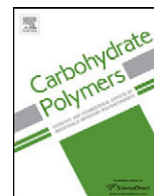




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Influence of TEMPO-oxidized cellulose nanofibril length on film properties

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ABSTRACT

Various mechanical disintegration conditions in water were applied to 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose to prepare TEMPO-oxidized cellulose nanofibrils (TOCNs) of uniform widths ~4 nm but with three different average lengths, 200, 680, and 1100 nm. The viscosity average degrees of polymerization of the TOCNs were 250, 350, and 400, respectively. Self-standing TOCN and TOCN-coated poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA) films were prepared, and the optical, mechanical and gas-barrier properties of the films were evaluated in terms of nanofibril length. Only small differences in density, water content, and elastic modulus of the films were observed but TOCN films prepared from longer nanofibrils clearly showed higher tensile strengths, elongations at break and crystallinity indices. The oxygen barrier properties of the TOCN-coated PET and PLA films increased with increasing nanofibril length. In contrast, nanofibril length had almost no influence on water vapor-barrier properties.

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1. Introduction

Crystalline nanofibrillated celluloses or nanocelluloses from 3 nm to 2 μm in width have attracted significant attention because they have potential applications as nano-reinforcing elements in polymer composites (Eichhorn et al., 2010), nano-filtration materials, rheology-control agents, hydro- and aero-gels with unique properties (Abe & Yano, 2011; Aulin, Netrval, Wågberg, & Lindström, 2010; Olsson et al., 2010; Pääkkö et al., 2008; Saito, Uematsu, Kimura, Enomae, & Isogai, 2011), and high gas-barrier films (Aulin, Gallstedt, & Lindström, 2010; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Fukuzumi et al., 2011; Hult, Lotti, & Lenes, 2010; Isogai, Saito, & Fukuzumi, 2011; Siró, Plackett, Hedenqvist, Ankerfors, & Lindström, 2010; Spence, Venditti, Rojas, Habibi, & Pawlak, 2010; Syverud & Stenius, 2009). Nanocelluloses are produced from native wood or cotton cellulose fibers with or without pretreatment by mechanical disintegration in water, during which the numerous hydrogen bonds between the microfibrils in native cellulose fibers are partially or extensively cleaved to form cellulose microfibrils/nanowhiskers individually or in bundles.

Microfibrillated celluloses (MFCs) with 10–2000 nm widths have been manufactured from wood celluloses by high-shear mechanical homogenization in water (e.g. Henriksson, Henriksson, Berglund, & Lindström, 2007; Turbak, Snyder, & Sandberg, 1983; Siró & Plackett, 2010) and are commercially available as CELISH®

(Daicel FineChem, Ltd., Japan). Cellulose nanowhiskers (CNWs) with 5–10 nm widths are produced from wood celluloses by hydrolysis with strong mineral acids (e.g. Dong, Revol, & Gray, 1998; Elazzouzi-Hafraoui et al., 2008; Marchessault, Morehead, & Walter, 1959). Other cellulose nanofibrils are prepared from native celluloses by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation and the subsequent mechanical disintegration of the oxidized celluloses in water (e.g. Isogai et al., 2011; Saito, Kimura, Nishiyama, & Isogai, 2007; Saito et al., 2009). Two important characteristics of TEMPO-oxidized cellulose nanofibrils (TOCNs) are: (1) TOCNs can be dispersed in water as almost completely individual fibrils with homogenous widths of 3–4 nm (Isogai et al., 2011) and (2) abundant sodium carboxylate groups are present on the crystalline cellulose fibril surfaces (~1.7 carboxylate groups nm^{-2}), by which electrostatic repulsion and/or osmotic behavior work effectively between the anionically charged TOCNs in water (Isogai et al., 2011; Okita, Saito, & Isogai, 2010).

Because individual TOCNs with 3–4 nm widths and high aspect ratios (>50) can be dispersed in water, highly transparent TOCN films can be prepared by aqueous TOCN dispersions on plates. Moreover, plastic films with thin TOCN layers can be prepared by coating an aqueous TOCN dispersion on surface-hydrophilized plastic base films. TOCN and TOCN-coated films have been studied in terms of optical, mechanical, thermal and gas-barrier properties (Fujisawa, Okita, Fukuzumi, Saito, & Isogai, 2011; Fukuzumi et al., 2009; Fukuzumi, Saito, Okita, & Isogai, 2010; Fukuzumi et al., 2011; Isogai et al., 2011). TOCN films have particularly high oxygen-barrier properties under dry conditions, although oxygen transmission rates clearly increase at high relative humidities (Fukuzumi et al., 2011).

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It has been reported that optical and mechanical properties of nanocellulose sheets are influenced by the degree of polymerization (DP), crystallinity and chemical composition of the celluloses used (Henriksson, Berglund, Isaksson, & Lindström, 2008). In the case of TOCNs, fibril length (and fibril length distribution) may be expected to influence optical, mechanical and gas-barrier properties to some extent. Although TOCNs prepared from wood celluloses have almost homogeneous widths (3–4 nm), their lengths and length distributions vary, depending on the preparation conditions, and the influence of these on film properties has not been studied in detail. The lengths of TOCNs can be controlled by the pH of the TEMPO-mediated oxidation system (Saito et al., 2009) or the amount of NaClO added in the TEMPO-mediated oxidation in water at pH 10 (Shinoda, Saito, Okita, & Isogai, 2012). In these cases, however, extensive changes in carboxylate content are unavoidable so the influence of fibril length alone on film properties cannot be extracted from the results.

