



# Preparation and characterization of TEMPO-oxidized cellulose nanofibril films with free carboxyl groups

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## ABSTRACT

A 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-oxidized wood cellulose with sodium carboxylate groups was completely converted to individual TEMPO-oxidized cellulose nanofibrils with free carboxyl groups (TOCN-COOH) dispersed in water at pH 4.6. Self-standing films prepared by casting and drying of the TOCN-COOH/water dispersion were flexible and highly transparent. Fourier transform infrared (FT-IR) spectra and sodium content determination confirmed that the sodium carboxylate groups of TOCN-COONa were almost completely converted to free carboxyl groups in TOCN-COOH. The TOCN-COOH and TOCN-COONa films had similar densities and tensile strengths, but the former had lower moisture content, higher Young's modulus and lower elongation values than those of the latter. The oxygen permeability of the TOCN-COOH films was  $0.049 \text{ mL } \mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ , which was clearly lower than that ( $15.5 \text{ mL } \mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ ) of poly(ethylene terephthalate) films.

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## 1. Introduction

Crystalline native cellulose nanofibers or nanowhiskers with widths of 3–100 nm dispersed at the nanolevel in water or organic solvents have been receiving wide attention in recent years as reproducible and environmentally friendly natural nanomaterials, which are applicable as nanofillers in composites or thin coated layers in laminated films to generic and cutting-edge products (e.g. Eichhorn et al., 2010; Henriksson, Berglund, Isaksson, & Lindström, 2008; Isogai, Saito, & Fukuzumi, 2010; Siqueira, Bras, & Dufresne, 2009). Nanocelluloses reported to date are roughly categorized into three groups; (A) cellulose nanocrystals or cellulose nanowhiskers prepared by acid hydrolysis of native celluloses and successive mechanical agitation of the acid-hydrolyzed residues in water (e.g. Dong, Revol, & Gray, 1998; Marchessault, Morehead, & Walter, 1959), (B) microfibrillated celluloses (MFCs) prepared by mechanical disintegration of cellulose/water slurries with or without energy-diminishable assistance by partial carboxymethylation or cellulase treatment (e.g. Henriksson, Henriksson, Berglund, & Lindström, 2007; Turbak, Snyder, & Sandberg, 1983; Wågberg et al., 2008), and (C) cellulose nanofibrils prepared by 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)-mediated oxidation of native celluloses followed by mechanical disintegration of the oxidized celluloses in water (e.g. Isogai et al., 2010; Saito, Kimura, Nishiyama, & Isogai, 2007; Saito et al., 2009).

Compared with the first two nanocellulose categories, TEMPO-oxidized cellulose nanofibrils (TOCNs) prepared from wood celluloses have mostly uniform widths of 3–4 nm and large aspect ratios of >50, and are dispersed as individual nanofibrils in water. Every one of two glucosyl units of the cellulose chains on the microfibril surfaces can be entirely and regularly oxidized to sodium glucuronosyl units by TEMPO-mediated oxidation, thus forming sodium carboxyl groups in high density on the microfibril surfaces (Hirota, Furihata, Saito, Kawada, & Isogai, 2010; Okita, Saito, & Isogai, 2010). Transparent and highly viscous TOCN/water dispersions are obtained by moderate disintegration of TEMPO-oxidized wood celluloses in water, due to the effective electrostatic repulsion between anionically charged TOCNs during and after the nanofibrillation process.

When TEMPO/NaBr/NaClO oxidation at pH 10 or TEMPO/NaClO/NaClO<sub>2</sub> oxidation at pH 7 is applied to wood celluloses, TEMPO-oxidized celluloses (TOCs) with sodium carboxylate groups up to approximately 1.7 and 0.8 mmol g<sup>-1</sup>, respectively, are obtained. Sodium carboxylate groups formed by TEMPO-mediated oxidation, are required at greater than a certain content for the preparation of TOCNs in high yields dispersed at the individual nanofibril level in water. However, for hydrogen bond formation between carboxyl groups and either other carboxyl groups or hydroxyl groups in TOCN films, it would be better to prepare aqueous dispersions of TOCNs with free carboxyl groups (TOCN-COOH) instead of sodium carboxylates. Sodium carboxylate groups cannot form hydrogen bonds with either hydroxyl or sodium carboxylate groups in TOCN-COONa films. Formation of inter-fibril hydrogen bonds in nanocellulose films is expected

