Interface Analysis of Composites Using AFM-Based Nanoscale IR and Mechanical Spectroscopy

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Introduction

Composite materials are becoming increasingly important in today's world, where lighter materials with enhanced properties are in high demand. Carbon fibers, carbon black, graphite, graphine, carbon nanotubes, quartz particles, nanocrystalline cellulose, and clays are among the materials being added to bulk polymers in an effort to achieve better properties and performance. It is important not only to determine the size and locations of nanoparticle inclusions in bulk polymers, but also to characterize the important interphase region where the components interact. This article describes how an atomic force microscope (AFM) combined with infrared (IR) spectroscopy and mechanical spectroscopy can be used to not only locate and determine the size of inclusions, but also to characterize them chemically and mechanically. After introducing AFM-IR spectroscopy and Lorentz contact resonance (LCR) methodology for obtaining nanoscale mechanical spectra and images, results from three specific applications will be discussed. These applications include an isotactic poly(propylene) film with added SiO_2 particles, a polymer with carbon black particles incorporated under different processing conditions, and a carbon-fiber/epoxy composite material. The first example uses AFM-IR spectroscopy and IR absorbance imaging. The second example employs LCR mechanical property spectroscopy and imaging. The final example includes a combination of AFM-IR and LCR to obtain corroborating information about the important interphase region between carbon fiber and epoxy domains.

Materials and Methods

Spectroscopy. The method of AFM-IR spectroscopy is based on the photothermal-induced resonance (PTIR) effect, which was first demonstrated at the Laboratoire de Chimie Physique, CLIO, Université Paris-Sud, Orsay, France, by Dazzi using the free electron laser at that facility [1]. The technique has since been commercialized by Anasys Instruments (Santa Barbara, CA). Figure 1 shows a diagram of the Anasys nanoIR2™ instrument, which uses a benchtop tunable IR source optically coupled to an AFM. This second-generation instrument excites molecular vibrations in the sample from the top side using a pulsed, tunable IR source, making it no longer necessary to mount the sample on an IR-transparent prism and illuminate from below, as in the earlier version [2–3]. The IR source used in the experiments described here is either an optical parametric oscillator (OPO) laser that is continuously tuneable within the mid-IR spectral ranges of 3600–2350 cm^{-1} and 2000–900 cm^{-1}, or a quantum cascade laser (QCL) that is tuneable between 1800 and 1200 cm^{-1}. When the laser light wavenumber matches the energy of a specific molecular vibration, the light is absorbed by the sample. A heat pulse is generated when the excited molecules return to their ground state, leading to a rapid thermal expansion of the sample that excites resonant oscillations in the AFM cantilever, whose sharp tip is in contact with the sample surface. The oscillations induced in the cantilever by absorption of the incident IR laser pulse, decay in a characteristic ringdown pattern,
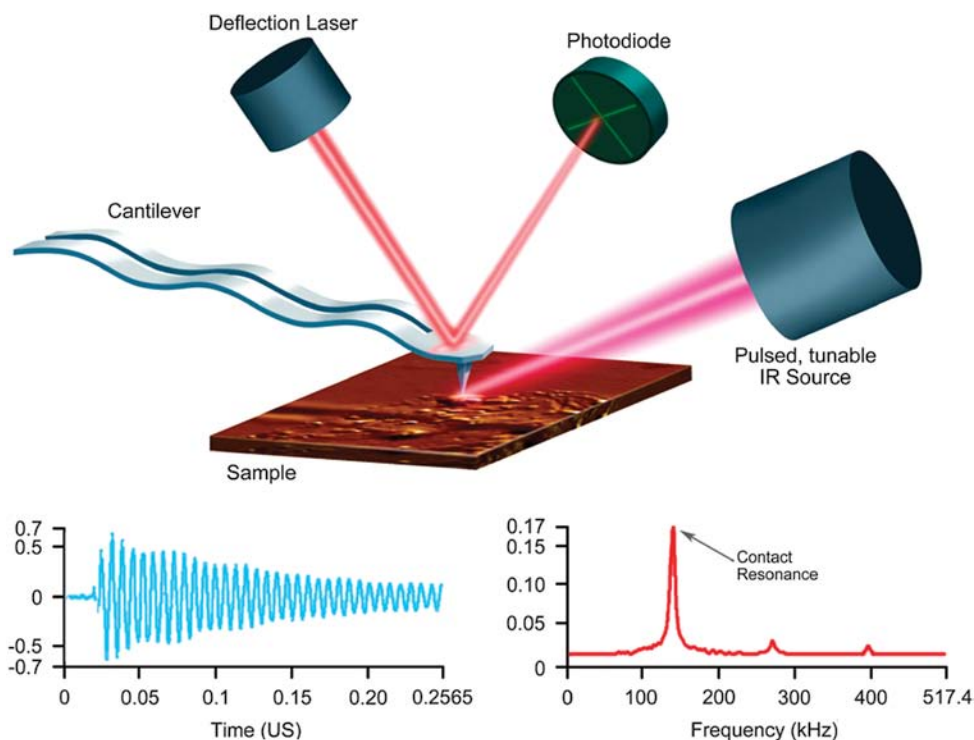

