

# **Identification and Validation of Analytical Chemistry Methods for Detecting Composite Surface Contamination and Moisture**

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## **Abstract**

In-field surface contamination and moisture detection are among the most critical issues in preparation of adhesive bonds between composite adherends for the construction and repair of structural composite components. In this paper, the feasibility of two analytical chemistry methods is explored to evaluate the preparedness of composite surfaces for bonding: 1) an all solid-state electrochemical sensor, and 2) atomic force microscopy. Electrical impedance spectroscopy measurements using the sensor were conducted on composite surfaces with a variety of contaminants. The sample surfaces were also examined using scanning electron microscopy and energy dispersive analysis of X-ray. Additionally, the capability of atomic force microscopy for adherend inspection was investigated using modified probe tips, force spectroscopy and force volume techniques. Results demonstrate that the electrochemical sensor can detect a wide range of surface contaminants and the atomic force microscope has the potential to discriminate contaminants based on the surface activity.

## **AFM**

Atomic force microscopy (AFM) is a useful tool for characterizing the topography and material properties of a solid substrate. AFM utilizes the nano-sized tip of a sharp probe to scan across the surface of a substrate and record surface topography and intermolecular forces between the probe tip and the sample. These interactions are monitored by position sensitive detectors, depicting maps of the material topography and other surface properties such as adhesion, mechanical, electrical, and magnetic properties. AFM can be operated in three different modes: contact, non-contact and tapping mode. The various images available from AFM include topography, friction, deflection and phase images. AFM offers the functionality of operating in various environmental conditions including with or without a vacuum and in a dry or fluid cell.

AFM has shown to be successful in probing surfaces with molecular and/or atomic resolution with very high sensitivity.<sup>1-3</sup> To identify and discriminate surfaces with varying chemistries, it is useful to modify the AFM tip surface with self-assembled monolayers (SAMs) of specific functional groups. The method of scanning surfaces using a modified AFM probe tip is called chemical force microscopy (CFM). Chemical force microscopy uses the chemical interaction between the functionalized tip and the surface for mapping, independent of surface morphology.

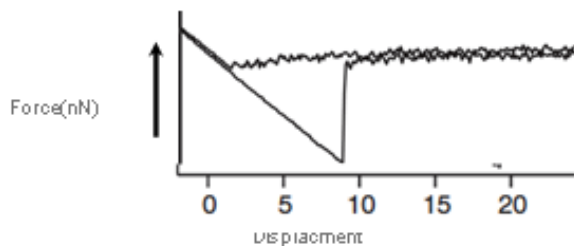
It has been shown that the presence of contaminants and moisture on composite surfaces prior to bonding, can affect the durability of the bond between the adhesive and the adherents. In addition, surfaces with improved surface activity have higher bond strength and durability.<sup>4,5</sup> Since CFM has been used to differentiate hydrophilic and

hydrophobic regions at nanoscale spatial resolution<sup>6-8</sup>, this analytical technique can be used to analyze the surface chemistry of various composite laminates. The mobilization of the epoxy function group on the AFM tip emulates the interaction with the chemical domains of typical bonding adhesives with composite surfaces and can potentially provide an improved mapping of the surface activity of the composite laminate prior to bonding. Since tips modified with the epoxy function group are not commercially available, it was required to develop a procedure to manufacture and validate tips with this type of SAM.

In the present study, the AFM tip has been modified using 3-Glycidoxypropyltrimethoxysilane (GPS) to improve the contrast between the hydrophobic and hydrophilic surface regions without liquid immersion and water vapor in the probe sample environment. Tips modified with GPS produce monolayers terminated by epoxy groups which have the ability to react with wide a range of nucleophiles. This property makes it an ideal compound to discriminate chemical compositions on surfaces. The approach presented in this study is useful to characterize and map the chemical heterogeneity of materials which are sensitive to solvents and humidity at nanoscale spatial resolution.

Studies were initially conducted on randomly patterned hydrophilic/hydrophobic SAM samples using unmodified and chemically modified epoxy terminated tips in normal room conditions. These experiments were intended to evaluate the performance of the epoxy terminated tip image contrast between chemically distinct domains with the unmodified tip. Results demonstrated that the AFM is a potential tool for discriminating different domains in normal room conditions.

Although scan images can provide a qualitative overview of changes in surface chemistry, force spectroscopy can be used to provide a qualitative measure. Force spectroscopy measures the intermolecular force between the tip and the sample by measuring the deflection of the tip when the piezoelectric controller of the AFM alternately moves and removes the tip near the substrate. This deflection of the tip occurs on a straight line normal to the surface. As the tip comes in close proximity to the surface, an attractive or repulsive forces is created between the tip and the surface causing the tip to deflect. If the force is attractive, the cantilever will be pulled down toward the substrate and if it is repulsive, the cantilever is pushed up. A typical force versus cantilever deflections curve is shown in Figure 1. The deflection is converted into a force using the spring constant of the cantilever. AFM can calculate the force as low as 10 pN ( $10^{-11}$ N). This adhesive interaction between similar or different functional groups is unique and reproducible, enabling the determination of functional groups simply on the bases of adhesive force.<sup>6</sup>



**Figure 1. Typical force spectroscopy curve.**

Multiple force displacement curves for a specimen can be obtained and adhesion forces for each curve can be plotted on a histogram representing the number of times a given adhesion force is observed during the measurements. Peaks in the histogram are

specific to the pair of functional groups and can assist in quantifying surface activity and contamination.

Force spectroscopy can be automated and provide more reliable results using a force volume technique. A force volume contains an array of force curves in an x-y plane over the entire scanned area. A unique x-y position in the area provides the force measurement data, and the force curves from the array of x-y points are combined into a 3-dimensional array or volume of force data. Force volume allows for the investigation of the spatial distribution of almost any force between the tip and sample that varies with distance. Since force is the derivative of energy with respect to distance, the volume data can be used to infer a potential energy map. Once the force volume data is generated, it can post-processed using SPIP software to generate adhesion maps, histogram of adhesion forces, etc.

### **Experimental – AFM**

AFM is a powerful tool for investigating changes in topography and surface chemistry of various surfaces. Modifying probe tips with various functional groups makes it chemically sensitive in imaging and also provides direct probing of intermolecular interaction. This chemical force microscopy is used in studying adhesion and frictional forces between various functional groups. A number of studies have been conducted to demonstrate and validate the use of AFM/CFM on composite laminates. Descriptions of these studies are provided in this section.

#### *Epoxy vs Unmodified Probe Study:*

Functionalizing the probe tips with chemically active groups such as epoxy provides a better contrast between different chemical groups present on the surface at the same

time providing intermolecular information between the probe tip and the surface. In order to evaluate the chemical sensitive nature of the epoxy probe, it was tested on chemically distinct domains created on gold-coated silicon substrates using hydrophobic (-CH<sub>3</sub>) and hydrophilic (-COOH) terminated SAMs and compared with the unmodified probe. Additionally, force spectroscopy tests were conducted on freshly cleaved mica substrates to quantify the improved sensitivity of the epoxy probe. Ten measurements were taken and mean values and standard deviations were obtained for the epoxy and unmodified probes.

