Methods for the Evaluation of the Fitness of Fiber Reinforced Composite Surfaces for Subsequent Adhesive Bonding

Bill Stevenson

Dept. of Chemistry

Wichita State University

Methods for the Evaluation of the Fitness of Fiber Reinforced Composite Surfaces for Subsequent Adhesive Bonding

- **Motivation and Key Issues**
- **With user safety in mind, the FAA has determined to coordinate and lead an effort to improve our understanding of current composite bonding methodology in the commercial aerospace and scientific community, with special emphasis on surface preparation and characterization prior to the bonding event.**
- **Objectives**
- **To develop nondestructive analytical techniques for application to the analysis of prebonded CF reinforced composite surfaces on the shop floor that can be used to support a decision to "go ahead" and bond the part or "stop" and have it re-cleaned, dried, or cured further prior to bonding**
- **To integrate these techniques of analysis into the joint FAA/NIAR scarf repair project to develop insights into the influence of surface contaminants on the integrity of composite patches for very thick CF reinforced composite laminates to be used in primary load bearing applications in next generation aircraft**

- **Approach - Techniques of analysis**
- **Contact angle measurement - Overall fitness for bonding**
- **Near Infrared Spectroscopy – Water**
- **Laser desorption – mass spectroscopy - Specific surface contaminents such as jet fuel, hydraulic oil, etc.**

FAA Sponsored Project Information

- **Principle Investigators & Researchers**
  - **William Stevenson, Irish Alkalen, Laura Stevenson, Michael VanStipdonk, Dennis Burns (Chemistry, Wichita State University) Chemical analysis**
  - **Lamia Salah, John Tomblin (National Institute for Aviation Research – NIAR, Wichita State University) Sample design, fabrication, mechanical testing, design of and interpretation**
  - **Charles Yang (NIAR & Aeronautical Engineering, Wichita State University) Finite element analysis**
- **FAA Technical Monitor**
- **Curt Davies**
- **Other FAA Personnel Involved**

  Larry Ilcewicz
- **Industry Advisory**
- **Michael Borgman, Robert Bohaty**

Water by near IR Spectroscopy

- Dissolved – entrained water in the composite will migrate to the surface and produce a poor bond.
- Even if the surface is dried by transient heating, water can migrate from the bulk to the surface to cause a poor bond
- Infrared spectroscopy can detect water if signals from water and hydroxyl groups in the resin can be separated – near infrared spectroscopy
- Instrument makers will custom build near IR configurations for the shop floor

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•Phase I (Dec 2005) goal

- To have a working Integrating Sphere diffuse reflectance Near IR system in place to analyze surface treated composite samples for water content

Progress: Completed

- Integrating sphere module was custom built to fit Nexus spectrometer.
- Hardware and software "glitches" were solved.
- Preliminary testing indicated that water in high performance composites containing Toray T-800 fibers can be observed by this method

Phase II (2006) goals

- To produce calibration curves relating spectrum to water content in epoxy resin based composite systems

Progress: Completed

- Calibration curves have been constructed for…
- A medium performance epoxy resin
- A high performance epoxy resin
- A carbon fiber reinforced composite containing the same high performance epoxy resin

Phase III (2006-07) goals

To integrate this technique into the joint FAA/NIAR scarf repair project to characterize "conditioned" repair surfaces made from high performance composite prior to repair layup for water content at and near the scarfed surface

