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

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Introduction

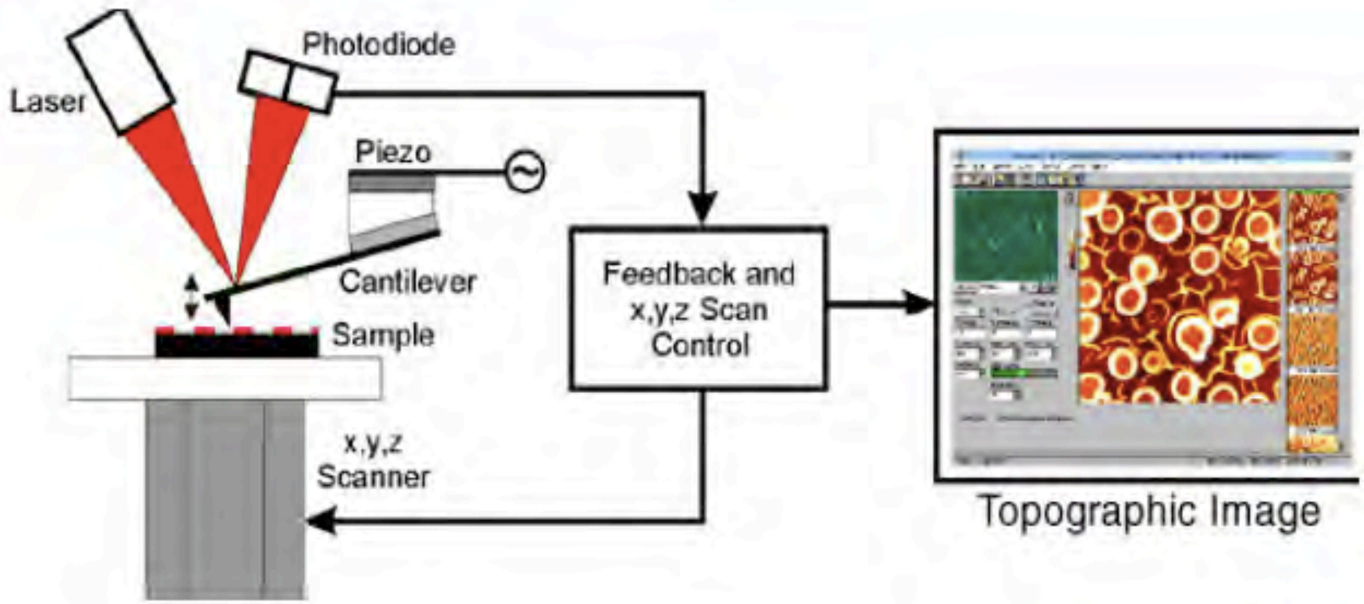
- Motivation and Key Issues
  - Adhesive bonding is now used in manufacture and repair and is beginning to predominate over mechanical fastening.
  - Adherend surface preparation is a critical issue to the structural integrity and durability of bonded structures.
- Objectives
  - benchmark knowledge of surface preparation quality assurance methods
  - identify and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.
- Approach
  - Literature review and analysis (complete)
  - Surface chemistry analysis
  - Electrochemical sensor study

Tasks Overview

- Accomplished tasks:
  - Electrochemical Sensor Study
  - Humidity Sensor Study
  - Atomic Force Microscopy Study (AFM)

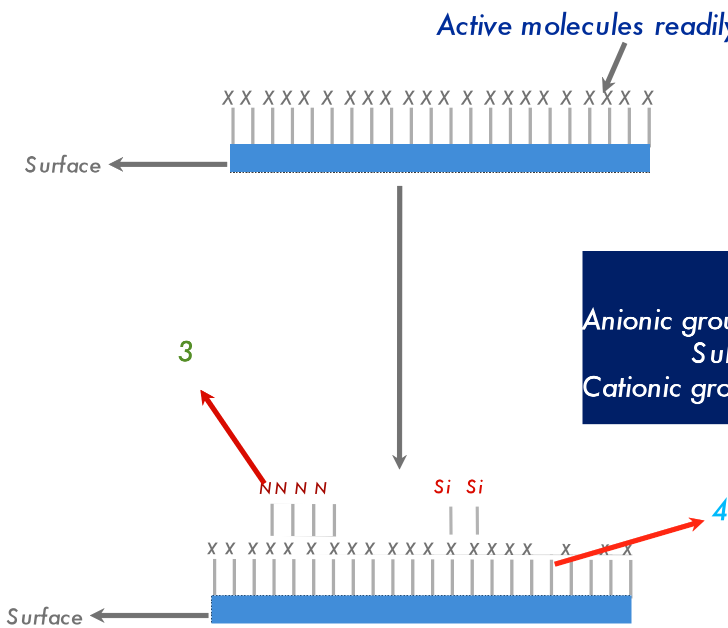
- Current tasks:
  - Advancement of Electrochemical Sensor
  - Chemical Force Microscopy

