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ATOMIC FORCE MICROSCOPY COVERS THE LANDSCAPE OF POLYMER CHARACTERIZATION

INTRODUCTION

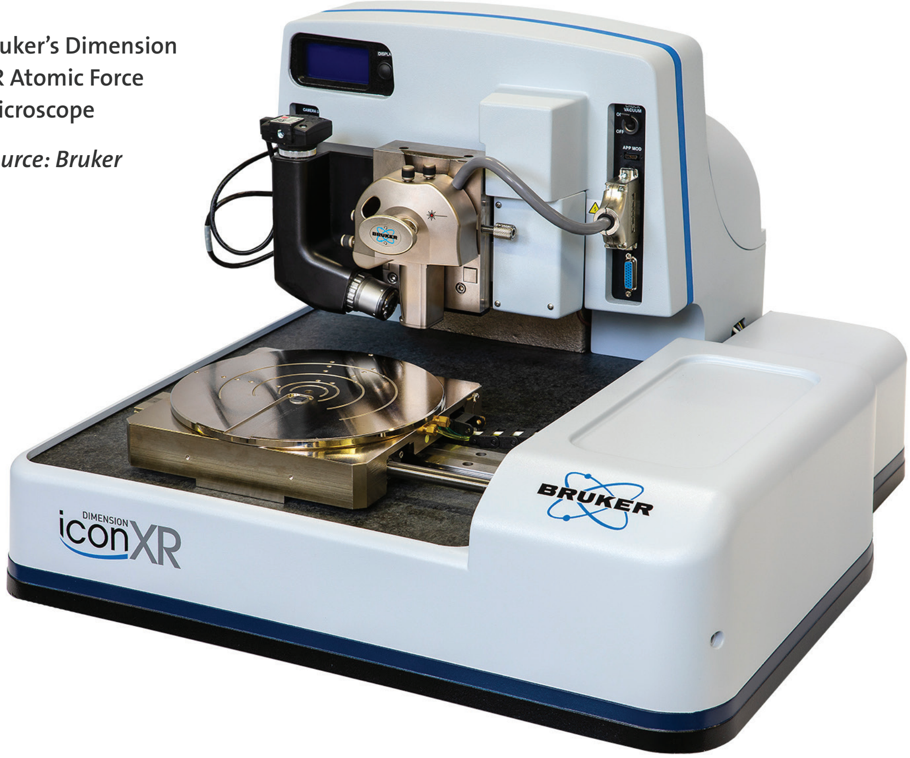
Polymers are ubiquitous in modern life. They're in our cars, our clothes, our electronics, our packaging—all possible because of the staggering diversity of properties that polymer-based materials can be made to have. Polymers are usually more lightweight than other materials such as glass or metal, but their mechanical properties can range from soft, sticky adhesives to tough enough to stop a bullet.[1] Some can even conduct electricity.[2]

What determines a polymer's properties? The chemical structure and how the monomeric building blocks are arranged relative to each other are both central. But the way a polymer-based material is processed for a given application—extruded into fibers, molded into shapes, blown into foams—can also have significant effects on how it performs. If a polymer is blended with additives or other polymers, the picture becomes even more complex.[3]

Materials scientists designing a polymer-based material for a specific application must analyze how and why all these factors come together to impact the final product. Understanding the structure and properties at the microscopic level is critical to a complete understanding of the material.

"Everybody wants to make their materials perform better at the macroscale," says Bede Pittenger, a senior staff development scientist at Bruker Nano Surfaces. "And they all know that the key to that is by changing how things are structured at the nano- or microscale."

And the key to changing how things are structured at the nanoscale is being able to analyze and understand what's happening at that level and how that connects to the bulk material. "My aim for 25 years has been to measure at the nanoscale—at the level of molecules—what is possible to measure in our



Bruker's Dimension XR Atomic Force Microscope

Source: Bruker

world," says Philippe Leclère, a researcher in the Laboratory for Chemistry of Novel Materials at the University of Mons.

A particularly powerful technique for analyzing a material at the nanoscale is atomic force microscopy (AFM). Invented in 1985, AFM uses a cantilever with sharp tip to probe a material's surface.[4] A laser measures the cantilever deflection from the surface as it encounters the nanoscale features of the material. Since the cantilever is a spring, the deflection can be used to find the force exerted on the sample beneath the tip.

