

Applications of AFM for Polymers

By: S. Magonov and M.G. Heaton

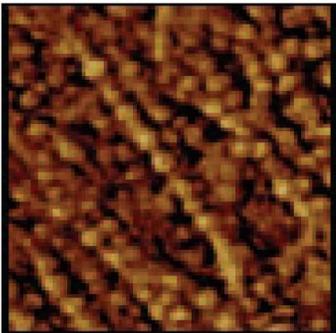


Figure 1. Caption to come.

Atomic force microscopy (AFM) has become an advanced microscopic method for examining polymer materials for such applications as engineering plastics, paints, coatings, rubber, packaging, fibers, and a wide range of consumer goods. Initially, AFM studies were aimed at visualization of polymer morphology, nanostructure, and molecular order, and these investigations have been performed on a large number of polymer samples.^{1,2} More recently, the spectrum of AFM applications to polymers has broadened substantially due to the discovery of new AFM capabilities. In addition to high resolution profiling of surface morphology and nanostructure, AFM allows determination of local materials properties and surface compositional mapping in heterogeneous samples. Furthermore, these techniques allow examination not only of the top-most surface features, but also the underlying near surface sample structure. Several examples illustrating these aspects of AFM as an advanced microscopic tool are collected in this application note.

Effect of Tip-Sample Force

Polymer materials are relatively soft (elastic moduli of a few Gpa or lower), therefore, minimization of force interactions between the AFM tip and the sample surface is required for non-destructive imaging of most polymer samples. This need was



Figure 2. The MultiMode microscope includes an optical detection head, scanner, and microscope base. The compact, rigid construction of the microscope gives it the mechanical stability and low noise needed for high resolution. NEED NEW IMAGE...

met with the introduction of TappingMode™ Imaging³, which allows examination — without damage or surface alteration — of a broader range of soft materials than the traditional AFM contact mode. Tapping of soft surfaces by the oscillating AFM tip prevents damage by eliminating the lateral forces that are inherent to contact mode (where the tip is simply dragged across the surface). Because of this gentler imaging, TappingMode is now the predominant technique for polymer studies.

With MultiMode™ and Dimension™ Series AFMs, the force of the tip applies to the sample surface can be adjusted by the user to obtain different kinds of information. Minimization of the tip-sample force on soft materials provides height images which most closely reproduce the sample topography - and the small tip-sample contact area which accompanies this low force imaging offers the best image resolution.* At elevated tip-forces, the sample surface may be deformed, and if the material is heterogeneous in structure, as many polymers are, the height image can represent a map of surface stiffness which is often quite different from the sample topography. Therefore, in practical applications it is worthwhile to conduct imaging at different forces in order to more rationally interpret the AFM images and to recognize features relevant to surface topography and composition.

Adjusting Tip-Sample Forces and Phase Imaging

In TappingMode, the level of the tip-sample interaction is defined by the relationship between the amplitude (A_0) of the free-oscillating cantilever (on which the tip is mounted) and the set-point amplitude (A_{sp})^{4,5}. Imaging is gentler when A_0 is small (2-5nm) and A_{sp} is close to A_0 . The difference between the phase of the freely oscillating tip and the phase of the tip as it interacts with the surface describes the nature and magnitude of the tip-sample interactions. Monitoring these phase changes has become one of the most useful characteristics of TappingMode, allowing the

* This concerns resolution for imaging of nonperiodic structures. Atomic-scale lattice images of crystals can be achieved at tip-sample contact areas substantially larger than a few atoms.

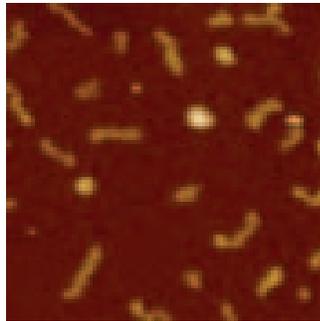


Figure 3. Caption to come???

compositional mapping mentioned above. In practice, the height and phase images are recorded simultaneously. On homogeneous materials, phase imaging provides higher contrast for morphological features. Phase images for heterogeneous materials often reflect differences in the properties of individual components, and are extremely useful for compositional mapping in blends, copolymers, composites, etc. Because of the increasing importance of phase imaging, we will discuss this mode in more detail while describing the compositional mapping.