Figure 1: The AFM-IR technique uses a pulsed, tunable IR source to excite molecular resonances in the sample (top). Absorption of IR radiation by the sample leads to a rapid thermal expansion that excites resonant oscillations of the cantilever. Cantilever oscillations decay in characteristic ringdowns (bottom left) that can be analyzed by Fourier techniques to extract their amplitude and frequency (bottom right). The contact resonance peak frequencies of the cantilever ringdowns are related to the mechanical stiffness of the sample.

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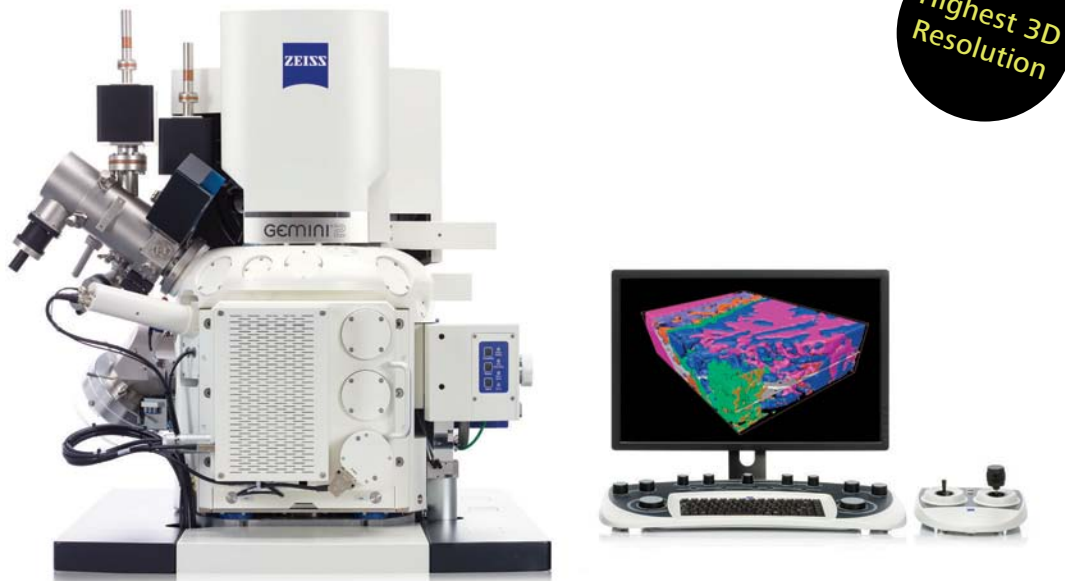
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such as that shown in Figure 1. The amplitude of this ringdown signal is directly proportional to the amount of IR radiation absorbed at that wavenumber. Photothermally detected AFM-IR spectra exhibit good correlation with bulk Fourier transform infrared (FT-IR) spectra, enabling the user to export spectra for digital searching against commercial IR databases. As illustrated in Figure 1, the raw cantilever ringdown signal usually contains multiple resonant frequency components, which become apparent after Fourier transforming the raw signal to extract the amplitudes and frequencies of the oscillations. The amplitudes and peak frequencies of the individual cantilever ringdown modes can change/shift depending on the mechanical properties of the area of the sample being probed by the AFM tip. Later, we will discuss how to take advantage of this using the LCR method to obtain extremely sensitive and specific mechanical spectra and images.

Imaging. AFM images of areas up to 80 cm^{-1} × 80 cm^{-1} can be obtained in a few minutes. AFM-IR spectra at selected points on the sample surface can then be collected at the rate of about one spectrum/min. Alternatively, the laser source can be tuned to a single wavenumber to obtain specific functional group IR absorption maps of compositional variations across the sample surface. This is accomplished by measuring the cantilever ringdown amplitudes for each AFM tip position as it is scanned across the surface at a rate of 0.1 Hz per image line.