AFM works with almost any type of surface, including polymers and biological samples, to produce images of the surface with nanometer resolution. "It can really localize the measurement very tightly—more so than any other mechanical measurement system," Pittenger says. The resolution is hundreds of times better than optical microscopy, in which features that are too close together relative to the imaging wavelength will appear blurry because the light diffracted by each object will interfere with each other. As a mechanically mediated technique, AFM isn't diffraction limited.

The most basic use for AFM is viewing topology: scanning over a given area and recording the deflection between the tip and the polymer surface. Dips or raised areas in the surface can be detected through changes in deflection. The result is a 3D map of the material's surface features.

AFM can also measure mechanical and electrical properties such as stiffness, adhesion, or conductivity for a close look at how a material's microstructure affects its bulk properties. The properties AFM can analyze and the materials it works on are as expansive as the world of polymers itself. Polymer researchers can apply it to uses as different as looking at an adhesive's stickiness and checking an organic solar cell's conductive response to sunlight.

"It's got an amazing amount of flexibility for just a little tip," Pittenger says.

DIVERSE AFM MODES FOR DIVERSE APPLICATIONS

AFM methods can be built on a number of modes, defined by how the cantilever tip interacts with the sample. There are three main types of modes: contact, resonant tapping, and nonresonant tapping. Polymer researchers can choose the mode that works best for the material they're working on and the type of measurement they're interested in.

Contact mode, in which the tip is touching the sample at all times, is the classic AFM topography method. It's fast and simple, according to Greg Meyers, a research fellow at Dow who specializes in polymer AFM. But it's not for every polymer—for example, it does not work very well with softer or delicate samples. The shear force from laterally pulling the cantilever across the sample cannot be controlled and may damage the sample and contaminate the tip.

In the mid-1990s, ~~researchers from Bell Laboratories and~~ Digital Instruments (later acquired by Bruker) introduced a new type of mode, resonant tapping,to protect samples. The mode uses an oscillating cantilever to "tap" the sample surface near the cantilever's free resonance frequency. Because the oscillation amplitude changes with the surface topography, tapping modes like Bruker's TappingMode are popular for mapping more delicate polymer samples.
It's a relatively fast method, making it a good choice for probing dynamic processes such as crystallization or diffusion in blended polymers, Meyers says. TappingMode Phase Imaging can also be used to map out polymer-based materials that have domains with distinct properties. Pittenger says the probe's force is not directly controlled, however, so it's best used for qualitative imaging.

In contrast, nonresonant tapping modes, such as Bruker's Force Volume and PeakForce Tapping, directly measure the interaction force between the probe and sample. In these modes, the probe approaches the surface until a user-specified force is reached and the probe retracts. In addition to mapping a polymer's topography, these modes can quantitatively measure and map other properties such as conductivity or stiffness over the same area so the topographical features can be correlated with other properties of interest.

With TappingMode Phase Imaging, different polymer properties (e.g., elasticity or adhesion) dominate at different tapping forces, which makes interpreting the role of each in the image contrast challenging. PeakForce Tapping mode, on the other hand, can unambiguously analyze a very wide range of samples because it produces separate signals for topography, elasticity, adhesion, and energy dissipation.

Traditionally, AFM measurements are either image based, mapping one property across the entire sample area, or point spectra, which show more complex data (for example, current as a function of voltage) taken at a single point. Researchers sometimes want the best of both worlds; Bruker's DataCube collects point spectra while mapping by adding a "dwell time" when the probe is in contact with the sample, creating multidimensional data at each pixel across the sample area.

TIP SELECTION AND SAMPLE PREPARATION

Researchers can swap out the tips on the AFM instrument depending on the particulars of an experiment. The best tip to use depends on the sample properties as well as the type, speed, and sensitivity of the AFM mode. Contact mode, for instance, works best with dull tips to minimize sample damage. For force measurements, such as those taken during PeakForce Tapping, knowing the tip's spring constant and tip geometry is essential for acquiring accurate data, as is choosing a tip with a spring constant that works with the polymer's mechanical properties. For example, softer polymers need stiffer cantilevers that won't get stuck.

"We have to pick a probe that is suitable to penetrate into the material enough to be able to measure its properties, but not so deep that when we go to a softer phase we will get unreliable data," Meyers says.