AFM Principles



Schematic representation of an atomic force microscopy (AFM) showing the force sensing cantilever.

CFM Principles

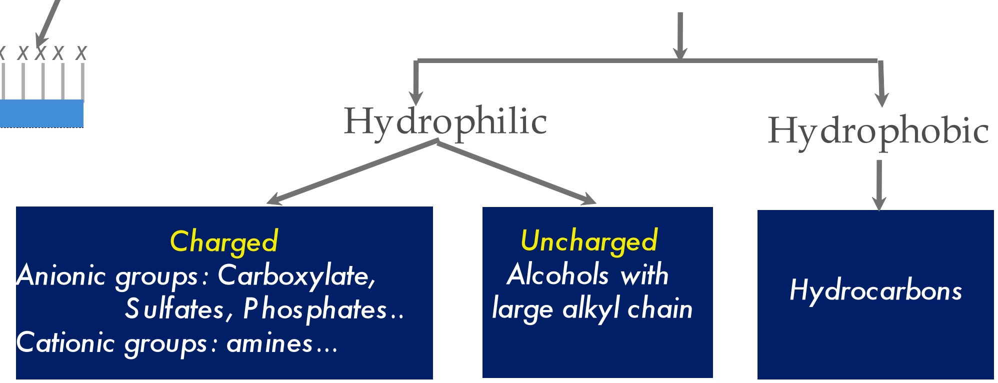


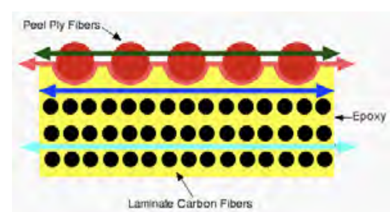
Shows decrese in active molecule for bonding

Laminate Surface Composition

Peel Ply	%C	%O	%N	%Si
Nylon	77.5	12.6	9.8	Tr.
Polyester	75.5	21.6	1.9	1.0
SRB	68	24.2	0.9	6.9

XPS results - UW





Fracture of the epoxy between peel ply and carbon fi bers(1)
Interfacial fracture between the peel ply fabric fi bers and the epoxy matrix (2)
Peel ply fi ber fracture(3)
Interlaminar failure(4)

CFM Principles

CHEMICAL FORCE MICROSCOPY 411

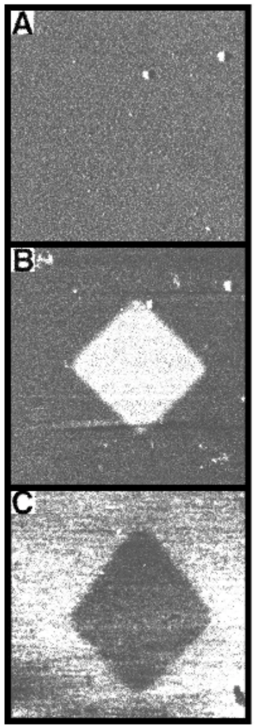


Figure 16 Force microscopy images of a photopatterned SAM sample. The 10×10 μm square region terminates in COOH, and the surrounding region terminates in CH_3. The images are of (*A*) topography, (*B*) friction force using a tip modified with a COOH-terminated SAM, and (*C*) friction force using a tip modified with a CH_3-terminated SAM. Light regions in (*B*) and (*C*) indicate high friction; dark regions indicate low friction (reproduced from Reference 33).

Force microscopy images of a photopatterned SAM sample. The 10 × 10 μm square region terminates in COOH, and the surrounding region terminates in CH3.

