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Impact of degree of oxidation on the physicochemical properties of microcrystalline cellulose

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ABSTRACT

Microcrystalline cellulose, a major component of cell wall of plants, is one of the most abundant natural materials, but the poor solubility of cellulose limits its applications. Cellulose is a linear glucan with exclusive β 1 → 4 linkage. Oxidation carried out with TEMPO–NaBr–NaClO system can selectively oxidize the C6 of glucose residues in cellulose. This modification improves polysaccharide solubility and other physicochemical properties. In this work, the impact of degree of oxidation on solubility, degree of crystallization, thermostability, molecular weight and the structures of the resulting oligosaccharide products of selectively oxidized cellulose were investigated using x-ray diffraction, thermogravimetric analysis, gel permeation chromatography–multiple angle laser light scattering and ultrahigh performance liquid chromatography–electrospray–quadrupole/time of flight–mass spectrometry, respectively. The physicochemical properties of selectively oxidized cellulose having different degrees of oxidation were carefully characterized providing a theoretical foundation for the more accurate selection of applications of oxidized celluloses.

1. Introduction

Microcrystalline cellulose (MCC), a linear glucan with exclusive β 1 → 4 linkage, is a major component of cell wall of plants (Klemm, Philip, Heinz, Heinz, & Wagenknecht, 1998; Li et al., 2015; Suhas et al., 2016). It is one of the most abundant natural materials. However, the pyknotic inter-molecular and intra-molecular hydrogen bonds in cellulose prevent most solvents from entering crystalline region and dissolving the cellulose (Bochek, Petropavlovsky, & Kallistov, 1993; Qin, Lu, Cai, & Zhang, 2013; Keshk, 2015). Concentrated alkaline solutions are one way to partially dissolve cellulose and include such solvents as concentrated aqueous NaOH and concentrated aqueous NaOH/urea solution (Qin, Lu, Cai, & Zhang, 2013; Keshk, 2015). This process of mercerization is used in limited areas, such as papermaking industry and production of macroporous cellulose membranes (Guo & Ruckenstein, 2002; Ruckenstein & Guo, 2001). Moreover, mercerized cellulose becomes insoluble again after the alkaline solution is removed, thus, this application of dissolving cellulose has limited utility.

Different derivatization reactions, such as carboxymethylation and oxidation have been used to improve the solubility and expand the application of cellulose (Kono, Oshima, Hashimoto, Shimizu, & Tajima, 2016; Isogai & Kato, 1998; Tahiri & Vignon, 2000). Carboxymethylated cellulose (CMC) is widely used in different areas, such as drug excipients (Ugwoke, Kaufmann, Verbeke, & Kinget, 2000). The degree of carboxymethylation affects both the solubility and viscosity of cellulose (Benchabane & Bekkour, 2008). Oxidation of cellulose improves polysaccharide solubility, viscosity and film-forming ability (Gomez-Bujedo, Fleury, & Vignon, 2004). Currently, there are two ways to produce oxidized cellulose, through specific and through nonspecific oxidation. Periodate is generally used for the nonspecific oxidation of cellulose (Jackson & Hudson, 1937; Sirvio, Hyvakko, Liimatainen, Niinimaki, & Hormi, 2011; Siller et al., 2015). In these reactions both the primary hydroxyl groups, at position 6, and the secondary hydroxyl groups at other positions on glucose (Glc) ring can be oxidized. The structures of these non-specifically oxidized products are always complicated. The better the structural characterization of an oxidized cellulose the more widely it can be used in different applications. The selective oxidation of cellulose with 2,2,6,6-tetramethylpiperidine-1-oxyl/sodium bromide/sodium hypochlorite (TEMPO – NaBr – NaClO) system has been recently reported (Isogai & Kato, 1998; Tahiri & Vignon, 2000; Gomez-Bujedo, Fleury, & Vignon, 2004; Shinoda, Saito, Okita, & Isogai, 2012; Benhamou, Dufresne, Magnin, Mortha, & Kaddami, 2014; Huang, Chen, Tsai, Hsieh, & Andrew Lin, 2015). In this selective oxidation, the primary hydroxyl groups at

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carbon-6 are oxidized to afford glucuronic acid (GlcA) residues. This selective oxidation process provides the opportunity to produce oxidized cellulose having different properties under good quality control. This selectively oxidized cellulose, called cellulosic acid, has been used in the textile, cosmetic, and medical industries (Gomez-Bujedo, Fleury, & Vignon, 2004). However, all these applications of selectively oxidized cellulose were based on a limited understanding of their industrial properties. Unfortunately, the relationship between the degree of oxidation (DO) and the corresponding physicochemical properties has not been studied in detail.

In the current study, selectively oxidized celluloses having different DOs were prepared using a TEMPO–NaBr-NaClO system from mercerized microcrystalline cellulose (MCC). Their DOs were determined and compared using infrared spectroscopy (IR) and solid-state nuclear magnetic resonance (NMR) spectroscopy. The impact of DO on polysaccharide solubility, degree of crystallization, thermostability, molecular weight, and the structures of the resulting oligosaccharide products of oxidized MCC were investigated using x-ray diffraction (XRD), thermogravimetric analysis (TGA), and gel permeation chromatography–multiple angle laser light scattering (GPC-MALLS) and ultrahigh performance liquid chromatography–electrospray–quadrupole/time of flight–mass spectrometry (UHPLC-ESI-Q/TOF-MS), respectively. The physicochemical properties of selectively oxidized MCC with different DOs, carefully characterized by systematic analysis, represent an important foundation for more informed and accurate application of oxidized MCC for different uses.

