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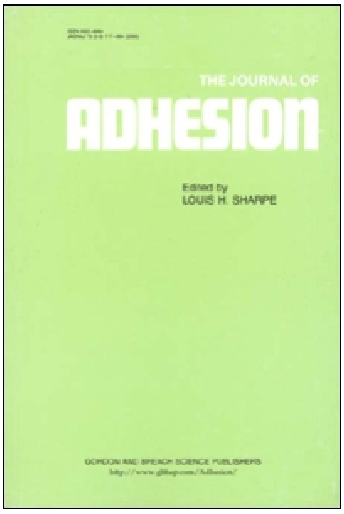

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Boerio, F. J. and Starr, M. J.(2008) 'AFM/FTIR: A New Technique for Materials Characterization', The Journal of Adhesion, 84: 10, 872 — 895

To link to this Article: DOI: 10.1080/00218460802445308

URL: http://dx.doi.org/10.1080/00218460802445308

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The Journal of Adhesion, 84:872–895, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460802445308

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AFM/FTIR: A New Technique for Materials Characterization

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A new type of infrared spectroscopy for obtaining the molecular composition of the surfaces of materials at ultra-high spatial resolution has been developed by combining atomic force microscopy (AFM) with Fourier-transform infrared spectroscopy (FTIR). This new analytical technique involves the use of an AFM to detect the response of a material to the absorption of modulated infrared radiation from an FTIR spectrometer and is referred to as AFM/FTIR spectroscopy. When the technique of AFM/FTIR spectroscopy is completely developed, we plan to use it to probe the molecular structure of interphases in polymer composites and adhesive bonds. Two approaches have been used to measure the response of polymer systems to infrared absorption. The first involves the use of a contact mode AFM probe to measure the thermal expansion of the polymer; the second involves using a scanning thermal microscopy (SThM) probe to measure the polymer's temperature increase. In either case, the output of the probe resembles an interferogram to which a Fourier-transform can be applied to obtain the infrared absorption spectrum. The first approach was used to obtain excellent quality AFM/FTIR spectra from various neat polymer films, including polystyrene, polycarbonate, and a model adhesive system consisting of an epoxy resin cross-linked with dicyandiamide. Excellent spectra were also obtained from polystyrene beads having a diameter of about 2 μ*m. The second approach, using an SThM probe to determine the temperature increase that accompanies infrared absorption, was also used to obtain interferograms of polymer samples such as polystyrene. However, the interferograms were noisy and the AFM/FTIR spectra obtained from them had a low signal-to-noise ratio. The present results, thus, show that AFM/FTIR spectroscopy is feasible but the spatial resolution of the technique remains to be shown.*

Keywords: AFM/FTIR spectroscopy; Atomic force microscopy; Dicyandiamide; Epoxy adhesive; Infrared spectroscopy; Interphases; Polycarbonate; Polystyrene; Scanning thermal microscopy

Received 17 April 2008, in final form 21 August 2008.

One of a Collection of papers honoring John F. Watts, the recipient in February 2008 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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I. INTRODUCTION

Our research group has been interested in "interphases" in composites and adhesive bonds for some time. The interphases in question represent transition regions near the surface of a fiber in a composite or the substrate in an adhesive bond over which the properties of a matrix material or adhesive vary from their "bulk" values to values that are strongly influenced by interactions with the fiber or substrate. These interphases are obviously very important since inferior properties within the interphase result in composites or adhesive bonds with inferior properties.

Many powerful analytical techniques are available to probe the molecular structure of interphases. However, characterization of the interphase is difficult since the interphase is usually a very thin region that is buried between much thicker phases. Techniques such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) can provide a great deal of information about interphases; however, it is usually necessary to prepare special samples or sputter through a thick layer of matrix material or adhesive in order to characterize the interphase when using these techniques. Thus, Bou, Martin, and Le Mogne used XPS to study the interphase between *in-situ* thermally evaporated aluminum and biaxially oriented films of poly(ethylene terephthalate) (PET). By monitoring the changes in the Al(2s), Al(2p), C(1s), and O(1s) spectra as a function of aluminum layer thickness, they were able to show that the aluminum metal atoms are very reactive with the PET surface, typically through sites of stronger basicity [1]. Subsequently, Leadley and Watts cast thin (~2 nm) poly(methyl methacrylate) (PMMA) films onto metal substrates and used high-resolution XPS to monitor changes in the C(1s) spectra as a result of specific interactions in the metal/polymer interphase. They observed a 0.1 eV shift in the C(1s) binding energy of the carboxyl carbon atoms due to interactions of PMMA with acidic sites on the substrates [2,3]. Possart and Fanter used XPS and reflection-absorption infrared spectroscopy (RAIR) to analyze model adhesives consisting of thin polymer films (3–100 nm) spin-coated or dip-coated onto aluminum or silicon substrates in atmospheric conditions. Although Possart and Fanter observed differences in resulting spectra of thin films near the interphase as compared with bulk material, they were unable to describe the specific adhesion mechanisms [4]. To avoid surface contamination by preparation in atmospheric conditions, Grundmeier and Stratmann introduced an *in-situ* method for RAIR analysis of the interphase between plasma-polymerized hexamethyldisilazane (HMDSZ) films and iron substrates [5]. Turner and Boerio used XPS and RAIR and somewhat similar *in-situ* sample preparation techniques to characterize the interphase between plasma-polymerized silica-like films and aluminum and titanium substrates; differences in the XPS and RAIR spectra that were related to film/substrate interactions were observed as the thickness of the plasma polymer films was decreased from several tens of nanometers to a few nanometers [6,7].

Dillingham and Boerio [8] used XPS and RAIR to characterize interphases between an amine-cured epoxide and mechanically polished aluminum substrates. They showed that the amino groups on the curing agent located adjacent to the substrate were more protonated ($\sim$50%) than the amino groups located farther away from the substrates. Protonated nitrogen atoms had a binding energy near 399.5 eV while un-protonated nitrogen had a binding energy near 398.0 eV. Barthes-Labrousse used several analytical techniques, including XPS, to examine the adsorption of monoethanolamine onto aluminum and hydroxylated aluminum substrates [9]. They found that the N(1s) binding energy was about 399.5 eV for adsorption onto clean aluminum but was about 401.9 eV for adsorption onto hydroxylated aluminum substrates. Bonding to clean aluminum involved coordination of nitrogen atoms to soft acidic sites (aluminum ions) on the substrate through the lone pair of electrons on the nitrogen atom. However, bonding to the hydroxylated substrate occurred by coordination of the lone pair of electrons on the oxygen atoms to hard, acidic aluminum ions and by formation of an alkoxide with elimination of water.

