Focus on Microscopy—Elasticity Imaging: New Views for Polymers, Proteins, Ceramics, and Advanced Materials

by Barbara Foster

Viscoelasticity has taken on new importance in the rapidly developing world of polymers, thin films, nanotechnology, and advanced materials. Various atomic force microscopy (AFM) modes such as phase, force modulation, pulsed force, and dynamic force modes have produced images based on this property, but quantitation has been a challenge, particularly in the direct measurement of Young's modulus. Atomic force acoustic microscopy (AFAM), a new member of the scanning probe microscopy (SPM) family, provides an easy-to-use solution. It solves several long-standing problems, including measurement of elastic properties of thin films unattainable by other methods and the ability to differentiate one polymer phase from another.

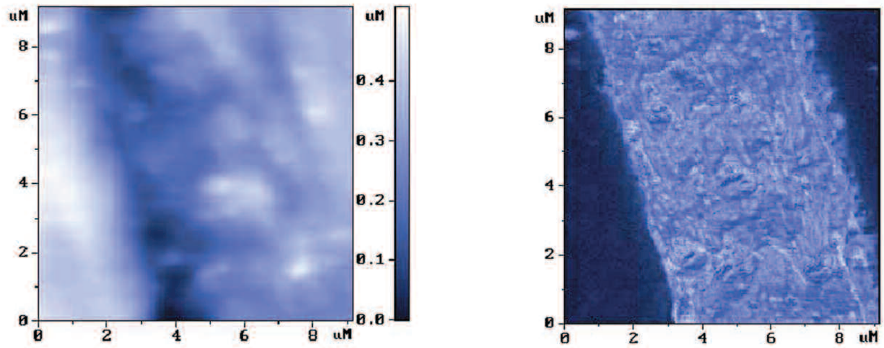

Figure 1 Differentiating polymer domains. Left: topography image. Right: AFAM detail in HDPE domain. Dark area = LDPE. Brigh area = HDPE. (Sample courtesy of Dr. Joachim Loos, TU/Eindhoven, The Netherlands. Image courtesy of NT-MDT.)

The value of this technique has already been demonstrated by a few pioneering groups who have successfully imaged the elastic properties of a wide array of materials ranging from conventional polymers[1] and thin films[2] to more exotic ceramic nanofiber composites,[3] polysilicon microelectromechanical systems (MEMs),[4] and multidomain piezoelectric materials.[5] Until recently, AFAM was purely a research device. It is now commercially available on a line of SPMs from NT-MDT (Zelenograd, Russia).[6]

Operation

Atomic force acoustic microscopy is based on the work of Prof. Walter Arnold of the Fraunhofer Institute for Nondestructive Testing (Saarbrücken, Germany).[7] Hirsekorn et al. best describe the differences between conventional AFM and AFAM.[8] In conventional AFM, the cantilever oscillates while the surface is scanned, resulting in force interactions between the tip and the sample. In AFAM, an acoustic modulator is placed below the sample, creating both vertical and horizontal acoustic vibrations. The system uses the resulting flexion and torsion of the cantilever to produce images based on the sample's local elastic, adhesive, and frictional properties. This type of analysis is called contact resonance spectroscopy and simultaneously produces topography and AFAM images.

The NT-MDT Web site uses animation to explain both the actual experiment and the derivation of the image and the measurements.[9] The tip is placed near the surface of the sample, and the sample is acoustically stimulated by a piezoelectric transducer. A four-sector photodiode coupled to a lock-in amplifier analyzes the cantilever motion. That motion depends on the stiffness of the tip–sample contact and on the contact radius, both of which are functions of Young's modulus of the sample and the tip, the tip radius, the load exerted by the tip, and the geometry of the surface. Applying Hertz's model of a clamped spring generates the contact stiffness, k*. By measuring k* for a reference sample for then the unknown, both Young's modulus and the indentation modulus can be calculated. Vertical and lateral elastic forces, adhesion, and friction are nonlinear with distance. However, if the tip-to-sample vibration is kept sufficiently small, the relationship fits a linear model, and Young's modulus can be calculated with a resolution of a few tens of nanometers.

continued

Distinguishing polymeric phases and fine structure

As illustrated in Figure 1, AFAM solves the longstanding problem of differentiating one polymer domain from another. A sample was made by clamping together alternating layers of high-density and low-density polyethylene (HDPE and LDPE), and then cross-sectioning them. The topography AFM image on the left fails to reveal much about the sample. However, because HDPE is stiffer than LDPE, it produces a brighter AFAM signal, clearly elucidating not only the difference between one domain and the other, but fine detail within the HDPE domain.

