Examination of Glass/Epoxy Interfaces in Printed Circuit Boards

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Abstract

Most manufacturers of electronics grade glass fiber reinforcement used in today's laminates apply treatments to enhance the bonding strength between the inorganic e-glass and the epoxy matrix which surrounds it in the laminate structure. These treatments, when properly formulated and applied on the glass fibers help to prevent glass-resin delamination due to mechanical stresses or due to thermal excursions during the laminate lifecycle. The thermal excursions can include multiple reflow cycles followed by wave soldering and in some common circumstances a cycle or two of rework. However, such laminates continue to develop glass-resin delamination that promotes a form of electro-chemical migration that leads to a loss of electrical insulation resistance between opposing biased conductors. This phenomenon is commonly known as conductive anodic filament (CAF). The glass-resin delamination can also contribute to a reduction in the mechanical flexural strength, which is not the focus of the present paper. The probability of CAF failure is a function of temperature, moisture content, the voltage bias, manufacturing quality and processes, materials and other environmental conditions and physical factors.

The present paper discusses the glass treatments and examines the effects of thermal and combined thermal/moisture exposure on the glass-resin interface. Atomic force microscopy is used for examination of sites to track the state of degradation and changes in the mechanical properties. Micro-Fourier transform infrared spectroscopy is used to track the progression and diffusion of the inter-penetrating network formed as a result of inter-diffusion between the glass-treatments and epoxy laminate material. The results of the studies are expected to show the progression of damage and provide unique quality assurance and failure analysis insights into this less reported contributor to printed circuit board quality.

Introduction

Printed circuit boards (PCBs) are the base for electronic packaging upon which electronic components are formed into electronic systems. PCBs are used in a variety of electronic circuits from simple one-transistor amplifiers to large super computers. A PCB serves three main functions: 1) it provides the necessary mechanical support for the components in the circuit 2) it provides the necessary electrical interconnections, and 3) it bears some form of legend which identifies the components it carries.

Printed circuit boards can be classified into three categories based on their construction and physical characteristics, namely rigid, flexible and rigid-flex boards. Rigid circuit boards are basically a composite layered structure in which solid copper sheets are laid down and separated with a dielectric material, which is commonly an epoxy resin system. Rigid boards represent the most widely used category and they can be built from different materials systems. Flexible printed circuits consist of thin copper foil bonded to a thin plastic base. The base material most frequently used is polyester film. This type of board is usually limited to a single- or double-sided board and only for very small components. The third category is the rigid-flexible boards which is a combination of rigid and flexible boards bonded together. The rigid portion supports the components while the flex portion allows the structure to be folded. Attention will be given to the rigid printed circuit boards since they represent the highest volume and it is within this category that the major challenges in terms of fabrication, materials, and applications are encountered [1].

Rigid printed circuit boards can be further categorized in terms of circuit complexity and base materials. Circuit density can force the design to be single-sided, double-sided, or multi-layer. A single sided board has circuit layout on one side only, while the double-sided board has artwork on both sides. On double sided boards, connections between the two layers are made with small conductive holes called "vias". A multilayer board has artwork on one or more internal layers in addition to the top and bottom.

A short circuit will occur whenever a low resistance path is formed between conductors in the presence of a voltage potential. This can sometimes result in catastrophic damage to the PCB or the whole system with fire or explosion in the worst case. This type of defect is also known to cause intermittent failures in electronic devices, which can be tedious to troubleshoot. A short circuit can be the start of a propagating fault that will burn or melt the PCB material leaving no evidence of the root cause.

As can be observed from **Error! Reference source not found.** there are multiple causes which contribute to short circuit failures. There are also a whole range of failure mechanisms that are activated by different factors occurring throughout the life cycle environment of the product. A short circuit is the observed effect or failure mode, but there are multiple possible

causes for this to happen and a variety of associated failure mechanisms. **Figure 1** provides a cause and effect diagram for the short circuit problem.

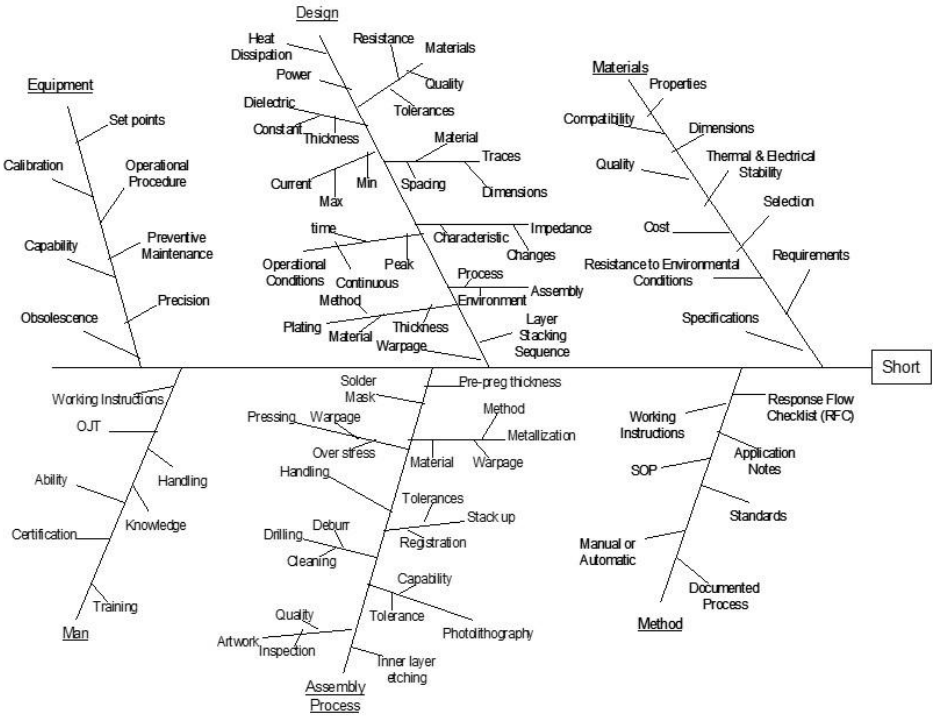

Figure 1 Cause and Effect Diagram for Short Circuit on a PCB.

Shorts due to Conductive Anodic Filament (CAF)

Multilayer organic laminates, which compose over 90% of the interconnecting substrates in electronics, with FR-4 representing 85% of the substrates used for laminates, can develop a loss of electrical insulation resistance between two biased conductors due to conductive anodic filament formation (CAF) [2][3][4][5]. CAF formation is a failure mechanism that occurs within glass-reinforced epoxy PCB laminates due to an electrochemical process involving the ionic transport of metallic ions through or across a non-metallic medium under the influence of an applied electric field [1][2][3][6] The growth of the metallic filament, a copper-chloride containing compound which starts from the anode, is a function of temperature, humidity, voltage, laminate materials, manufacturing processes, and the geometry and spacing of the conductors [1]. The growth of these filaments can result in either leakage currents, which reduce performance, or catastrophic shorts, which cause complete failure.

The filament formation typically takes place in two steps: a degradation of the resin/glass interface followed by an electrochemical reaction. Bond degradation provides a path along which electrodeposition may occur due to electrochemical reaction. The path may result from poor glass treatment, hydrolysis of the silane glass finish, and mechanical stresses. Once the path is formed, an aqueous medium will develop through the adsorption, absorption, and capillary action of water. The presence of hollow glass fibers inside the laminate can make the CAF a one-step process, effectively removing the first step, namely the need for path formation [7][8][9][10][11]. The path in the PWB may be viewed as an electrochemical cell in which the metal conductors are the electrodes, the driving potential for the electrochemistry is the operating potential of the circuit, and the electrolyte is the absorbed moisture. In other words, CAF is a process by which a metal, in contact with insulating materials and under an electric potential, is removed ionically from its initial location and is redeposited at some other location. The result can be intermittent or permanent leakage currents or short circuit failures.

Modes of Path Formation in Printed Wiring Boards

Prior to or simultaneously with the formation of the filament, a pathway connecting the oppositely biased conductors must be formed. Three of the common pathways (PTH/PTH, PTH/plane and plane/plane) in addition to vertical filament formation are observed. In the case of vertical filament formation, the PCBs experience a drop in insulation resistance by shorted internal planes, which was verified after physical identification of a hydrolyzed silica particle at a failure site [7]. Other path configurations include formation between PTHs and power/ground planes, between internal traces, between an internal trace and a PTH, and between internal and surface traces. It is hypothesized that path formation, proposed to be voltage-independent, is the rate-limiting step in CAF. In other words, it takes a much longer time for the pathway to form than for the

metal migration and formation of the conductive filament to bridge and short the two conductors. The rate-limiting step of CAF induced failure is the creation of the path. Hollow fibers, discussed previously [6], can also contribute to CAF by creating an open path between biased conductors.

Chemical Degradation

One manner in which the pathway between conductors is formed in PCBs is chemical hydrolysis of the silane glass finish or coupling agent. Past work has shown that the glass epoxy interface absorbs 5 to 7 times more moisture than the bulk epoxy [12]**Error! Reference source not found.**. A common cross-linking agent used in FR-4 and many other epoxy-based laminated systems is dicyandiamide (DICY). DICY and glass surfaces are both hydrophilic. This combination of a hydrophilic surface and a hydrophilic cross-linking agent is one of the factors responsible for degradation of the glass fiber/epoxy resin interface due to hydrolysis. Williams [13] **Error! Reference source not found.** has shown that PCBs manufactured with non-DICY cross-linked epoxy resins are more resistant to CAF failures than PCBs manufactured with DICY cross-linked epoxy resins.

Organosilanes are bifunctional molecules that act as adhesion promoters, cross-link agents, and moisture scavengers in adhesive and sealant products [14]**Error! Reference source not found.**. Silane adhesion promoters act as molecular bridges between two chemically different materials and have been shown to dramatically improve the adhesion of polymeric resins to substrates such as glass, silica, alumina, or active metals [15] **Error! Reference source not found.**.

Figure 2 illustrates a typical alkoxysilane coupling agent and its hydrolysis reaction. Typically, the silane is functional at both ends. R is an active chemical group, such as amino (NH_2), mercapto (SH), or isocyanato (NCO). This functionality reacts with functional groups in an industrial resin or biomolecule such as DNA fragments. The other end consists of a halo (most often chloro) or alkoxy (most often methoxy or ethoxy) silane. This functionality is converted to active groups on hydrolysis called silanols. The silanols can further react with themselves, generating oligomeric variations. All silanol variations can react with active surfaces that contain hydroxyl (OH) groups. A pathway between conductors may also be formed by chemical hydrolysis of the silane glass finish or coupling agent. Research has demonstrated that this type of chemical degradation might be reversible [16][17] **Error! Reference source not found.Error! Reference source not found.**.

