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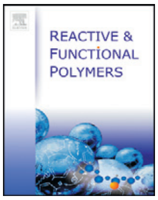

Creation of a new material stream from Japanese cedar resources to cellulose nanofibrils

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ABSTRACT

Japanese cedar is one of the most abundant plantation softwoods in Japan, although it is not effectively utilized as a wood resource. Japanese cedar cellulose was isolated and subjected to one-pot catalytic oxidation and reduction with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and $NaBH_4$, respectively. The TEMPO-oxidized and $NaBH_4$-reduced Japanese cedar celluloses (TOCs-$NaBH_4$) had carboxylate content of up to 1.4 mmol/g and viscosity-average degrees of polymerization from 2000 to 3000. The X-ray diffraction patterns of the TOCs-$NaBH_4$ showed that the crystal widths were ~3 nm, indicating that the C6-OH groups present on the crystalline cellulose microfibril surfaces were selectively oxidized to C6-carboxylate groups. When the TOCs-$NaBH_4$ with carboxylate content of 0.9–1.4 mmol/g were mechanically disintegrated in water, transparent TEMPO-oxidized cellulose nanofibril (TOCN) dispersions were obtained. The lengths of the TOCNs, determined from their atomic force microscopy images, varied from 800 to 1500 nm, depending on the oxidation conditions. The TOCNs prepared from Japanese cedar cellulose have an average of high aspect ratios (>300), which is greater than that (~150) prepared from wood pulp and thus advantageous.

1. Introduction

Approximately 66% of Japan's total land area is forest. The cumulative stock of forest was 4.43 billion m^3 in 2009, and has increased annually by 80 million m^3 [1]. Japan therefore has abundant forest resources. The enhancement of the quantitative and qualitative use of these abundant wood biomass resources as materials (not fuels), together with adequate artificial management of forests and tree plantations, would help to create a sustainable and low-carbon society, decrease CO_2 emissions, and prevent global warming. In particular, softwood trees represent ~53% of the total trees in Japan, with Japanese cedar accounting for ~21% (or ~40% of softwood trees) [2]. Japanese cedar wood is therefore a significant potential source of materials.

Japanese cedar trees are generally felled ~60 years after planting, but they have not been efficiently and quantitatively used [1,2]. Moreover, the wood resources produced from forest thinning, which correspond to ~20 million m^3 per year, have been left in forests as logging residues rather than being used. Japanese cedar is therefore one of the most abundant but unused softwoods in Japan [2]. Conventionally, wood resources have mainly been used in areas such as housing and furniture timbers, pulp and paper, and wood fuel, and these have been the driving forces in establishing a carbon-neutral society. However, quantitative and qualitative increases in these conventional uses of wood resources in the future are no longer expected, because of the decreasing population and growing paperless society in Japan [3,4].

Nanocelluloses, including nanocrystalline celluloses and nanofibrillated celluloses, with low and high aspect ratios, respectively, are categorized as new, wood-based, and crystalline nanomaterials. They have potential applications as biomaterials for commodity goods and high-tech materials [5,6]. Nanocelluloses are prepared from wood celluloses by various pretreatments and mechanical disintegration of the pretreated wood celluloses in water; they have widths from a few nanometers to several hundred nanometers [7]. In various pretreatments, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation of wood cellulose fibers to papermaking-grade materials provide typical TEMPO-oxidized cellulose nanofibrils (TOCNs) with homogeneous widths of ~3 nm and high aspect ratios, i.e., >100 [8,9]. Cast films of wood TOCNs, TOCN networks, TOCN hydrogels, TOCN aerogels, and wood- TOCN-containing composites have been reported to have unique oxygen barrier, mechanical, optical, thermal, hydrophilic/hydrophobic, electric, and catalytic properties, different from those of materials prepared from other nanocelluloses [10–16].

