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

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ABSTRACT

A 2,2,6,6-tetramehylpiperidine-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 mL μm m^{-2} day^{-1} kPa^{-1}, which was clearly lower than that (15.5 mL μm m^{-2} day^{-1} 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/$NaClO_2$ 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^{-1}, 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, & Lindstöm, 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 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 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 (Physcotron, Microtec Nition 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 × *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 ∼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 × *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 °C for 2 days without forced air-flow to obtain self-standing TOCN-COONa and TOCN-COOH films. 50 μm 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 μm 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 ζ-potentials of the dispersions were measured at 25 °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 μA 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 cm^{-1} with a 4 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 Multimode, Digital Instruments, USA) in the tapping mode. Tensile tests of films with ca. 15 μm 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 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 °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 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 × *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 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 mmol g^{-1}) determined by X-ray fluorescence analysis was close to the carboxylate content

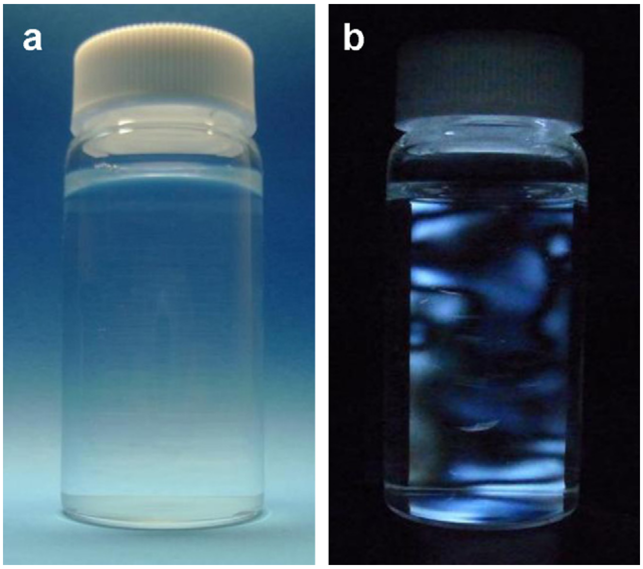

Fig. 1. Photographs of a 0.1% TOCN-COOH/water dispersion at pH 4.6 (a) and that taken between cross polarizers (b).

of the TEMPO-oxidized cellulose (1.74 mmol g^{-1}) determined by the conductivity titration method (see Section 2). Consequently, TOCN-COOH/water dispersions at 0.1% solid content without any gel particles were obtained by this procedure.

ζ-Potential measurements are applicable to rod-like TiO_2 nanotubes and carbon nanofibers dispersed in solvents for approximate evaluation of their surface charges on the basis of Smoluchowski theory (Bavykin et al., 2005; Kvande et al., 2008). Hence, the surface charges of TOCN-COONa and TOCN-COOH dispersed in water at 0.01% solid content were estimated by their ζ-potentials, in which the pH values became 7.8 and 5.6, respectively, by dilution with distilled water. There was no remarkable difference in ζ-potential between the two dispersions, and the values were −51 and −58 mV for TOCN-COONa and TOCNs-COOH, respectively. This indicates that almost all free carboxyl groups in TOCN-COOH were dissociated to provide anionic surface charges in water at pH 5.6 under the conditions of ζ-potential measurement.

pK_a values of C6-carboxyl groups of polyuronic acids have been reported to be 2.8–3.7 (Cesaro, Delben, & Paoletti, 1990; Fourest & Volesky, 1996; Kötz, Phillipp, Nehls, Heinze, & Klemm, 1990; Milas, Shi, & Rinaudo, 1990; Morel, Andreux, Habib, & Cuckert, 1987; Morvan, Demarty, & Thellier, 1979; Zhu, Kumar, & Banker, 2004), indicating that most of C6-carboxyl groups on the TOCN-COOH surfaces are dissociated in an aqueous dispersion at pH 4.6. Therefore, it is likely that electrostatic repulsion acts between TOCN-COOH in water at pH 4.6 by the anionically charged C6-carboxyl groups present on the TOCN-COOH surfaces in high density, which provides mostly individualized and stable TOCN-COOH/water dispersions.

