Application News

No. A579

Spectrophotometric Analysis

An Evaluation of the Dispersibility and Functional Group Information of Networked CNFs and the Optical Properties of CNF Film

Cellulose is a polysaccharide that is the primary component of plant cell walls. Cellulose that is fibrillated down to the order of nanometers is called nanocellulose and of such nanocelluloses, those that have a high aspect ratio (100 or higher) with a width of 4 to 100 nm and a length of a few µm are called cellulose nanofibers (CNFs). CNFs are gaining attention as state-of-the-art biomass material.

There are generally two types of CNFs: monodisperse CNFs and networked CNFs. Monodisperse CNFs have a width of approx. 3 to 5 nm and each fiber is dispersed. They are therefore transparent and can easily be added functions such as water-resistance and enzymatic barriers. Networked CNFs on the other hand are larger with a width of approx. 20 to 100 nm and only require mechanical fibrillation to make. They feature easy adhesion with resins and also easy processing. Regarding monodisperse CNFs, an evaluation of dispersibility is introduced in Application News No. S31.

This article studies the dispersibility and function group information of networked CNFs. The measurement samples are CNFs (wood-derived etc.) purchased from Sugino Machine Ltd., and fermented nanocellulose (product name: Fibnano) provided by Kusano Sakko Inc., and Prof. Kenji Tajima of Hokkaido University. We also evaluated the optical properties of CNF film purchased from Sugino Machine Ltd., the results of which are also introduced in this article.

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Dispersibility Evaluation of a Networked CNF Solution

Four types of samples were prepared for measurement as shown in Table 1: wood-derived CNF, cellulose made from carboxymethyl cellulose and powdered chitin respectively, and fermented nanocellulose (materials: glucose, fructose). After diluting each sample to a concentration of 0.1 wt%, the linear transmission and total light transmission were measured using the conditions listed in Table 2.

According to the linear transmission spectra shown in Fig. 1, wood-derived CNF indicates low transmission under 20 %T including the visible range. CMC exhibits high transmission exceeding 90 %T in the visible range, but drops steeply in the ultraviolet range at about 200 to 240 nm. Both chitin and fermented nanocellulose show a gradual decline in transmission from the long-wavelength range through to the short-wavelength range. All samples show a lower transmission in the linear transmission spectra compared to the total light transmission spectra (Fig. 2), suggesting that the samples are cloudy with a concentration of 0.1 wt%.

Table 1 List of Measurement Samples

Sample Name	Material
Wood-derived CNF	Cellulose
CMC	Carboxymethyl cellulose
Chitin	Powdered chitin
Fermented nanocellulose	Glucose, fructose

Table 2 Measurement Conditions

Instrument Used	:	UV-2600, ISR-2600 Plus
Measuring Wavelength Range	:	200 nm - 800 nm
Scan Speed	:	Medium speed
Sampling Interval	:	1.0 nm
Slit Width	:	2 nm (UV-2600) 5 nm (UV-2600+ISR-2600 Plus)
Light Source Changing Wavelength	:	323 nm

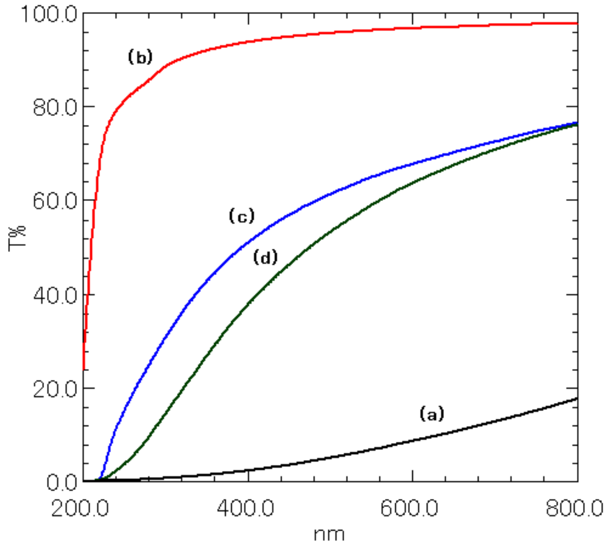

Fig. 1 Linear Transmission Spectra
(a) Wood-Derived CNF, (b) CMC, (c) Chitin, (d) Fermented Nanocellulose

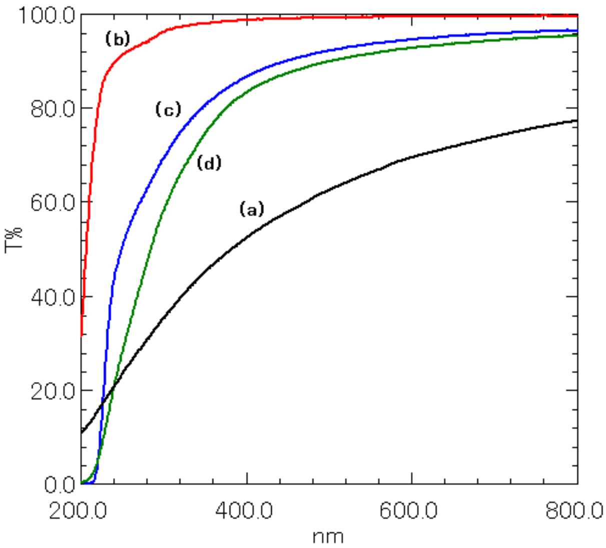

Fig. 2 Total Light Transmission Spectra
(a) Wood-Derived CNF, (b) CMC, (c) Chitin, (d) Fermented Nanocellulose

Functional Groups of Networked CNFs

Each sample in Table 1 was applied to and dried on aluminum foil as shown in Fig. 3 and then measured using the ATR method on an FTIR instrument. Table 3 lists the measurement conditions and Fig. 4 shows the measured infrared spectra.

