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Application News

No. S55

Scanning Probe Microscope / Atomic Force Microscope SPM-9700HT™

Quantitative Evaluation of Elastic Modulus of Polymeric Materials: For Material Design/Material Evaluation

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User Benefits

- Enables quantitative evaluation of the elastic modulus of polymeric materials.
- Supports judgments of the validity of measurements performed.

■ Introduction

Polymeric materials include rubber and plastics, and are widely used in industrial products. Remarkable improvement has been achieved in their functions, and techniques which enable quantitative evaluation of the nanoscale structure and viscoelasticity of these materials are demanded.

This article introduces an example in which the elastic modulus of polymeric materials was measured by using the dedicated nanophysics evaluation software Nano 3D Mapping™ of the Shimadzu scanning probe microscope (SPM/AFM), and the quantitativeness of the measurement results was verified.

The samples used in these measurements were provided by Prof. Ken Nakajima of the School of Materials and Chemical Technology, Tokyo Institute of Technology.

■ Nano 3D Mapping

The SPM/AFM is a microscope 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 tiny probe called a cantilever. In this measurement of the elastic modulus (Young's modulus), the Nano 3D Mapping nanophysics evaluation software was used. In Nano 3D Mapping, mapping of the elastic modulus is done by acquiring force curves for a designated region and number of datapoints and calculating the elastic modulus at each point (Fig. 1). Force curve measurement is a technique for analyzing the viscoelasticity of a sample by measuring the force acting on the cantilever when the cantilever is pressed into the sample surface in the vertical (Z) direction. Details can be found in Application News No. S26.

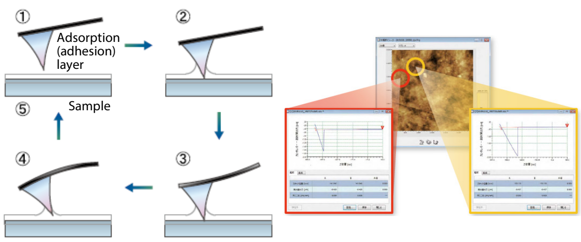

Fig. 1 Nano 3D Mapping™

■ Elastic Modulus Mapping of SBR

The measurement samples were two types of styrene-butadiene rubber (SBR High Tg, SBR Low Tg) with different glass transition temperatures (Tg), which were prepared in advance by Soxhlet extraction. The samples were measured after sectioning with a cryo-ultramicrotome (Leica Microsystems, EM FC7, glass knife; SBR High Tg: –90 ˚C, SBR Low Tg: –120 ˚C). The measurement area was 3 µm x 3 µm, and the number of datapoints was 128 x 128. The JKR 2-point method was used in calculations of the elastic modulus.

Fig. 2 shows the topographic images and elastic modulus images of the two samples, and Fig. 3 shows the elastic modulus histograms. The elastic modulus (median values) of the two samples was SBR High Tg: 2.40 MPa and SBR Low Tg: 1.41 MPa. These results were also in good agreement with the results of measurements in prior research (Fig. 4).

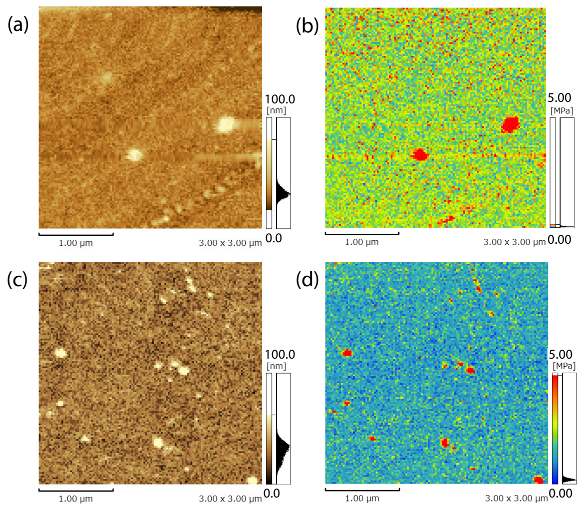

Fig. 2 Results of Elastic Modulus Mapping of SBR Samples
SBR High Tg: (a) Topographic Image, (b) Elastic Modulus Image,
SBR Low Tg: (c) Topographic Image, (d) Elastic Modulus Image

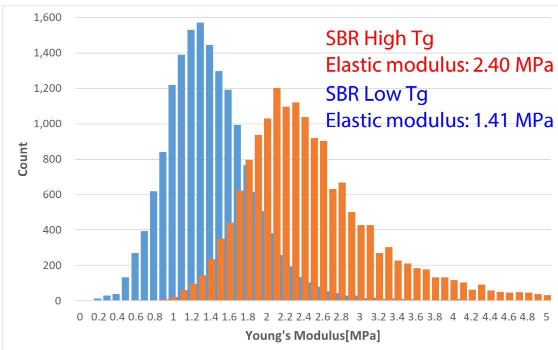

Fig. 3 Elastic Modulus Histograms

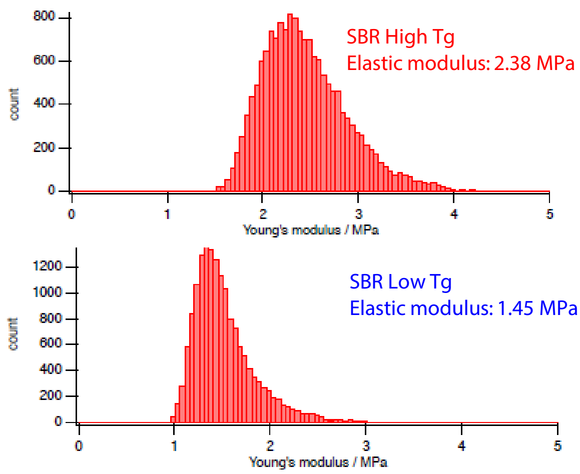

Fig. 4 Elastic Modulus Histograms (Prior Research)