In this study, therefore, we first prepared TEMPO-oxidized wood cellulose with a carboxylate content of 1.5 mmol g⁻¹, and various mechanical disintegration conditions were applied in water to prepare TOCNs with different nanofibril lengths. TOCN and TOCN-coated plastic films were prepared, and their optical, mechanical and gas-barrier properties were evaluated in terms of nanofibril length.

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 DP (DP_v) of 1200, when 0.5 M copper ethylenediamine (cuen) was used as the solvent (Sihtola, Kyrklund, Laamanen, & Palenius, 1963). The pulp contained approximately 90% cellulose and 10% hemicelluloses. Laboratory grade TEMPO, sodium bromide, and 13% sodium hypochlorite solution (Wako Pure Chemicals, Co. Ltd., Tokyo, 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 using NaClO at 5 mmol g⁻¹-cellulose (Saito et al., 2007). The TEMPO-oxidized cellulose thus prepared had a DP_v of 550 and a sodium carboxylate content of 1.5 mmol g⁻¹. Commercial poly(ethylene terephthalate) (PET) (Teijin DuPont Films, Japan), and poly(lactic acid) (PLA) films (Mitsui Chemical Tohcello, Inc., Japan) were used as coating substrates.

2.2. Preparation of TEMPO-oxidized cellulose nanofibrils (TOCNs)

An aqueous 0.15% slurry of the TEMPO-oxidized cellulose was subjected to blender-type homogenization at 15,000 rpm (Excel Auto ED-4, Nissei, Japan) for 5 or 10 min, and subsequently sonicated at 19.5 kHz and 300 W output power (26 mm probe tip diameter, US-300T, Nissei, Japan) for 2, 4 or 20 min (Table 1). Three transparent aqueous dispersions (TOCNs-A, -B, and -C) were obtained after centrifugation of the dispersions at 12,000 × g for

10 min to remove unfibrillated and partly fibrillated fractions. The yields of TOCNs after centrifugation are given in Table 1. The homogenization and sonication conditions for TOCN-C have been generally adopted in our laboratory to prepare longer TOCNs with less damage. The more harsh disintegration conditions for TOCNs-A and -B were selected in this study to prepare TOCNs in smaller and different length.

2.3. Preparation of TOCN films

Self-standing TOCN films ~10 μm in thickness were prepared by pouring the TOCN dispersions into polystyrene petri dishes and drying at 40 °C for 3 days. The TOCN films were easily detached from the dish after drying. TOCN-coated films ~1.5 μm in TOCN thickness were prepared as follows. The PET films (thickness 50 μm; area 9 cm × 9 cm) and PLA films (thickness 25 μm; area 9 cm × 9 cm) were surface-hydrophilized by plasma exposure at 5 mA for 5 min in vacuum using a soft-etching device (DSDE-AF, Meiwafofosis Co., Ltd., Japan). The 0.15% TOCN/water dispersion (10 ml) was uniformly cast onto the hydrophilized surface of the base film and allowed to dry naturally at room temperature for 3 days.

2.4. Analyses

Freeze-dried TOCNs (0.5 g) were reacted with NaClO₂ (0.1 mmol) in an acetate buffer (50 ml) at pH 4.5 and room temperature for 2 days to selectively oxidize small amounts of C6-aldehydes to C6-carboxylates (Saito & Isogai, 2004; Shinoda et al., 2012). After subsequent conversion of carboxyl groups to sodium carboxylate groups using a diluted NaOH solution, the NaClO₂-oxidized TOCNs were purified and isolated by dialysis against water followed by freeze-drying. Freeze-dried samples (0.04 g) were dissolved in 0.5 M cuen and their viscosities measured using a capillary viscometer. The DP_v values of the NaClO₂-oxidized TOCNs were calculated from their intrinsic viscosities (Sihtola et al., 1963).

A 10 μl aliquot of 0.015% (w/v) TOCN/water dispersions was mounted on a glow-discharged carbon-coated electron microscopy grid and the excess liquid was absorbed by a filter paper. One drop of 1% uranyl acetate negative stain was added before drying and the excess solution was also removed with a filter paper. The stained TOCN dispersions were allowed to dry by natural evaporation. The sample grids were observed at 200 kV using a JEOL electron microscope (JEM 2000-EX, Tokyo, Japan). The sizes of TEM images were approximately 1 μm × 1.3 μm for TOCNs-A and -B, and 5 μm × 6.7 μm for TOCN-C.

The films were conditioned in desiccators at desired relative humidities for at least 48 h, and their weights measured at a resolution of ±2 μg. Dry weights of the films were measured after drying the films at 105 °C for 3 h followed by storage in desiccators with P₂O₅ for 3 h. Water contents of the self-standing TOCN films at various relative humidities under equilibrium conditions were calculated gravimetrically from the conditioned and dried weights. Fourier transform infrared (FT-IR) spectra of the TOCN films were recorded using a JASCO FT/IR-6100 spectrometer (Tokyo, Japan)

Table 1
Preparation conditions and properties of TOCNs.

	Homogenization time (min)	Sonication time (min)	Nanofibril yield (%)	Length-weighted average nanofibril length (nm)	DP _v ^a
TOCN-A	10	20	ca. 100	200	250
TOCN-B	10	4	98	680	350
TOCN-C	5	2	85	1100	400

^a Viscosity-average degree of polymerization determined using 0.5 M cuen as the solvent during preparation.

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