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Application News

No. S54

Scanning Probe Microscope SPM / Atomic Force Microscope AFM

Evaluation of Elastic Modulus of Cellulose Nanofiber

Introduction

Cellulose is a polysaccharide which is the main component of plant cell walls. Among the types of nanocellulose obtained by defibrating cellulose to the nanometer size, fiber with a diameter of approximately several nm to 100 nm is called cellulose nanofiber (CNF). CNF has attracted attention as an advanced biomass-type new material, as it is a plant fiber-derived material with low environmental loads in the production and waste disposal processes, is lightweight and has high strength, and also possesses various excellent functions, including a high gas barrier property, adsorption, and transparency. In the future, application of composites of CNF and automotive materials, electronic materials, and packaging materials is expected. In composite materials, it is important to select CNF of the proper type and strength, as the strength, weight, and other specifications of the composite must be optimized corresponding to the intended application. However, the lack of a fully established method for evaluating the strength of nanometer-order individual CNF fibers in the development and production processes is an issue.

This article introduces an example using measurement of the elastic modulus as a CNF strength evaluation method employing the scanning probe microscope (SPM/AFM).

E. Iida

Nano 3D Mapping™

The SPM/AFM is an instrument which enables high-magnification observation and measurement of the 3-dimensional topography and local physical properties of samples by scanning the sample surface with a minute probe called a cantilever. Fig. 1 shows the appearance of the instrument. In measurement of the elastic modulus in this article, the Nanophysics Evaluation System "Nano 3D Mapping" was used. Nano 3D Mapping makes it possible to map the elastic modulus by acquiring force curves for designated regions/numbers of data points and calculating the elastic modulus at each point. In the force curve technique, the force acting on the cantilever when it is pressed onto a sample surface in the vertical (Z) direction is measured and the viscoelasticity of the sample is analyzed. Details of the force curve technique are presented in Application News No. S26.

Fig. 1 SPM-9700HT™ Scanning Probe Microscope

Elastic Modulus Mapping of CNF

A commercially-available water dispersion type cellulose[*1] was used as the measurement sample. This CNF has been mechanically defibrated to the nanometer size. The sample was adjusted to 0.001 wt%, dripped on a cleaved mica surface and dried, and its elastic modulus was mapped. Fig. 2 shows the results. The measurement region was 1 µm × 1 µm, and the number of data points was 128 × 128. In the topography image in Fig. 2(a), a condition of complex intertwining of large and small diameter fibers can be observed. In the elastic modulus image in (b), the size distribution of the elastic modulus is clear, and it can be understood that the elastic modulus of the CNF is low in comparison with the mica part.

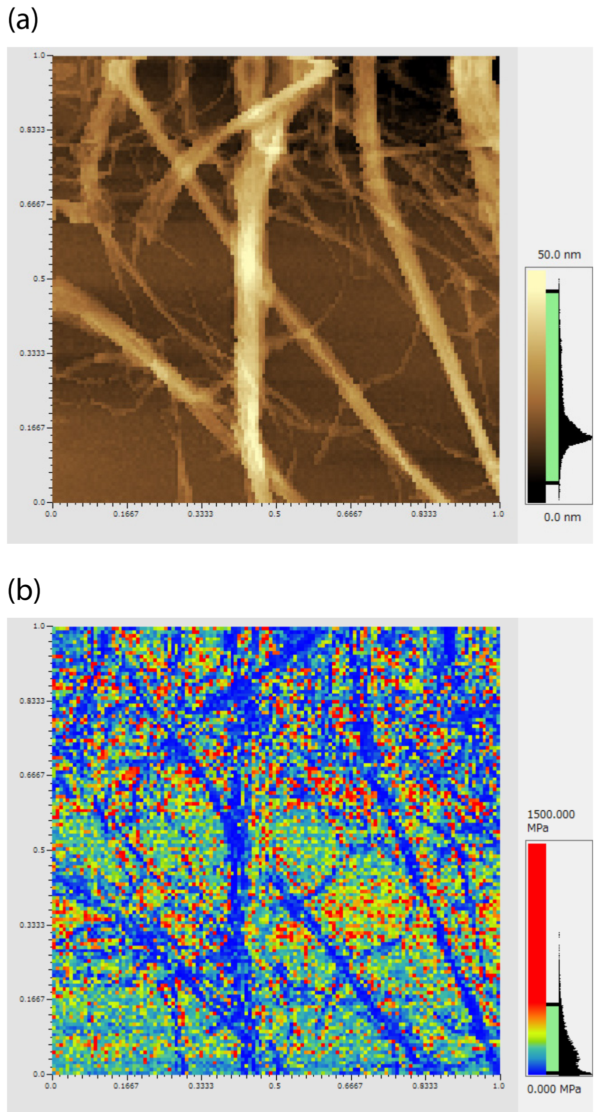

Fig. 2 Elastic Modulus Mapping of CNF
(a) Topography Image, (b) Elastic Modulus Image

Fig. 3 shows a superimposed image of the topography image and elastic modulus image in Fig. 2(a) and (b), and Fig. 4 shows the histogram of the elastic modulus of the CNF and mica parts. The median value of the elastic modulus of the CNF is 364 MPa, while that of the mica part is 1234 MPa, and the difference between the elastic modulus of the two is captured clearly. The variations in the histogram suggest the possibility that contaminants in the sample solution may be present on the sample surface. Because an accurate value can be obtained by a measurement of the elastic modulus of a cylindrical sample conducted by pressing the probe vertically onto the sample at the peak of the side surface, the elastic modulus at the peak of the side surfaces of 11 fibers (Fig. 3, 1 to 11) were used as reference.