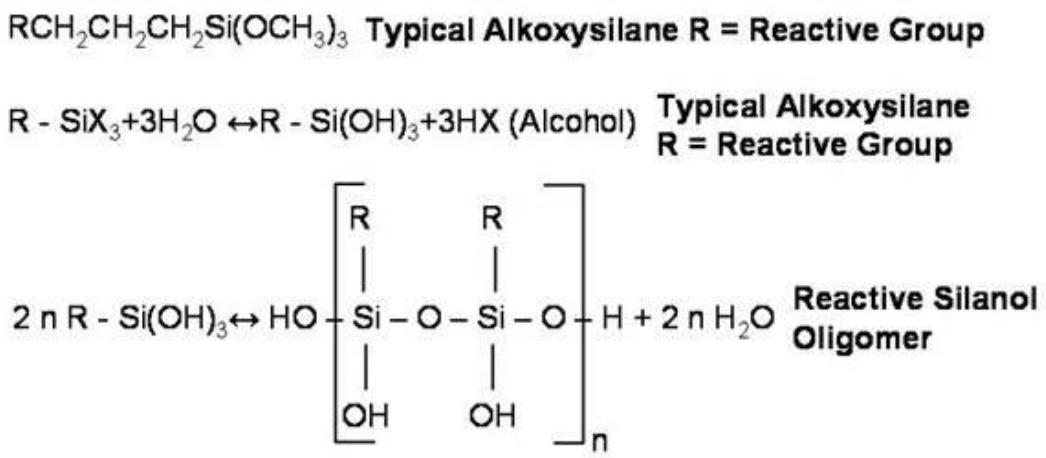

Figure 2 Alkoxysilane coupling agent and its hydrolysis reaction.

The three main classes of silanes are chloro-, methoxy-, and ethoxysilanes. Chlorosilanes are the most reactive, but evolve into corrosive hydrogen chloride on hydrolysis; methoxysilanes are of intermediate reactivity; ethoxy-silanes are the least reactive and evolve into non toxic ethanol [18]**Error! Reference source not found.**. The difference in reactivity between methoxy- and ethoxysilanes is small; at typical hydrolysis pH (acidic ~5, basic ~–9), both versions hydrolyze in under 15 minutes at 2% silane concentrations.

The bifunctional silane molecules act as a link between the glass fiber and resin by forming a chemical bond with the glass surface through a siloxane bridge, and the organofunctional group bonds to the polymeric resin [19] **Error! Reference source not found.**. This allows silanes to function as surface-treating or "coupling" agents. The formation of an interpenetrating network (IPN) through interdiffusion is the next step in the process. Figure 3 Figure 2 shows a schematic for interdiffusion and creation of an IPN in a silane-treated glass fiber [15]**Error! Reference source not found.**. Interdiffusion and intermixing take place in the coupling agent/polymer resin interface region due to penetration of resin into the chemisorbed silane layer and migration of the physisorbed silane molecules into the resin phase. The migration and intermixing of silane and other sizing ingredients with polymer resin create an interface of substantial thickness.

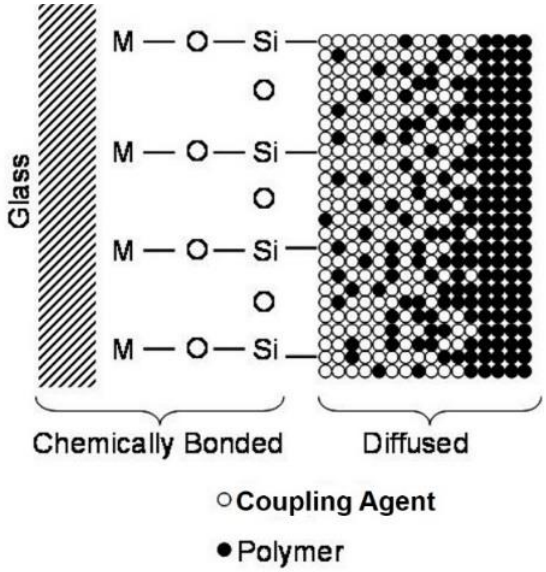

Figure 3 Schematic for conventional interdiffusion and IPN Error! Reference source not found.Error! Reference source not found..

A single layer of silane may be sufficient to bond with the glass surface; however, to ensure uniform coverage, more than one layer of silane is usually applied by the glass manufacturers. This results in a tight siloxane polymeric network close to the inorganic surface that diffuses into subsequent overlays. The siloxane remains in high concentration at the glass/epoxy interface and may be dissolved into the matrix during curing of the matrix resin, as shown in Figure 4. Coupling to the organic matrix is a complex phenomenon. The reactivity of a thermoset polymer is matched to its reactivity with the silane. For example, an epoxysilane or aminosilane will bond to an epoxy resin; an aminosilane will bond to a phenolic resin; and a methacrylate silane will bond through styrene cross-linking to an unsaturated polyester resin. The large differences in composition and chemical characteristics of the individual components, such as antistats on the glass, lubricants, surfactants, and film formers, further complicate the formation of this interface with different formulations. While the silane chemistry and its interactions with the glass surface and the polymer have been extensively studied, relatively little information is available about the influence of these sizing components on the formation of the interface. The interface is the region where stress transfer occurs between the two composite constituents, but its material properties and effective thickness are unknown. The extremely thin layers of the interface are difficult to probe and present a challenge to investigation of the mechanical properties.

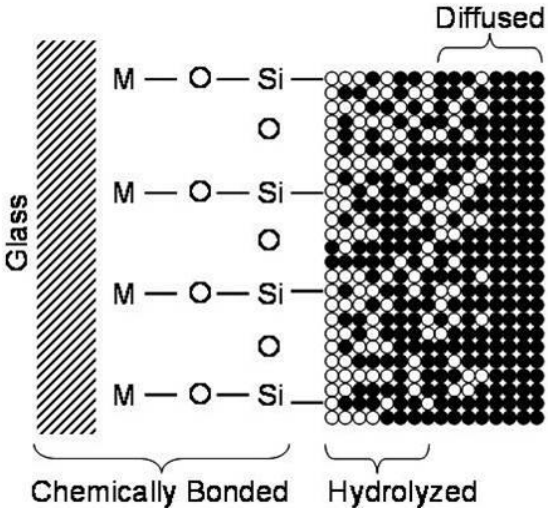

Figure 4 Schematic for hydrolyzed diffused interface after aging in water in a silane-treated glass fiber [15][16] Error! Reference source not found.Error! Reference source not found..

The silicon atoms in the silanes are bonded to the silicon atoms in the glass through oxygen atoms, and the silicon atoms in the glass are bonded to each other. If the water produced in the forward reaction is continuously removed (e.g., by evaporation), then the bonding of silane to glass will continue until either there is no more silane or no more attachment sites

on the glass surface. Conversely, if water is added to the silane bonded to glass, the reverse reaction can debond the silane from the glass. The rate of hydrolysis is influenced by the pH.

Instrumented indentation testing is an appropriate method to characterize the degradation in the glass/resin interface. It is a technique for measuring the mechanical properties of materials and was developed from traditional hardness tests such as Brinell, Rockwell, Vickers, and Knoop. Instrumented indentation testing is similar to traditional hardness testing in that a hard indenter, usually a diamond, is pressed into contact with the test material. However, traditional hardness testing yields only one measure of deformation at one applied force, whereas during an instrumented indentation test, force and penetration are measured for the entire time that the indenter is in contact with the material. Nearly all of the advantages of instrumented indentation derive from this continuous measurement of force. Instrumented indentation is particularly well suited for testing small volumes of material such as thin films, particles, or other small features. Even for larger volumes of material that could be tested in a tensile configuration, instrumented indentation is often preferred for its speed and simplicity; sample preparation is relatively easy, and many tests can be performed on a single sample.

Experimental Method

In order to assess the quality of glass to resin adhesion of commercially available printed circuit boards, experiments were performed. Samples consisted of two different laminate materials, a pre-preg with two glass bundles of 2116 glass type and a core with also two glass bundles with a glass type 3113. The second core sample was thermally degraded at 530 ºC to remove all epoxy material and also the coupling agent. Figure 5 shows the bare glass bundle from top view, this sample was mounted using epoxy after the epoxy was removed, and then the sample was cross sectioned and polished. Cross section view was used for observation using optical microscopy, FTIR microscopy, and atomic force microscopy. The thermally degraded sample was designated uncoated and the prepreg samples are designated as “coated”. This nomenclature was selected to ease in distinction between samples. Samples were baked in an oven until the weight loss due to the egress of moisture had stabilized. These samples are labeled as dried, and then samples were exposed to 85 ºC and 85% RH. These samples are labeled as humidified.

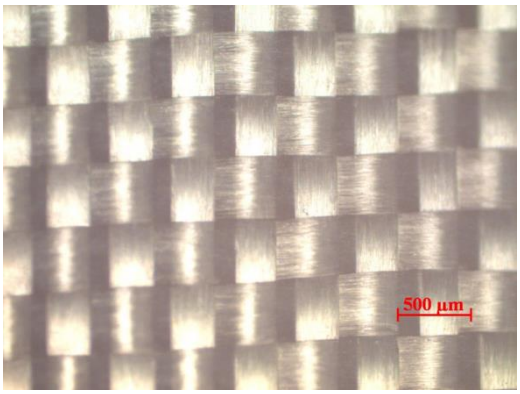

Figure 5 Laminate material thermally etched at 530 °C. Only glass bundle remained. The epoxy and the coupling agent were removed

Fourier Transform Infra-Red (FTIR) spectroscopy Analysis

In order to analyze the chemical changes after high temperature/high humidity test a FTIR spectrometer and a FTIR microscope with a 32 by 32 focal plane array (FPA) detector were used to acquire the FTIR spectra, and also to map images that contain 1064 microspectra Each scan area represents 70 by 70 microns. Images were generated using a 15X Optical/IR objective lens. FTIR microscopy was selected as a tool for this analysis because it can acquire accurately FTIR spectra from small samples, providing spatial and spectral information. Images were analyzed, and the identification of the functional groups was made, Si-O bonds were identified in the coated and uncoated samples due to the presence of silicon atoms in the glass fiber samples. Vibrations between atoms in Si-O molecules excited by infrared radiation could be either absorb or transmit. Figure 6 a) is an optical image of the cross section of a dried coated sample, it can be noticed the glass bundle and the epoxy. Figure 6 b) is the IR mapping image, lighter colors are related to the Si-O molecules. The IR spectrum showed in Figure 4 corresponds to the signal acquired from the glass bundle, and the Si-OH and OH functional groups were detected.