High-Resolution Surface Profiling

To illustrate the high resolution of AFM in studies of morphology and nanostructure, we consider a Langmuir-Blodgett film of poly(styrene)-b-poly(methylmethacrylate), (PS-b-PMMA) copolymer. This film was prepared on water as a subphase, and then transferred onto a mica substrate. The height image (Figure 3) reveals that hydrophilic PMMA blocks form a compact layer (0.6-0.8nm in height) immediately on the substrate, whereas individual monoblocks of hydrophobic PS are assembled on the PMMA layer in the form of string-like aggregates (1.5nm in height) or ball-like patterns (2.5nm in height). Individual monoblocks of PS ($M_w=15K$) exhibit diameters in the 8-14nm range, which is close to the size of a polymer coil.⁶ This image has been recorded with $A_0 = 2nm$ and the largest possible A_{sp} (1.6nm). As A_0 increases, the resolution becomes poor, and mechanical deformation and film damage are observed.

In studies of commercial PVDF film with a biaxial orientation (Figure 4), fine details of the nanostructure are best visualized in the phase image (4b).

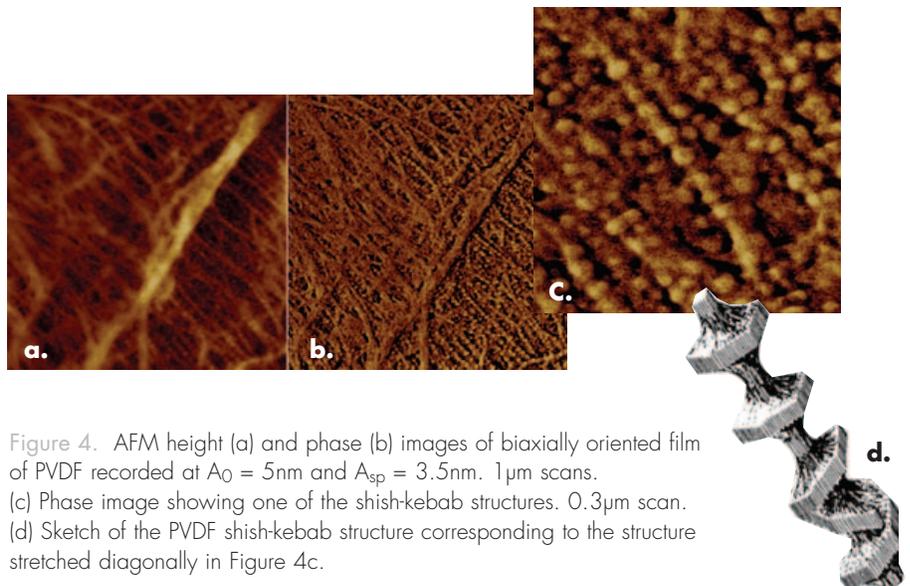


Figure 4. AFM height (a) and phase (b) images of biaxially oriented film of PVDF recorded at $A_0 = 5nm$ and $A_{sp} = 3.5nm$. $1\mu m$ scans. (c) Phase image showing one of the shish-kebab structures. $0.3\mu m$ scan. (d) Sketch of the PVDF shish-kebab structure corresponding to the structure stretched diagonally in Figure 4c.

This phase image distinctively shows not only nanofibrils oriented in orthogonal directions, but also so-called "shish-kebab" nanostructures formed in this material during stretching and crystallization. One such structure is shown at higher magnification in (4c). A core thread of the "shish-kebab" is about 5nm in diameter and lamellar blocks attached to the thread are in the 15-25nm range. A sketch of a "shish-kebab" nanostructure, which was found earlier in TEM micrographs of a number of polymers is shown in (4d).

Another high-resolution example is taken from studies of hot rubbed films of PVDF (Figure 5). The phase images distinguish oriented nanofibrils, some of them with diameters as small as 2-3nm, demonstrating that resolution of a few nanometers can be routinely achieved. The AFM visualization of nm-scale structures substantially complements the results of electron microscopy studies. In addition, AFM allows the visualization of structural features, such as sub-lamellar organization in polymer spherulites⁷, which are not accessible by electron microscopy.