Progress: To commence this summer

Background Info

Combination stretching/deformation band

@ 5215cm^{-1} $\nu_{assym} + \delta_{in\ plane}$

Pro's

Free of interference from resin hydroxyls

Quantitative measure of water

Con's

Little info on state of water in resin

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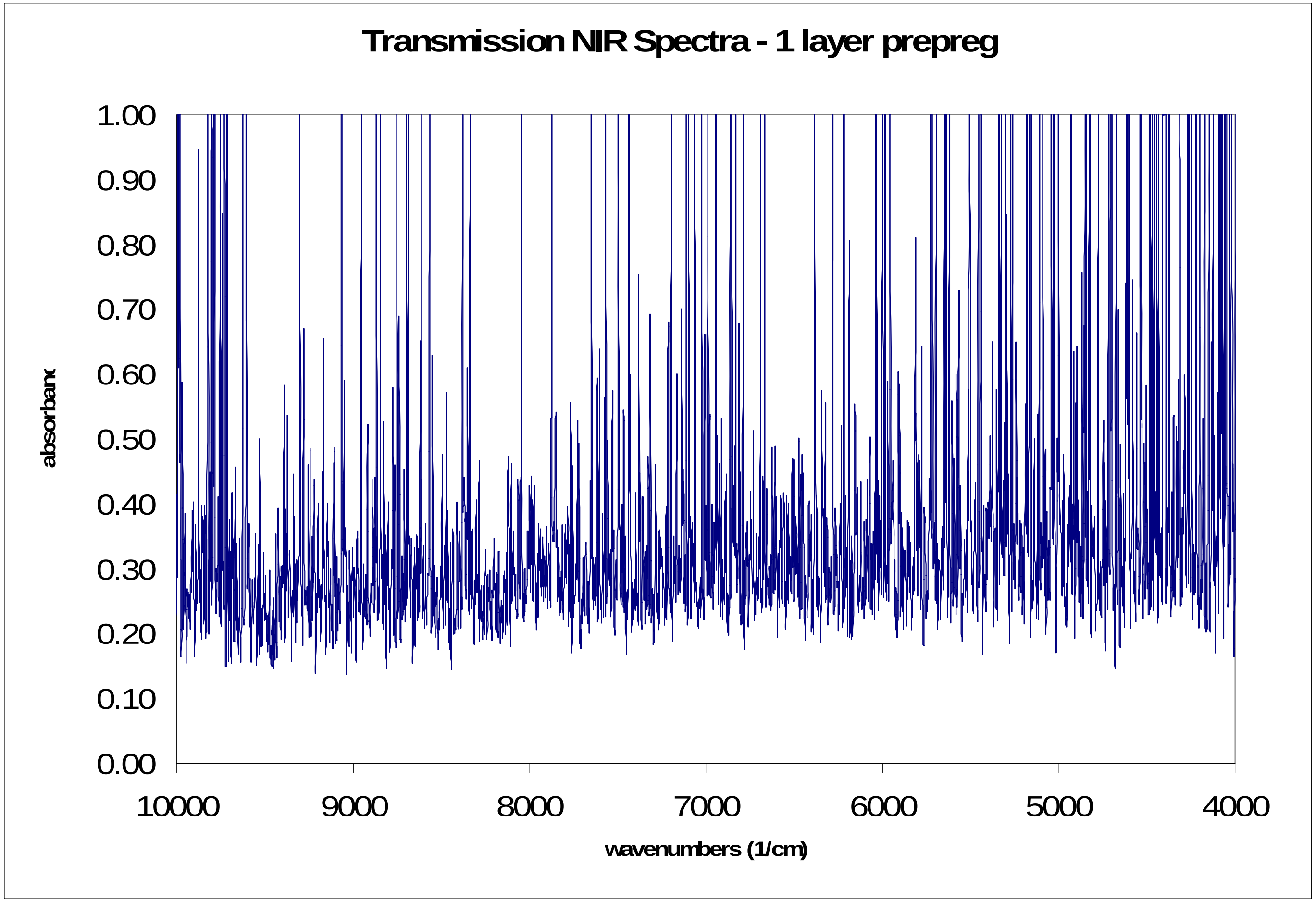
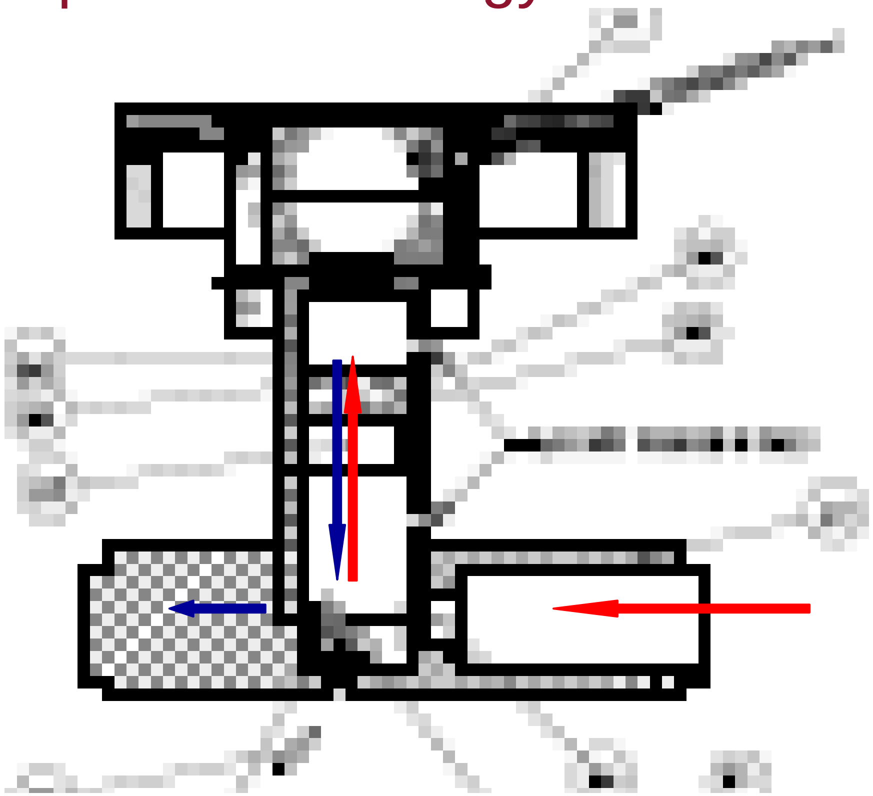
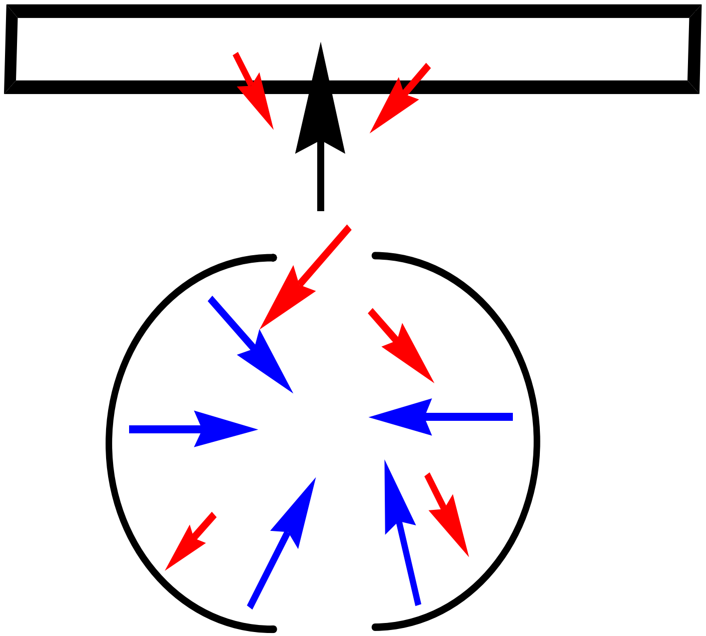
Unfortunately near IR spectroscopy of composites does not work in transmission