3.2. Self-standing TOCN-COOH films

Self-standing, approximately 15 μm thick TOCN-COOH films were prepared by casting and drying of the dispersion. The films were transparent and flexible (Fig. 2 upper photograph), and the AFM image (Fig. 2 lower image) showed that the film surface consisted of individual nanofibrils with similar widths. The surface of the TOCN-COOH film had a random nanofibril orientation, and apparent nanofibril widths were quite similar to those of previously reported TOCN-COONa films (Fukuzumi et al., 2008). Thus, almost all TOCN-COOH nanofibrils are probably dispersed in water at the individual nanofibril level (3–4 nm width) in a similar manner to that of TOCN-COONa in aqueous dispersions (Isogai et al., 2010; Saito et al., 2006, 2008, 2009).

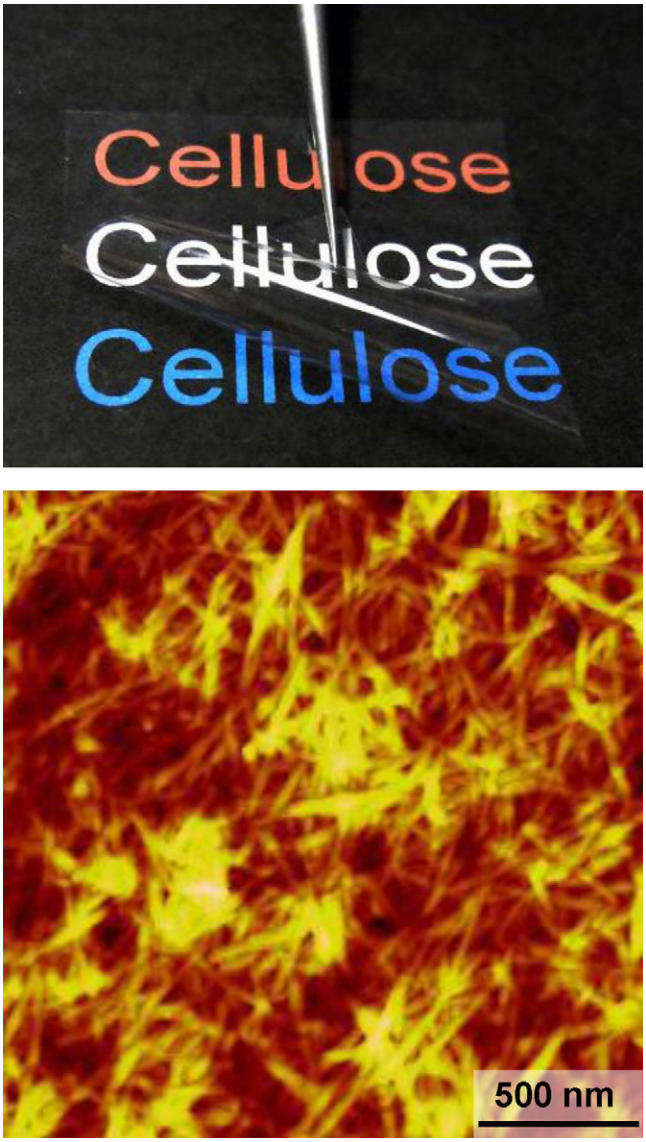

Fig. 2. Photograph (upper) and AFM image (lower) of a TOCN-COOH film.

Fig. 3 presents FT-IR spectra of the TOCN-COONa and TOCN-COOH films. The absorption band due to C=O stretching of sodium carboxyl groups at ca. 1600 cm^{-1} for the TOCN-COONa film was shifted to 1720 cm^{-1} for the TOCN-COOH film. Moreover, the absorption band around 1400 cm^{-1} due to C–O symmetric stretching of dissociated carboxyl groups disappeared in the FT-IR spectra of the TOCN-COOH film, which indicates that the sodium carboxylate groups in TOCN-COONa were converted to free carboxyl groups by the acid treatment. The C=O absorption band at 1720 cm^{-1} is assigned to C=O stretching of carboxyls forming hydrogen bonds, while isolated carboxyl groups without hydrogen bonds exhibit C=O absorption around 1740 cm^{-1} (Creager & Steiger, 1995; Dueval & Corn, 1992; Smith, Alves, Anderegg, & Porter, 1992; Sun & Crooks, 1993). Thus, carboxyl groups in the TOCN-COOH films mostly form intra- or inter-nanofibril hydrogen bonds with hydroxyl groups or other carboxyl groups.