LCR spectroscopy and imaging. As alluded to earlier, information regarding the nanoscale mechanical properties at specific locations on the sample surface is contained in the frequency values of individual resonant modes of the cantilever. The contact resonant frequency of the cantilever correlates with the stiffness of the sample and can be used to qualitatively map the elastic modulus of the sample. Higher cantilever contact resonance frequencies correspond to stiffer regions of the sample. We can take advantage of this and collect extremely information-rich mechanical spectra and images using methodology referred to as Lorentz contact resonance (LCR) [4]. A diagram of the LCR configuration (available commercially as part of the nanoIR2 instrument) is shown in Figure 2. A special U-shaped AFM
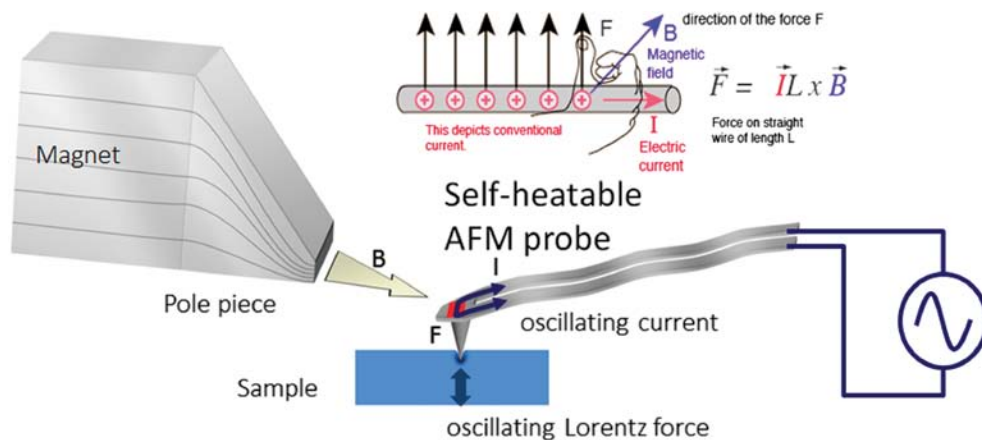

Figure 2: The Lorentz contact resonance (LCR) technique mechanically perturbs the sample surface as a function of frequency. The signal acquired is based on the Lorentz "right-hand rule" of electromagnetism. A frequency generator is used to send an alternating current through a conducting U-shaped AFM cantilever. The frequency is rapidly swept from 0 to 1 MHz. A permanent magnet with a pole piece directs the magnetic field toward the cantilever at a 90-degree angle, producing an oscillating force of the AFM tip down on the sample. The response of the AFM cantilever to the applied force modulation is measured using the same detection scheme shown in Figure 1 [4].
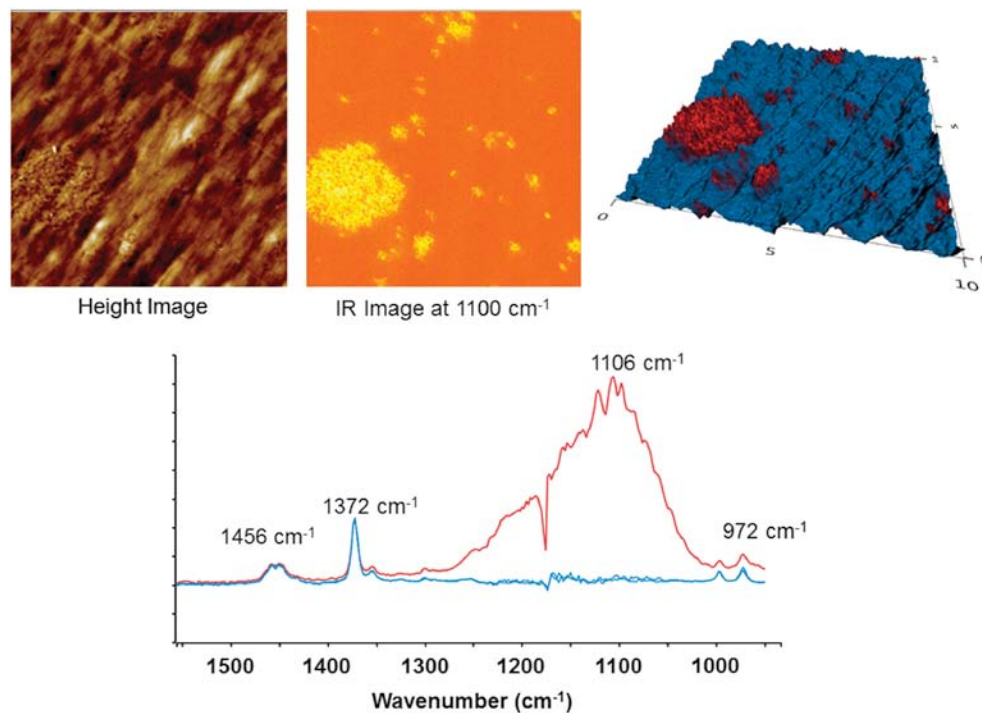