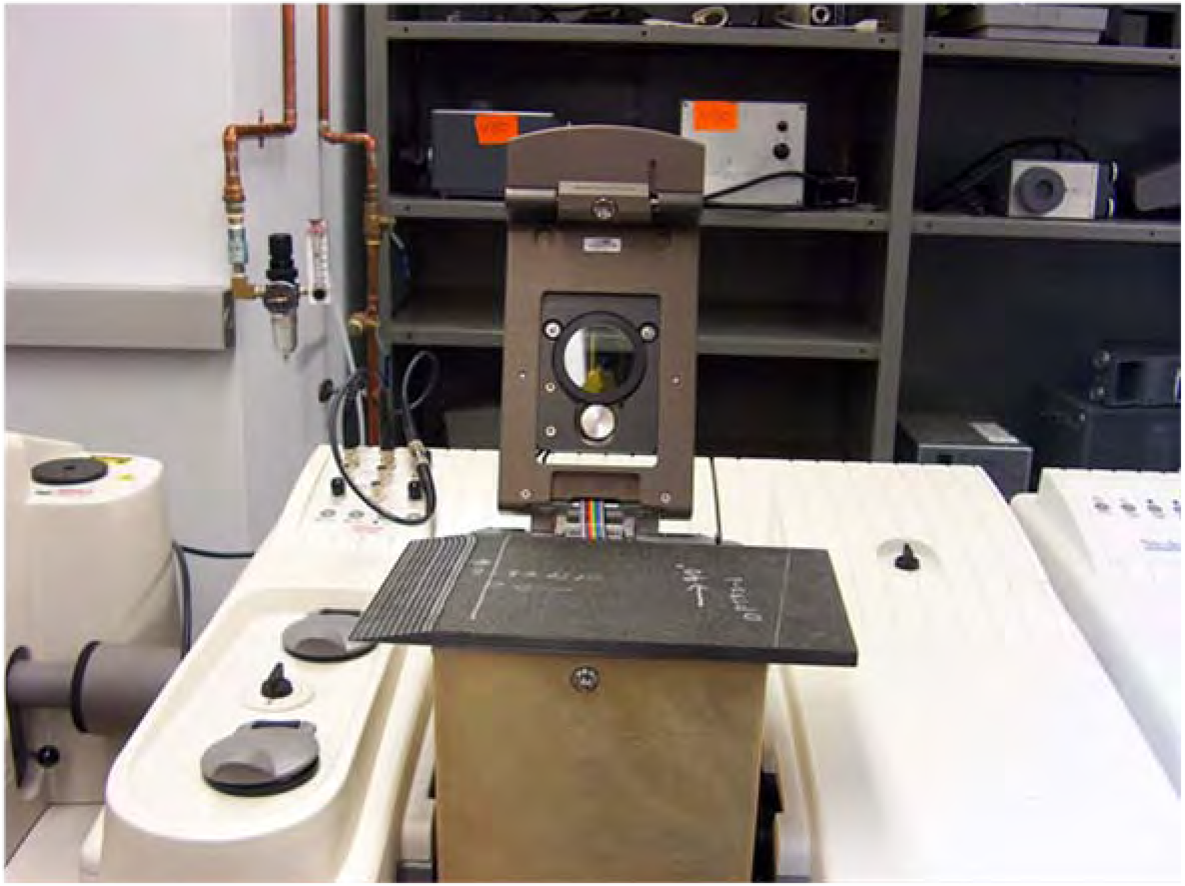
Diffuse reflectance Near IR spectroscopy using integrating sphere technology





TE Nexus with Integrating sphere module

A composite sample placed on top of the integrating sphere module and ready for analysis



Procedure for resin samples

(1). Resin cured between steel plates

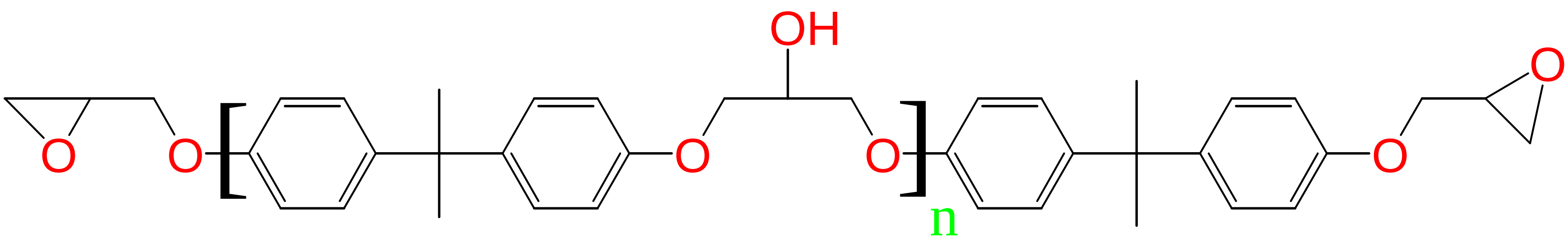
(2). Near IR spectrum acquired

(3). Weighed then exposed to water vapor @ 140 ^{o}F

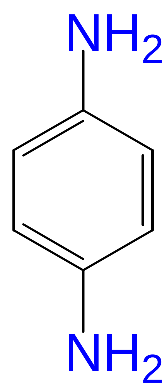
(4). Reweighed then near IR spectrum acquired

(5). Dried @ 50^{o}C, reweighed, and near IR spectrum acquired

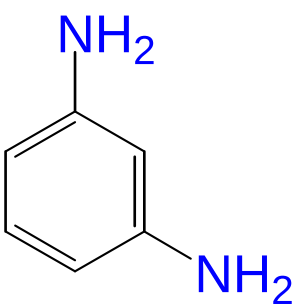
Cured 2h at 120ºC then 2h at 180ºC and stored in a dessicator



