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

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The Joint Advanced Materials and Structures Center of Excellence

- **Motivation and Key Issues**
  - **Adhesive bonding has been used in the manufacture and repair as a direct competition to mechanical fasting.**
  - **Adherend surface preparation is a critical issue to the structural integrity and durability of bonded structures.**
- **Objective**
  - **benchmark surface preparation quality assurance methods**
  - **identify and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.**
- **Approach**
  - **Literature review and analysis**
  - **Surface chemistry analysis**
  - **Electrochemical sensor development**
  - **Experimental validation**

FAA Sponsored Project Information

- Principle Investigators & Researchers
  - Xiangyang Zhou, Richard Burton
  - Rajiv Srivastava, Dwayne McDaniel, Weihua Zhang, Wongbon Choi,
  - Sam Hill, Yao Ge, Shejie Tang, Ling Wang (Graduate Students)
- FAA Technical Monitor

  Curtis Davies
- Industry Participation
  - **DME Corporation**
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Main Results

- Literature database
- Summary of literature review
  - Surface treatment
  - Surface chemistry analyses
- An electrochemical sensor for surface chemistry analysis
- Novel carbon nanotube sensor for humidity sensing
- AFM study of the peel plies

Research Roadmap

Information collection and analyses	→	Strength & durability versus surface pretreatment
		↓
Chemical analyses	→	Surface analysis criteria
		↓
Information collection and analyses	→	Candidate field analysis technologies
		↓
Technology validation	→	Effective field analysis technology

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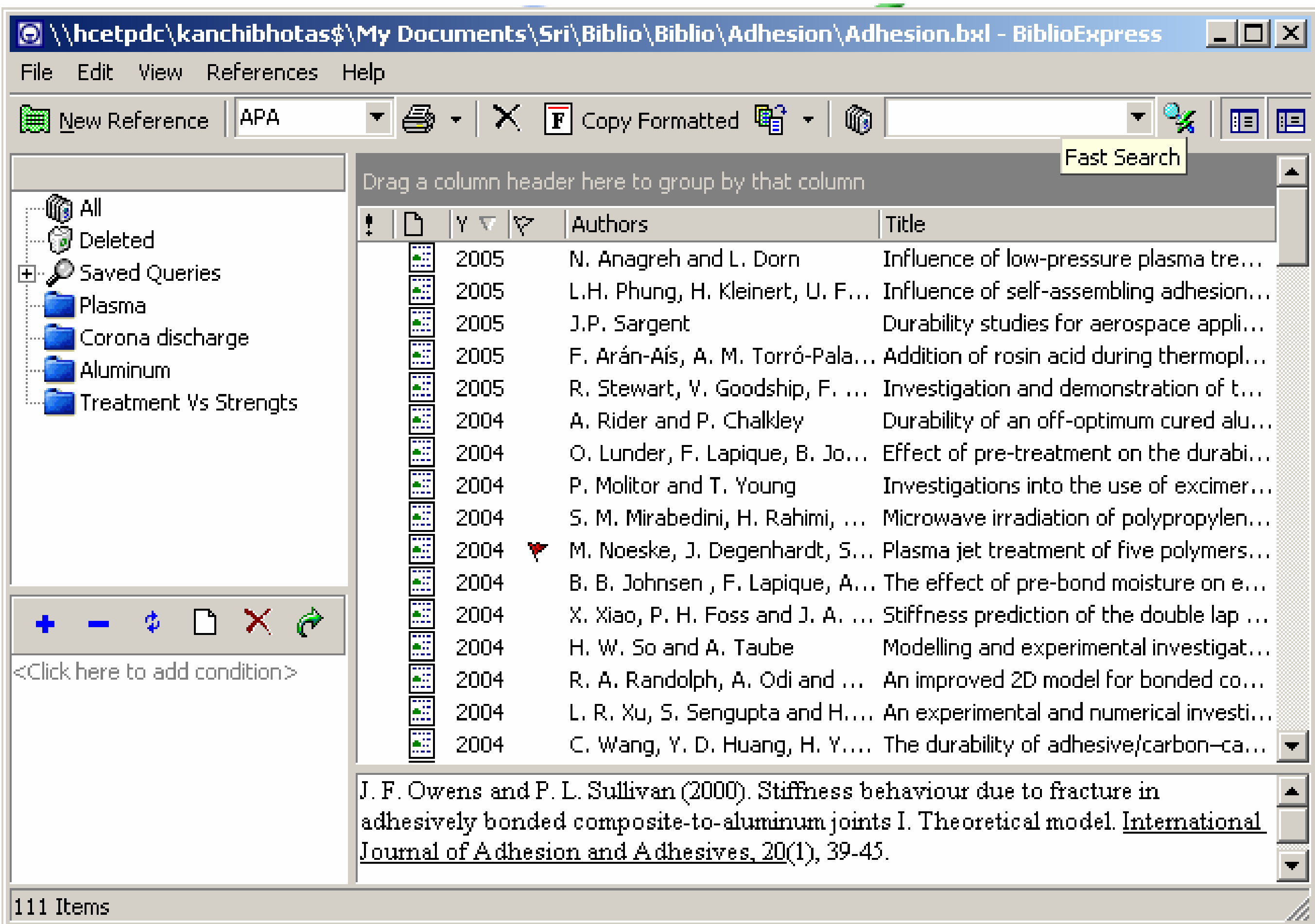
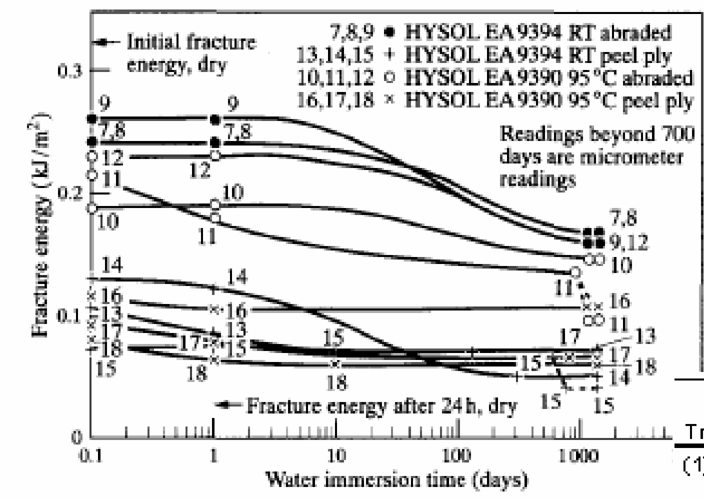
Literature Database



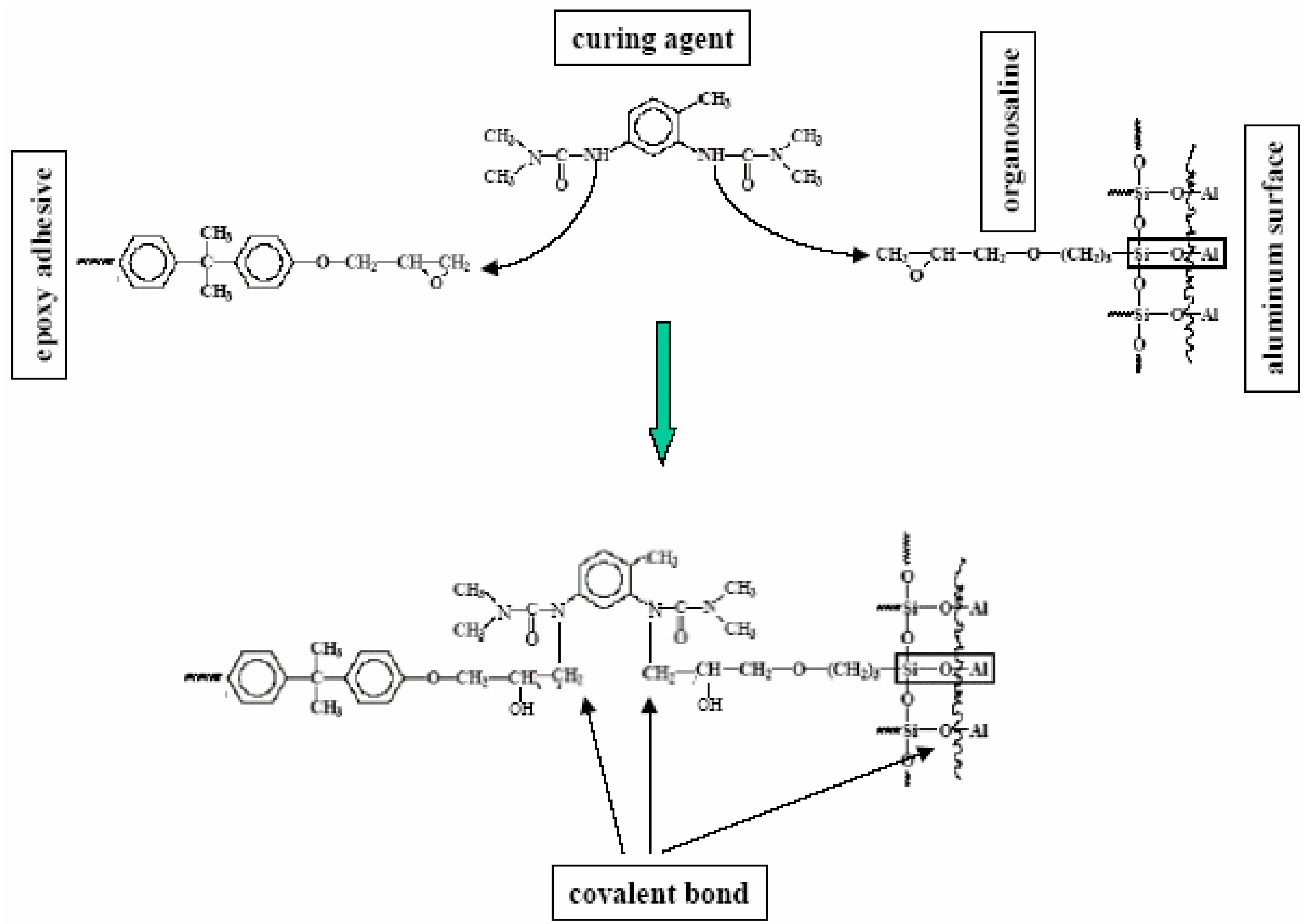
Effect of Various Surface Pretreatment Method



