AM-FM Viscoelastic mapping mode

ASYLUM RESEARCH

Atomic force microscopy (AFM) is mainly known for its ability to measure high resolution 3D topographical images. Due to its inherent spatial resolution and force sensitivity, AFM can also measure a myriad of nanomechanical properties such as hardness, adhesion and viscoelasticity. Nanoscale mechanical properties impact the behavior of many materials and are useful in both theoretical understanding and commercial deployment of such materials. However, the diversity of material properties limits any single AFM technique from providing the most relevant and accurate data for every application. Asylum Research provides multiple techniques to measure a broad spectrum of nanomechanical properties, providing flexibility for different samples and greater insight through comparison of results. Here, we discuss the nanomechanical technique known as AM-FM Viscoelastic mapping mode.

Tapping mode-based nanomechanical imaging

Force curve acquisition is a well established method to explore nanomechanical properties of samples. Nanomechanical imaging was initially introduced in the form of force curve arrays also known as force volume or force maps and was followed by the introduction of Fast Force Mapping (FFM). Unfortunately, force curve acquisition is inherently slower than tapping mode imaging based on the fact that a force curve needs to be collected for every single image pixel. It was only with the emergence of tapping mode-based nanomechanical mapping that sample characterization became as quick and simple as acquiring a topography image. Tapping mode is easy to set up, gentle on samples, fast and provides the highest resolution images. Combined with the capability of probing nanomechanical properties of the sample, AM-FM viscoelastic mapping mode is the fastest way to obtain quantitative nanomechanical data. See table 2 for summary of differentiating properties for tapping mode-based (AM-FM) and force curve-based (FFM) modes.

How AM-FM works

AM-FM viscoelastic mapping mode is a tapping mode-based imaging technique. In contrast to regular tapping mode, during AM-FM imaging, two different vibrational modes (resonance frequencies) of the cantilever are excited simultaneously. The first resonance is operated in amplitude modulation (AM) and the second frequency is operated in frequency modulation (FM), hence the name AM-FM viscoelastic imaging mode. Figure 1 shows a schematic representation of AM-FM imaging of a multilayer polymer film.

Specifically, the first resonance frequency of the cantilever is driven with a large amplitude (A1), while the second resonance frequency is simultaneously driven with a small amplitude (A2). The cantilever drive signal (blue), which is the sum of the two excitations, is compared with the cantilever detection signal (green) after the tip interacts with the sample. Just like regular tapping mode, the topography feedback loop uses A1 to track surface topography and the sample's viscous response in the form of loss tangent measurement.

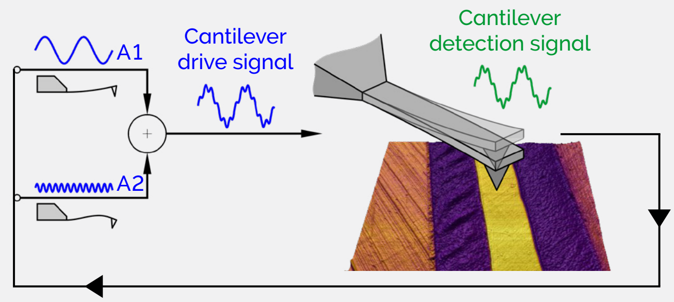

Figure 1: Schematic representation of AM-FM imaging of multilayer polymer film composed of from left to right: polyethylene terephthalate (PET), polyethylene (PE), ethyl vinyl alcohol (EVOH), PE and polypropylene (PP).

Another feedback loop maintains the higher frequency A2 oscillation constant. Finally, the phase feedback loop tracks the changes in frequency of the second resonance mode. The observed frequency shifts are related to the sample's elastic properties through modeling and reference samples.[1]

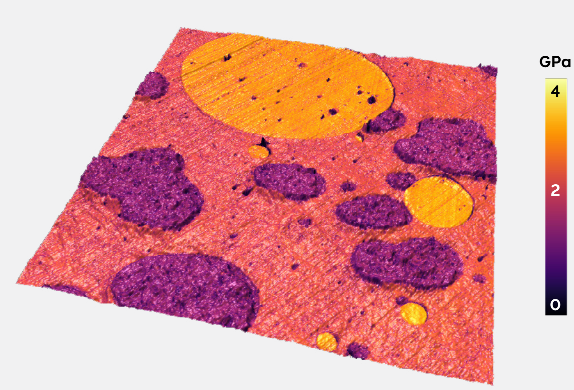

Figure 2: Polymer blend sample composed of polyethylene (darkest), polypropylene (matrix) and polystyrene (brightest). The 3D overlay of elastic modulus on topography. Image size: 25 um.

Characterization of polymers

AM-FM provides both elastic and viscous response of materials which makes it particularly well suited for characterization of polymers such as thin film polymer coatings, multilayer polymer films, and molecular lever features of polymer samples.