Water in a stoicheometrically balanced mid performance epoxy resin



Curative - PPDA : MPDA
1:1 mole : mole



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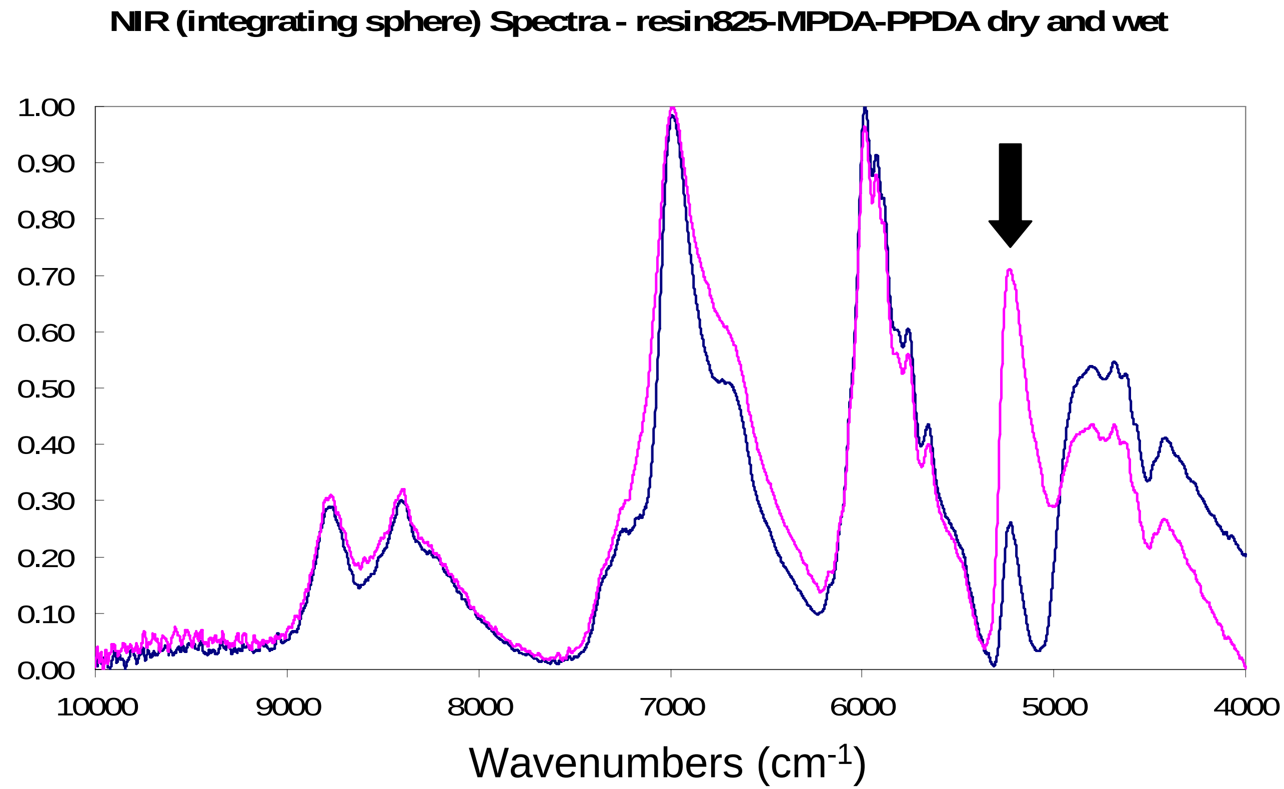