Treatment type	Material	Nature of treatment	Surface tension	Surface roughness	Surface chemistry	Bond strength	Durability
(1) Abrasion and solvent wipe	Thermoset and thermoplastic	Remove mold release		Y		Increased found for thermosets	Good for thermosets
(2) Grit blasting	Thermoset and thermoplastic	Remove mold release		Y		Increased found for thermosets	Good for thermosets
(3) Acid etch	Thermoset and thermoplastic	Etcha	Y		Y	Slight increase	Poor
(4) Peel-ply	Thermoset	Remove mold release		Y		Increase	Good
(5) Tear-ply	Thermoset	Remove mold release				Increase	Good
(6) Corona discharge	Thermoplastic	Oxidising	Y		Y	Double	Good (90 days)
(7) Plasma treatment	Thermoplastic	Ablation and/or oxidation[a]	Y	Y	Y	Increase	Good (90 days)
(8) Flame treatment	Thermoplastic	Oxidasing[a]	Y			Increase	
(9) Laser treatment	Thermoset and thermoplastic	Ablation and or oxidation		Y	Y	Increase	More research is necessary

[a]Depends on polymer matrix material. Y - Yes

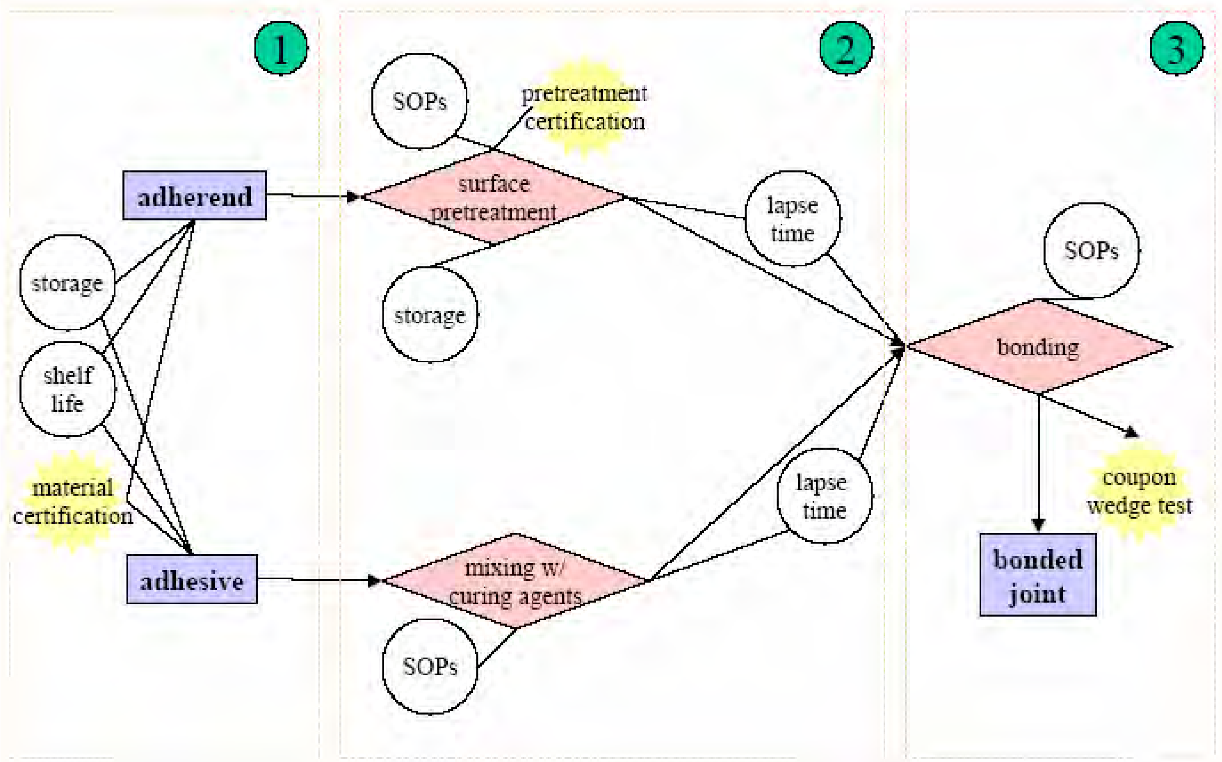
Covalent bond formation between adherend and adhesive-Effect of Surface O- and N- Functional Groups (Anchor Groups)



Concentration of O versus Strength

Polymer	Treatment	Surface composition (at%)		Failure load/N
		C	O	
HDPE	No treatment	100.0	0.0	400
	2.1 V, Pt edge, 50 passes	95.5	4.5	1330
	2.4 V, Pt edge, 50 passes	96.2	3.8	1320
	2.9 V, Pt disc, 5 min	92.4	7.6	1110
PP	No treatment	100.0	0.0	0
	3.25 M nitric acid, 60 s	—	—	267
	2.1 V, Pt edge, 50 passes	92.6	7.4	2060
	2.4 V, Pt edge, 50 passes	93.1	6.9	2560
	2.9 V, Pt edge, 50 passes ($H_2SO_4^-$)	100	0	50
	2.9 V, Pt disc, 300 s, not touching	—	—	270
	2.9 v, Pt disc, 300 s, far removed	—	—	390
SBS	No treatment	100.0	0.0	—
	2.5 V, Pt edge, 50 passes	83.6	14.6[b]	—
PS	No treatment	100.0	0.0	550
	2.9 V, Pt disc, 300 s	94.5	5.5	670

Quality Control

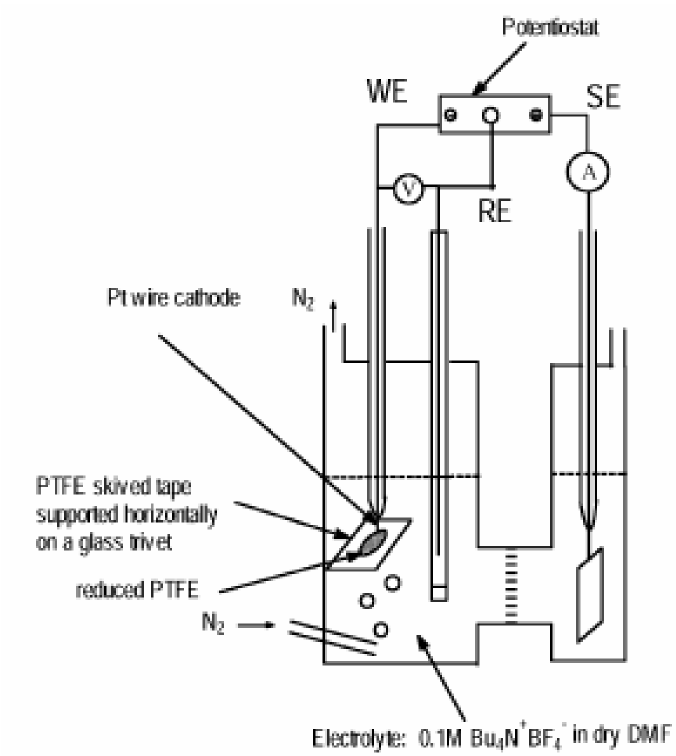


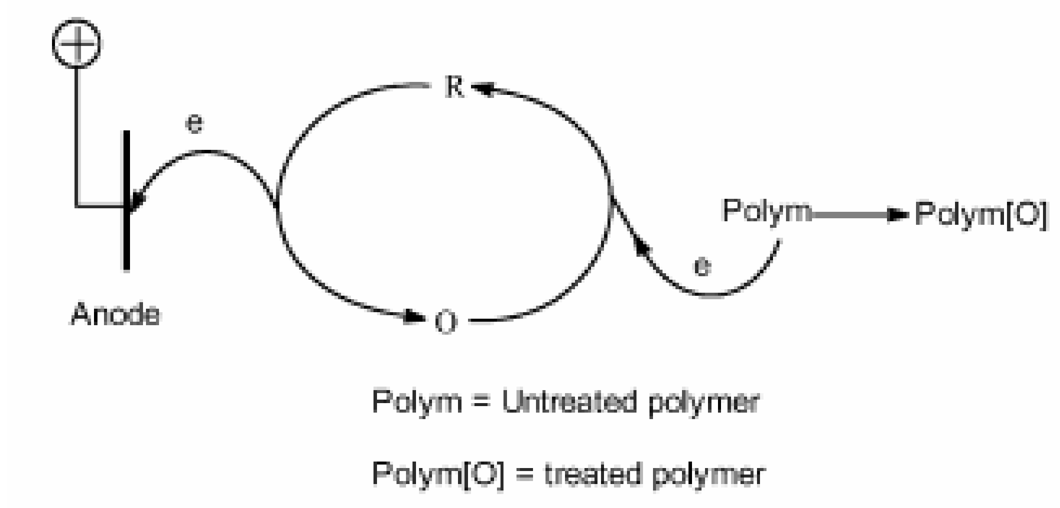
- **Materials certification,**
- **Pretreatment certification**
- **Adhesive application certification,**
- **Bonding certification,**
- **Technician certification,**
- **Process flow management**