Figure 3: AFM topography image (top left), IR absorbace image collected at 1100 cm^{-1} QCL excitation wavenumber (top center), and a composite overlay of the AFM topography and IR absorbance images (top right) from a 300 nm thick cross section of a poly(propylene)/SiO$_2$ nanocomposite sample. Single-point AFM-IR spectra (bottom) collected in a region of high SiO$_2$ concentration (blue) and from the iPP matrix (red). Image width = 10 μm.

cantilever that conducts electricity enables the frequency of an alternating current applied to the cantilever to be rapidly swept from 0 to 1 MHz [4]. Using a permanent magnet with a pole piece to direct a magnetic field toward the U-shaped cantilever at a 90° angle produces an oscillating force, which pushes the AFM tip down on the sample [4]. This force is a clean excitation producing clean, well-formed resonance peaks over a broad frequency range. The response of the AFM cantilever to the applied force modulation is measured using the same detection scheme shown in Figure 1, which
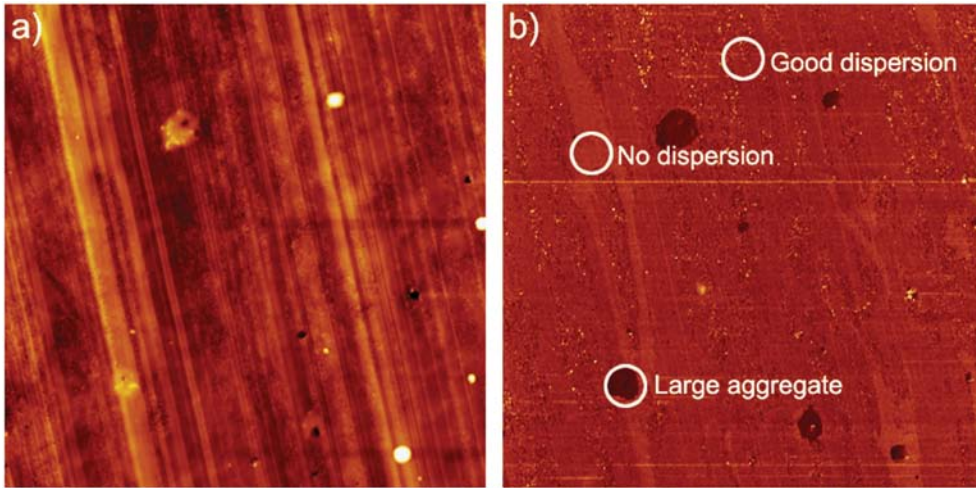
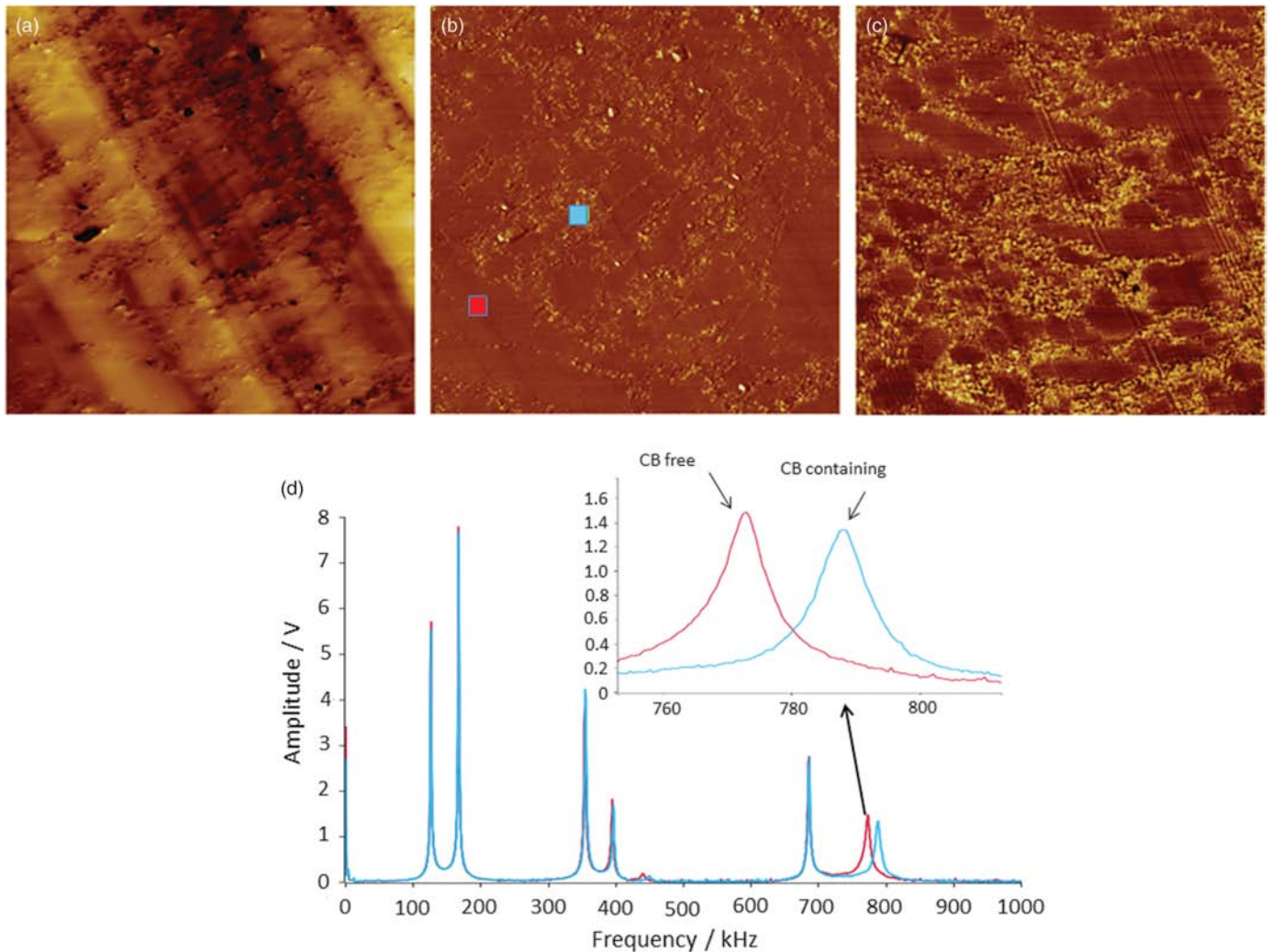**Figure 4:** AFM topography image (a) and LCR amplitude image (b) of a carbon-black-filled polymer sample. Darker areas in the LCR image represent locations of high carbon black concentration. Image width = 60 μm.