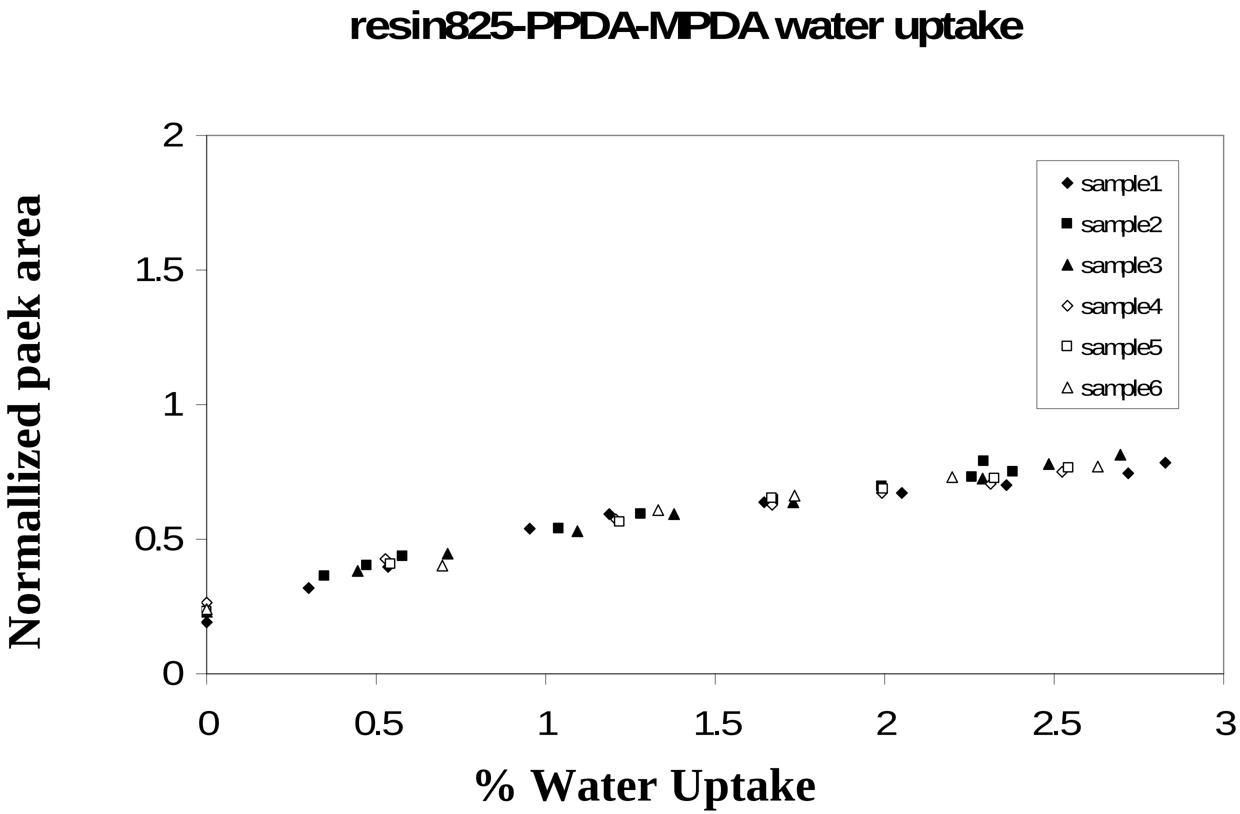
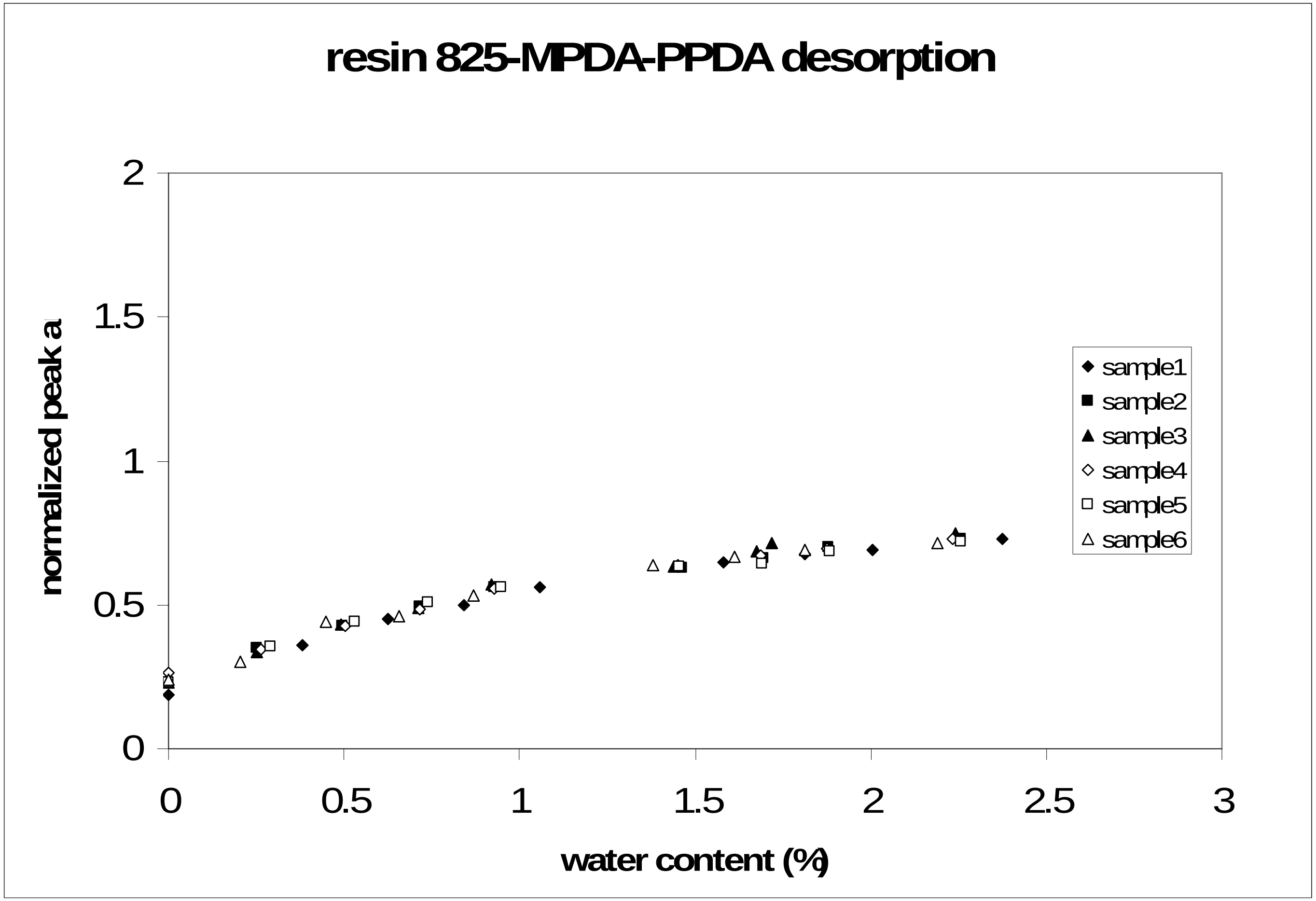
Near IR spectra of mid performance DGEBA epoxy resin before (blue) and after (wine) water absorption. The water absorption (overtone) is denoted by the arrow.