Kieffer and Hartwig used photoacoustic infrared spectroscopy (PAS) and attenuated total reflection (ATR) infrared spectroscopy to analyze the interphase reactions of isocyanates with an epoxy adhesive system. They solution cast phenyl isocyanate for various reaction times onto the surface of the cured epoxy and used PAS and ATR spectroscopy techniques to analyze the interactions between the isocyanate and cured epoxy system. For the parameters used in PAS, the penetration depth into the sample was 10 to 20 μm. For ATR, the penetration depth was 0.16 to 3.5 μm, depending on the crystal used (germanium or KRS5). Kieffer and Hartwig found that the isocyanate diffused into the cured epoxy and reacted with the secondary hydroxyl groups of the epoxy. They also found that if excess amine groups from the curing agent were present in the cured epoxy, they, too, reacted with the isocyanate [10].

One very interesting technique was reported by Boerio *et al.* [11] who used surface-enhanced Raman scattering (SERS) to probe the interphase in adhesive bonds consisting of an acrylic adhesive cured against a silver substrate. In SERS, the Raman scattering by a thin layer of organic molecules adjacent to the surface of certain metals such as silver, gold, and copper is enhanced by as much as 10^6 compared with its value well away from the metal surface. Thus, it is possible to observe the Raman scattering by an interphase even when the interphase is buried under a few hundred nanometers of adhesive. This is a very powerful technique for probing interphases but it is limited to those few metals that support SERS. Nevertheless, Boerio *et al.* were able to show that an interphase with unique structure existed in which saccharin, a component of the adhesive cure system, reacted with metal ions to form a metal salt. The metal ions extracted from the surface were important to the cure since they catalyzed the formation of free radicals from cumene hydroperoxide, another component of the cure system.

Hinder *et al.* described an ultra-low-angle microtomy (ULAM) sample tapering technique that was well suited to exposing polymer interphases since the resulting taper did not exhibit sample smearing [12]. Hinder *et al.* used XPS and ULAM to characterize the interphase formed by poly(vinylidene fluoride) (PVF_2) topcoat and polyurethane (PU) primer [13]. The same group also used time-of-flight TOF-SIMS and ULAM to characterize the interphase formed by the PVF_2 topcoat and PU primer [14]. The TOF-SIMS technique allowed much greater spatial resolution because of the smaller area illuminated.

Sum-frequency generation (SFG) is another very interesting technique with applications to interphases. SFG is a nonlinear optical process in which two light waves at frequencies ν_1 and ν_2 mix in a medium to generate a wave at the sum frequency $\nu_3 = \nu_1 + \nu_2$. This process is forbidden in a medium that has a center of inversion as one of its symmetry elements but is permitted at a surface or interface where no center of inversion can exist. Therefore, SFG is highly surface-specific and has been developed into a powerful and versatile surface probe. A review of this technique as applied to interfaces between dissimilar materials was given by Vidal and Tadjeddine [15]. Harp *et al.* [16] and Chen *et al.* [17] have also discussed the use of SFG to probe polymer interphases.

Kruger *et al.* [18] described a technique based on microscopic Brillouin spectroscopy that could be used to probe the mechanical properties of the adhesive in adhesive joints with a spatial resolution of approximately 1 μm. They found unexpectedly wide interphases of tens to hundreds of micrometers in diglycidylether of bisphenol-A (DGEBA) epoxy resins that were cured between substrates of glass and aluminum using diethylene triamine as the curing agent.

Fourier-transform infrared spectroscopy (FTIR) is a very powerful technique for characterizing polymer systems and is in many ways ideal for probing interphases. FTIR provides an unparalled amount of information about polymer systems, including information about chemical composition and molecular orientation. Infrared microspectroscopy can be used to obtain spectra of interphases if the bond is cross-sectioned. However, the spatial resolution of FTIR microspectroscopy is limited by the so-called diffraction limit to approximately the wavelength of the infrared radiation (about 10 μm in the mid-IR region of the electromagnetic spectrum).

Atomic force microscopy (AFM) is another powerful technique for probing interphases on a nanometer scale and can provide a great deal of information regarding topography as well as properties such as modulus and adhesion. With new thermal probes, images can be obtained showing the way in which thermal properties, such as glass transition temperatures, vary across the surface of a sample. Unfortunately, AFM does not provide any direct information about the composition of a material. Thus, AFM can be used to show that some property, say modulus, varies across a surface but it cannot show why the property varies.

The goal of our current research on interphases is to develop a new analytical technique for obtaining infrared spectra of polymer systems at ultra-high spatial resolution by using an AFM to detect absorption of infrared radiation from an FTIR spectrometer by the polymers. In this technique, referred to as AFM/FTIR, the sample of interest essentially becomes the detector and an AFM is used to measure the response of the sample to infrared absorption. This technique is a form of photothermal spectroscopy (PTS) which is an indirect form of optical absorption spectroscopy since it measures some effect that optical absorption has on a sample instead of measuring the intensity of light transmitted through the sample. Sample responses of interest include variations in the temperature and volume.

The spatial resolution of this type of AFM/FTIR spectroscopy is related to the contact area that the probe makes with the sample and the use of AFM probes is obviously advantageous in that regard. According to Pethica and Oliver [19], the contact area between an AFM probe and the sample surface is given by

$$a^3 = 3PR/4E^* \tag{1}$$

$$1/E^* = (1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2. \tag{2}$$

In these expressions, P is the force applied to the probe tip, E_1 and E_2 are the elastic moduli of the sample and tip materials, respectively, n_1

and n_2 are the Poisson ratios of the sample and probe materials, respectively, and R is the radius of curvature of the probe tip.

Spatial resolution also depends on the effect that infrared absorption occurring in volume elements not in contact with the probe has on the properties of the volume element in contact with the probe. It is, thus, important to limit the spread of perturbations from one volume element to another. If the effect being measured is the temperature of the volume element in contact with the probe, the thermal diffusion length should be minimized. This can be done by modulating the intensity of the infrared radiation. The thermal diffusion length is given by the expression

$$\mu = (\alpha/\pi\nu)^{1/2}, \tag{3}$$

where ν is the modulation frequency and α is the thermal diffusivity [20]. If the effect measured is the volume of the sample or its thermal expansion, it is more difficult to limit the spread of perturbations from one volume element to another since elastic waves are relatively un-damped.

Hammiche *et al.* [21] illuminated the surface of a polymer sample with modulated infrared radiation from an FTIR spectrometer and used a miniature scanning thermal microscopy (SThM) probe to record photo-thermally induced temperature fluctuations at the surface. The probe was fabricated from a length of so-called “Wollaston wire” (75 µm silver wire with a 5 µm diameter platinum/10% rhodium core). The wire was made into a loop and the silver was electrochemically etched away over a length of about 50 µm to expose the core. A sharp bend near the mid-point of the exposed “core” made contact with the sample surface and served as the sensor. The contact region between the probe and the sample was on the order of a few hundred nanometers. Changes in probe resistance were amplified and routed to the external input of an FTIR spectrometer where the Fourier-transform was performed, yielding the infrared spectrum of the sample. FTIR spectra of several polymers, including poly(butylene terephthalate), were obtained and compared with spectra of the same polymers that were obtained by attenuated total reflection (ATR). In these experiments, spatial resolution was determined in part by the area of the probe/sample contact and was reported to be about 250 nanometers for the type of probe employed. Hammiche *et al.* noted, however, that the resolution would be greater with improved probes and could approach 20–50 nm with a passive detector such as a miniaturized thermocouple [21].