Japanese cedar wood is therefore a potential resource for the preparation of TOCNs for high-tech bio-based nanofibers, after isolation of cellulose from the wood, because softwood cellulose provides completely and individually nanofibrillated TOCNs more efficiently than hardwood celluloses do [11]. We previously prepared TOCNs from commercially available softwood bleached kraft pulps for papermaking. However, for environmental reasons, sulfur-free pulping of, and cellulose-isolation from Japanese cedar wood is necessary, because

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the odor of methyl mercaptan is a serious problem [17–19]. Puangsin et al. [20] and Kuramae et al. [21] used various wood and non-wood holocelluloses containing significant amounts of hemicelluloses for the preparation of TOCNs.

In this study, Japanese cedar holocellulose was extracted with 4% aqueous NaOH to remove as much of the hemicelluloses as possible, while maintaining the original cellulose I crystal structure. The alkali-treated Japanese holocellulose or Japanese cedar cellulose was oxidized using a TEMPO-mediated system under various conditions in water at pH 10. The obtained TEMPO-oxidized and the $NaBH_4$-reduced Japanese cedar celluloses (TOCs-$NaBH_4$) and TOCNs prepared from them were characterized to be used as bio-based nanomaterials for the creation of a new material stream from forest to high-tech industry.

2. Materials and methods

2.1. Materials

Japanese cedar (*Cryptomeria japonica*) powder (80 mesh pass, particle size < 0.2 mm) was used as the wood resource. It was delignified with $NaClO_2$ in water at pH 4–5 and 75 °C for 1 h, according to the Wise method [22]. This delignification treatment was repeated five times with fresh chemicals to prepare Japanese cedar holocellulose [23], and the holocellulose was extracted with 4% aqueous NaOH at room temperature for 1 h to remove hemicelluloses. The obtained Japanese cedar cellulose was neutralized by washing it with acidic water at pH 4–5, washing it thoroughly with water, and keeping it in a wet state at 4 °C before use. TEMPO, NaBr, 70% $NaClO_2$ solution, 13% NaClO solution, and other chemicals and solvents were of laboratory grade (Wako Pure Chemicals Ind., Tokyo, Japan) and used without further purification.

2.2. TEMPO-mediated oxidation of Japanese cedar cellulose

Japanese cedar cellulose (1 g) was stirred in water (100 mL) containing TEMPO (0.016 g), NaBr (0.1 g), and NaClO (2.5–12.5 mmol/g) at pH 10 and room temperature. The mixture was maintained at pH 10 with 0.5 M NaOH until no NaOH consumption was confirmed using a pH stat [9]. Oxidation was stopped by adding a small amount of ethanol to the mixture, and $NaBH_4$ (0.1 g) was added to the slurry at room temperature for 3 h to reduce the small amounts of aldehyde and ketone groups present in the oxidized cellulose to hydroxyl groups, in a one-pot reaction [24]. The resulting TEMPO-oxidized and $NaBH_4$-reduced cellulose (TOC-$NaBH_4$) was washed thoroughly with water by filtration, and stored in a wet state for further treatment or analyses. The yields of the water-insoluble TOCs-$NaBH_4$ were calculated from their dry weights before and after the TEMPO-oxidation and $NaBH_4$-reduction. The carboxylate contents of the TOCs-$NaBH_4$ were determined using an electrical conductometric titration method [9].

2.3. Nanofibrillation of TOCs-$NaBH_4$ in water

The never-dried TOC-$NaBH_4$ was suspended in water (100 mL) at a 0.1% (w/v) solid content, and the slurry was homogenized at 7500 rpm for 6 min at room temperature using a double-cylinder-type homogenizer (Physcotron NS-56, Microtec). The slurry was sonicated for 6 min using an ultrasonic homogenizer equipped with a 26-mm probe tip (US-300T, Nihon Seiki) to prepare an aqueous dispersion of TEMPO-oxidized cellulose nanofibrils (TOCNs). The small amounts of partly unfibrillated fractions present in the dispersion were removed by centrifugation at 7500 rpm for 20 min.

