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Abstract

A new type of infrared spectroscopy for obtaining the molecular composition of the surfaces of materials has been developed by combining the inherently high spatial resolution of the atomic force microscope (AFM) with the powerful chemical characterization capabilities of Fourier transform infrared (FTIR) spectroscopy. When the new technique is fully developed, we plan to use it to determine the molecular structure of polymer systems on a sub-micrometer scale, or about several orders of magnitude greater than currently possible using “conventional” infrared spectroscopy techniques. We are especially interested in probing the molecular structure of “interphases,” the transition regions between an adhesive and a substrate in polymer composites and adhesive bonds. We have used both contact mode AFM probes and thermal mode AFM probes to measure the response of polymer systems to infrared absorption. In either case, when the probe is engaged with a sample that is absorbing infrared radiation from the FTIR spectrometer, the output from the AFM probe resembles an interferogram to which a Fourier-transform can be applied to obtain the infrared spectrum. The contact mode approach was successfully used when various neat polymer samples, including polystyrene, polycarbonate and a model epoxy adhesive system, were characterized by AFM-FTIR techniques. Excellent spectra were also obtained from polystyrene beads having a diameter of about 2 μm . AFM thermal mode probes have been used to obtain preliminary interferograms and infrared spectra from neat polystyrene samples, but the signal-to-noise ratio was low. AFM-FTIR spectroscopy results to this point show that this new method is feasible, but the spatial resolution of the technique remains to be shown.

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I. Introduction

Adhesives and adhesive technologies have improved a great deal in the last 20 years. Adhesives have seen increasing use in structural applications, aerospace applications and in many other high tech fields, often in place of heavier and sometimes inferior mechanical fasteners. With increased use of adhesive technology there is a need to thoroughly understand all that goes into making a superior bond between two materials. Adhesion is a combination of chemical as well as physical interactions within the adhesive and between the adhesive and the materials being joined. When an adhesive is used to join materials, as in a composite or an adhesive bond between substrates, there exists an “interphase” or transition region near the surface of a fiber or substrate. In this transition region the properties of an adhesive vary from its bulk properties to properties that are strongly influenced by interactions with the fiber or the substrate. Therefore, it is important to intimately understand these transition regions or “interphases,” since inferior properties within the interphase result in composites or adhesive bonds with inferior properties. There are many powerful analytical techniques available for probing the molecular structure of the interphase region. However, characterization of the interphase is often difficult since the transition region between adhesive and fiber or substrate is typically a very thin region, usually less than 1 μm , buried between much thicker phases.

A. Adhesive Interphase Characterization Techniques

The interphase in adhesive bonds has been the subject of study for many years. Many different techniques for analyzing the interphase have been introduced all with advantages and disadvantages. Possart and Röder used the primary beam of a scanning

electron microscope (SEM) to cause the emission of secondary electrons from a composite sample of low-density polyethylene (LDPE) solution cast on an aluminum substrate. Cross-sectioned samples of the interface between the LDPE and aluminum were prepared by microtomy and coated with an evaporated carbon layer to prevent electron charging of the polymer layer. They investigated the electrical interactions between the aluminum and LDPE by collecting secondary electron (SE) energy spectra of the samples and studying the distribution of the electrical potential across the interface. Results indicate that an area of negative potential exists near the interphase and spreads at least 10 μm into the LDPE. One would expect an area of positive potential in the aluminum at the surface near the contact with LDPE; however, it could not be resolved using this method¹. Measuring the electrical potential distribution is one way of studying the interphase of adhesive bonds; however, additional experimental data would be needed to comment on specific composition and molecular structure of the sample. The authors also did not mention steps taken to prevent smearing of the composite sample due to cross-sectioning using microtomy, which could affect actual spectral resolution results. Additionally this method has additional factors affecting the SE spectrum accuracy including inhomogeneities of the sample. Examples of inhomogeneities are chemical composition, surface geometry, and local electric fields.

X-ray photoelectron spectroscopy (XPS) is another excellent technique for obtaining information concerning adhesive interphases. Using high-resolution monochromated XPS, Beamson, Bunn and Briggs investigated factors affecting the carbon 1s, C(1s), spectra of poly(methyl methacrylate) (PMMA) spin-coated on silicon substrates. Beamson et al showed the presence of additional peaks in the C(1s) spectra of

thin films of PMMA on a silicon substrate as compared to the C(1s) spectra of bulk PMMA. Their results indicated that high resolution XPS was capable of observing interactions occurring in the interphase region between PMMA and the silicon substrate; however, they were unable to distinguish between three possible models for the curve-fitting scheme used².

Chehimi and Watts investigated the use of XPS as a potential analytical technique to probe acid-base properties of polymers in the solid state. They used XPS to investigate the effect of substrate acidity/basicity on the orientation of the carbonyl group (C=O) of PMMA. The underside of PMMA films cast from solution onto glass microscope slides and substrates of thermally grown layers of SiO₂ on silicon wafers were analyzed by peeling the cast films from the substrates after solvent evaporation was complete. The glass slide and SiO₂ substrates were treated with solutions of hydrochloric acid with varying pH; additionally a glass slide was treated with a solution of sodium hydroxide (NaOH). The oxygen 1s, O(1s), and silicon 2p, Si(2p), XPS spectra were studied from the PMMA film samples. It was found that when changing from acidic to basic pretreatment the expected additional SiO⁻ groups generated at the surface caused a lower O(1s) binding energy as well as a lower Si(2p) binding energy in the PMMA films cast on modified glass substrates. The authors were unable to draw any firm conclusion about SiO₂ substrate acid pretreatment due to limited data. However, Chehimi and Watts were able to reach some conclusions concerning the effect of orientation of the carbonyl groups as related to surface acidity. The effect of orientation of the C=O group towards the surface acidic silanols, on both glass and SiO₂, was enhanced by casting PMMA on the highly acidic solution treated substrates³. One of the drawbacks of this method for

studying interphases is sample preparation, as the cast film has to be peeled from the substrate in order to analyze the underside.

Bou, Martin, and Le Mogne used XPS to study the interphase between in-situ thermally evaporated aluminum and biaxially oriented film of polyethylene terephthalate (PET). A pre-prepared 12 μm thick PET film was placed in a reaction chamber and the aluminum was evaporated in-situ to coat the PET films at rate of about 1 $\text{\AA}/\text{s}$. The Al(2s), Al(2p), C(1s) and O(1s) spectra were evaluated for a range of aluminum thicknesses on the PET film. As aluminum coverage increased the intensities of the C(1s) and O(1s) spectra decreased, while the Al(2s) and Al(2p) intensities increased. This effect was attributed to photoelectrons initially coming from the PET surface and with increasing Al thickness from the interphase until mainly coming from the Al layer. The results from Bou et al showed that the aluminum atoms were very reactive with the PET surface and the interphase was found to be composed of Al-O-C (PET) compounds, Al-C (PET)-like species and Al clusters. They were also able to infer that the reaction was preferential towards the sites of stronger basicity, with carbonyl groups first, ether linkages second and finally benzene rings⁴.

Leadley and Watts also used high-resolution XPS to monitor the changes in the C(1s) spectra as a result of interactions between spin-coated thin films ($\sim 0.5 - 2 \text{ nm}$) of PMMA and poly(acrylic acid) (PAA) on various oxidized metal substrates including iron, copper, nickel, and aluminum. The authors chose to study oxidized metal substrates as opposed to pure metal substrates, such as those used by Bou et al, as the oxidized surface would better represent samples prepared in ambient laboratory environments. They observed a 0.1 eV binding energy shift of the carboxyl carbon in the C(1s) spectra due to

PMMA interacting with acidic sites on the substrate. Additionally the authors stated that interactions between PMMA and strongly basic sites likely involved nucleophilic attack of the carboxyl carbon atom. This statement was supported by observations of a further increase in binding energy of the carboxyl carbon in the C(1s) spectra from sample substrates with strong basic sites. Leadley and Watts also supported the claim of a possible 5 peak fitting scheme for the C(1s) spectra of the PMMA-oxidized-metal samples due to weaker basic sites interacting with PMMA *via* the hydrolysis of the methyl ester to a carboxylate. They were also able to identify specific acid-base interactions that occurred in the interphase for the PAA-oxidized-metal samples. A shift of 0.1 eV up from bulk PAA values indicated acidic sites by fitting the carboxylic acid carbon peak to the carboxylic acid component. Additional peak fitting in the C(1s) spectra indicated the formation of a carboxylate complex due to basic site interactions. However, degradation of polymer in the C(1s) spectra was observed for the PAA thin film samples, thus revealing a weakness of XPS as an interphase analysis technique. The authors had to include a fourth peak in the C(1s) fitting scheme indicating the presence of hydroxyl or ether functionalities introduced by X-ray damage. Leadley and Watts believed the X-ray induced electron damage caused cross-linking in the PAA, but further investigation would be required to determine the damage mechanism more accurately^{5, 6}. An additional drawback of XPS as an analytical technique for characterizing adhesive interphases is that special sample preparations are often required, such as thin films in this case (films should be less than 5 nm to allow photo-electrons to escape from the interface), special substrate preparation, in-situ or laboratory conditions, or sputtering through thick layers of matrix material or adhesive to reach the interfacial region.

Infrared spectroscopy is another method widely used to study adhesive interphases. Possart and Fanter analyzed adhesive models of ultra-thin films of dicyanate bisphenol-A prepolymer on aluminum or silicon substrates. Thin films were prepared in atmospheric conditions by spin-coating or dip-coating and were from 3 nm to 100 nm thick. They used reflection-absorption infrared (RAIR) spectroscopy and XPS to analyze the thin films and their interaction with the substrate surface. The substrates had to be very flat in order to obtain thin continuous prepolymer layers. An atomic force microscope (AFM) was used to show the layer thickness of prepolymer could be as low as 10 nm on the aluminum substrate or as low as 2 nm on the silicon substrate before discontinuous distribution of the prepolymer was observed. As film thickness went to thinner values the spectroscopic intensities of features due to the interphase became greater relative to the intensity of features due to the bulk film, thus providing an analysis of the interphase. Possart and Fanter reported the energy and orientation of the triazine rings was affected by some possible adhesive interaction of the cyanurate prepolymer with the aluminum substrate, but experimental results were unable to describe the specific adhesion mechanism. Preparing thin films in atmospheric conditions represented the laboratory environment; however, such conditions could have introduced surface contaminants, which could lead to erroneous interpretation of resulting spectra from thin film metal substrate samples⁷.