■ Improvement of Elastic Modulus Evaluation Accuracy

The cantilever used in this experiment was an OMCL-AC240TS (Olympus Corporation). However, the shape of the cantilever probe tip may change in some cases, depending on the sample material and the circumstances of the measurement. The accuracy of the measured elastic modulus is improved by accurately determining the shape of the probe tip and reflecting this in the analysis. Therefore, the measured value of the spring constant was obtained by the Sader method [1], and the probe tip radius was obtained by observing a commercial sample for tip shape evaluation after the mapping measurements of the two SBR samples and calculating the tip radius from the acquired topographic images (Table 1).

Table 1 Measurement Values of Cantilever

Sample material	SBR High Tg	SBR Low Tg
Spring constant k [N/m]	1.86	1.92
Probe tip radius R [nm]	10.0	15.3

■ Validation of Measured Values of Elastic Modulus

Fig. 5 shows representative force curves in these measurements, and Fig. 6 shows the load-displacement curves obtained from the force curves. In Fig. 5, the adhesive force of the release curves (parts indicated by the arrows) influences the difference in the elastic modulus.

The JKR theoretical curve in Fig. 6 can be obtained by calculating the load and sample displacement from parameters such as the spring constant and probe tip radius at the time of the measurement. The validity of the measurement value of the elastic modulus calculated by the JKR 2-point method can be judged from the coincidence between the measured curve and the JKR theoretical curve. In Fig. 6, the measured release curves and JKR theoretical curves show good agreement in both cases, indicating that the values of the elastic modulus calculated by the JKR 2-point method is valid. It can also be understood that the analysis results obtained in prior research shown in Fig. 7 are in good agreement with our results (Fig.6).

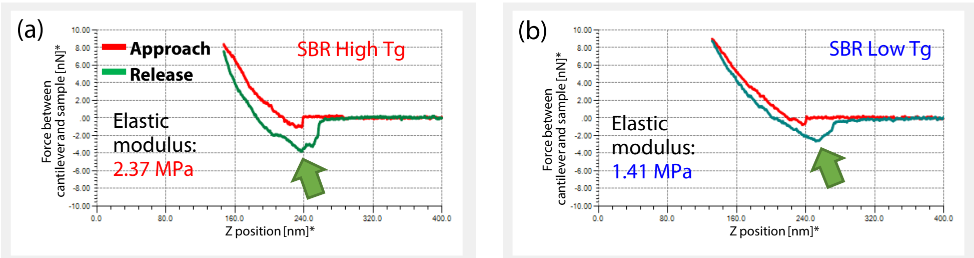

Fig. 5 Representative Force Curves
(a) SBR High Tg, (b) SBR Low Tg

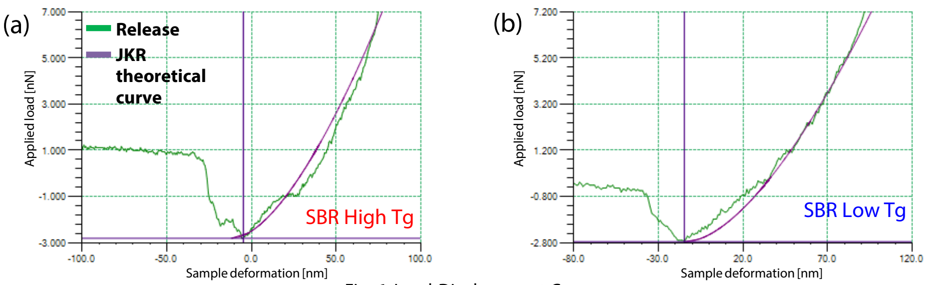

Fig. 6 Load-Displacement Curves
(a) SBR High Tg, (b) SBR Low Tg

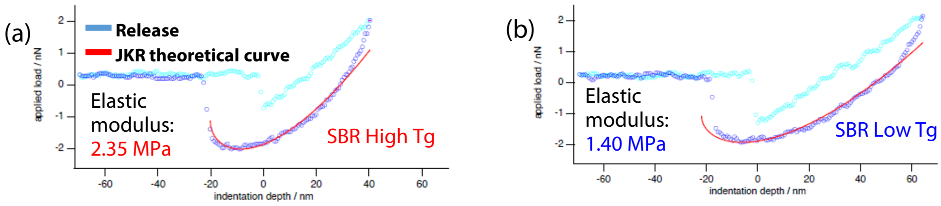

Fig. 7 Load-Displacement Curves (Prior Research)
(a) SBR High Tg, (b) SBR Low Tg

■ Conclusion

Quantitative evaluation of the elastic modulus of polymeric materials was possible by using the Shimadzu Nano 3D Mapping nanophysics evaluation software. The validity of the measurement values obtained by the JKR 2-point method was confirmed by agreement with the JKR theoretical curve. The results of this research were also the same as those of prior research.

The Shimadzu SPM/AFM is an effective tool for evaluation of the local elastic modulus of polymeric materials.

<Reference>
(1) J.E. Sader, J.W.M. Chon, and P. Mulvaney, Rev. Sci. Instrum. 70, 3967 (1999)

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