Additionally, since AM-FM mode is based on tapping mode, images are acquired quickly, at very high resolution and the low indentation depth preserves thin and delicate samples during imaging. For example, constituents of a polymer blend sample, such as the one shown in figure 2, can be differentiated and their distribution assessed in the time it takes to acquire one tapping mode image.

Highest resolution imaging

Tapping mode is known to provide the highest resolution AFM data. The advantage of using tapping mode in the form of AM-FM mode is that nanomechanical properties and topography are obtained simultaneously. AM-FM nanomechanical data, such as modulus or tip-sample interaction stiffness, can be particularly useful for differentiation of crystalline (higher stiffness) versus amorphous (lower stiffness) regions of polymer samples and thus provide comprehensive sample characterization. Molecular level images of various polymers are shown in figure 3.

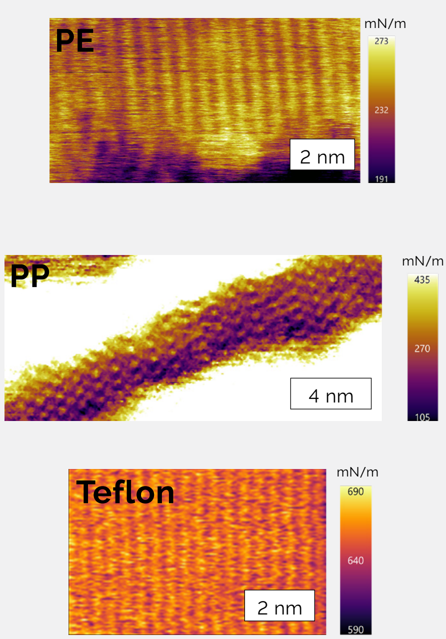

Figure 3: Molecular level tip-sample stiffness images of polyethylene (PE) chains, polypropylene (PP) and Teflon.

Viscous response - Loss Tangent (tan δ)

For many polymeric materials, loss tangent is a very sensitive probe of phase transitions, which can relate to performance-critical properties such as toughness and impact resistance. When measured on bulk samples with traditional techniques, loss tangent (also known as tan δ) typically ranges from less than 0.001 for metals and ceramics to more than 1 for elastomers and biological materials. In AFM experiments, loss tangent is measured as the ratio of dissipated energy to stored energy of the tip-sample interaction. Practically, these values are determined from the amplitude and phase AFM data and have the advantage of being independent of the tip-sample contact area.[2] AFM-measured loss tangent is useful in assessing viscoelastic behavior of samples and adds valuable information for a more complete materials characterization as shown in figure 4.

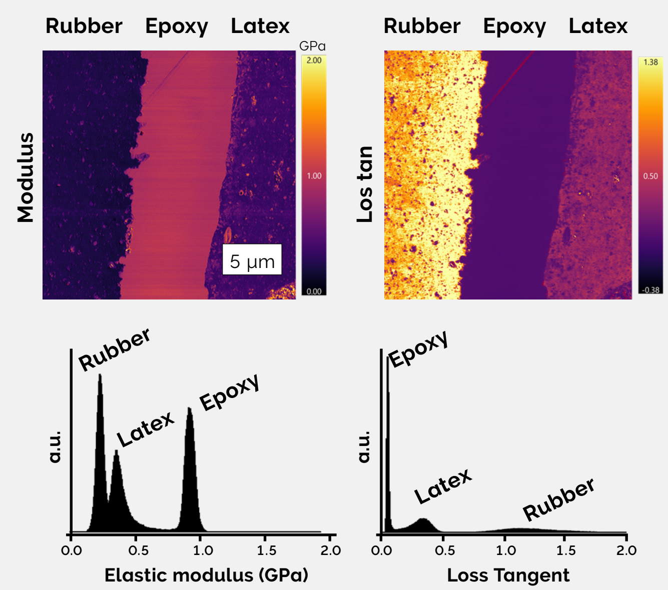

Figure 4: Elastic modulus (left) and loss tangent (right) images of a rubber-epoxy-latex sample. Rubber and latex have a very similar modulus which is not easily distinguishable in the modulus image. However, the additional information from the loss tangent image helps to identify the three materials.

Wide dynamic range of modulus mapping

AM-FM can characterize materials with a wide range of moduli using a single type of cantilever. This is an advantage over force curve-based nanomechanical mapping modes where the spring constant of the cantilever should roughly match the tip-sample stiffness. This is possible as AM-FM nanomechanical data is derived from frequency shift as opposed to cantilever deflection. Figure 5 demonstrates the range of sample moduli that can be measured by AM-FM with one type of cantilever.

