

Applications of AFM-IR—Diverse Chemical Composition Analyses at Nanoscale Spatial Resolution

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Introduction

The combination of infrared (IR) spectroscopy and atomic force microscopy (AFM) has produced a technique, called AFM-IR, which is becoming one of the most important recent developments in the field of IR spectroscopy and chemical imaging. Conventional Fourier transform infrared (FT-IR) microspectroscopy is well established as a technique for chemical characterization of small samples down to the 3–10 μm size range. This diffraction-imposed size limit has prevented the application of FT-IR microspectroscopy to smaller analysis regions that are relevant to analysis problems in polymer materials and the life sciences. The nanoIR™ instrument (Anasys Instruments, Santa Barbara, CA) described here uses an AFM probe as the IR absorbance sensor and hence breaks through the diffraction limit to attain spatial resolution improvements of between one and two orders of magnitude beyond previous techniques. Thus, the AFM-IR concept provides chemical information from nanoscale regions of polymers and other organic materials. This article describes the physics behind the technique, followed by results from several applications.

How AFM-IR Works

The heart of the AFM-IR technique is a patented technology based on the effect of photothermal-induced resonance (PTIR). The technique was pioneered by Dr. Alexandre Dazzi from the Laboratoire de Chimie Physique, CLIO, Université Paris-Sud, Orsay, France, using the free electron laser source at that facility [1–3]. For the nanoIR instrument, a laboratory-scale tunable IR source was optically coupled to an AFM as shown in Figure 1.

IR signal generation. The nanoIR system uses a pulsed, tunable IR source to excite molecular vibrations in a sample that

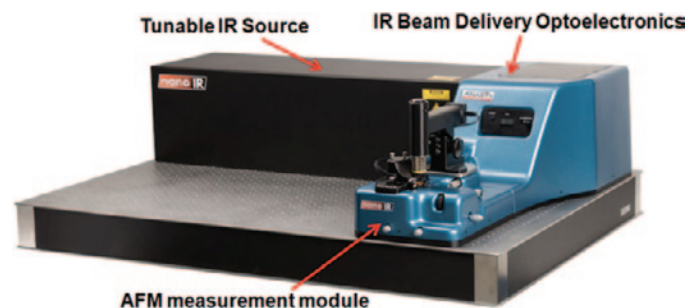


Figure 1: The nanoIR AFM-IR instrument, including a tunable IR source, IR-beam delivery optoelectronics, and AFM measurement module.

is mounted on an IR-transparent prism of zinc selenide (ZnSe). The incident light is totally internally reflected at the interface between the prism and sample for most organic materials. A standing wave, or evanescent field, is produced, which extends through the sample film to a distance on the order of the wavelength of light. Importantly, the total internal reflection conditions of the experimental setup reduce background interactions of the source radiation with the AFM cantilever. This creates an illumination configuration similar to conventional attenuated-total-reflectance (ATR) spectroscopy. The system's IR source is designed using proprietary technology and is continuously tunable from 900 to 3600 cm^{-1} covering a broad range of the mid-IR spectrum. As the sample absorbs radiation, it heats up, leading to a rapid thermal expansion that excites resonant oscillations of the cantilever. An operational schematic of the AFM-IR instrument is shown in Figure 2. The oscillations induced in the