(A) Topography,

(B) friction force using a tip modified with a COOH-terminated SAM,

(C) friction force using a tip modified with a CH3-terminated SAM.

NOTE: Light regions in (B) and (C) indicate high friction; dark regions indicate low friction.

Why Epoxy Probe?

- CFM with epoxy functional group modified probe will mimic the interactions between composite surfaces and epoxy resin adhesive.
- Interactions between composites and epoxy resin are important for bonding strength.
- The epoxy functional group has the ability to interact with a wide range of nucleophiles which make it an ideal probe in detecting contaminants on surfaces.
- No prior use of an epoxy modified probe has been recorded according to our literature review. Epoxy modified probes are not available commercially - this study is the first research effort that seeks to synthesize these modified probes.

Methodology

- Modify AFM probe with epoxy functional group.
- Testing of probe on pre-defined gold surface.
- Contaminating the composite with known contaminants and developing signature peaks for various contaminants.
- Building a database of adhesive forces for the various contaminants.
- Testing the probe efficiency.
- Epoxy probe testing on various laminates with and without peel ply for surface contaminants.

Mapping the Laminate Surface Using the Epoxy Probe (Force Spectroscopy)

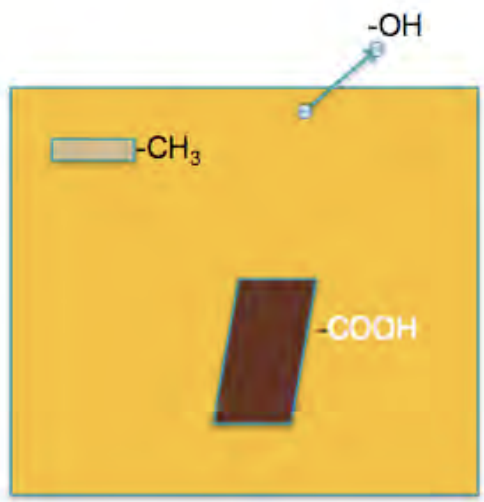
Run CFM using epoxy probe

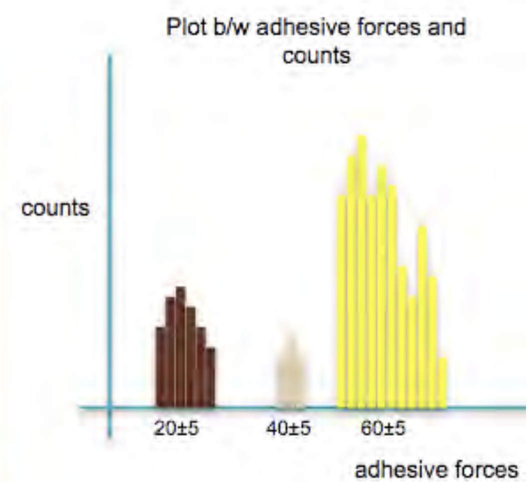
↓

Record force vs. distance traces between samples and functionalized tip

↓

Record the histograms of adhesion forces between tip and sample.

