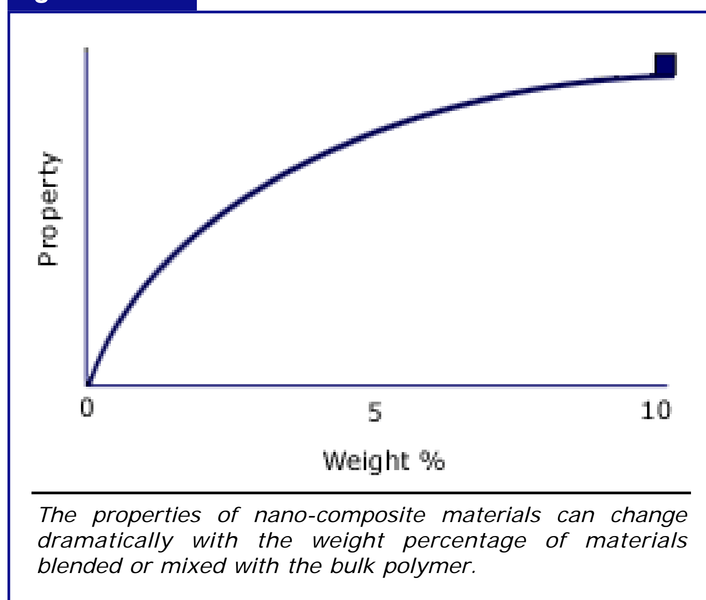
APPLICATION NOTE

Atomic Force Microscopy for
Polymer Applications:

Historically, polymer materials were characterized solely by their bulk properties including stiffness, elongation, gas permeability, impact and modulus. Because the bulk polymers were essentially homogeneous, characterization of substructure was not important. Recent advances in polymer science require advanced methods for polymer micro and nano structure characterization.

Polymer nano-composite materials are now created having clusters, layers, rods, and networks of nanometer sized materials blended with a bulk polymer. These new materials, such as Nylon-6/clay nano-composites, can have desirable properties such as a high modulus and low gas permeability. Ideally, nano-composite polymer materials show a dramatic increase in a physical property with a small amount of nano-particle additive.

Figure 1



The properties of nano-composite materials can change dramatically with the weight percentage of materials blended or mixed with the bulk polymer.

A unique aspect of the new class of nano-composite polymer materials is the high interfacial volume of the materials, just the opposite of traditional bulk polymers. The chemical and physical properties of the interfaces are what give rise to the unique and often desirable properties of nano-composite polymer materials.

Additionally, polymer materials are being developed for a host of new applications in the high technology and industrial sectors. As an example, low K materials derived from polymers are under development and may replace SiO2 in semiconductor devices. Polymer coatings are routinely used in packaging applications in the food industry. Such applications require characterization of surface structure and surface properties.

Traditional methods for surface structure characterization are optical and electron microscopes. Besides giving a 2-D projection of the sample topography, the optical microscope can give contrast associated with polarization. However, the optical microscope is limited to resolutions of greater than .5 microns. Electron microscopes such as SEM and TEM give high-resolution images but require sample coating to make the polymer electrically conductive. The Atomic Force Microscope is well suited for the characterization of nano-composite polymer materials when compared to traditional microscopes such as the electron and optical microscopes.

Atomic force microscopes give direct 3-D measurements of the surface structure of polymers. Further, using materials sensing modes such as lateral force and phase contrast, it is possible to differentiate the types of materials at a polymer surface.