To avoid surface contamination, Grundmeier and Stratmann introduced an in-situ method for analyzing adhesive interphases between plasma deposited hexamethyldisilazane (HMDSO) and iron substrates. The in-situ preparation method was similar to that practiced by Bou et al above, but in this case the polymer was deposited on

the metal substrate instead of the metal being deposited on the polymer film. They cleaned the iron surface with oxygen plasma then deposited the monomer and polymerized it using the plasma energy. Coupling the reaction chamber with an infrared spectrometer allowed for in-situ analysis of the thin films, as they increased in thickness, on the iron substrates using RAIR spectroscopy techniques. Carrying out their investigations in-situ allowed identification of interfacial molecular structures without concern for atmospheric contamination or hydration. Grundmeier and Stratmann reported that an additional layer of iron oxihydroxide was formed during the oxygen plasma cleaning of the substrate. This resulted in a high density of surface hydroxyls, which leads to the hydrolysis of the adsorbed silazane. They also showed that the concentration of siloxane and N-H units was higher near the iron surface and decreased as the film thickness increased, especially within the first 4 nm of the film thickness⁸.

Turner and Boerio further investigated the characterization of plasma-polymerized thin polymer films on aluminum and titanium substrates through in-situ RAIR and XPS. RAIR and XPS spectra were collected as the films were progressively deposited. The resulting spectra provided information about how the silica-like films interacted with the metal substrates as the RAIR and XPS spectra of thinner films had additional infrared bands and C(1s) peaks present as compared to thicker films, which exhibited spectra characteristic of the bulk film material. They reported that during the initial stages of plasma deposition, metal atoms from the substrate migrated to the metal-oxide surface. This resulted in the formation of silicon sub oxide at the film/metal interphase, which was shown to be dependant upon the diffusivity of the metal substrate atoms through the surface oxide of the metal. Therefore, more interfacial sub oxide was

observed to form for depositions on titanium substrates as compared to aluminum substrates as diffusivity of metal through the surface oxide was greater in titanium than in aluminum^{9, 10}. Thin film deposition methods have successfully been used to analyze adhesive interphases, but the method still does not allow for analysis of pre-prepared adhesive joints.

Sample preparation has been an important factor influencing the results obtained by the various characterization techniques described thus far. Being able to characterize prepared adhesive joints would be advantageous as it could lead to the ability of characterizing industrially made adhesive joints. Using specially prepared adhesive model samples Hinder, Lowe, and Watts described an ultra-low-angle microtomy (ULAM) sample preparation technique developed to expose a larger area of the adhesive interface by precise sectioning of an adhesive sample at low angles. The ULAM technique exposed the interfacial region without polymer smearing across the interphase¹¹. Hinder, Watts, and Lowe also used ULAM and XPS to obtain a depth profile of the adhesive interphase of a poly(vinylidene difluoride) (PVdF) topcoat and a poly(urethane) (PU) primer on an aluminum substrate. Using ULAM prepared samples having a taper of $< 0.05^\circ$ with high resolution XPS, having a spot size of approximately 15 μm , the effective depth resolution was calculated to be $< 20\text{nm}$. XPS cross-sectional analysis of the sample indicated diffusion of the fluorine-containing components of the PVdF topcoat formulation into the uppermost nanometers of the underlying poly(urethane) primer¹². The same group, including Maxted, expanded on these results by using ULAM with time-of-flight secondary ion mass spectrometry (ToF-SIMS) on a similar PVdF topcoat PU primer system on aluminum substrates. The ToF-SIMS

allowed greater depth resolution than XPS because of the smaller area illuminated. Results indicated the presence of a methacrylate-based component or additive in the interphase, which were attributed to the PVdF topcoat as it contained methyl methacrylate (MMA)/ethyl acrylate (EA) co-polymer components¹³. ULAM is a technique that shows promise for analyzing the interphase of adhesive joints, but sample prep by microtomy can be finicky and is highly dependant on the materials involved in the adhesive joint; a realization that may not make it as broad reaching as one would hope, but nonetheless a very good technique for exposing the interphase for analysis.

Another interesting technique for adhesive interphase characterization was described by Boerio, Hong, Clark, and Okamoto, who utilized surface enhanced Raman scattering (SERS) to probe the interface between an acrylic adhesive cured against a silver substrate. SERS is a phenomenon in which 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 to its value well away from the metal surface. This makes it possible to observe the Raman scattering by adhesive interphases even when the interphase is buried beneath hundreds of nanometers of adhesive. Boerio et al were able to show that the structure described by Raman scattering at the interface of the sample was unique as compared to the structure described by Raman scattering of the bulk adhesive. They found that saccharin and benzoic acid were preferentially adsorbed at the silver surface to form metal salts¹⁴. SERS is a powerful technique for probing adhesive interfaces, but it is limited to the few metals that support the technique.

More recently, Chehimi, Kjouani, Connan, and Benarti have combined several of the described techniques to analyze the interphase chemistry of an epoxy adhesive

[diglycidylether of bisphenol-A (DGEBA) resin with diethylenetriamine (DETA) hardener] on hydrated cement paste. They reported an XPS, FTIR and differential scanning calorimeter (DSC) study of the interfacial chemistry of stoichiometric and nonstoichiometric epoxy mixtures coated on the surface of hardened-cement pastes. XPS data revealed the cross-linking of epoxy resin by the hardener and allowed the detection of hydrogen bonding between the minerals in the cement and the DETA hardener component of the epoxy system. The evidence for these hydrogen bonds was further supported by examination of the OH-stretching frequency shifts in the FTIR spectra indicating interaction with portlandite, one of the constitutive hydrates of the cement substrate. DSC was used to show that the glass transition temperature of the epoxy adhesive increased as a result of interactions with the cement substrate¹⁵.

Possart, Meiser, Willstrand, and Fehling used FTIR micro-spectroscopy to study the local aging of epoxy interphases with air and with several metals. DGEBA epoxy resin was hardened using DETA on both gold and copper substrates. The samples were sectioned using the ULAM method and exposed to two environmental conditions to age the samples: wet air and dry air, both at 60°C for up to 500 days. Quantitative FTIR analysis showed that in the bulk air to surface region three aging mechanisms formed a gradient region of more than 200 μm depending upon the environmental conditions. It was shown that the epoxy-metal interphases were unaffected by aging in the dry conditions; however, in the humid environment a 50 μm thick region was formed where the copper substrate accelerated aging¹⁶.

The techniques described above show the capability of probing adhesive interphases for chemical characterization, molecular structural information and even

adhesive joint aging characteristics. However, there are certain drawbacks that limit their use whether be it spatial resolution limits, sample preparation, or material limitations. Each drawback leaves something more to be desired for the characterization of adhesive interphases. This document describes a new technique that utilizes scanning probe microscopy along with FTIR spectroscopy and is potentially capable of characterizing the structure and composition of adhesive interphases of various polymer adhesive systems at sub-micrometer spatial scales.

B. Scanning Probe Microscopy

With the development of the scanning tunneling microscope (STM) in 1983 the field of scanning probe microscopy was introduced¹⁷. Scanning probe microscopy further established itself as a powerful characterization technique with the development of the atomic force microscope (AFM) just a few years after the STM was introduced¹⁸. The AFM has opened the door to many discoveries and advances as it can be used to characterize, on a nanometer scale, both conducting and insulating materials in an ambient environment. Contact mode AFM is a common method using silicon or silicon nitride probes prepared by acid etching techniques. The AFM obtains information from the sample through ultra-weak van der Waals interactions between the atoms at the tip of the probe and on the surface of the sample as shown in Figure 1. In the case of contact mode AFM, as the probe is raster scanned, the cantilever to which the probe is attached will deflect as the morphology of the sample changes. A photosensitive electronic feedback system is used to monitor the cantilever deflection and adjust the z-piezoelectric

controller to maintain constant cantilever deflection as the probe is scanned. The result is a three dimensional profile of the sample surface.

The wide range of applications for the AFM has led to rapid developments in scanning probe microscopy through the introduction of specialized probes and techniques. These specialized probes and techniques can provide surface properties of samples other than topography. One example is phase imaging, done by tapping mode or non-contact AFM¹⁹. In tapping mode AFM, the cantilever is oscillated at its resonant frequency so the probe periodically comes in to contact with the surface as it is scanned. A piezoelectric transducer in the SPM electronic feedback loop is used to drive the oscillation of the cantilever. The feedback system, which monitors cantilever deflection, also monitors the phase lag between the transducer and the cantilever and plots phase lag as a function of scanning probe position. As the tip scans the sample surface, it may encounter regions where composition, adhesion, or other properties differ, resulting in a difference in the sample/probe interaction, which causes a phase lag between the cantilever oscillation and its drive frequency. If the sample being imaged contains regions with different properties, the result is an image with contrasting regions representative of different compositions or surface properties, but the image does not give any specific information concerning chemical composition or molecular structure.

Scanning thermal microscopy (SThM) further developed the field of scanning probe microscopy. Scanning thermal microscopy uses a special SPM probe capable of measuring changes in temperature within a sample²⁰. An example probe for measuring temperature change is a micro-fabricated resistive thermometer. A resistive thermometer operates on the phenomenon that the electrical resistance of a material changes with

changing temperature. By calibrating the resistance value of the probe to corresponding temperature values and monitoring the resistance of the probe interacting with the sample, the temperature changes and differences on the surface can be monitored as a result of the surface being exposed to an external radiation source, such as infrared radiation.

Although scanning probe microscopy contains a multitude of tools for obtaining various surface properties of materials on a nanometer scale, the techniques do not provide any direct information regarding chemical composition of materials.

C. Fourier Transform Infrared Spectroscopy

In contrast to the field of scanning probe microscopy Fourier transform infrared (FTIR) spectroscopy is an excellent tool for chemically characterizing a wide variety of materials including polymers and ceramics. In a conventional FTIR spectrometer, infrared radiation emitted by the source is split into two beams by a beam-splitter; one beam is reflected off of a fixed mirror while the other is reflected off of a moving mirror as shown in Figure 2. Because the two beams travel different distances to reach the detector there is a phase difference between them at the detector. This phase difference is referred to as the optical retardation and is represented by the symbol δ . The sweeping motion of the movable mirror causes a continuous change in the optical retardation. Therefore, the output from the detector consists of the intensity, I , as a function of δ and is referred to as an interferogram. In the experiments described in this work, the intensity is described in units of volts. In traditional infrared spectroscopy techniques, such as transmission FTIR spectroscopy, the sample is generally placed just before the detector

(see Figure 2) and its absorption spectrum is encoded within the interferogram. Fourier-transformation of the interferogram yields the absorption spectrum of the sample.