involves detecting the instantaneous angle of the cantilever via reflection of a visible laser off its top surface. Lorentz contact resonance mechanical spectra are recorded at a single point on the sample surface by sweeping the excitation frequency applied to the AFM tip from 0 to 1 MHz, allowing us to interrogate a number of resonant modes of the cantilever. Higher modes in the cantilever have a higher effective stiffness allowing us with a single cantilever to cover a broad range of material stiffness as demonstrated by measurements on materials having modulus ranging from 100 MPa to 100 GPa. LCR images are collected by holding
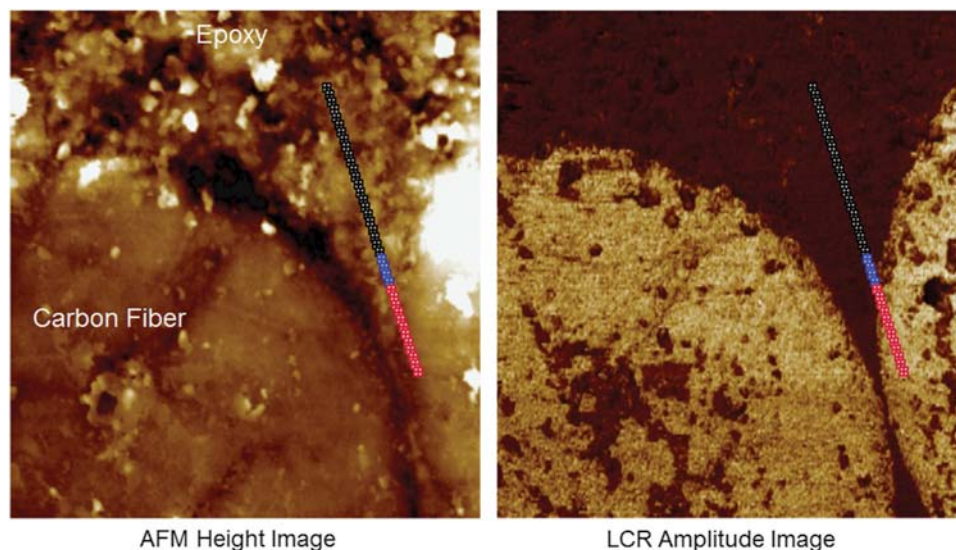