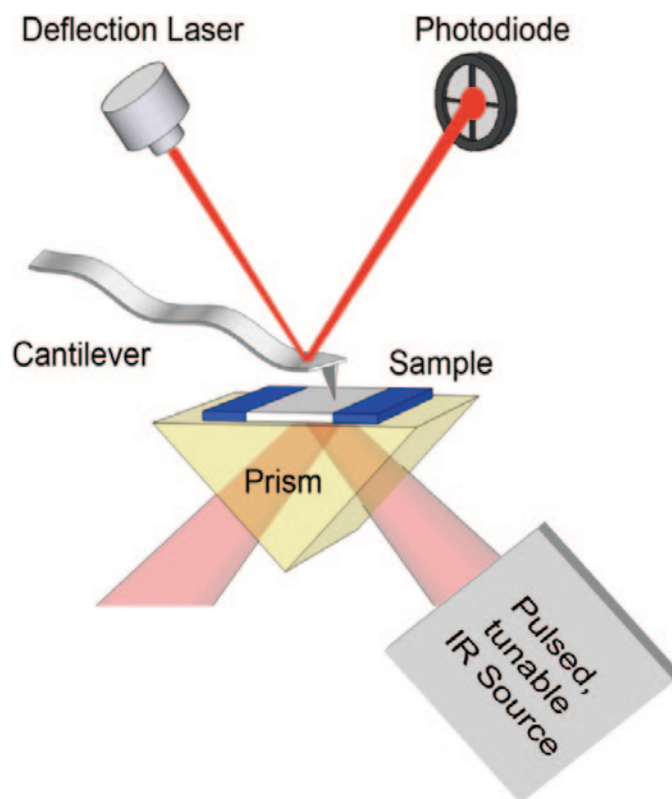


Figure 2: The AFM-IR technique uses a pulsed, tunable IR source to excite molecular resonances in the sample. Absorption of IR radiation by the sample leads to a rapid thermal expansion that excites resonant oscillations of the cantilever.

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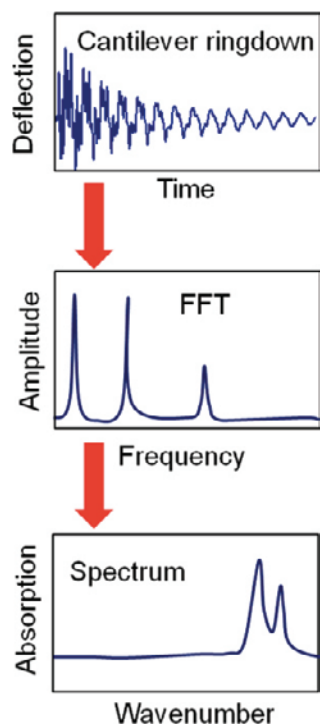


Figure 3: Cantilever oscillations decay in characteristic ringdowns (top) that can be analyzed by Fourier techniques to extract their amplitude and frequency (middle). Measuring the amplitude of the cantilever oscillation as a function of the source wavelength creates local absorption spectra (bottom). The oscillation frequencies of the ringdown are also related to mechanical stiffness of the sample.

cantilever by absorption of the incident IR laser pulse decay in a characteristic ringdown as shown in Figure 3.

IR signal analysis. The raw cantilever ringdown signal usually contains multiple resonant frequency components. The signal amplitude at each individual cantilever ringdown frequency can be determined by Fourier transforming the raw signal to extract the amplitudes and frequencies of the oscillations (Figure 3). Measuring the amplitudes of the cantilever oscillation as a function of the source wavelength creates local absorption spectra. Typically, the height of the most intense cantilever ringdown peak in the fast Fourier transformed (FFT) spectrum (middle of Figure 3) is measured for each wavelength as the laser source is stepped one wavelength at a time through the spectral region of interest. The IR spectrum is obtained by plotting the laser wavenumber on the x axis versus the cantilever ringdown amplitude on the y axis.

Users of the AFM-IR instrument can quickly (~ 60 s) survey regions of a sample via AFM imaging and then acquire 8 cm^{-1} resolution chemical spectra at selected regions on the sample at a rate of about one spectrum/min. Polymer spectra acquired with the nanoIR system have exhibited good correlation with bulk FT-IR spectra [4]. This allows the user to export AFM-IR spectra to be compared with standard spectra in commercial IR databases where they can be digitally searched in order to chemically identify the materials at specific sample locations.

Alternatively, the IR source can be tuned to a single wavelength of a specific functional group absorption band to map compositional variations across the sample surface. This is accomplished by measuring the cantilever ringdown amplitudes, as shown in Figure 3, for each AFM tip position as it is scanned across the surface at a rate of 0.1 Hz per image.

