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Advanced Nanoscale Characterization with diCaliber™

Phase Imaging of Polymer Materials

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INTRODUCTION

TappingMode™ imaging has proved to be the most versatile mode of atomic force microscopy (AFM) in ambient conditions where the presence of a fluid layer (condensed water vapor and other contaminants) severely limits the applicability of both, contact mode and non-contact techniques. Overcoming the challenges posed by friction, adhesion, and other issues, TappingMode has provided a means of greatly extending AFM applications.

Phase Imaging is an important extension of TappingMode imaging. By mapping out the phase of the oscillating cantilever, phase imaging goes beyond simple topographical mapping. Being sensitive to variations in adhesion and viscoelasticity, phase imaging can provide information about sample composition and microphase separation.

TappingMode phase imaging is a standard feature on the new Caliber scanning probe microscope (see Figure 1). With its proprietary low-noise electronic control, closed-loop scanning tip technology, and comprehensive software, the Caliber system offers big utility in a small footprint. The powerful software package includes full control over the two integrated dual lock-in amplifiers, thus enabling a suite of imaging modes, including phase imaging.

Figure 1: The portable diCaliber mini-SPM

APPLICATION EXAMPLES

Phase imaging can reveal microphase separations occurring in block copolymers. Obtaining this information with alternative techniques involves complications, such as chemical staining for TEM. With TappingMode phase imaging, AFM can provide the visualization of the microphase separation pattern directly from images obtained in ambient conditions of an untreated thin film. Figure 2 shows two phase images of a PS-*b*-PB-*b*-PS triblock copolymer (PS, polystyrene; PB, polybutadiene). Both channels clearly show the expected worm-like microphase separation pattern. The microphase domains exhibit a width of ~ 35nm. The stiffer PS lamellae appear bright in both, topography (implying taller features) and phase (implying more positive phase angle).

For a phase image to reflect differences in viscoelasticity or modulus of a material, the AFM probe needs to penetrate the material. More precisely, the probe needs to penetrate sufficiently far such that the tip-sample interactions are influenced by material properties from the layer of interest. In the case of a PS-*b*-PB-*b*-PS film, an amorphous, PB-enriched top-layer is usually present. Thus, the combination of a soft cantilever (e.g., FESP, k ~ 2-5N/m) with light tapping conditions would fail to uncover the microphase separation pattern. Images such as those shown in Figure 2 are usually obtained with hard tapping conditions, that is, fairly high ratios of free amplitude to amplitude setpoint. On Caliber, probe tuning at moderate amplitude (input gain setting ~ 8) and significant increase of the cantilever drive amplitude upon engaging, in conjunction with high proportional feedback gains, will yield the desired result.

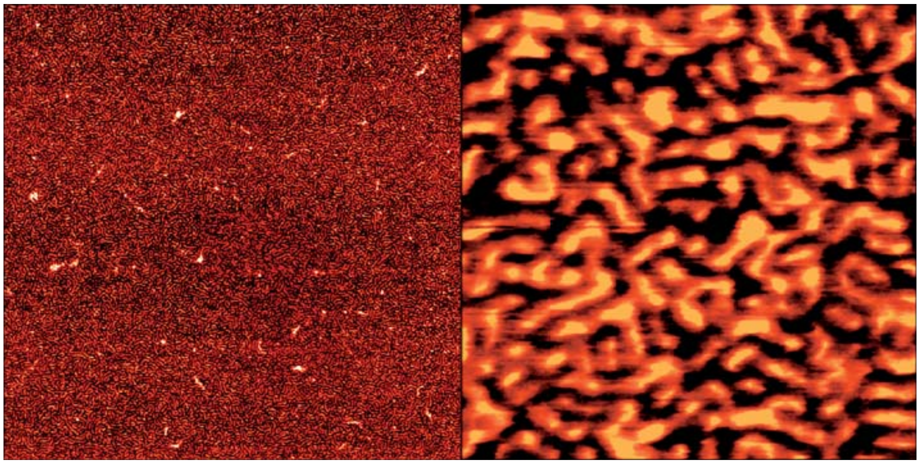


Figure 2: 5μm (left) and 500nm (right) phase image of PS-b-PB-b-PS triblock copolymer. Sufficiently hard tapping conditions have ensured probe penetration into the subsurface layer, where a wormlike microphase separation pattern is present as can be seen clearly in both channels. Images acquired with Closed-loop active.