Fig. 4 shows UV–vis transmittance spectra of the TOCN-COONa and TOCN-COOH films. Both films have high transmittance values at 600 nm of approximately 90 and 87%, respectively, irrespective of the different carboxyl structures in the TOCN-COONa and TOCN-

Table 1
Tensile properties[a] of TOCN films prepared from aqueous TOCN-COOH and TOCN-COONa dispersions.

	Moisture content (%)	Density (g cm^{-3})	Tensile strength (MPa)	Young's modulus (GPa)	Elongation (%)
TOCN-COOH film	5.9	1.51	178 ± 9	10.0 ± 1.7	5.1 ± 0.6
TOCN-COONa film	7.8	1.47	191 ± 25	7.2 ± 0.6	11.7 ± 3.7

[a] Measured at 23 °C and 50% relative humidity.

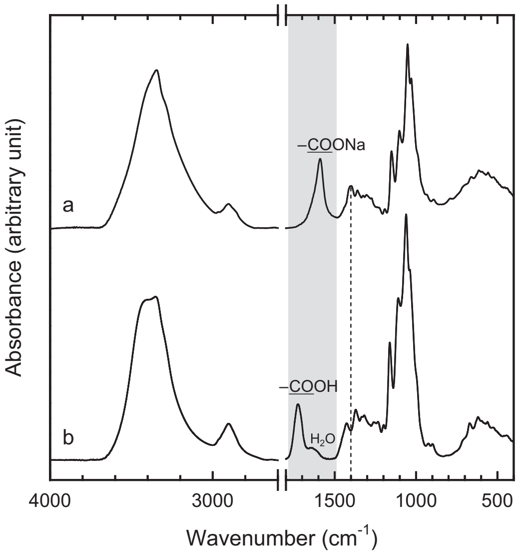

Fig. 3. FT-IR spectra of the TOCN-COOH and TOCN-COONa films.

COOH films. Therefore, the TOCN-COOH films have similar optical properties and surface structures to those of the TOCN-COONa films (Fukuzumi et al., 2008).

The moisture content, density and tensile properties of the TOCN-COONa and TOCN-COOH films at 23 °C and 50% relative humidity are listed in Table 1. There were no significant differences in the densities and tensile strengths of the two films, whereas the moisture content, Young's modulus and elongation were clearly different; the TOCN-COOH films had lower moisture content, higher Young's modulus and lower elongation than those of the TOCN-COONa films. These differences are likely to be due to different hydrogen bonding patterns between the two films. Free carboxyl groups in the TOCN-COOH films can form intra- and inter-nanofibril hydrogen bonds, while the sodium carboxylate groups cannot. In the TOCN-COONa films, intra- and inter-fibril hydrogen bonds can be formed only between alcoholic hydroxyl groups. The lower moisture content in the TOCN-COOH film than that of the TOCN-COONa film is due to the less hydrophilic nature of free carboxyl groups forming hydrogen bonds than that of isolated and hydrophilic sodium carboxylate groups. The lower moisture content of the TOCN-COOH films may also result in the higher Young's modulus and lower elongation.

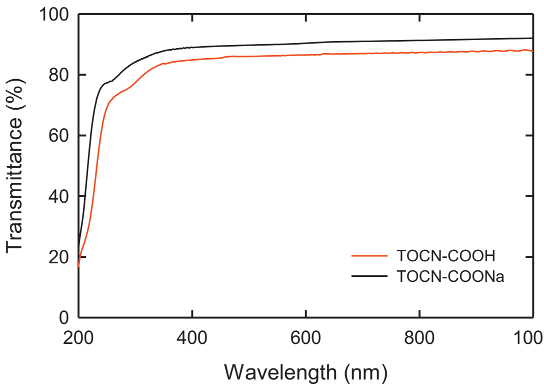

Fig. 4. UV–vis transmittance spectra of the TOCN-COOH and TOCN-COONa films.