Specimen requirements. The spatial resolution of the IR spectra measured is determined by the AFM tip size and thermal diffusion in the sample, which can lead to a deterioration in spatial resolution for thicker samples. For sample thicknesses from 100 to 500 nm, we estimate the spatial resolution of the IR spectra to be about 100 nm. It is also important that there be good contact between the ZnSe prism and the sample for best results. We have prepared samples using a number of techniques, including deposition from solution, spin coating, and microtomy to create thin sections.

Other signals. In addition to its ability to provide 8 cm^{-1} resolution infrared spectra and compositional mapping at high spatial resolution, the nanoIR system provides information on the mechanical properties of the sample. This is accomplished by monitoring the frequency of the fundamental or higher resonant modes of the cantilever. This is analogous to the contact resonance method used for a number of years in the AFM community. The contact resonant frequency of the cantilever correlates to the stiffness of the sample and can be used to qualitatively map the modulus of the sample. Higher cantilever ringdown frequencies correspond to stiffer regions of the sample. The nanoIR platform can also perform nanoscale thermal analysis using special AFM cantilevers that incorporate a resistive heating element in the end of the cantilever. These cantilevers, in combination with the system, allow local measurement of certain transition temperatures, such as the melt temperature (T_m) or glass-to-rubber transition temperature (T_g) of materials at a single point or at an array of points across a sample. This allows identification or mapping of amorphous/crystalline content, stress, extent of cure, or other material properties that can be characterized through the thermal properties (for example, T_g) of the material.

Multifunctional analysis. This tool provides nanoscale surface morphology, as well as chemical, mechanical, and thermal properties. The nanoscale spatial resolution provided by this approach enables IR spectroscopic and thermal characterization of materials at length scales an order of magnitude smaller than previously possible using conventional instrumentation.

Applications for AFM-IR

Polymer blends. Using the nanoIR instrument, AFM-IR absorption variations within distances less than the

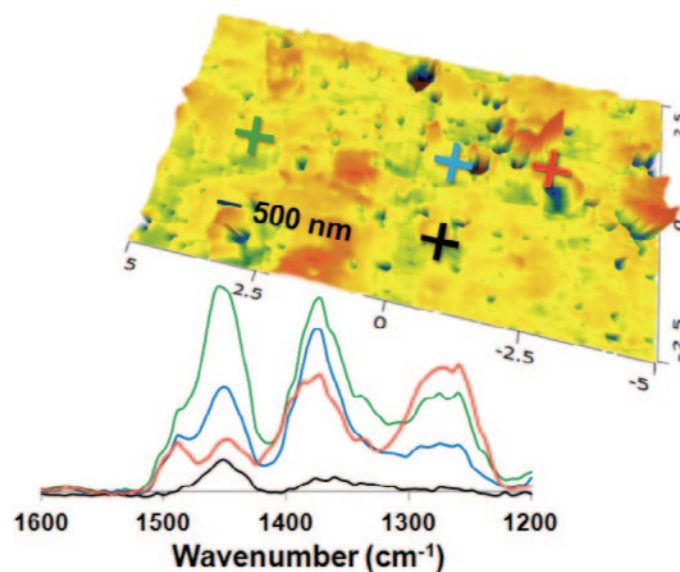


Figure 4: AFM topography image (top) for a blend of four different polymer components. The IR spectra shown at the bottom were recorded at the AFM tip locations on the image, indicated by the correspondingly colored “plus” signs. The band at 1490 cm^{-1} in the red spectrum indicates it contains the largest percentage of aromatic components, while the green spectrum contains a higher percentage of aliphatic compounds as indicated by the stronger bands at 1460 and 1375 cm^{-1} . The blue spectrum with a strong intensity at 1375 cm^{-1} likely contains a significant PP contribution.