Bozec *et al.* [22] used synchrotron radiation in a similar approach to obtain photothermal infrared spectra of several polymers, including PET and polypropylene (PP). They used a microscope to focus the infrared radiation onto the surface of a thermal probe that was in contact with the sample. The probe itself consisted of a small pyramid that was grown at the free end of a silicon nitride cantilever. A strip of palladium was formed on the flattened apex of the pyramid; a constriction in the palladium strip served as the resistive sensing element. High quality spectra of PET and PP were obtained by co-adding 1,000 scans at 16 cm^{-1} resolution.

Anderson [23] described a different approach that did not involve the use of specialized probe tips. In his investigations, a very simple set-up was used to focus a modulated beam of infrared radiation onto a sample. Absorption of the infrared radiation resulted in modulated thermal expansion by the sample that was detected by an AFM. Anderson suggested that the spatial resolution in this approach was determined by several factors, including the incident power, the frequency at which the IR radiation was modulated, and the thermal conductivity of the sample but could be as small as 100 nm. Although Anderson"s simple apparatus did not enable actual FTIR spectra of polymers to be obtained, he did show that the output of the AFM had the characteristic appearance of an interferogram from the unprocessed output of an FTIR detector. Anderson suggested that the output from the AFM could be used as input to the FTIR spectrometer and that signal averaging would result in a much improved signal-to-noise ratio.

It seems likely that the two approaches described above will have different applications. Some materials, such as oxides, have strong infrared absorption bands but relatively low coefficients of thermal expansion. On the other hand, polymers, which are of most interest in our work, usually have somewhat weaker absorption bands than oxides but much greater coefficients of thermal expansion. As a result, polymers may give stronger signals using Anderson's approach while oxides give stronger signals using the approach of Hammiche *et al.*

The primary purpose of this paper is to report results that we have obtained using Anderson's approach to record AFM/FTIR spectra of several polymer systems by using an AFM and contact mode probes to measure the thermal expansion of the polymers resulting from absorption of modulated infrared radiation from an FTIR spectrometer. Preliminary results obtained using SThM probes to obtain AFM/FTIR spectra are also reported.

II. EXPERIMENTAL

All of the experiments described here were performed using a Nexus 870 FTIR spectrometer from Thermo Electron Corporation (Madison, WI, USA) and a Dimension 3100 atomic force microscope (AFM), NanoScope IIIa controller, and a NanoScope Signal Access Module (SAM) from Veeco Metrology Inc. (Santa Barbara, CA, USA). Both the FTIR system and the AFM were mounted on an RS-2000 vibration isolation table equipped with I-2000-428 legs (Newport Corporation, Irvine, CA, USA). The AFM was contained within a purpose-built Plexiglas® enclosure that was covered with sound-absorbing felt provided by Auralex Corporation (Indianapolis, IN, USA).

In a conventional FTIR spectrometer, infrared radiation emitted by the source is split into two beams by a beamsplitter; one beam is reflected off of a fixed mirror while the other is reflected off of a moving mirror. Because the two beams travel different distances to reach the detector, they are out of phase at the detector by an amount δ that is referred to as optical retardation. Moreover, δ changes constantly due to movement of the moving mirror. The output of the detector, thus, consists of intensity I as a function of δ and is referred to as an interferogram. The sample is usually placed just before the detector and its absorption spectrum is encoded within the interferogram. Fourier-transformation of the interferogram yields the infrared absorption spectrum of the sample.

In AFM/FTIR, the sample becomes the detector and an AFM probe is used to measure the response of the sample to absorption of infrared radiation. The general approach that we have used for AFM/FTIR is shown in Figure 1. We have used the schemes suggested by Anderson [23] and Hammiche *et al.* [21] to measure the response of the sample. Anderson's scheme is referred to as "Approach #1;" in this case, standard gold-coated NPG Si_3N_4 contact mode probes (spring constant 0.6 N/m) from Veeco Metrology were used to measure the thermal expansion that occurred when the sample absorbed infrared radiation. Output of the probe was accessed through the SAM and returned to the FTIR spectrometer through an external input for processing. The scheme suggested by Hammiche *et al.* is referred to as "Approach #2;" in this case, SThM probes provided by AnaSys Instruments (Santa Barbara, CA, USA) were used to measure the temperature increase that occurred when the sample absorbed infrared radiation. The SThM probes were interfaced with the "Nano-TA2" thermal analysis hardware provided by AnaSys; the output of the probe was accessed through the Nano-TA2 hardware and input to the FTIR spectrometer for processing.

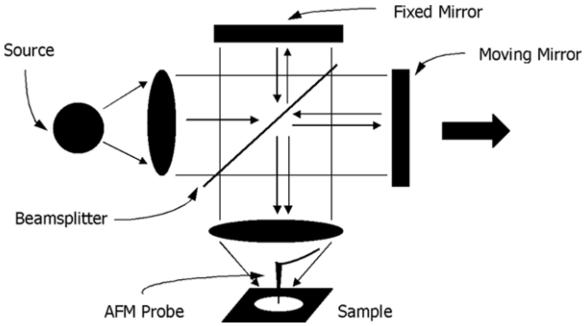


FIGURE 1 General approach used for AFM/FTIR. The sample was the detector and an AFM probe was used to measure the response of the sample to absorption of infrared radiation. The output of the AFM probe resembled an interferogram; performing a Fourier-transform on the interferogram resulted in the infrared absorption spectrum of the sample.

In both cases, the unprocessed output of the AFM probe was expected to resemble an interferogram. However, the Nexus 870 spectrometer permits the interferogram to be obtained in two different ways. In one way, the moving mirror of the Michelson interferometer is scanned through its entire range continuously to obtain the interferogram as described above. In this case, the modulation frequency (ν) is given by

$$\nu = 2\mathrm{V}/\lambda, \tag{4}$$

where V is the velocity of the moving mirror and λ is the wavelength of the infrared radiation. In this case, the modulation frequency depends on the wavelength and, thus, varies throughout the spectrum.

Alternatively, the interferogram can be obtained by "stepping" the interferometer through a series of discrete values of retardation and collecting intensity information at each value of retardation for a period of time (P). In this approach, the modulation frequency is the inverse of the time period but does not vary with wavelength:

$$\nu = 1/\mathrm{P}. \tag{5}$$

We have used both continuous scanning and step scanning in this work.

In all cases, the infrared radiation was diverted from the sample compartment by a motorized mirror and allowed to exit the left side of the spectrometer through a port. Several different experimental configurations referred to as top, side, and bottom illumination were used to focus the infrared radiation onto the samples of interest (see

Figure 2). Top illumination can obviously be used for probing surfaces. Bottom illumination can also be used for surfaces if the polymer film sample is microtomed from a surface.