#### *Environmental Effects on Force Spectroscopy:*

The environment in which force spectroscopy is conducted plays a crucial role in measured adhesion forces. Force spectroscopy conducted in ultrahigh vacuum can only provide the bare chemical adhesion forces between the tip and the surface. Force spectroscopy carried out in air are difficult to interpret as they are influenced by capillary condensation<sup>9</sup> and the measured adhesion forces are 1 to 2 orders higher in magnitude than specific chemical interactions between tip and the sample surface. In order to investigate the change in laboratory conditions from day to day and its effect on force spectroscopy measurements, temperature and humidity changes were monitored at different time periods using unmodified probes on freshly cleaved mica wafers.

#### *Force Spectroscopy Composite Laminate Study*

Performing force spectroscopy on the regions that show discrepancies in phase/frictional images quantify the adhesion force between the possible contaminant and the probe tip and provides an evaluation of the effect of contaminant on the surface/tip. This current research focuses on the study of the contamination of

composite laminates resulting from various peel plies including nylon and polyester. In this evaluation, nylon peel-ply prepared samples were selected and topography and frictional images were obtained for a scanning range of 3.80um. Based on the frictional image, anomalies at different locations were selected and labeled from A thru D and force spectroscopy was performed on those selected regions. Ten measurements were taken at each location and mean adhesion force values and standard deviations were obtained.

### Force Volume Study

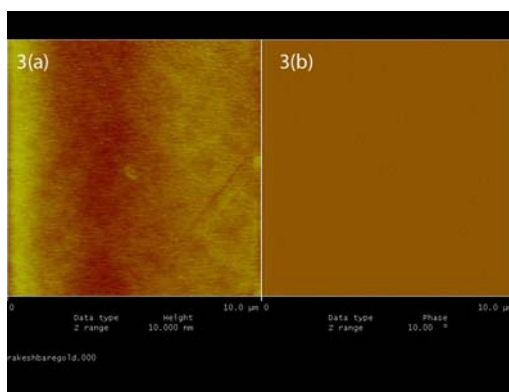
In order to examine the difference in adhesion forces between the nylon and polyester prepared peel-ply samples (of 1um scan area and 256 × 256 pixel resolution), force volume imaging was performed. Force volume provides a more systematic approach for recording force curve data when compared to the previous, more random approaches that were utilized for data analysis. Additionally, the information from the entire scan area will be utilized instead of the specific areas that are selected, providing a better representation of the adhesion forces. In this study, the force volume technique was used with both a modified epoxy probe and an unmodified probe.

## **Results and Discussions – AFM**

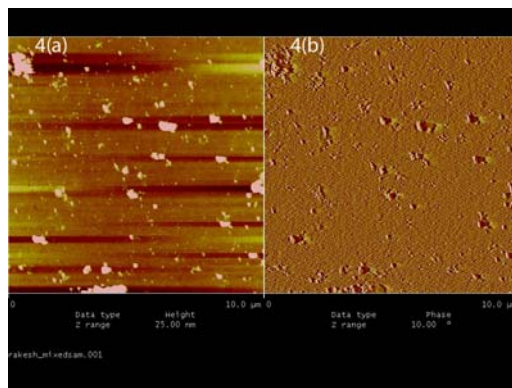
### Epoxy vs Unmodified Probe Study:

Figure 2(a) and (b) shows a height and phase image of an unmodified gold plated silicon wafer surface using an unmodified probe, respectively. Figure 3(a) and (b) shows the same for a surface mixed with hydrophobic and hydrophilic regions using an unmodified probe and Figure 4(a) and (b) shows the same images for the mixed surface using an epoxy modified probe, The important detail to note is that the phase image

obtained using an epoxy modified probe shows improved sensitivity detecting the chemically distinct domains on the surface when compared with the unmodified probe. Table 1 shows the mean adhesion force values for both the unmodified probe and the epoxy probe taken from a mica substrate. The average value for the epoxy modified probe is 65.4nN which is significantly greater than 2.7nN for the unmodified probe. These values demonstrate a greater sensitivity for the epoxy probe.

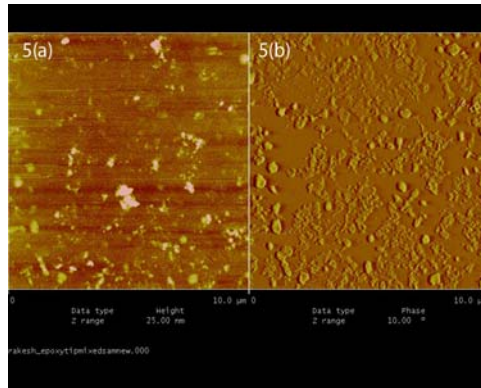


**Figure 2. (a) Topography (b) Phase image of unmodified gold coated silicon substrate, using unmodified AFM probes.**



**Figure 3. (a) Topography (b) Phase image of partially modified gold coated silicon substrate with 11-mercaptopundecanoic acid and 1-octadecanethiol self assembled monolayer, using unmodified AFM probes.**





**Figure 4. (a) Topography (b) Phase image of partially modified gold coated silicon substrates with 11-mercaptoundecanoic acid and 1-octadecanethiol self assembled monolayer, using epoxy modified AFM probes.**

**Table 1. Force Spectroscopy on Mica Surfaces**

Probe	Adhesion Force (nN)	SD
Epoxy	65.36	1.85
Unmodified	2.66	0.194

*Environmental Effects on Force Spectroscopy:*

The experimental data using AFM with the force spectroscopy technique was gathered on two consecutive days. Table 2 shows the 1st day of trials in which 5 new probe tips were utilized. Table 3 shows the 2<sup>nd</sup> day of trials using the same 5 probes. The tables document the changes in environmental conditions. The time gap between each set of readings for each tip was approximately 15 minutes. The average adhesion force for similar AFM tips are approximately the same, except for tips 1 and 2 (from Table 2). The slight variation in adhesion forces for tips 3, 4, 5 may be due to the difference in contact area of the probe. Probe tips have a specified range of cross sectional area and variations within this range can explain small differences observed from tip to tip. The results show a similar trend on day 2, but with significantly lower adhesion forces relative to day 1. This is likely due to the change in humidity, which will further cause a

change in capillary condensation on the mica surface. From the above analysis, it appears that both tip area of contact and the humidity have an effect on the adhesion force measurements. The data highlighted in yellow does not appear to follow any trend and requires further investigation.

**Table 2. Environmental Conditions - Day 1**

<b>Humidity</b>	<b>Temperature (C)</b>	<b>Tip No.</b>	<b>Mean of 50 adhesion force</b>	<b>S.D</b>
52.2	22.5	1	10.997	1.7966
50.4	23.4	2	32.803	0.97307
50.3	23.5	3	19.967	1.3857
49.6	23.7	4	13.714	2.2984
49.0	23.8	5	18.056	6.0413

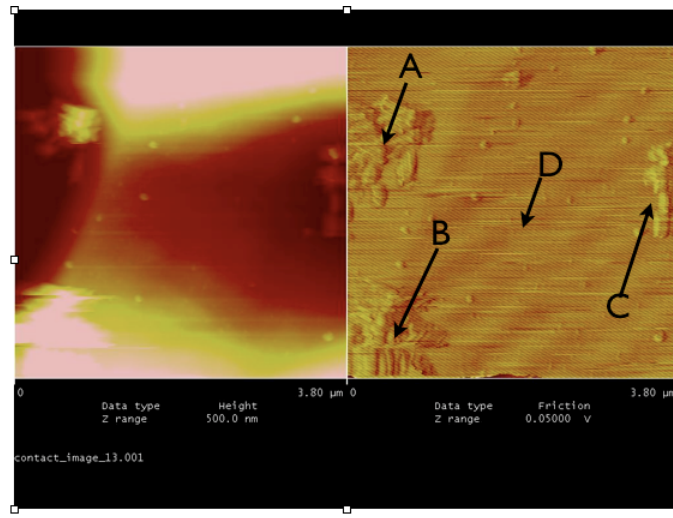
**Table 3. Environmental Conditions - Day 2**