2. Experimental

2.1. Materials

Commercial microcrystalline cellulose (MCC) was supplied by Sinopharm Chemical Reagent CO. Ltd. (Shanghai, China). Sodium hydroxide (NaOH) and concentrated hydrochloric acid (HCl) were both purchased from Chinasun Specialty Products CO., LTD. (Changshu, China). Sodium bromide (NaBr), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and sodium hypochlorite (NaClO, 5% active chlorine) were obtained from Aladdin Industrial Co. (Shanghai, China). Methanol (chromatographic grade) was obtained from Merck Chemicals (Darmstadt, Germany). Ammonium acetate (NH_4OAc, chromatographic grade) was supplied by Sigma-Aldrich (Shanghai, China). Deuteroxide (D_2O, atm.%D ≥ 99.9%) was purchased from Energy Chemicals (Shanghai, China). High-purity water (resistivity ≥ 18.2 MΩ × cm, 25 °C) was used throughout the study. All other chemicals were of analytical reagents.

2.2. Methods

2.2.1. Procedure for oxidation of MCC with TEMPO mediated system

MCC, freshly mercerized with alkaline solution, improves its reactivity towards chemical modification (Guo & Ruckenstein, 2002; Ruckenstein & Guo, 2001; Assa, Belgacemb, & Frollinia, 2006; Gurgel, Melo, Lena, & Gil, 2009). All reactions in this work were carried out on MCC at a 1 g scale. MCC was freshly mercerized in 30 mL of 10% NaOH solution with magnetic stirring for 24 h before using. Each mercerized MCC solution was neutralized with 6 M HCl followed by desalting with 500 Da cut-off dialysis bag against DI water, which was afforded a volume of each reaction system of ~180 mL. After 32 mg TEMPO and 320 mg NaBr were added each reaction system was adjusted to pH 10 by the dropwise addition of 20% NaOH solution. Oxidations were carried out with different amounts of NaClO (1, 5, 10, 15 mL, 5% active chlorine) at 50 °C to afford oxidized MCC of various DOs. A pH meter was used to monitor the pH and 20% NaOH solution was used to maintain the pH at 10 during the reaction. Each reaction was terminated by adding 1 mL of ethanol after 4 h. The mixture was neutralized with 4 M HCl and dialyzed against DI water by using 500 Da molecular weight cut-off (MWCO) dialysis bag to eliminate TEMPO and other salts. The products remaining in the bag were concentrated with a rotary evaporator at 45 °C and then lyophilized. The oxidized MCC powders with different DOs were next ready to be analyzed.

2.2.2. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of initial, mercerized, and oxidized MCCs (2 mg of each) were recorded using a FT-RI spectrometer (Vertex 70, Bruker, Germany) with the resolution of 4 cm^{-1}. The transmittance mode and 16 s scanning number were selected. The scanning was performed ranging from 4000 to 600 cm^{-1}. The data was processed and analyzed with OPUS.

2.2.3. NMR spectroscopic analysis

Solid-state ^{13}C NMR spectra of initial, mercerized, and oxidized MCCs were obtained on a WB/AVANCE III 400 MHz spectrometer (Bruker, Germany) with cross polarization and magic angle sample spinning. The spinning rate, pulse delay and contact time were set at 10 kHz, 3.5 s and 0.5 ms, respectively. The chemical shift was calibrated from an external standard of Adamantane. The NMR data was processed and analyzed using MestReNova.

2.2.4. X-ray diffraction (XRD) measurement

The XRD patterns of initial, mercerized, and oxidized MCCs (~30 mg of each) were performed on an X'Pert Pro MPD diffractometer (PANalytical B. V. Co., Netherlands). The X-ray source was Ni-filtered Cu Kα radiation at 40 kV and 30 mA and the 2θ range was set at 5 ~ 50°.

2.2.5. Thermogravimetric analysis (TGA)

The TG analysis of initial, mercerized and oxidized MCCs (~1 mg/each) were performed on a SDT 2960 thermal analyzer (TA Instruments, USA) under N_2 atmosphere. The heating rate was set at 10 °C/min and the scanning range was 20 ~ 490 °C.

2.2.6. Water solubility analysis

Water solubility of oxidized MCC is important for different applications (Keshk, 2015). Twenty milligrams of each sample was weighed out accurately (W) and dissolved in 4 mL distilled water before vigorous mixing on vortex mixer. The suspension was then centrifuged at 12000 rpm for 10 min. The supernatant was transferred out, lyophilized and weighed accurately (Ws). The solubility was calculated according to the following equation: Water solubility (%) = Ws/W × 100, where Ws is the mass of dissolved material in supernatant and W is the mass of total material (20 mg). The experiments were performed in triplicate.

2.2.7. Measurement of the molecular weight (MW) and distribution by GPC-MALLS

The weight-average MW of dissolved portion of each oxidized starch sample was determined by GPC-MALLS. In this experiment, an Agilent 1260 HPLC system (CA, USA) was coupled with an 18-angles MALLS (Wyatt, USA) and a refractive index (RI) detector (Agilent, USA). The dn/dc value was set at 0.138 mL/g. The separation was performed on an ACQUITY UPLC@BEH125 SEC column (1.7 μm, 4.6 × 300 mm, Waters, USA) at 0.1 mL/min and 25 °C. The mobile phase was 80 mM ammonium acetate aqueous solution. The injection volume was 20 μL solution. The data were processed with ASTRA software of version 6.1.