MRS CORPORATE PARTNER

WHITE PAPER

Mapping nanomechanical properties of polymers with AFM

ASYLUM RESEARCH

The atomic force microscope (AFM) is an invaluable instrument for characterizing polymer materials at small length scales.[1–4] Its spatial resolution enables visualization of submicrometer and subnanometer polymer morphology as well as mapping nanomechanical properties. Mechanical properties of polymers are an important consideration in applications ranging from food packaging to flexible electronics. To optimize mechanical performance, one or more phase-separated components or fillers may be included in polymers. The length scales of such inclusions demand mechanical-property measurements with nanoscale spatial resolution. AFM offers a wide range of techniques for investigating nanomechanical properties, ranging from simple qualitative techniques to more sophisticated quantitative methods. In many cases, these techniques are complementary and can be used together to learn more about polymer samples.

Tapping mode has been and still is the most widely used scanning technique, whereby the AFM tip is oscillated above the surface, avoiding sample damage.[5] When a phase shift in tapping mode was discovered to yield material property contrast, phase imaging became a source of much excitement beginning in the late 1990s. Since then, phase imaging has become a valuable technique for polymer characterization, where it can often resolve fine structural details and discriminate between various material components. Interpretation is not always straightforward, however, because the phase response depends on how the material stores elastic energy and dissipates viscous energy (i.e., the loss tangent) as well as other dissipative forces. Notwithstanding these challenges, phase imaging remains a simple and popular means of obtaining qualitative material property contrast (Figure 1).

Bimodal imaging (Dual AC)* is another option for qualitative mapping of material property variations. It operates the same as the regular tapping mode with phase imaging, except that an additional resonance mode of the cantilever is driven simultaneously with operation at the first mode. The amplitude and phase response at this second mode is measured along with topography and phase from the first mode. Like regular phase imaging, interpretation of the results is not always easy, but the technique can be useful for obtaining contrast in cases where phase imaging does not provide it, as shown in Figure 2.

Most recently, AM-FM Viscoelastic Mapping Mode* has been adopted as the only mode compatible with small cantilevers for fast scanning and is especially well suited for polymers. Similar to bimodal imaging, it uses tapping mode operating simultaneously at two different cantilever mode frequencies. However, the frequency of the second mode is tracked and related to the sample stiffness while the amplitude and phase of the first mode is related to the sample loss tangent. This enables unambiguous, quantitative mapping of elastic storage

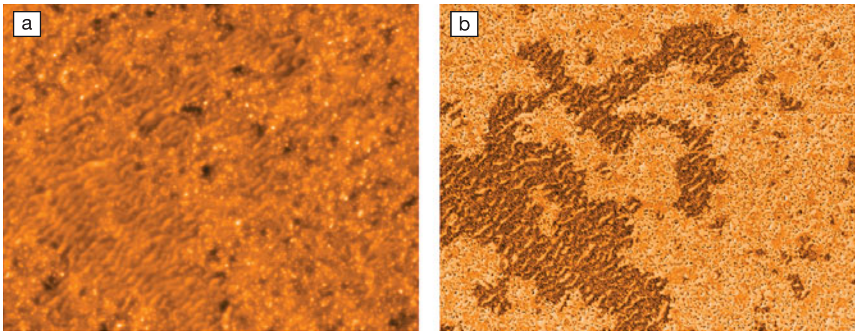

Figure 1. (a) Tapping mode topography and (b) phase of semiconducting polymer blends EVA/EPP carbon black.[7]

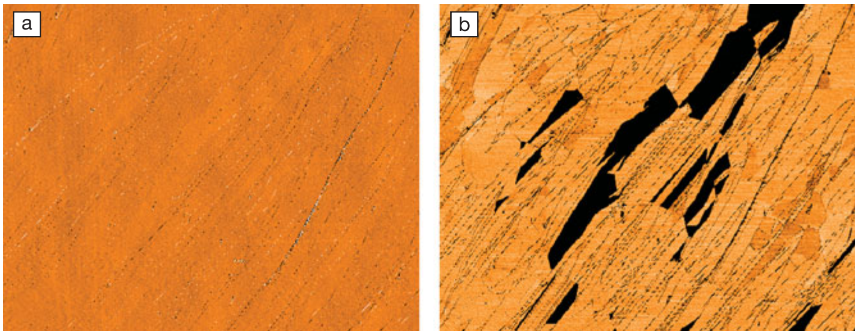

Figure 2. Phase image of (a) graphite and (b) bimodal second mode amplitude, 30-μm scan.[8]

Asylum Research
The MRS Corporate Partner Program supports the Materials Research Society Foundation.