A plot of normalized water absorbance at 5215 cm^{-1} , versus % water uptake for this resin system



Spectra were also obtained during desorption (drying) cycles @ 50°C



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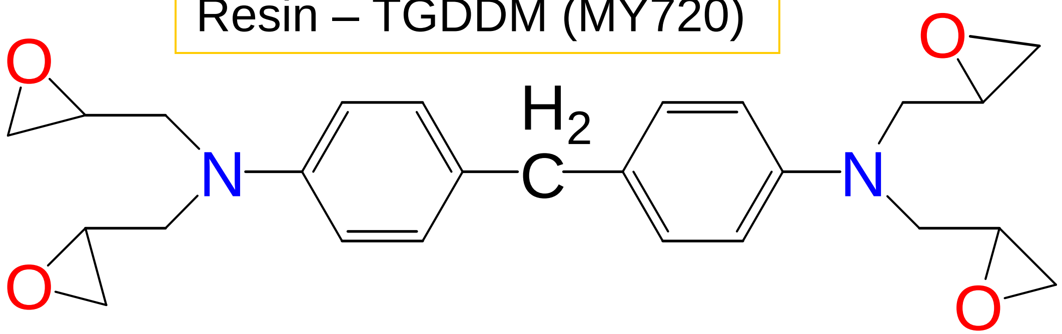
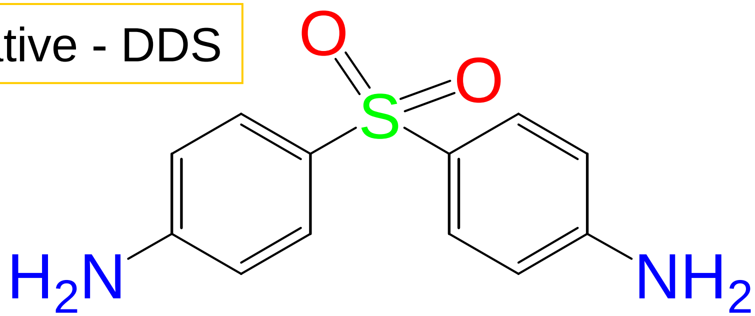
Water in a stoicheometrically balanced high performance epoxy resin formulated to “mimic” 934 resin

Resin – TGDDM (MY720)



