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Application News

No. A610

Spectrophotometric Analysis

Evaluation of Dispersibility of Individualized Cellulose Nanofiber (CNF)

Cellulose is a type of polysaccharide which is the main component of plant cell walls. Cellulose with a fiber diameter of 4 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, as a plant-derived material, its production- and waste-related environmental impacts are low. Future applications are expected to include automotive components, electronic materials, and packaging.

Application News No. A579 introduced an evaluation of networked CNF. In the present article, the dispersibility of monodisperse CNF was evaluated by using a Shimadzu UV-2600i ultraviolet-visible light (UV-VIS) spectrophotometer.

In addition, the monodisperse CNF was compared with commercially-available aqueous dispersions of wood-derived CNF and carboxymethyl cellulose (CMC), which are networked CNFs. Those results are also introduced here.

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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 to 100 nm and is produced by mechanical defibration. In contrast, the monodisperse type has a fiber diameter of about 3 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 to 4 nm, and has the distinctive features of high dispersibility in solutions and transparency.

Because the modification functional group attached to the CNF is changed from a hydrophilic group to a hydrophobic group by the TEMPO oxidation catalyst, it is possible to mix TEMPO-oxidized CNF with resins, which are hydrophobic. As a result, a wide range of industrial application, including paints, composites with resins and rubber, and others, is expected.

Dispersibility Evaluation of CNF Solutions

In this experiment, 0.1 wt% aqueous dispersions of wood-derived CNF, CMC and TEMPO-oxidized CNF were evaluated by using the UV-2600i ultraviolet-visible light (UV-VIS) spectrophotometer in Fig. 1. Fig. 2 shows the appearance of the sample solutions used in the evaluation. Transparency was evaluated by measuring the linear transmittance and total light transmittance of the samples.

Fig. 1 UV-2600i Ultraviolet-Visible Light (UV-VIS) Spectrophotometer

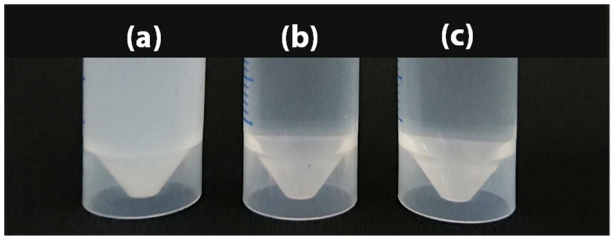

Fig. 2 Appearance of Sample Solutions (0.1 wt%)
(a) Wood-derived CNF, (b) CMC, (c) TEMPO-oxidized CNF

First, linear transmittance measurement and total light transmittance measurement will be explained. Fig. 3 shows the principle of the general transmittance measurement method. As shown in Fig. 3, in linear transmittance measurement, the light transmitted linearly through a sample is measured. In contrast, as shown in Fig. 4, both linear transmitted light and diffuse transmitted light (scattered light) are measured in total light transmittance measurements using the integrating sphere which is one of UV accessories. In cloudy sample solutions, color films with low transmittance, and similar objects, the scattered light component is large. Therefore, an evaluation of high transparency is possible as the difference between the two transmittance ratios becomes smaller.