Figure 5: AFM topography image (a) and LCR amplitude image (b) of a carbon-black-filled polymer sample. The small red and blue squares shown on the LCR amplitude image indicate locations where the LCR mechanical spectra shown in the corresponding colors (d) were collected. The zoomed inset shows a clear separation between the contact resonance peak frequency of the bulk polymer and carbon black domains, with the carbon black peak frequency being significantly higher. LCR amplitude image (c) collected at the carbon black contact resonance peak frequency (790 kHz) indicated (in blue) in the inset of the bottom left frame. Lighter areas have higher carbon black concentration. Image width = 10 μm.

Figure 6: AFM topography image (left) and LCR amplitude image (right) of a carbon fiber/epoxy composite cross section. The LCR amplitude image was collected at an LCR frequency of 124.82 kHz, consistent with a contact resonance peak frequency for the carbon fiber domain. The red, blue, and black locations shown along a line extending from the bulk carbon fiber into the bulk epoxy are spaced by 50 nm and correspond to the colors of the spectra in Figure 7 [5]. Image width = 5 μm.
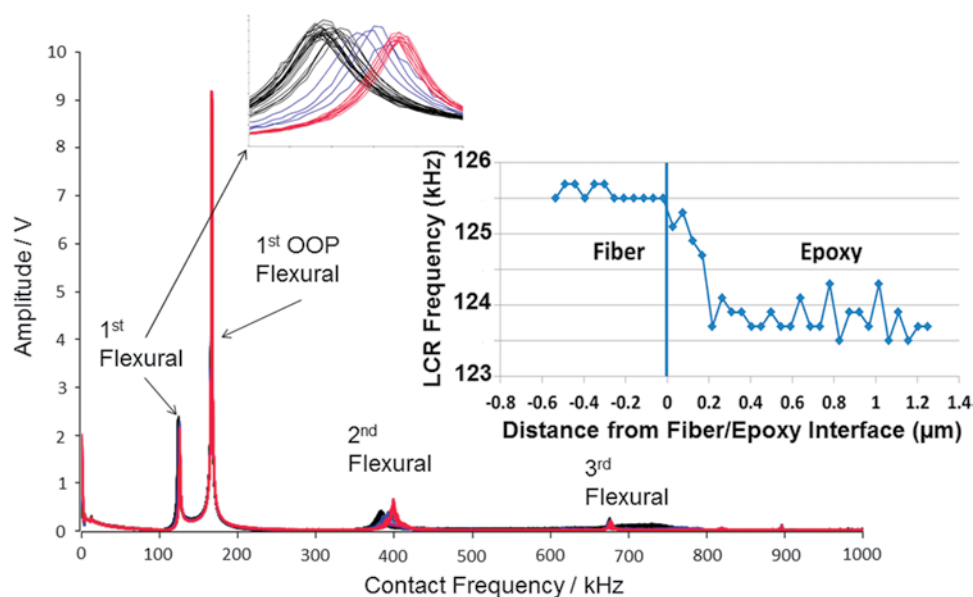

Figure 7: LCR spectra (left) showing cantilever mode changes across the interface between the carbon fiber and epoxy domains. Plot of the LCR peak frequency as a function of distance (Figure 6) from the carbon fiber/epoxy interface (right) [5].

the excitation frequency constant and monitoring the amplitude and phase of the oscillating cantilever while scanning the AFM tip over a specified region of the sample surface.

Multifunctional analysis. This AFM-based technology provides nanoscale surface morphology as well as chemical, thermal (not discussed here), and mechanical properties. The nanoscale spatial resolution provided by this approach enables IR spectroscopic chemical characterization of materials at length scales two orders of magnitude smaller than previously possible using conventional FT-IR microspectroscopic instrumentation [1–3].