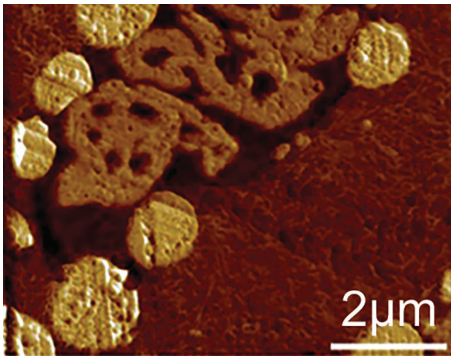
Bruker offers a range of precalibrated tips with known spring constant and tip shapes suitable for a range of mechanical properties. There's no need for a reference sample; all the user has to do is scan a barcode to load the tip information into the instrument.

Sample preparation for AFM depends on the properties of the sample and what the researcher wants to learn about it. Though it's a surface analysis method, there are still ways to see inside a material with AFM. One approach is to take thin slices from the sample's interior with a microtome, then apply AFM to the slices.

MECHANICAL CHARACTERIZATION

The mechanical properties and nanoscale environment of each component in a polymer blend—how large the domains are, what their interfaces look like—have a large role in the blend's bulk properties. In a two-polymer blend, "the properties of component A and component B, if they're mixed, will be some averaging of the two," Meyers says. "So we need to spatially localize what the properties are, especially when you get to an interface between two materials."

PeakForce quantitative nanoscale mechanical characterization (PF-QNM)



PeakForce quantitative nanoscale mechanical (PF-QNM) characterization produced this modulus map, which shows microscale features that contribute to bulk properties of a polymer-based material.

Source: Reference 5

Snack foods, such as potato chips, are often packaged in layered polymer-based materials. AFM can reveal details about the junctions between these layers.

Credit: Shutterstock

provides localized information about mechanical properties—such as Young's modulus, which measures how deformable a polymer is—that are essential to figuring out which microscale features contribute to the overall stiffness or bendability of the material and how to influence it for a given application.

In a virtual symposium in 2020, Pittenger discussed using PF-QNM to look at the interfaces of a polymer-based material being developed for packaging snack foods.[5] The material had several layers: a nylon barrier layer to keep moisture out, a soft polyethylene blend layer that can be heated and pressed together to seal the package, and a polyethylene "tie" layer in the middle meant to stick the barrier and sealant together.

The interphase between the tie and sealant is invisible by optical microscopy because they are chemically similar. Carrying out PF-QNM and looking at the resulting modulus map make it possible to see the junction because the sealing layer is softer than the tie layer. The modulus map also showed lamella from the tie layer infiltrating the sealant, binding them together. Examining the polymer layers' interaction on a microscopic level tells researchers how the material is held together. This snack food packaging example also illustrates the power of AFM to distinguish chemically similar materials by their relative stiffness.

Dynamic mechanical analysis on the nanoscale

A polymer near its glass transition temperature is viscoelastic, with its long, entangled chains providing the properties of both an elastic solid and a fluid. Viscoelasticity gives polymers a complex response when force is applied. Whether a flexible piece of plastic will snap back to its original shape after being bent or become permanently deformed depends on multiple factors: the temperature, the amount of force applied, the time over which the force is applied, and how good the material is at dissipating energy.

Relating a polymer's composition to its viscoelastic properties helps researchers understand why a material has a particular response to being bent or stretched.

Dynamic mechanical analysis (DMA) is a common technique to measure viscoelastic properties. DMA looks at complex mechanical responses by applying an oscillating force to a polymer and measuring its deformation as a function of force and time. Bruker recently developed an AFM-nanoscale DMA (nDMA) method to make quantitative measurements of those same properties at the nanoscale.

AFM-nDMA takes advantage of PeakForce QNM (PF-QNM), Force Volume, and point measurements. The method starts with surveying the mechanical properties across the sample area to create a high-resolution PF-QNM map. From there, researchers choose areas of interest for dynamic point spectroscopy or maps of viscoelastic properties.

To take the point spectra, the tip is brought into contact with the sample with a known force. After a rest period to allow the polymer to "relax" into a slightly deformed state after the initial force, the tip oscillates at several different frequencies. Measuring the deformation as a function of an oscillating force gives the storage modulus, which corresponds to elastic energy stored by the polymer, and loss modulus, which represents energy lost to heat. According to Pittenger, each point measurement can take 1–5 min, depending on the frequencies used.