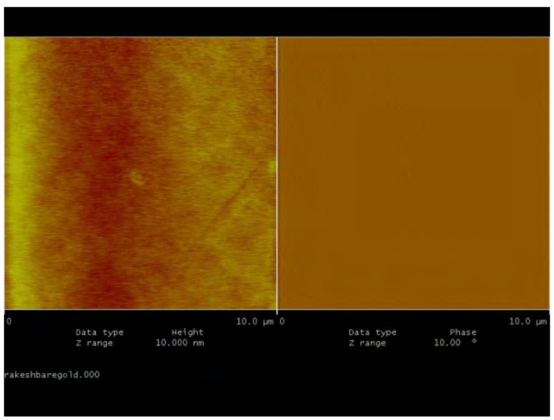




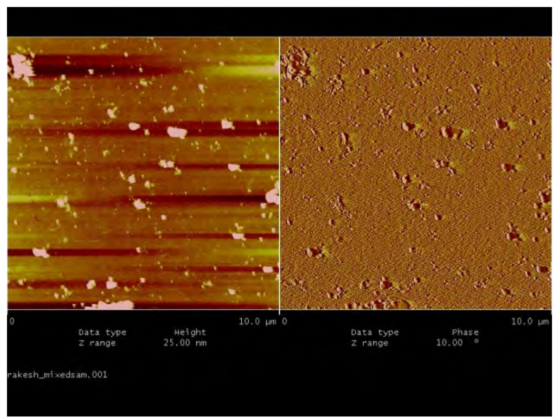
Results - Phase Imaging

Topography Image Phase Image

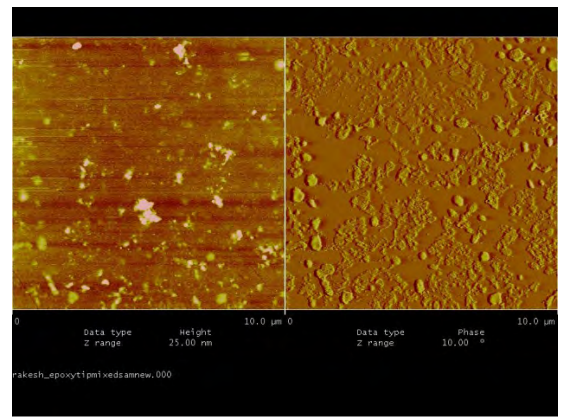
Mixed surface having hydrophobic and hydrophilic domains



Unmodified surface - unmodified probe



Modified surface - unmodified probe



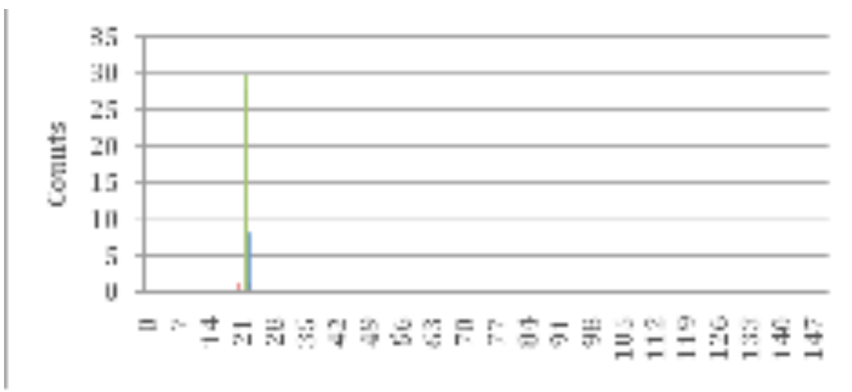
Modified surface - Modified probe

Epoxy modified probes are more sensitive in detecting the chemically distinct domains.

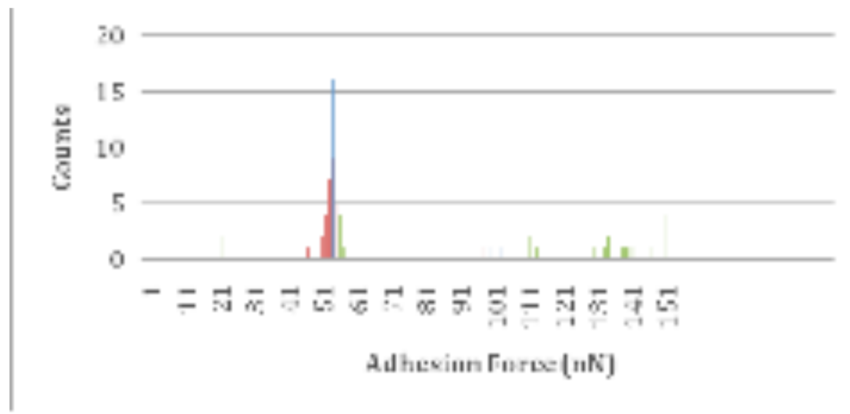
Results – Force Spectroscopy

Histogram for the epoxy tip and the unmodified surface.

Histogram for the epoxy tip and the CH3 surface.



Histogram for the epoxy tip and the COOH surface.



Histogram for the epoxy tip and the epoxy surface.

