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Application News

SPM-Nanoa™ Scanning Probe Microscope (Atomic Force Microscope)

SPM-Nanoa Enables Evaluating Dispersion Status of CNF/Polymer Composite Fibers

Eiji Ida

User Benefits

- The CNF dispersion status on the surface of composite materials can be easily evaluated at the nano-scale level.
- The quantitative modulus of elasticity distribution on the surface of composite materials can be visualized at high resolution.

■ Introduction

Cellulose nanofibers (CNF) are cellulose that has been broken apart into nanometer-sized fibers. CNFs are increasingly being used as a reinforcing material in light-weight high-strength composite materials. To improve the mechanical properties of CNF/polymer composite materials, the CNFs must be dispersed uniformly throughout the polymer material. That dispersion status is evaluated using a scanning probe microscope (SPM [AFM]).

This article describes an example of using an SPM-Nanoa with Nano 3D Mapping™ Fast nano-properties evaluation software to evaluate the CNF dispersion status on the surface of a fiber composite material by qualitatively observing phase images and quantitatively mapping physical property values at high speed.

■ SPM-Nanoa

SPM scan sample surfaces with a microscopic probe (cantilever) to observe or measure three-dimensional shapes or localized physical properties at high magnifications. The SPM-Nanoa is a new SPM that includes an advanced high-sensitivity detection system and automatic viewing functionality as standard features for observing target features more easily, in more detail, and more quickly. It offers powerful assistance for everything from observing shapes in micro areas to measuring their physical properties. The SPM-Nanoa system is shown in Fig. 1. It offers the following three key features:

(1) Automatic Observation:
Adjusts laser beam, adjusts parameter settings during observation, and performs image processing automatically

(2) Extensive Functionality:
Captures sharp images with optical microscopy to the SPM Microscopy Modes

(3) Save Times:
High-throughput observations and fast physical property mapping

This article describes fast physical property mapping, which is one of the features in item (3) above for save times. Nano-3D Mapping Fast software is used to quickly map physical properties. It measures the force acting on the probe (force curve[1)]) as it moves perpendicularly toward and away from the sample surface. It quickly measures the force at each point in the specified area to calculate the modulus of elasticity and adhision forces. The previous model required 24 hours to map physical properties in a 256 × 256 pixel area, but now this only takes about 20 to 60 minutes with the SPM-Nanoa. Due to the tiny loads applied to samples during measurements, it is especially useful for thin films or soft materials with a modulus of elasticity of only about a few kPa to 1 GPa, which are difficult to measure with a nanoindenter.

Fig. 1 SPM-Nanoa™ Scanning Probe Microscope

■ Evaluating Dispersion Status Based on Observing Phase Image

A composite solution was prepared by mixing a 1:2 ratio of CNF in water (1 wt%) with an aqueous solution of polyvinylpyrrolidone (PVP) (30 wt%). This was sprayed onto a silicon substrate by the electrospinning method to observe the CNF/PVP composite fibers. The observation conditions are indicated in Table 1. The electrospinning process applies high pressure to the composite solution in the nozzle to form fibers by ejecting (spinning) them from the nozzle.

Table 1 Observation Conditions

Instrument:	SPM-Nanoa scanning probe microscope
Scanner:	HT scanner (10 µm)
Observation Mode:	Phase mode
Observation Field:	4 µm × 4 µm
Number of Pixels:	512 × 512

A 3D overlay image of the CNF/PVP composite fiber shape and phase images is shown in Fig. 2. The flat areas are the silicon substrate, which appears in contrast to the areas presumably originating from the composite solution. On the left side of the field of view is an orange rectangle that indicates the CNF/PVP composite fiber. The areas with CNF and PVP properties on the fiber surface are differentiated by the contrast between light blue areas (marked with a white arrow) and dark blue areas (marked with black arrows). Using the particle analysis software, the proportional surface area of the dark blue area was calculated to be 22.1 % of the overall composite fiber surface area. Considering that the composite solution contains more PVP than CNF, it can be inferred that the dark blue area is CNF. Thus, the dispersion status can be easily evaluated by observing the phase image.

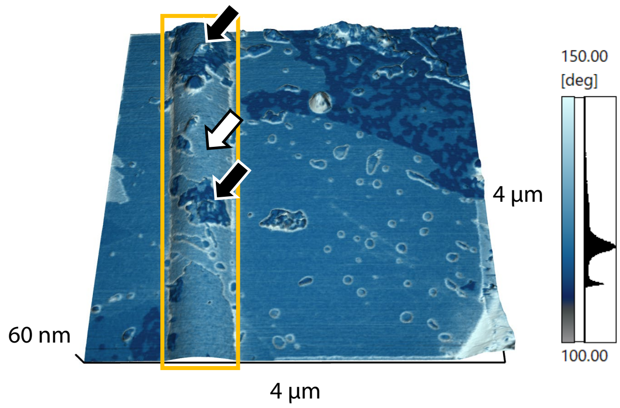

Fig. 2 Shape + Phase Image of the CNF/PVP Composite Materials

■ Evaluating Dispersion Status by Fast Physical Property Mapping

PVP fiber was created by electrospinning using only the PVP water solution. The properties of the CNF/PVP composite fiber used for measurements in the previous section and the PVP fiber above were mapped by fast physical property mapping. The measurement conditions are indicated in Table 2. The JKR 2-point method[2)] was used to calculate the modulus of elasticity.