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to improve their mechanical and oxygen barrier properties. In particular, the oxygen barrier properties of nanocellulose films have been extensively studied in recent years for application of nanocelluloses as biodegradable, carbon-neutral and thus environmentally friendly film components in the field of packaging technology (Aulin, Gallstedt, & Lindström, 2010; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai (2008); Hult, Lotti, & Lenes, 2010; Siró, Plackett, Hedenqvist, Ankerfors, & Lindström, 2010; Sreekala, Goda, & Devi, 2008; Syverud & Stenius, 2009). Therefore, in this study, a method for the preparation of TOCN-COOH/water dispersions is demonstrated, and the oxygen barrier and other fundamental properties of the TOCN-COOH films prepared are investigated.

## 2. Materials and methods

### 2.1. Materials

A never-dried softwood bleached kraft pulp was used as the cellulose source for TEMPO-mediated oxidation. The pulp had a viscosity average degree of polymerization ( $DP_v$ ) of 2600, when 0.5 M copper ethylene diamine (cuen) was used as the solvent (Evans & Wallis, 1989). The pulp contained approximately 90% cellulose and 10% hemicelluloses. Laboratory grade TEMPO, sodium bromide, and 13% sodium hypochlorite solution (Wako Pure Chemicals, Co. Ltd., Japan) were used as received. TEMPO-oxidized cellulose was prepared from the softwood cellulose using the TEMPO/NaBr/NaClO system at pH 10 according to a previously reported method with NaClO at  $10 \text{ mmol g}^{-1}$ -cellulose (Okita et al., 2010; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006; Saito et al., 2007). The TEMPO-oxidized cellulose thus prepared had a  $DP_v$  of 1440 and a sodium carboxylate content of  $1.74 \text{ mmol g}^{-1}$ , which was determined by the conductivity titration method (Saito & Isogai, 2004).

### 2.2. Preparation of aqueous TOCN-COONa and TOCN-COOH dispersions

A 0.1% (w/v) slurry of TEMPO-oxidized cellulose in water (150 mL) was disintegrated at 7500 rpm for 1 min using a double cylinder-type homogenizer (Physoctron, Microtec Niton Co. Ltd., Japan). The gel-like dispersion obtained was further sonicated for 3 min to prepare a mostly transparent and flowable dispersion using an ultrasonic homogenizer (US-300T, Nihonseiki, Japan) with a 7 mm diameter probe tip at 19.5 kHz and 300 W output power. The dispersion was centrifuged at  $12,000 \times g$  for 15 min to remove a small amount of unfibrillated and partly fibrillated fraction (<5%) to obtain TEMPO-oxidized cellulose nanofibrils with sodium carboxylate groups (TOCN-COONa) dispersed in water. 1 M HCl was slowly added to the 0.1% TOCN-COONa dispersion under magnetic stirring to set the pH to  $\sim 2.0$ . The mixture was then stirred at room temperature for additional 30 min, in which the viscous and flowable TOCN-COONa dispersion changed into a non-flowable gel by conversion of the sodium carboxylate groups to free carboxyl groups. The gel was sequentially washed with 0.01 M HCl and distilled water by repeated centrifugation at  $12,000 \times g$ . The gel suspended in water was then subjected to sonication for 1 min for conversion to a 0.1% (w/v) transparent and flowable dispersion consisting of TEMPO-oxidized cellulose nanofibrils with free carboxyl groups (TOCN-COOH).

