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Application News

No. S31A

Surface Observation

Evaluation of Fiber Length and Dispersibility of Mono-Dispersed Cellulose Nanofibers

Introduction

Cellulose is a polysaccharide consisting mainly of plant cell walls. Nanocellulose is produced by defibrating cellulose to the nanometer size. Nanocellulose with a diameter of 4 to 100 nm, length of approximately several μm, and high aspect ratio (100 min.) is called cellulose nanofiber (CNF), and is a focus of attention as an advanced new biomass material.

In addition to light weight and high strength, CNF also offers outstanding functions such as a high gas barrier property, adsorption, and transparency. Moreover, because CNF is a plant fiber-derived material, the environmental impacts associated with production and disposal are small. Application to automotive, electronic, packaging and other materials is expected in the future.

The lack of an established method for evaluating the basic physical properties of CNF is one current issue. As basic measurements, establishment of a method for measuring the fiber length and diameter of CNF is demanded, as they are thought to influence the mechanical strength of CNF composites. Application News No. S30[1] introduced a method for measuring the fiber length/diameter by using a scanning probe microscope (SPM).

This research examined the use of a particle size analyzer and UV-visible spectrophotometer in addition to SPM.

The particle size analyzer is used to evaluate a large quantity of fibers rapidly, for example, in quality control applications, and the UV-visible spectrophotometer is used to evaluate the correlation between fiber length and dispersibility with the aim of enhancing the dispersibility of CNF in the matrix.

The following introduces evaluation of fiber length by using the Shimadzu single nano particle size analyzer IG-1000 Plus and scanning probe microscope SPM-9700HT™, and evaluation of dispersibility by using the UV-visible spectrophotometer UV-2600. Fig. 1 shows these instruments.

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Fig. 1 **Single Nano Particle Size Analyzer IG-1000 Plus (Upper Left), Scanning Probe Microscope SPM-9700HT™ (Upper Right), and UV-visible spectrophotometer UV-2600 (Bottom)**

Mono-Dispersed TEMPO-Oxidized CNF

CNF consisting of completely disaggregated fibers kept in a solution in a dispersed, aggregation-free condition is called the mono-dispersed type. The material evaluated here was mono-dispersed TEMPO-oxidized CNF, which was disaggregated to the nanometer size by a combination of a TEMPO-catalyzed oxidation reaction (TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl) and slight mechanical treatment. TEMPO-oxidized CNF has a homogeneous fiber diameter of 3 nm to 4 nm and high dispersibility and transparency in solutions, and is expected to find wide industrial application in paints and composites with resin and rubber.

Evaluation of Fiber Length by Induced Grating Method

Fig. 2 shows TEMPO-oxidized CNF solutions after mechanical treatment for 10 min and 120 min. These samples were adjusted to a concentration of 0.1 wt% and measured with the IG-1000 Plus.

In the induced grating (IG) method, a diffraction grating consisting of particle groups is created in a solution by applying an AC voltage to regularly-arranged electrodes, and then disintegrates and disperses when the AC voltage is discontinued. Large particles disperse slowly, while smaller particles disperse rapidly. This diffusion process is detected as a change in the intensity of diffracted light and is output as peaks showing the particle size distribution. The results of measurement of the particle size distribution are shown in Fig. 3.

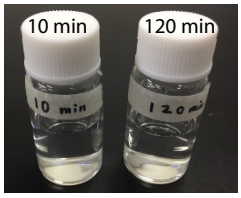


Fig. 2 **TEMPO-Oxidized CNF**

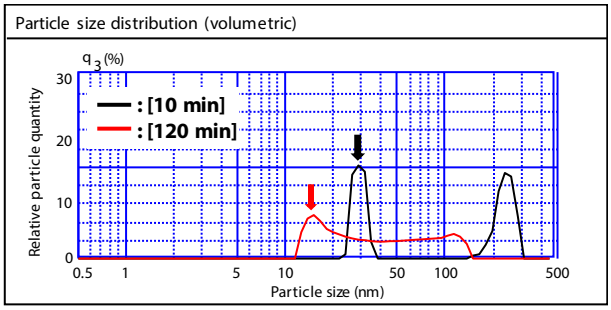


Fig. 3 **Results of Measurement of Particle Size Distribution**

With the sample treated for 10 min, peaks were detected at 30 nm and 250 nm, whereas a broad peak extending from 10 nm to 150 nm was observed with the 120 min sample. As shown by the arrows in Fig. 3, the largest relative particle quantity was around 30 nm with the 10 min sample and around 15 nm with the 120 min sample, indicating that the particle size decreases as the mechanical treatment time is extended. However, there is a possibility that IG may detect not only the fiber length, but also averaged information for the fiber length and fiber diameter as the particle diameter.

Therefore, in order to verify that the results of the IG measurements were in fact the measured fiber length, samples were observed with a nanometer-level resolution SPM.

Evaluation of Fiber Length by SPM

TEMPO-oxidized CNF solutions treated mechanically for 10 min and 120 min were adjusted to a concentration of 0.001 wt%, dripped on cleaved mica and dried, and observed with the SPM-9700HT.

Particle analysis software was used in measurements of the fiber length/diameter. The software first extracts the contours of the CNF from the obtained 3D shape image as particles, and then calculates the feature values of multiple extracted particles, enabling statistical analysis. The dedicated particle analysis software[2] of the SPM-9700HT supports 29 types of feature values, including length and height.

Because CNF has a high aspect ratio and its diameter-to-length ratio is negligibly small, the fiber length was calculated as "circumference/2" using the feature values after extraction.