Local Mechanical Properties

The ability of the AFM to study local mechanical (stiffness, friction) and adhesive properties has been demonstrated by many research groups. In experiments using contact mode AFM, force induced elastic surface corrugations were found at different dimensional scales.⁸ These effects can be consequences of different local stiffness of atoms in layered materials, of chain blocks in oriented polymers, or of layers with different density in microlayer samples. More recently, researchers have

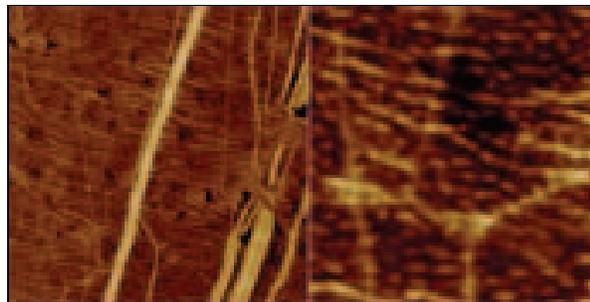


Figure 5. Height (left) and phase (right) images of hot-rubbed film of PVDF. Scan size?

intentionally elevated the tip sample forces to cause plastic deformation and indentation of polymer materials. Such "nanoindentation" experiments using AFM include not only making an indent, but also subsequent low-force imaging of the indent in TappingMode.⁹ Traditional commercial nanoindentors lack this capability. In this paper we restrict the illustration of nanoindentation to one example (Figure 6), however more detailed examples are available in an application note from Veeco Instruments entitled "Nanoindentation, Scratching and Wear Testing Using Atomic Force Microscopy" (AN13), available on www.veeco.com/afm. The figure shows an array of indents made in the multilayer PE material, where the central 2µm strip is a layer of high-density PE surrounded by wider layers of low-density PE. The different size of the indents (larger indents are on broad layers) reflects differences in the density of these layers.

More information concerning local studies of adhesive and mechanical properties using so-called force curves can be found elsewhere.¹⁰ There is growing interest in stretching of single macromolecules with the AFM tip in order to study their mechanical properties. In such experiments, the AFM tip is first engaged into the

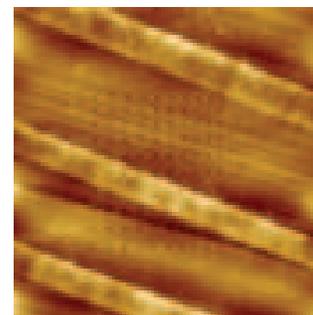


Figure 6. Nanoindentations of high-density and low-density polyethylene.

sample, upon which some of the macromolecules adhere to the tip. Therefore, as the tip is withdrawn, the adhered molecules will be stretched between the sample and the tip until they break. This sequence of events is recorded by the force curves with the ultimate goal of measuring mechanical characteristics of single macromolecules. Please see the Veeco Instruments brochure for the MultiMode PicoForce AFM.

Compositional Mapping

The ability of the AFM to distinguish components in heterogeneous samples was demonstrated using a technique called force modulation imaging, which is performed in the contact mode. With the adoption of TappingMode and phase imaging, this capability has been much more broadly applied because of the elimination of damaging lateral forces.

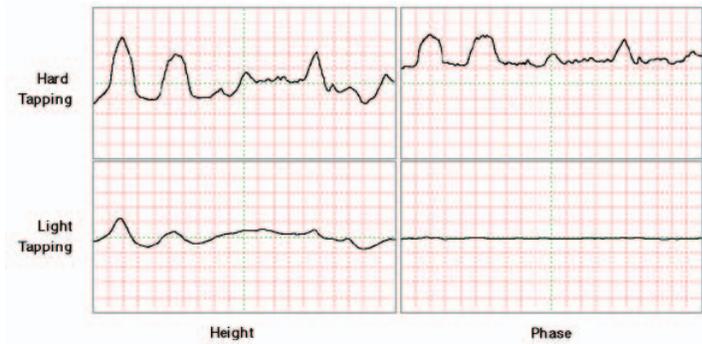


Figure 7. Dissecting a cell membrane locally by applying too high forces.

Analysis of the mechanics of phase imaging has shown that the difference between the phase of free-oscillating vs. the interacting cantilever is defined by the energy dissipated in the tip sample contact.¹¹ Therefore, the differences in adhesive or mechanical properties of different components of a heterogeneous sample might be expected to influence the energy dissipation and, therefore, phase contrast when such a sample is examined with TappingMode. Indeed, in AFM measurements of many polymer blends, the high sensitivity of phase contrast to sample composition has been proven.^{2,5} Assigning the cause of phase contrast to specific differences in individual properties of components is difficult. However, it is reasonable to suggest that with increase of A_0 and decrease of A_{sp} the difference in the energy dissipating on different components will be defined by differences in their mechanical properties.