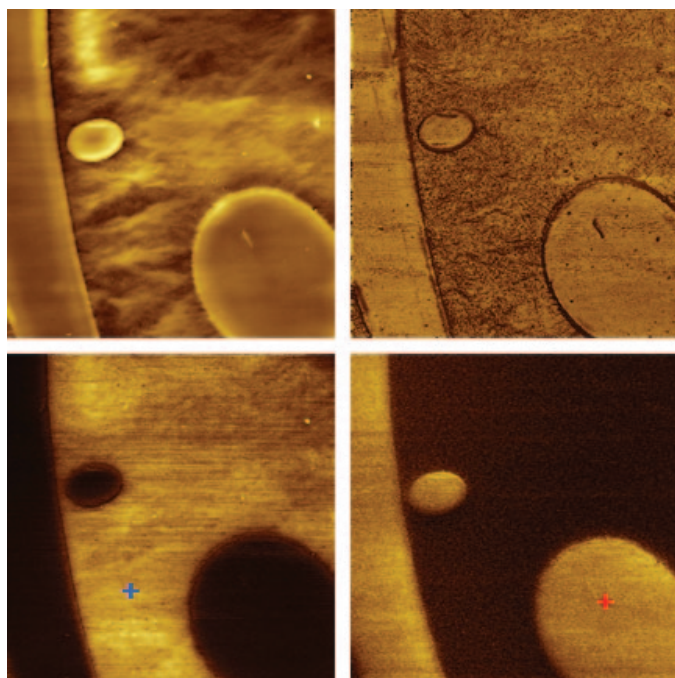


Figure 5: Images of two sulphur-containing poly(arylene) polymers in a polymer blend: one amorphous (A) and the other semicrystalline (B). (top left) AFM topographic image. (top right) Contact resonance frequency image showing the relative stiffness between the amorphous (uniform stiffness) and the semicrystalline polymer, which exhibits significant variations in stiffness. (middle left) IR absorption image collected with the light source tuned to a fixed wavenumber of 1388 cm^{-1} characteristic of polymer B. (middle right) IR image collected with the light source tuned to a fixed wavenumber of 1248 cm^{-1} characteristic of polymer A. Brightness in these images highlight the location of the two polymers comprising the blend. (bottom) IR spectra of polymer A (red) and polymer B (blue) collected from the correspondingly colored locations in the middle panels (+). Image width = 20 μm .

diffraction limit (3–10 μm) may be demonstrated with a commercial polymer blend sample (Figure 4). The blend is composed of four different components, including poly(ethylene terephthalate) (PET), poly(ethylene) (PE), poly(propylene) (PP), and poly(maleimide) (PMI). These components are not readily identifiable from the AFM image alone, as is often the case for blended polymer materials. However, as shown in Figure 4 the area under the black cross marker was identified through the IR spectrum as the aliphatic component, most likely PE. Spectra at the other locations show varying relative peak ratios, indicating changes in the local chemical signatures. Specifically, the red spectrum with an intense shoulder at 1490 cm^{-1} is mostly due to PET,

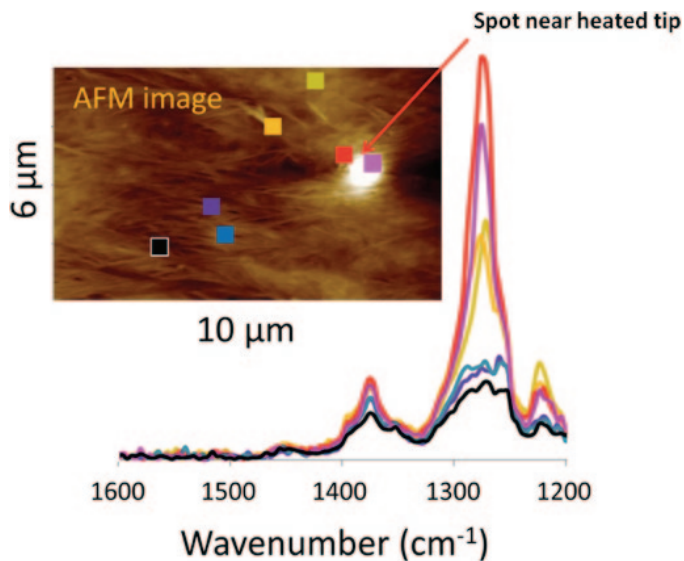


Figure 6: Local microdomains of semicrystalline polymer. (top) Contact mode AFM height image and (bottom) IR spectra at selected positions (bottom) of P(HB-co-HHx) (7.6 mol % HHx) [4].