Fig. 4 shows the shape images, and Fig. 5(a) and (b) show the images of the extraction process and the measurement results for the 10 min sample and 120 min sample, respectively.

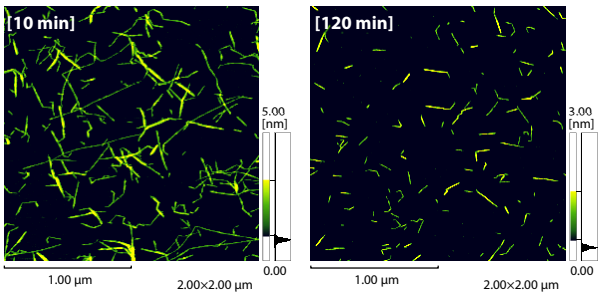
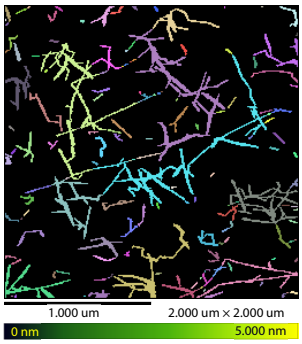
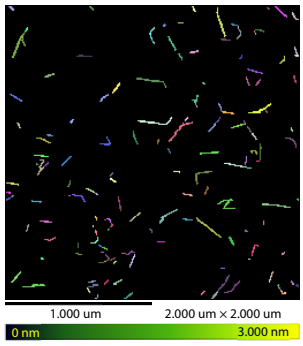


Fig. 4 **Shape Images of CNF**
Left: 10 min, right: 120 min (observation field: 2 µm × 2 µm)



Number of extracted fibers	152
Average circumference	400 nm
Average fiber length (Average circumference/2)	200 nm

Fig. 5 **(a) Image of Extraction Process and Measurement Results of 10 Min Sample**



Number of extracted fibers	157
Average circumference	100 nm
Average fiber length (Average circumference/2)	50 nm

Fig. 6 **(b) Image of Extraction Process and Measurement Results of 120 Min Sample**

The average fiber lengths of the 10 min and 120 min samples were calculated as 200 nm and 50 nm, respectively. Thus, these SPM results showed partial agreement with the IG results, in which peaks were detected at 30 nm and 250 nm with the 10 min sample and in the range of 10-150 nm with the 120 min sample. This suggests that the fiber length can be evaluated by IG. The fact that the IG results showed peaks in a range that did not coincide with the SPM results presumably occurred because the IG results also contained averaged information for the fiber length and diameter.

Evaluation of Dispersibility by UV

To evaluate the dispersibility of CNF in solutions, in-line transmittance was measured with the UV-2600 and total light transmittance was measured by using an integrating sphere as an attachment. In in-line transmittance measurement, only the light that passes straight through the sample is measured, whereas in total transmittance measurement, all the light that passes through the sample is measured, including scattered light. It can be presumed that the sample is transparent if the results of the two methods are the same, and the sample is cloudy if the results are different. The measurement conditions and results are shown in Table 1 and Fig. 6, respectively.

Table 1 Measurement conditions of UV-2600

Attachment	: Integrating sphere ISR-2600 Plus
Wavelength range	: 200 nm to 900 nm
Scan speed	: Medium
Sampling pitch	: 1.0 nm
Photometric value	: Transmittance
Slit diameter	: 2 nm (UV-2600) 5 nm (UV-2600 + ISR-2600 Plus)
Light source switching wavelength	: 323 nm

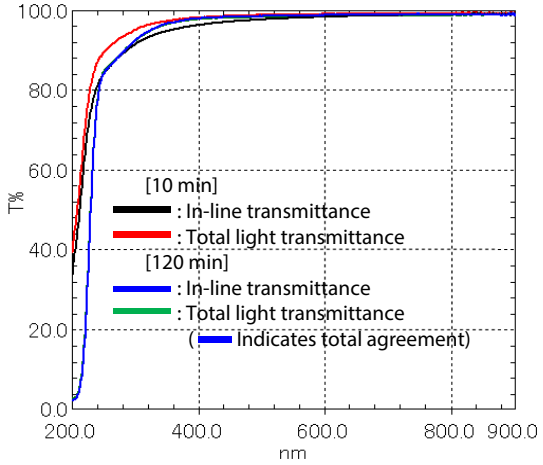


Fig. 7 **Measurement Results**

With the 10 min sample, the transmittance of the UV region (200-400 nm) was higher in the total light transmittance measurement than in the in-line transmittance measurement. From this, it can be inferred that light was scattered as a result of partial aggregation of CNF in solutions. On the other hand, with the 120 min sample, the two transmittance values coincided perfectly, indicating that virtually no CNF aggregation occurred and the dispersibility of the CNF was high.

Conclusion

This study showed that IG enables direct measurement of CNF in solutions, and the results of IG measurements display a good correlation with the results of measurements of the fiber length by SPM. Use of IG as a faster method for evaluating large quantities of fibers can be expected. In particle size analyzers, IG with a measurement range of 0.5 nm to 200 nm is suitable for measurements of mono-dispersed CNF, which have a comparatively short fiber length and high dispersibility in solutions. In the future, it will be necessary to study sample materials other than TEMPO-oxidized CNF.

The dispersibility of CNF could be evaluated by in-line transmittance and total light transmittance by UV. The sample that was mechanically processed for 120 min had a shorter fiber length and showed less aggregation and higher dispersibility than the sample processed for 10 min.

<Acknowledgement>
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Reference

(1) Application News No. S30, Observation of Cellulose Nanofibers and Measurement of Fiber Length/Diameter.

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