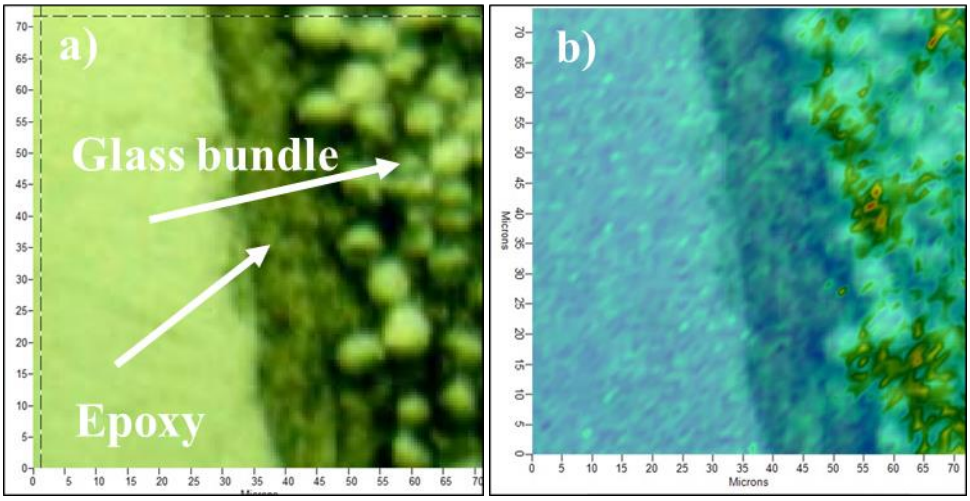

Figure 6 a) Optical image and b) IR image of cross section view of non-coated siloxane sample.

The organic functional group detected by the FTIR in the dried uncoated sample was the Si-O, which was found at 1038 cm^{-1}, shown in Figure 7. In Figure 8, after the sample was exposed to humidity test, the hydroxyl group around 3200 cm^{-1} is present. There is an evidence of water absorption and also it can be noticed that there are new peaks associated to Si-OH functional groups.

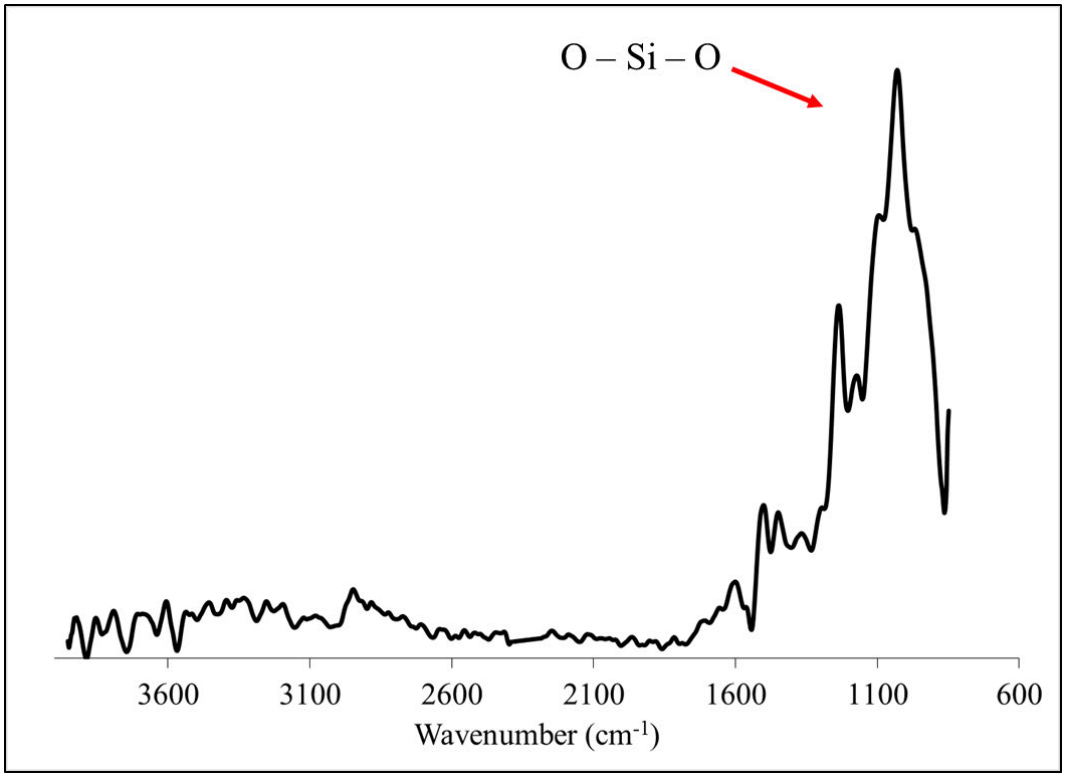

Figure 7 IR spectrum of dried uncoated sample. Evidencing the presence of Si-O bonds from the glass fiber.

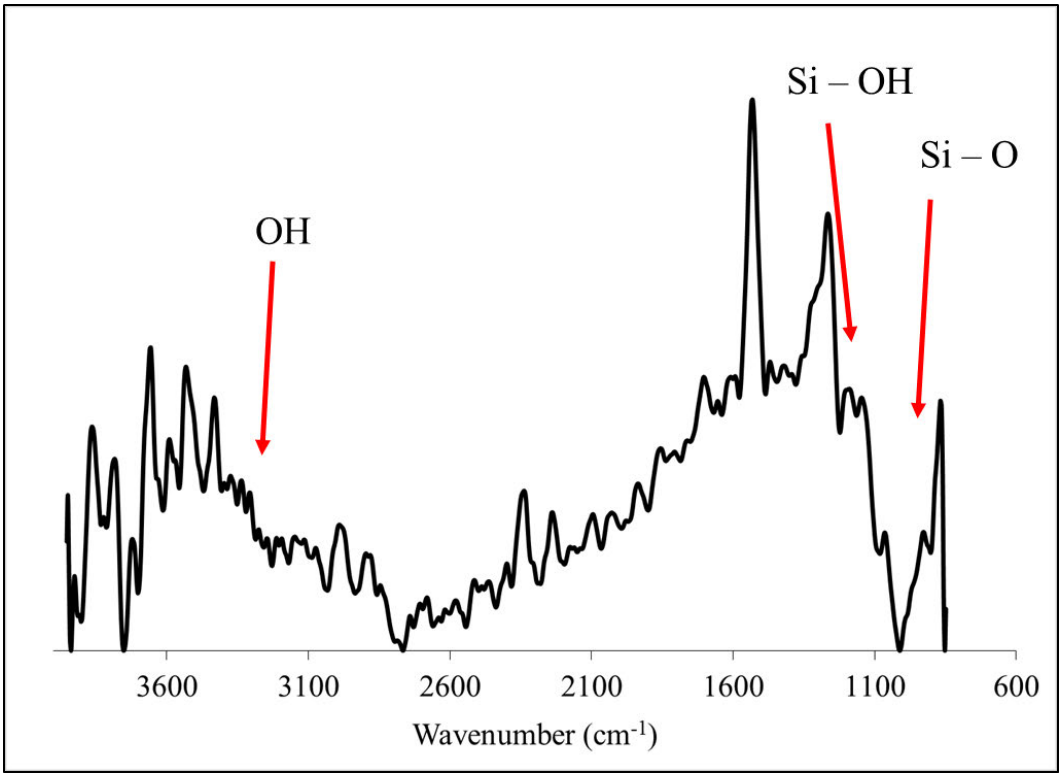

Figure 8 IR spectrum of uncoated sample after humidity test.

AFM Analysis

Since epoxy materials that are used in the fabrication of laminate materials in PCB are viscoelastic, the technique that was selected for this analysis was based on atomic force microscopy (AFM) static force spectroscopy (SFS), which is based on the interaction between the cantilever tip and the glass/epoxy interphase on dried and humidified samples. For this analysis the cantilever approaches the interphase at different velocities, the aim of this analysis is to obtain information about the viscoelastic behavior of interphase. In the analysis of AFM, Figure 9, Figure 10 and Figure 11, it was found that the slope of the above curves for humidified sample is higher. Higher slope refers to higher compliance / less stiff material. However, the dry sample is more viscoelastic and has higher dissipation behavior. The analysis was performed in contact mode, there was no vibration involved in the measurement, and the test was performed 100 times at the same location.