whereas the blue spectrum with an intense band at 1375 cm^{-1} likely consists mostly of PP.

Figure 5 shows four images of the same region of a polymer blend sample consisting of two sulphur-containing poly(arylene) polymers: one amorphous (polymer A) and the other semicrystalline (polymer B). This polymer blend was microtomed at ambient temperature to prepare it for measurement with the nanoIR system. The upper-left image shows the AFM topographic image with lighter areas representing higher elevations of the sample surface. A significant portion of the variation in the topography is a result of the microtoming process, with the small white spots caused by contamination occurring during the deposition of the sections. The upper-right image shows a contact resonance frequency image collected by the AFM tip, with the lighter areas representing stiffer regions of the sample. The contact frequency image shows the amorphous material as a more uniform light-brown color in contrast with the more variable semicrystalline polymer, which is composed of both amorphous and crystalline polymer, leading to significant variations in stiffness. In both the topography and contact resonance images there is evidence of a ring of the semicrystalline phase surrounding the amorphous regions in the lower part of the image.

The middle two images are IR absorption images. The middle-left image was collected with the tunable IR source fixed at 1388 cm^{-1} , where semicrystalline component B of the polymer blend absorbs strongly. The middle-right image was collected with the tunable IR source fixed at 1248 cm^{-1} , where the amorphous component A absorbs strongly. The light areas in these images indicate regions with higher IR absorbance at the respective wavenumbers, indicating that the upper-right portion of the image is largely polymer B, while there are domains of polymer A in the lower-right and on the left of the image. Representative spectra of polymer A (red) and polymer B (blue) are shown at the bottom of

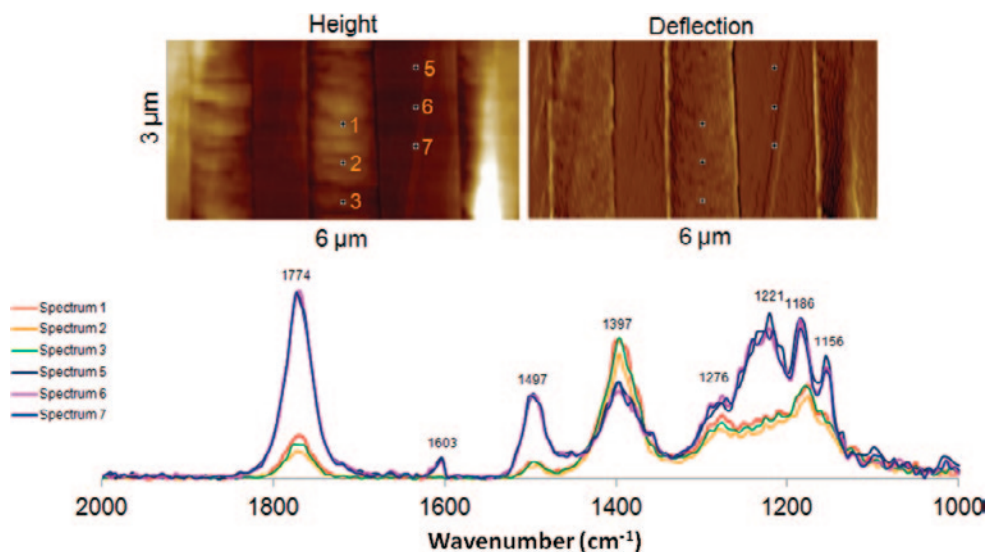


Figure 7: Analysis of a multilayer film of P[VDF-HFP] and PC using AFM-IR. The intensity of 1774 and 1186 cm^{-1} bands due to PC are weak in spectra 1–3 and increase dramatically in intensity in spectra 5–7. The strongest absorbance of P[VDF-HFP] occurs at 1397 cm^{-1} .