Preliminary investigations were carried out to demonstrate that the thermal expansion due to absorption of infrared radiation of the polymer could be detected by the AFM. A polystyrene plate was placed onto the stage of the AFM and illuminated with infrared radiation using the top illumination technique (see Figure 2A). The infrared radiation was focused onto the sample using a ZnSe lens (ISP Optics, Irvington, NY, USA) with a 3-inch focal length. A mechanical chopper (SR-540, Stanford Research Systems, Sunnyvale, CA, USA) was used

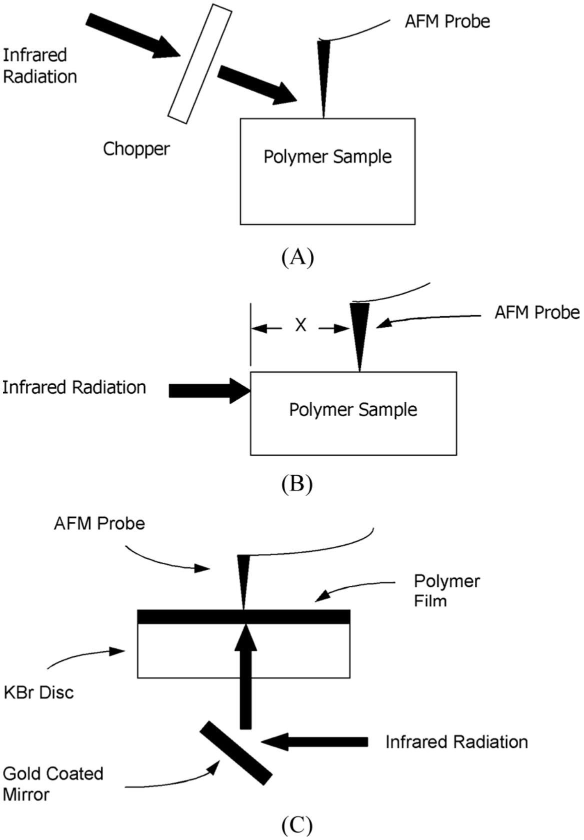


FIGURE 2 Sampling techniques used in AFM/FTIR spectroscopy. Top illumination is useful for surfaces. Bottom illumination is also useful for surfaces if samples are microtomed from a surface.

to modulate the infrared radiation from the spectrometer at frequencies of 6 and 12 Hz. The scan size of the AFM was set to zero and the refresh rate (scan rate) was set to 0.1 Hz. Integral and proportional gains were set to 0.001 and 0.002, respectively, while the probe was making contact with the sample. The AFM scope trace displayed the height data that was collected by the AFM as a function of time. The height scale of the scope trace was adjusted to values that would enable the full range of thermal expansion and contraction of the polystyrene sample to be observed in one frame. In a few experiments conducted at a chopping frequency of 12 Hz, a polystyrene film with thickness 76.2 μm was placed in line with the infrared radiation before the sample to act as a filter for the infrared radiation.

Next, a polystyrene plate sample was prepared and mounted on the AFM stage on its side. The AFM probe was engaged with the top surface of the sample as close to the front edge as possible and infrared radiation was focused onto the edge using an aluminum-coated off-axis converging mirror in the side illumination technique as illustrated in Figure 2B. An AFM/FTIR step scan spectrum of the polystyrene sample was collected using a period (P) equal to 100 msec and a resolution of 16 cm^{-1}. A "depth analysis" was also conducted on the polystyrene sample by moving the AFM probe away from the front edge of the sample where the infrared radiation was incident in increments of 10 μm up to a maximum of 770 μm.

AFM/FTIR spectra were obtained from thin films of polycarbonate and of a model epoxy adhesive system. Films of polycarbonate (Aldrich Chemical Co., Milwaukee, WI, USA) were cast from solution in chloroform onto KBr discs and the solvent was allowed to evaporate. The model epoxy adhesive consisted of a typical epoxy resin (DER 332, Dow Chemical Co., Midland, MI, USA) crosslinked with dicyandiamide (DDA, Aldrich). Thin films of the epoxy were cast onto KBr discs from solutions in dimethylformamide and then crosslinked by heating at 150°C in an oven overnight. Infrared radiation from the FTIR spectrometer was focused through the sample onto the probe using an aluminum-coated off-axis converging mirror with 6-inch (16.2 cm) focal length and a gold-coated glass slide adhered to a variable angle mirror mount as illustrated by the bottom illumination setup in Figure 2C. Spectra were obtained by illuminating the films while the AFM probe was in contact with the films; 8,192 scans were collected at 8 cm^{-1} resolution in the continuous scanning mode with a mirror velocity of 0.1581 cm/sec. The AFM refresh rate was set at 1.97 Hz, integral and proportional gains were set to 0.001 and 0.002, respectively, and the z-limit was set to 500 nm.

The spatial resolution of AFM/FTIR using Approach #1 was evaluated using polystyrene beads having a diameter of about 2 μm (Bangs Laboratories Inc., Fishers, IN, USA). In some experiments, polystyrene beads were embedded in a KBr disc and illuminated using the bottom illumination method. An AFM/FTIR spectrum of the embedded polystyrene beads was collected in continuous scan mode with a mirror velocity of 0.0475 cm/s and an average of 1,692 scans at a spectral resolution of 8 cm^{-1}. In other experiments, the 2 μm diameter polystyrene beads were embedded in a thin layer of stretched paraffin film on a KBr disc. An AFM/FTIR spectrum of this sample was collected in continuous scan mode with a mirror velocity of 0.0475 cm/s and an average of 1,320 scans at a spectral resolution of 8 cm^{-1}.

Using Approach #2, the thermal probes were used to obtain an AFM/FTIR step scan spectrum at a resolution of 32 cm^{-1} of a polystyrene plate sample illuminated from the side as shown in Figure 2B. Additionally, a 38 μm thickness polystyrene film standard from Thermo Electron Corp. was stretched over a KBr pellet and illuminated using the bottom illumination set up. An AFM/FTIR step scan spectrum of the stretched polystyrene film was collected at a spectral resolution of 32 cm^{-1}.

Transmission spectra of polystyrene, polycarbonate, the model epoxy adhesive, and paraffin films were obtained for comparison with the AFM/FTIR spectra by averaging 64 scans at a spectral resolution of 4 cm^{-1}. The polystyrene film was a standard (Thermo Electron Corp.) with a thickness of 38 μm. Polycarbonate and epoxy films were cast from solution onto KBr discs as described above while the paraffin film was stretched over a KBr disc.

