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Water-resistant and high oxygen-barrier nanocellulose films with interfibrillar cross-linkages formed through multivalent metal ions

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ABSTRACT

Once-dried 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibril (TOCN) films with sodium carboxylate groups (TOCN–COONa) were soaked in aqueous $MgCl_2$, $CaCl_2$, $AlCl_3$ and $FeCl_3$ solutions to change the counterion to TOCNs–COOM films (M: metal ion). Dry TOCN–COOM films had high Young's moduli (11–20 GPa) and tensile strength (170–280 MPa). In particular, the wet TOCN films with aluminum and iron (III) carboxylates had high Young's moduli and tensile strengths of $\sim$3 GPa and 30–40 MPa, respectively, even at water contents of $\sim$470%. Moreover, the dry TOCN films with calcium and aluminum carboxylates had extremely low oxygen permeabilities of 0.08 and 0.15 mL μm m^{-2} day^{-1} kPa^{-1}, respectively, even at 80% relative humidity, which are outstanding values compared to those of other films reported previously. These results are explained in terms of the high water resistance of the films, which is caused by the formation of interfibrillar cross-linkages through multivalent metal ions.

1. Introduction

The films constituted of nanofibrillated celluloses show excellent physical properties such as high modulus, high tensile strength and low oxygen permeability [1–3]. Nanocellulose-containing films are thus promising candidates for packaging films for food and pharmaceutical products or as the substrates of electronic devices [4–7]. However, the properties of these films are impaired by humidity, because they have abundant hydroxyl groups and are therefore hydrophilic. Water molecules preferentially adsorb on cellulose nanofibril surfaces, resulting in the swelling of the films. This hydrophilic nature of nanocelluloses causes serious problems in practical applications, when nanocellulose films and nanocellulose-containing composites are used under humid conditions or in water.

Water molecules adsorbing onto the hydroxyl groups plasticize nanocellulose films by partial cleavage of interfibrillar hydrogen bonds that form under dry conditions [8,9]. When these interfibrillar hydrogen bonds are cleaved by water or under humid conditions, the stiffness and tensile strength of the nanocellulose films are drastically decreased. This also causes the oxygen permeability to increase as the relative humidity (RH) is increased [10,11]. Oxygen can easily penetrate water- or moisture-containing films, and it becomes more diffusible when water molecules are present between the nanofibrils. This increase in the mobility of oxygen molecules accelerates the oxygen permeability through the films under humid conditions [12].

Thus, improving the water or moisture resistance of hydrophilic nanocelluloses is a challenge of interest in practical applications. The water resistance of films is often evaluated by the wet tensile strength, which is measured in water-containing films prepared by soaking once-dried films in water for a certain amount of time [13–17]. The wet tensile strength of nanocellulose films has been improved by making composites with poly(vinyl alcohol), starch, chitosan or carboxymethyl cellulose, although these composite materials need multiple and time-consuming procedures for their preparations [13–17]. Chemical modifications of the cellulose hydroxyl groups have been tried to add hydrophobicity to nanocellulose films. However, these modifications often decrease the crystallinity of nanocelluloses, resulting in a decrease in their mechanical performance [18,19]. Large amounts of chemicals and organic solvents are often required to introduce sufficient amounts of hydrophobic ester or ether groups to the hydroxyl groups of nanocellulose, which is not environmentally friendly.

When 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation is applied to wood celluloses suspended in water, completely individualized TEMPO-oxidized cellulose nanofibrils (TOCNs) with homogeneous widths of 3 nm and lengths of $>$300 nm are obtained as aqueous TOCN dispersions [2]. Sodium carboxylate groups are densely, regularly and position-selectively present on the crystalline TOCN surfaces. The surface modification

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of these carboxylate groups of TOCNs has been reported to increase the hydrophobicity of the TOCNs [20–23]. Surfactants have amphiphilic chemical structures, so the adsorption of cationic surfactants on anionic TOCN surfaces often plays an important role in efficiently making TOCNs hydrophobic without damaging the crystalline nanofibril structures. However, the self-standing films of surface-modified TOCNs have low mechanical performance, probably because the formation of interfibrillar hydrogen bonds is partially prevented by the introduction of hydrophobic surfactants onto the TOCN surfaces.

In our previous study, hydrophobic nanocellulose films with quaternary alkylammonium (QA) carboxylate groups were prepared from aqueous TOCN–COOQA dispersions [24]. The TOCN–COOQA films with tetrabutylammonium carboxylate groups showed water contact angles of ~100° and higher mechanical performance than those of commercially available synthetic polymer films. However, the oxygen permeability of the TOCN–COOQA films increased with RH. This is probably because the ionic bonds of the QA carboxylate groups are still hydrophilic, and water molecules adsorbing on the ammonium carboxylate groups in the TOCN–COOQA films could accelerate the diffusivity of oxygen molecules inside the films.

In this study, we prepared TOCN films with metal carboxylate groups, TOCNs–COOM (M: metal ion), to improve their water resistance. The TOCN–COOM films with interfibrillar cross-linkages through multivalent metal ions had high wet tensile strengths and low oxygen-permeabilities even under humid conditions, depending on the metal ions introduced.