Fig. 5 shows a typical force curve (approach line) of the peak of fiber 8, which is a single fiber. Since the deformation of the fiber when pressed was 0.72 nm, or 12 % relative to the 5.9 nm diameter of the fiber, measurement with deformation relatively unaffected by the substrate was possible. The pressing load, which was calculated by "Load = Spring constant of cantilever × Amount of deflection," was approximately 13 nN.

Conclusion

The elastic modulus of a CNF sample was evaluated by elastic modulus mapping using the Shimadzu analysis software "Nano 3D Mapping." It was also possible to capture the deformation of fibers when the probe was pressed onto the individual CNF fibers from their force curves. As a strength evaluation method for CNF, measurement of the elastic modulus by SPM/AFM is recommended, as this method enables measurement of individual single fibers at the nanometer level.

*1 BiNFi-s™ water-dispersed cellulose, manufactured by Sugino Machine Limited.
Product No.: WMa-10002 (Standard)

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BiNFi-s is a trademark of Sugino Machine Limited.

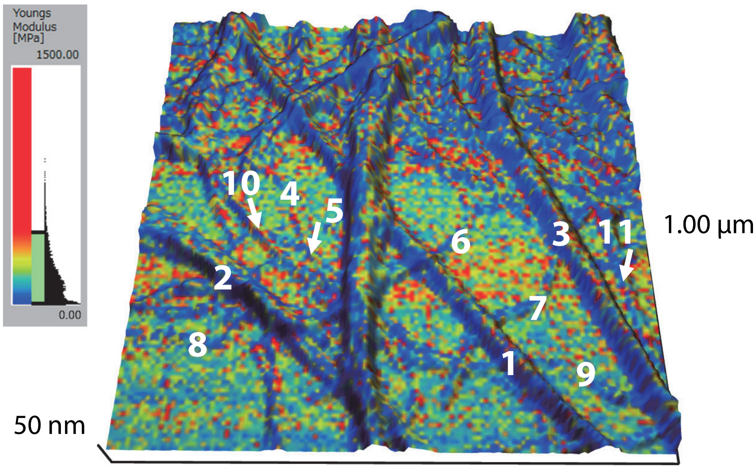


Fig. 3 Superimposed Image of Topography Image and Elastic Modulus Image

Table 1 Diameters of Fibers

Fiber No.	Fiber diameter [nm]
1	26.8
2	24.0
3	23.6
4	4.1
5	5.4
6	4.8
7	3.8
8	5.9
9	6.5
10	8.2
11	4.1

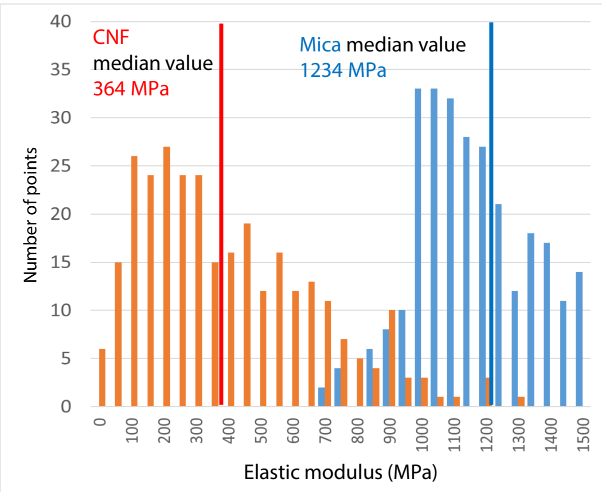
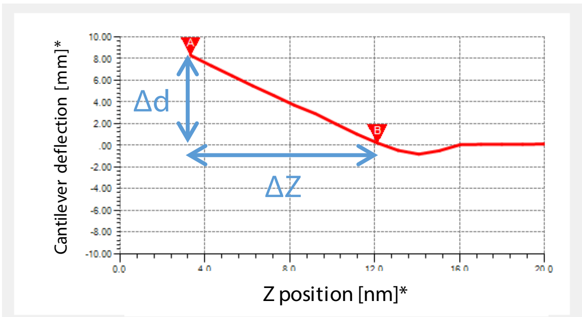


Fig. 4 Histogram of Elastic Modulus of CNF and Mica Parts



[Change in pressing process]
Z position (pressing amount) : ΔZ = 8.80 nm
Cantilever deflection : Δd = 8.08 nm
Sample deformation : ΔZ – Δd = 0.72 nm

* Cantilever probe tip diameter : 7 nm (manufacturer's nominal value)

Fig. 5 Representative Force Curve of Fiber 8

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