FTIR spectroscopy provides an unparalleled amount of information about polymer systems, including information about chemical composition and molecular orientation. The technique is in many ways ideal for probing adhesive interphases. Infrared micro-spectroscopy uses mirrors, lenses and apertures to focus infrared light. It can map or image the surface composition of materials as well as provide molecular orientation information. By cross-sectioning an adhesive bond the interphase region can be mapped by the infrared micro-spectroscopy technique. However, the spatial resolution of FTIR micro-spectroscopy 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). The spatial resolution of a microscope can be described mathematically by equation 1 and is determined by the wavelength of radiation, λ , and the numerical aperture, NA, of the focusing mechanism²¹:

$$SP = \frac{0.61 \cdot \lambda}{NA} \quad (1)$$

$$NA = n \cdot \sin \theta \quad (2)$$

Numerical aperture is a value that represents the range of angles over which a microscope lens can accept or emit light, n represents the refractive index of the medium in which the lens operates and θ is the half angle of the maximum cone of light that can enter or exit the lens. For typical infrared microscopes, the NA value is about 0.6, giving a spatial resolution approximately equal to the wavelength of radiation used. Placing an aperture behind the sample before the detector can improve the situation; however, diffraction still limits the spatial resolution to no greater than the micrometer scale.

Although FTIR spectroscopy is a powerful characterization technique for determining composition and molecular orientation, with potential for adhesive interface analysis, it is limited to a spatial resolution no greater than approximately 1 μm .

Based on the above descriptions of atomic force microscopy and FTIR spectroscopy it becomes clear that by combining the high spatial resolution of the AFM with the powerful chemical characterization capabilities of FTIR spectroscopy a very powerful new characterization technique would be introduced. This new technique would be capable of providing topographic and other surface properties along with composition and molecular orientation information on a nanometer scale and would be ideal for analyzing adhesive interfaces.

D. Combining Scanning Probe Microscopy with Spectroscopic Techniques

As mentioned above, this document describes a new materials characterization technique potentially capable of determining molecular structure and other surface properties on the nanometer scale. We were concerned with combining the inherently high spatial resolution capabilities of scanning probe microscopy with a different characterization technique involving electromagnetic radiation and we were not the only ones. There have been several efforts by various investigators to combine scanning probe microscopy with some form of radiation and absorption detection for chemical and optical characterization purposes. Weaver, Walpita, and Wickramasinghe presented a microscope based on the STM, capable of recording optical absorption spectra with nanometer resolution. They utilized photothermal spectroscopy techniques in which the temperature rise due to the absorption of light was measured. Using a tunable

monochromatic light to illuminate the sample, the STM was scanned across the surface and measured the differences in tunneling current as a result of the thermoelectric effect. The thermoelectric effect can be described as the change in tunneling current with change in temperature. Thus, by maintaining a constant tunneling current by moving the probe up and down, a thermal profile of a surface exposed to external radiation can be obtained. Weaver et al stated the instrument provided a map of optical absorption by the sample at a spatial resolution of $\sim 1 \text{ nm}^{22}$. Although this method may provide optical absorption data on the nanometer scale, it does not directly correlate to chemical composition of the sample and the technique is limited to conducting samples only.

Durig, Pohl, and Rohner proposed work in Near-Field Scanning Optical Microscopy or NSOM. NSOM uses a detector or aperture with dimensions smaller than the wavelength of light being used and therefore, below the diffraction limit. By bringing the aperture and detector into close proximity of the sample surface the diffraction effects from the edge of the aperture can be minimized²³. Radmacher, Hillner, and Hansma introduced micro fabricated hollow SPM probes capable of simultaneously providing topographic and optical absorption information from a material's surface. To obtain topographic information, the hollow probe interacted with the sample in a way similar to contact mode AFM. Light emitted through the apex of the hollow SPM tip traveled through transparent portions of the sample to a photo-detector²⁴. Betzig et al were able to achieve an optical resolution of $\sim 12 \text{ nm}$ by placing fabricated probes, similar to Radmacher's, with apertures from $20 \text{ nm} - 500 \text{ nm}$ in diameter at a distance less than $\lambda/50$ away from the sample surface, where λ is the wavelength of the light. By placing the aperture this close to the surface, referred to as the 'near field' the diffraction from the

edge of the aperture did not have a chance to spread out much further than the size of the aperture itself²⁵. This method only works when the aperture is very close to the surface it is imaging, hence the use of a specialized SPM probe. The delicacy of SPM probes and the high cost associated with specialized probes of this nature does not make this method easily accessible. The low intensity of light passing through the small aperture would lead to lower signal-to-noise ratios, which is not desirable in FTIR spectroscopy techniques. Additionally special sample preparation is required to make samples thin enough so light passes through to the detector. This preparation could compromise the surface properties of the sample, which would be important when investigating properties such as surface preparation for adhesion. An ideal technique would require little sample preparation.

Knoll and Keilmann presented work using an aperture-less approach to scanning near-field optical microscopy. They focused infrared radiation from a tunable CO₂ laser onto commercially available silicon SPM tips coated with a 100 nm layer of gold. The cantilever was oscillated at its resonant frequency (~40 kHz) by a piezoelectric transducer in the SPM system. A mercury-cadmium-telluride (MCT) detector observed the scattering of light by the tip and provided a contrasting infrared image as a function of probe position. A topographic image can be collected from the sample at the same time as the contrasting infrared image. A polystyrene (PS) region, approximately 100 nm in diameter, embedded in a poly (methyl methacrylate) (PMMA) matrix was imaged and it was observed that as the wavelength of infrared radiation was tuned to a wavelength that is more absorbed in either PS or PMMA, the infrared image of the more absorbing material darkened in comparison to the less absorbing material. They reported contrast

infrared absorption imaging of PS and PMMA at a spatial resolution of $\sim 100\text{ nm}^{26}$. Knoll and Keilmann's tip scatter approach was able to provide infrared absorption information at sub-micron spatial resolutions; however, it was in the form of contrast imaging, analogous to that observed in phase mode SPM imaging. A great step forward would be a corresponding infrared spectrum at each data point in the spatial infrared map of the sample. This would provide a compositional profile of the surface, which could be used to better understand the molecular structure in the adhesive interphase region.

Foster et al described nano-Raman spectroscopy and scanning nano-Raman spectroscopy using a technique referred to as tip-enhanced Raman spectroscopy (TERS). TERS operates on the same phenomenon as SERS as described in Section I-A by Boerio et al, where the Raman scattering by organic molecules adjacent to a surface of certain metals such as silver, gold, and copper is enhanced by as much as 10^6 compared to its value well away from the metal surface. In TERS an SPM probe is coated with the metal used to enhance the Raman signal. Foster et al were able to show significant enhancement of Raman signals when the tip-enhanced probe was in contact with the sample as compared to when the probe was withdrawn. Because the SPM probes for TERS are on the nanoscale at the tip, the region of signal enhancement is on the same level of nanoscale resolution^{27, 28}. This method has only been shown to work on a select number of samples and requires specialized SPM probes. Additionally the wavelengths of interrogation are limited to the narrow regions around the wavelength of the Raman laser source. Different laser sources would have to be used to look at different regions of the spectrum.

Hammiche et al illuminated the surface of a sample with infrared radiation from an FTIR spectrometer as a miniaturized Wollaston wire resistive thermometer SPM probe monitored thermally induced temperature fluctuations at the sample surface. The Wollaston wire consisted of 75 μm diameter silver coating over a 5 μm diameter platinum/10% rhodium core. The wire was made into a loop and where the loop was formed the silver was electrochemically etched away, revealing the core over a length of 50 μm . The exposed length of the core acted as the sensor and the photothermal response of the sample resulted in changes in resistance of the core. The signal was amplified and routed to the external input of an FTIR spectrometer where a Fourier-transform was performed, resulting in the infrared spectrum of the sample. Peaks on the resulting spectrum represented peaks of absorption by the sample. FTIR spectra of several polymers including poly(butylene terephthalate) and polycarbonate were obtained and compared to attenuated total reflection (ATR) spectra of the same polymers. The authors claimed the spatial resolution in these experiments was about 250 nm depending on the type of probe employed. Hammiche et al noted that the resolution could approach 20 – 50 nm with improved probes²⁹. It was reported that the spatial resolution in these investigations was about 250 nm. Lack of supporting spectral information for this spatial resolution claim leads one to question whether such high spatial resolutions were achieved using this method. Obtaining spectral information from a composite sample where it would be necessary to resolve spectral information of one material that is chemically joined to another material through an interphase region would better support the claim that this method is capable of such high spatial resolutions.

Anderson described an approach that used relatively inexpensive contact mode AFM probes rather than specialized probes. A simple setup with an infrared lens was used to focus modulated infrared radiation on to the sample surface at the point of AFM tip contact. Absorption of the modulated infrared radiation resulted in modulated thermal expansion by the sample that was detected by the SPM. Anderson suggested that the spatial resolution in this approach could be as small as 100 nm based on several factors including the incident power, the frequency at which the IR radiation was modulated, and the thermal conductivity of the sample^{30, 31}. Although Anderson's simple apparatus did not enable actual FTIR spectra of polymers to be obtained, he did show that the output of the SPM had the characteristic appearance of an interferogram from the unprocessed output of an FTIR detector. Anderson suggested that the output from the SPM could be used as input to the FTIR spectrometer and that signal averaging would result in much improved signal-to-noise ratio. However, Anderson did not report any successful results concerning this suggestion.

The spatial resolution of the two types of infrared spectroscopy combined with SPM probes as described by Hammiche et al and by Anderson is related to the contact area that the probes makes with the sample. Because of this relationship, the use of AFM probes is obviously advantageous to the development of ultra-high spatial resolution infrared spectroscopy. Pethica and Oliver described the contact area between an AFM probe and the sample surface by the following equations:

$$a^3 = \frac{3PR}{4E^*} \quad (3)$$

$$\frac{1}{E^*} = \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \quad (4)$$

In equations 3 and 4, a is the radius of the contact area, P is the probe/sample interaction force, E_1 and E_2 are the elastic moduli of the sample and probe materials, respectively, ν_1 and ν_2 are the Poisson ratios of the sample and probe materials, respectively, and R is the radius of curvature of the tip of the probe³².

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

$$\mu = (\alpha/\pi\nu)^{1/2} \quad (5)$$

where ν is the modulation frequency and α is the thermal diffusivity³³. 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.

We have observed above the delicate balance of parameters such as sample preparation and analysis technique for investigating the interphase region in adhesive bonds. Is it possible to design a simple system based on two proven techniques in order to greatly improve the capabilities of each? Can relatively cheap contact mode AFM probes be used to provide chemical information on the nanoscale from samples absorbing infrared radiation? These are questions this work attempted to answer. A large portion

of this work is concerned with expanding and improving upon the work started by Anderson and investigates the use of an AFM as an absorption detector of infrared light from an FTIR spectrometer. We have taken his initial work further by successfully processing the output signal from an AFM probe engaged with an absorbing sample into that samples infrared absorption spectrum. We have also begun investigating the spatial resolution capabilities of the technique. Another smaller portion focuses on expanding the work by Hammiche et al using newly available thermal AFM probes to measure the temperature fluctuations of samples absorbing infrared radiation from an FTIR spectrometer.