Figure 5, and these spectra can be used to unequivocally identify the two materials. The correspondingly colored plus signs in the middle panels identify the locations where the spectra at the bottom were collected.

Microdomain-forming semicrystalline polymers. Local microdomains of semicrystalline poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P(HB-*co*-HHx)), a biodegradable polymer produced by bacteria, can be probed with the nanoIR instrument [4]. Figure 6 shows a contact mode AFM image and seven AFM-IR spectra collected on a sample film of P(HB-*co*-HHx) at the locations indicated. The white spot near the right edge of the AFM image in Figure 6 is a “high” area generated when an AFM tip was brought close to the sample surface, heated to 350°C for 90 s and then withdrawn. The AFM and AFM-IR measurements shown were recorded after the sample had cooled back to room temperature. Spectra collected near

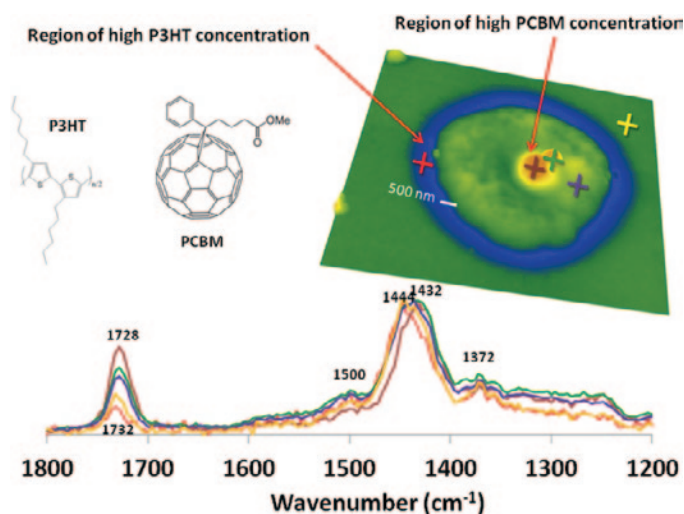


Figure 8: Molecular structures of the P3HT and PCBM components of a photovoltaic material (top left). AFM image (top right) and normalized spectra (bottom) of a heat-treated PCBM-doped P3HT sample [5].

the site of the heated spot have much higher IR absorbance near 1276 cm^{-1} than spectra collected farther away. The observed local differences in the relative IR absorbance intensities and band shapes in the vicinity of the 1276 cm^{-1} band, where C-O-C backbone stretching vibrations occur, would be impossible to resolve at this spatial resolution using conventional FT-IR micro-spectroscopy [4].

Multilayer film. The nanoIR instrument can distinguish two alternating components in a cross section of a poly(vinylidene fluoride-*co*-hexafluoropropylene)-polycarbonate (P[VDF-HFP]-PC) multilayer film. Figure 7 shows height and deflection AFM images, as well as 6 individual AFM-IR spectra collected from

the P[VDF-HFP] and PC layers of the multilayer film. The intensities of the 1774 and 1186 cm^{-1} bands due to PC are weak in spectra 1–3 and suddenly increase dramatically in intensity in spectra 5–7. The strongest absorbance of P[VDF-HFP] occurs at 1397 cm^{-1} .