<b>Humidity</b>	<b>Temperature (C)</b>	<b>Tip No.</b>	<b>Mean of 50 adhesion force</b>	<b>S.D</b>
56.7	22.2	1	17.036	1.1987
55.2	22.5	2	7.7828	0.71156
55.6	22.6	3	9.7174	1.1738
54.7	22.6	4	6.0493	0.61482
54.2	22.8	5	7.7124	0.8806

*Force Spectroscopy Composite Laminate Study:*

Figure 5, shows the height (left) and frictional (right) image of a carbon fiber specimen manufactured using nylon peel-ply. The friction image shows the variation in composition of the composite surface. At each individual region, 10 force curves were

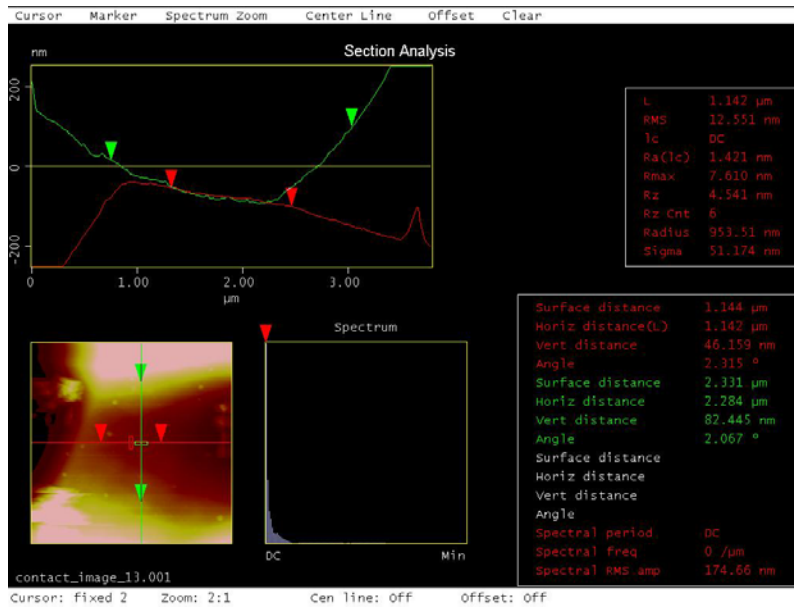
performed and the mean and standard deviation results were tabulated and are provided in Table 4. As expected, the force curves were different from one region to another showing the difference in composition of the material between the regions of interest and the overall area of the specimen. Figure 6 provides detailed information of the surface topography of the cross-section of the composite. This figure clearly depicts the complexity of the composite surface giving a detailed picture of peaks and valleys.



**Figure 5. CFM contact mode: height and friction image of nylon peel-ply sample.**

**Table 4. Force Curves on Nylon Peel-Ply Samples**

<b>Points</b>	<b>Mean Adhesion Force (nN)</b>	<b>SD</b>
<b>A</b>	0.772	0.01
<b>B</b>	0.215	0.013
<b>C</b>	0.023	0.015
<b>D (background)</b>	0.579	0.013



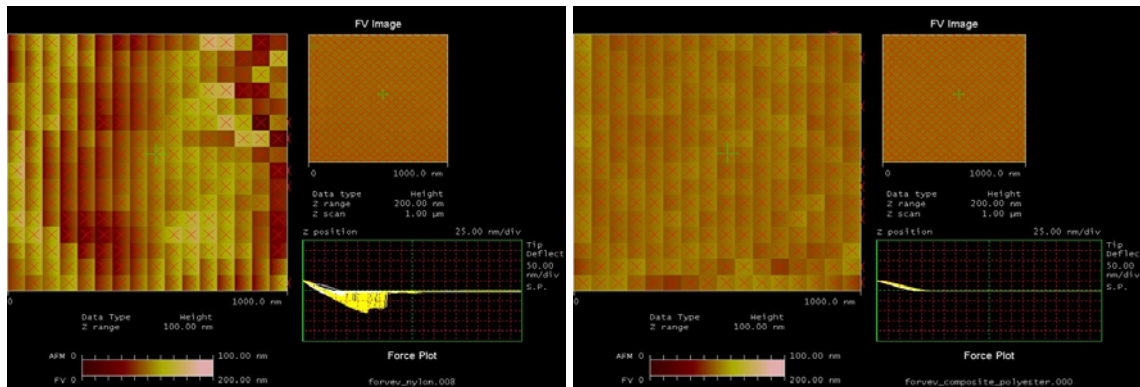
**Figure 6. Sectional analysis of composite laminate.**

*Force Volume Study:*

Figure 7a and b show force volume scans using a nylon and polyester prepared peel-ply samples using an unmodified probe. The contour on the left of each figure shows a discretization of the topography and the image on the right of each figure shows the adhesion force contour. Figure 8 shows the histogram of adhesion forces for the nylon and polyester prepared peel-ply samples. The region shows a maximum adhesion force range of 5.299 nN for nylon prepared sample and 15.58 pN for polyester prepared sample. Because the force volume imaging is not performed under vacuum conditions, the adhesion forces obtained do not directly correspond to the chemical bond adhesion; they also include the capillary adhesion forces. The adhesion forces range on the nylon prepared peel-ply sample is higher in magnitude than the polyester prepared peel-ply samples which demonstrates the dominant response of the capillary condensation. AFM silicon probes are hydrophilic in nature and its interaction with nylon prepared peel-ply surface (hydrophilic) results in higher adhesion forces since hydrophilic-

hydrophilic interactions are stronger than hydrophilic-hydrophobic interactions (i.e., silicon tip and polyester). From Figure 8 it is clear that adhesion forces fall under one region for nylon 0-28nN and for polyester 0.06-0.12nN, indicating that unmodified probes are less sensitive in differentiating the contaminant.

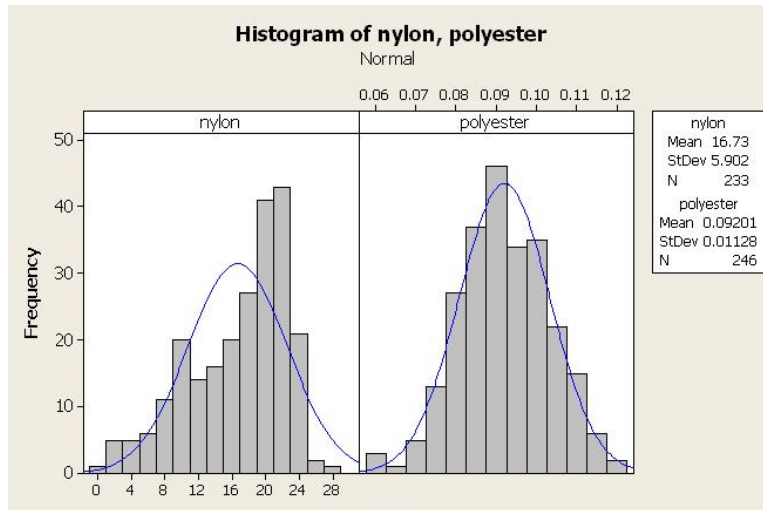
Figure 9a and b show the force volume scans for the nylon and polyester prepared peel-ply samples using an epoxy probe. Figure 10 clearly shows two significant regions of adhesion forces: 0-7.5nN and 30-40nN (for the nylon sample) and 0-15nN and 60-80nN (for the polyester sample). The histogram plots (Figure 8 and Figure 10) demonstrate the chemical sensitive nature of the epoxy probe in terms of the adhesion force range and magnitude when compared with the unmodified probe.



