrI) and crystallite size of the samples were continuously decreased with the increase of the oxidant.

Introduction

Periodate oxidation approach offers a facile and important method for functionalization of hydroxyl groups in cellulose. It is well known for its highly selective oxidative fragmentation of the C2-C3 glycol bond of the glucose ring into C2/C3 dialdehyde product, without significant side reactions, which acts as a reactive intermediate for further derivatization[1]. Some studies[2, 3] have shown that dialdehyde cellulose (DAC) was successfully synthesized by sodium periodate oxidation using microcrystalline cellulose (MCC) and cotton fiber as raw materials.

Nanocrystalline cellulose (NCC), which has high Young's modulus, high aspect ratio, high crystallinity, and special optical, rheological and mechanical properties, shows great prospect in high-performance composite material[4]. Due to the wide application of bio-medical and chemical industry for DAC, periodate oxidized from lignocellulosic materials, the periodate oxidation of NCC has attracted great attention.

In this study, a series of DANC were prepared by sodium periodate oxidation of NCC, and characterized by FT-IR, XRD and conductimetric titration.

Experimental

Material. Bleached hardwood kraft pulp (BHKP) was provided by Asia-Pacific Forest Fair APP Co., Ltd. Sodium periodate (NaIO₄) and ethylene glycol were purchased from Tianjin Damao Chemical Reagent Factory. Hydroxylamine hydrochloride was purchased from Tianjin Bodi Chemical Industry Co., Ltd. All chemicals were analytic grade and used as received without further purification.

Preparation of NCC via H₂SO₄-hydrolysis. The NCC was prepared by sulfuric acid hydrolysis of BHKP according to the method of Bondeson et al[5]. 10.0 g (oven dried weight) BHKP which was passed through a 40-mesh screen was hydrolyzed by sulfuric acid (85 mL, 64 wt%) with continuous stirring for 30 min at 45°C. After adding 900 mL of deionized water to terminate the reaction, the suspension was successively centrifuged at 5,000 rpm for 10 min to remove the residual acid. Then the precipitate was dialyzed (MWCO: 14,000) until the solution pH became neutral. The suspension was sonicated for 10 min, and then was stored at 5°C.

Preparation of dialdehyde nanocellulose (DANC) via sodium periodate oxidation. The DANC was prepared according to the method of Kim et al[6]. After mixing varied amounts of sodium periodate with 1.0 g NCC (oven dry weight), acetate buffer (25 mL, pH value 3.5, acetic

acid/sodium acetate) was added to the mixture stirring for 48 h in the absence of light at 40°C. Then 20.0 mL of ethylene glycol was added to remove residual oxidant. The obtained product was then placed into dialysis membranes (MWCO:14,000) and dialyzed until the solution pH became neutral.

Characterization of NCC and DANC. X-ray diffraction analysis of NCC and DANC was performed on a Bruker D8 Advance powder X-ray diffractometer (Bruker AXS, Germany) equipped with a CuXa X-ray tube. The FT-IR spectra of NCC and DANC were performed with an IRPrestige-21 Fourier Transform Infrared Spectrometer (Shimadzu Company, Japan). The samples were pressed into pellets with KBr before measuring. The spectra were collected at a resolution of 2 cm⁻¹, in the range of 400 and 4,000 cm⁻¹. Zeta potential of NCC and DANC was recorded on a Malvern Zetasizer Nano-ZS90 (Malvern Instruments, UK).

Determination of aldehyde group content (AGC). AGC was determined according to the method of Veelaert et al [7]. The pH of DANC suspension (0.50 g oven dry weight) was adjusted to 5.0, and then hydroxylamine hydrochloride solution (20 mL, 0.05 g/mL) was added to the system. After stirring for 4 h at 40°C, the suspensions were titrated against 0.01 M NaOH standard solution until the pH value was 5.0. Control experiment of NCC was carried out under the same conditions.