III. RESULTS AND DISCUSSION

The AFM deflection that was observed when infrared radiation was chopped at approximately 6 Hz and focused onto a polystyrene sample is shown in Figure 3A. Since the vertical scale was 0.25 nm/div, the total amplitude of the deflection was approximately 2.25 nm while the observed period was about 1.25 sec. When the chopping frequency was 12 Hz, the observed deflection was 1.25 nm and the observed period was about 690 msec as seen in Figure 3B. An additional preliminary experiment consisted of illuminating a polystyrene sample with infrared radiation chopped at 12 Hz; however, in this case, a polystyrene "filter" with a thickness of 76.2 μm was placed between the chopper and the sample to remove most of the wavelengths that would be absorbed by the sample while allowing other wavelengths to

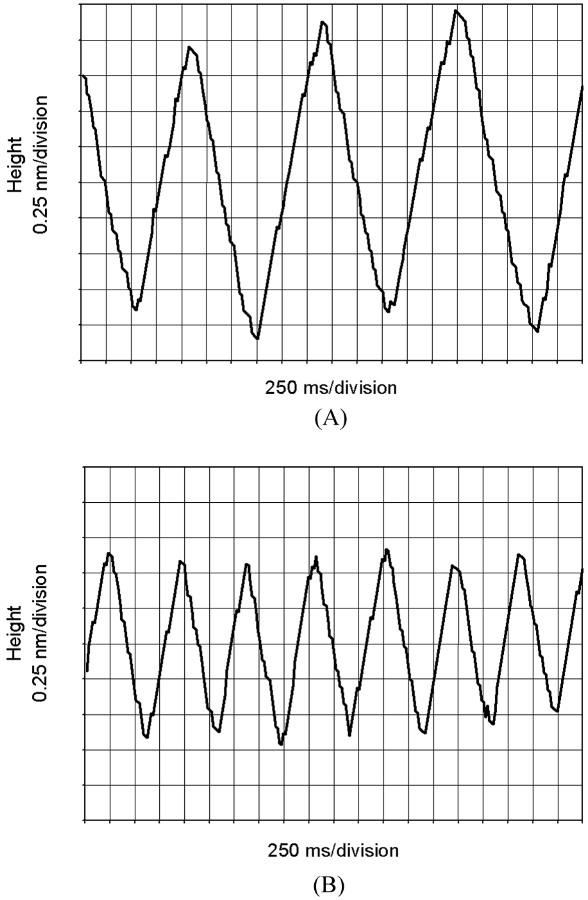


FIGURE 3 AFM deflection observed when a polystyrene sample was illuminated with infrared radiation that was chopped at frequencies of (A) 6 Hz and (B) 12 Hz.

impinge on the sample. Thus, absorption by the sample was expected to be greatly reduced while the period of any residual signal remained the same. That is exactly what was observed (see Figure 4). The amplitude of the deflection in this experiment was only about 0.25 nm but the period was still about 690 msec. These results demonstrated that the signal being measured was indeed the thermal expansion that occurred when polystyrene absorbed infrared radiation.

Next, we obtained the AFM/FTIR spectrum of polystyrene using step-scanning and side illumination and compared it with the transmission FTIR spectrum (see Figure 5). The AFM/FTIR spectrum

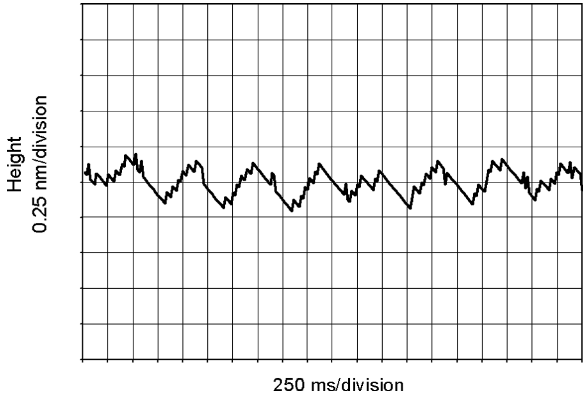
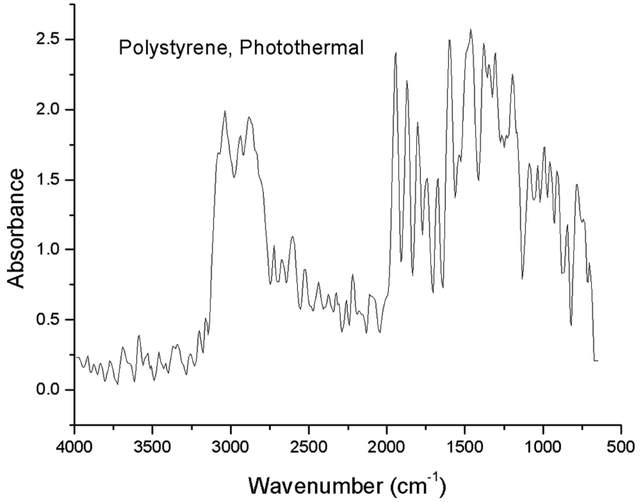


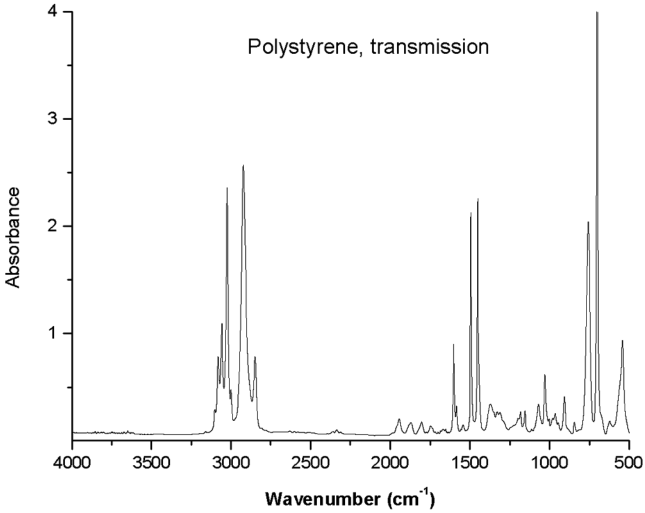
FIGURE 4 AFM deflection observed when a polystyrene sample was illuminated with infrared radiation that was chopped at a frequency of 12 Hz and passed through a polystyrene "filter" having a thickness of 76.2 μm.

clearly resembled the transmission spectrum but there were significant differences in relative intensity of many of the bands. For example, the relatively weak bands at 1945, 1874, 1804, 1744, 1665, and 1600 cm^{-1} in the transmission spectrum were remarkably strong in the AFM/FTIR spectrum while the very strong band near 690 cm^{-1} in the transmission spectrum was not observed in the AFM/FTIR spectrum. These differences in relative intensity were related to the side-illumination sampling technique. In side illumination AFM/FTIR, wavelengths that are strongly absorbed in transmission will be completely absorbed before they reach the vicinity of the probe; thus, no signal will be measured by the probe. On the other hand, wavelengths that are weakly absorbed in transmission should travel a considerable distance into the sample and produce absorption in the vicinity of the probe, thus resulting in a signal in AFM/FTIR.

In order to demonstrate this effect further, we obtained AFM/FTIR spectra of polystyrene using the side illumination technique while placing the probe at different distances from the side that was illuminated; selected results of this "depth analysis" are shown in Figure 6. When the probe was placed near the edge of the specimen that was being illuminated, bands in the region from 2700 to 3100 cm^{-1} that were strong in transmission spectra appeared to be saturated while the peaks at 1945, 1874, 1804, 1744, and 1665 cm^{-1}, which were weak in the transmission spectra, were strong to medium in intensity in the AFM/FTIR spectra; strong bands near 756 and 690 cm^{-1} in transmission spectra were absent from the AFM/FTIR spectra.