2. Experimental

2.1. Materials

A never-dried softwood bleached kraft pulp (SBKP, Nippon Paper Industries, Japan) was used as the original cellulose. Sodium chloride (NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), aluminum chloride ($AlCl_3$) hexahydrate, iron (III) chloride ($FeCl_3$) hexahydrate and other chemicals were laboratory grade (Wako Pure Chemicals, Japan) and used as received.

2.2. Preparation of TOCN-COONa films

Aqueous 0.1% w/v TOCN dispersions with sodium carboxylate groups (TOCN–COONa) were prepared according to our previous report [25]. In brief, SBKP was oxidized with TEMPO/NaBr/NaClO system in water at pH 10. After post-oxidation with $NaClO_2$ in water at pH 4.8, the resulting TEMPO-oxidized cellulose had a carboxylate content of 1.6 mmol g^{-1} and a viscosity-average degree of polymerization of 500 [26]. The TEMPO-oxidized cellulose/water slurry was mechanically disintegrated using a double-cylinder-type homogenizer (Microtec NS-56 Physcotron, Japan) for 1 min and an ultrasonic homogenizer (Nihon Seiki US-300T, Japan) at 300 W for 8 min, to obtain a 0.1% w/v aqueous TOCN dispersion. An unfibrillated fraction ($< 10\%$) present in the dispersion was removed by centrifugation at 12,000 g for 15 min, and the supernatant was used as the TOCN–COONa dispersion. The TOCN–COONa dispersion was poured into poly(styrene) Petri dishes and dried at 40 °C for 3 days. The resulting TOCN–COONa films with thicknesses of 15 ± 1 μm were conditioned at 23 °C and 50% RH before use.

2.3. Preparation of TOCN–COOM films

The TOCN–COONa films (25–30 mg and 7×7 cm^2 each) were soaked in aqueous 0.1 M NaCl, HCl, $MgCl_2$, $CaCl_2$, $AlCl_3$ or $FeCl_3$ solutions (100 mL each) for 2 h. The original dried and conditioned TOCN–COONa film without any soaking treatment was coded as "original TOCN–COONa", and the TOCN films after soaking in dilute HCl or metal chloride solutions were coded as TOCN–COOH, TOCN–COONa, TOCN–COOCa, TOCN–COOMg, TOCN–COOAl and TOCN–COOFe, respectively. These TOCN–COOM films were soaked in fresh distilled water three times to ensure they were washed, placed on silicone rubber plates, and dried at 23 °C and 50% RH for 2 days.

2.4. Analyses

The amounts of sodium and chloride ions in the TOCN–COOM films were determined on an energy-dispersive X-ray fluorescence analyzer (XRF) (Shimadzu EDX-8000, Japan). Fourier transform infrared (FTIR) and light transmittance spectra of the films were obtained using a FTIR spectrometer (JASCO FT/IR-6100, Japan) and a UV–vis-NIR spectrometer (JASCO V670, Japan), respectively. The film thicknesses were calculated from the interference patterns in the transmittance spectra according to a previously reported method [24,27]. The film densities were calculated from the volumes and weights of the dry films after conditioning at 23 °C and 50% RH. The moisture contents of the conditioned films were calculated from the weights before and after heating at 105 °C for 3 h. Tensile test on dry films was carried out at 23 °C and 50% RH using a tensile tester (Shimadzu EZ-TEST, Japan) equipped with a 500 N load cell. The film specimens were 3 mm wide and 40 mm long. At least five specimens were measured for each sample with a span length of 15 mm at a rate of 1.0 mm min^{-1}. Oxygen permeability (P–O_2) of the TOCN films was measured at 23 °C and at 46%, 65% and 80% RH, using an apparatus for determination of oxygen transmission rates (MOCON OX-TRAN 2/21, Modern Control Inc., USA) according to a standard method (ASTM D-3985) [6,24].

The TOCN–COOM films, which were prepared by soaking the original TOCN–COONa film in aqueous HCl or metal chloride solutions, and successive washing with water, were soaked in fresh water for 1 h (without drying), and the wet films were picked up and excess water was removed with blotting paper. The water contents of the wet films were calculated from the weights before and after soaking in water. Wet tensile test was carried out for the water-containing and swollen films using the same apparatus as above at a span length of 10 mm according to TAPPI T 456 om-87 [28]. The thickness of the wet films was measured using a micrometer (Mitutoyo CLM1-15QM, Japan).

3. Results and discussion

3.1. Structures of TOCN-COOM films

In the present study, the counterions of the carboxylate groups on the TOCN surfaces of the original TOCN–COONa film were exchanged with H^+ and/or metal ions by soaking the original TOCN–COONa film in dilute HCl or metal chloride solutions followed by washing with fresh water and drying. Neither sodium nor chloride ions were detected in any of the ion-exchanged TOCN–COOH nor TOCN–COOM films by XRF (Fig. 1). When the original TOCN–COONa film was soaked in aqueous NaCl solution, the washed TOCN–COONa film contained no chloride ion. Thus, the washing procedure of the soaked films with water used in this study is sufficient to completely remove any salt components physically trapped in the wet films. When the original TOCN–COONa film was soaked in each metal chloride solution, only the corresponding metal signal was detected in the XRF spectrum (Fig. 1). Quantitative analysis of the metal ions present in the films was,