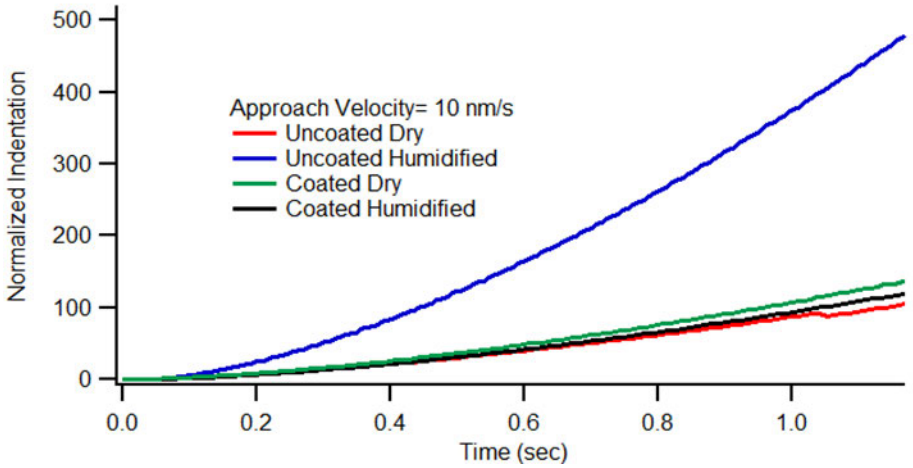

Figure 9 Comparison between the normalized indentation of dried and humidified samples at 10nm/s

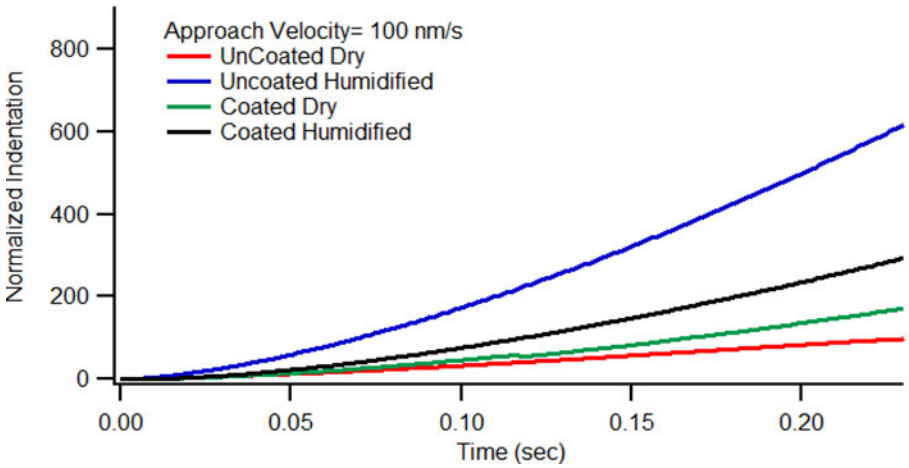

Figure 10 Comparison between the normalized indentation of dried and humidified samples at 100nm/s

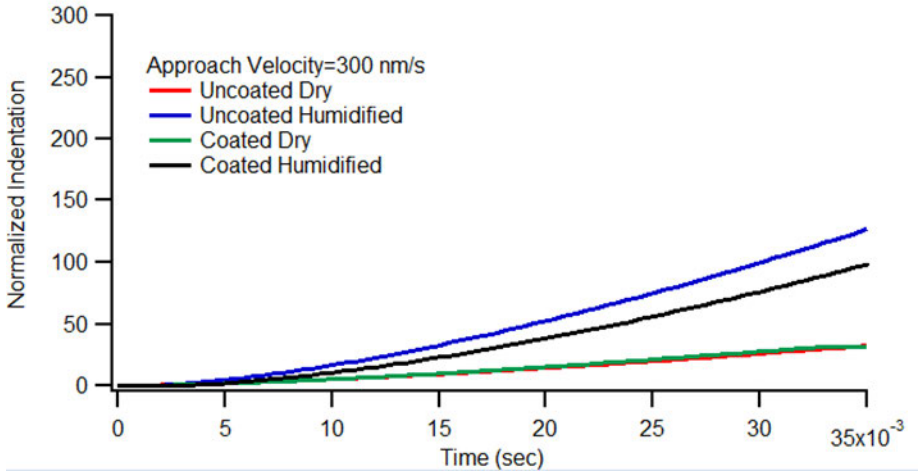

Figure 11 Comparison between the normalized indentation of dried and humidified samples at 300nm/s

There are many printed circuit board laminate manufacturing steps, each of which can install an unrepairable defect into the board. PCBs are an integrated item which cannot be disassembled for repair. Most PCB defects cannot be repaired, and PCBs are not made in production lots but are instead made in panels. For understanding CAF type of electrical shorts in printed circuit boards, the behavior of the glass-resin interface in "off-the-shelf" PCB materials is key. Analytical techniques such as AFM atomic force spectroscopy have the advantage of providing a rapid evaluation of the critical interfaces which can contribute to overall PCB reliability and quality. AFM atomic force spectroscopy experiments have the potential to target the changes to viscoelastic properties of the glass-resin interface in FR4 materials. Process variations can occur from panel-to-panel and across a single panel. With few exceptions (e.g. electrical test, external visual), groups of boards cannot be screened for defects, instead, destructive quality conformance inspection such as the ones described here can be performed on a representative sample of each manufacturing lot.

Conclusions

Microscopic examination of failure sites in printed circuit boards have shown that conductive filaments can be formed along debonded or delaminated fiber glass and epoxy resin interfaces. The conductive filaments can bridge between conductors that leads to intermittent electrical behavior. The debonding between the glass and epoxy is largely attributed to the breaking of the organosilane bonds. The organosilane bonds can be chemically degraded by hydrolysis (adsorption of water at the fiber glass/epoxy resin interface) or by repeated thermal cycling, which induces stresses at the interface due to coefficient of thermal expansion mismatches.

To determine the feasibility of analysis and detection of silicon functional groups and moisture ingression in printed circuit boards, coupons were made of laminate materials, with and without siloxane coatings and exposed to 85ºC and 85%RH, it was possible to detect functional groups associated to silicon and moisture absorption using FT-IR. Regarding the mechanical behavior after temperature and moisture exposure, samples presented a more elastic response to an AFM cantilever tip approach. Original equipment manufacturers and researchers can use the methodology developed in this work as an

alternative to characterize and screen laminate materials. This paper showed a unique approach where laminate materials are chemically and mechanically analyzed at a microscopic level using an AFM atomic force spectroscopy technique.

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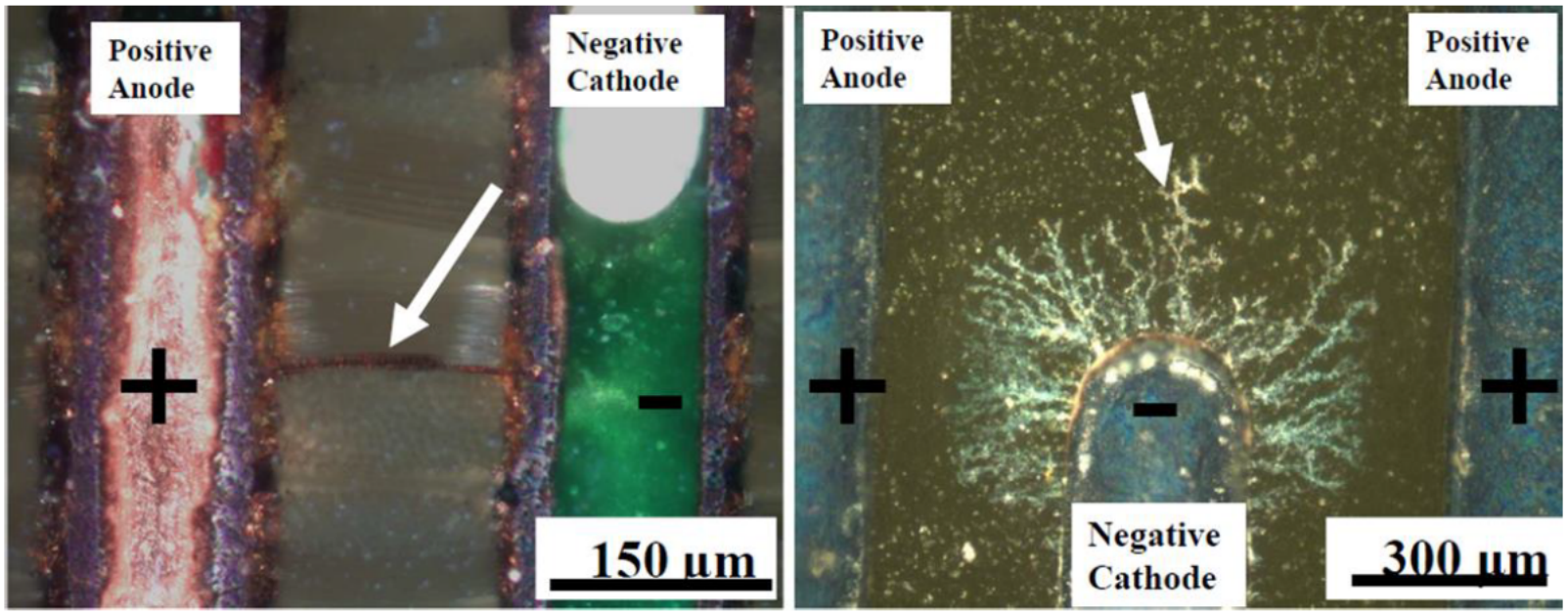
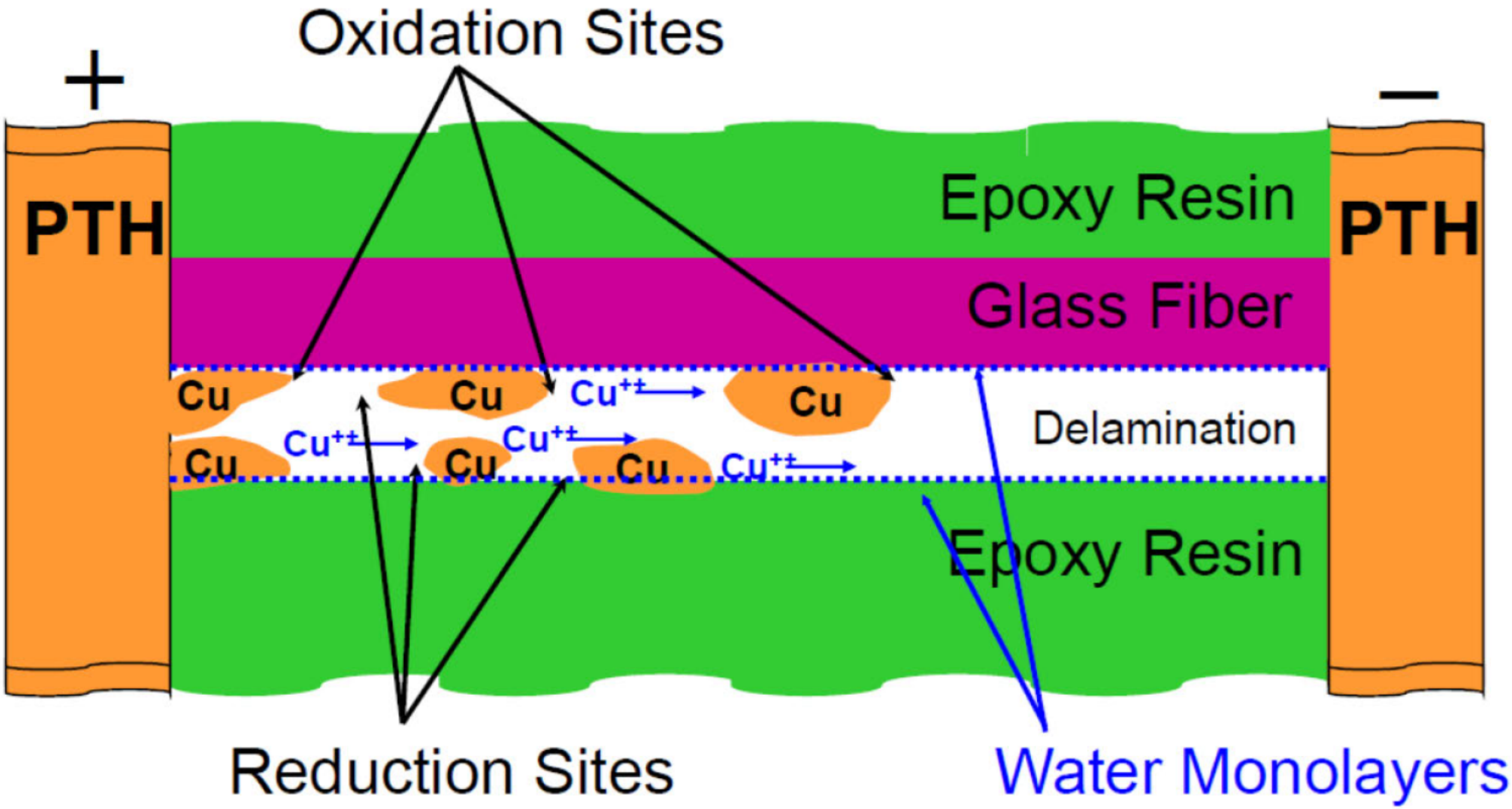
Comparison of PCB Surface and Sub-surface Leakage Mechanisms