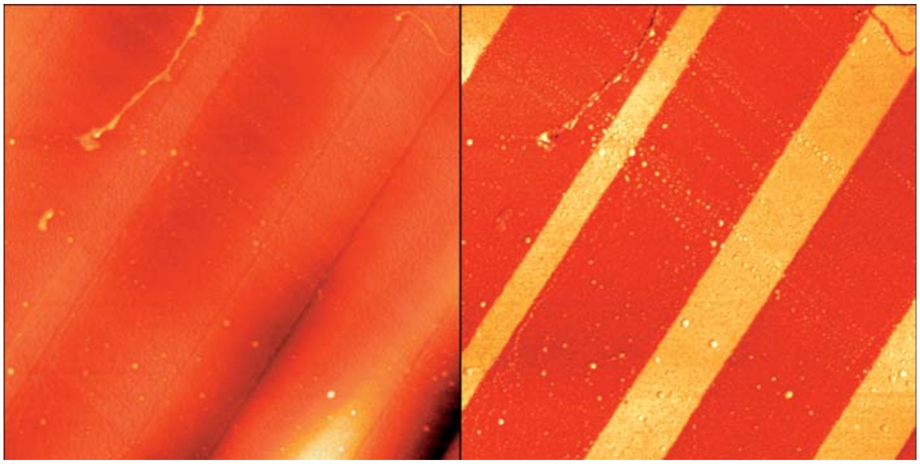


Figure 3: Topography (left) and phase image (right) of a cryo-microtomed multilayer polyethylene sample. While topography is dominated by large-scale undulations, phase provides a clean view of the layered structure. Additional fine structure shows the presence of small droplets. Image size 55μm.

As phase imaging is sensitive to local variations in mechanical properties, it can afford an efficient means for mapping out the distribution of components in composite samples. Figure 3 shows topography and phase images of a cross-sectioned multilayer polyethylene sample, composed of alternate high and low density layers. The topography image is dominated by the large scale, low frequency height undulation that has apparently resulted from cross-sectioning by cryo-microtoming. The phase image has an entirely different appearance, clearly providing complementary information. The phase image is dominated by an alternating set of stripes, obviously representing the sought after alternation in material properties and thus component layers. In addition, topographic fine features are readily apparent, such as droplets, indicating an ageing sample surface. The droplets are clearly not distributed randomly. Rather, they appear to form along lines, presumably small scratches imparted on the sample by the microtoming process.

While the phase image in Figure 3 provides a particularly clean map of alternating density components, the differing material properties can also have an effect on the observed AFM topography, depending on the choice of imaging mode, cantilever, and other factors. For more details, see the application note *Advanced Nanoscale Characterization with Caliber: Force Spectroscopy and Local Mechanical Properties*.

Aside from compositional mapping and the visualization of microphase separations, phase imaging can aid in the detection of fine structures. Figure 4 shows AFM images of an oriented film of isotactic polypropylene, also known