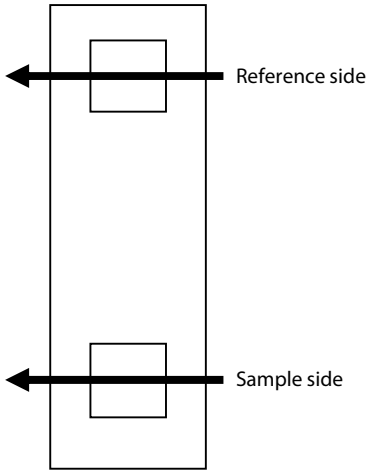

Fig. 3 Linear Transmittance Measurement

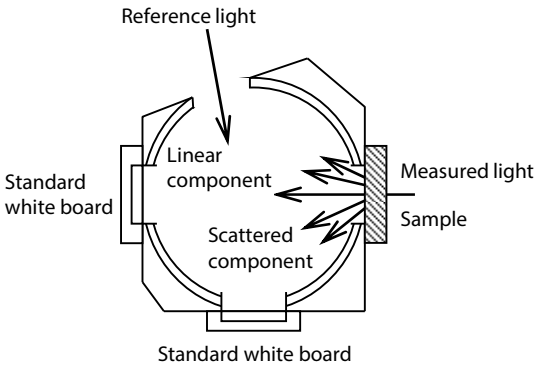

Fig. 4 Total Light Transmittance Measurement

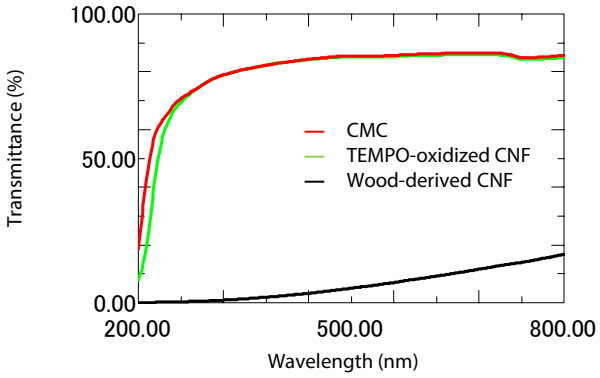

Fig. 5 Linear Transmittance of Cellulose Samples

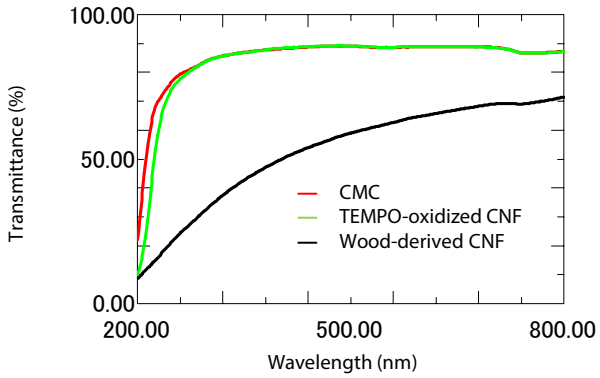

Fig. 6 Total Light Transmittance of Cellulose Samples

Table 1 shows the measurement conditions. Fig. 5 and Fig. 6 show the linear transmittance and total light transmittance of the samples, respectively. The linear transmittance of the wood-derived CNF shown in Fig. 5 was low in the visible region, at 20% or less. On the other hand, the linear transmittance of the TEMPO-oxidized CNF and CMC was high in the visible region, at nearly 80%, but decreased rapidly at around 200 to 240 nm in the ultraviolet (UV) region.

In contrast, in the total light transmittance results shown in Fig. 6, the transmittance of the wood-derived CNF in the visible region was approximately 60%.

The difference between linear transmittance and total light transmittance is small in the TEMPO-oxidized CNF and CMC, while the difference between the two is large in the wood-derived CNF. These results show that the transparency of the TEMPO-oxidized CNF and CMC is high, and can be measured satisfactorily by linear transmittance. It is known that CNF with a fiber diameter smaller than the wavelength of visible light disperses without aggregating and becomes transparent [(1)]. From these measurement results, it can be thought that the TEMPO-oxidized CNF was nano-dispersed in water, and aggregation did not occur.

Table 1 Measurement Conditions

Instrument	:	UV-2600i UV-VIS spectrophotometer ISR-2600 Plus integrating sphere attachment
Wavelength range	:	200 nm - 800 nm
Scan speed	:	Medium
Sampling pitch	:	1.0 nm
Slit width	:	2 nm (UV-2600i) 5 nm (UV-2600i + ISR-2600 Plus)
Light source switching wavelength	:	323 nm

Conclusion

The linear transmittance and total light transmittance of monodisperse CNF was compared, and its dispersibility was evaluated. In comparison with wood-derived CNF, TEMPO-oxidized CNF displayed high transmittance of approximately 80% for both linear transmittance and total light transmittance. From this, it was understood that monodisperse CNF has high dispersibility and excellent transparence.

<Acknowledgement>
In conducting these measurements, Prof. Akira Isogai of the University of Tokyo provided useful knowledge concerning the sample materials and CNFs. We wish to take this opportunity to express our deep gratitude to Prof. Isogai for his assistance.

<Reference>
(1) A. Isogai, T. Saito, H. Fukuzumi: TEMPO-oxidized cellulose nanofibers, Nanoscale, 3, 71-85 (2011)

First Edition: May 2020

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