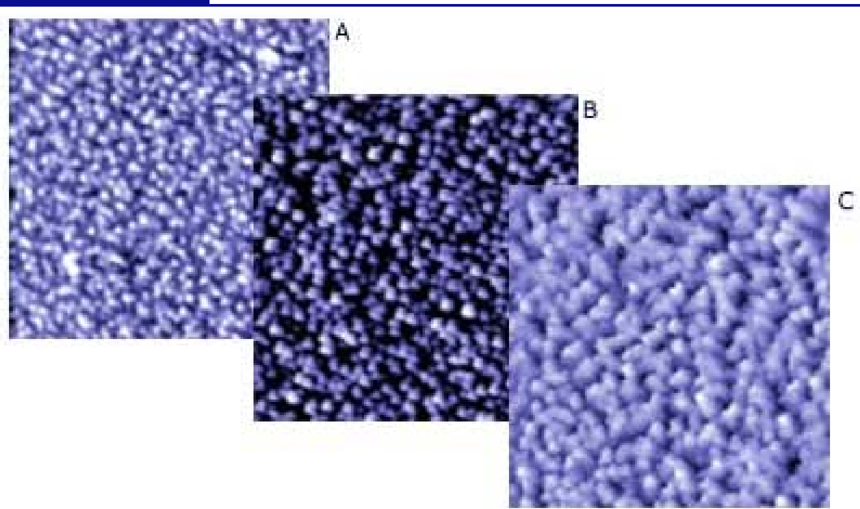
Visualization

Two imaging modes, continuous and vibrating, may be used for imaging polymer samples. If the sample is relatively "hard", then "contact" mode may be used. However if the sample is relatively "soft", then it is necessary to use "close contact" mode. The forces placed on the sample surface with "close contact " mode are about 10 - 100 times less than in "contact" mode.

Direct visualization of 2-D and 3-D images of polymer surfaces is helpful for understanding the effects in changes in process conditions. Because the AFM does not require conductive samples, there is little or no sample preparation required.

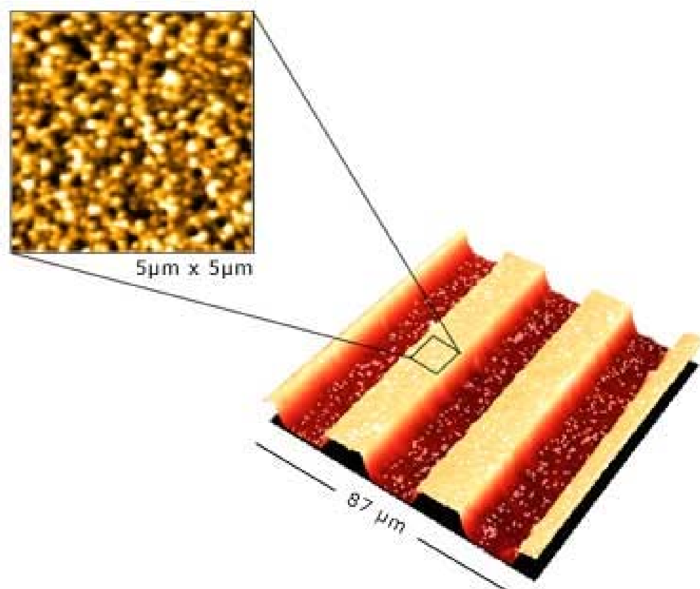
Below are three polymer samples prepared from the introduction of polypeptides. In figures 2a, 2b, and 2c, the density of peptides is 1%, 10 %, and 100 %.

Figure 2



Atomic force microscopes are ideal for visualizing the surface texture of polymer materials. In comparison to a scanning electron microscope, no coating is required for an AFM. Images a, b, and c are of a soft polymer material and were measured with close contact mode.

Figure 3



At the bottom is an illustration of a 3-Dimensional image of a patterned polymer material deposited on silicon substrate. At the top is a 2-Dimensional image of the polymer structure at the top of one of the lines.

Metrology

Many methods are available for measuring the size of particles suspended in a liquid. However, such techniques give only a statistical average of particle size. Detailed visualization and metrology of nano-particles is possible with traditional electron microscopy. However, SEM and TEM require sample preparation such as coating and micro-toning. AFM allows the direct measurement of particle metrology. Sample preparation requires finding a substrate to which the particles naturally adhere.

Below are images of two sizes of latex spheres measured with the AFM. The size of the particles can be directly measured with a line profile.

Figure 4

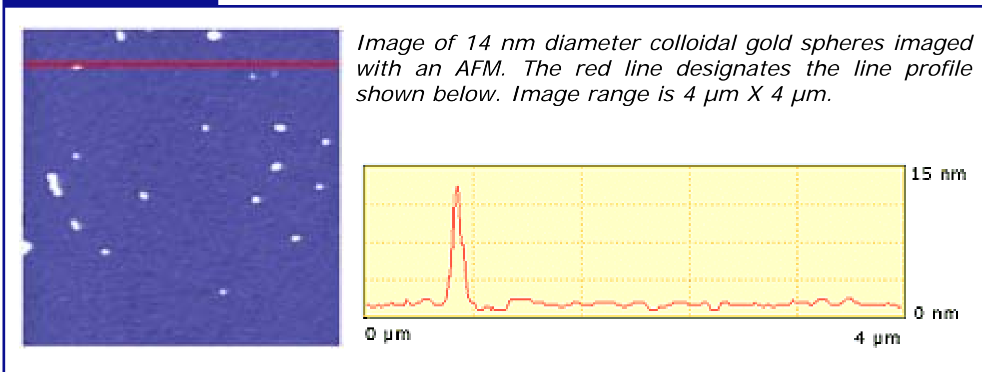


Image of 14 nm diameter colloidal gold spheres imaged with an AFM. The red line designates the line profile shown below. Image range is 4 µm X 4 µm.