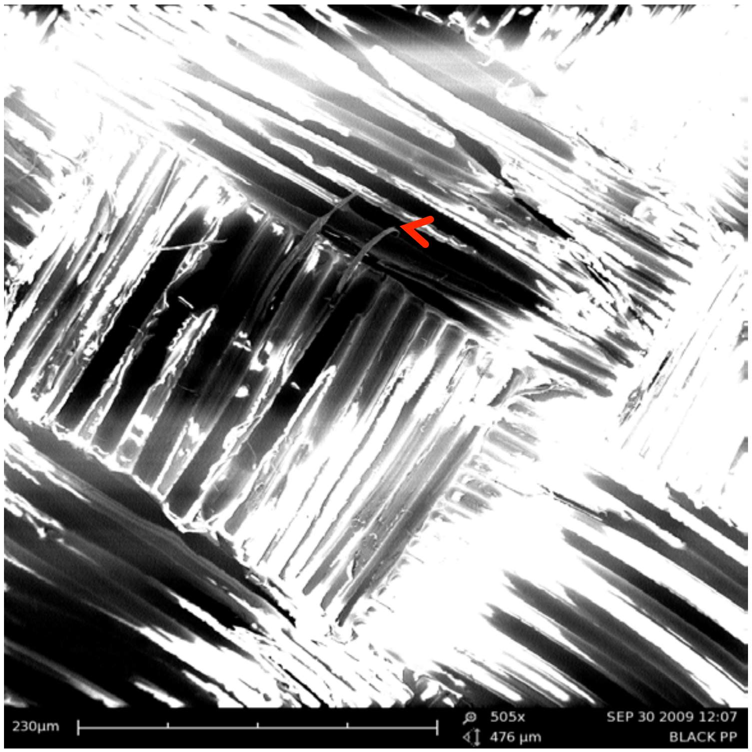
Results – Force Spectroscopy

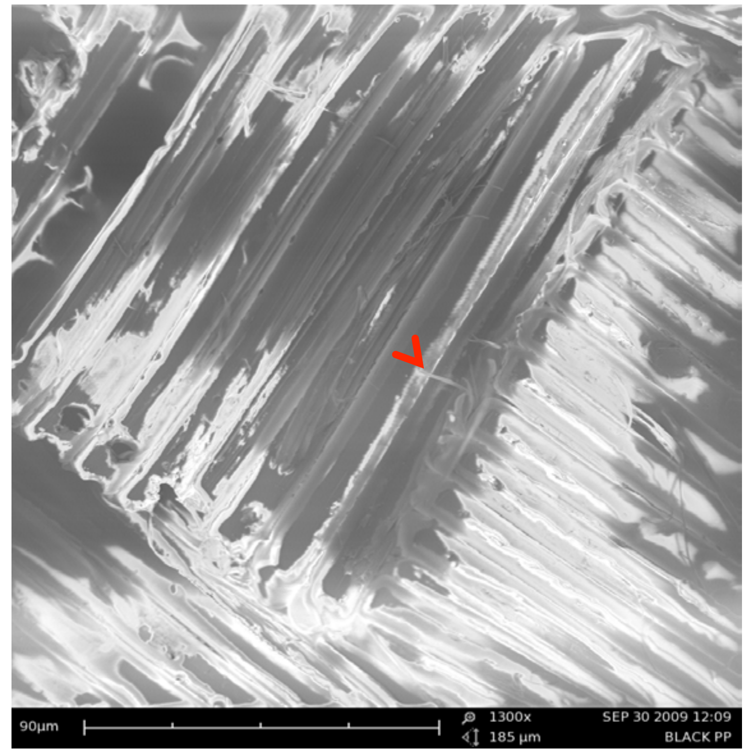
Table 1. Force Spectroscopy Results for Various Substrates

Type of Tip	Unmodified Surface (Average adhesion force in nN)	CH_3 Surface (Average adhesion force in nN)	COOH Surface (Average adhesion force in nN)	Epoxy Surface (Average adhesion force in nN)
Epoxy	39	8	21	84
Hydroxyl	-	6	~0	5

Force spectroscopy on four different surfaces i.e, unmodified surface, -CH3 surface, -COOH surface, epoxy surface using epoxy modified and hydroxyl modified (commercially available). Results indicate that epoxy modified functional groups have higher adhesion forces when compared to the hydroxyl modified functional groups.

