



# The role of heteropolysaccharides in developing oxidized cellulose nanofibrils



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## ABSTRACT

A fundamental study was undertaken to determine the general role of heteropolysaccharides during the production of TEMPO-oxidized cellulose nanofibrils (TOCNs). Four major fiber resources, viz., fully bleached kraft pulps of softwood and hardwood varieties (pine, eucalyptus) and non-woods (bamboo, bagasse) were used because of their substantial morphological differences and relative abundance. The effect of heteropolysaccharides during TEMPO-mediated oxidation and high-pressure homogenization for TOCNs production was investigated under constant conditions. Most galactoglucomannans were removed during oxidation, whereas the majority of xylans were retained. The galactoglucomannans, however, non-beneficially consumed NaClO, the terminal TEMPO oxidant, while xylans adversely affected carboxylate group formation by limiting chemical accessibility to cellulose. However, lower xylans content led to more transparent and processable suspensions, while during mechanical processing, heteropolysaccharides supported nanofibrillation. The average length of the final TOCNs from eucalyptus, bamboo, bagasse, and pine were 290, 350, 360 and 370 nm, respectively, with average widths of ~4 nm.

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## 1. Introduction

Nanocelluloses as an engineered material not only display widely acclaimed and highly prized renewability and biodegradability to meet today's environmental compliancy demands, but also exhibit outstanding mechanical strength, large surface area, superior biocompatibility, high hydrophilicity, and a broad chemical-modification capacity (Habibi, 2014; Klemm et al., 2011). As a result, they are galvanizing a revolution in the domain of sustainable materials for diverse applications: pharmaceutical carriers, food packaging, flexible electronic devices, tissue engineering scaffolds, biomimetic materials, reinforcement of nanocomposites, etc (Isogai, 2013; Siró, Plackett, Hedenqvist, Ankerfors, & Lindström, 2011).

Nowadays, one of the most widely used methodologies used to prepare oxidized nanocelluloses is the application of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) with mechanical treatment (Saito et al., 2009; Saito, Kimura, Nishiyama, & Isogai, 2007; Saito, Okita, Nge, Sugiyama, & Isogai, 2006; Saito & Isogai, 2004). During TEMPO-mediated oxidation, the primary (C6) hydroxyls of

cellulose are selectively converted into carboxylate groups. As a result of such chemistry, strong electrostatic repulsions among negatively charged fibers have been shown to remarkably reduce energy consumption and facilitate nanofibrillation by reducing bonding among fibrils and thus encouraging defibrillation (Isogai, Saito, & Fukuzumi, 2011). Generally, the TEMPO-oxidized cellulose nanofibrils (TOCNs) consist of individualized nanofibers with 3–4 nm widths of high aspect ratios (>100).

Given the stated materials importance of oxidized nanocelluloses, thus far no study has been done to ascertain the fundamental factors within the major starting materials that substantially contribute to their development. Bleached pulps from woods and non-woody plants have often been used as the starting materials to prepare nanocellulose (Okita, Saito, & Isogai, 2009; Qian, Qin, Vu, Tong, & Chin, 2012; Saito et al., 2007). Cellulose is typically composed of microfibrils that are embedded in a matrix of lignin and heteropolysaccharides. The lignin content in pulps can be entirely removed by pulping and bleaching, while keeping a significant amount of heteropolysaccharides in the bleached pulp. It is well known that the presence of heteropolysaccharides contribute to pulp and paper properties such as beatability, brightness, physical strength, and printability (Ban, Chen, Andrews, & Van Heiningen, 2011; Hu, Fu, & Liu, 2013). Unlike cellulose, heteropolysaccharides are branched compounds consisting of pentoses (arabinose,

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xylose), hexoses (glucose, mannose, galactose), and sugar acids. The structure and content of heteropolysaccharides in pulps are a function of its sources. Generally, softwood heteropolysaccharides contain mainly galactoglucomannan and a certain amount of xylan, whereas xylan is the primary heteropolysaccharide in hardwoods (glucuronoxylan) and plants (arabinoxylan) (Saha, 2003). The chemical composition of pulp is an important factor that determines the feedstock suitability for producing nanofibrils (Chirayil, Mathew, & Thomas, 2014). The role of xylans in hardwood on the efficiency of TEMPO-mediated oxidation and ensuing TOCNs properties were investigated (Meng, Li, Fu, & Lucia, 2014). A recent study made by Kuramae et al. demonstrated the unfavorable influence of heteropolysaccharides on nanofibrillation through a comparison of different plant holocelluloses (softwood, hardwood, gymnosperm, and herbaceous species) (Kuramae, Saito, & Isogai, 2014). Additionally, the importance of heteropolysaccharides on nanofibrillation and subsequent nanocellulose properties has been previously alluded (Arola, Malho, Laaksonen, Lille, & Linder, 2013; Chaker, Alila, Mutjé, Vilar, & Boufi, 2013; Iwamoto, Abe, & Yano, 2008; Pönni, Pääkkönen, Nuopponen, Pere, & Vuorinen, 2014; Rodionova et al., 2013).