Results and Discussion

Poly(propylene) film with added SiO$_2$ particles. This example demonstrates how AFM-IR spectroscopy and IR absorption images can chemically identify and spatially characterize SiO$_2$ domains in a bulk polymer matrix, where the domains are much smaller in size than the diffraction limit of conventional FT-IR microspectroscopy (3–10 μm). Figure 3 shows (top, from left to right) an AFM topography image, an IR absorption image recorded with the QCL at an excitation wavenumber of 1100 cm^{-1}, and an overlay of the two on a sample of isotactic poly(propylene) (iPP) with intermixed small particles of SiO$_2$. The bottom of Figure 3 shows IR spectra recorded from the bulk polymer (in blue) and from a region where the SiO$_2$ is present in high concentration (in red). The IR absorption bands due to iPP are clearly seen in both spectra at 1456, 1372, 995, and 975 cm^{-1}. The strong band centered at 1104 cm^{-1} is due to the IR absorption of an SiO$_2$-stretching vibration. The yellow and red areas seen in the 1100 cm^{-1} IR absorption and overlay images, respectively, show the locations of highest SiO$_2$ concentration, some of which are on the order of 20 nm in size. The 2 μm region where the SiO$_2$ particles have aggregated forming a domain several micrometers in diameter is also clearly observed. This characterization of the nanoparticle mixing would not be possible from the AFM topography image alone.

Carbon black dispersion. Figure 4 shows a comparison of an AFM topography image (left) and an LCR mechanical spectroscopy amplitude image (right) of a polymer sample with carbon black particles dispersed in it. Darker regions in the LCR image, recorded at one of the contact resonance peak frequencies of the bulk polymer, indicate locations of higher carbon black concentrations. This LCR image is exquisitely sensitive to relative stiffness differences across the sample surface. It is clear from the LCR image that the dispersion of the carbon black is not occurring consistently in the sample. Areas of no dispersion, good dispersion, and regions where large aggregates have formed are each observed within the 60 μm × 60 μm area examined. The location of carbon black domains is not at all clear from the AFM topography image. The depth sensitivity of the LCR technique is fairly shallow, of order of the AFM tip diameter. That said, it can sometimes sense the presence of objects that are buried well below the

sample surface if the object has an impact on the mechanical properties of the surrounding matrix over larger distances. The depth sensitivity of the AFM-IR technique is related to the size of the absorbing object. For an object of diameter D, the AFM-IR technique can sense the object to roughly a distance D beneath the surface, and it is not detected at a distance of ~3 D. This conclusion is based on models and simulations performed by Alex Dazzi.

The top half of Figure 5 shows an AFM topography image (5a) and LCR amplitude image (5b) of a 10 μm × 10 μm area of a different carbon black/polymer dispersion. The small red and blue squares shown on the LCR amplitude image indicate locations from which complete LCR mechanical spectra (shown in corresponding colors at the bottom of Figure 5) were collected. The zoomed region of the LCR mechanical spectrum around 780 kHz shows a clear separation between the contact resonance peak frequency of the bulk polymer and carbon black domains, with the softer polymer peak frequency being significantly lower. The image shown in Figure 5c was collected at a new location on the sample modulating the probe at the unique carbon black contact resonance peak frequency (790 kHz). The light areas of this image clearly highlight locations of high carbon black concentration. It is difficult to determine the specific locations of carbon black in Figure 4, because the image was collected at a scan size and pixel resolution in which the carbon black particles are the scale of individual pixels in the image. This was done to see the dispersion of the carbon black at a larger scale across the sample surface. The few dispersed white spots can be seen in the image when a carbon black particle corresponds to a pixel. In other locations we are measuring the mechanical properties of the polymer material, which incorporates the carbon black. The carbon black shows up brighter in Figure 5 because the image was collected at the fixed contact resonance peak frequency of 790 kHz, which corresponds to the carbon black component. We know that the carbon black is stiffer than the surrounding bulk polymer because the contact resonance peak frequency is higher. Thus, this LCR contact resonance peak frequency is ideal for imaging the uniformity of the carbon black dispersion in this polymer as a function of the dispersion conditions.