This is confirmed by the chart in Figure 7, which shows height and phase profiles recorded on a blend of polyethylenes (PE) with different densities. These profiles were determined by imaging with $A_0 = 100$ nm and $A_{sp} = 0.95$ and 0.5 . At $A_{sp} = 0.95$, the height profile shows a sequence of elevated regions

which become more pronounced with decreasing A_{sp} (i.e. by stronger indentation of low density PE regions relative to high density PE regions). At $A_{sp} = 0.95$, the phase of the interacting cantilever almost coincides with that of the free oscillating cantilever, indicating low-force imaging or "light" tapping. As mentioned above, at light tapping, the height profile most closely reproduces true surface topography. With decreasing A_{sp} the phase profile exhibits step-like changes, which differentiate regions of low and high density PE. The largest phase difference was found at $A_{sp} = 0.5$, where the height difference between low-density and high-density regions was also maximal. The imaging conditions just described can be defined as "hard" tapping.

It should be noted that in this latter PE blend, elastic moduli of low density and high-density components differ by at least two orders of magnitude, making it possible to directly correlate phase contrast with differences in mechanical properties. In many other cases the differences in the elastic properties can be smaller, and the changes in the height images at different A_{sp} might be less apparent. However, even in such cases, the phase images exhibit higher sensitivity to materials properties and allow easy visualization of the different components.

In the following sections, we present several examples of imaging in light tapping ($A_0 = 50$ - 100 nm, $A_{sp} = 0.9$ - $0.8 A_0$) and compositional mapping in hard tapping ($A_0 = 50$ - 100 nm, $A_{sp} = 0.5$ - $0.4 A_0$). The changes in height and phase images observed in light and hard tapping are reversible, and they do not cause permanent damage to polymer samples.

Linear Low Density Polyethylene (LLDPE) Film

The images recorded on the surface of a commercial film of LLDPE are shown in Figure 8. In light tapping, the height

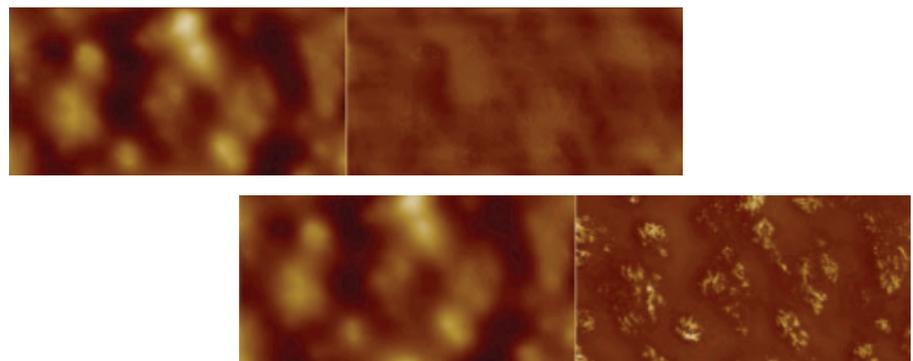


Figure 8. AFM height (left) and phase (right) images recorded on linear low-density polyethylene (LLDPE). Top images were recorded in light tapping. Bottom images were recorded in hard tapping.

image reveals slightly corrugated sample topography, and the phase image does not exhibit well-defined features. In hard tapping, the height image is relatively unchanged; however, the difference in the phase images is dramatic; i.e., aggregates of bright "strips" appear at the locations shown to be elevated in the height image.¹² The "strips" of about 20nm in width can be assigned to lamellae, which are embedded in amorphous polymer (dark contrast). Brighter contrast of lamellae — compact arrays of folded polymer chains — is consistent with the previous finding that more dense PE layers exhibit brighter phase contrast when subjected to hard tapping.