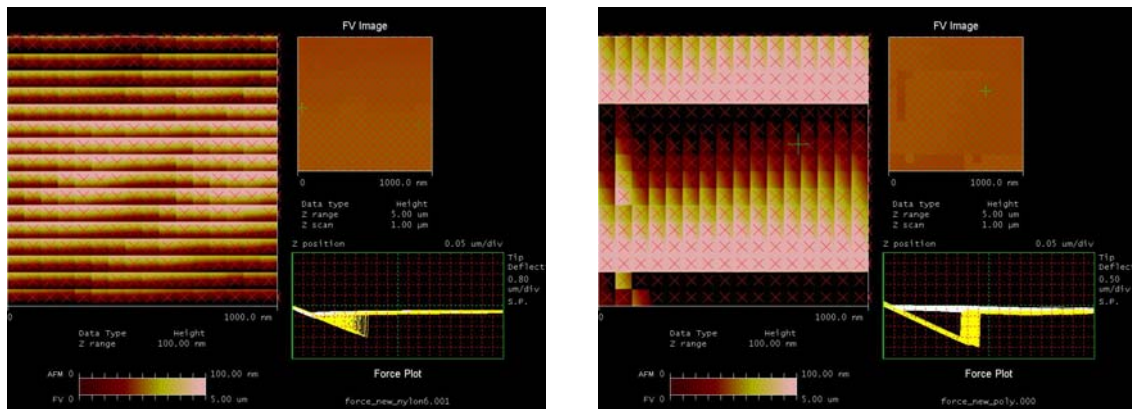
(a) nylon prepared peel-ply sample surface

(b) polyester prepared peel-ply sample surface

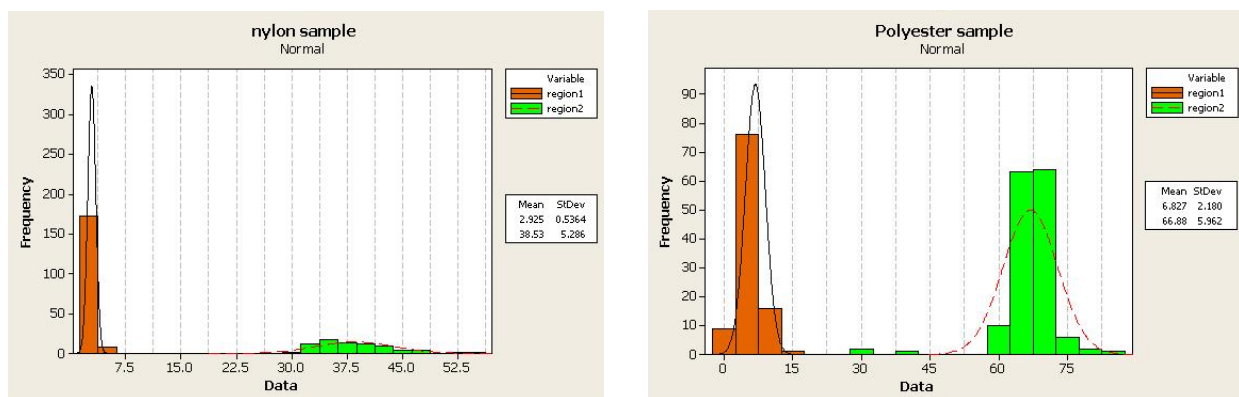
**Figure 7. Force volume scans of composite laminate with unmodified probe.**



**Figure 8. Histogram of adhesion forces from force volume scans with an unmodified probe.**



**Figure 9. Force volume scans of composite laminate with unmodified probe.**



**Figure 10. Histogram of adhesion forces from force volume scans with an epoxy modified probe.**

## **Solid-State Electrochemical Sensor**

Electrochemical sensing technology includes a variety of devices based on conductimetry, polarization measurement, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (ENA). Electrochemical sensing technology simply requires a small input energy density ( $<0.1$  mW cm<sup>2</sup>). Many electrochemical humidity sensors are based on conductimetry. One of the most promising sensors for water moisture detection is the four-probe electrochemical cell which is fabricated using water sensitive conductors such as carbon powder (electron conductor) and proton conducting polymer electrolyte (PCPE) (proton conductor).<sup>10</sup> EIS and ENA technologies have been used to detect water ingress or accumulation at the interfaces between polymer and metallic components.<sup>11</sup> Stripping electrochemical sensors (SESS)<sup>12</sup> technology utilizes the fact that a specific atom or molecule is oxidized at a specific voltage with a specific reaction rate. This allows spectral analysis of the composition and quantity of surface contaminants. However, classical electrochemical sensors with liquid electrolytes are usually rather bulky and awkward. Moreover, leakage of the electrolyte may corrode the device and contaminate the studied composite component. In addition, traditional electrochemical sensors cannot be used to analyze the surfaces of inert polymer materials including polytetrafluoroethylene (PTFE), acrylics, and epoxies. Brewis and Dahm<sup>13</sup> found that mediators or redox pairs (organo-silver ions) can directly react with the surface groups of inert polymers and transfer the electrons between an electrode and the surface of a polymer. This finding opens a door for direct detection of the chemical properties of inert polymer materials. However, Brewis and Dahm's experiments were conducted

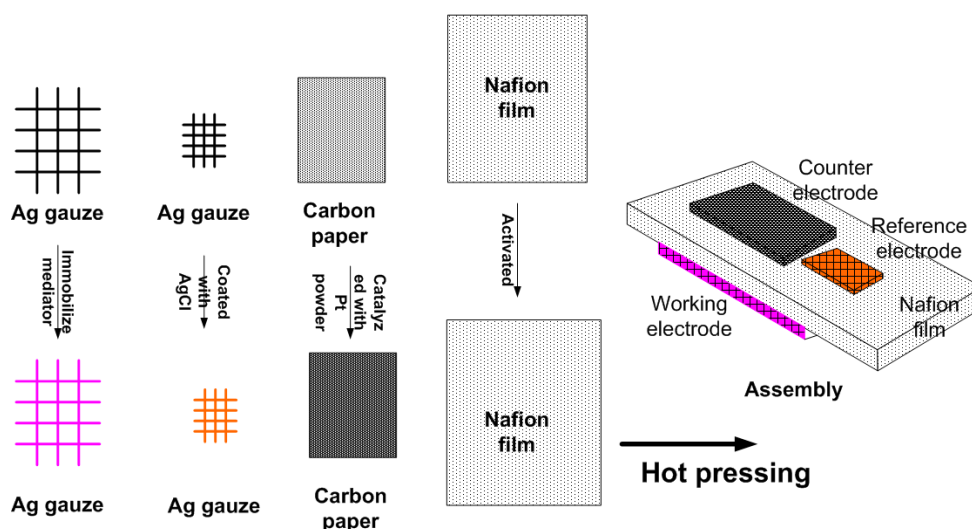
using liquid electrolytes. This section of the paper is focused on demonstrating the feasibility of an all solid-state electrochemical sensor for detecting surface contamination of composite laminates.

