

Application News

No. A611

Spectrophotometric Analysis

Evaluation of Modification Functional Groups of Monodisperse Cellulose Nanofiber (CNF)

■ Introduction

Cellulose is a type of polysaccharide which is the main component of plant cell walls. Cellulose with a fiber diameter of 4 nm to 100 nm, length of several μm , and aspect ratio of 100 or more is called cellulose nanofiber (CNF), and has attracted attention as a leading-edge biomass new material. CNF has a number of outstanding functions. In addition to light weight and high strength, it also has a high gas barrier property, adsorption, and transparency. Moreover, because CNF is a plant-derived material, environmental impacts associated with production and waste disposal are low. Future applications are expected to include automotive components, electronic materials, and packaging.

Application News No. A579 introduced an evaluation of the modification functional groups of networked CNFs. This article introduces an example of evaluation of the modification functional groups of monodisperse CNF by using an IRSpirit™ Fourier transform infrared spectrophotometer.

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■ What is Cellulose Nanofiber (CNF)?

CNF can be broadly divided into the monodisperse type and the networked type. The networked type has a fiber diameter of about 20 nm to 100 nm and is produced by mechanical defibration. In contrast, the monodisperse type has a fiber diameter of approximately 3 nm to 5 nm, and the individual fibers are dispersed. Among monodisperse CNF, TEMPO-oxidized CNF (TOCN) is defibrated to the nanometer size by a combination of a chemical reaction called TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation and gentle mechanical processing. TEMPO-oxidized CNF has a uniform fiber diameter of 3 nm to 4 nm, and has the distinctive features of high dispersibility in solutions and transparency.

The modification functional group CH_2OH attached to networked CNF is changed to COO^- by the TEMPO oxidation catalyst, as shown schematically in Fig. 1. Because the hydrophilic group is changed to a hydrophobic group, mixing with resins is possible, as resins are also hydrophobic. Taking advantage of this feature, a wide range of industrial application is expected, including composites with resins and rubber and use in paints.

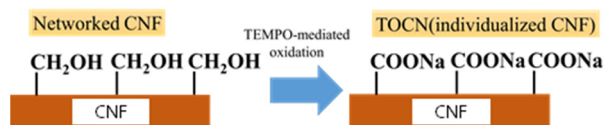


Fig. 1 Change of Modification Functional Group by TEMPO Oxidation Catalyst

■ Evaluation of Modification Functional Groups of CNF

A TOCN film was used as a monodisperse CNF. This monodisperse CNF was compared with a film of wood-derived CNF, which is a networked-type CNF, and a carboxymethyl cellulose (CMC) film.

Fig. 2 shows the appearance of the film samples used in the evaluation of functional groups. Table 1 shows the samples and modification functional groups evaluated in this experiment. These were measured by the attenuated total reflection (ATR) method using an IRSpirit-T Fourier transform infrared spectrophotometer shown in Fig. 3. In the ATR method, samples are measured by placing the film in close contact with the prism, as shown in Fig. 4.

Table 1 List of Samples and Modification Functional Groups

	Sample name	Raw material	Modification functional group
(a)	TOCN	Cellulose	Carboxy group
(b)	Wood-derived CNF	Cellulose	Hydroxy group
(c)	CMC	Carboxymethyl cellulose	Carboxymethyl group

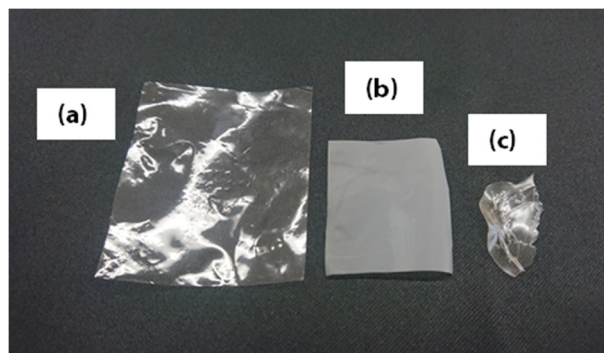


Fig. 2 Appearance of Film Samples
(a) TOCN, (b) Wood-Derived CNF Film, (c) CMC



Fig. 3 IRSpirit™-T Fourier Transform Infrared Spectrophotometer with QATR™-S Single-Reflection ATR Accessory with a Diamond for Use with IRSpirit™ Series