Table 2 Measurement Conditions

Instrument:	SPM-Nanoa scanning probe microscope
Scanner:	Medium-range scanner (30 µm)
Measurement Mode:	Nano 3D Mapping Fast
Observation Field:	0.3 µm × 0.3 µm (PVP fiber)
	4 µm × 4 µm (CNF/PVP composite fiber)
Number of Pixels:	256 × 256
Sweep Speed:	20 Hz (measurement time: 55 min)
Elastic Modulus Calculation Method:	JKR 2-point method

Fig. 3 shows (a) an optical microscope image of the PVP fiber and (b) a 3D overlay of the shape and modulus of an elasticity image viewed and magnified near the top of a circular cylindrical fiber. Fig. 4 shows (a) an optical microscope image of the CNF/PVP composite fiber and (b) a 3D overlay of the shape and modulus of elasticity images. Fig. 3 (a) shows the linearity of the PVP fiber, whereas (b) shows that it has a very smooth surface. The modulus of elasticity is about 100 MPa. The fact that the modulus of elasticity increases across a portion of the right side of the field of view is presumably due to the curved surface of the PVP fiber.

Fig. 4 (a) shows how the composite fibers are mutually entangled. Just as in Fig. 2, the flat portions in Fig. 4 (b) are the silicon substrate, whereas the contrast between the light and dark blue areas is presumably because of the composite liquid. The orange rectangle near the center of the field indicates the CNF/PVP fiber and clearly shows yellow areas (marked by white arrows) where the modulus of elasticity is higher than other areas of the composite fiber surface.

Because the value for CNF is known to be between 200 and 400 MPa,[3)] it can be inferred that the yellow region with values from 250 to 300 MPa is CNF. Also, using the particle analysis software to calculate the proportional surface area shows that the yellow area accounts for 28.2 % of the overall composite fiber surface area, which corresponds closely with the phase image results.

By using the fast physical properties mapping function to quantitatively measure the modulus of elasticity, both the dispersion status and the modulus of elasticity of CNF can be evaluated easily.

■ Conclusion

With the SPM-Nanoa scanning probe microscope, the fiber dispersion status on composite materials' surface can be evaluated both qualitatively, based on the phase image, and quantitatively, based on the modulus of elasticity measurements. Simply viewing phase images is recommended for quick and easy evaluations of fiber dispersions, whereas fast physical properties mapping is recommended for accurately evaluating the modulus of elasticity in addition to evaluating dispersions. The SPM-Nanoa shows you what you want to see.

Reference
1) Hiroyuki Akinaga et al.: Introduction to Scanning Probe Microscopes, Ohmsha, 76 (2013)
2) K. L. Johnson, K. Kendall, and A. D. Roberts, Proc. R. Soc. Lond. A324, 301-313 (1971).
3) Application News No. S54 Evaluating to Modulus of Elasticity of Cellulose Nanofibers

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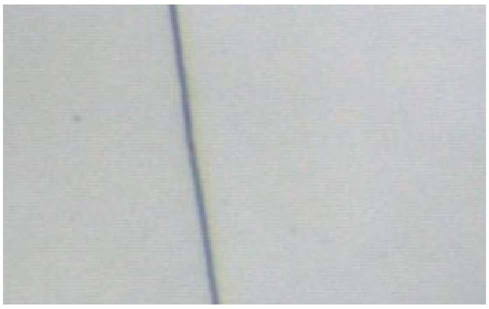
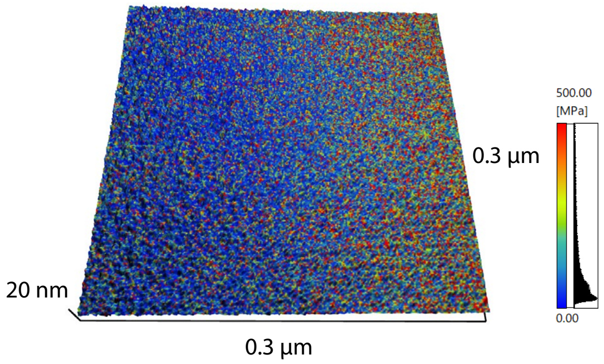
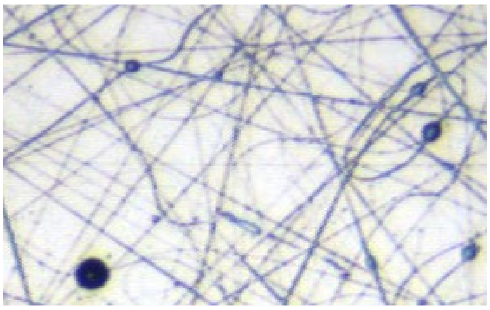


(a) Optical Microscope Image

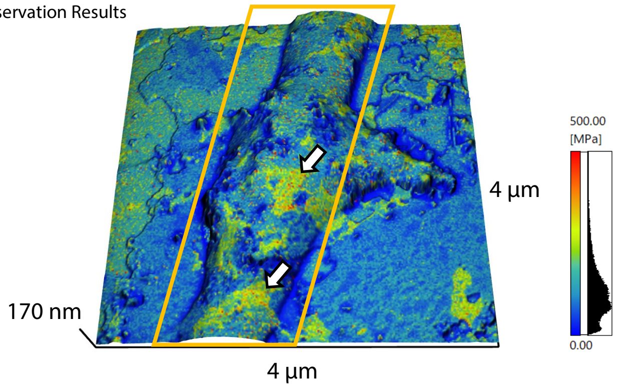


(b) 3D Overlay of Shape and Modulus of Elasticity Images

Fig. 3 PVP Fiber Observation Results



(a) Optical Microscope Image



(b) 3D Overlay of Shape and Modulus of Elasticity Images

Fig. 4 CNF/PVP Composite Fiber Observation Results

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