### Experimental – Electrochemical Sensor

Two types of sensors were developed; one for CV tests and another for EIS tests.

#### Sensor for CV Tests:

The structure of the sensor and the procedure for fabricating the sensor is illustrated in Figure 11. The detailed procedure for fabricating the parts and assembly of the sensor is provided below.



**Figure 11. Procedure of fabricating a solid-state electrochemical sensor.**

#### Working electrode

A silver gauze of 2 cm × 2 cm was cut as the electrode. An electrochemical deposition method was used. An electrochemical deposition bath contained saturated  $\text{AgNO}_3$  and 1 M  $\text{HNO}_3$ . An electrical power source was used to provide an appropriate voltage and current. A voltage of 0.2 V was applied for 2-4 minutes between the Ag gauze and a Pt wire that was used as a counter electrode. The Ag gauze was then immersed in a



Nafion solution (Liquion™). When the solvent (mainly isopropanol) is vaporized, the Ag gauze was placed in the saturated AgNO<sub>3</sub> solution again for electrochemical oxidation and impregnation. These steps were repeated several times. The coated Ag gauze was washed with deionized water and then dried.

#### Counter electrode of the sensor

A square 2 cm by 2 cm piece of carbon cloth or carbon paper was used as the electrode. Activated Pt catalysts (40% Pt on carbon, Alfa Aesar) were mixed into a Nafion ionomer solution (Alfa Aesar). The mixture was loaded on to a carbon cloth. The counter electrode was wired with an Ag wire.

#### Reference electrode

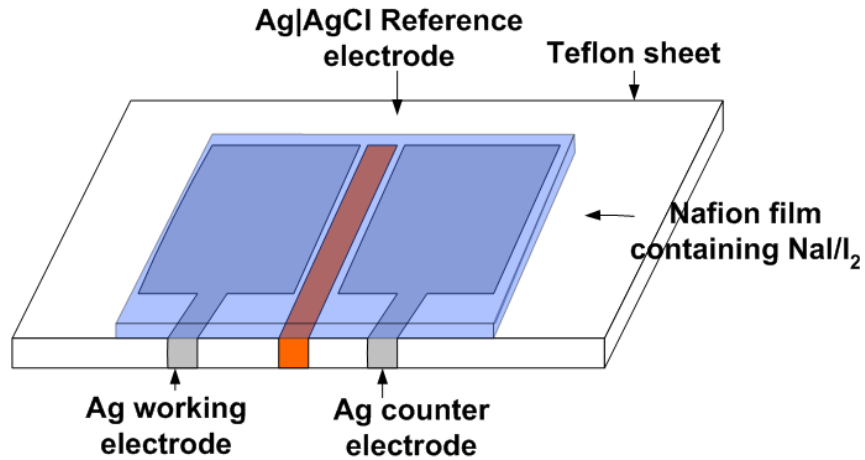
The reference electrode was a piece of Ag gauze (1 cm x 1 cm) that was coated with AgCl. An original Ag gauze was immersed into saturated HCl solution. A 0.3 V voltage was applied between the Ag gauze and a Pt wire for a period of 2 minutes. The resulting coated Ag gauze was washed with deionized water and dried.

#### Sensor assembly

The working electrode was attached to one side of a piece of Nafion 117 proton conducting membrane whereas the counter and reference electrode was attached to the other side. The electrodes were hot pressed using a hot press machine. The pressure for pressing was 1500 psi and the temperature was 100°C.

#### Sensor for EIS Tests:

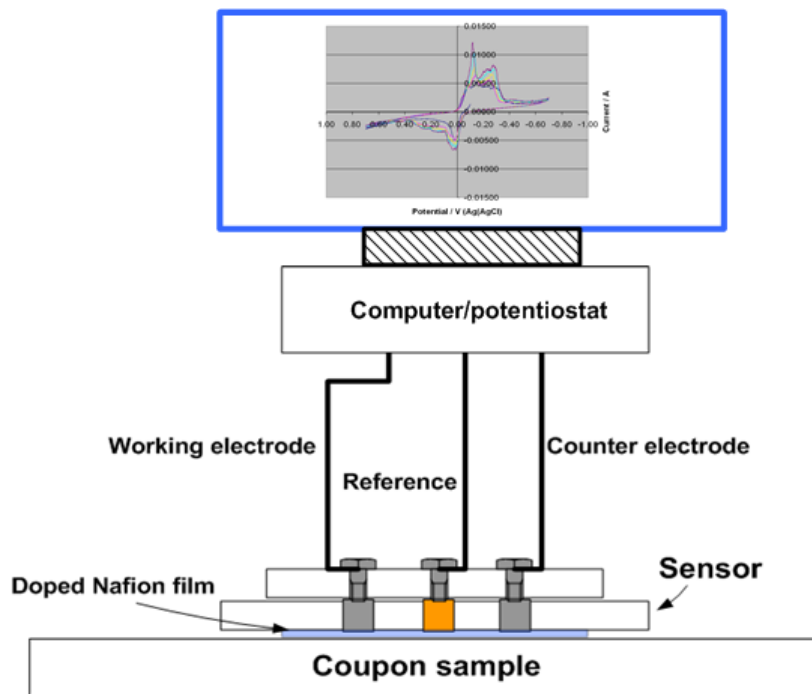
The schematic of the sensor for the EIS measurements is shown in Figure 12. Two pieces of Ag film are painted on a Teflon sheet, one as the working electrode and the other as the counter electrode. A piece of Ag|AgCl film is painted in the middle of the working and counter electrodes and is used as a reference electrode.



**Figure 12. Schematic for the sensor used for EIS measurements.**

Experimental Setup:

The experimental setup is shown in Figure 13. A polymer or composite coupon sample is set at the bottom. The sensor is placed on the top of the surface with the Nafion film or the working electrode impregnated with Nafion in contact with the surface. The sensor is slightly pressed using a weight of about 1 kg.



**Figure 13. Experimental setup for both CV and EIS tests.**

### Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis of X-Ray (EDAX) Study:

In order to correlate the form and composition of the contamination with the EIS measurements, SEM/EDAX examinations were conducted on the composite coupon samples that were either pristine or contaminated with various sources.

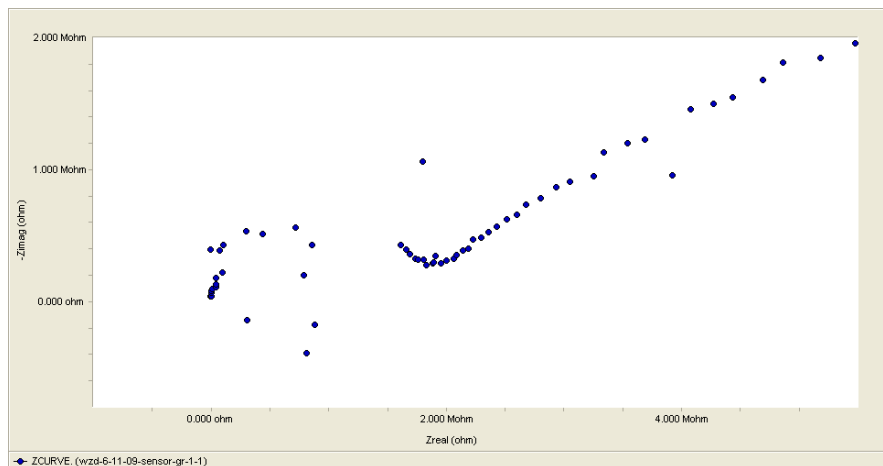
### **Results and Discussions – Electrochemical Sensor**