$$N_{adsorbed} < N_{adsorbed}(critical)$$

$$N_{O-\&N-} > N_{O-\&N-}(critical)$$

Electrochemical Sensor



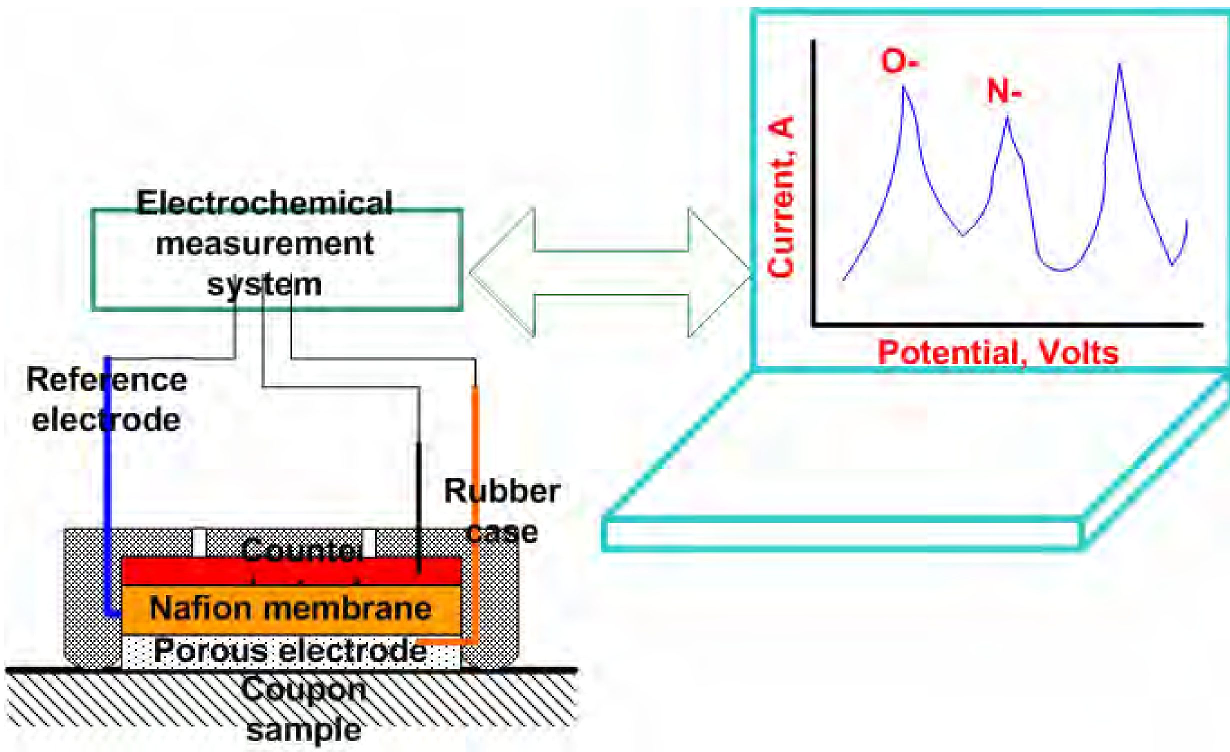


XPS analysis of unformulated elastomers before and after electrochemical treatment

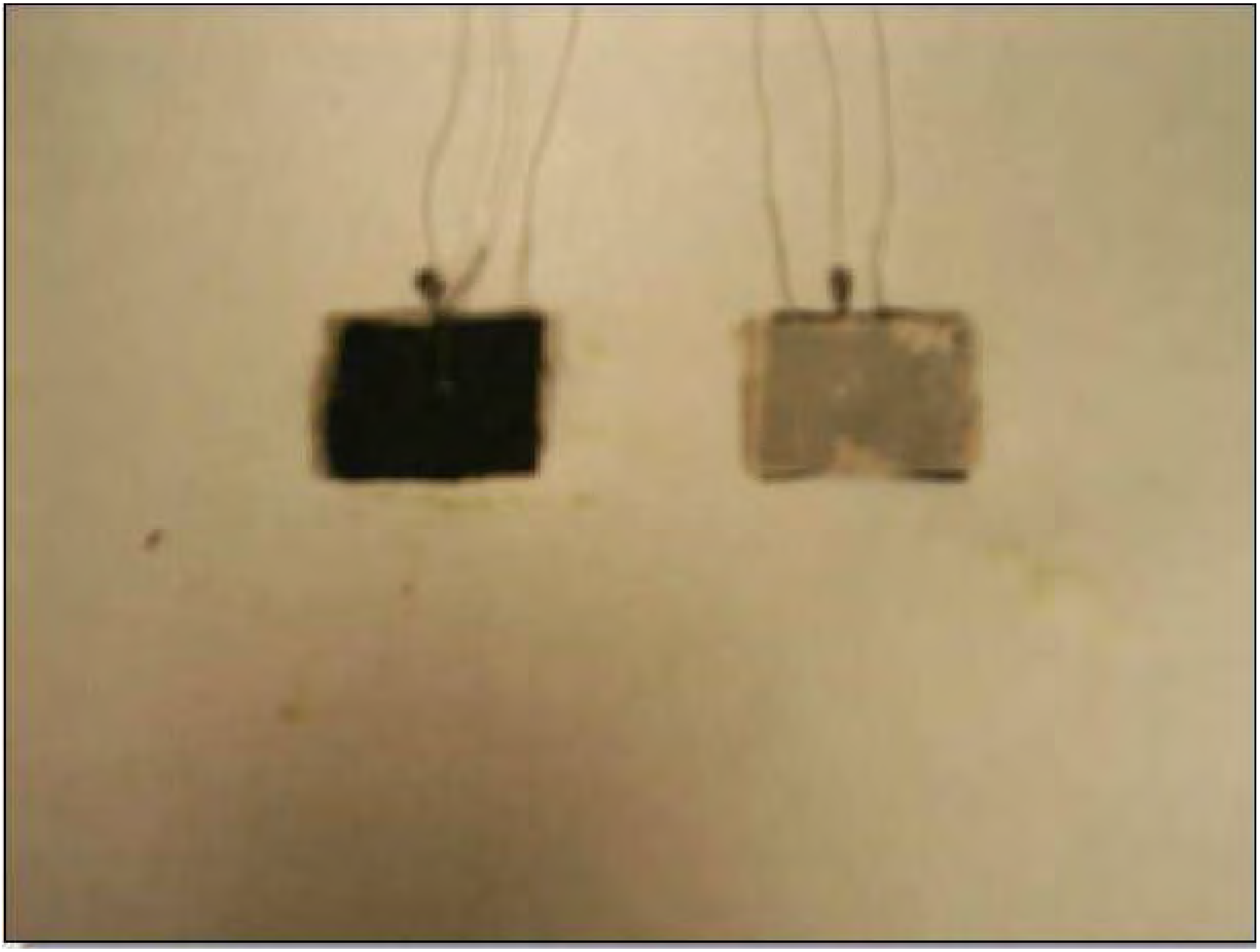
Sample	Treated[a]	Surface composition (at%)		
		C	O	N
SBS	No	97.9	1.4	—
SBS	Yes	83.9	13.8	2.3
SBR	No	94.5	5.5	—
SBR	Yes	83.7	15.8	0.2

D.M. Brewis, R.H. Dahm / International Journal of Adhesion & Adhesives 21 (2001) 397–409