Figure 5

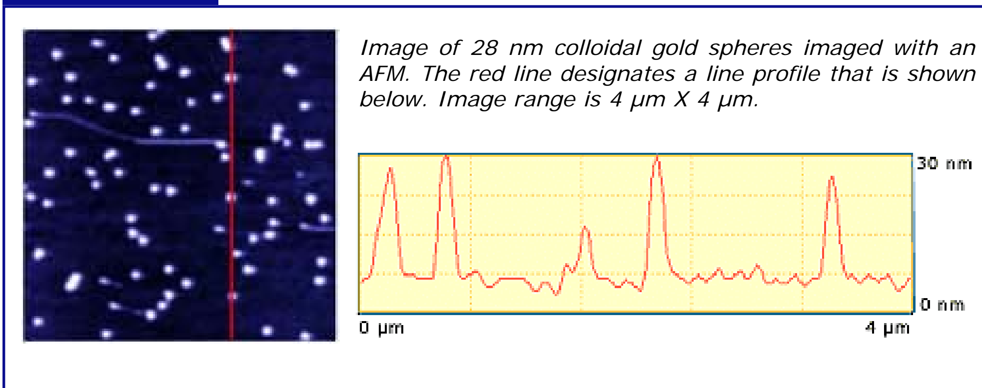


Image of 28 nm colloidal gold spheres imaged with an AFM. The red line designates a line profile that is shown below. Image range is 4 µm X 4 µm.

Materials Sensing

The AFM makes it possible to measure not only the topography of the sample but also changes in the mechanical properties of the surface. The two most common types of material sensing modes are Lateral Force Microscopy(LFM) and Phase Contrast Mode(PCM).

The torsion of the cantilever is monitored with the AFM scanning head in lateral force microscopy. As the cantilever is scanned across the surface, the amount of torsion changes depending on the types of materials at the surface. It is possible to acquire both an LFM image and a topographic image simultaneously with an AFM.

Figure 6

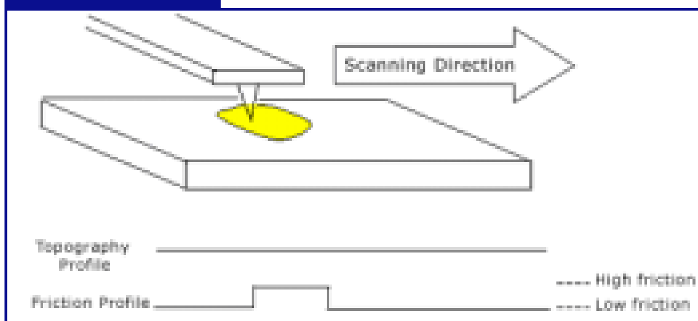
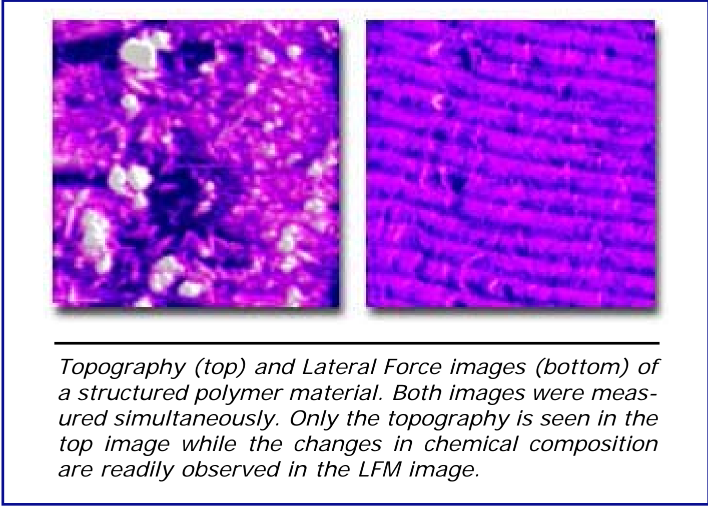


Figure 6: As the probe is scanned across a surface, any change in chemical composition can be detected by a change in the lateral torsional motion of the cantilever. In this example the yellow area will show different "friction" than the white area.