#### EIS Results:

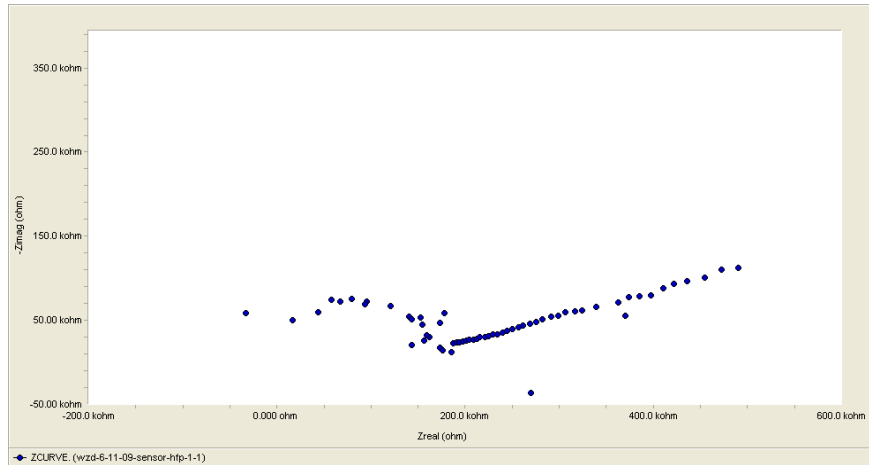
Electrochemical impedance measurements on peel-ply samples with various surface conditions were conducted. Contaminants included Diestone HFP cleanser, UV dye, ultrasonic coupling gel, silicone glove residue, solution from marker, tape residue (no silicone, MTI RAE1000), soda, coffee and protective cream. The impedance for the protective cream is the least ( $1.2 \times 10^3$  ohm) while that for the non-contaminated surface is the greatest ( $2 \times 10^6$  ohm). Figure 14 through Figure 22 show the EIS curves for each of the samples studied. The results are also summarized in Table 5 with a list of polarization impedance values for the samples. The lower the polarization impedance, the higher the reaction rate at the interface between the sensor and the polymer or composite surface.<sup>11</sup> The silicone rubber glove residue has been found to significantly impact the surface tension. The polarization impedance of the sample is very close to that for the pristine sample. Thus, for the current composition of the sensor, it is difficult to detect the silicone rubber residue. This problem may be solved by using other type of mediators or redox pairs including Mn(II)/Mn(III) and Ce(III)/Ce(IV).

**Table 5. Summary of Polarization Impedance Values for the Pristine and Contaminated Samples**

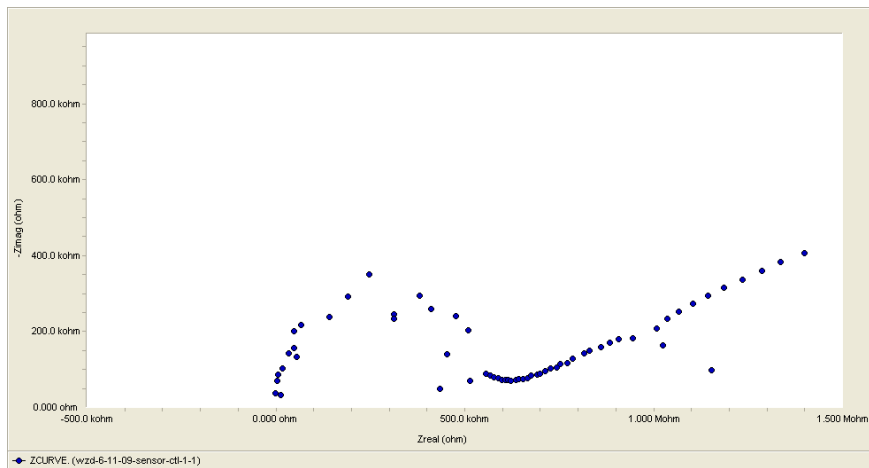
Sample	Polarization Impedance (ohm)
Pristine	$2.0 \times 10^6$
Cleanser (Diestone HFP) residue	$1.8 \times 10^5$
UV dye	$6.0 \times 10^5$
Ultrasonic coupling gel	$6.0 \times 10^5$
Silicone rubber glove residue	$1.8 \times 10^6$
Solution from a marker	$8.0 \times 10^5$
Tape Residue no silicone (MTI RAE1000)	$1.7 \times 10^6$
Soda	$6.5 \times 10^5$
Coffee	$6.0 \times 10^5$
Protective cream	$1.2 \times 10^3$



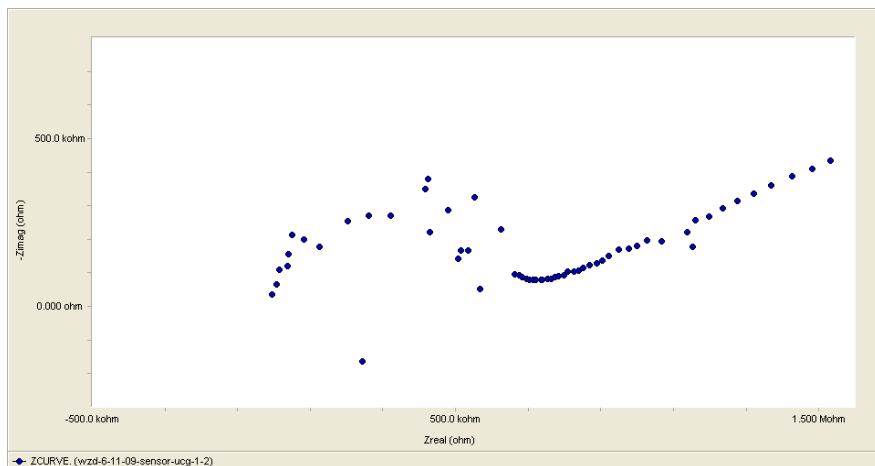
**Figure 14. EIS for a pristine non-contaminated surface.**



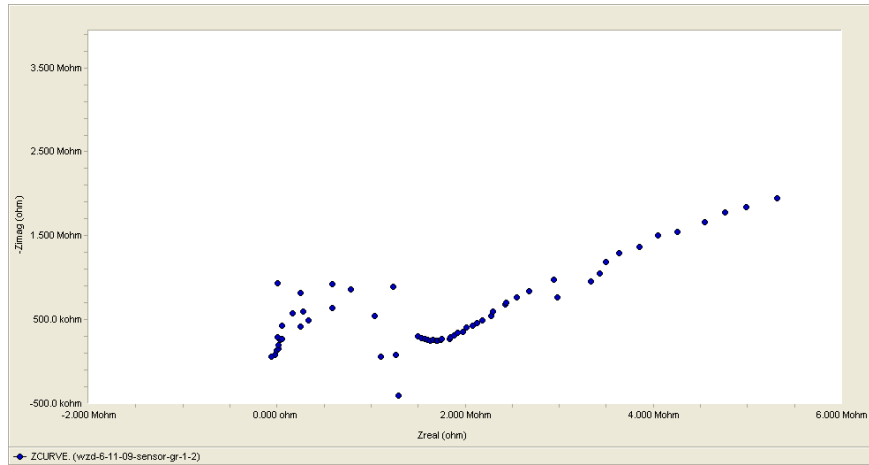
**Figure 15. Surface with cleanser (Diestone HFP) residue.**