ECM	Conductive Anodic Filament (CAF)	Dendritic Growth
Growth Direction	Anode to Cathode	Cathode to Anode
Filament Composition	Metallic salt	Pure metal
Growth Position	Internal	Surface

Formation of Conductive Filaments



Glass Fibers and Silane Coupling Agents

- Coupling agents act as adhesion promoters [1] [2] [3]
  - Silane based adhesion promoters act as molecular bridges between two chemically different materials.
  - Silane molecules act as a link between a silicon based filler and organic resin by forming a chemical bond with the surface through a siloxane bridge.
  - Examples: Organo silanes $Y-(CH_2)n-Si\ (OX)_3$

    (Y-organo functional group; OX- silicon functional group)

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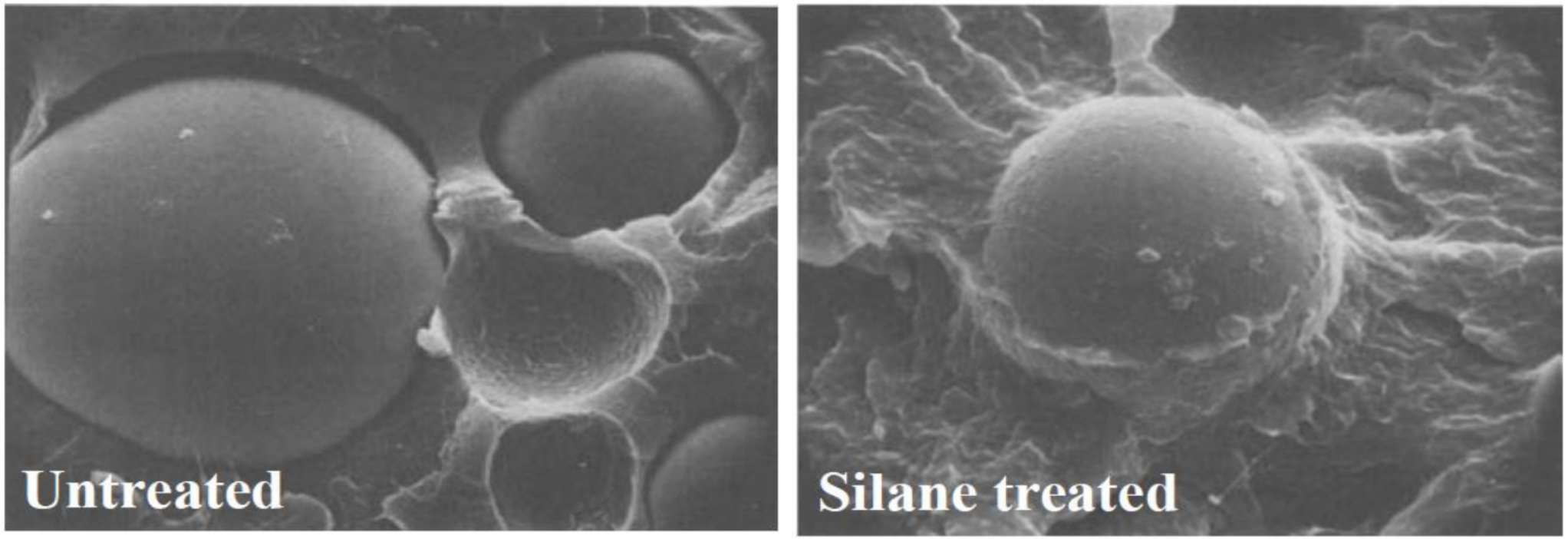
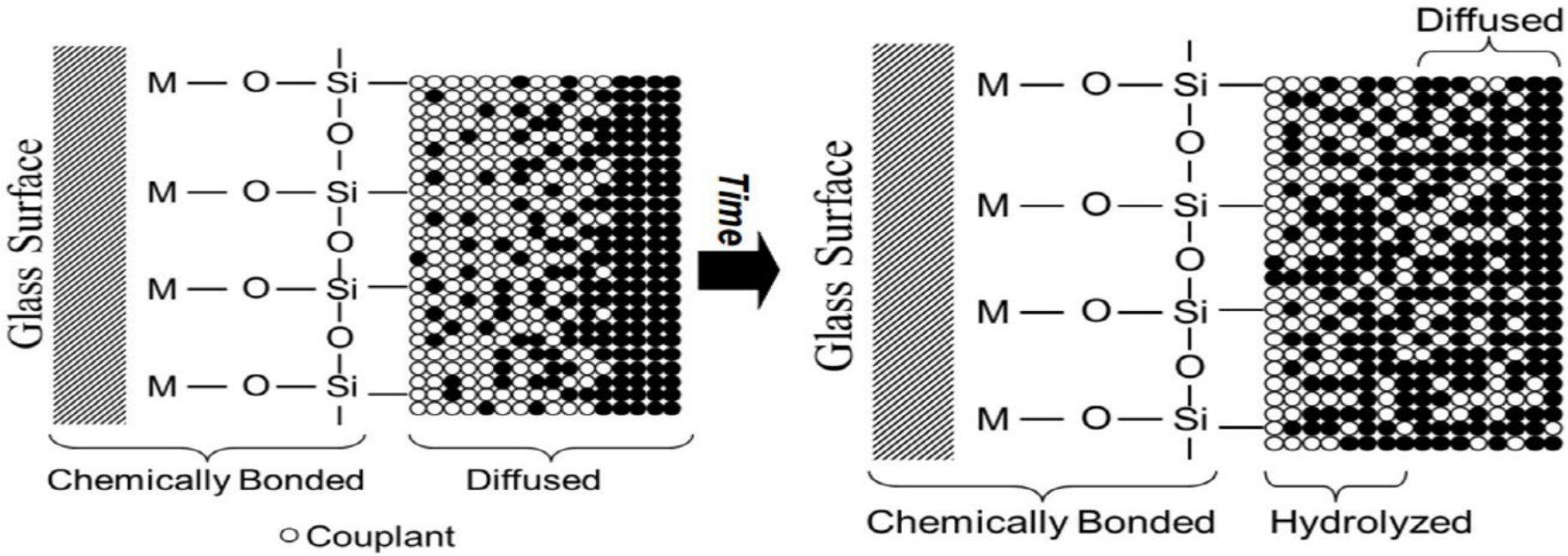
Effects of Coupling Agents



SEM images of glass filler/polyamide composite shows silane treated and untreated fillers.

[1]

Formation of Inter-penetrating Networks



1. Present status and research needs in silane coupling, H. Isheda (Ed.), Proc. ICCI—II, Polymer, Ceramic and Metal Matrix Composites, Elsevier Sci. Pub, New York (1988), pp. 17–33.
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Problem Statement

- Cost and schedule prohibitive 85/85 tests are performed in order to assess laminate systems
  - *Key step in a CAF failure is the fiber/resin delamination. Characterization of this delamination could reduce time and costs in assessing CAF risk.*
- What is the thickness and hardness of the fiber-epoxy interfacial region in FR-4 materials? How do changes in the interfacial region due to process temperature exposures affect bulk properties?
  - *What is the progression in the change of the mechanical properties of the interface after moisture absorption?*
  - *Does the cure state of the FR-4 epoxy influence the interfacial properties?*
- How does moisture influence the dielectric properties of silane treated glass fibers?
  - *Can changes in dielectric properties at the interface govern the bulk dielectric response?*

Coupon Preparation

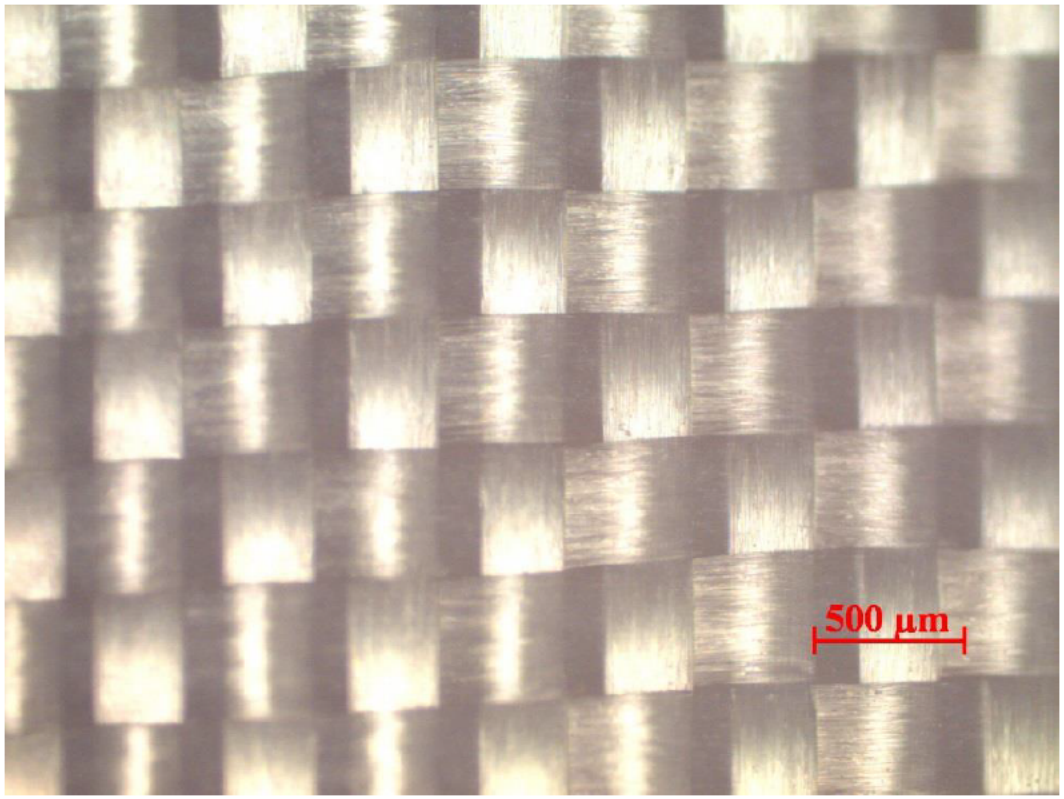
Laminate material coupons

Uncoated

- Laminate type: pre-preg.
- Glass type: 2116.