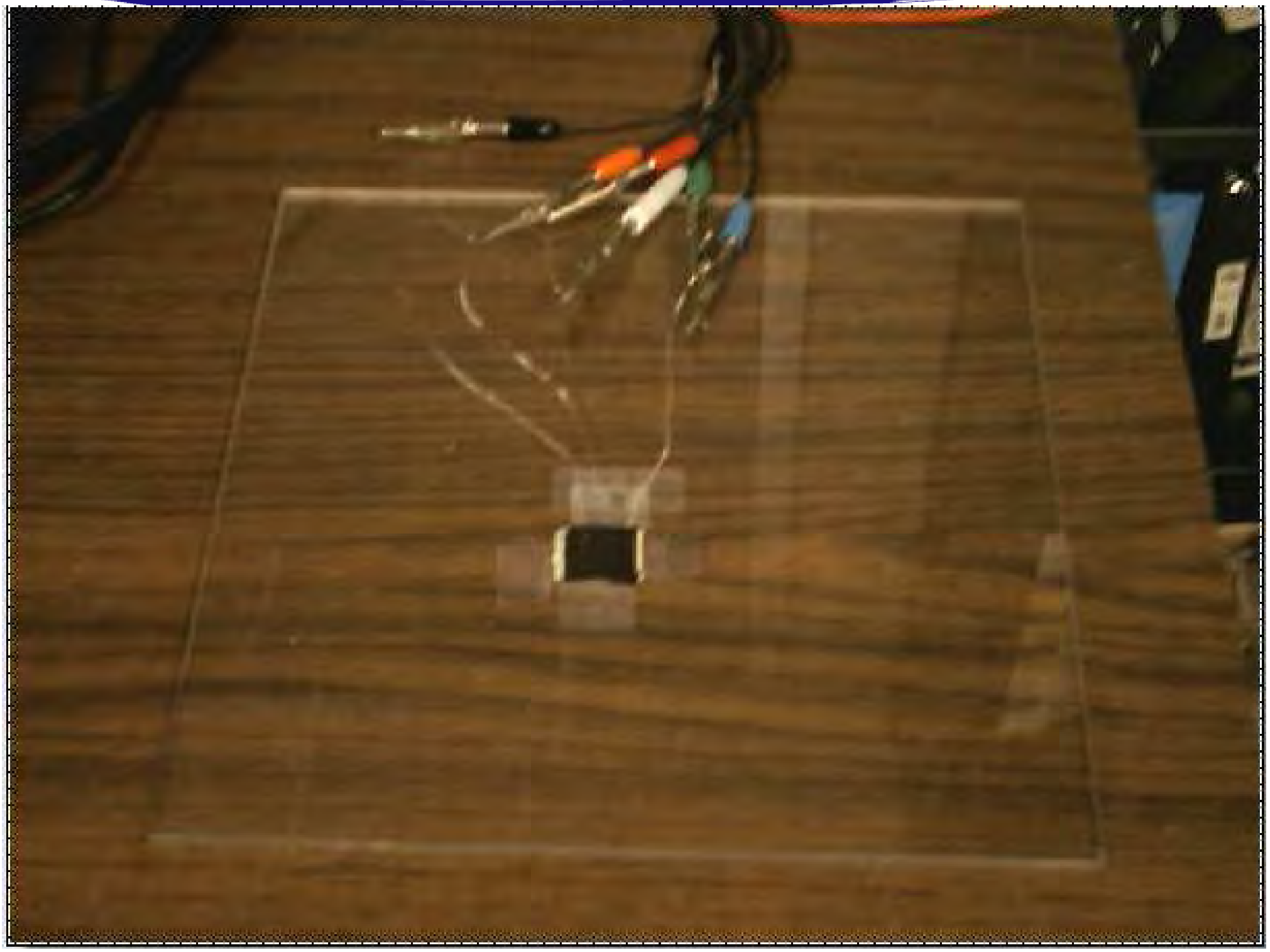
Solid-State Electrochemical Sensor



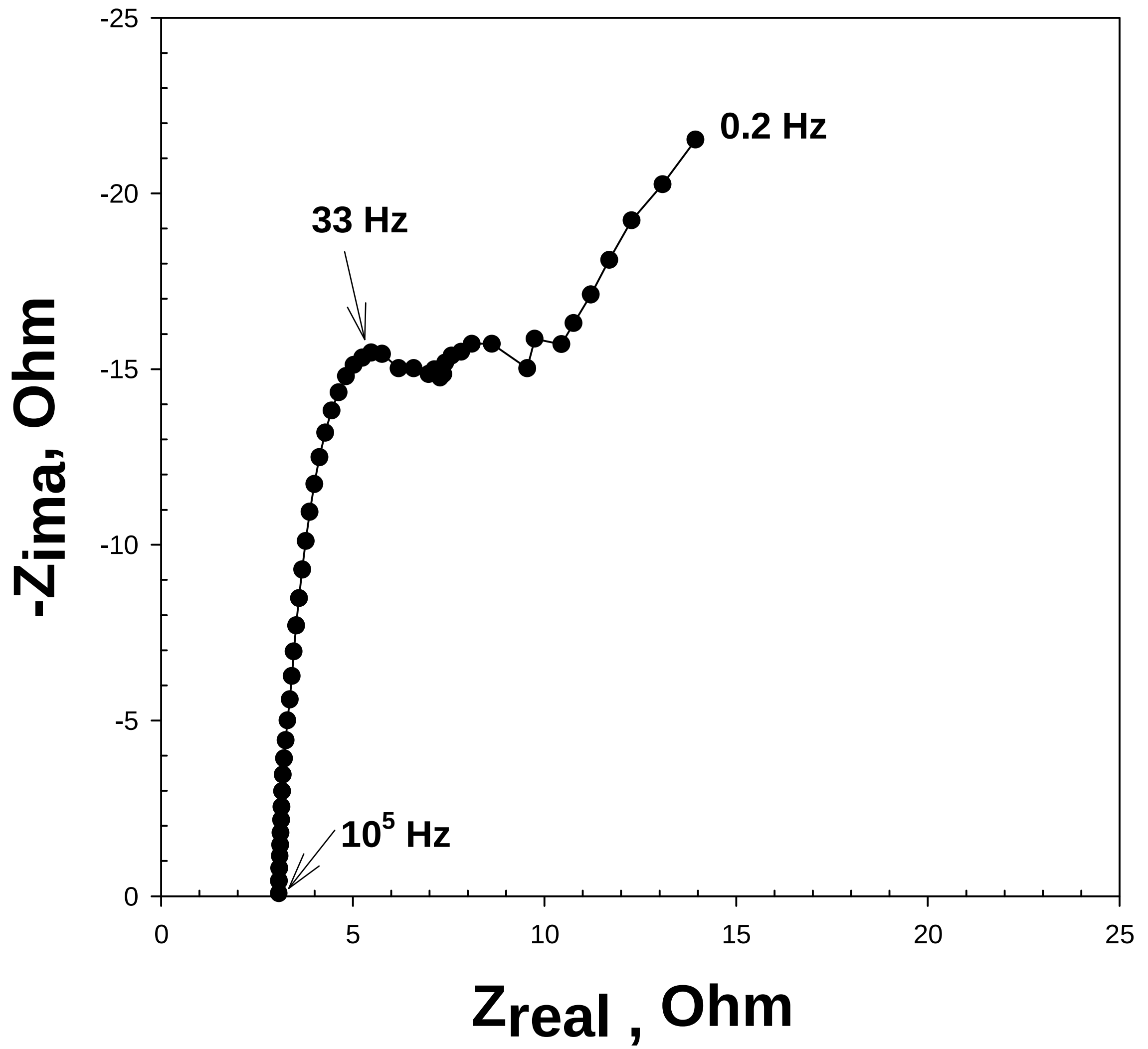
Solid-state Electrochemical Sensor



Solid-state Electrochemical Sensor



Test results



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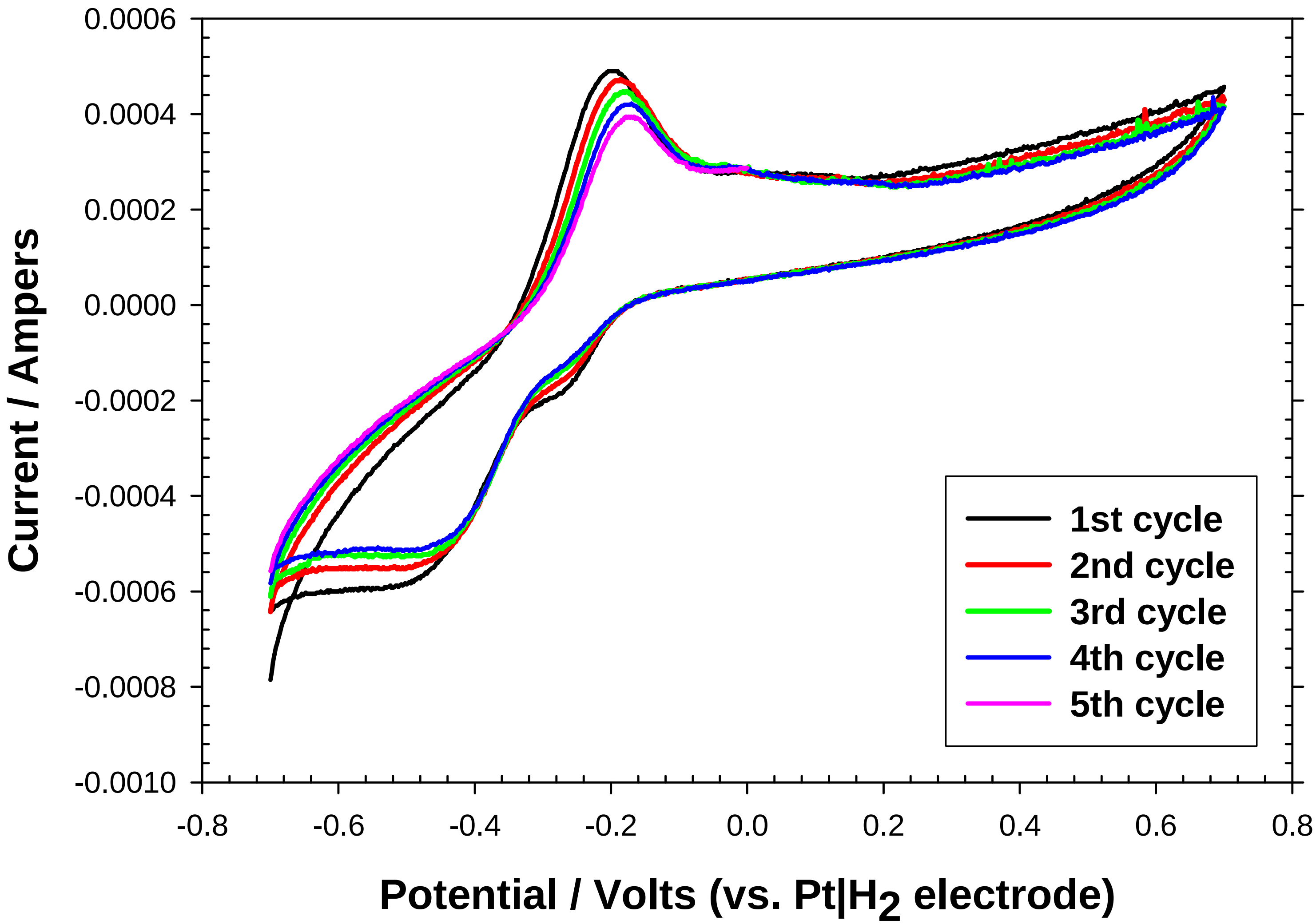