### 2.3. Preparation of aqueous TOCN-COONa and TOCN-COOH cast films

The aqueous TOCN-COONa and TOCN-COOH dispersions were poured into poly(styrene) petri dishes, and dried in a ventilated oven at  $45^\circ\text{C}$  for 2 days without forced air-flow to obtain self-standing TOCN-COONa and TOCN-COOH films. 50  $\mu\text{m}$  thick

poly(ethylene terephthalate) (PET) films (Tetron G2, Teijin Ltd., Japan) were surface-hydrophilized for 5 min using a plasma apparatus (DEDE-AF, Meiwa Fosis, Japan) at 5 mA. 0.1% TOCN-COONa and TOCN-COOH dispersions were then cast on the PET films to obtain ca. 1  $\mu\text{m}$  thick TOCN-COONa and TOCN-COOH films after drying at room temperature for 2 days, which were then subjected to oxygen permeability tests.

### 2.4. Analyses

The 0.1% TOCN-COONa and TOCN-COOH dispersions were diluted with distilled water to 0.01% (w/v) solid content, and  $\zeta$ -potentials of the dispersions were measured at  $25^\circ\text{C}$  using a laser-Doppler-electrophoresis-type analyzer (DelsaTM Nano C, Beckman Coulter, USA). The aqueous TOCN-COONa and TOCN-COOH dispersions were freeze-dried, and converted to pellets by pressing at 750 MPa for 1 min. The pellets (0.1 g each) were subjected to sodium content determination using an X-ray fluorescence analyzer (MESA 500, Horiba, Japan), in which X-rays generated at 15 kV and 500  $\mu\text{A}$  were irradiated onto the sample for 100 s in vacuum (Koshikawa & Isogai, 2004). The thicknesses of the PET films coated with TOCN-COONa and TOCN-COOH were determined using an optical measurement system (F20, Filmetrics Japan, Co.). Fourier transform infrared (FT-IR) spectra of the TOCN-COONa and TOCN-COOH films were recorded using a Jasco FT/IR-6100 spectrometer under transmission mode from 400 to  $4000 \text{ cm}^{-1}$  with a  $4 \text{ cm}^{-1}$  resolution. Light transmittance spectra of the films were measured from 200 to 1000 nm with a Shimadzu UV-1700 spectrometer. The surface morphology of the TOCN-COOH film was observed by atomic force microscopy (AFM; Nanoscope III Multi-mode, Digital Instruments, USA) in the tapping mode. Tensile tests of films with ca. 15  $\mu\text{m}$  thickness were carried out using a Shimadzu EZ-TEST tensile tester equipped with a 500 N load cell. Specimens with at least 20 mm length and 2 mm width were measured at  $1.0 \text{ mm min}^{-1}$  and a 10 mm span length, and at least 5 specimens were measured for each sample. The PET films coated with TOCN-COONa and TOCN-COOH were subjected to oxygen permeability determination at  $23^\circ\text{C}$  and 0% relative humidity using oxygen permeability testing apparatus (MOCON ML & SL, Modern Controls Inc., USA) according to a standard method (ASTM 3985). The test cell was composed of two chambers separated by a  $50 \text{ cm}^2$  film under test.

## 3. Results and discussion

### 3.1. TOCN-COOH/water dispersion

When the pH of the TOCN-COONa/water dispersion was adjusted to 2.0 with 1 M HCl, the flowable dispersion changed into a non-flowable gel by conversion of the sodium carboxylate groups to free carboxyls. The gel structure was maintained even after washing with water to remove residual HCl and NaCl. Sonication of the gel suspended in water provided a flowable TOCN dispersion with 0.1% solid content, and the pH of the dispersion became 4.6. The TOCN-COOH/water dispersion thus obtained was transparent, and exhibited clear birefringence between cross polarizers (Fig. 1). No gel-like particles were present in the dispersion, which was confirmed by centrifugation of the dispersion at  $12,000 \times g$  for 5 min. Birefringence is usually taken as an indication of individual nanofibril dispersions (de Souza Lima & Borsali, 2004). The sodium contents of freeze-dried TOCN-COONa and TOCN-COOH were 1.79 and  $0.00 \text{ mmol g}^{-1}$ , respectively, and thus, the sodium carboxylate groups in TOCN-COONa were completely converted to free carboxyl groups by the acid treatment. Moreover, the sodium content of the freeze-dried TOCN-COONa ( $1.79 \text{ mmol g}^{-1}$ ) determined by X-ray fluorescence analysis was close to the carboxylate content

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