Carbon fiber/epoxy composite. Carbon fiber composite materials are used to reduce overall weight while maintaining or exceeding the mechanical strength of metallic counterparts in products such planes, automobiles, boats, and sporting goods. The chemical nature of the interphase region between the carbon fiber and surrounding epoxy matrix is important for understanding the ultimate mechanical properties of the composite material. Characterization tools with submicron spatial resolution, such as AFM-IR spectroscopy and imaging and LCR mechanical spectroscopy and imaging, should be useful for understanding and enhancing the properties of carbon fiber composites.
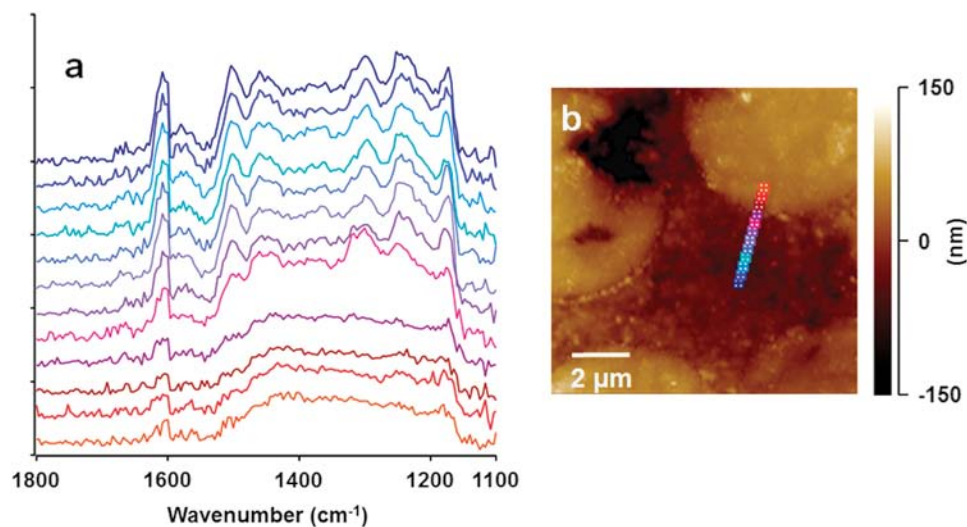

Figure 8: AFM-IR spectra (a) and AFM topography image (b) collected on a cross section of a carbon fiber/epoxy composite film. Spectra of various colors were recorded from the similarly colored locations on the AFM image spaced at 300 nm apart [5].

Figure 6 shows AFM topography (left) and LCR amplitude (right) images of a polished cross section of a 5 μm × 5 μm region of a carbon fiber/epoxy composite sample. The LCR amplitude image, collected at a contact resonance peak frequency of the carbon fiber component shows dramatically better contrast between the carbon fiber and epoxy domains than the AFM topography image. The red, blue, and black locations shown along a line extending from the bulk carbon fiber into the bulk epoxy are spaced 50 nm apart, with the blue locations representing the key interphase region between the two domains of the composite [5].

The left side of Figure 7 shows LCR mechanical spectra collected at the corresponding color-coded locations shown on the images in Figure 6 [5]. The inset represents a blow-up of the first flexural AFM cantilever mode centered around 125 kHz. The inset on the right side of Figure 7 is a plot of the LCR peak frequency as a function of distance from the carbon fiber/epoxy interface. The peak frequency is observed to be relatively constant within the carbon fiber and epoxy regions. The stiffer carbon fiber region with the higher contact resonance peak frequency exhibits less point-to-point variation than the same signal from the epoxy region. The gradual mechanical stiffness change, occurring in the 300-nanometer-wide interphase region, is likely a factor in why this material is so strong and does not shear easily at the interface when under strain.

The right side of Figure 8 shows a 10 μm × 10 μm AFM topography image of the same carbon fiber/epoxy material as in Figures 6 and 7 [5]. The left side of Figure 8 shows a series of 300-nanometer-spaced AFM-IR spectra collected using the OPO laser source along the line shown on the AFM image. The spectra recorded in the region of the carbon fiber (red) are very broad and featureless, as would be expected from a carbonized carbon fiber with only the aromatic ring stretching band remaining at 1600 cm⁻¹. The IR absorption from the epoxy matrix is stronger and clearly changes as a function of distance from the interface with the carbon fiber. Note the first epoxy AFM-IR spectrum (purple) collected closest to the interface between the two composite domains differs significantly from the remainder of the spectra that

extend into the bulk of the epoxy showing a stronger band at 1350 cm^{-1}. This band indicates a higher concentration of methylgroups and suggests a significantly different chemical nature of the epoxy component immediately adjacent to the carbon fiber domain, consistent with the location where the LCR mechanical spectra show a gradient in stiffness.

Conclusion

The ability to perform chemical and mechanical spectroscopy and imaging measurements at the nanoscale opens many new opportunities for characterizing composite materials. Although conventional scanning probe microscopies are useful for visualizing materials at high spatial resolutions, they provide limited chemical information. The combination of AFM-IR spectroscopy and imaging with LCR mechanical spectroscopy and imaging provides a multifunctional characterization tool for the analysis of composite materials at sub-micrometer length scales.

Acknowledgement

iPP/SiO$_2$ sample courtesy of Dr. Fischer, IPF Dresden.

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