Impact-Modified Plastics

Microscopic studies of sample composition and component distribution at micron and sub-micron scales can be applied to understand structure-property relationships in polymer materials. Transmission electron microscopy (TEM) is often used for such studies; however, laborious preparation of ultra-thin

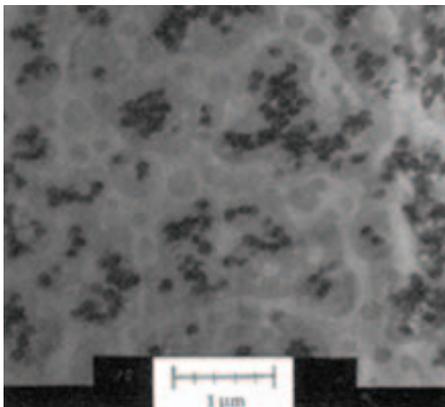


Figure 9. Transmission electron micrograph of impact-modified plastic containing three components. Differences in the contrast are a consequence of chemical staining of the sample.

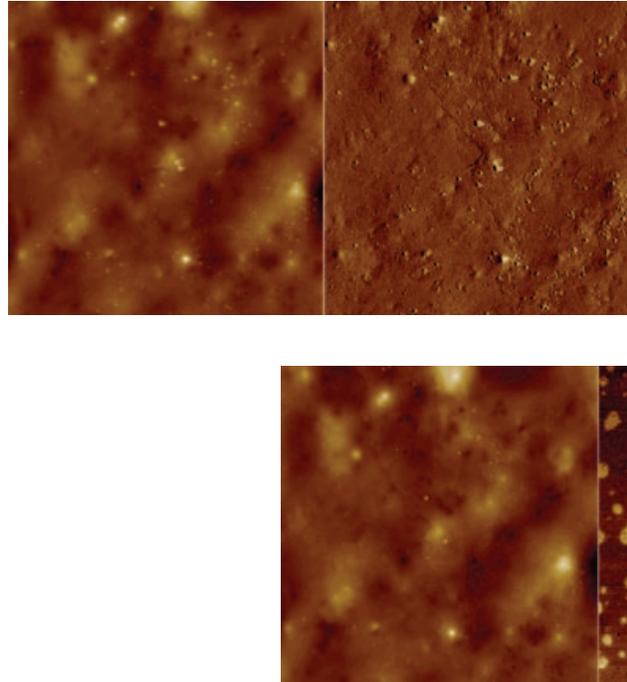


Figure 10. AFM height (left) and phase (right) images of impact-modified plastics containing three components. Top images were recorded in light tapping. Bottom images were recorded in hard tapping.

slices and chemical staining are needed to reveal contrast relevant to different components in TEM micrographs. The TEM image in Figure 9 shows micrograph of ultra-thin sections of an impact modified plastic, a blend of two polymers and rubber particles. The AFM study of the same blend — which requires neither staining nor elaborate preparation of ultra-thin slices — provides similar morphological information.

The height and phase images recorded on this sample at different Aspare shown in Figure 10. As expected, in light tapping the height image shows sample topography, and only minor contrast variations are found in the phase image. The image recorded in hard tapping, however, reveals the composition of this sample. Three components are well distinguished in the phase image (b),

where rubbery particles of about 1nm in size are the brightest features. The phase contrast is strongly different for the two major polymer components: one (darker contrast) is seen as a matrix and the other is presented as brighter domains within it.

Polymer Latex Systems

Polymer latex films are formed by spreading dispersions of polymer particles on a substrate, where they organize into close-packed arrays during solvent evaporation. During thermal annealing, these arrays develop into homogeneous films, which are widely used as paints and coatings for textiles and paper.¹³ Polymer latex systems have been intensively examined with AFM in order to reveal their morphology, composition, and film formation

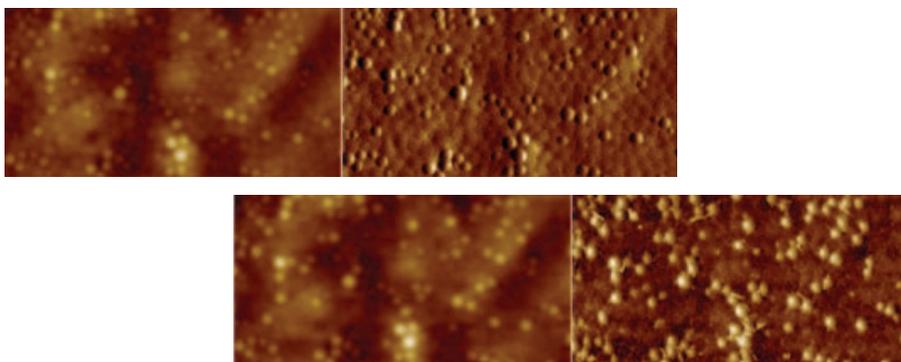


Figure 11. AFM height (left) and phase (right) images of a two-component latex blend consisting of spheres of about 120nm diameter. Top images were recorded in light tapping. Bottom images were recorded in hard tapping.