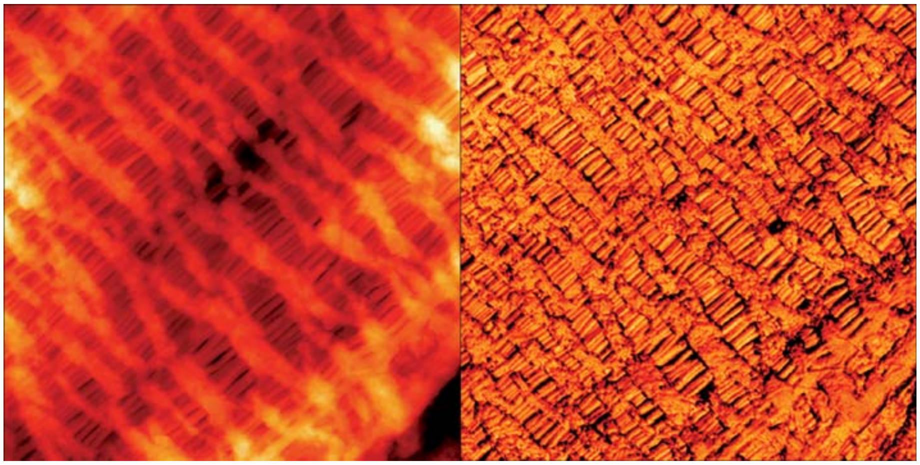


Figure 4: Topography (left) and phase image (right) of Celgard. While oriented fibrillar structures are evident in topography, the phase image additionally reveals lamellar fine structure. Image size 3.5µm.

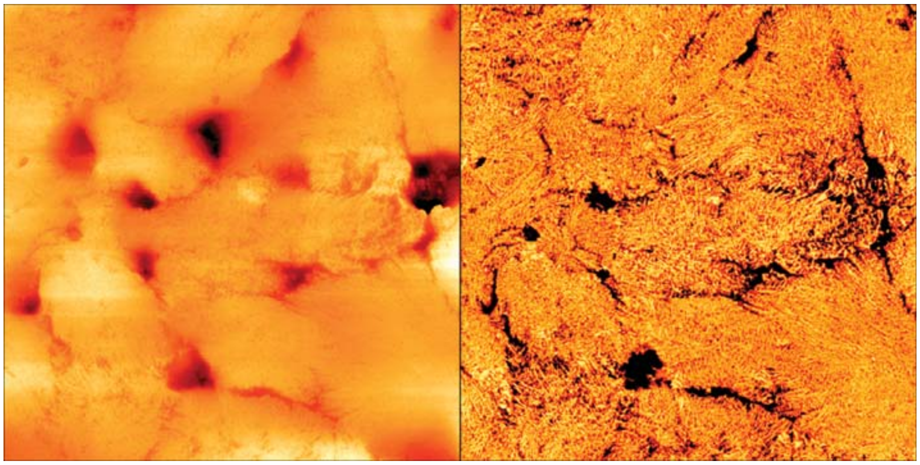


Figure 5: Topography (left) and phase image (right) of thermoplastic vulcanizate. The phase image clearly shows lamellar fine structure, indicating enrichment of the polypropylene component in this region. Image size 7.6µm.

as the microporous membrane Celgard. Both, topography and phase clearly show the pattern of oriented fibrillar structures that is characteristic of this sample. With the overall height scale (~ 200nm) dominated by large variations, finer structures are not evident in the topography data. In contrast, the phase image clearly reveals finer, partially oriented lamellar structures (~ 20nm wide) in between the rows of fibrils. As the phase signal is sensitive to deviations of the oscillation amplitude from the amplitude setpoint, it can serve as an edge detection technique and thus highlights such fine structures that are easily overlooked in the topography channel.

The appearance of fine structure in phase images not only complements the sensitivity to material properties. By identifying components in composite samples, the appearance of fine structure in phase images aids in compositional imaging. Figure 5 shows topography and phase images of a thermoplastic vulcanizate, a multi-component material consisting of isotactic polypropylene, rubber, and carbon black filler.

A lamellar fine structure can be discerned in the topography image and is much more clearly seen in phase, indicating that this region is enriched in the polypropylene component. Other AFM imaging modes can help to obtain additional information about this composite sample. In particular, electric force microscopy can uncover the distribution of carbon black filler material near the surface. See the application note: *Advanced Nanoscale Characterization with Caliber: Electrical Characterization with EFM and SEPM.*

SUMMARY

With TappingMode phase imaging, the Caliber system can efficiently map variations in sample properties at high resolution. Phase imaging can complement other modes such as force modulation and lateral force microscopy, see the application note *Advanced Nanoscale Characterization with Caliber: Force Spectroscopy and Local Mechanical Properties*, often with superior image detail. Phase imaging applications include the characterization of composite materials, mapping of variations in adhesion and viscoelasticity, and identification of surface contamination. Phase imaging makes Caliber a powerful tool for the study of material properties at the nanometer scale.