II. Experimental

A. Instrumentation

All of the infrared spectroscopy experiments were conducted using a Nicolet Nexus 870 FTIR spectrometer from Thermo Electron Corporation. The atomic force microscope system consisted of a Dimension 3100 atomic force microscope (AFM), Nanoscope IIIa controller, Nanoscope Signal Access Module (SAM) and Quadrex module from Veeco Metrology, Inc. The SAM allowed access to various output signals from the AFM, which could be input into the FTIR spectrometer for processing. The AFM probes used for all thermal expansion experiments were made of silicon nitride, part number DNP (un-coated tip) or DNPG (gold coated tip), with a nominal spring constant of 0.32 or 0.56 N/m, from Veeco Metrology, Inc. Both the FTIR system and AFM were mounted on an RS-2000 vibration isolation table equipped with I-2000-428 legs from Newport Corporation. A purpose-built Plexiglas enclosure lined with acoustic foam from Auralex Corp. was used to aid in isolation of the AFM from the ambient environment. The AFM enclosure and the FTIR system were purged with dried, filtered air from a Parker Balston FT-IR purge-gas generator from Parker Hannifin Corporation. The AFM-FTIR system was setup so that each instrument could be used separately or together depending upon experimental needs.

B. AFM-FTIR Spectroscopy

In AFM-FTIR spectroscopy infrared light was focused on an infrared absorbing sample near the point of the stationary engaged, not scanned, AFM probe (see Figure 3). In a sense the sample and AFM probe took the place of the infrared absorption detector in

a transmission FTIR experiment. The SAM was used to extract the desired signal from the AFM probe, which was expected to resemble an interferogram. The extracted signal was routed into one of two inputs of the FTIR spectrometer, depending upon the type of experiment being conducted. The Nexus 870 spectrometer permitted the interferogram to be obtained in two different ways. In one way, referred to as step scan, the moving mirror of the Michelson interferometer was stepped through a series of discrete values of retardation while intensity information was collected for a short period of time at each value of retardation. In the other way, referred to as continuous scan, the moving mirror of the interferometer was scanned through its entire range continuously; multiple scans were averaged to obtain the interferogram. Fourier-transformation of the interferogram signal from the AFM probe yielded the AFM-FTIR spectrum of the sample. Three different methods for focusing the infrared radiation on the sample and probe were used to generate AFM-FTIR spectra and are described in the following section.

C. AFM-FTIR: Infrared Focusing Techniques

1. Top Illumination

The FTIR spectrometer was set up for a custom experiment and the infrared radiation was diverted out the left side of the spectrometer. A flat adjustable angle aluminum mirror was used to re-direct the infrared radiation into a ZnSe converging lens with a focal length of 76.2 mm, from ISP Optics. The converging lens was used to focus the radiation on the top of the sample surface at the AFM probe (see Figure 4). The approximate angle of incidence for the infrared radiation on the top of the sample surface

was 10° . The focusing lens was positioned using optical mounting components on the breadboard top of the RS-2000 vibration isolation table.

2. Side Illumination

The FTIR spectrometer was set up for a custom experiment and the infrared radiation was diverted out the left side of the spectrometer. An aluminum off-axis elliptical converging mirror with a focal length of 152.4 mm (Thermo Electron Corporation) was mounted on a 23° range goniometer (Melles Griot) and placed directly in front of the AFM probe at a distance of approximately 150 mm. The angle was adjusted to focus the infrared radiation so that it was incident on the front edge of the sample at an angle of no less than 85° to the plane of the front edge (see Figure 5). Therefore, if any infrared radiation was incident on the top surface where the AFM probe was engaged with the sample it was at an angle of incidence less than 5° .

3. Bottom Illumination

The FTIR spectrometer was again set up for a custom experiment and the infrared radiation was diverted out the left side of the spectrometer. An aluminum off-axis elliptical converging mirror with a focal length of 152.4 mm (Thermo Electron Corporation) was mounted on a 23° range goniometer (Melles Griot) and placed directly in front of the AFM probe at a distance of approximately 150 mm and set up higher than the point of engagement of the probe so the radiation had to be angled downward for proper focusing. A purpose built sample mounting stage was constructed and adhered to the AFM stage with an opening in the top surface such that a 13 mm diameter KBr disc

could be placed over the opening and still be exposed to radiation from below. This allowed for a stable surface to be engaged by the AFM. A custom cut, gold-coated microscope slide was adhered to an adjustable angle optical mount and adhered to the AFM stage. The sample mounting stage for bottom illumination was positioned over the gold mirror so that light could be focused up through the opening to the AFM probe using the off-axis elliptical converging mirror as shown in Figure 6. Using the white light source of the FTIR spectrometer, the elliptical mirror was adjusted to focus the light as near to the AFM probe as possible using the AFM optics as a rough feedback on proper focusing; the source was then switched back to infrared radiation. The angle on the goniometer was between 5 and 15° for all AFM-FTIR bottom illumination experiments.

D. Thermal Expansion Experiments

An investigation was conducted to determine if the AFM was capable of detecting and measuring the thermal expansion effects as a result of a polymer sample being exposed to and absorbing infrared radiation. A polystyrene plate sample was cut from a Petri dish (Fisher Scientific) and was placed over the vacuum chuck on the AFM stage. The infrared radiation was focused using the top illumination method and the AFM probe was engaged with the sample. For the thermal expansion experiments, an SR-540 mechanical chopper (Stanford Research Systems, Inc.) was placed in line with the radiation before the converging lens (see Figure 7). The chopper was mounted on a laboratory jack, which was attached to the RS-2000 breadboard table surface. The AFM probe was engaged with the sample roughly in the area where the infrared radiation was focused on the top surface of the sample. The AFM scan size was set to zero so that the

probe was “parked” on the sample surface. The integral and proportional gains of the AFM were set to 0.001 and 0.002, respectively, to reduce the response of the feedback electronics to cantilever deflection. The AFM z-limit was reduced to 500 nm to increase the sensitivity of the z-piezo controller, making it easier to execute smaller movements in response to cantilever deflection. A chopping wheel with four slits was fabricated from paper and attached to the SR540 chopper. The height data from the AFM probe was monitored as the infrared radiation was chopped at various angular frequencies between 6 and 62 Hz. The AFM scope trace was scaled such that five seconds of data were displayed in each frame (scan rate of 0.1 Hz), with a height scale showing a total of 2.5 nm. A single frame of the chopping data was collected for the approximate angular frequencies of 6, 12, 24, 48, and 62 Hz. After data was collected at the frequencies of 6, 12 and 24 Hz, a 76.2 μm thick polystyrene transmission standard film (Thermo Electron Corp.) was placed in line with the infrared radiation after the chopping wheel, but before the polystyrene sample to act as a filter for the infrared radiation as shown in Figure 7. A single frame of chopping data was collected at each frequency with the polystyrene filter in place. For the 6 Hz chopping frequency, an additional polystyrene filter was used in place of the 76.2 μm filter. The additional filter used was a cut piece of polystyrene plate from the same Petri dish the sample was cut from and had an approximate thickness of 1.02 mm.

E. Interferogram Collection by AFM

An investigation was performed to determine if the AFM was capable of detecting the interferogram pattern observed in FTIR spectroscopy. In this case, the AFM would

be measuring the variation in thermal expansion of the sample due to absorption of infrared radiation modulated by the interferometer. The same polystyrene sample used in the thermal expansion experiments, mentioned above, was used for this investigation. The ‘top-illumination’ method was utilized for AFM engagement of the sample and focusing of the infrared radiation. The FTIR spectrometer was set up to run step scan experiments, where the movable mirror in the interferometer is stepped at small increments, as described in Section II-B.

For the purposes of this particular experiment, the step scan preview function was utilized. The preview function swept the movable mirror of the interferometer through the positions closest to zero optical retardation or where complete constructive interference occurs, so that the center burst of the interferogram was observed. As the interferometer cycled through multiple preview mini scans, the AFM scope trace was set so that 5 seconds of data were displayed in each frame. Multiple frames of data were captured over several minutes to ensure that if the AFM did detect the center-burst of an interferogram, it would have been captured in the time frame of data collection by the AFM scope trace. The AFM scope trace was set to “trace” mode only instead of “trace-retrace” so that only one line was displayed on the scope trace during interferogram collection. The scope trace height was scaled so that 2.5 nm of deflection were displayed in each frame.

F. Step Scan AFM-FTIR Spectra

It was determined that the AFM was capable of detecting the center-burst of an interferogram, so the next logical step was to conduct complete step scan experiments

with the AFM outputting deflection data throughout the entire experiment. The cantilever deflection signal from the AFM probe was extracted using the SAM connected in line with the AFM feedback electronics. This signal was then input into Channel A of the FTIR spectrometer.

1. ZnSe Converging Lens Focusing

Using the ‘top-illumination’ method, interferogram patterns were collected in the FTIR spectrometer software. However, Fourier transformation of the collected signals did not result in any spectral information characteristic of the polystyrene sample. The lack of success using the ‘top-illumination’ method led to an experiment using a variation of the eventual ‘side-illumination’ method. A polystyrene plate sample was cut in the shape of a triangle from a Fisher Scientific Petri dish. The sample was then hand sanded so the cut edges were smoothed and removed of any burrs. One point of the triangle was sanded flat and smooth, parallel to the opposite leg of the triangle, to create a flat surface for the AFM to engage the sample when sitting on its edge. The sample was mounted in a Cross-Sectional Sample Holder (P/N SD-103 from Veeco Metrology, Inc.) and secured using a setscrew so the flattened point of the triangle sample was facing upward. The sample holder was held firmly on the AFM stage using a vacuum chuck. The AFM probe was engaged with the sample on the flattened point surface as close to the front edge as possible and the infrared radiation was focused on the probe and sample from the side using the ZnSe converging lens. A step scan experiment was conducted averaging 32 scans at a resolution of 16 cm^{-1} . Other notable step scan settings were a settling time of 1 ms, a settling factor of 1, and an average time per step of 100 ms. The settling time parameter defines a delay after each mirror step to allow the detector to stabilize before

data collection begins. The settling factor parameter defines a factor by which the settling time will be increased for 32 data points on each side of the zero path difference (ZPD) point or point of zero retardation. The average time per step parameter defines the length of time spent collecting data at each moving mirror position. The signal is continually sampled at a rate of 100,000 Hz and increasing the timer per data point increases the amount of signal averaging and the quality of demodulation for each point of the interferogram.