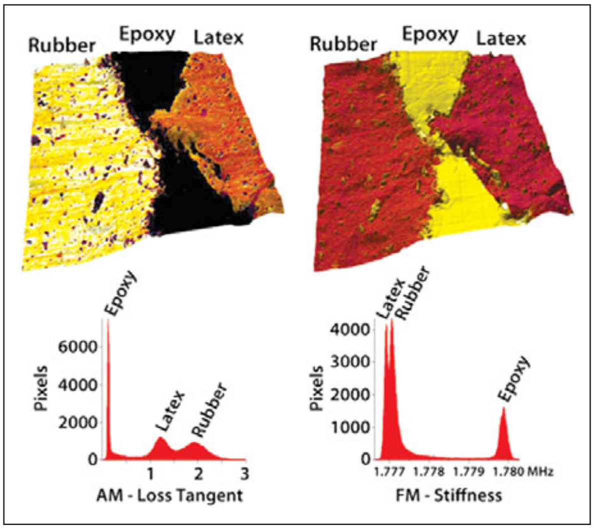

Figure 3. AM-FM viscoelastic mapping mode images and histograms of (left) loss tangent and (right) second mode frequency overlaid on topography for a rubber-epoxy-latex bonded polymer. Different components are clearly distinguished by the AM loss tangent of viscoelastic damping and resolved by the FM frequency, which is proportional to elastic.[7]

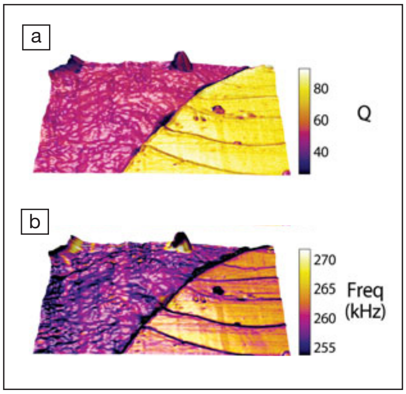

Figure 5. Contact resonance image of the cryotomed surface of an 80/20 PP-PS blend, where (a) shows the calculated quality factor overlaid on topography, and (b) is the contact resonance f_0 on topography. The PP and PS regions display less contrast in f_0 consistent with a small difference in their bulk storage moduli, while the higher contrast in Q between PP and PS is consistent with a large difference in their bulk loss moduli. Adapted with permission from Reference 6. © 2011 Institute of Physics.

modulus and viscoelastic loss modulus or loss tangent, all with the usual speed and nondestructive nature of tapping mode. AM-FM Mode's huge range of applicability— from less than 1 MPa to more than 100 GPa—means it can be used on virtually any polymer. An example of AM-FM mapping on a multicomponent polymer assembly is shown in Figure 3.

Force curves are a well-known method to measure elastic modulus. The technique is well suited for point measurements but frustratingly slow for mapping; at a typical rate of 1 second per pixel, a 256 × 256 array takes over 18 hours to acquire. Fast Force Mapping Mode solves this problem by acquiring force curves at pixel rates up to 300 Hz. A 256 × 256 image of complete deflection versus Z sensor force curves takes less than 10 minutes to capture with Fast Force Mapping, with no missing curves or hidden data manipulation. Figure 4 shows an example of Fast Force Mapping on a phase-separated polystyrene (PS)-polycaprolactone (PCL) blend.

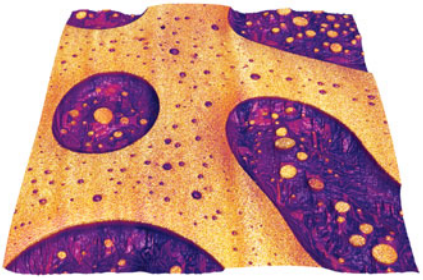

Figure 4. Elastic modulus mapping overlaid on topography for a PS-PCL blend. As expected from bulk literature values, PS regions (yellow) have a higher modulus (approximately 3 GPa) than PCL regions (purple, approximately 350 MPa). The biodegradable nature of the PS is valuable in the development of new bioblend materials.[7]

Contact Resonance Viscoelastic Mapping Mode* measures elastic storage modulus and viscoelastic loss modulus on relatively stiff polymers (modulus approximately 1 GPa or higher). The Contact Resonance Mode exploits the sensitivity of the cantilever resonance to small changes in sample mechanical properties when the tip is in contact. Like all of the techniques mentioned here, Contact Resonance can be operated with either minimal calibration for fast, qualitative mapping, or it can be calibrated with a material of known properties for quantitative results. Figure 5 shows a Contact Resonance image of a PP-PS blend.