Therefore, the current fundamental study was undertaken to definitively identify how major compositional differences in the classes of cellulose, in this case, heteropolysaccharides, affect nanofibrillation. In that spirit, four common bleached kraft pulps (pine, eucalyptus, bamboo, and bagasse) were used to prepare TOCNs via TEMPO/NaClO/NaBr oxidation and high-pressure homogenization. The influence of heteropolysaccharides on the oxidation was assessed according to the carboxylate content and reaction rate. The thermal properties and the size distribution of obtained nanofibrils were compared and the optical and rheological properties were characterized.

## 2. Experimental

### 2.1. Materials

Commercial fully bleached kraft pulp boards of pine, eucalyptus, bamboo, and bagasse were kindly provided by Yueyang Paper Co., Ltd., China. The subsequent pulps used for nanofibers preparation were produced from these paperboards by treating them in a laboratory disintegrator for 10,000 revolutions at ambient temperature. TEMPO was purchased from Aladdin Chemistry Co., Ltd., China and other chemicals were obtained from Guangzhou Chemical Reagent Factory, China. All chemicals used in this study were of analytical grade and used as received without further purification.

### 2.2. TEMPO-mediated oxidation

The TEMPO-mediated oxidation used the TEMPO/NaClO/NaBr system at 25 °C and pH 10. Approximately 10 g oven-dried pulps (o.d.p.) from different raw materials were used, and the chemical dosages of TEMPO, NaBr and NaClO were 0.015 g/g o.d.p., 0.1 g/g o.d.p. and 5.5 mmol/g o.d.p., respectively. The detailed steps of the oxidation were essentially repeated according to a previous report (Meng et al., 2014). The TEMPO-mediated oxidation was started by adding NaClO solution to the substrates until no further decrease in pH was observed. During the oxidation, the reaction time and its corresponding 0.5 mol/L NaOH consumption were recorded. The oxidation of each material was performed by two parallel experiments.

### 2.3. High-pressure homogenization

Before mechanical treatment, oxidized fibers were diluted with deionized water to a uniform dispersion of 0.4% (w/w) by mag-

netic stirring. Then this suspension was homogenized by 4 passes through a high-pressure homogenizer (JN-10C, Guangzhou Juneng Biology & Technology Co., Ltd., China) operating at a pressure of 1800 Bar at 6 °C.

### 2.4. The chemical composition and morphology of fibers

The carbohydrate composition in pulp before and after TEMPO-mediated oxidation was determined according to standardized methods from NREL Laboratory Analytical Procedure NREL/TP-510-42618 (Sluiter et al., 2008). After a successive two-step hydrolysis with 72% and 4% sulfuric acid, the monosaccharides in the hydrolysate were analyzed by ion chromatography (DIONEX ICS-3000, CarboPac PA20).

### 2.5. Determination of carboxylate content

To convert the sodium carboxylate groups (-COONa) to free carboxyl groups (-COOH), pulps were pretreated with 0.1 mol/L HCl for 1 h at 1% consistency at room temperature with continuous stirring. The carboxylate contents of pulps were measured by Headspace Gas Chromatography (HSGC) according to an accepted method (Chai et al., 2003). At least three replicates were performed.

### 2.6. X-ray diffraction analysis

The crystal structures of original and oxidized pulps were determined by wide-angle X-ray diffraction (XRD) with a Bruker D8 Advance Diffractometer (Bruker AXS, Inc.) using Cu K $\alpha$  radiation at 40 kV and 40 mA. Prior to XRD analysis, the membrane of each cellulose sample with a thickness of  $\sim 25$   $\mu$ m was prepared according to a method mentioned below. The angular region ( $2\theta$ ) from 10° to 60° was scanned with steps of 0.04° at a rate of 1°/min. The crystallinity index (CrI) of cellulose was calculated from XRD pattern according to the Segal method:  $CrI(\%) = (I_{002} - I_{am})/I_{002} \times 100$ , where  $I_{002}$  is the maximum intensity of the (002) lattice diffraction at  $2\theta = 22.5^\circ$  and  $I_{am}$  is the intensity of diffraction at  $2\theta = 18^\circ$  (Segal, Creely, Martin, & Conrad, 1959).

### 2.7. Atomic force microscopy (AFM)

Atomic force microscopy (Multimode 8, Bruker, Germany) was used for studying the surface characteristics and aggregation state of the nanofibers. A drop of sample was air dried overnight on a clean mica surface at ambient conditions for the analysis. Images from several different places on the samples were scanned. One drop of 0.005% (w/w) TOCNs suspension was deposited onto a clean mica plate and vacuum dried prior to AFM observation. Images were acquired in tapping mode using RTESP Si cantilevers (Antimony-doped Si, Bruker AFM Probes) with tip radius of 8 nm.

### 2.8. Transmission electron microscopy (TEM)

The micromorphology and size of TOCNs were characterized by TEM (H-7650, Hitachi, Japan) operating at an accelerating voltage of 80 kV. Approximately 3% phosphotungstic acid solution (pH 7) was used as negative stain for 2 min. At least ten different areas on the sample were scanned. To obtain the length distribution of TOCNs, the number of measured nanofibrils was 100 for each sample from its corresponding TFM images.

### 2.9. Thermal properties

Thermogravimetric (TG) analyses of the freeze-dried cellulosic samples were performed by means of a TGA Q500 (TA Instruments, USA) with nitrogen flow rate of 25 mL/min and heating rate

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