The aldehyde group content was calculated using the following equation,

$$AGC (\%) = \frac{c \times (V_1 - V_2)}{m \times 1000} \times 100\% \quad (1)$$

Where, AGC is the CHO number per 100 glucose units (%); *c* is the concentration of NaOH (mol/L); *m* is the oven dry sample mass (g) of DANC; *V*₁ and *V*₂ are the consumptions of NaOH for DANC and NCC in the titration process (mL).

Calculation of crystallinity index (CrI) and crystallite size (D). The CrI of NCC and DANC was defined as,

$$CrI (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

Where, *I*₀₀₂ is the maximal intensity of the 002 planes reflection located at 2θ = 22°-23°; *I*_{am} is the minimal intensity at 2θ = 18°-19°.

The crystallite size was calculated using the Scherrer equation with the method based on the width of the diffraction patterns [8],

$$D (nm) = \frac{k\lambda}{B \cos \theta} \quad (3)$$

Where, *D* is the average width of the crystallite in the 002 lattice plane (nm); *k* is the Scherrer constant (0.89); *λ* is the wavelength of the X-ray source (0.15406 nm); *B* is the half-band width in radians, and *θ* is the Bragg angle.

Results and discussion

DANC was prepared by sodium periodate oxidation of NCC, and the reaction equation is shown in Fig. 1.

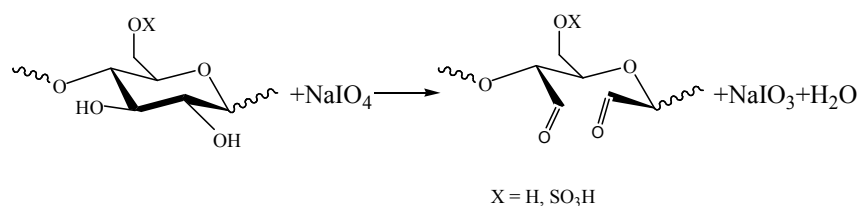


Fig. 1. Sodium periodate oxidation of NCC

The effect of the dosage of oxidant on the aldehyde group content and Zeta potential is shown in Fig. 2. As expected, the aldehyde group content continuously increased with the increase of sodium periodate equivalents. As can be seen from Fig. 2, maximum aldehyde group content can be achieved when oxidant dosage is 9 mmol/g. Further increasing the amount of oxidant, the aldehyde

group content increased insignificantly. Periodate Oxidation makes hydrogen bond, intermolecular force and other covalent bonds between molecules become weak, which can destroy the internal crystal structure of the NCC. Meanwhile, the probability of collision increased of the secondary hydroxyl in the C₂-C₃ bond with oxidant, which accelerated the oxidation reaction. The negative Zeta potential firstly declined and then became gradually stable with the increase of oxidant. This was because that an increasing negative secondary hydroxyl were transferred into aldehyde which was neutral with the increase of oxidant amount. Therefore, the trend of Zeta potential was in agreement with that of aldehyde group content.

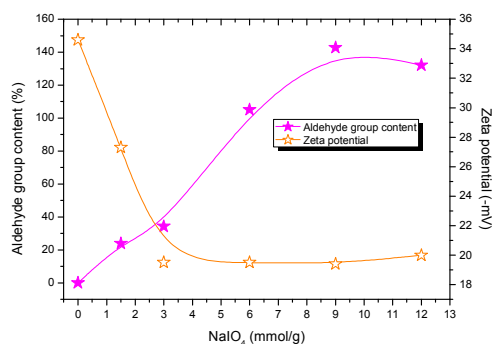


Fig. 2. Effect of dosage of oxidant on aldehyde group content and Zeta potential (reaction time, 48 h; reaction temperature, 40°C)

The evidence of the successful synthesis of DANC was obtained from the FT-IR spectra, as shown in Fig. 3. As can be seen from the Fig. 3, the absorption band around 1,730 cm⁻¹ in the spectra of DANC (b, c, d, e, and f), which was attributed to the stretching vibration of C=O in aldehyde groups, was absent from the spectra of NCC (a), indicating the introduction of the aldehyde groups during the process of sodium periodate oxidation of NCC. Furthermore, the intensity of the absorption peaks of aldehyde band increased with the increase of the addition of oxidant, which corresponded well with the increase of aldehyde group content [9].