Coated

- Laminate type: Core
- Glass type: 3313.

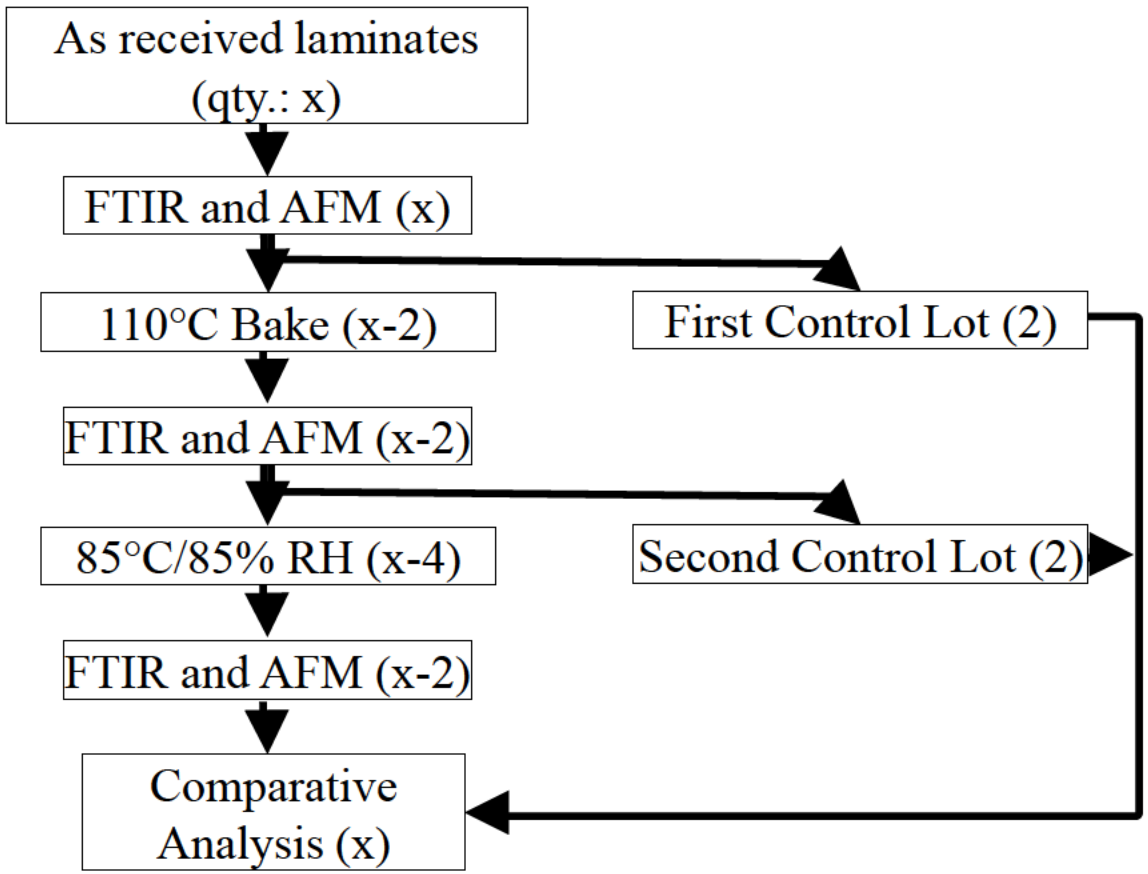


Laminate material thermally etched at 530 °C. Only glass bundle remained. The epoxy and the coupling agent were removed

Recommended Test Flow

Note 1: Test sequence can be duplicated for laminates that are sourced with different glass styles.

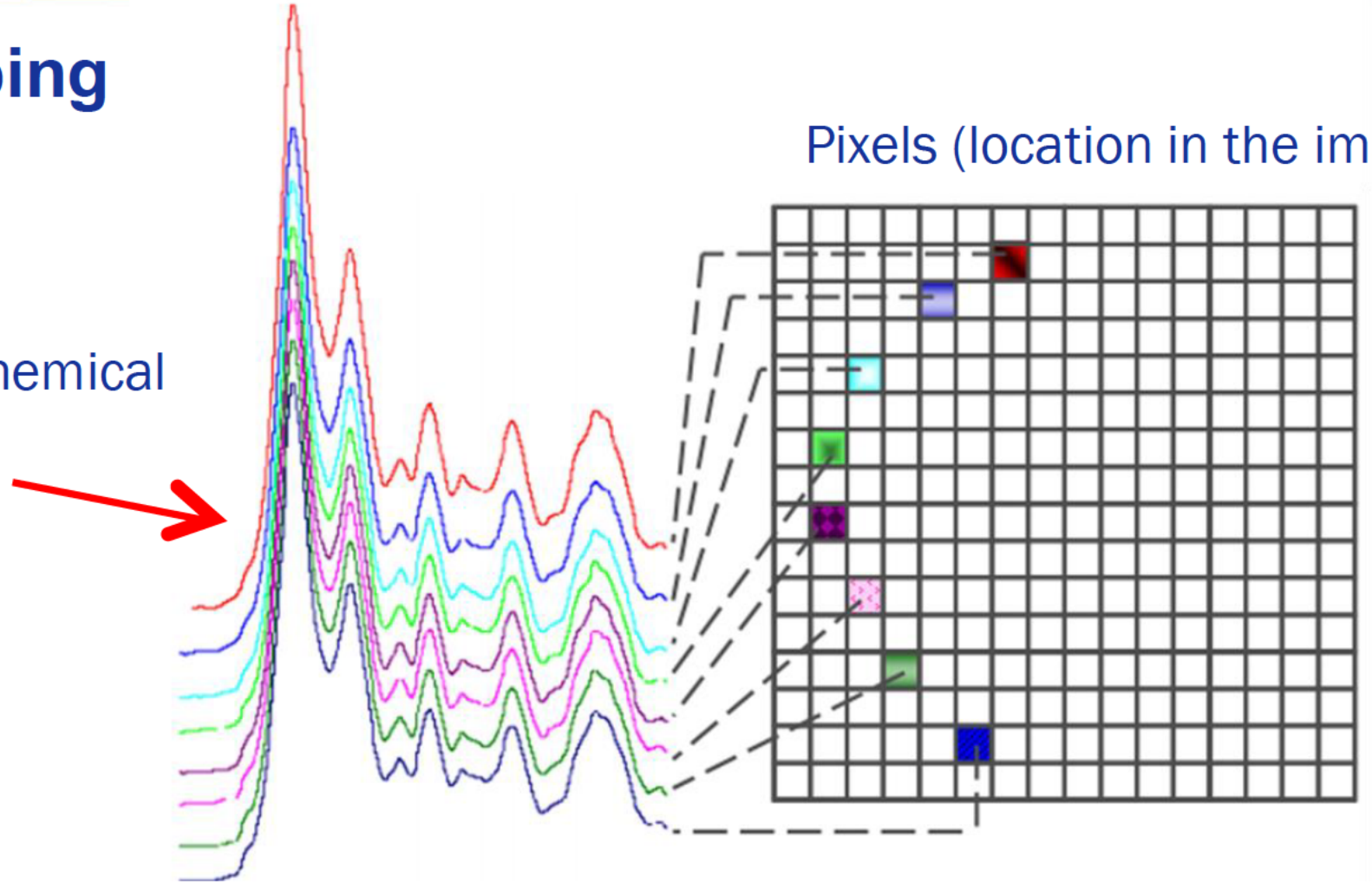
Note 2: Quantity x reflects samples of both types – containing siloxane treatment and the alternate treatment.



FTIR Mapping

Pixels (location in the image)

FTIR spectra (chemical information)



Each pixel in a FTIR mapping image corresponds to a specific location that contains chemical information

What is FTIR microscopy?