Today, many more AFM nanomechanical mapping techniques are available to researchers than ever before. There is no one technique that can be called "the best," and each technique has its strong suit depending upon the sample being measured. Ultimately, researchers can now do more experiments with this large variety of techniques and can correlate their findings, resulting in more accurate and quantitative results.

*All techniques and images described in this note are exclusively available on Oxford Instruments Asylum Research Cypher and MFP-3D AFMs. *Denotes techniques patented/patent pending by Oxford Instruments Asylum Research. Portions of the text were taken from "AFM Applications in Polymer Science and Engineering." The PDF can be downloaded at www.oxford-instruments.com/afm-polymers. Asylum Research also has several Webinars on this topic. They can be viewed at www.oxford-instruments.com/afm-webinars.*

References

1. P. Samori, M. Surin, V. Palermo, R. Lazzaroni, P. Leclere, *Phys. Chem. Chem. Phys.* **8**, 3927 (2006).
2. L. Sawyer, D. Grubb, G. Meyer, *Polymer Microscopy*, 3rd ed. (Springer, New York, 2008).
3. M.E. McConney, S. Singamaneni, V.V. Tsukruk, *Polym. Rev.* **50**, 235 (2010).
4. H. Schönherr, G.J. Vancso, *Scanning Force Microscopy of Polymers* (Springer Laboratory, Heidelberg, 2010).
5. A. Payman, D. Martin-Jimenez, R. Garcia, *Nanotechnology* **26**, 18 (2015).
6. A. Gannepalli, D.G. Yablon, A.H. Tsou, R. Proksch, *Nanotechnology* **22**, 355705 (2011).
7. "AFM Applications in Polymer Science and Engineering," Oxford Instruments Asylum Research Application Note.
8. "Bimodal Dual AC™ Imaging," Oxford Instruments Asylum Research Application Note. □

Sheraton Society Hill Hotel
Philadelphia, Pennsylvania, USA

May 8-12, 2016

SIAM Conference on

Mathematical Aspects of Materials Science

MRS® ENDORSED MEETINGS

ORGANIZING COMMITTEE

Peter Smereka, Co-Chair
University of Michigan, USA

David Srolovitz, Co-Chair
University of Pennsylvania, USA

Aleksandar Donev, *Courant Institute of Mathematical Sciences, New York University, USA*
Dimiry Golovaty, *University of Akron, USA*
Robert P. Lipton, *Louisiana State University, USA*
Kristin Persson, *University of California, Berkeley and Lawrence Berkeley National Laboratory, USA*
Ellad B. Tadmor, *University of Minnesota, USA*
Florian Theil, *The University of Warwick, United Kingdom*
Axel Voigt, *Technische Universität Dresden, Germany*
Peter W. Voorhees, *Northwestern University, USA*
Jonathan Weare, *The University of Chicago, USA*
Yang Xiang, *The Hong Kong University of Science and Technology, Hong Kong*
Pingwen Zhang, *Peking University, China*
Dana Zöllner, *University of Magdeburg, Germany*

FOCUS

The 2016 SIAM Conference on Mathematical Aspects of Materials Science covers all areas of the science and engineering of materials, including all electronic structure, atomistic simulation, microstructures, continuum descriptions, thermodynamics, kinetics, analytical methods, stochastic methods, and computational methods. Of particular interest are innovative mathematical and computational approaches to materials science and engineering, including those approaches and questions that are arising within the Materials Genome.

Instructions on how to participate and more at

http://www.siam.org/meetings/ms16/

siam®

Society for Industrial and Applied Mathematics
3600 Market Street, 6th Floor
Philadelphia, PA 19104-2688 USA
Telephone: 800-447-7426 (USA & Canada)
1-215-382-9800 (Worldwide)
meetings@siam.org