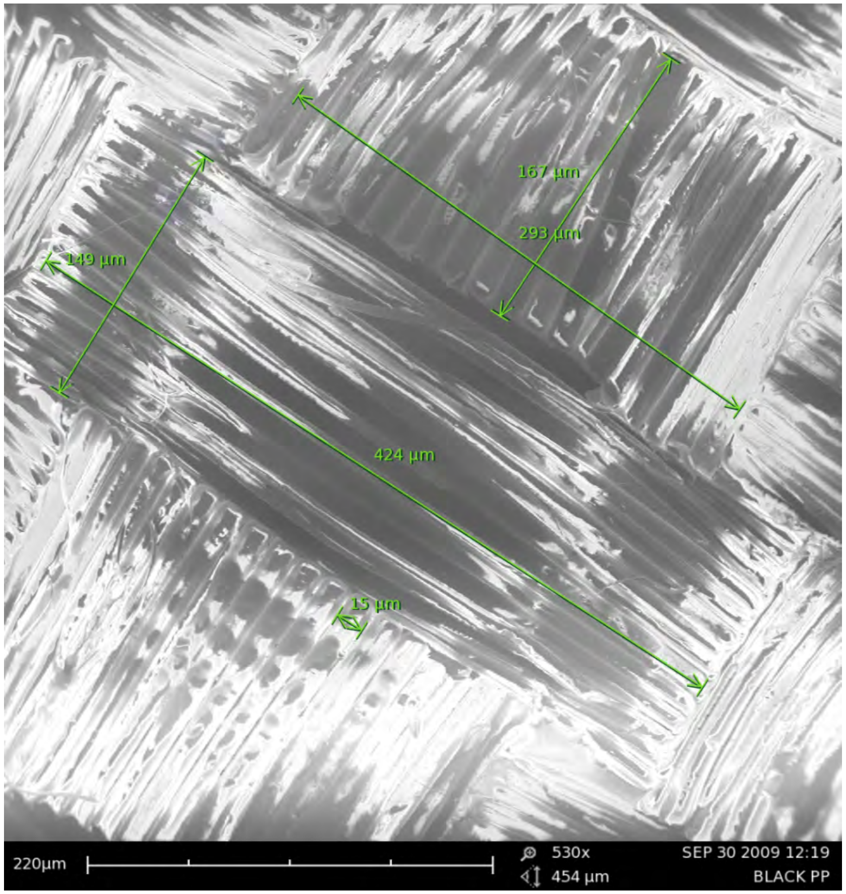
SEM Results





Polyester peel-ply sample showing fiber remnants

SEM Results



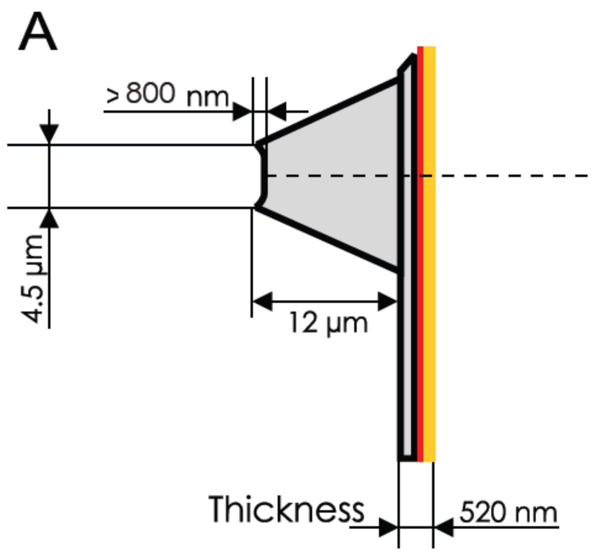
The diameter of the fiber imprint on the epoxy matrix is ~15µm

~7.5µm the depth

Imprint of polyester fibers on the epoxy matrix

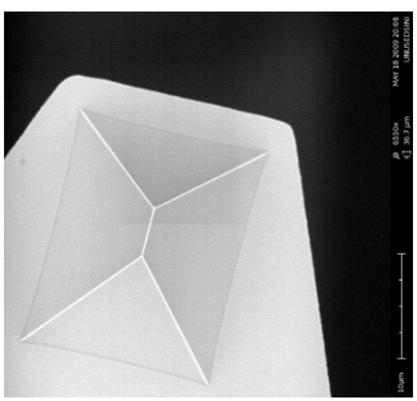
Note: The dimensions are approximately the same with nylon peel-ply samples