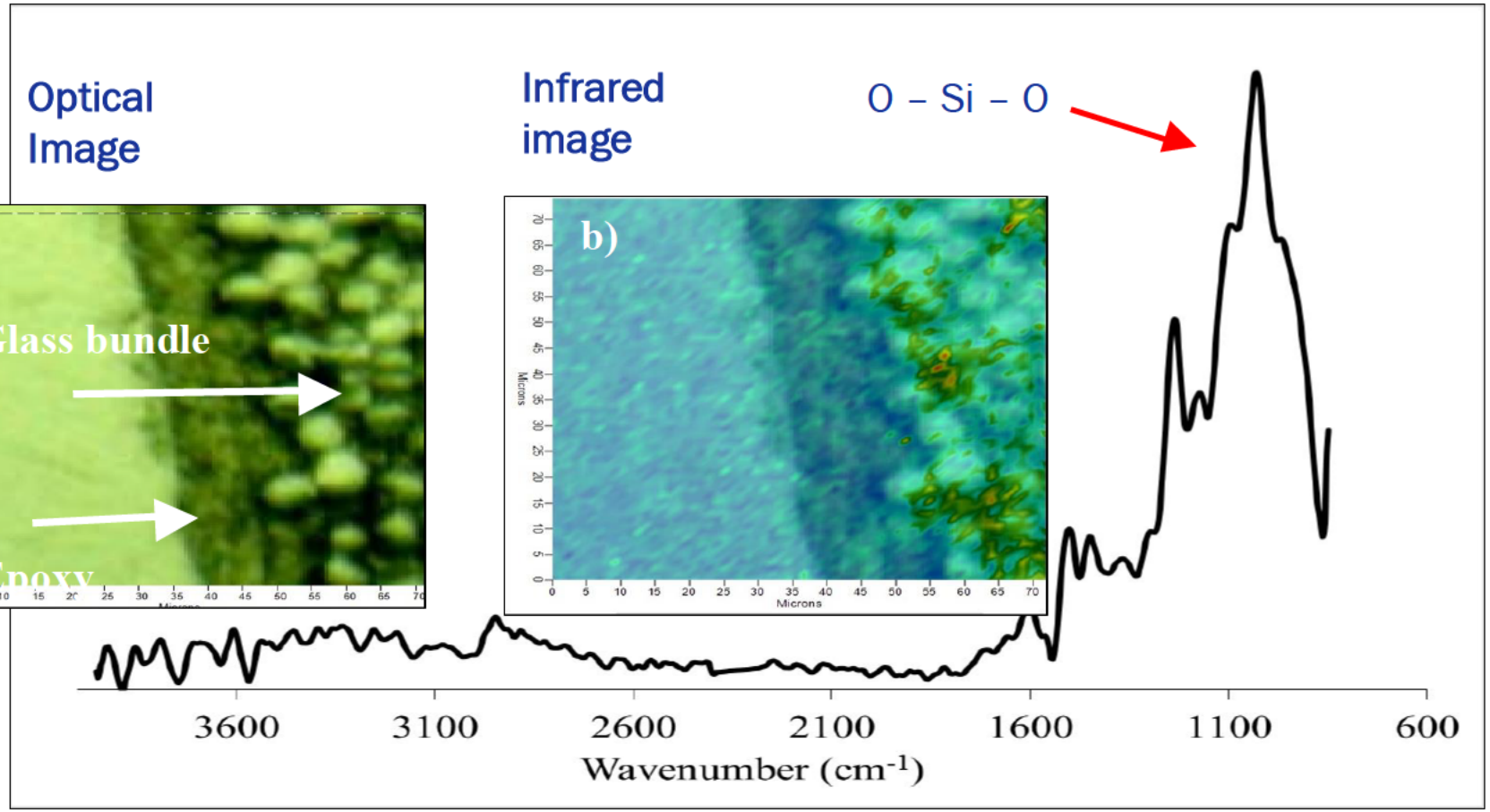
- FTIR Microscopy
  - *1. Visualize small (micron) sized samples*
  - *2. Collect accurate FTIR spectra from small samples*

- FTIR Imaging enables spatial and spectral information from an area of a sample.

Infrared Spectroscopy Analysis, Dried Sample

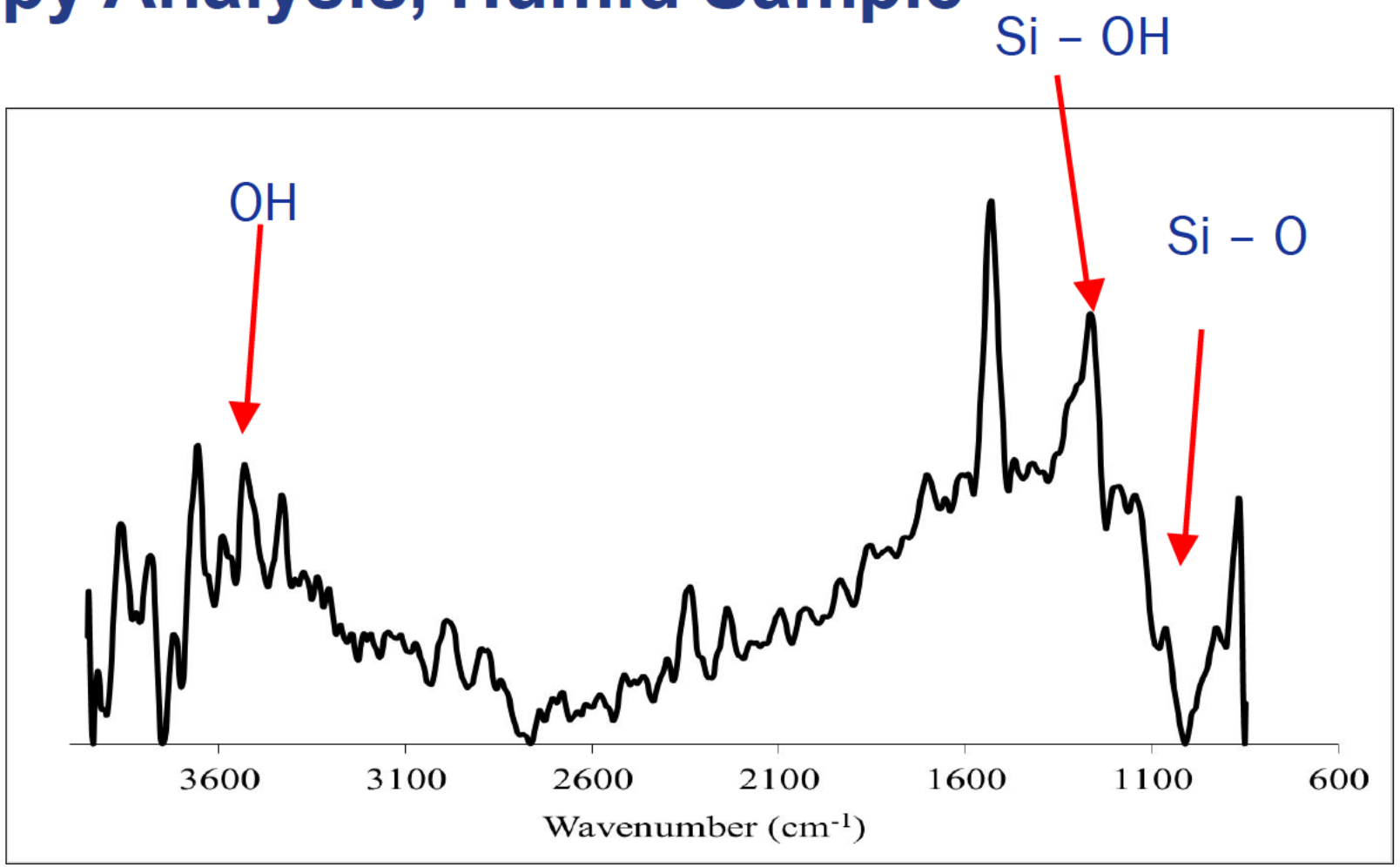
Optical image and infrared images shows a cross section of PCB coupon, where the interface between the glass bundle and epoxy was studied.

IR spectrum showed the peaks associated to Si and O bonds

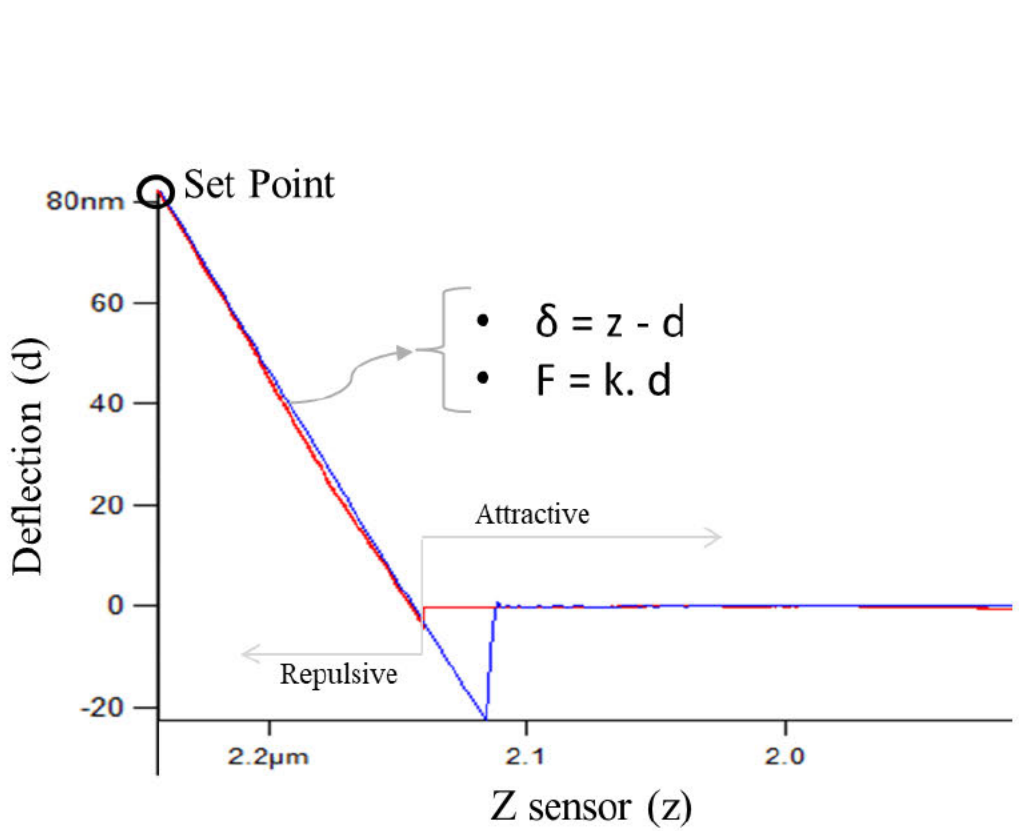


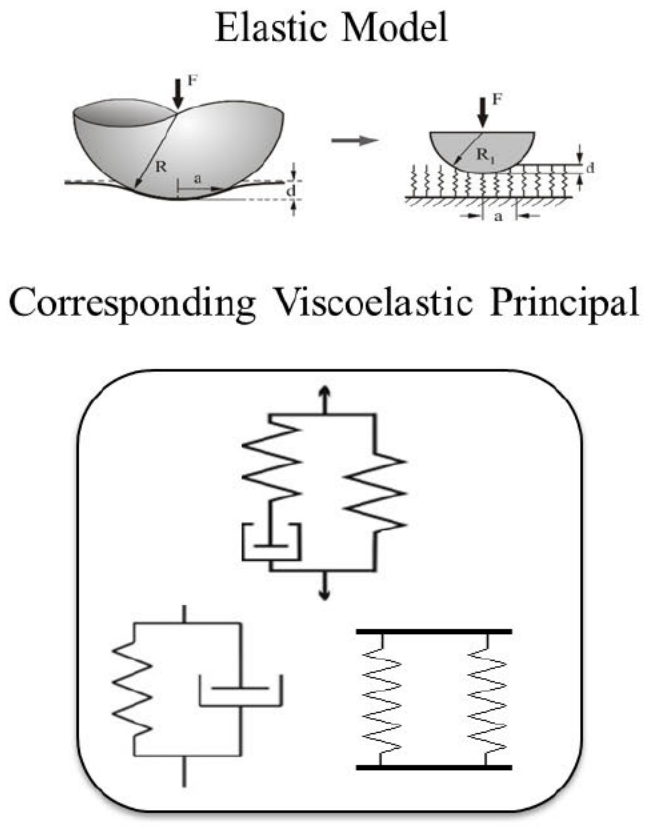
Infrared Spectroscopy Analysis, Humid Sample

