SHIMADZU
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Application News

No. X269

X-Ray Analysis

# Measurement of Degree of Crystallinity of Cellulose Nanofiber

## Introduction

Cellulose is a polysaccharide, a major component of plant cell walls. Among the types of nanocellulose produced by defibrating cellulose to the nanometer size, fiber with a width of 4 nm to 100 nm, length on the order of several μm, and a high aspect ratio (100 or more) is called cellulose nanofiber (CNF), and has attracted considerable attention as a leading-edge biomass new material.

CNF is a lightweight, high strength material and possesses various outstanding functions such as a high gas barrier property, absorption, and transparency. Because CNF is plant-derived, it is also a low environmental impact material in production and waste disposal processes. Future applications are expected to include automotive components, electronic materials, and packaging materials.

This application news introduces an example of measurement of the degree of crystallinity of CNF by X-ray diffraction.

Y. Okamoto

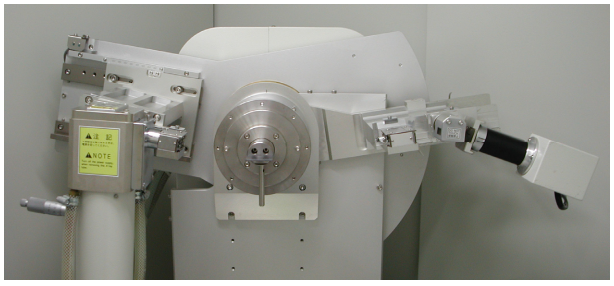

**Fig. 1 XRD-7000 Goniometer**

## Measurement of Degree of Crystallinity

Measurement of the degree of crystallinity is one method for evaluation of the main characteristics that influence the chemical and physical properties of cellulose. For example, strength tends to increase with the degree of crystallinity. X-ray diffraction is one technique for measurement of the degree of crystallinity.

Polymers that contain cellulose are generally divided into crystalline polymers, in which the atoms are arranged regularly, and amorphous polymers, which display low regularity. Patterns having two regions comprising crystalline and amorphous, as shown below, can be obtained by acquiring the X-ray diffraction patterns of these materials.

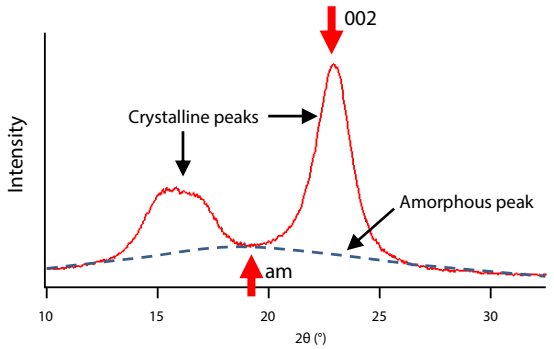


**Fig. 2 Intensity Values Used in Calculation of Degree of Crystallinity of CNF**

The Segal method (1959) is widely used in evaluations of cellulose crystallinity and was also used in this application news. In the Segal method, the index of crystallinity $C_i$ (%) is obtained by the following equation by using $I_{am}$, which is the intensity of the valley between the two crystalline peaks in Fig. 2 and corresponds to the height of the amorphous peak, and $I_{002}$, which is the height of the 002 peak.

$$C_i(\%) = \left(1 - \frac{I_{am}}{I_{002}}\right) \times 100$$

The samples measured here were commercially-available aqueous cellulose dispersions. Five types (A, B, C, D, and E) with different fiber lengths were measured.

## Sample Pretreatment

In order to acquire X-ray diffraction patterns of CNF samples that can be obtained as ordinary aqueous dispersion samples, sheets were prepared by removing water in the following procedure. First, the sample material was diluted by approximately 10 times and homogenized by stirring, and was captured on a filter by suction filtration. To prevent warping of the samples, the sheets were then inserted between two plates and dried by pressurization.

**Fig. 3 Aqueous Cellulose Dispersion (2 wt%)**

The following Fig. 4 shows an example of a sheet (φ 35 mm, 0.11 g) obtained by this pretreatment.

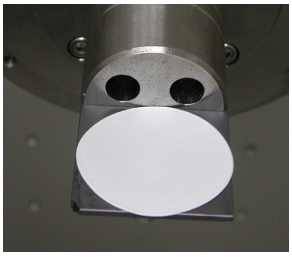

**Fig. 4 Cellulose Sheet (φ 35 mm, 0.11 g) on Zero Background Sample Holder**

## Measurement Conditions

The following table shows the measurement conditions. A zero background sample holder was used to enable X-ray transmission through the cellulose sheets. A Shimadzu XRD-7000 X-ray diffractometer equipped with a sample horizontal goniometer was used in the measurements.

**Table 1 Measurement Conditions**

| | |
|---|---|
| Instrument | XRD-7000 X-ray diffractometer |
| X-ray target | Cu |
| Tube voltage-tube current | 40 kV-40 mA |
| Monochromatization | Counter monochromator |
| Measurement range | 2θ: 10-32.5° |
| Scanning speed | 2°/min |
| Detector | Scintillation detector |
| Measurement mode | Continuous scan |
| Sample holder | Zero background sample holder |

## Measurement Results

Fig. 5 shows the measured patterns of the five types. Table 2 shows the results of calculation of the degree of crystallinity by the Segal equation. Differences could be seen in the degree of crystallinity by sample type.

**Table 2 Results of Degree of Crystallinity**

| Sample | $C_I$ (%) |
|---|---|
| A | 84 |
| B | 86 |
| C | 76 |
| D | 77 |
| E | 82 |

## Conclusion

It was possible to evaluate the degree of crystallinity of CNF by X-ray diffraction. Application of this technique to quality control of parts and materials is expected.

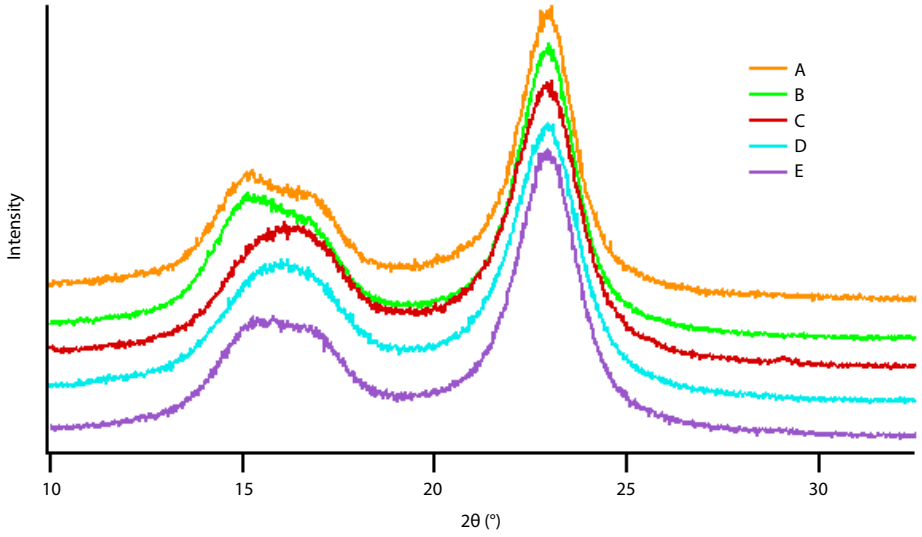


**Fig. 5 Measured Patterns (Intensity Normalized by 002 Plane Peak)**

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