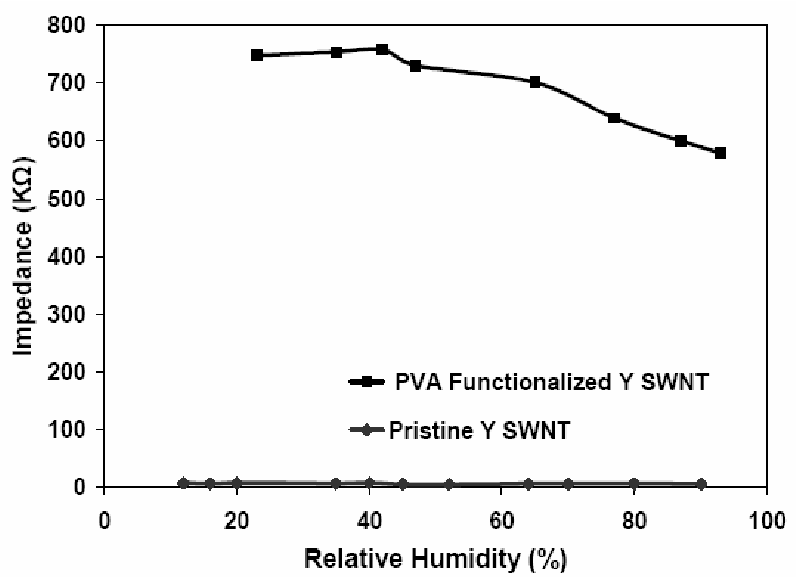
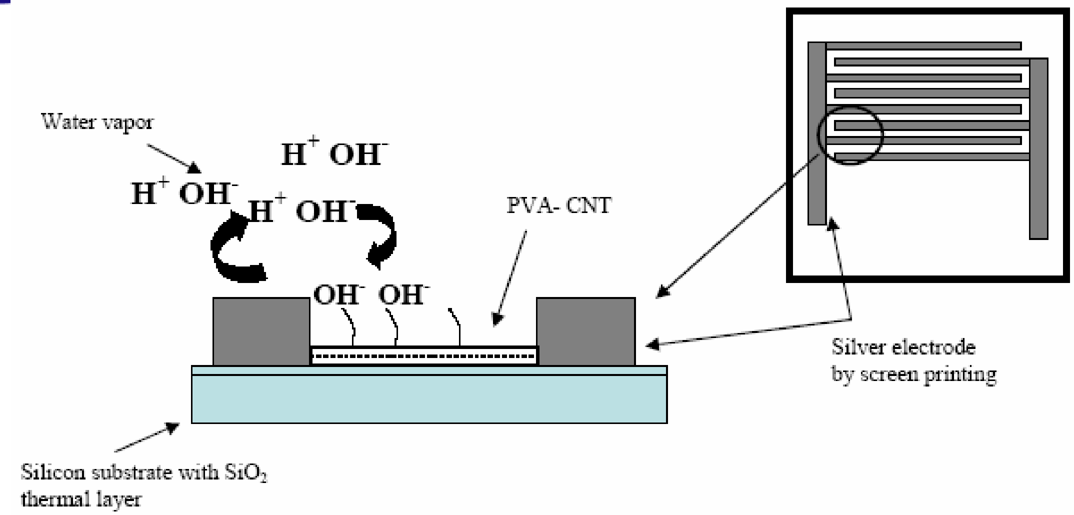
Test Results

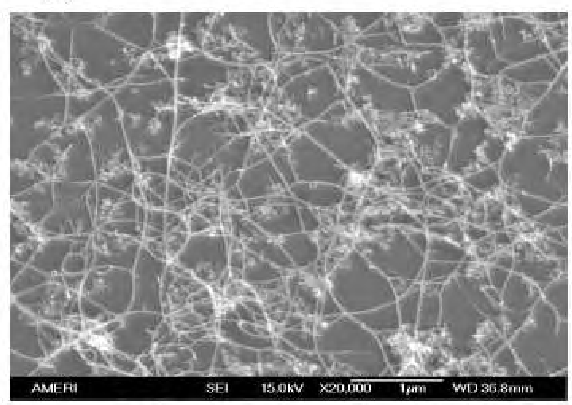


Carbon Nanotube Based Humidity Sensor

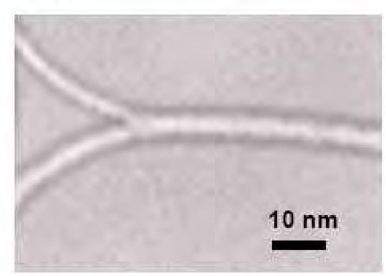




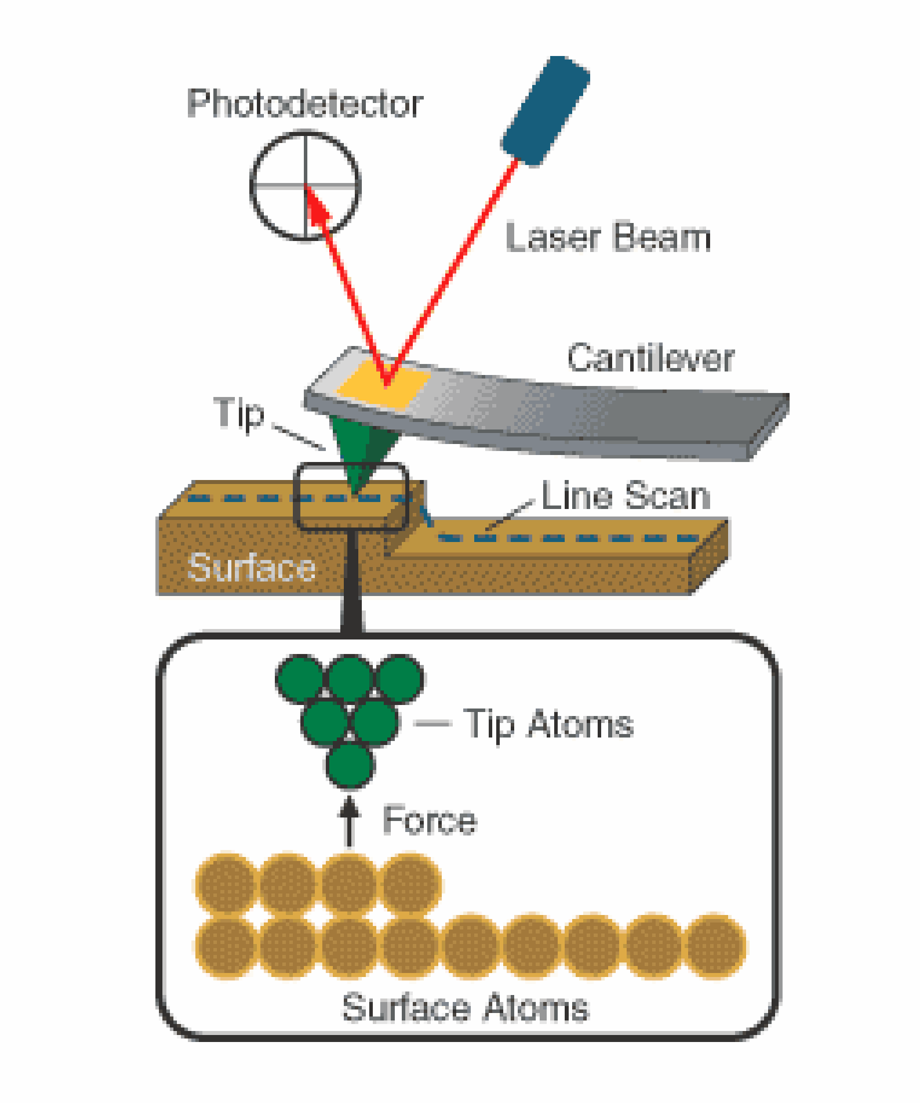
(c)