A standard polystyrene film of 38 μm thickness (Thermo Electron Corporation) was used for a transmission experiment to generate an absorption spectrum averaging 32 scans at a spectral resolution of 4 cm^{-1} . This was done for comparison with the AFM-FTIR spectra.

2. Aluminum Elliptical Mirror Focusing

A rectangular polystyrene sample was cut from a Petri dish and the edges were sanded smooth and free of any burrs. The sample was mounted on its edge in the cross-sectional sample holder and placed on the vacuum chuck of the AFM stage. The AFM probe was engaged with the sample as close to the front edge as possible and the infrared radiation was focused on the probe and sample using the ‘side illumination’ method. The difference between this setup and the previous side illumination setup, in Section II-F-1, was the angle of the focused beam to the horizon was less and an aluminum off-axis elliptical mirror was used to focus the infrared radiation, see Section II-C for a more detailed description. An AFM-FTIR step scan spectrum of the polystyrene sample was collected from only 1 scan at a spectral resolution of 32 cm^{-1} , settling time of 1 ms, settling factor of 1, and average time per step of 100 ms.

Through the course of running different experiments, it was noticed that different step scan settings resulted in spectral results of various quality. The settings that seemed to most affect spectral quality were settling time, settling factor and average time per step. It was found that the most ideal settings resulting in quality spectra were a settling time of 10 ms, a settling factor of 10 and average time per step of 100 ms.

3. Depth Profile

While collecting AFM-FTIR spectra using the ‘side illumination’ method it was noticed that varying the distance of AFM probe engagement from the front edge of the polystyrene sample resulted in varying relative peak intensities in the spectra. An investigation was conducted to view the effects on relative peak intensities as a function of AFM probe distance from the front edge. Since the majority of the infrared radiation was incident upon the front surface of the sample in the ‘side illumination’ setup this was in effect a measure of absorption affects as the probe is moved “deeper” into the sample; hence, the title ‘depth profile’ was assigned to this investigation. The AFM probe was engaged with the sample as close to the front edge as possible by scanning perpendicular to the edge and parking the probe nearest to the point where the scope trace indicated the probe was “falling off” the edge. An AFM-FTIR step scan spectrum was collected using 1 scan at a resolution of 16 cm^{-1} , a settling time of 10 ms, a settling factor of 10 and average time per step of 100 ms. The AFM probe was moved $10\text{ }\mu\text{m}$ from the front edge of the sample by withdrawing the probe from the sample, stepping the stage the correct amount and reengaging the probe with the sample. This was necessary because the maximum movement in one direction by the piezoelectric controllers that position the probe was around $96\text{ }\mu\text{m}$, depending upon calibration. At each $10\text{ }\mu\text{m}$ step an AFM-

FTIR step scan spectrum was collected using the same settings as mentioned above. The same probe was used throughout the entire experiment and the focus of the infrared radiation was not adjusted. The depth profile of the sample was investigated up to a distance of 770 μm from the front edge.

G. Continuous Scan AFM-FTIR

1. Bottom Illumination – Neat Polymer Samples

An approximately 1% by weight solution of Poly [Bisphenol-A carbonate-co 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (Sigma Aldrich) in chloroform was prepared. A 13 mm diameter potassium bromide disc was prepared using infrared grade KBr powder (Thermo Electron Corporation), a KBr pellet press and die kit (Thermo Electron Corporation) and a Carver laboratory press. One aliquot of the polycarbonate solution was cast on the KBr pellet and allowed to dry overnight in an exhaust hood. The solution cast sample of polycarbonate on a KBr pellet was placed over top of the hole in the bottom illumination stage. Infrared radiation was focused on the AFM probe through the sample. The AFM cantilever deflection signal was routed through the black box accessory and into the accessory port on the back panel of the infrared spectrometer. The spectrometer was set to collect 8,192 scans at a resolution of 8 cm^{-1} with an interferometer mirror velocity of 0.1581 cm/s .

The same sample of solution cast polycarbonate thin film on a KBr pellet was placed in the FTIR transmission sample holder and an FTIR transmission spectrum of the sample was collected averaging 64 scans at a resolution of 4 cm^{-1} with an interferometer mirror velocity of 0.6329 cm/s .

An epoxy thin film sample was prepared on a KBr pellet for collection of an AFM-FTIR continuous scan spectrum using the 'bottom illumination' method. 0.1 g of Dicyandiamide (DDA, Sigma Aldrich) was dissolved in 5 ml of N, N, Dimethyl Formamide (DMF, Fisher Scientific). 2.5 ml of Di-Glycidyl Ether of Bisphenol A (DGEBA, The Dow Chemical Company) was added to the solution of DDA in DMF, for a 7:1 mole ratio of DGEBA:DDA, and stirred using a magnetic stirrer for 2-3 minutes. One aliquot of mixture was spread on a KBr pellet and the DMF was allowed to evaporate overnight. The thin film of resin and hardener mixture was then cured overnight in a vacuum oven at a temperature of 150°C. The solution cast and cured epoxy sample on a KBr pellet was placed over top of the hole in the bottom illumination stage. Infrared radiation was focused on the AFM probe through the sample. The AFM cantilever deflection signal was routed through the black box accessory and into the accessory port on the back panel of the infrared spectrometer. The spectrometer was setup to collect 8,192 scans at a resolution of 8 cm⁻¹ with an interferometer mirror velocity of 0.1581 cm/s.

The same sample of solution cast and cured epoxy thin film on a KBr pellet was placed in the FTIR transmission sample holder and an FTIR transmission spectrum of the sample was collected averaging 64 scans at a resolution of 4 cm⁻¹ with an interferometer mirror velocity of 0.6329 cm/s.

A 38 µm polystyrene film transmission standard from Nicolet was stretched over a KBr pellet resting over the hole on the bottom illumination stage. The AFM was engaged with the polystyrene film in the area where the infrared radiation was focused using the bottom illumination method. A continuous scan spectrum of the polystyrene

film was collected averaging 4,116 scans at a spectral resolution of 8 cm^{-1} with an interferometer mirror velocity of 0.1581 cm/s .

2. AFM-FTIR Spatial Resolution Capability

To investigate the spatial resolution capabilities of the AFM-FTIR instrument in continuous scan mode, polystyrene micro spheres were obtained from Bangs Laboratories, Inc. Two different size spheres were obtained with mean diameters of $1.97\text{ }\mu\text{m}$ and $0.53\text{ }\mu\text{m}$. Each size sphere was stored in an aqueous suspension at a concentration of approximately 10 % solids. Several 13 mm diameter KBr pellets were prepared and stored in a dry location. The suspension of polystyrene spheres with a diameter of $1.97\text{ }\mu\text{m}$ was further diluted to 0.1 % solids, ultrasonicated for 45 minutes, and one aliquot of this suspension was deposited on the anvil of the KBr die and press kit and placed in an oven at $60\text{ }^{\circ}\text{C}$ for 30-60 minutes. The water in the suspension was evaporated leaving behind the micro spheres. The KBr die kit was assembled and one of the KBr pellets previously prepared was placed over top of the micro spheres on the anvil. The spheres were pressed into the surface of the KBr pellet at a pressure of 5,000 psi for 10 seconds then removed from the die kit. The sample was then placed over the opening of the bottom illumination stage and engaged by the AFM for contact mode scanning. The zoom feature of the AFM microscope was used to zoom in on a cluster of 5 micro spheres packed closely together. One of the outer spheres was zoomed in on until the probe was only scanning on the one sphere, at which point the scan size was set to 0 nm so the AFM probe was “parked” on the micro sphere. The infrared radiation was focused on the AFM probe through the sample by the bottom illumination method. A continuous scan spectrum was collected with the AFM probe parked on the one polystyrene micro

sphere of 1.97 μm diameter. 1,692 scans were averaged at a spectral resolution of 8 cm^{-1} and an interferometer mirror velocity of 0.0475 cm/s .

Using the 0.53 μm micro spheres, another sample embedded in a KBr pellet was prepared in the same way as the 1.97 μm micro sphere sample. The AFM was used in contact mode to image the sample and zoom in on one micro sphere embedded in the KBr. The infrared radiation was focused on the AFM probe through the sample using the bottom illumination method. An attempt was made to collect a continuous scan AFM-FTIR spectrum of a 0.53 μm diameter polystyrene micro sphere.

To investigate if a single 1.97 μm diameter polystyrene micro sphere could be spectrally resolved when embedded in a different polymer material a sample was prepared where the micro spheres were embedded in paraffin film, all on top of a KBr pellet. A blank KBr pellet was prepared using the KBr Die press kit, the Carver laboratory press and infrared grade KBr powder. A piece of paraffin film (Fisher Scientific) was stretched to as thin as it could be without breaking and a piece smaller than the 13 mm diameter KBr pellet was cut out. Using Nitrile gloves the cut out piece of paraffin film wax was hand pressed onto the KBr. Next the 10% solids suspension of 1.97 μm diameter polystyrene micro spheres was diluted to a 0.1% solids suspension and one aliquot was deposited on the anvil from the KBr die kit and placed in an oven at 60 $^{\circ}\text{C}$ for 30-60 minutes to evaporate the water. The die kit was assembled and the KBr pellet with the thin film of paraffin film on it was placed so the film side was facing the surface of the anvil. The pellet with the film was pressed onto the anvil to a pressure of 5,000 psi for 10 seconds then removed and the sample was placed over the opening of the bottom illumination stage. The AFM was engaged with the sample and a contact mode

image was collected of the 1.97 mm diameter polystyrene micro spheres embedded in paraffin film wax all on top of a KBr pellet. A single micro sphere was zoomed in on as before and the infrared radiation focused on the probe by the bottom illumination method. A continuous scan spectrum was collected over 1,320 scans at a spectral resolution of 8 cm^{-1} and an interferometer mirror velocity of 0.0475 cm/s . A transmission spectrum of the same sample was collected averaging 64 scans at a spectral resolution of 4 cm^{-1} . Another sample was prepared with just a thin stretched film of paraffin film on a KBr pellet. A transmission infrared spectrum of this sample was captured over 64 scans at a resolution of 8 cm^{-1} and an interferometer mirror velocity of 0.6329 cm/s .