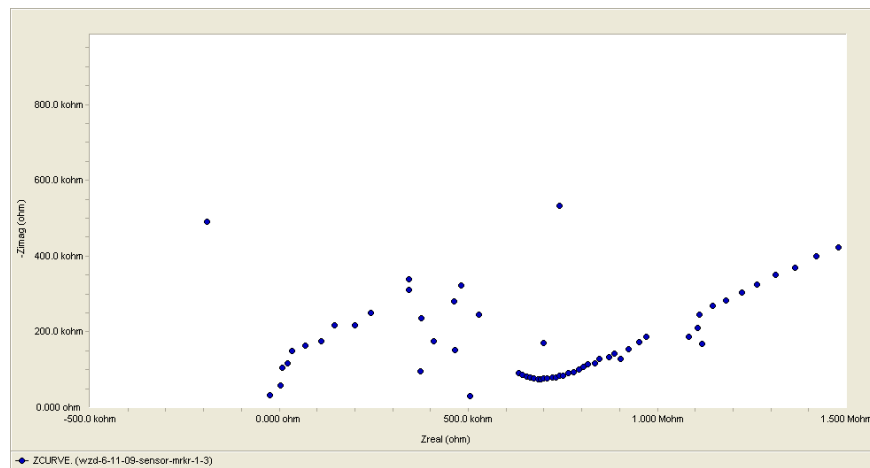
**Figure 16. Surface with an UV dye.**



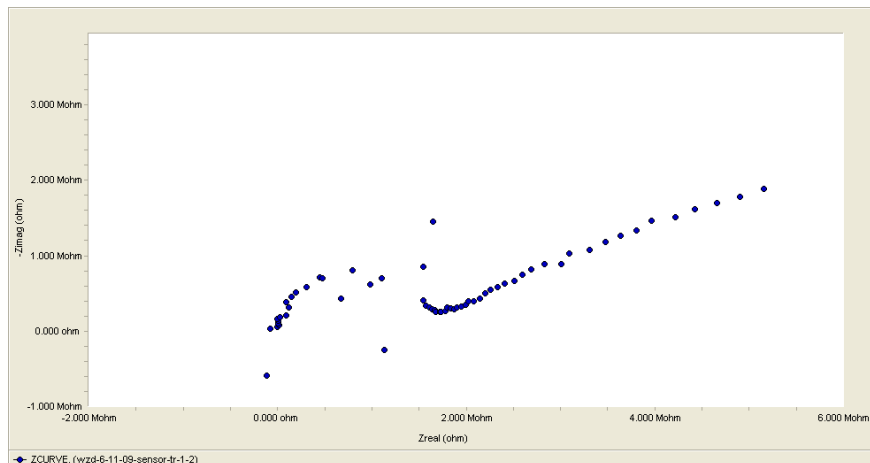
**Figure 17. Surface with an ultrasonic coupling gel.**



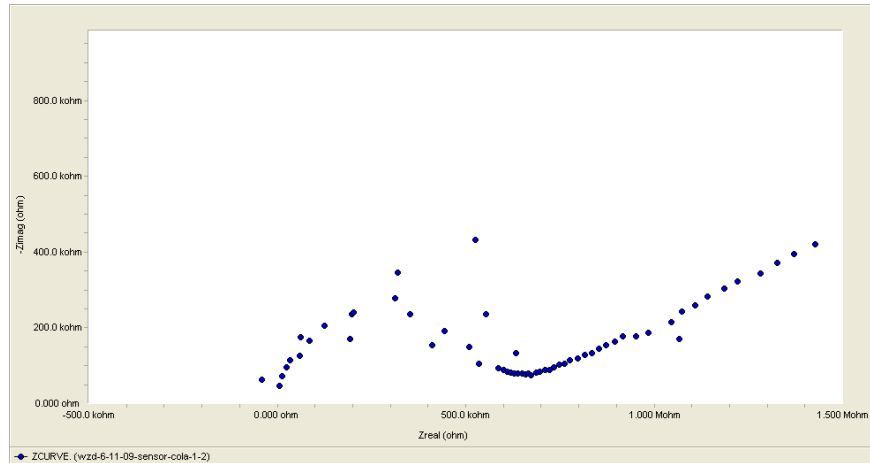
**Figure 18. Surface with silicone rubber glove residue.**



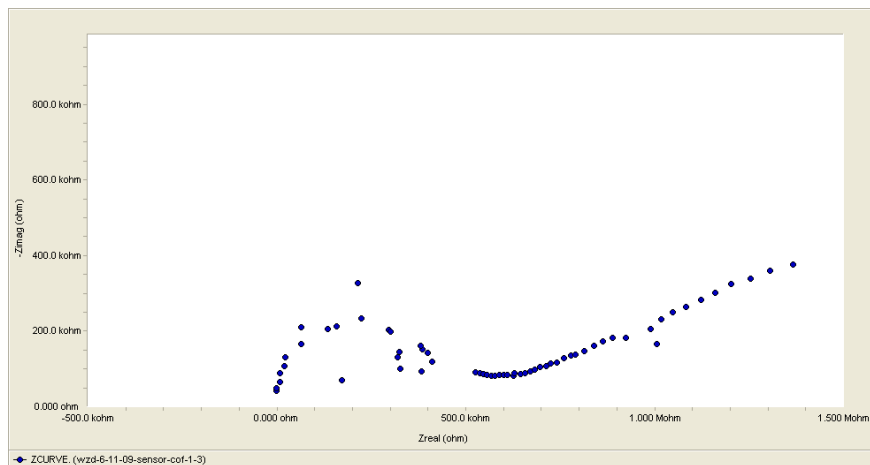
**Figure 19. Surface with solution from a marker.**



**Figure 20. Surface Tape Residue no silicone (MTI RAE1000).**



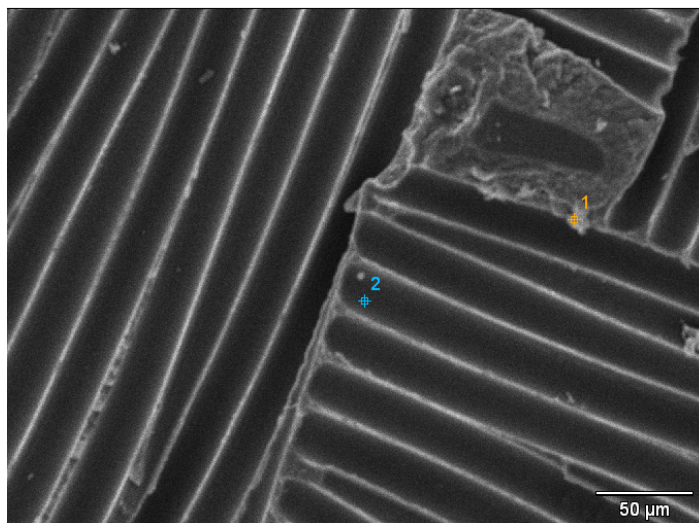
**Figure 21. Surface with soda.**



**Figure 22. Surface with coffee.**

**SEM/EDAX Results:**

Figure 23 shows the surface of a pristine sample. This sample was freshly prepared by tearing off the peel-ply. In order to prevent discrimination between different samples, EDAX area scans on a surface area of about 0.3 cm<sup>2</sup> for all samples were conducted. EDAX analysis results show that the pristine sample only has C, O, and Al (Table 6).