(A)



(B)

FIGURE 5 Infrared spectra of (A) a polystyrene plate obtained by AFM/FTIR and (B) a polystyrene film obtained by transmission.

When the probe was moved away from the edge by approximately 300 or 550 μm, all of the bands in the AFM/FTIR spectrum decreased in intensity and when the probe was approximately 770 μm from the

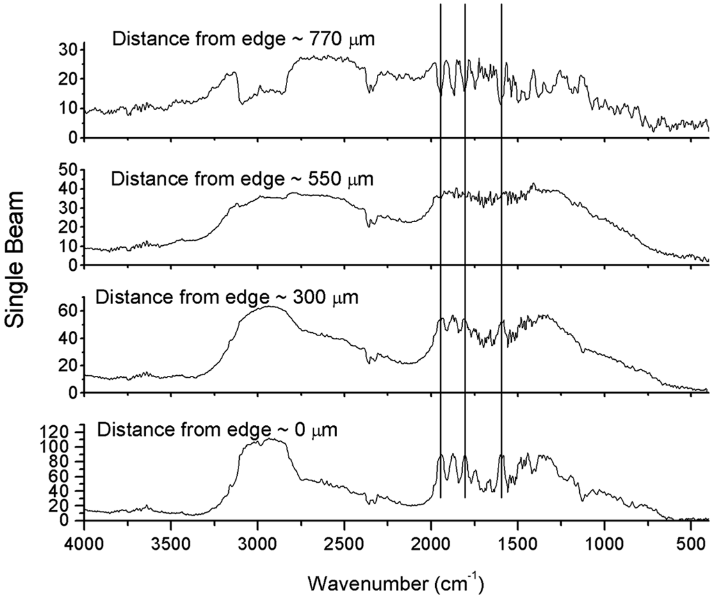


FIGURE 6 AFM/FTIR spectra of polystyrene obtained using step-scanning and side illumination.

edge, several bands, including those between 2700 and 3100 cm^{-1} and those near 1945, 1874, 1804, and 1744 cm^{-1}, appeared to become negative (see Figure 6). In AFM/FTIR spectroscopy, the AFM only measures a signal when the sample absorbs infrared radiation. When the AFM probe was placed approximately 770 μm from the edge, all of the infrared radiation at 1945, 1874, 1804, and 1744 cm^{-1} was absorbed before reaching the vicinity of the probe; thus, very little signal (no thermal expansion) was measured by the probe. The vertical lines in Figure 5 highlight the behavior of the bands at 1945, 1804, and 1600 cm^{-1}. It can be seen that those bands and others were positive when the probe was located close to the edge of the sample ($X = 0$) but negative when the probe was located well away from the edge ($X = 770$ μm).

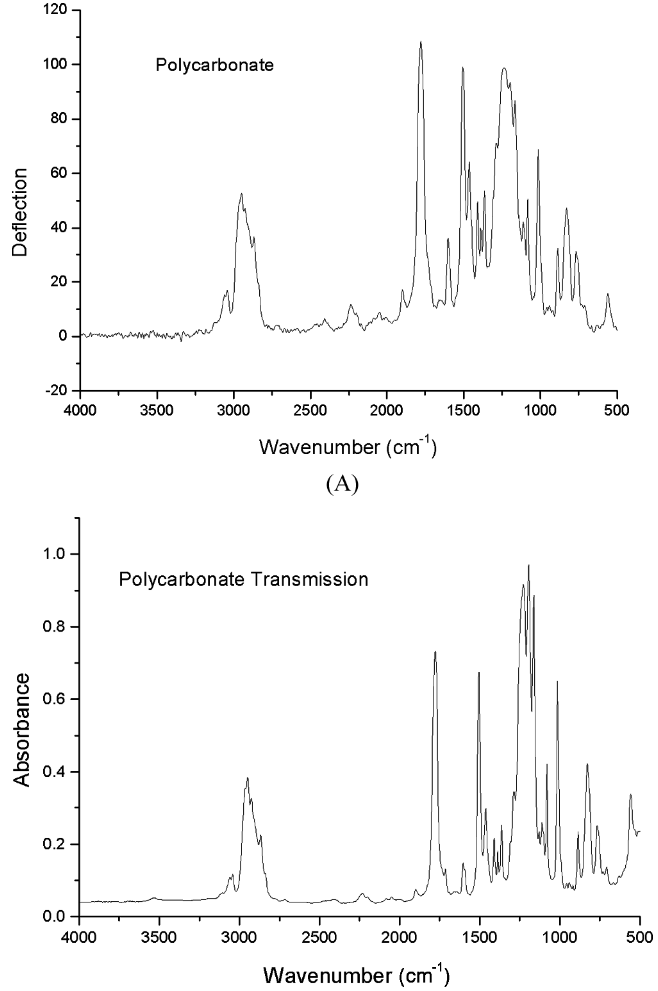
A somewhat similar explanation was obtained for the two bands near 2350 cm^{-1} that were related to absorptions by CO_2. CO_2 in the path of the infrared radiation absorbed near 2350 cm^{-1} but the sample in contact with the probe did not. Thus, there was no thermal expansion by the sample due to absorption at 2350 cm^{-1} and the signal measured by the probe dropped toward zero, giving the appearance of “negative” absorption bands near 2350 cm^{-1}. This is, of course, a characteristic of photothermal spectroscopy; there is no response by the sample if there is no absorption by the sample.

The experiment described above was very similar to the experiment that was used to obtain the results shown in Figure 4 except that in this case the "filter" was integral with the sample and had a variable thickness. Previously, the filter was separate from the sample and had fixed thickness. Therefore, it was expected that at some value of X, the AFM signal would disappear and the intensity of the bands in the AFM/FTIR spectrum would go to zero.

It was evident that thermal saturation was a problem with the side illumination approach. Therefore, we considered another approach consisting of bottom illumination combined with continuous scanning. The AFM/FTIR spectrum of polycarbonate obtained using this technique and averaging 8192 scans at 8 cm^{-1} resolution is shown in Figure 7 along with a reference transmission infrared spectrum of polycarbonate. Bottom illumination and continuous scanning led to excellent AFM/FTIR spectra of polycarbonate that were very similar to the transmission spectra in terms of relative intensities, peak positions, and spectral resolution. Moreover, the signal-to-noise ratio in the AFM/FTIR spectrum was outstanding. These results indicated that very high quality AFM/FTIR spectra could be obtained from polymer systems.