2.4. Analyses

The neutral sugar composition of the Japanese cedar holocellulose, Japanese cedar cellulose, and TOCs-$NaBH_4$ were determined using myo-inositol as an internal standard, according to a previously reported method [21]. A high-performance liquid chromatography system with a Shodex Asahipak NH2P–50 4E column (ψ 4.6 mm × 250 mm) and a refractive index detector (Optilab T-rEx, Shodex, Wyatt Technology, USA) was used for the sugar composition analysis; acetonitrile/250 mM H_3PO_4 (3:1 v/v) was used as the mobile phase, at flow rate of 1.0 mL/min, at 30 °C [20].

Freeze-dried samples (0.04 g each) were dissolved in 0.5 M cupriethylenediamine for 30 min. The intrinsic viscosities $[\eta]$ of the solutions were measured using a capillary viscometer, and the viscosity-average degrees of polymerization (DP_v) were calculated from the $[\eta]$ values using the Mark–Houwink–Sakurada equation: $[\eta] = 2.84 \times DP_v^{0.67}$ [25].

Solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a JEOL JNM-ECA500 spectrometer operated at a ^{13}C frequency of 500 MHz, with a combination of proton dipolar decoupling, magic-angle sample spinning (MAS), and cross-polarization (CP). The spectra were acquired at room temperature with a MAS spinning rate of 6 kHz. CP transfer was achieved using a ramped amplitude sequence for an optimized total time of 2 ms. The relaxation time was 5 s, and the average number of scans acquired for each spectrum was 1024.

X-ray diffraction (XRD) patterns of pressed disk-pellet samples (0.1 g each) were obtained in reflection mode, using an RINT 2000 diffractometer (Rigaku, Tokyo, Japan) with monochromator-filtered Cu Kα radiation, at 40 kV and 40 mA. Scans were obtained from 2θ values of 4° to 40° and a scanning speed of 1°/min. The crystallinity index and (2 0 0) crystal size of cellulose I were calculated from the XRD patterns using conventional methods [20,26].

The mechanically disintegrated aqueous TOCN dispersion (without removal of the unfibrillated fraction) was placed in a disposable poly(methyl methacrylate) cuvette and the optical transmittance of the dispersion was measured from 300 to 800 nm using an ultraviolet–visible (UV–vis) spectrophotometer (JASCO V-670).

Atomic force microscopy (AFM) images of the TOCNs (after removal of the unfibrillated fraction) were obtained using a Nanoscope III Multimode (Digital Instruments, USA) instrument. Aqueous dispersions of TOCN (~0.0005%) were deposited on freshly exfoliated mica plates of dimensions ~1×1 cm^2, and subjected to tapping-mode AFM after drying in air. The widths and lengths of TOCNs in each sample were determined from the AFM height profiles.

3. Results and discussion

3.1. Chemical structures of TEMPO-oxidized Japanese cedar celluloses

Japanese cedar powder was delignified five times with fresh $NaClO_2$ and acetic acid to prepare holocellulose by the Wise method. The yield of the obtained holocellulose was about 71.5%, indicating that most of the lignin was removed [23]. The obtained never-dried holocellulose was extracted with 4% aqueous NaOH to remove hemicelluloses, keeping the original cellulose I crystal structure. The yields of the alkali-treated holocellulose were 72.4% and 51.1% based on the holocellulose and original wood powder, respectively. The alkali-treated holocellulose was regarded as Japanese cedar cellulose. The neutral sugar compositions of the Japanese cedar holocellulose and cellulose are discussed later.

The never-dried Japanese cedar cellulose was oxidized using a TEMPO/NaBr/NaClO system in water at pH 10, followed by reduction with $NaBH_4$ at the same pH in a one-pot procedure without isolation/purification of the TEMPO-oxidized cellulose. The post-reduction of TOCs with $NaBH_4$ is required to convert C6-aldehydes and C2/C3 ketones slightly present in TOCs to hydroxyls, which can prevent discoloration by heating and maintain high TOCN yields from completely dried TOCs in the following disintegration process in water [24]. The amounts of NaClO added varied from 2.5 to 12.5 mmol/g. As the amount of NaClO added increased from 2.5 to 12.5 mmol/g, the time required for