Dynamic data can be measured for each component in a blend, as illustrated in an application note Pittenger coauthored.[6] The detailed data on each component's mechanical properties help predict how they come together to influence the final blend. Measuring mechanical properties as a function of temperature can give quantitative information about thermal transitions that agrees with data obtained by bulk DMA and other methods. It's even possible to obtain a detailed understanding of each component's time and temperature dependence.

ELECTRICAL CHARACTERIZATION

By applying a voltage to the tip, researchers can also use AFM to measure electrical properties, including current and surface potential. Electrical characterization techniques are useful for conductive polymers and applications where a polymer is used as a binder for conductive materials.

Analyzing lithium-ion battery cathodes

In a 2019 application note, Pittenger and colleagues used AFM to generate conductivity maps of a battery cathode, consisting of lithium-metal domains and carbon nanoparticles embedded in a polymer matrix.[7] Their method collected data on the sample's topography, modulus, and tunneling current between the tip and sample at a range of voltages between –2 and +2 V.

The researchers easily identified the cathode's components by both their mechanical and electrical properties. Mapping the current revealed the dynamic electrical performance of each lithium domain. This nanoscale examination identified “dead” areas, where there was no conductive path, which should be minimized in a practical battery as they add weight without contributing to capacity.

Photoconductive AFM

Hybrid bulk heterojunctions are the interface between inorganic semiconductor nanomaterials and conjugated polymers. They’ve attracted attention from researchers as a less expensive approach to photovoltaic devices, in which the inorganic domains transport electrons and the organic domains transport holes to create a current.

Once again, morphology—especially at the interfaces—strongly affects the photovoltaic performance of these hybrid materials. Leclère and his colleagues at the University of Mons used photoconductive AFM, which measures how the material’s electrical conductivity responds to light, to characterize the electrical properties of a bulk heterojunction material.[8]

The interface between the material’s two domains is where the action happens, according to Leclère. “We were able to measure that the current is generated exactly at the interface, and we were also among the first to show that,” he says. When the material absorbs light, electron-hole pairs are generated. Correlating the morphology to the local photoconductivity and surface potential, he and his team were able to determine that the electron-hole pairs travel to the interface. There, the pair separates—with the holes going to the cathode and the electrons going to the anode— which generates a current.

The research illustrates that “interfaces are extremely important, and everything is occurring at the nanoscale,” Leclère says. That’s why knowing how to influence nanoscale interfaces is immensely important to figuring out how to create better photovoltaic materials.

CHEMICAL CHARACTERIZATION

AFM can’t by itself answer every question about polymer-based materials. Fortunately, the method plays well with others and can be combined with complementary techniques in innovative ways. For example, Meyers has coupled AFM with infrared (IR) spectroscopy to overcome the diffraction limit of traditional IR to map a material’s chemistry as well as its morphology. “With an infrared microscope, you’re limited to a few microns or so of spatial resolution. Now, with this methodology, we’re at about 30 nm resolution,” he says. “That gives us a whole new look at things—not only do we see the mechanical response but we can see the chemistry.”

The chemical structures of polyethylene (PE) and polypropylene (PP) are separated by just a single methyl group, yet that’s enough to make them immiscible in blends unless they’re compatibilized with a copolymer. Meyers used AFM-IR in contact mode to look at the morphology and chemical composition of a compatibilized PE-PP blend by identifying the regions with and without the methyl group IR stretch.[9]

To distinguish the compatibilizer by IR, the copolymer was tagged with deuterium in place of some of the hydrogens. Using this approach, Meyers and his colleagues determined that the copolymer largely dispersed in the PE domains. More broadly, they showed the power of AFM-IR to distinguish between chemically similar materials.

PROBING THE FUTURE

Ultimately, Pittenger says, the hope for AFM advances is to speed up data collection without sacrificing quality. Getting mechanical properties with very high resolution relatively quickly is what “everybody would like to see,” he says

The next big breakthrough in AFM technology may actually come from data analysis and computing. Given the amount and complexity of data that can be collected with AFM-nDMA and DataCube, machine-learning approaches are increasing. “If you have this huge amount of data, it’s better to ask a computer to do the job for you,” Leclère says. DataCube files can be analyzed using Bruker’s analysis software or exported to other software.

Polymer research as a field will likely undergo significant changes in the coming years as more applications shift toward recyclable or degradable materials, and exciting new applications arise.[10] Through it all, AFM will remain an essential tool for researchers to connect materials’ nanoscale structures to their macroscale properties.

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