One of our long term goals is to use AFM/FTIR spectroscopy to probe the interphase region in adhesive bonds and in composites. Therefore, we investigated the use of bottom illumination and continuous scanning to characterize a model epoxy system. The model system consisted of the diglycidyl ether of bisphenol-A (DGEBA) crosslinked by dicyandiamide (DDA) in a 1:7 mole ratio. The epoxy was dissolved in dimethyl formamide; a few drops of the solution were deposited on a KBr pellet and the solvent was allowed to evaporate overnight. Then the KBr pellet with uncured epoxy was placed in an oven at 150°C overnight until curing was complete. AFM/FTIR and transmission spectra of the sample were then obtained (see Figure 8). The AFM/FTIR spectrum was obtained using bottom illumination, 8192 scans, and 8 cm^{-1} resolution while the transmission spectrum was collected using 64 scans at resolution of 4 cm^{-1}.

Except for some differences in relative intensities that were related to the thickness of the sample used to obtain the AFM/FTIR spectrum, the AFM/FTIR and transmission spectra were very similar. Some bands that were strong in the transmission spectrum were relatively weak in the AFM/FTIR spectrum (*e.g.*, 1495 cm^{-1}) while some that were weak in transmission were strong in AFM/FTIR (*e.g.*, 1740 cm^{-1}). These differences in relative intensities of bands in the AFM/FTIR



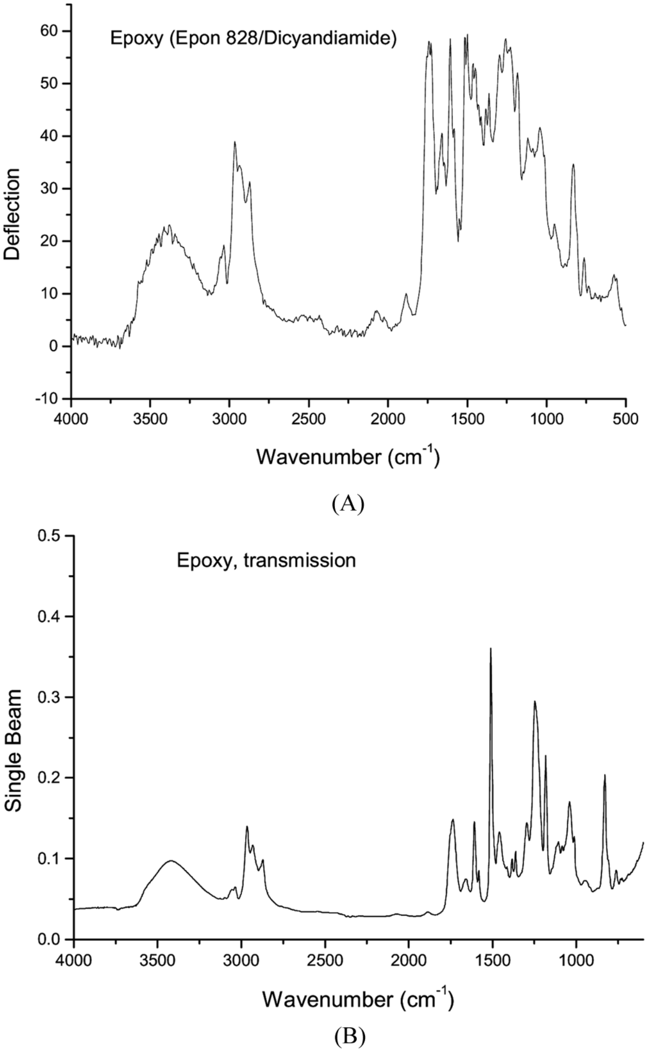
(A)

(B)

FIGURE 7 FTIR spectra of polycarbonate. In (A) the spectrum was obtained by AFM/FTIR using continuous scanning and bottom illumination. In (B) the spectrum was obtained by transmission.

and transmission spectra were similar to those previously observed in AFM/FTIR and transmission spectra of PS (see Figure 5) and were related to the thickness of the film that was used to obtain the AFM/FTIR spectrum.

It was especially interesting to note the bands near 1740 and 1660 cm^{-1} in the spectra of the model epoxy adhesive. Reaction of an



(A)

(B)

FIGURE 8 FTIR spectra of a model epoxy system consisting of an epoxy resin cross-linked with dicyandiamide. In (A) the spectrum was obtained by AFM/FTIR using continuous scanning and bottom illumination. In (B) the spectrum was obtained by transmission.

epoxy resin with dicyandiamide results in a complex series of intermediates and eventually in a urethane [24]. The intermediate 2-iminooxalidine contains an imine bond that is expected to absorb near 1660 cm^{-1} while the urethane end product is expected to absorb near

1740 cm^{-1}. Both bands were observed in the AFM/FTIR spectra, confirming the ability of AFM/FTIR to identify specific functional groups of interest in adhesion and interphases.

Several investigations were carried out to determine the lower limit on sample size for obtaining AFM/FTIR spectra. In one investigation, polystyrene beads having a diameter of 2 µm were embedded in a KBr disc and examined using the bottom illumination method (Figure 2C) while the AFM probe was "parked" on a single bead. The spectrum obtained is shown in Figure 9. This spectrum was very similar to the transmission spectrum of polystyrene (see Figure 5). In particular, the bands near 760 and 690 cm^{-1} that were not observed with side illumination and step-scanning were observed with good intensity. However, the bands at 1945, 1874, 1804, 1744, and 1665 cm^{-1}, which were weak in the transmission spectra, were relatively strong in the AFM/FTIR spectrum; these differences in relative intensities of bands in AFM/FTIR and transmission spectra were again related to the thickness of the sample used to obtain the AFM/FTIR spectra. Considering the excellent signal-to-noise ratio of the spectrum shown in Figure 9, it was concluded that AFM/FTIR spectra could be obtained from samples that were much smaller then 2 µm using bottom illumination and continuous scanning and measuring thermal expansion with the AFM.

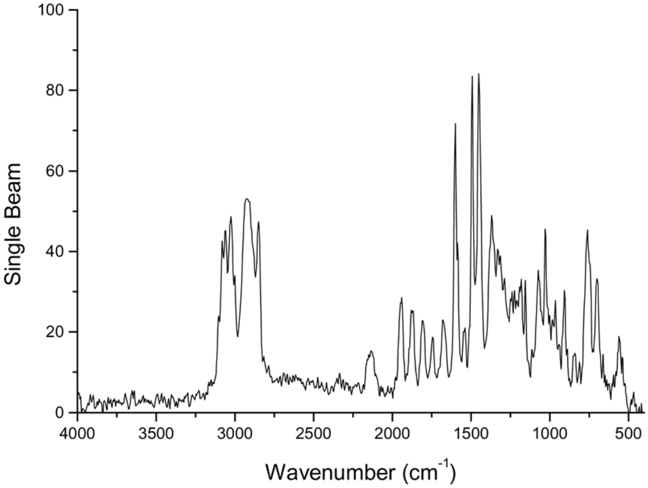


FIGURE 9 AFM/FTIR spectrum obtained from a polystyrene pellet having an approximate diameter of 2 µm. The pellet was pressed into the surface of a KBr disc and the spectrum was obtained using continuous scanning and bottom illumination.