Although this technique is not quantitative, it provides a contrast mechanism for differentiating chemical materials at a sample surface. LFM is best applied to samples with small topographic features because changes in topography can also cause changes in the cantilever torsion.

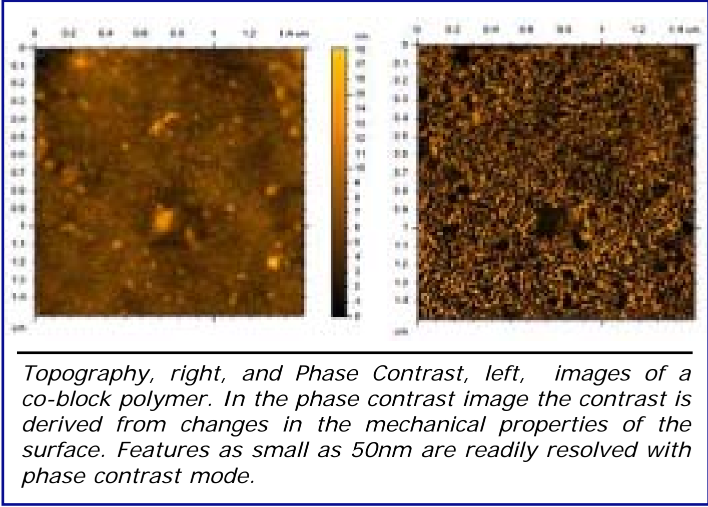
Figure 7



Topography (top) and Lateral Force images (bottom) of a structured polymer material. Both images were measured simultaneously. Only the topography is seen in the top image while the changes in chemical composition are readily observed in the LFM image.

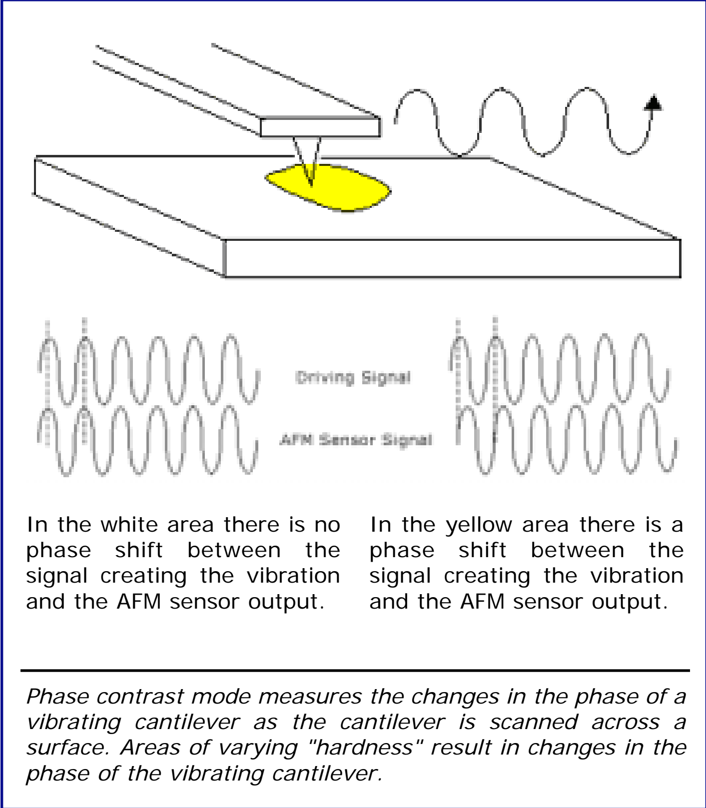
It is possible to measure changes in the mechanical properties at a polymer surface with PCM. Close contact mode operates by maintaining the amplitude of a vibrating cantilever constant while scanning over a polymer surface. At the same time, monitoring changes in the phase of the cantilever gives an image that is related to the localized "hardness" of the surface. A harder section of a sample will give More (or Less) phase shift of the vibrating cantilever as it scans across a sample.

Figure 8



Topography, right, and Phase Contrast, left, images of a co-block polymer. In the phase contrast image the contrast is derived from changes in the mechanical properties of the surface. Features as small as 50nm are readily resolved with phase contrast mode.

Figure 9



In the white area there is no phase shift between the signal creating the vibration and the AFM sensor output.

In the yellow area there is a phase shift between the signal creating the vibration and the AFM sensor output.

Phase contrast mode measures the changes in the phase of a vibrating cantilever as the cantilever is scanned across a surface. Areas of varying "hardness" result in changes in the phase of the vibrating cantilever.