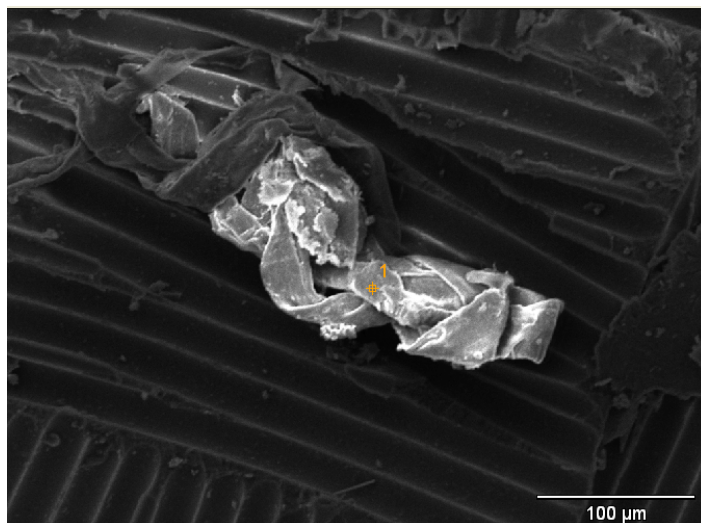
**Figure 23. SEM micrograph obtained from a pristine surface.**

**Table 6. Elemental Weight Percentages for an Area (0.3 cm<sup>2</sup>) Analyzed with EDAX for the Pristine Surface**

Element Line	Weight %	Weight % Error
C K	92.38	+/- 1.49
O K	3.41	+/- 1.03
Al K	4.21	+/- 0.35
S K	0	
S L	---	
K K	0	
K L	---	
<b>Total</b>	100.00	

A micrograph showing the contaminants from ultrasonic coupling gel is presented in Figure 24. The contaminant is at the middle of the micrograph. The EDAX results on the spots of the contaminants are listed in Table 7. The contaminants contain C, O, Al, S, and K. S concentration is a significant content.





**Figure 24. SEM micrographs obtained from a peel-ply surface that was contaminated with an ultrasonic coupling gel.**

**Table 7. Elemental Weight Percentages for an Area (0.3 cm<sup>2</sup>) Analyzed with EDAX for the Surface Contaminated with Ultrasonic Coupling Gel**

Element Line	Weight %	Weight % Error
C K	70.52	+/- 1.21
O K	21.15	+/- 1.36
Al K	4.36	+/- 0.29
S K	1.83	+/- 0.25
S L	---	---
K K	2.15	+/- 0.21
K L	---	---
<b>Total</b>	100.00	

The sample that is contaminated with protective cream shows a composition that is significantly different from the other types of contaminations. As can be seen in Table 8, the surface contains O, Al, Na, Si, and Zn. A location analysis was conducted on the same sample (Table 9), revealing a very complicated composition which was not observed using the area analysis mode. As many as 13 elements excluding C were detected, including O, Si, K, Zn, Ti, Cl, Ca, Fe, and Zn. In specific locations, Ti and Fe

were the major elements. S was detected at a low value of 0.2 wt% in one location but was not significant at other locations and in the area scan.

**Table 8. Elemental Weight Percentages for an Area (0.3 cm<sup>2</sup>) Analyzed with EDAX for the Surface Contaminated with a Protective Cream**

Element Line	Weight %	Weight Error %
C K	86.38	+/- 1.51
O K	9.31	+/- 0.81
Na K	0.58	+/- 0.03
Al K	0.88	+/- 0.06
Si K	0.10	+/- 0.01
S K	0.00	
S L	---	
Zn K	2.75	+/- 0.21
Zn L	---	
Total	100.00	

**Table 9. Elemental Weight Percentages for Six Locations with EDAX for the Surface Contaminated with a Protective Cream**

	C-K	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Fe-K	Cu-K	Zn-K	Ag-L	Ce-L
P1	39.7	24.2	0.27	0.06	0.22	0.00	0.00	0.00	0.00	0.00	34.1	0.00	0.13	0.00	1.10
P2	75.5	13.5	1.45	1.07	0.48	0.00	0.66	0.83	0.54	0.00	1.07	0.00	4.69	0.00	0.04
P3	34.2	1.09	0.32	2.24	1.67	0.00	0.44	1.37	1.56	46.9	0.49	5.24	1.94	2.43	0.00
P4	83.9	7.8	0.64	4.41	0.78	0.23	1.23	0.21	0.04	0.18	0.00	0.51	0.00	0.00	0.00
P5	81.2	7.7	1.71	0.73	0.28	0.00	0.09	0.08	0.06	0.00	0.00	0.11	7.94	0.00	0.07
P6	90.8	6.2	0.92	0.13	0.01	0.00	0.06	0.07	0.08	0.00	0.07	0.11	1.38	0.00	0.00

The results of the EDAX measurements are summarized in Table 10 with the weight percentages and the polarization impedance for the corresponding sample. Essentially, for the pristine sample, the percentages of O and Al are very low. However, the number of data does not allow a statistically meaningful correlation between the EIS impedance

and composition. Nevertheless, the “clean” or “non-contaminated” area of the pristine sample that show low O and S contents may be used as a baseline for the EIS analysis.

**Table 10. Summary of Composition of the Contaminants on Surfaces of the Coupon Samples**

Sample	[O], wt%	[Al], wt%	[K], wt%	[Si], wt%	[Na], wt%	[S], wt%	[Zn] Wt%	Polarization Impedance (ohm)
Pristine	3.41	4.21	0	0	0	0	0	$2.0 \times 10^6$
Cleanser	18.63	4.51	0	0	0	1.63	0	$1.8 \times 10^5$
UV dye	17.19	4.03	0	0	0	2.55	0	$6.0 \times 10^5$
Ultrasonic coupling gel	21.15	4.36	2.15	0	0	1.83	0	$6.0 \times 10^5$
Silicone rubber glove residue	18.15	4.46	0	0	0	2.09	0	$1.8 \times 10^6$
Solution from a marker	17.69	3.64	0	0	0	2.63	0	$8.0 \times 10^5$
Tape Residue	16.02	4.55	0	0	0	2.85	0	$1.7 \times 10^6$
Soda	25.12	3.77	0	0	0	1.07	0	$6.5 \times 10^5$
Coffee	15.07	4.57	0	0.75	0	2.37	0	$6.0 \times 10^5$
Protective cream	9.31	0.88	0	0.10	0.58	0	2.75	$1.2 \times 10^3$

## Conclusions

1. The epoxy modified probe provides better sensitivity than the unmodified probes and can be used to detect variations in the surfaces of composite materials.
2. Environmental effects, particularly humidity, effect adhesion force results. To obtain the chemical adhesion forces, force spectroscopy analysis should be conducted in a vacuum.
3. Force volume is a promising technique that provides a more systematic and reliable procedure for obtaining adhesion force data.

4. The all solid-state electrochemical sensor can differentiate the pristine and a variety of contaminated laminate surfaces. The simple designs, fabrication protocols, and testing setup allow implementation of an online and in-field technology for pre-bonding inspection of the laminate surface.
5. The EIS results show that a specific mediator or redox pair may be sensitive to certain compounds but insensitive to others. The sensitivity of other mediators or redox pairs needs to be examined.
6. SEM and EDAX analyses indicate that the pristine sample has a low concentration of oxygen and sulfur and hence may be used as a baseline for the EIS measurements.

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