ABOUT THE IMAGING TECHNIQUES

Conventional Approaches

Two conventional AFM scanning modes – contact mode and noncontact mode have been used for some time with varying success. Each has its limitations, particularly for imaging delicate samples in ambient conditions, see also application note: *TappingMode Imaging Applications and Technology.*

Contact mode AFM represents the simplest imaging technique. The sample is simply moved laterally relative to the probe such that the probe is dragged across the surface. While this technique has been successful for many samples, it is subject to serious drawbacks. In essence, the dragging motion of the probe combined with adhesive tip-surface forces can lead to substantial damage to probe and sample, creating artifacts in the image and often degrading the resolution severely.

Under ambient air conditions, most surfaces are covered by a fluid layer, composed of water and other contaminants, which is typically several nanometers thick. An AFM tip touching this layer will cause a meniscus to form and surface tension will pull the tip onto the surface. Additional adhesive forces can arise from trapped electrostatic charges (see Figure 6).

Tip-sample forces are thus larger than the cantilever deflection would seem to indicate. Correspondingly, lateral motion during contact mode imaging is associated with larger lateral forces, resulting in severe tip or sample damage or involuntary displacement of weakly bound surface adsorbates. Capillary forces can be eliminated by completely submersing the sample and probe tip in liquid. However, sample surfaces are often either less robust in liquid (e.g., adsorbates are more weakly bound) or are not compatible with a liquid environment at all.

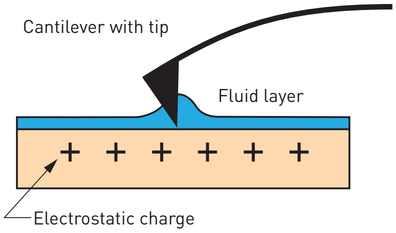


Figure 6: In contact mode AFM, electrostatic and/or surface tension forces from the adsorbed fluid layer lead to destructive lateral shear forces. From application note AN04, TappingMode Imaging Applications and Technology.

Non-contact mode represents an attempt to overcome the deleterious tip-surface forces associated with contact mode. Unfortunately, ambient air conditions are rarely conducive to non-contact AFM imaging.

Non-contact mode is based upon the detection of weak attractive van der Waals forces that exist between tip and sample a few nanometers above the surface. It is important to note that the fluid layer present in ambient conditions partially shields these forces and occupies a large fraction of their useful range, i.e., when compared to operation in ultra-high vacuum, where no fluid layer is present. Due to the limited range of any residual van der Waals forces, their detection necessitates very small oscillation amplitudes. At the same time, a cantilever operated at very small amplitudes is easily trapped inside the fluid layer, once it touches. In the ideal case, operation remains outside the fluid layer – and therefore several nanometers away from the sample surface. The consequences are substantially degraded resolution (as compared with TappingMode) and an inability to map out variations in local mechanical properties (see the preceding sections of this application note for many examples of probing local mechanical properties with TappingMode phase imaging). In practice, the probe is frequently drawn onto the sample surface and remains trapped there while the scanning motion proceeds, leading to unusable data and sample damage similar to that caused by contact mode.

TappingMode Imaging in Air

Veeco's patented TappingMode imaging overcomes the limitations of the conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the sample. TappingMode imaging is implemented in ambient air by oscillating the cantilever at or near its fundamental flexural resonance, usually a frequency in the range of 50 to 500 kHz. "Free air" amplitudes are typically greater than 20nm. During the engage process, the tip-sample separation is reduced until the tip begins to interact with the surface. The interaction with the surface ("tapping") leads to energy loss and a reduced oscillation amplitude (see Figure 7 and application note AN04: TappingMode Imaging Applications and Technology). Deviations of the amplitude from a setpoint value serve as error signal in the feedback loop that drives the Z-motion to track surface features. In phase imaging, the phase lag of the cantilever oscillation, relative to the drive signal, is simultaneously monitored with topography data. As the phase lag is influenced by energy dissipation experienced during the oscillation cycle, it is very sensitive to material properties such as adhesion, viscoelasticity, and modulus. Phase imaging can also act as a real-time contrast enhancement technique. Because phase imaging highlights edges and is not affected by large-scale height differences, it provides for clearer observation of fine features, such as grain edges, which can be obscured by rough topography.