Organic photovoltaic materials. Identification of chemical defects in organic photovoltaic materials is a promising application for the nanoIR instrument (Figure 8). The (6,6)-phenyl- C_{61} -butyric acid methyl ester (PCBM) component (the orange circular feature at the center) tends to phase-separate from the bulk poly(3-hexylthiophene) (P3HT). Using the 1728 cm^{-1} band as the marker for PCBM, AFM-IR spectra show that the orange feature has absorption characteristics of pure PCBM (brown spectrum), whereas the blue rim of the defect is mostly P3HT (red spectrum). The purple spectrum has an intermediate intensity at 1728 cm^{-1} , and the broadened

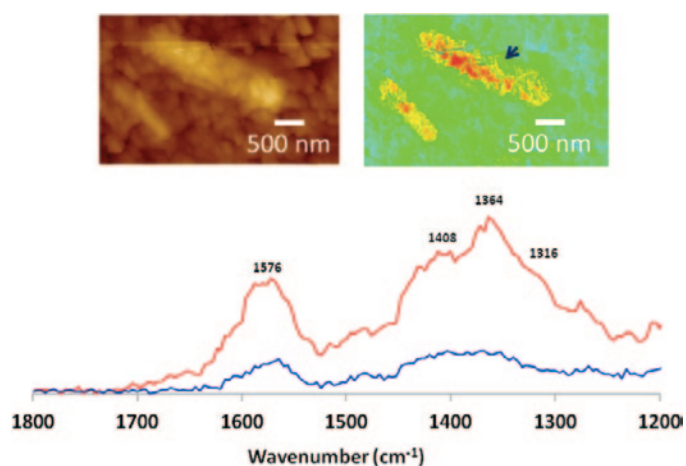


Figure 9: AFM image (top left) and IR absorption image collected with the light source tuned to a fixed wavenumber of 1360 cm^{-1} (top right) of a cellulose sample containing microfibrillated cellulose (MFC). AFM-IR spectra (bottom) collected from a MFC particle (red), indicated by the arrow, and from the surrounding matrix (blue).

band near 1440 cm^{-1} is the result of P3HT and PCBM contributions [5].

Microfibrilated cellulose. The AFM-IR imaging capability of the nanoIR instrument has also been used to visualize microfibrilated cellulose (MFC). This material typically has higher local crystallinity and mechanical strength than cellulose and is being investigated for use as a paper additive and as a component of polymer nanocomposites. Figure 9 shows an AFM topographic image and an IR absorbance image collected at the same sample location by the AFM tip while the sample was being illuminated at the fixed wavenumber of 1360 cm^{-1} by the tuneable pulsed source. The red regions of the IR absorbance image indicate locations where approximately 500 nm wide pieces of microfibrilated cellulose are differentiated from the bulk cellulose (green areas). Figure 9 also shows representative AFM-IR spectra taken from the MFC (red) and bulk (green) regions of the sample. The overall IR spectral intensity in the more dense MFC regions is higher than in the bulk, likely indicating higher crystallinity. From the chemical image of the microfibril (red) in Figure 9, the spatial resolution of analysis can be estimated to be about 50 nm.

Conclusion

Chemical spectroscopy on the nanoscale opens many new opportunities for materials characterization in the growing world of nanotechnology. While scanning probe microscopies are now entering their third decade and are used

widely, the arrival of AFM coupled with chemical identification is an important step forward. Analytical spatial resolutions in the 50–100 nm range have been demonstrated with AFM-IR, compared to 3–10 μm with conventional diffraction-limited FT-IR microspectroscopy. Adding the capability of mechanical and thermal property mapping to the topographic and spectral information available through the nanoIR system results in a comprehensive multifunctional characterization tool for the analysis of polymers and biological materials at sub-micrometer length scales.

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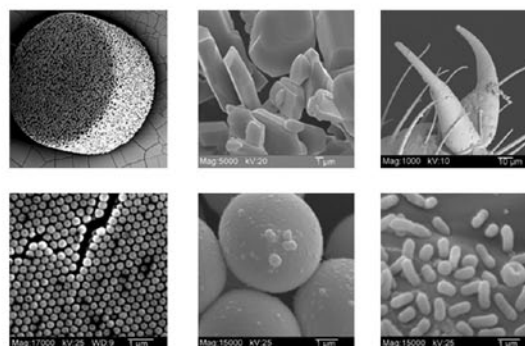
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