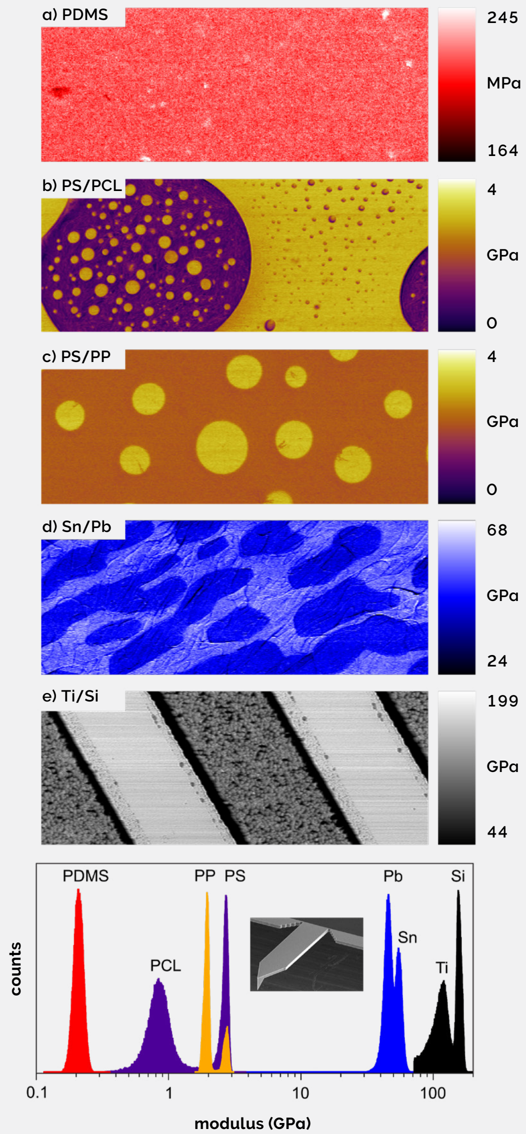

Figure 5: AM-FM modulus images of a) PDMS, b) PS/PCL polymer blend, c) PS/PP polymer blend, d) Sn/Pb solder alloy, and e) Ti thin-film stripes on Si. Bottom: Combined histogram of all the images using the same type of cantilever. The inset shows a scanning electron micrograph of an Olympus AC160 cantilever that was used in all these measurements.

Conclusions

AM-FM Viscoelastic Mapping mode from Asylum Research is a nanomechanical imaging mode that offers unique benefits and when coupled with other nanomechanical modes, such as FFM, provides a comprehensive suite of tools for a wide range of samples.

Advantages of Asylum Research AM-FM

- AM-FM is a tapping mode imaging technique which makes it simple to set up. When combined with faster cantilevers, it can acquire nanomechanical data much faster than force curve-based techniques (Speeds up to 20 Hz line rate).
- blueDrive photothermal excitation available on Cypher and Jupiter AFMs simplifies cantilever tuning and assures quantitative results.
- A wide range of sample elastic moduli (MPa to GPa) can be imaged with the same type of cantilever since the mechanical properties are extracted from frequency shifts instead of cantilever deflection.
- AM-FM measures the viscoelastic response of the sample in addition to the elastic modulus (E'). The loss tangent is the ratio of the loss modulus (E") over the elastic modulus (E'). The viscoelastic response (expressed as either loss tangent or loss modulus) is an important design parameter for polymers and elastomers.
- GetReal™ proprietary software automatically calibrates the cantilever spring constant and deflection sensitivity required for quantitative measurements.

Table 1: Advantages of Asylum Research AM-FM

Considerations	AM-FM	FFM
Speed of image acquisition	Fast	Generally slower
Quantitative sample properties	Yes, mathematical analysis of tapping mode signals	Yes, fitting of indentation force curves
Sample thickness allowed due to indentation depth requirements	Thin and thick samples can be imaged (indentation depth is very low, < 1 nm)	Generally best on thicker samples to reduce surface effects (large indentation depths)
Resolution	Highest resolution is achieved in tapping mode techniques	Indentation depth vs. imaging resolution trade-off
Sample types especially well-suited for the technique	Small features that require molecular resolution, high modulus samples	Sticky samples, high aspect ratio samples, weakly bound samples
Properties measured	Loss tangent, Youngs modulus stiffness, dissipation	Adhesion, hardness, Youngs modulus, current (in Fast Current mapping)

Table 2: Comparison of tapping mode-based and force curve-based nanomechanical imaging modes

References

1. Labuda, A., Kocun, M., Meinhold, W., Walters, D., Proksch, R. Beilstein J. *Nanotechnol.* 2016, **7**, 970–982.
2. Proksch, R., Kocun, M., Hurley, D., Viani, M., Labuda, A., Meinhold, W., Bemis, J. *Journal of Applied Physics*, 2016, **119,** 134901.
3. Kocun, M., Labuda, A., Meinhold, W., Revenko, I., Proksch, R. *ACS Nano* 2017, **11,** 10, 10097–10105.