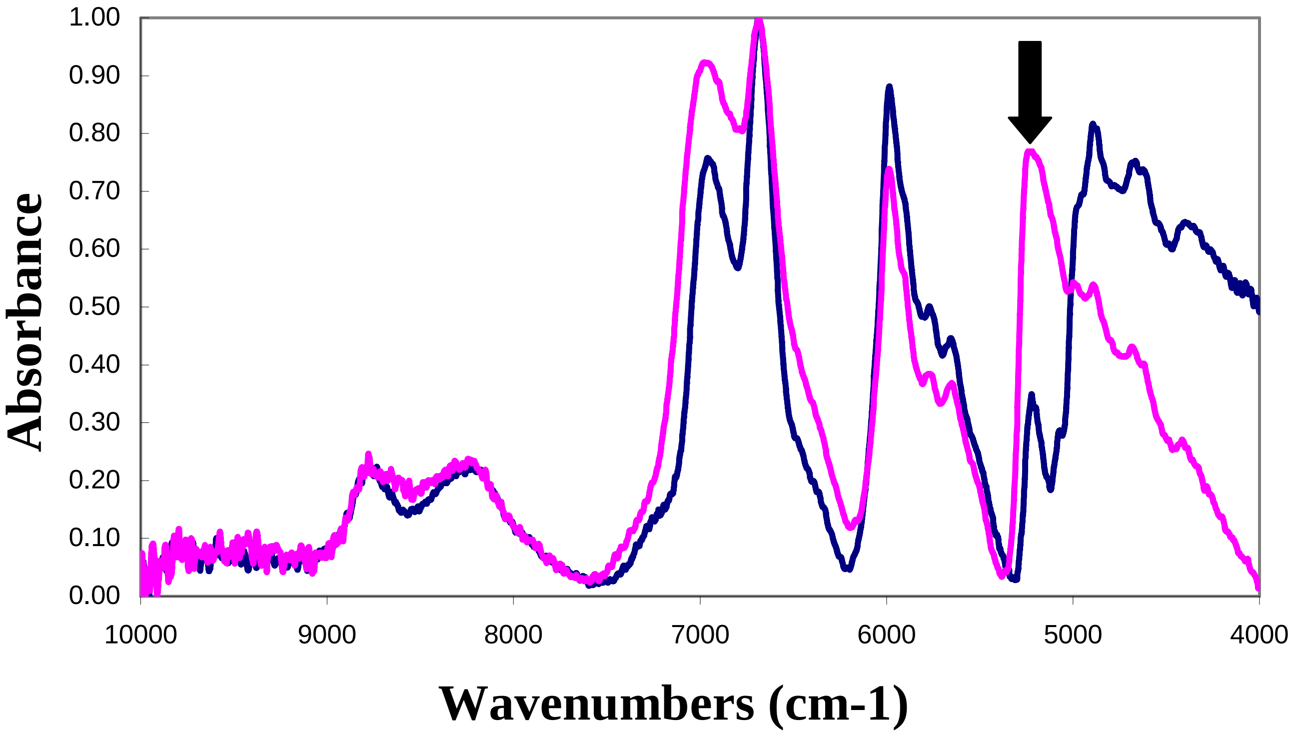
Curative - DDS



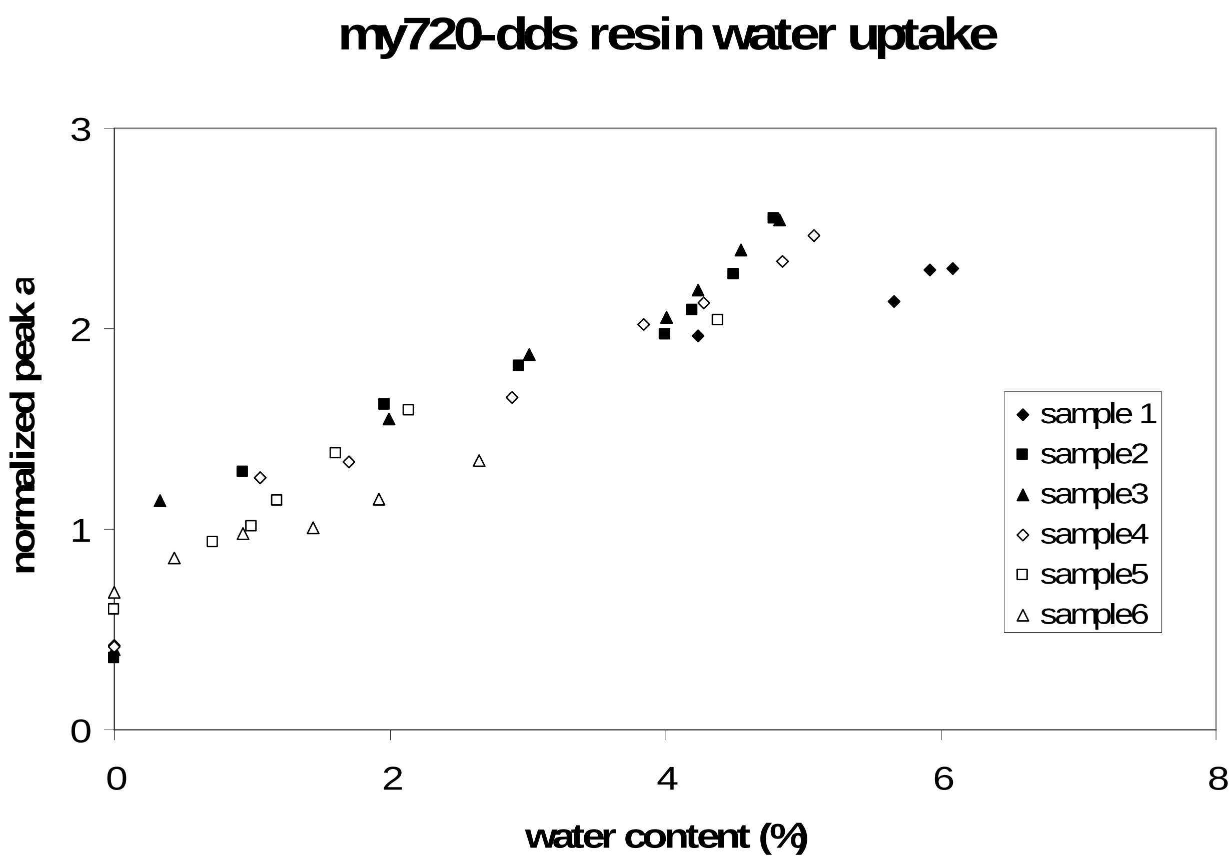
Resin cured between steel plates 2h at 140°C then 4h at 200°C

Near IR spectra of a high performance epoxy resin containing MY720 epoxy resin and DDS curative before (blue) and after (wine) water absorption. The water absorption (overtone) is denoted by the arrow

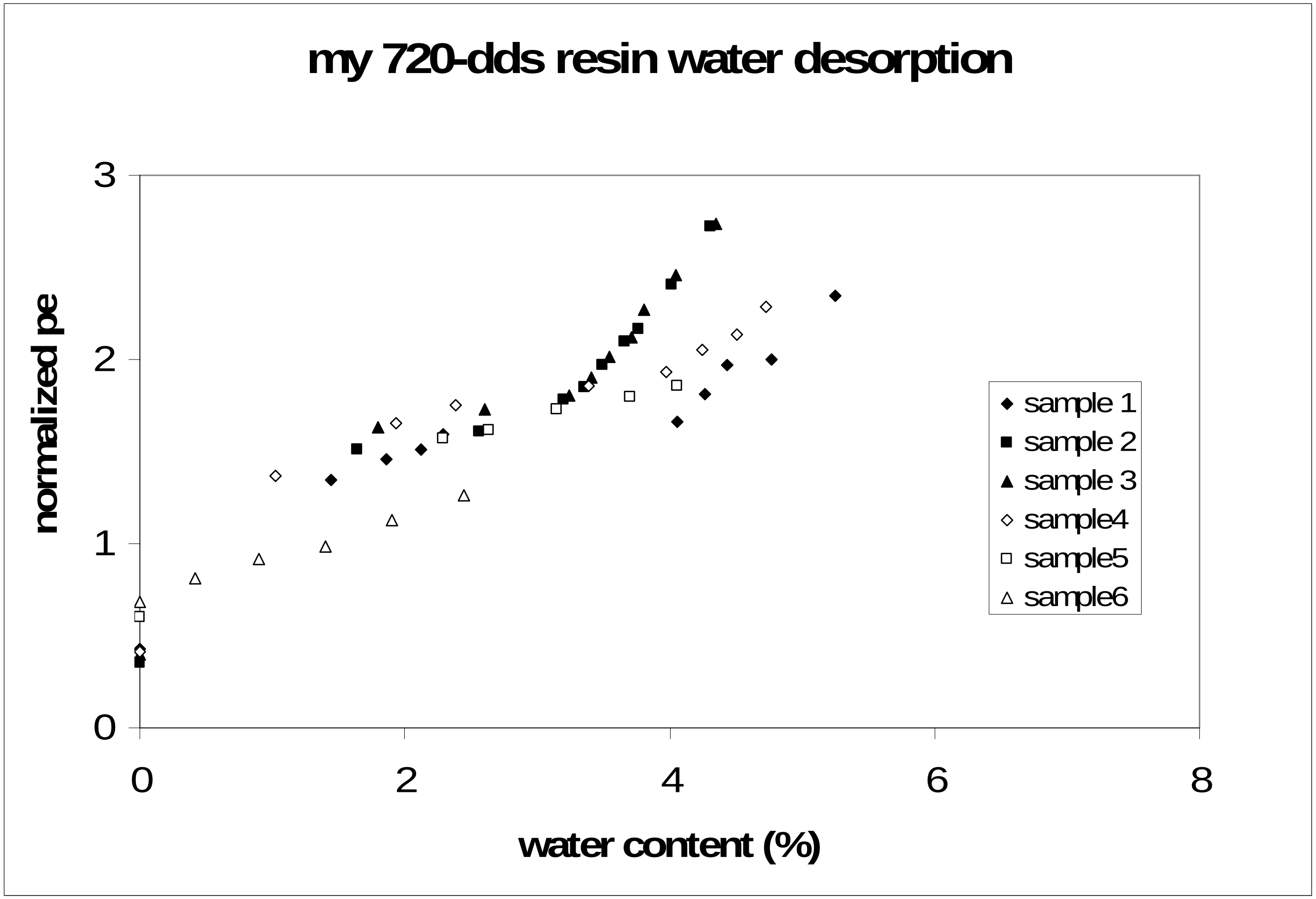
NIR (integrating sphere) Spectra - my720-dds resin dry and wet