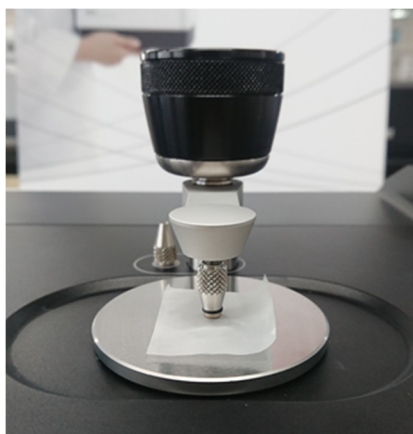


Fig. 4 Condition of ATR Measurement

Table 2 Measurement Conditions

Instruments	: IRSpirit-T (KBr window plate) QATR-S (wide-band diamond prism)
Resolution	: 4 cm ⁻¹
Accumulation	: 20 times
Apodization function	: Happ-Genzel
Detector	: DLATGS

Table 2 shows the measurement conditions, and Fig. 5 shows the measurement results. In the infrared spectra of all samples, peaks of cellulose originating from the stretching vibration of the O-H bond at 3,600 cm⁻¹ to 3,200 cm⁻¹ and the stretching vibration of the C-O bond at 1,100 cm⁻¹ to 900 cm⁻¹ can be observed. In addition, a peak originating from the antisymmetric stretching vibration of COO⁻ of carboxylate can also be seen around 1,600 cm⁻¹ in the TOCN and CMC spectra. Fig. 6 shows the result of a spectrum search for the wood-derived CNF. The spectrum of the wood-derived CNF is in good agreement with the library spectrum of cellulose. Thus, a simple investigation of functional groups is possible by using FTIR.

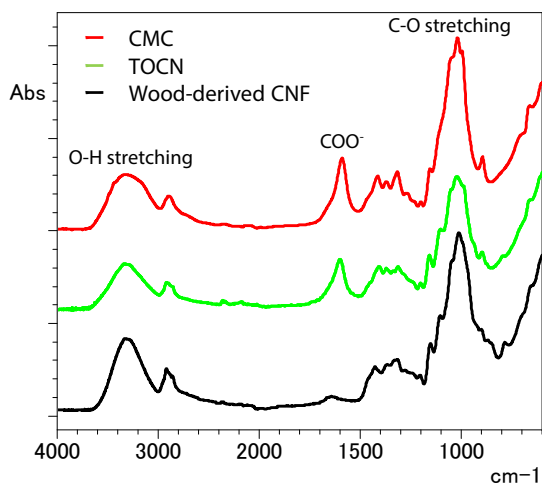


Fig. 5 Infrared Spectra of Various Cellulose Materials

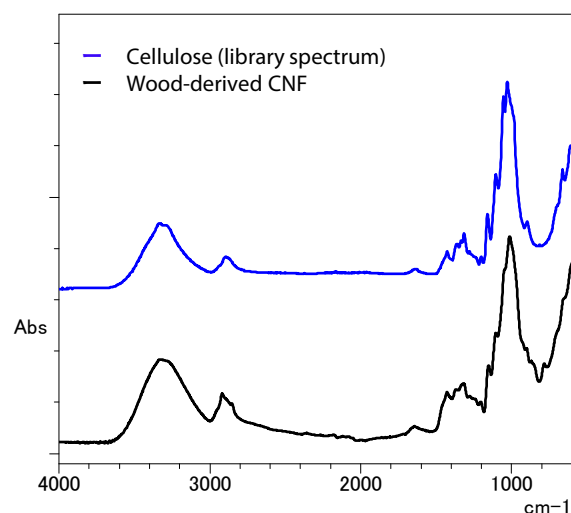


Fig. 6 Result of Spectrum Search for Wood-Derived CNF

Conclusion

The modification functional groups of monodisperse CNFs were evaluated by the ATR method using FTIR. The results revealed that the modification functional groups are different in TOCN and CMC, which are monodisperse-type CNFs, and wood-derived CNF, which is a networked-type CNF. In particular, the facts that the monodisperse-type CNFs have the carboxy group and the wood-derived CNF shows good agreement with the library spectrum of cellulose could be confirmed by a simple and easy analysis.

<Acknowledgement>

In conducting these measurements, Prof. Akira Isogai of the University of Tokyo provided the samples and valuable knowledge in connection with CNF. We wish to take this opportunity to express our deep appreciation to Prof. Isogai.

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