characteristics. Figure 11 above shows the height and phase images of a blend of two acrylic latex components with glass transitions (T_g) at 37°C (1 part) and 11°C (3 parts). The diameter of latex spheres of both polymers is about 120nm. Under light tapping, the height image (a) of the blend exhibits a close-packed array of latex particles, and the phase image (b) shows contrast variations which emphasize topographic features. The phase image recorded with hard tapping (d), distinguishes particles of individual components. The smaller number of bright spheres can be assigned to the high T_g polymer and the surrounding dark areas to the low T_g polymer, consistent with the expectation that latex spheres with lower T_g are softer than those with higher T_g . The height images (a and c) show less changes than the phase images when the imaging conditions were changed.

Near Surface Structure

Polymer samples are often coated with a soft, thin surface layer, which can differ in composition from underlying materials, for example due to different affinity of the materials to air.

Therefore, one can expect that at small forces, the topmost surface layer can be observed, whereas with increased tip sample force, underlying structures might be detected. This possibility is illustrated by two examples next.

Triblock Copolymer Film

Poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) triblock copolymer has been intensively studied by transmission electron microscopy (TEM). For this purpose ultra-thin sections of the chemically stained material are usually prepared with an ultramicrotome. TEM micrographs revealed that the topmost layer (about

10nm in thickness) at the copolymer/air interface consists mostly of PB blocks, which have lower surface energy than PS blocks. These results are confirmed by XPS data. In bulk, PS and PB (polybutadiene) blocks are microphase separated, leading to a morphology with curved nanostructures of 20-30nm in width. Such morphology has also been detected in AFM images of spin-cast PS-PB-PS films;¹⁴ however, generation of more detailed information about this material requires imaging at different tip-sample force levels.

With light tapping, the height images (Figure 12a) reflects a smooth copolymer film topography with corrugations in the 0-3nm range, and the corresponding phase image (12b) shows no pronounced contrast variations. As A_{sp} decreases, these images exhibit substantial changes: dots of diameters in the 15-20nm range begin to appear and increase in number.

Finally, at hard tapping the height (Figures 12d) and phase images both exhibit "worm-like" patterns consistent with the microphase morphology found in TEM micrographs of the bulk material. It has been shown that brighter patterns in these height and phase images can be assigned to the

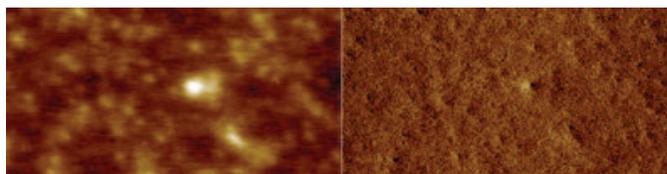


Figure 12. AFM height (left) and phase (right) images of the poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) triblock copolymer film. Top images were obtained in light tapping. Bottom images were obtained in hard tapping.

stiffer PS blocks.¹⁵ These results can be explained as follows: At light tapping the height images of a PS/PB/PS film reveal the surface topography of the butadiene-rich topmost layer. From TEM data it has been established that this layer is about 10nm thick. At ambient conditions, PB is in a rubbery state and, therefore, can be deformed by the AFM tip. Under hard tapping, the tip “feels” the more rigid underlying structure associated with the microphase separation of PS and PB blocks.

Mesomorphic Polysiloxanes

Some polymer materials, including liquid crystalline polymers, exist not only in crystalline and amorphous states but also in partially ordered (mesomorphic) phases. One of these polymers — polydiethylsiloxane (PDES) — was recently examined with AFM.¹⁶ The height and phase images of PDES revealed the coexistence of mesomorphic and amorphous phases at room temperature and allowed monitoring of the polymer crystallization at -7°C. In an AFM study of another mesomorphic polymer — cyclolinear polydimethylsiloxane deposited on an Si substrate by rubbing — the transition from light to hard tapping revealed different nanostructural features of the polymer (Figure 13). With light tapping, the height image reveals the relatively smooth morphology of the polymer patches and the phase image emphasizes edges of layers, especially at the elevated region in the center of the image. With hard tapping, a striped morphology becomes evident in the phase image, with linear elements aligned perpendicular to the rubbing direction.