H. Thermal Probes for FTIR Spectroscopy

As was described in Section II-G-1, the $38\text{ }\mu\text{m}$ thick polystyrene standard film from Nicolet was stretched over a blank KBr pellet on the AFM-FTIR bottom illumination stage. A Nano-TA2 thermal analysis system (Anasys Instruments) was used to obtain thermal fluctuation information from samples on a nanometer scale. The system was run in Scanning Thermal Microscopy (SThM) mode using GLA probes (Anasys Instruments). The thermal probes were engaged with the polystyrene film on the KBr pellet and parked inside of the focus of the infrared radiation focused by the bottom illumination method. The thermal signal was extracted from the Nano-TA2 system via the output and was input into Channel A of the Nexus 870 FTIR spectrometer. A step scan spectrum of the polystyrene film was collected using a single scan at a resolution of 32 cm^{-1} . The settling time, settling factor and average time per step for the experiment were 50 ms, 50 and 100 ms, respectively.

III. Results and Discussion

A. Thermal Expansion Experiments

With the AFM probe engaged with the top surface of the polystyrene sample it was immediately apparent that the AFM was capable of measuring thermal expansion resulting from absorption of infrared radiation. As soon as the sample was exposed to infrared radiation, the AFM scope trace indicated the AFM probe was moving upwards away from the surface. However, the probe was moving upwards as a result of the sample surface moving upwards because of the thermal expansion. When the chopping wheel was set to an angular frequency of approximately 6 Hz saw tooth like waves were observed in the AFM scope trace (see Figure 8A). The peak-to-peak height difference between the top and bottom of the waves was approximately 2.25 nm, as summarized in Table 1. The frequency calculated from the scope trace was approximately 0.83 Hz, which can be converted to an angular frequency by the following equation:

$$\omega = 2\pi f \quad (6)$$

Using equation 6, the frequency of 0.83 Hz was converted to an angular frequency of 5.24 Hz. The difference between the observed frequency and the angular frequency setting on the mechanical chopper can be attributed to a controller accuracy of only 1 Hz as well as the possibility of being out of calibration due to using a hand made chopping wheel. When the 76.2 μm thick polystyrene film was placed in the path of the infrared radiation the peak-to-peak height of the saw tooth waves was reduced to 0.312 nm, as seen in Figure 8B. This was an 86.1 % reduction in peak-to-peak height as compared to

the un-filtered saw tooth waves at a setting of 6 Hz (see Table 2). When the 1.02 mm thick polystyrene plate sample was placed in the path of the infrared radiation there was no apparent repeating pattern observed in the AFM scope trace, as shown in Figure 8C. Any variation due to cantilever deflection observed in the scope trace were attributed to ambient noise and vibrations from the mechanical chopper since it was mounted on the same table surface as the AFM.

When the angular frequency was increased to 12 Hz, saw tooth like waves were again observed in the AFM scope trace at a frequency of approximately 2.7 Hz, as seen in Figure 9A. The peak-to-peak height of the waves was approximately 1.25 nm (see Table 1), which was less than that observed for the 6 Hz frequency. This was expected as the time increments of exposure to infrared radiation had decreased as compared to the frequency of 6 Hz. When the 76.2 μm polystyrene film was placed in the path of the infrared radiation, the peak-to-peak height decreased (see Figure 9B) by 81 % to 0.240 nm as summarized in Table 2. Increasing the angular chopping frequency of the mechanical chopper to 24 Hz, saw tooth like waves were observed in the AFM scope trace at a frequency of approximately 3.33 Hz (see Figure 10A), which converted to an angular frequency of 21 Hz by using equation 3. The peak-to-peak height of the waves was approximately 0.625 nm (see Table 1), continuing the trend of decreasing range of expansion and contraction with increasing chopping frequency. Placing the 76.2 μm polystyrene film in the path of the infrared radiation resulted in no observable repeating pattern in the AFM scope trace (see Figure 10B). The apparent reduction in deflection signal as a result of filtering the infrared radiation at a chopping frequency of 24 Hz was approximately 88.2%. Increasing the angular frequency further to 48 Hz resulted in a

frequency of approximately 7.3 Hz observed in the AFM scope trace, as shown in Figure 11. Again the peak-to-peak height of the saw tooth waves decreased as frequency increased in this case measuring 0.280 nm (see Table 1). Finally, increasing the angular frequency to 62 Hz resulted in saw tooth waves observed in the AFM scope trace at a frequency of approximately 9.3 Hz (see Figure 12). The peak-to-peak height of the observed saw tooth waves for this chopping frequency was approximately 0.200 nm (see Table 1).

Increasing the chopping frequency above 62 Hz resulted in too much vibration noise from the mechanical chopper and made it difficult to discern a saw tooth wave pattern in the AFM scope trace. However, the results of these experiments demonstrated that the AFM was capable of measuring thermal expansion of polystyrene as a result of absorption of infrared radiation. A trend was observed of decreasing peak-to-peak height with increasing chopping frequency following an approximate exponential decay pattern, as shown in Figure 13. The decrease in peak-to-peak height of the saw tooth waves as a result of placing the 76.2 μm thick polystyrene film indicates that the observed expansion and contraction of the sample was a result of absorption of infrared radiation by the sample at the frequencies characteristic of polystyrene, since the filtering material was the same as the material engaged by the AFM. For each frequency the reduction in peak heights, when the 76.2 μm thick PS film was in-line, were similar at 86.1 %, 81%, and 88.2%. These results indicated that the AFM was capable of measuring thermal expansion of polystyrene. Therefore, it was likely that the AFM was capable of measuring thermal expansion of other polymers as a result of absorption of infrared radiation.

B. Interferogram collection by AFM

During set up for this experiment it was necessary to allow the AFM a certain amount of time to stabilize. Upon engaging the sample the AFM probe would appear to drift either away from the sample or into the sample at a relatively slow rate, but enough to affect experimental results. With time this drifting rate would decrease and the “stabilization time” was found to be in the range of 5 to 15 minutes. After the AFM stabilized, the step scan preview feature could be used. Capturing multiple frames of the AFM scope trace allowed capture of the center burst pattern of an interferogram, as shown in Figure 14. The peak-to-peak height of the interferogram center burst was 1.61 nm, which calculated to approximately 0.14 V peak-to-peak (see Table 4). The voltage value was determined from the AFM calibration setting for the z-piezoelectric controller, which was 440 V equivalent to 5.196 μm . This gave 11.8 nm/V or 8.47×10^{-2} V/nm as conversion values for peak-to-peak measurements made in either height or voltage. The results of this experiment indicated that the AFM was capable of detecting the center burst pattern of an interferogram as a result of a polystyrene sample absorbing infrared radiation. This was a promising indication that the AFM could be used to generate infrared spectra of various polymer materials.

C. Step Scan AFM-FTIR Spectra

In the previous sections the AFM showed the ability to measure the thermal expansion of polystyrene and collect interferogram patterns due to absorption of

modulated infrared radiation. The next step was to collect a full step scan experiment using the sample and AFM probe as the infrared absorption detector and performing a Fourier transform on the resulting cantilever deflection signal, which was input into the FTIR spectrometer. As stated in Section III-B, the approximate center-burst peak-to-peak voltage for the interferogram generated by step scan using top illumination method was 0.14 V. Upon investigating whether infrared spectra could be generated by Fourier transformation of the AFM cantilever deflection signal from a step scan experiment, this peak-to-peak voltage proved to be too low to generate any useful spectral information. Thus, new methods for focusing the infrared radiation were investigated in order to increase this peak-to-peak voltage of the generated interferogram. The idea for side illumination was developed. However, initially the ZnSe converging lens was used and results are described below.

1. ZnSe Converging Lens Focusing

Placing the sample on its side allowed for more infrared radiation to be incident on the sample near the AFM probe, resulting in a greater degree of thermal expansion due to absorption. Performing a Fourier transform on the resulting 32 scan averaged interferogram pattern, from the cantilever deflection signal, resulted in spectral bands characteristic of polystyrene, as observed in Figure 15A. Comparing the AFM-FTIR step scan spectrum of polystyrene to a transmission infrared spectrum of polystyrene, shown in Figure 16A, it was observed that the AFM-FTIR spectrum clearly resembled the transmission spectrum. However, there were significant differences in the 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. One marked improvement made from the top illumination method was the interferogram peak-to-peak voltage; in this case it measured 2.70 V, equivalent to a cantilever deflection of 32.92 nm, which indicated a much higher signal-to-noise ratio. However, the relative peak intensities being different than their transmission counterpart left more to be desired and the search for even greater signal strength lead to focusing using the aluminum elliptical mirrors and the set up for the current method of side illumination.

2. Aluminum Elliptical Mirror Focusing

It proved unnecessary to collect multiple interferogram scans for step scan experiments since data was already averaged at each step of the interferometer mirror. Therefore, all subsequent AFM-FTIR step scan spectra consist of only one scan, or one full sweep of the interferometer mirror. Using the ‘side illumination’ method with an aluminum-focusing mirror a single step scan AFM-FTIR spectrum of polystyrene was obtained (see Figure 17). Again the AFM-FTIR spectrum clearly resembled the transmission spectrum, but as with the previous AFM-FTIR spectrum of polystyrene, there were significant differences in relative intensity of the some bands. As stated at the beginning of Section II-F-3, it was noticed that the relative peak intensities would vary as probe distance from the front edge of the sample varied. These differences in relative intensity were related to the side-illumination method. Because side-illumination was essentially a depth analysis, the wavelengths that were strongly absorbed in transmission were completely absorbed before they reached the vicinity of the probe; thus, little or no signal was measured by the probe. On the other hand, wavelengths that were weakly

absorbed in transmission traveled a considerable distance into the sample and produced absorption in the vicinity of the probe, thus resulting in a signal in AFM-FTIR. This effect was further demonstrated by performing the depth profile experiment described in Section II-F-3.

3. Depth Profile

Additional AFM-FTIR spectra of polystyrene were obtained using the side illumination method, while placing the probe at 10 μm increments from the front edge of the sample. Results are shown in Figure 18 and are from AFM-FTIR step scan spectra collected at distances from the front edge of 0, 300, 550, and 770 μm . The spectrum generated when the distance from the edge was $x=0$ μm was very similar to the spectrum reported in Section III-C-2. That is, the bands in the region from 2700 to 3100 cm^{-1} that were strong in transmission spectrum appeared to be saturated in the AFM-FTIR spectrum, while the peaks at 1945, 1874, 1803, 1744, and 1665 cm^{-1} , which were weak in the transmission spectra were strong to medium in intensity in the AFM-FTIR spectra. The band at 690 cm^{-1} was not present in any of the AFM-FTIR spectra. Moving the probe further away from the front edge of the sample to approximately 300 and 550 μm resulted in all of the bands in the AFM-FTIR spectra decreasing in intensity. When the probe was placed at a distance of approximately 770 μm from the front edge of the sample, 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 18). In AFM-FTIR spectroscopy, the AFM only measured a signal when the sample was absorbing infrared radiation near the probe. The value for the peaks in the 770 μm spectrum were still positive, but they appeared to be inverted because all of the radiation at the absorption

bands of polystyrene was absorbed by the sample prior to reaching the vicinity of the AFM probe.