Next, the AFM/FTIR spectrum was obtained from a 2-µm polystyrene bead that was pressed into a paraffin film (see Figure 10). This spectrum was identical to that obtained from the transmission spectrum of the neat paraffin film. No bands characteristic of the polystyrene were observed. This result indicated that the spatial resolution when using Approach #1 to obtain AFM/FTIR spectra was limited. The reason was that a relatively large area of the paraffin was illuminated by the beam of infrared radiation; absorption in the paraffin resulted in thermal expansion that was detected by the AFM and represented a background signal. Any absorption and thermal expansion by the polystyrene bead was buried within the background even though the radius of the contact area between the probe and the PS bead was much smaller than the PS bead. The radius of the contact area between the probe and the bead was calculated using Equations (1) and (2) assuming typical values for the relevant parameters ($E_1 = 3.3 \times 10^9$ Pa for polystyrene, $E_2 = 2.5 \times 10^{11}$ Pa for Si_3N_4, $\nu_1 = 0.33$ for polystyrene, $\nu_2 = 0.24$ for Si_3N_4, tip radius of curvature = 20–90 nm), and taking the applied force as between 10^{-7} and 10^{-8} N. Values of the radius of the contact area between the Si_3N_4 probes and polystyrene between approximately 3.5 to 12.5 nm were obtained. These results demonstrated the

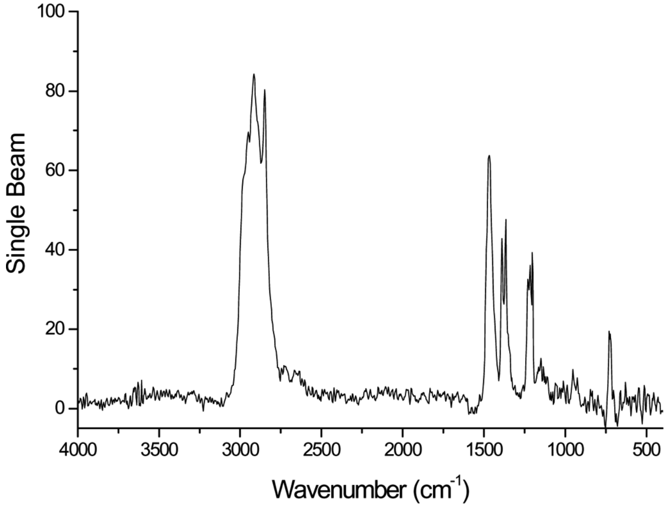


FIGURE 10 AFM/FTIR spectrum obtained from a 2-µm polystyrene pellet that was pressed into a paraffin film that was cast onto the surface of a KBr disc; the spectrum was obtained using continuous scanning and bottom illumination.

tendency of information from adjacent volume elements to affect the volume element that was in contact with the AFM probe when using Approach #1.

Very recently, we have begun experimenting with Approach #2, using a SThM probe to detect the temperature increase that occurs when a polymer sample absorbs infrared radiation. This approach is of interest because of the small contact area that the SThM probes make with the sample and because the thermal diffusion length can be controlled by modulating the infrared radiation (see Equation 3). The radius of curvature is described by the manufacturer (AnaSys) as less than 100 nm. Using equations 1 and 2, assuming that the applied load was between 10^{-7} and 10^{-8} N, and assuming that the radius of curvature was 100 nm, the contact area was calculated to have a radius of less than 13 nm. This was obviously much smaller than the Wollaston wire type of probes used by Hammiche *et al.* [21].

Figure 11 shows an interferogram that was obtained from a polystyrene sample using this approach. The side illumination technique was used to illuminate a polystyrene plate as shown in Figure 2B while the interferometer was operated in step-scan mode. The period (P) was nominally set to 100 msec; however, the software increased the period by a factor of approximately 100 at retardations where the intensity of the interferogram was significant. The interferogram had a low signal-to-noise ratio; when it was transformed into an

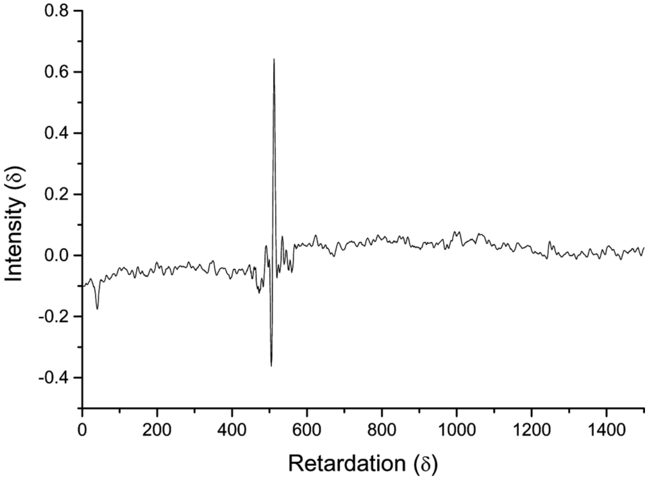


FIGURE 11 Interferogram of a polystyrene plate obtained using a SThM probe, side illumination, and step-scanning.

absorption spectrum, the only bands that were recognizable as being characteristic of polystyrene were those near 3,000 cm^{-1}. Nevertheless, the fact that we were able to obtain an interferogram using this technique was encouraging for the future development of high-resolution AFM/FTIR spectroscopy. Assuming that the thermal diffusivity of polystyrene was $10^{-7}\ \text{m}^2/\text{sec}$ [21], the thermal diffusion length was calculated to be approximately 6 μm. This would appear to be too large to prevent the spread of information from adjacent volume elements into the volume element in contact with the probe and, thus, too large for AFM/FTIR spectroscopy at high spatial resolution. However, the spatial resolution is a complex function of the thermal diffusion length and the probe/sample contact area. Thus, the spatial resolution with this technique remains to be determined. Improved techniques for delivering infrared radiation to the sample should result in interferograms with less noise and in usable AFM/FTIR spectra when using SThM probes.

IV. CONCLUSIONS

The results obtained here show that AFM/FTIR spectroscopy is very feasible. When contact mode probes are used to detect the thermal expansion that accompanies infrared absorption, high quality infrared spectra can be obtained with excellent signal-to-noise ratios. The spatial resolution of this technique has yet to be evaluated but may be limited by the relatively un-damped nature of elastic waves. The spatial resolution may be substantially better when SThM probes are used to measure the temperature increase that occurs when a polymer system absorbs infrared radiation since thermal waves are very highly damped; however, in that case, the signal-to-noise ratio is expected to be lower. Nevertheless, with continued development, AFM/FTIR spectroscopy should be a powerful technique for determining the molecular structure of interphases in polymer composites and in adhesive bonds.

V. ACKNOWLEDGMENTS

This research was supported in part by grants from the National Science Foundation and the Ohio Board of Regents (Hayes Investment Fund and Action Fund). The numerous contributions of Dr. Forrest Weesner (Thermo Electron Corporation) regarding the acquisition and processing of FTIR signals from external detectors are gratefully acknowledged as are the contributions of Brian Stephens who assisted with much of the early work on this project.

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