Dimensional Analysis



Area of contact for probe and composite surface

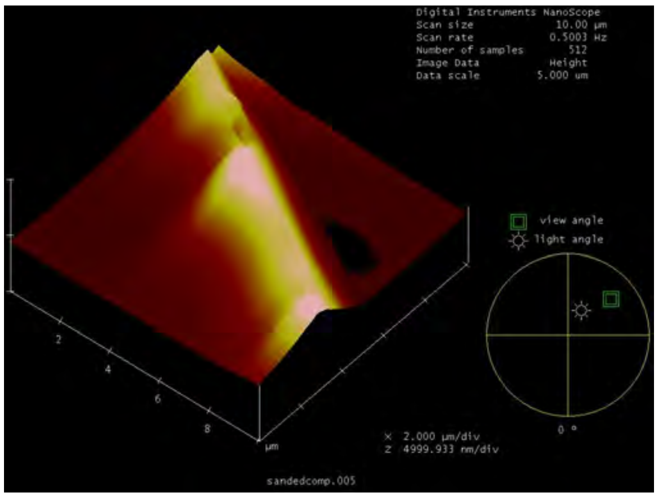
- AFM Z-range parameter will limit the topography range of operation
- Currently investigating other tips that will optimize scanning range



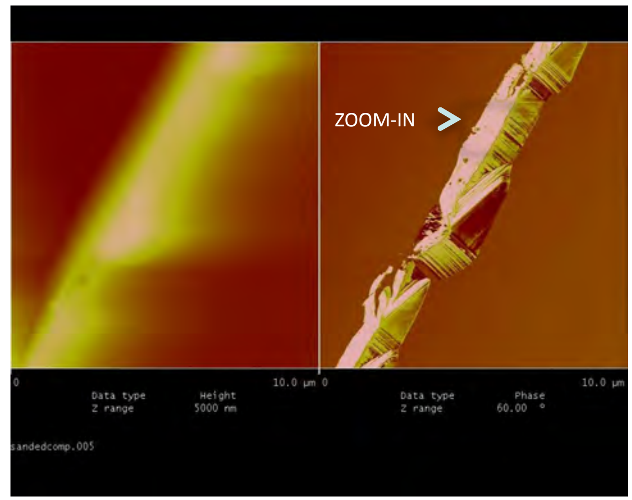
SEM- AFM TIP

AFM Composite Images

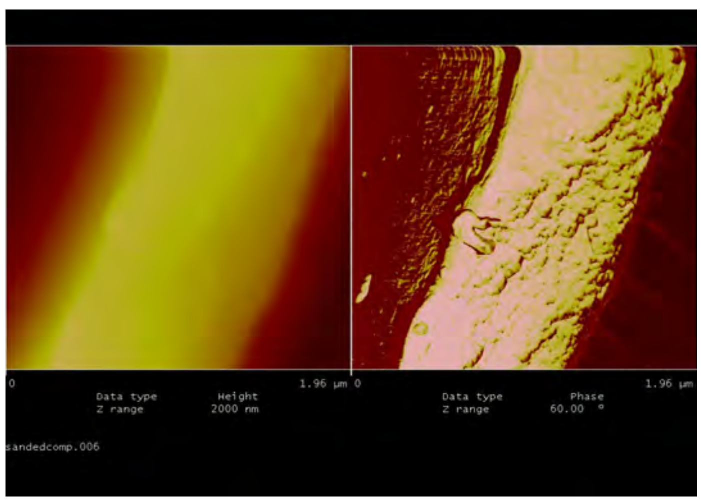
Polyester prepared peel-ply composite samples



3D Height Image



10 μm Height & Phase Image



2 μm Height & Phase Image

AFM – Environmental Effects

Day 1

Humidity	Temperature (C)	Tip No.	Mean of 50 adhesion force	S.D
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

Day 2

Humidity	Temperature (C)	Tip No.	Mean of 50 adhesion force	S.D
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