The depth profile experiment was analogous to the experiment that was used to obtain the results described in Section III-A where a filter was used to decrease the amount of thermal expansion observed in the polystyrene sample. In the thermal expansion experiments the filter was separate from the sample and had a fixed thickness. Therefore it was expected that at some value x away from the front edge of the sample the AFM signal would disappear and the intensity of the bands in the AFM-FTIR spectrum would go to zero.

D. Continuous Scan AFM-FTIR

1. Bottom Illumination – Neat Polymer Samples

From the side illumination results described above, it was apparent that thermal saturation was a problem. Therefore, a different approach was investigated using the bottom illumination method and continuous scan FTIR spectroscopy as described in Section II-G-1. An AFM-FTIR spectrum of polycarbonate was obtained using this technique and is shown in Figure 19. Comparing the AFM-FTIR spectrum of polycarbonate to that of the transmission spectrum of the same sample (see Figure 20) resulted in excellent correlation between absorption bands observed as well as relative peak intensities. Additionally, the signal-to-noise ratio of the AFM-FTIR spectrum was outstanding. These results showed that AFM-FTIR spectroscopy is capable of producing very high quality spectra of polymer systems.

One of the long-term goals for use of the AFM-FTIR instrument is to probe the interface region in adhesive bonds and composite materials. For this reason we prepared a model epoxy adhesive system for AFM-FTIR analysis through bottom illumination as described in Section II-G-1. As with the polycarbonate sample, an AFM-FTIR spectrum of the model epoxy system was obtained using the bottom illumination continuous scan method and is shown in Figure 21. Comparing the AFM-FTIR spectrum of the model epoxy system to that of the transmission spectrum of the same sample (see Figure 22) also resulted in excellent correlation between the observed absorption bands. There were some differences in relative peak intensities where weaker absorbing bands in the transmission spectrum appeared to be stronger in the AFM-FTIR spectrum; this was related to the thermal saturation due to the sample being slightly too thick. Thus, it became apparent that the bottom illumination method was dependant upon film thickness. It is especially interesting to note the bands near 1740 and 1660 cm^{-1} in the AFM-FTIR spectrum of the model epoxy adhesive. These bands were representative of a reaction that occurred between the epoxy resin with dicyandiamide, resulting in a complex series of intermediates and eventually the end result of a urethane³⁴. The intermediate 2-iminooxalidine contained an imine bond that was expected to absorb near 1660 cm^{-1} , while the urethane end product was expected to absorb near 1740 cm^{-1} . The presence of these bands indicated the ability of the AFM-FTIR instrument to spectrally resolve specific functional groups.

An AFM-FTIR spectrum of a $38\text{ }\mu\text{m}$ thick polystyrene sample was obtained using the bottom illumination continuous scan method and is shown in Figure 23. Comparing the AFM-FTIR bottom illumination continuous scan spectrum of polystyrene to the

transmission spectrum of polystyrene (see Figure 16) resulted in excellent correlation between absorption bands and the best AFM-FTIR spectrum of polystyrene to this point. Relative peak intensities were still a bit different with weaker bands in the transmission spectrum appearing relatively more intense in the AFM-FTIR spectrum, indicating the polystyrene film was slightly too thick. However, it was noted that the absorption bands near 690 and 756 cm^{-1} were present and strong in this AFM-FTIR spectrum of polystyrene.

2. AFM-FTIR Spatial Resolution Capability

The AFM-FTIR spectra described thus far have all been of single-phase materials or neat polymer samples. Since interrogation of interphase regions on the sub-micron scale was one of the goals of this research the polystyrene micro sphere samples embedded in KBr and in paraffin film were prepared as described in Section II-G-2. In the first investigation where the 2 μm diameter polystyrene micro spheres were embedded in a KBr pellet, the AFM probe was parked on one of the outlying spheres of a small cluster as shown in Figure 24. The AFM-FTIR spectrum obtained (see Figure 25) was very similar to the AFM-FTIR spectrum obtained of the 38 μm thick polystyrene film described in Section III-E-1. There are some differences in relative peak intensities, which indicated that this sample was actually thicker than the polystyrene film. This indicated that there were multiple layers of micro spheres stacked on top of one another. However, the excellent signal-to-noise ratio of the spectrum indicated that AFM-FTIR spectra could possibly be obtained from samples that were much smaller than 2 μm using bottom illumination and continuous scanning. Therefore a sample was prepared using the 0.53 μm diameter micro spheres embedded in a different KBr pellet. However, upon

attempting to collect an AFM-FTIR a stable and strong enough signal was unable to be achieved in order to collect a continuous scan spectrum. The failure to obtain a continuous scan spectrum from the 0.53 μm diameter micro spheres sample could have had to do with the observations of inverted peaks in the step scan AFM-FTIR spectra of the same sample. The absorption peaks observed were similar to those observed in the depth profile experiment as described in section III-C-3. This indicated that the polystyrene micro spheres were stacking on top of one another and the layers were forming a much too thick layer for a significant amount of infrared radiation, at the characteristic absorption bands of polystyrene, to reach the sphere being engaged by the AFM probe. It was likely that static interactions between the sub-micron size spheres made it too difficult to isolate one bead because they tended to cluster together, forming multiple layers.

Since a successful AFM-FTIR spectrum of 2 μm diameter polystyrene micro spheres was obtained by bottom illumination continuous scan methods, a composite sample was prepared consisting of the micro spheres embedded in a thin film of paraffin all on a KBr pellet. The AFM was used in contact mode to focus in on and “park” the probe on one micro sphere embedded in the wax (see Figure 26). An AFM-FTIR continuous scan spectrum of this composite sample was obtained and is shown in Figure 27. The spectrum obtained did not contain any bands characteristic of polystyrene. However, when compared with the transmission spectrum of a neat paraffin film sample shown in Figure 28 it was observed that the AFM-FTIR spectrum of the composite sample had identical absorption bands compared to the neat paraffin film spectrum. This result indicated that the spatial resolution when using AFM-FTIR spectroscopy and

measuring thermal expansion using contact mode probes was not substantially better than that obtained using FTIR micro-spectroscopy. This result could have been related to the relatively large area of paraffin film being illuminated by the infrared radiation as compared to the area illuminated of embedded polystyrene micro spheres. This lead to the polystyrene absorption signal reaching the AFM probe being much smaller as compared to the paraffin film absorption signal and therefore being buried in the signal from the paraffin wax. It was a problem possibly related to contact area of the AFM probe with sample, as described by equations 3 and 4 in section I-D. Table 5 shows examples of calculated contact areas for polystyrene and polycarbonate materials when engaged by a silicon nitride contact mode AFM probe. Because the sample/probe contact area for this composite sample was similar to those calculated in table 5 it was likely that the spatial resolution problem in this case was more related to the thermal diffusion length as given by the expression in equation 5 in section I-D. It was likely that the AFM probe was measuring the thermal expansion of the overall sample due to a large spread of perturbations from one volume element to another in the paraffin film and this was why the absorption signal from the polystyrene micro sphere was buried in the absorption signal from the surrounding paraffin material, since the elastic waves being measured by the probe were relatively un-damped. Being able to measure the temperature change in a sample as a result of absorption of infrared radiation would allow measurement of a signal more representative of the volume elements in close proximity of the probe in the sample/probe contact area, as thermal diffusion through a sample is much more damped as compared to elastic waves.

E. Thermal Probes for AFM-FTIR Spectroscopy: SThM-FTIR

Initial experiments were conducted using newly acquired thermal probes for the AFM in order to measure the thermal fluctuations within the sample as a result of exposure to infrared radiation. Using the bottom illumination method, step scan AFM-FTIR spectra were generated of the 38 μm thick polystyrene film stretched over a KBr pellet as was done in previous bottom illumination experiments. The so-called thermal AFM-FTIR step scan spectrum of the polystyrene film is shown in Figure 29. The absorption bands from 2700 to 3100 cm^{-1} were observed in the spectrum as well as indications of the bands around 1500 cm^{-1} . Relative intensities of the bands were off in a similar way observed in step scan AFM-FTIR spectra collected using side illumination. Attempts to collect continuous scan thermal AFM-FTIR spectra have failed to date due to low signal-to-noise ratio. As with AFM-FTIR the initial spectra were of poor quality, but with continued work the signal-to-noise ratio can be increased and spectral quality can be improved. The spatial resolution of thermal AFM-FTIR spectroscopy has not yet been determined. However, as mentioned, it is expected to be substantially better than AFM-FTIR spectra obtained using contact mode probes. The reason is that the spread of thermal energy in this type of photothermal spectroscopy was related to the thermal diffusion length as described by equation 5 in section I-D. It was evident from the spectrum shown in Figure 29 that the realization of ultra-high spatial resolution AFM-FTIR spectroscopy is a realistic goal.

IV. Conclusions

The AFM was capable of detecting the thermal expansion of polymer systems as a result of absorption of infrared radiation. By Fourier transformation of the cantilever deflection signals, high quality infrared spectra were obtained with excellent signal-to-noise ratios, a significant advancement compared to the work conducted by Anderson using a similar setup. However, the spatial resolution of this technique did not appear to be better than that obtained using infrared micro-spectroscopy, but more rigorous testing could prove otherwise. The use of thermal AFM probes showed promise in generating high quality infrared spectra at ultra-high spatial resolutions. However, use of this method was limited due to low signal-to-noise ratios. With further work on both methods AFM-FTIR spectroscopy could become a powerful technique for determining molecular structure of interface regions in adhesive bonds and polymer composites.

V. Future Work

Continued efforts using the AFM-FTIR technique using contact mode measuring the thermal expansion could include collecting spectra of better prepared samples for testing the spatial resolution limits. Such samples could include a sample similar to that used by Knoll and Keilman²², or phase separating block co-polymer systems such as styrene-butadiene-styrene block co-polymers. Of course careful sample preparation would be in order to use such phases separating samples in the bottom illumination method to ensure that there exists only one layer of phase separated material in the thin cast film on KBr pellet.

Additionally further work is needed in increasing the signal-to-noise ratio when using thermal probes for AFM-FTIR spectroscopy when measuring the thermal change in the sample upon absorption of infrared radiation. Similar samples as described above for thermal expansion AFM-FTIR could be used to determine the spatial resolution of AFM-FTIR spectroscopy using thermal probes.