Similar features are barely distinguishable in the height image. By analogy with imaging of PS-PB-PS tri-block copolymer, the observed changes reflect the presence of a topmost layer with characteristics different from the bulk. The height of the central polymer patch (c) is about 8-10nm less than that in (a). This effect is caused by the tip-force induced deformation of the sample at hard tapping, and this difference (8-10nm) can be used as a rough estimate of the thickness of the topmost layer. Note that the striped morphology of the bulk materials is similar to the lamellar structure found in mesomorphic PDES. Indeed, DSC (Differential Scanning Calorimetry) measurements of cyclolinear polydimethylsiloxane found that at ambient conditions this polymer exists in a fully mesomorphic state. The detection by AFM of a topmost layer with differing organization relative to the bulk was unexpected from the DSC measurements and clearly illustrates the

higher sensitivity of phase imaging to sample heterogeneity at micron and sub-micron scales when compared with the sensitivity of thermal techniques.

Summary

We have demonstrated the increasing number of AFM capabilities useful in studies of polymer materials. In these applications, AFM goes far beyond high-resolution profiling by providing local properties, maps of sample composition and the ability to examine underlying surface layers. Already a widely used tool in the study of polymers, these results illustrate additional potential for using AFM for recognizing the structure/property relationships in advanced polymer characterization for rubber, paints/coatings, packaging, engineering plastics, consumer goods and other applications.

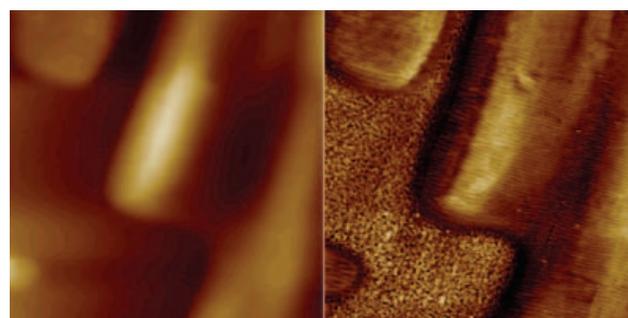
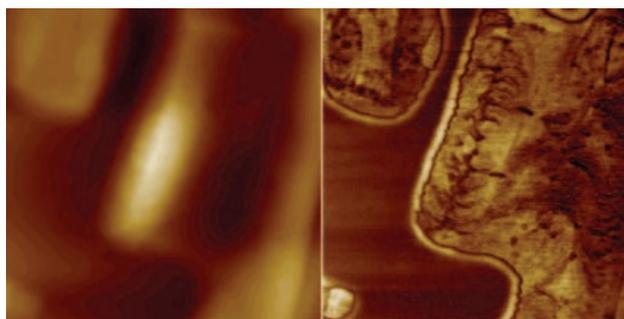


Figure 13. AFM height (left) and phase (right) images of cyclolinear polydimethylsiloxane patches deposited on Si substrate by rubbing. Top images were recorded in light tapping. Bottom images recorded in hard tapping.

Footnotes

* Reprinted with permission from American Laboratory, May 1998, pages 9-16. All images and measurements in this article were generated on the Digital Instruments MultiMode AFM. Samples for AFM measurements described in this article were kindly provided by Prof. T. Hashimoto (Kyoto University), Dr. A. Ghanem (Solvay Company), Dr. S. Nazarenko, Profs. E. Baer, A. Hiltner and S. Nazarenko (Case Western Reserve University, Cleveland), Prof. Y. Godovsky (Moscow), Dr. R. Antrim (Rohm & Haas Company) and Dr. D. Denley (Shell Company), and the authors are grateful to them.

What does this asterik refer to? Could not find it in the main text. Do we even need to use the heading of "Footnotes"? Seems weird!!! We can call it "Acknowledgements" like in previous App Notes.....

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???? this was tacked on to the end of Reference #8, but I think it belongs somewhere else....

morphic state. The detection by AFM of a topmost layer with differing organization relative to the bulk was unexpected from the DSC measurements and clearly illustrates the higher sensitivity of phase imaging to sample heterogeneity at micron and sub-micron scales when compared with the sensitivity of thermal techniques.

There should be 16 references.....

Is it correct to have hyphens for "Hennemann O-D" and "Whangbo M-H"?



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