The atomic force microscope (AFM) is an invaluable instrument for characterizing polymer materials at small length scales. 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. 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
The development of new bioblend materials is valuable in degradable nature of the PS is valuable in (approximately 3 GPa) than PCL regions (yellow) have a higher modulus expected from bulk literature values, PS on topography for a PS-PCL blend. As an example of AM-FM mapping on a multicomponent polymer assembly is shown in Figure 3.

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.

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.

Force curves are a well-known method to measure elastic modulus. The 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.

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.

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 f₀ on topography. The PP and PS regions display less 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.

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