VI. References

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VII. Tables

Frequency (Hz)	P-P Height (nm)
6	2.25
12	1.25
24	0.625
48	0.280
62	0.200

Table 1: AFM peak-to-peak deflection values for thermal expansion experiment using chopping wheel at various frequencies with no polymer filter in place.

Frequency (Hz)	P-P Height (nm)	% Reduction
6	0.312	86.1%
12	0.240	80.8%
24	0.074	88.2%

Table 2: AFM peak-to-peak deflection values for thermal expansion experiment using chopping wheel at frequencies 6, 12 and 24 Hz with 76.2 μm polystyrene film in line with radiation acting as a filter.

Frequency	Filter Size (μm)	P-P Height (nm)	% Reduction
6	0	2.25	-
6	76.2	0.312	86.1%
6	1022	N/A	-
12	0	1.250	-
12	76.2	0.240	80.8%
24	0	0.625	-
24	76.2	0.074	88.2%
48	0	0.280	-
62	0	0.200	-

Table 3: AFM peak-to-peak deflection values for thermal expansion experiment using chopping wheel. Compiled table showing all filters used for each chopping frequency.

Sample Description	IFG Centerburst peak-to-peak Voltage (V)	Equivalent peak-to-peak height (nm)	Focusing Method	Experiment Method
Polystyrene: section II-D, IFG capture	0.14	1.61	Top Illumination	Step Scan
Polystyrene: section II-E-1, step scan ZnSe focusing lens	2.79	32.92	Side Illumination, ZnSe focus	Step Scan
Polystyrene: section II-E-2, step scan aluminum mirror focus	7.50	88.50	Side Illumination	Step Scan
Polystyrene: section II-F-1	13.90	164.02	Side Illumination	Continuous Scan
Polycarbonate: section II-F-2	11.40	134.52	Bottom Illumination	Continuous Scan
DGEBA-DDA Epoxy: section II-F-2	12.00	141.60	Bottom Illumination	Continuous Scan
Polystyrene: section II-F-2	5.90	69.62	Bottom Illumination	Continuous Scan
Polystyrene microspheres: section II-F-3	5.10	60.18	Bottom Illumination	Continuous Scan

Table 4: Comparison of peak to peak voltages and deflection heights for the center burst from the different experiment setups from which quality infrared spectra were generated.

Material	P (N)	R (m)	a³ (m³)	a (m)	a (nm)	area (nm²)
Polystyrene	1.0E-08	2.0E-08	4.10E-26	3.45E-09	3.45	37.3
Polystyrene	1.0E-07	2.0E-08	4.10E-25	7.43E-09	7.43	173.3
Polystyrene	1.0E-08	9.0E-08	1.84E-25	5.69E-09	5.69	101.8
Polystyrene	1.0E-07	9.0E-08	1.84E-24	1.23E-08	12.26	472.4
Polycarbonate	1.0E-08	2.0E-08	5.94E-26	3.90E-09	3.90	47.8
Polycarbonate	1.0E-07	2.0E-08	5.94E-25	8.41E-09	8.41	222.0
Polycarbonate	1.0E-08	9.0E-08	2.67E-25	6.44E-09	6.44	130.4
Polycarbonate	1.0E-07	9.0E-08	2.67E-24	1.39E-08	13.88	605.2

Table 5: Calculations for contact area between Polystyrene and Polycarbonate and a silicon nitride AFM contact mode probe with a radius of curvature from 20 nm to 90 nm and sample/probe interaction force between 10 and 100 nN.

VIII. Figures

Figure 1: Interaction between AFM probes and sample surface for a typical contact mode topographic image.

Figure 2: Fourier Transform Infrared Spectroscopy setup for transmission experiment.

The signal reaching the detector undergoes a fast Fourier transform to generate an infrared spectrum of the sample being analyzed.

Figure 3: AFM/FTIR setup. Infrared radiation is focused on the sample near the point at which the AFM probe is engaged (parked, not scanning) on the sample surface. The sample becomes the detector and as it absorbs infrared radiation it thermally expands and thermal waves propagate to the surface causing it to oscillate. The cantilever will deflect with these oscillations and this deflection signal is Fourier transformed into infrared spectra of the sample. Alternatively if a thermal probe is used temperature fluctuations can be measured as a result of IR absorption and this signal can be Fourier transformed into infrared spectra of the sample.

Figure 4: Top Illumination focusing method for AFM-FTIR spectroscopy.

Figure 5: Side Illumination focusing method for AFM-FTIR spectroscopy. Distance from the front edge can be changed and measured.

Figure 6: Bottom illumination focusing method for AFM-FTIR spectroscopy, where thin polymer film is required for spectroscopic purposes.

Figure 7: Top illumination method with chopper and filter in line before sample as used for the thermal expansion saw tooth wave experiments. Polymer filter is same material as the polymer sample and is in place only when indicated in the experimental section.

(A)

(B)

(C)

Figure 8: AFM deflection signal when engaged with polystyrene sample exposed to infrared radiation via top illumination, chopped at a radial frequency of approximately 6 Hz (A) with no filter, (B) with a 76.2 μm polystyrene filter placed in line with the radiation, before the sample, and (C) with a thicker (~ 1.02 mm) polystyrene filter placed in line with the radiation, before the sample.

(A)

(B)

Figure 9: AFM deflection signal when engaged with polystyrene sample exposed to infrared radiation via top illumination, chopped at a radial frequency of approximately 12 Hz (A) with no filter and (B) with a 76.2 μm polystyrene filter placed in line with the radiation, before the sample.

(A)

(B)

Figure 10: AFM deflection signal when engaged with polystyrene sample exposed to infrared radiation via top illumination, chopped at a radial frequency of approximately 24 Hz (A) with no filter and (B) with a 76.2 μm polystyrene filter placed in line with the radiation, before the sample.

Figure 11: AFM deflection signal when engaged with polystyrene sample exposed to infrared radiation via top illumination, chopped at a radial frequency of approximately 48 Hz with no filter in place, before the sample.

Figure 12: AFM deflection signal when engaged with polystyrene sample exposed to infrared radiation via top illumination, chopped at a radial frequency of approximately 62 Hz with no filter in place, before the sample.

Figure 13: Reduction in peak to peak deflection as a function of chopping frequency measured by AFM for thermal expansion of polystyrene exposed to chopped infrared radiation.

Figure 14: AFM deflection signal engaged with polystyrene sample exposed to infrared radiation via top illumination with infrared red spectrometer operating in step scan mode. Deflection signal shows characteristic center burst as seen in a typical interferogram.

(A)

(B)

Figure 15: (A) infrared spectrum of a polystyrene plate sample obtained by AFM-FTIR via side illumination method and step scan amplitude modulation at a resolution of 16 cm^{-1} resolution with a settling time of 1 ms, settling factor of 1 and average time per step of 100 ms. (B) Interferogram from AFM/FTIR spectrum in (A).

(A)

(B)

Figure 16: (A) Transmission FTIR spectrum of a 38 μm thick polystyrene film, 32 scans, 4 cm^{-1} resolution (B) Interferogram from transmission FTIR spectrum in (A)

(A)

(B)

Figure 17: (A) AFM-FTIR spectrum of a polystyrene plate sample obtained by side illumination method using an aluminum 6" focal length off axis elliptical converging mirror to focus the radiation and step scan amplitude modulation at a resolution of 32 cm^{-1} , with a settling time of 1 ms, settling factor of 10 and average time per step of 100 ms. (B) Interferogram from AFM-FTIR spectrum in (A)

Figure 18: AFM-FTIR spectra from depth profiling experiment using side illumination method and polystyrene plate sample. Peaks appear to go negative as distance is increased, but actually the radiation at the absorbing wavenumbers have all been absorbed and so it only appears to be negative, the values are still positive, just less positive than the weak absorption vibrations that were still reaching the point of contact with the probe. Red lines indicate how peaks invert.

(A)

(B)

Figure 19: (A) AFM-FTIR continuous scan spectrum of a solution cast polycarbonate film on KBr pellet using bottom illumination method, an average of 8192 scans at 8 cm^{-1} resolution and interferometer mirror velocity of 0.1581 cm/s . (B) Interferogram of AFM-FTIR continuous scan spectrum from (A).

Figure 20: FTIR transmission spectrum of solution cast polycarbonate film on KBr pellet.

Same sample as used in the AFM-FTIR experiment, an average of 64 scans at 4 cm⁻¹ resolution and interferometer mirror velocity of 0.6329 cm/s.

(A)

(B)

Figure 21: (A) AFM-FTIR continuous scan spectrum of a solution cast and subsequently cured DGEBA/DDA epoxy adhesive system on KBr pellet using bottom illumination method, an average of 8192 scans at 8 cm^{-1} resolution and interferometer mirror velocity of 0.1581 cm/s . (B) Interferogram of AFM-FTIR continuous scan spectrum from (A).

Figure 22: FTIR transmission spectrum of solution cast and subsequently cured DGEBA/DDA epoxy adhesive film on KBr pellet. Same sample as used in the AFM-FTIR experiment, an average of 64 scans at 4 cm⁻¹ resolution and interferometer mirror velocity of 0.6329 cm/s.

Figure 23: (A) AFM-FTIR continuous scan spectrum of a 38 μm thick polystyrene film transmission standard from Nicolet, stretched over a KBr pellet using bottom illumination method, an average of 4116 scans at 8 cm^{-1} resolution and interferometer mirror velocity of 0.1581 cm/s .

Figure 24: AFM contact mode image of polystyrene micro spheres, 1.97 μm in diameter, pressed into a KBr pellet.

Figure 25: AFM-FTIR continuous scan spectrum of 2.0 μm diameter polystyrene spheres pressed into KBr pellet using bottom illumination, an average of 1692 scans at 8 cm^{-1} resolution and interferometer mirror velocity of 0.0475 cm/s .

Figure 26: AFM contact mode image of 1.97 μm diameter polystyrene micro spheres pressed into a stretched paraffin film layer on a KBr pellet.

Figure 27: AFM-FTIR continuous scan spectrum of 2.0 μm diameter polystyrene spheres pressed into paraffin wax layer on KBr pellet using bottom illumination method, an average of 1320 scans at 8 cm^{-1} resolution and interferometer mirror velocity of 0.0475 cm/s

Figure 28: FTIR transmission spectrum of a stretched paraffin wax sample on KBr pellet, an average of 64 scans at 8 cm⁻¹ resolution and interferometer mirror velocity of 0.6329 cm/s

(A)

(B)

Figure 29: (A) Thermal AFM-FTIR step scan spectrum of 38 μm thick polystyrene film pressed over KBr pellet using bottom illumination method with a resolution of 32 cm^{-1} . (B) Interferogram from the thermal AFM-FTIR step scan spectrum in (A)