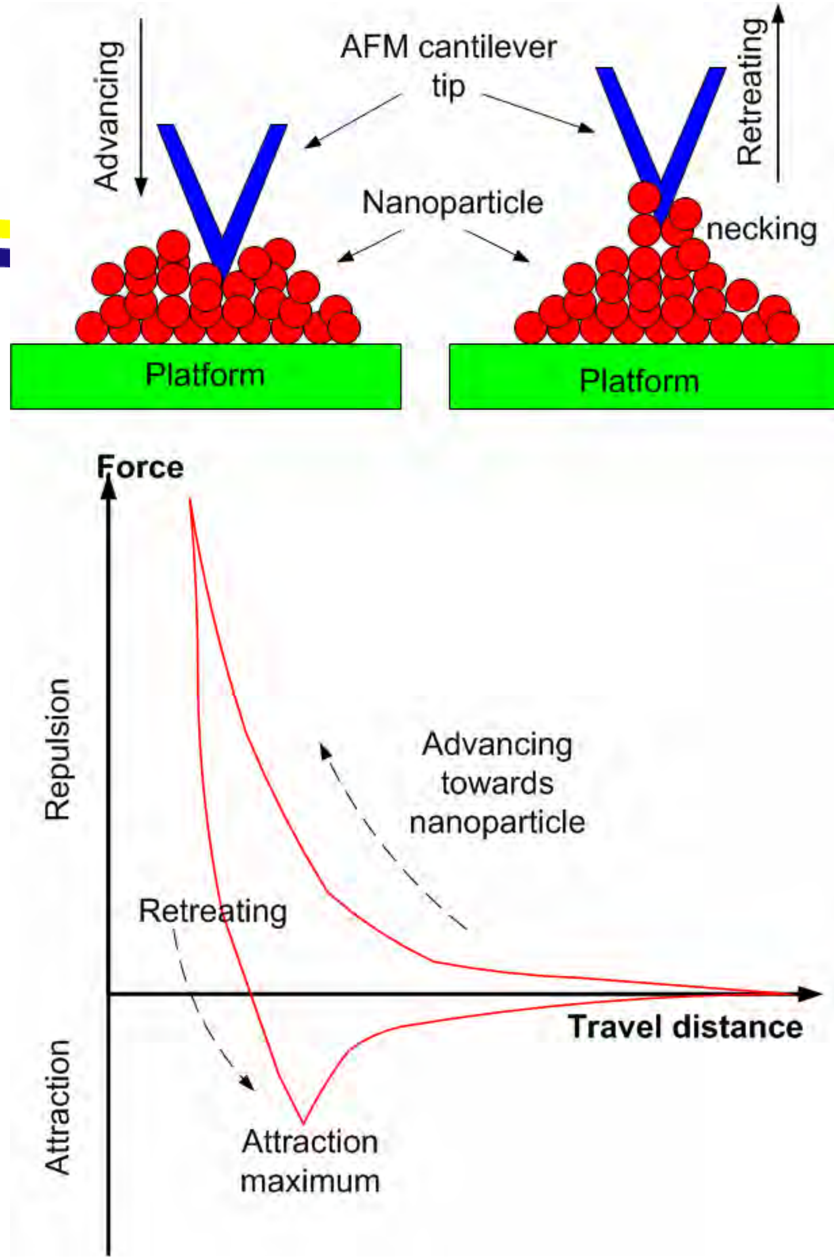


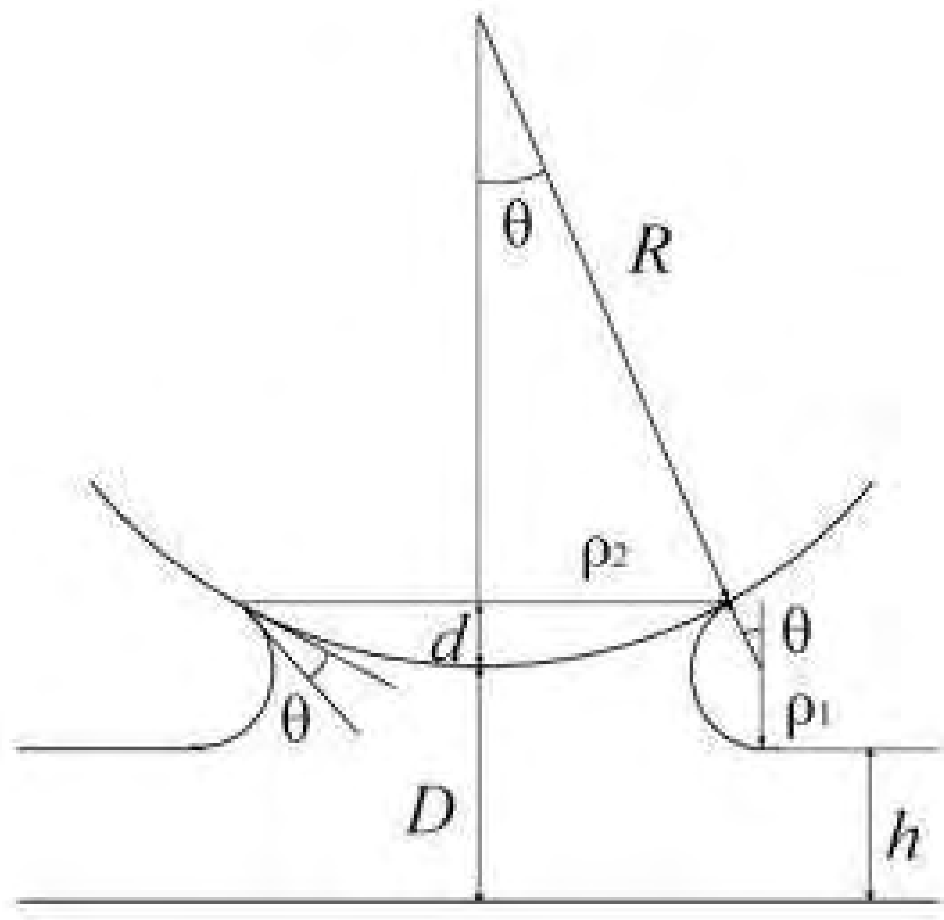
(d)



Atomic Force Microscopy Study of Peel Ply




Advancing
AFM cantilever
tip
Retreating
Nanoparticle
necking
Platform
Platform
Force
Repulsion
Attraction
Advancing
towards
nanoparticle
Retreating
Travel distance
Attraction
maximum



$$\sigma = \frac{F_{\max}}{4\pi R\cos\theta}$$

Atomic Force Microscope

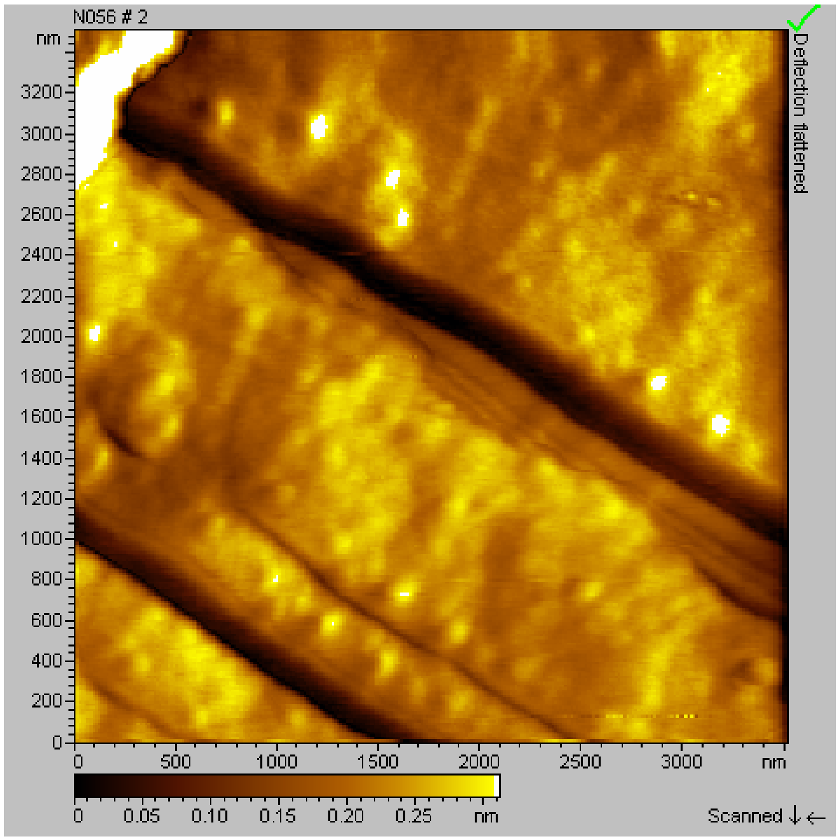
Previous SEM and XPS Results on Peel Ply Surfaces