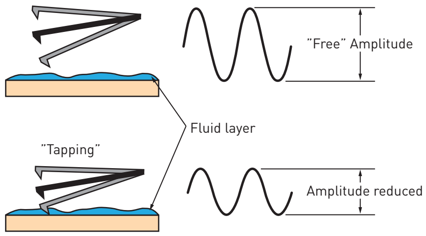
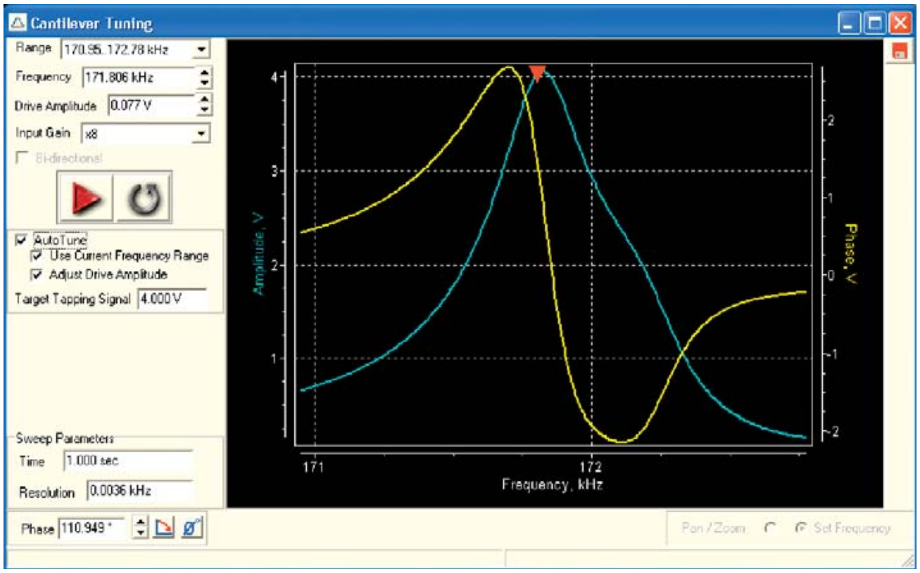


Figure 7: TappingMode cantilever oscillation amplitude in free air and during scanning. From application note AN04, TappingMode Imaging Applications and Technology.

TappingMode prevents the tip from sticking to the surface and causing damage during scanning. In contrast to non-contact mode, the oscillation amplitude and energy is sufficient to overcome tip-sample adhesion in every oscillation cycle. In addition, TappingMode provides a large linear operating range, i.e., linear dependence of cantilever amplitude on tip-sample separation, making the feedback system highly stable and allowing routine reproducible sample measurements at high resolution.

Selection of the optimal cantilever oscillation frequency is a critical step in preparing for TappingMode imaging. On Caliber this is accomplished in the Cantilever Tuning dialog (see Figure 8). Choice of drive frequency and adjustment of lock-in parameters for proper phase imaging are all taken care of by the autotune function. The user just chooses the desired cantilever oscillation amplitude by selecting a target amplitude and lock-in sensitivity ("input gain") factor. As shown in Figure 8, both, amplitude and phase are displayed in the Cantilever Tuning dialog.


Cantilever Tuning

Range 170.95..172.78 kHz
Frequency 171.806 kHz
Drive Amplitude 0.077 V
Input Gain x8
☐ Bi-directional
☑ AutoTune
☑ Use Current Frequency Range
☑ Adjust Drive Amplitude
Target Tapping Signal 4.000 V

Sweep Parameters
Time 1.000 sec
Resolution 0.0036 kHz

Phase 110.949 °

○ Pan / Zoom
● Set Frequency

Figure 8: Selecting drive frequency and phase in preparation for TappingMode imaging using the autotune function in the Cantilever Tune dialog.

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