Fig. 3 Wood-Derived CNF Applied to and Dried on Aluminum Foil

Table 3 Measurement Conditions

Instrument Used	: IRSpirit™-T (KBr window), QATR™-S (wide-band diamond prism)
Resolution	: 4 cm^{-1}
Accumulation	: 32 times
Apodization Function	: Happ-Genzel
Detector	: DLATGS

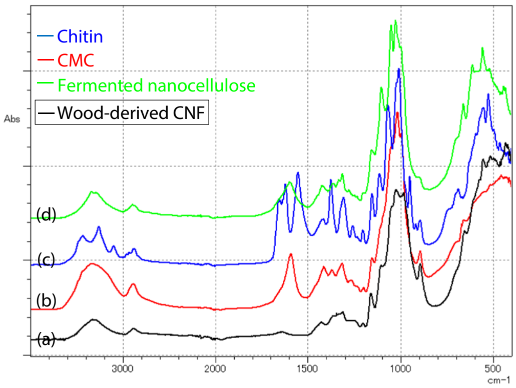

Fig. 4 Infrared Spectra
(a) Wood-Derived CNF, (b) CMC, (c) Chitin, (d) Fermented Nanocellulose

For wood-derived CNF, we can see a peak at 3600 to 3200 cm^{-1} caused by O-H stretching vibrations and a peak at 1100 to 900 cm^{-1} caused by C-O stretching vibrations. This matches with the cellulose included in the ATR and food additive libraries of LabSolutions™ IR. For CMC, in addition to the peaks observed for wood-derived CNF, there is a peak near 1600 cm^{-1} caused by COO^- asymmetrical stretching vibrations. Overall, the spectrum is similar to that of fermented nanocellulose. Regarding chitin, there is a peak near 3300 cm^{-1} caused by NH stretching vibrations from amide bonds, a peak near 1650 cm^{-1} caused by C=O stretching vibrations, and a peak near 1550 cm^{-1} caused by NH bending vibrations and CN stretching vibrations. As described, functional groups can be determined by using FTIR.

Optical Properties of CNF Film

The optical properties of CNF film were measured using the conditions listed in Table 2. For comparison reasons, commercially available polypropylene (PP) film and polyethylene (PE) film shown in Fig. 5 were measured as well. The measurement results are shown in Fig. 6

The linear transmission spectra show that the transmission of CNF film is low compared to that of PP film and PE film, and that there is only about 10 % of linear light transmission in the entire visible range. From the total light transmission spectra, we can see that if scattered light is included, CNF film transmits the same level of light as PP film and PE film in the visible range. Whereas PP film and PE film show a sharp drop in transmission due to the absorbance by additives in the ultraviolet range for wavelengths shorter than 250 nm, CNF film shows a gradual drop.

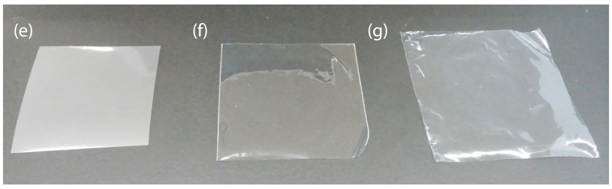

Fig. 5 (e) CNF Film, (f) PP Film, (g) PE Film

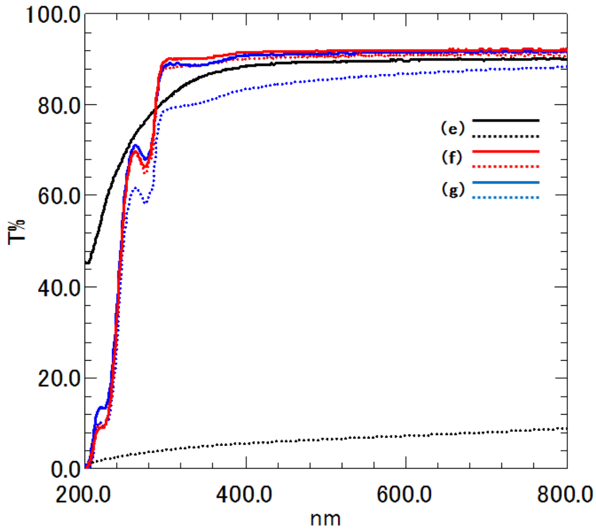

Fig. 6 Transmission Spectra
(Solid line: Total light, Dotted line: Linear)
(e) CNF Film, (f) PP Film, (g) PE Film

Conclusion

In this research, we studied the dispersibility and functional group information of networked CNF samples made of differing materials. By evaluating the dispersiblity of networked CNF solutions diluted to a concentration of 0.1 wt%, we determined that the CNFs are cloudy. It was also found that the transmission of each sample declines differently in the visible range and the ultraviolet range.
The functional groups of each sample were easily determined by measuring dried samples using the ATR method on an FTIR. Measurements suggested that CMC and fermented nanocellulose have a similar structure.
Evaluation of the optical properties of samples in film form was possible by comparing linear transmission and total light transmission. The CNF film we measured had a low linear transmission compared to PP film and PE film, but the total light transmission was at about the same level in the visible range.

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