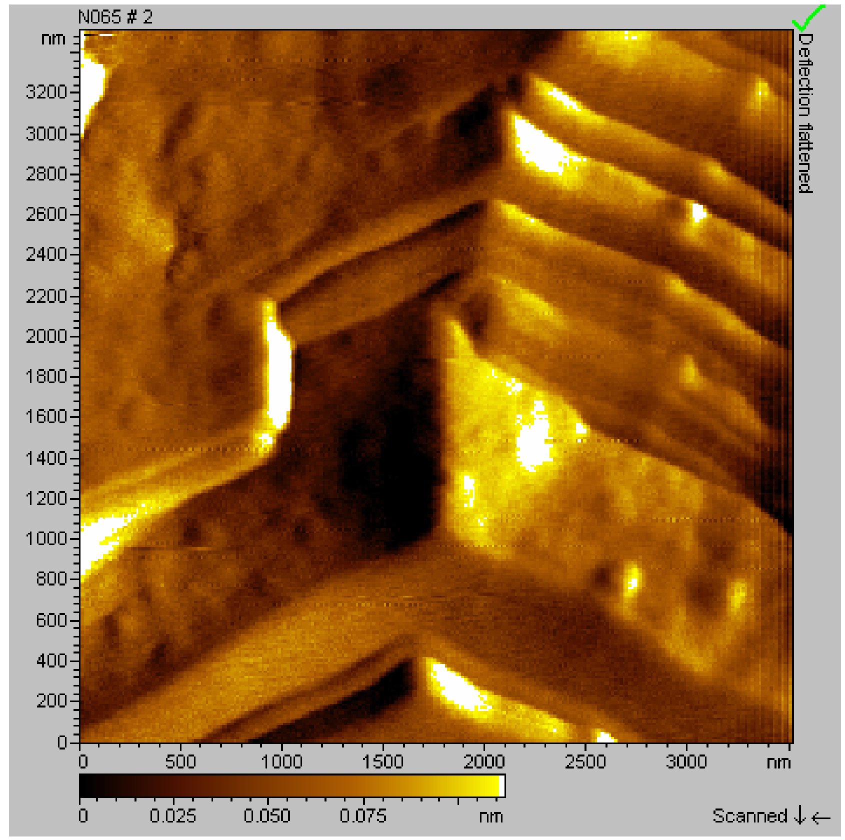
- **Polyester (PF 60001): No transfer, strong bonds**

- **SRB (PF 60001): Siloxane coating transfer, weak bonds**

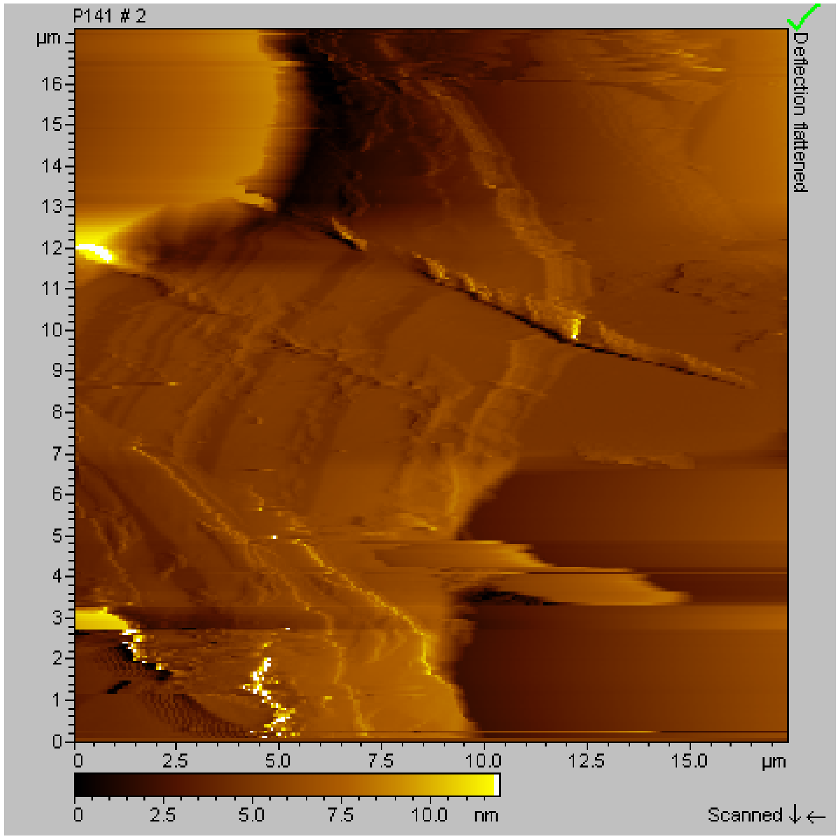
- **Nylon (PF 52006): Fiber transfer, bond strength depends on adhesive**