IR spectrum of a humid sample, showed the peaks associated to Si and O bonds, also Si-O-H and OH radical, evidence of moisture ingress into the PCB coupon



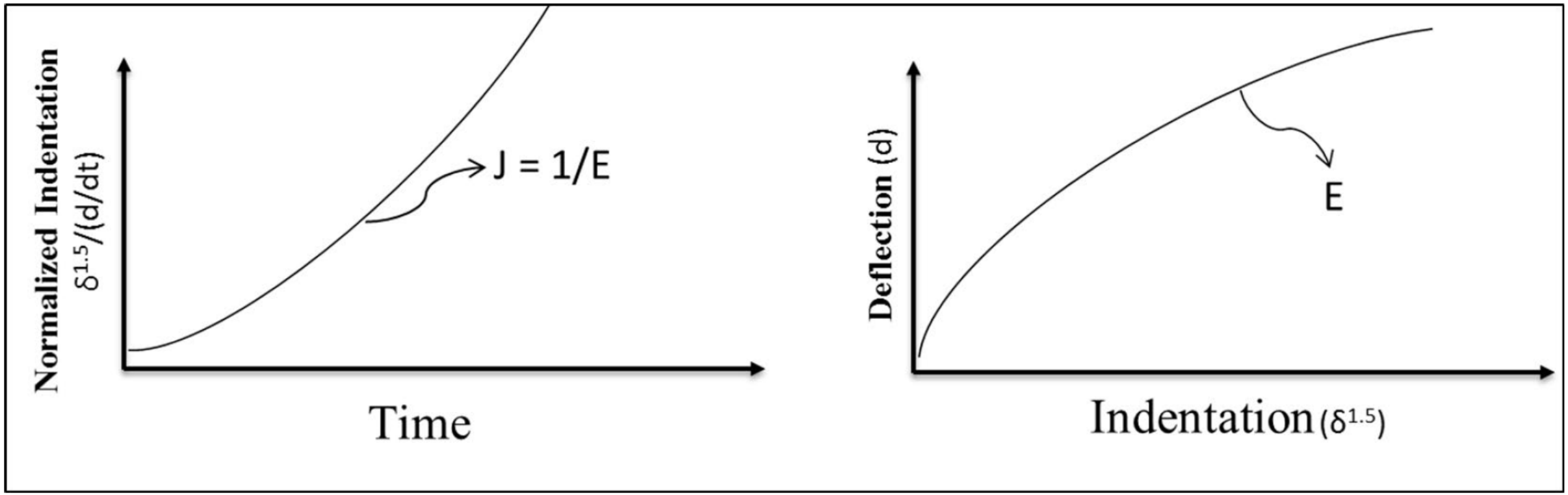
AFM Analysis





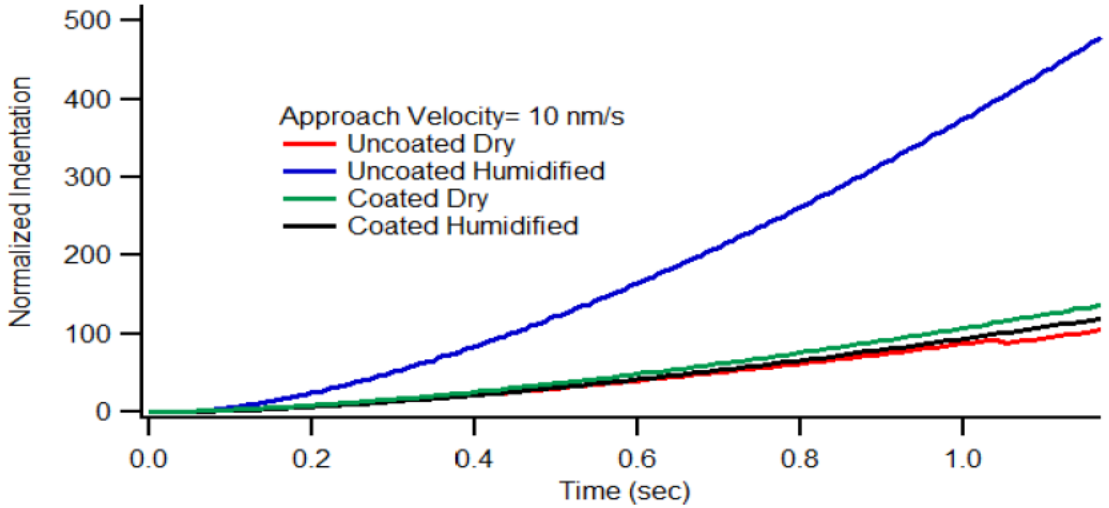
AFM was used to study the mechanical response of the epoxy-glass bundle interface

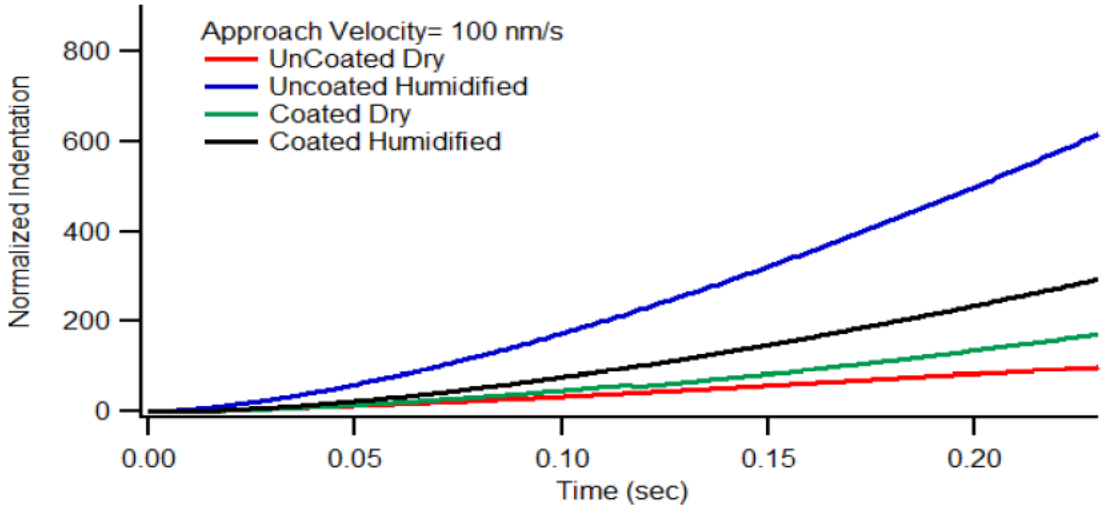
Correlation to Material Properties

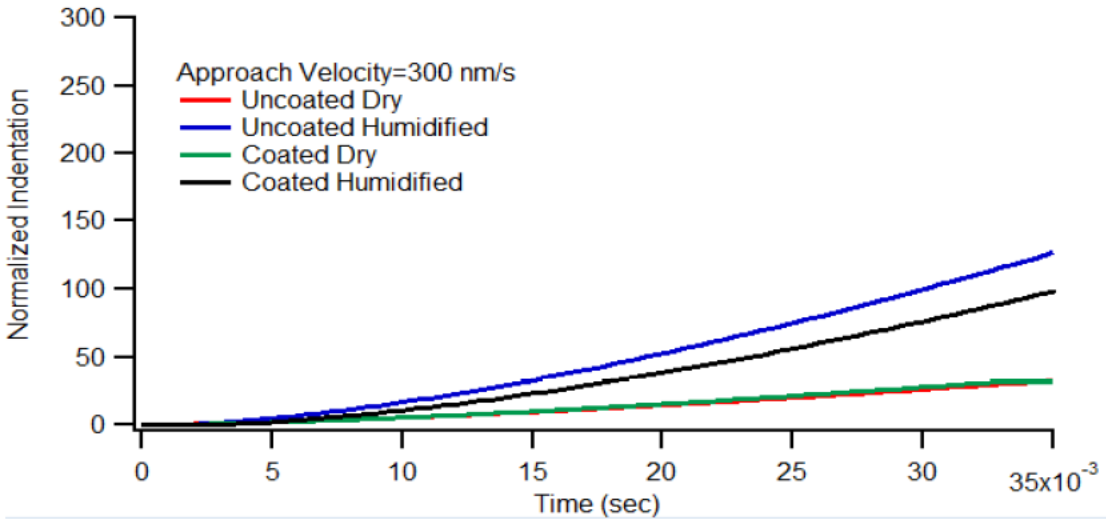


When the AFM cantilever interacts with the surface material the stiffness and viscoelasticity can be estimated.

Atomic Force Analysis Uncoated Sample







Uncoated Humidified Sample is the least stiff among all samples.

Dried samples are more viscoelastic.

The samples are in the following order (stiff to less stiff): Uncoated Dried, Coated Dried, Coated Humidified, Uncoated Humidified.

Conclusions

- Degradation of mechanical properties and stiffness of glass/epoxy interface can be estimated by indentation techniques
- Organic functional groups in glass/fiber epoxy samples can be imaged and identified using FTIR microscopy.
- Changes in material properties due to moisture ingression can be measured using FTIR imaging, allowing laminate characterization for CAF risk.

Acknowledgement

- Atomic Force Microscopy analysis was performed at
  - *University of Maryland by Dr. Babak Eslami, Mr. Mied*
  - *George Washington University by Ernesto Lopez and Prof. Santiago Solares*

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