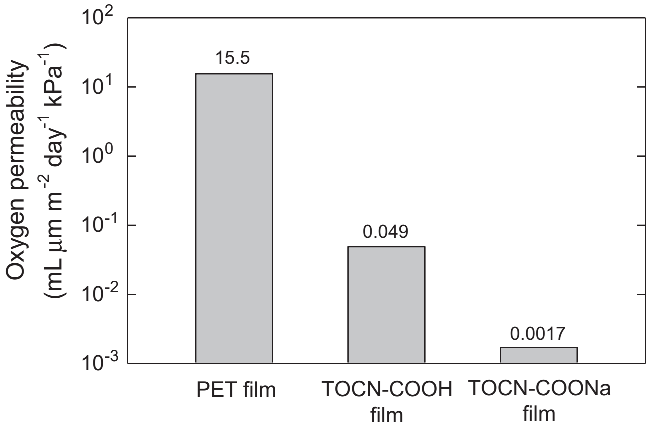

Fig. 5. Oxygen permeability of poly(ethylene terephthalate) (PET), TOCN-COOH and TOCN-COONa films with 1 µm thickness. PET films and those coated with TOCN-COOH or TOCN-COONa were used as samples.

3.3. *Oxygen permeability of PET films coated with TOCN-COOH*

50 µm thick PET films coated with 1 µm thick TOCN-COONa or TOCN-COOH layer were subjected to oxygen permeability measurements at 23 °C and 0% relative humidity. The oxygen permeability of the PET films decreased from 0.31 to 0.049 mL m^{-2} day^{-1} kPa^{-1} by coating with TOCN-COOH. The oxygen permeability of PET film at the 1 µm thickness is calculated to be 15.5 mL µm m^{-2} day^{-1} kPa^{-1} (Fig. 5). Thus, the TOCN-COOH films had oxygen barrier properties clearly higher than those of PET and other petroleum-derived synthetic polymer films at 0% relative humidity (Lange & Wyser, 2003). However, the PET films coated with TOCN-COONa had an extremely low oxygen permeability value, 0.0017 mL m^{-2} day^{-1} kPa^{-1}. The densities of the TOCN-COOH and TOCN-COONa films were quite similar; therefore, a detailed mechanism for the significantly different oxygen barrier properties of the PET films coated with TOCN-COONa and TOCN-COOH is unknown at present. However, it is conclusive that sodium carboxylate groups present on cellulose nanofibril surfaces can effectively improve the oxygen barrier properties of cellulose nanofibril films (Siró et al., 2010).

4. Conclusions

A TEMPO-oxidized cellulose gel with free carboxyl groups, prepared from a TOCN-COONa/water dispersion, was individually dispersed at the nanofibril level in water at pH 4.6 by sonication treatment. Transparent and flowable TOCN-COOH/water dispersions having birefringence when observed between cross polarizers were obtained. The ζ-potential of TOCN-COOH in water was −58 mV, which indicates that sufficient electrostatic repulsion acts between TOC nanofibrils with dissociated C6-carboxyl groups in water at pH 4.6 and results in the formation of individual TOCN-COOH/water dispersions. The self-standing TOCN-COOH films were flexible and highly transparent. AFM images revealed that the TOCN-COOH film surfaces consisted of individualized TOC-COOH nanofibrils with random orientation. The TOCN-COOH films had higher Young's modulus (ca. 10 GPa) and lower elongation (ca. 5.1%) than those of the TOCN-COONa films, which was considered to be due to increased intra- and inter-nanofibril hydrogen bonding in the TOCN-COOH films and the resultant lower moisture content. The oxygen permeability of the TOCN-COOH films was 0.049 mL μm m^{-2} day^{-1} kPa^{-1}, which was lower than that of the PET films (15.5 mL μm m^{-2} day^{-1} kPa^{-1}) but higher than that of the TOCN-COONa films (0.0017 mL μm m^{-2} day^{-1} kPa^{-1}).

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