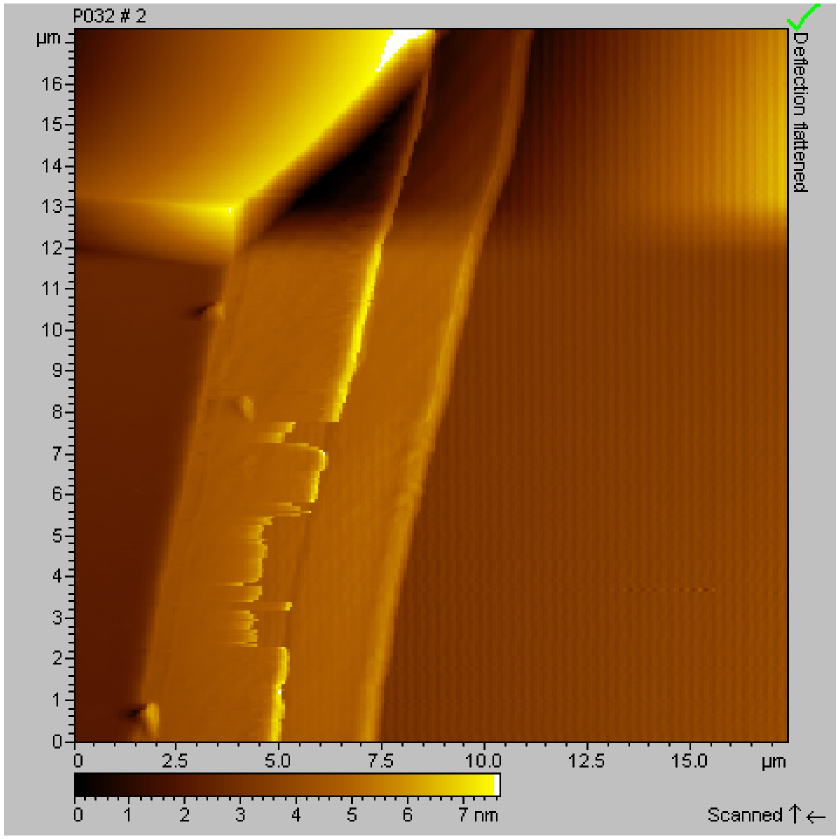
Nylon Peel Ply Surface



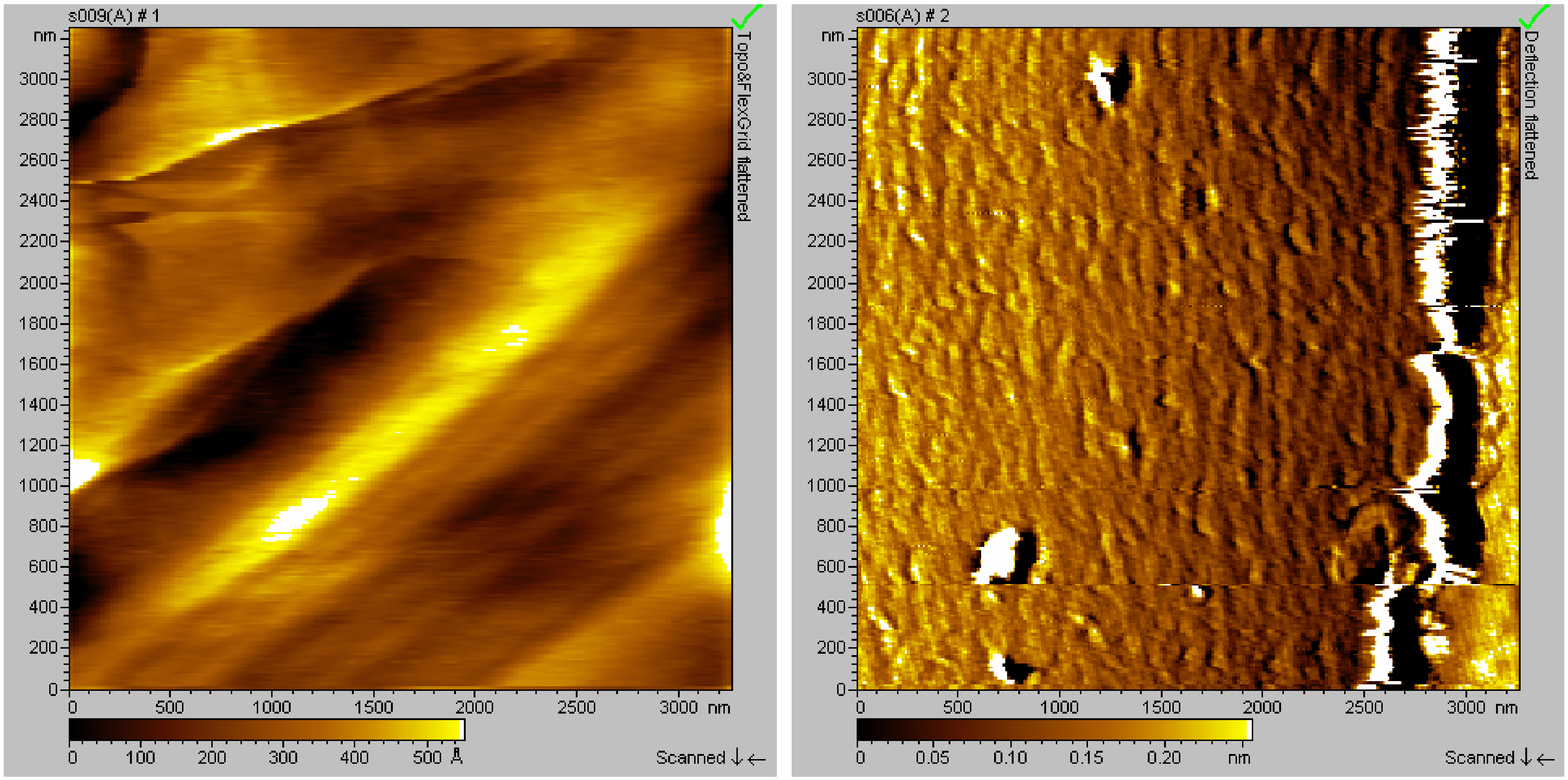


Polyester Peel Ply Surface

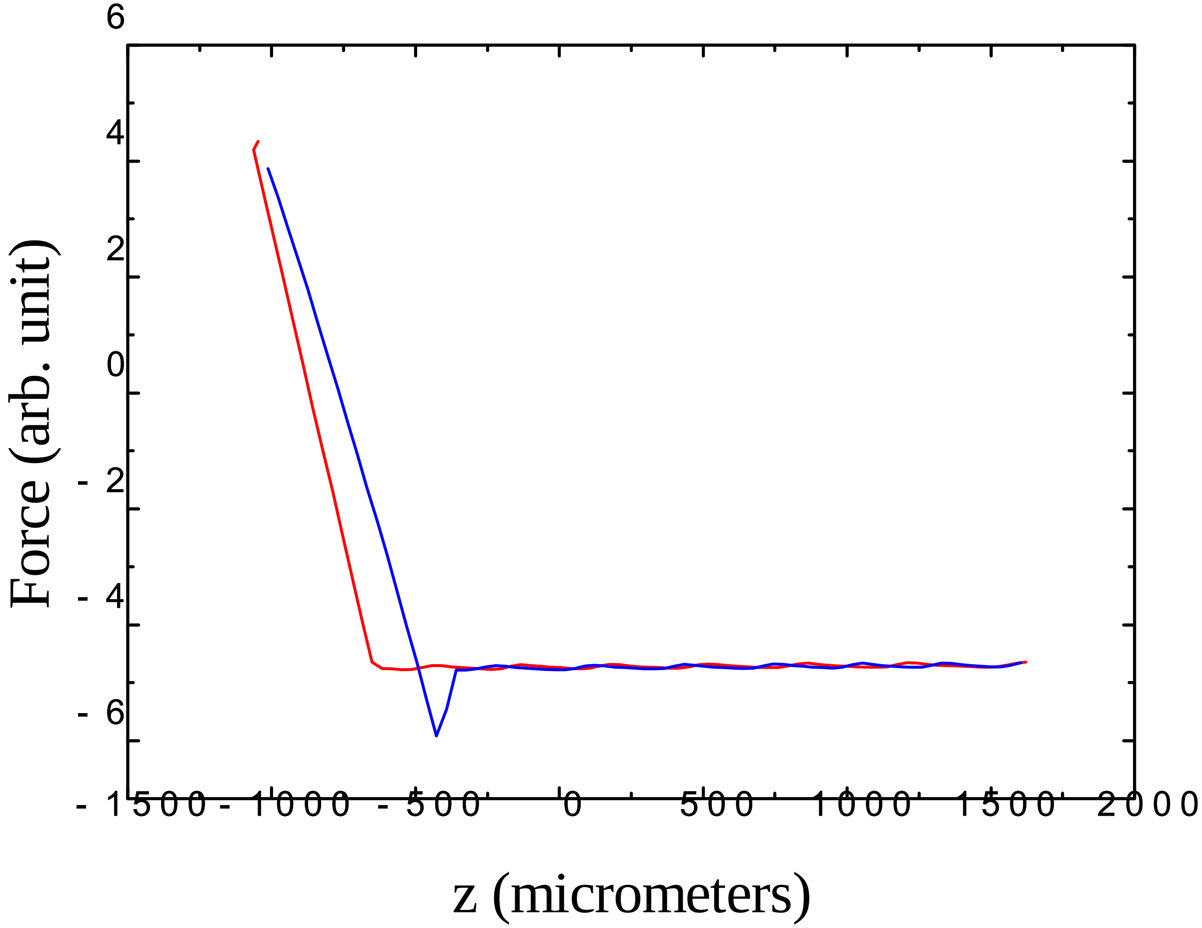




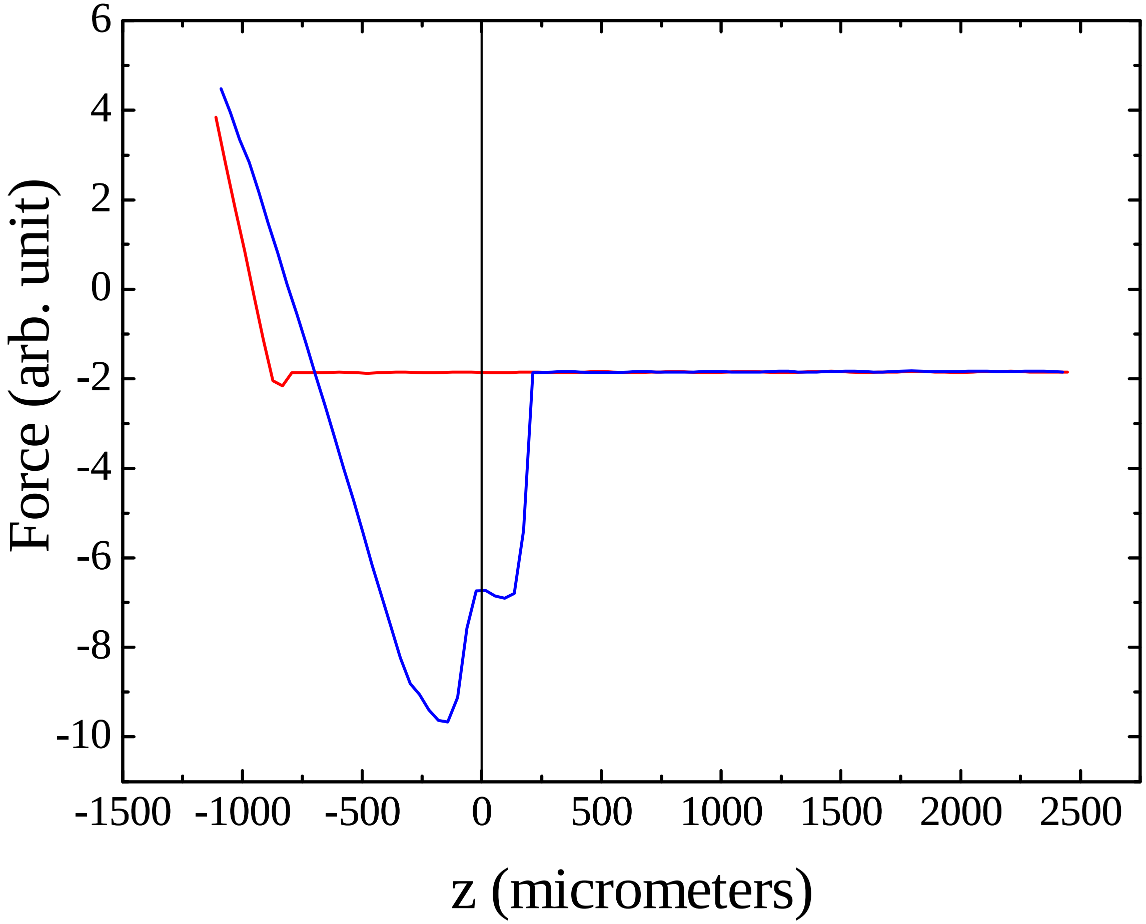
SRB Peel Ply Surface



Force vs. distance for nylon peel ply surface



Force vs. distance for SRB peel ply Surface



Conclusions

- Certification of pre-bond surface preparation quality requires implementation of effective surface chemistry inspection technologies for each and every step of the surface preparation procedure to ensure the strength and durability of the bonded aviation structures.
- Solid-state electrochemical sensor is a promising candidate technology for in-field surface chemistry analysis

Conclusions

- No sign of contamination was found on polyester peel ply surface
- Some small size particles were found on nylon peel ply surface
- Some contaminating particles were found on SRB peel ply surface
- The SRB surface shows a more complicated force spectrum than the nylon peel ply surface.

A Look Forward

- Benefit to Aviation
  – Better understanding of the pre-bond surface preparation methods
  – Better understanding of bond strength and durability versus surface preparation
  – Novel in-field, online certification and assurance technology for surface preparation
  – Reduced costs for surface preparation and adhesive bonding processes
- Future needs
  – In-field, online analytical detection and monitoring technologies for manufacture, chemical, environmental, and energy industries.