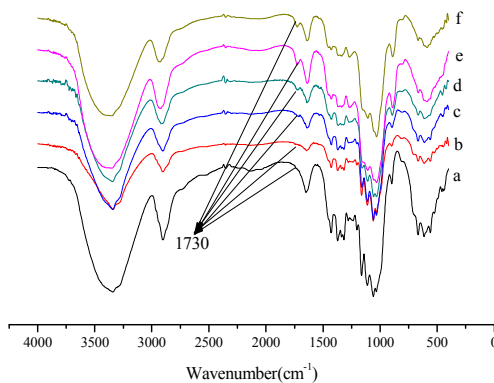


Fig. 3. FT-IR spectra of the samples: a, NCC; b, c, d, e, and f, oxidized with 1.5, 3.0, 6.0, 9.0 and 12.0 mmol/g of sodium periodate, respectively

The typical wide angle X-ray diffraction patterns of freeze-dried NCC and DANC are shown in Fig. 4. The peaks at $2\theta=14.18^\circ$, 22.5° , and 34.5° were characteristic of the structure of cellulose I, indicating that the crystal structure was retained after oxidation.

The CrI and crystallite size of NCC and DANC are calculated and shown in Table 1. As can be seen from Table 1, the CrI and crystallite size of the samples were continuously decreased with the increase of the oxidant, indicating that an increasing crystalline regions of NCC were destroyed according to the oxidation level by sodium periodate. The NCC initially has a crystallinity of 63.68% and the crystallite size in the 002 lattice plane (L002) is 3.63 nm, whereas the values declined to 13.91% and 0.74 nm when the dosage of oxidant reached to 12 mmol/g with a decrease of 78.16% and 79.01% for CrI and crystallite size, respectively.

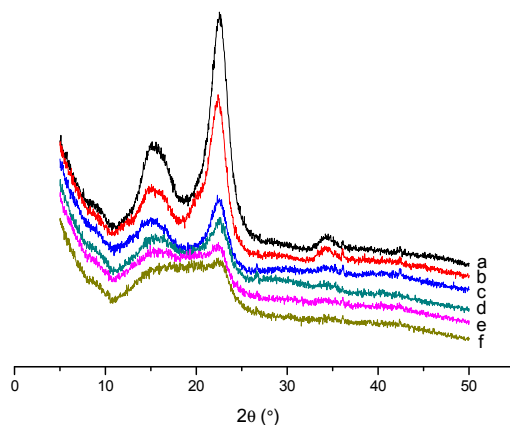


Fig. 4. XRD spectra of the samples: a, NCC; b, c, d, e, and f, oxidized with 1.5, 3.0, 6.0, 9.0 and 12.0 mmol/g of sodium periodate, respectively

Table. 1. The CrI and crystallite size of NCC (a) and DANC (b, c, d, e, and f, oxidized with 1.5, 3.0, 6.0, 9.0 and 12.0 mmol/g of sodium periodate, respectively)

| Sample | a | b | c | d | e | f |
|-----------------------|-------|-------|-------|-------|-------|-------|
| CrI (%) | 63.68 | 60.57 | 48.74 | 32.50 | 18.05 | 13.91 |
| crystallite size (nm) | 3.63 | 3.56 | 3.32 | 2.39 | 0.76 | 0.74 |

Conclusions

- Dialdehydenanocellulose was successfully prepared by sodium periodate oxidation of nanocrystalline cellulose. The introduction of aldehyde group was confirmed by FT-IR spectra. With the increase of the sodium periodate, the aldehyde group content of the DANC increased, while Zeta potential declined and then became gradually stable.
- The crystal form of DANC was not changed in the process of oxidation, and maintained cellulose I structure, and the CrI and crystallite size of the samples were continuously decreased with the increase of the oxidant.

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