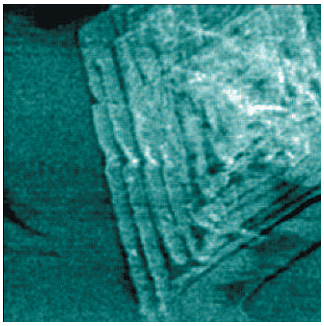

Figure 2 Fine structure in polyethylene single crystals. (Image courtesy of NT-MDT.) Scan area: 7 × 7 μm.

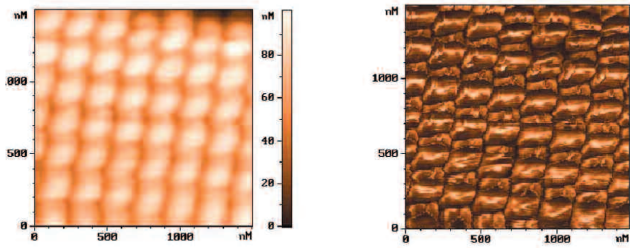

Figure 3 Comparison of conventional AFM topography image (left) and enhanced definition of AFAM (right). Object: permalloy nanoparticles on niobium substrate. (Image courtesy of Fraunhofer Institute for Nondestructive Testing.)

AFAM can also be used to image other polymeric fine structures. Figure 2 shows the delicate detail of a polyethylene single crystal. When coupled with a thermal stage, the AFAM can be used to track changes on heating and cooling.

AFAM can operate either in air or in liquid. Since proteins are large biopolymers, it is not surprising that this technique has also been applied to the analysis of composite protein films.

New applications for ceramics and advanced materials

The new technique has been used for the analysis of common nonpolymeric materials such as clay. Prasad et al.[10] reported that the presence of clay minerals, especially those with grains smaller than 2 μm, "alter the elastic and plastic behavior of materials significantly . . . As pore-filling materials, they block hydraulic pathways and decrease permeability. In the presence of water, [they] can swell and cause considerable formation damage." AFAM provides quantitation that was previously inaccessible.

The technique also reveals information for exotic advanced materials such as nanoparticles and carbon nanotubes. While it still faces challenges when the substrate is very soft and sticky, AFAM provides high-definition images for firmer materials such as the submicron permalloy nanoparticles shown in Figure 3.

Summary

AFAM is a powerful new technique for investigating the surface elasticity of soft, as well as very stiff materials where other AFM techniques such as force modulation have failed. Easily added to existing atomic force microscopes, its images improve contrast and reveal detail unavailable through conventional phase or topography images and, unlike nanoindentation, it is much less destructive. Furthermore, it provides direct, quantitative measurement of both the indentation and Young's modulus on a nanoscale.

References

1. Efimov AE, Saunin SA. Atomic force acoustic microscopy as a tool for polymer elasticity analysis. Proceedings SPM 2002, Lancaster University, Lancaster, U.K.:79.
2. Hurley DC, Shen K, Jennett NM, Turner JA. Atomic force acoustic microscopy methods to determine thin-film elastic properties. J App Phys Aug 15, 2003; 94(4):2347–54.
3. Dzenis Y, Feng R, Larsen G, Turner J, Zeng X. Manufacturing of novel continuous nanocrystalline ceramic nanofibers with superior mechanical properties. NSF Nanoscale Science and Engineering Grantees Conference, Arlington, VA, Dec 16–18, 2003.
4. Nilchiani R. MS thesis. Atomic force acoustic microscopy for materials characterization of polysilicon microelectromechanical systems. University of Nebraska/Lincoln, Oct 15, 2001. Abstract downloaded from www.unl.edu/emhome/seminars/2001-02/Rnilchiani.html.
5. Arnold W. Quantitative contact spectroscopy by atomic-force acoustic microscopy. University of Nebraska/Lincoln, seminar series, Sept 17, 2001. Abstract downloaded from www.unl.edu/emhome/seminars/2001-02/WArnold.html.
6. www.nt-america.com.
7. U.S patent 5675075 and U.S. patent 5852233.
8. Hirsekorn S, Kopycinska-Muller M, Rabe U, Reinstadtler M, Caron A, Arnold W. Quantitative imaging of elastic, piezoelectric, and frictional properties of material surfaces using atomic force acoustic microscopy. Proceedings W.C.U. 2003, Paris, Sept 2003:325–8.
9. www.nt-mdt.com.
10. Prasad M, Kopycinska M, Rabe U, Arnold W. Measurement of Young's modulus of clay minerals using atomic force acoustic microscopy. Geophys Res Ltrs Apr 2002; 29(8).

Ms. Foster is President, Microscopy/Marketing & Education, Inc., 126 Paridon St., Ste. 102, Springfield, MA 01119, U.S.A.; tel.: 413-746-6931; fax: 413-746-9311; e-mail: bfoster@mme1.com. The author welcomes comments on her articles.