Trials were conducted with unmodified tips on a freshly cleaved mica wafer

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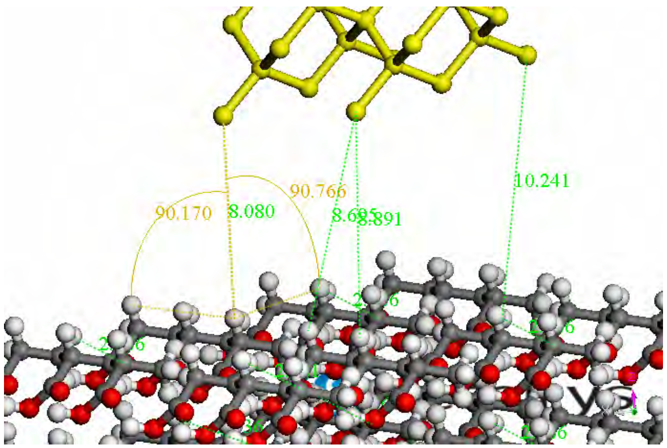
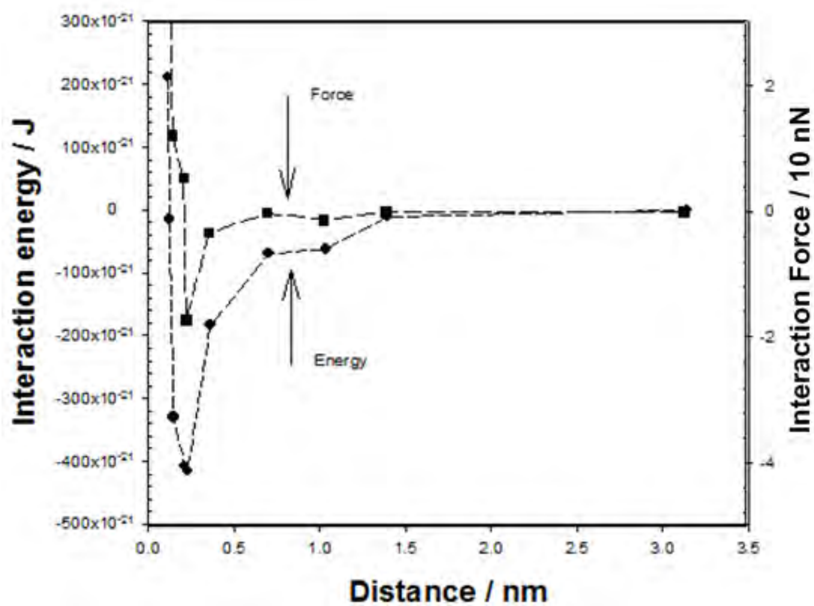
Quantum Chemistry Simulation of Force Spectroscopy

Quantum chemistry model of the interaction between Si tip (top) and epoxy sample (below). The relative positions and orientations of the Si tip of the AFM and the epoxy sample are defined in the model as shown.





Interaction energy and force spectra for a Si tip on an epoxy sample. For the non-functionalized tip, the maximum adhesion force is approximately 20 nN which is within the range of experimental results.

Future Work

- Developing signature peaks for various known contaminants (from XPS analysis).
- Establishing correlation between the electrochemical cyclic voltammetry and chemical essence of contaminants.
- Building a database of these signature peaks.
- Testing epoxy probe wear and tear.
- Testing epoxy probe on composite laminates with and without peel ply for surface contaminants.
- Theoretical analysis of the force spectroscopy.

Thank you!

Design of Epoxy Probe

Protocol

- Clean silicon or silicon nitride tips with ethanol for 5 minutes followed by rinsing with milli-Q water for 5 minutes.

↓

- Treat with a freshly prepared acidic mixture (H_2SO_4:H_2O_2) ratio 7:3 v/v for 15 minutes, followed by rinsing with milli-Q water for 5 minutes.

↓

- Dry in vacuum for 10 minutes to remove the water layer on the surface.

↓

- Treat with 2 % 3- Glycidoxypropyltrimethoxysilane (GPS) in dry toluene for 2 hrs.

↓

- Rinse with toluene, ethanol and milli-Q water for 3 minutes each.

↓

- Dry in vacuum for 1 hr and store in desiccators until use.