A plot of normalized water absorbance at 5215 cm-1 versus % water uptake for the MY720-DDS resin system



Spectra were also obtained during desorption (drying) cycles @ 50ºC



Conclusions

- More water is absorbed by the high performance resin than the mid performance resin (free volume)
- More scatter with the high performance resin than with the mid performance resin
- Reproducible calibration curves

Water in an epoxy resin – carbon fiber based composite

Fibers – woven T300 carbon
Resin – generic "934" high performance resin
Details of cure – double vacuum bagged and cured in a forced air oven, 2h at 120°C followed by 2h at 200°C

Component	Percent Composition by Mass	Methods
Carbon Fiber	62.0 – 63.1%	solvent extraction & HNO_3 resin burn off
TGDDM (MY720 epoxy resin)	22%	^{1}H NMR spectroscopy, prep TLC
DDS (amine curative)	14%	^{1}H NMR spectroscopy, prep TLC
BF_3 (catalyst)	< 1 %	^{11}B & ^{19}F NMR spectroscopy
Acetone solvent	< 1%	mid IR & ^{1}H NMR spectroscopy

Strength

Works well with fiber reinforced composite on resin rich vacuum bag and peel ply surfaces

Weakness

Does not work well on resin poor (tool) surfaces

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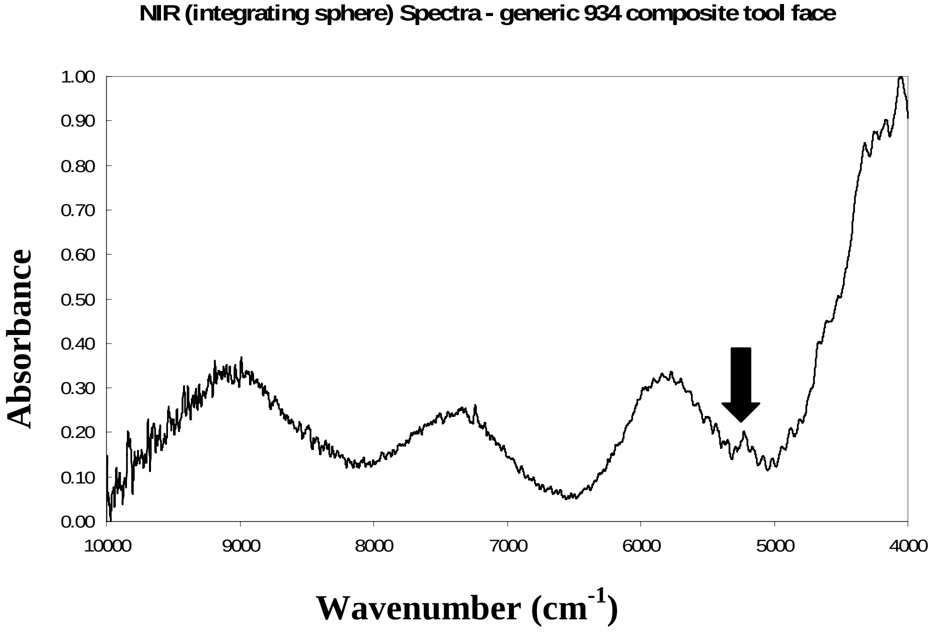
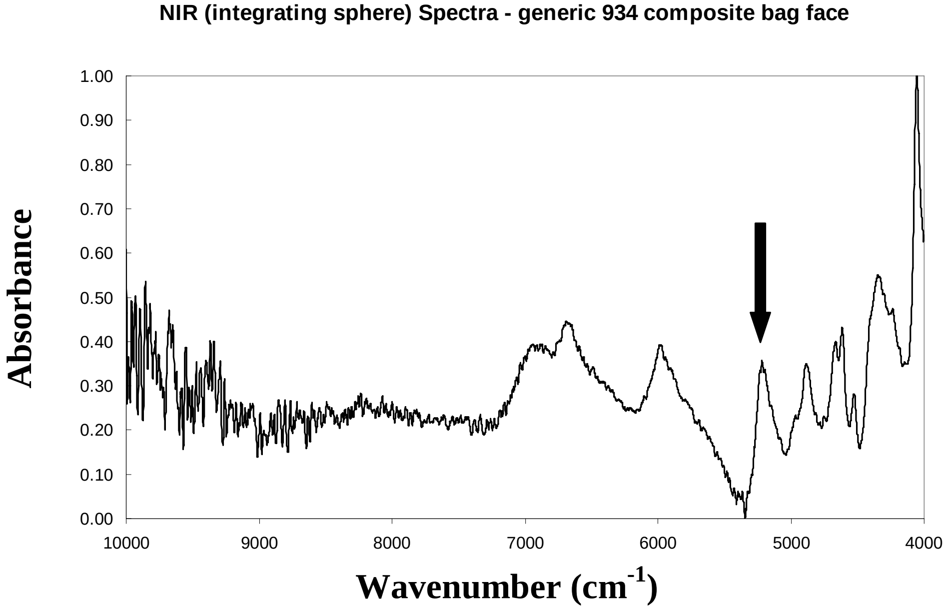
Near IR spectra of tool face (left) and bag face (right) of composite. “Bag face” spectra can be normalized

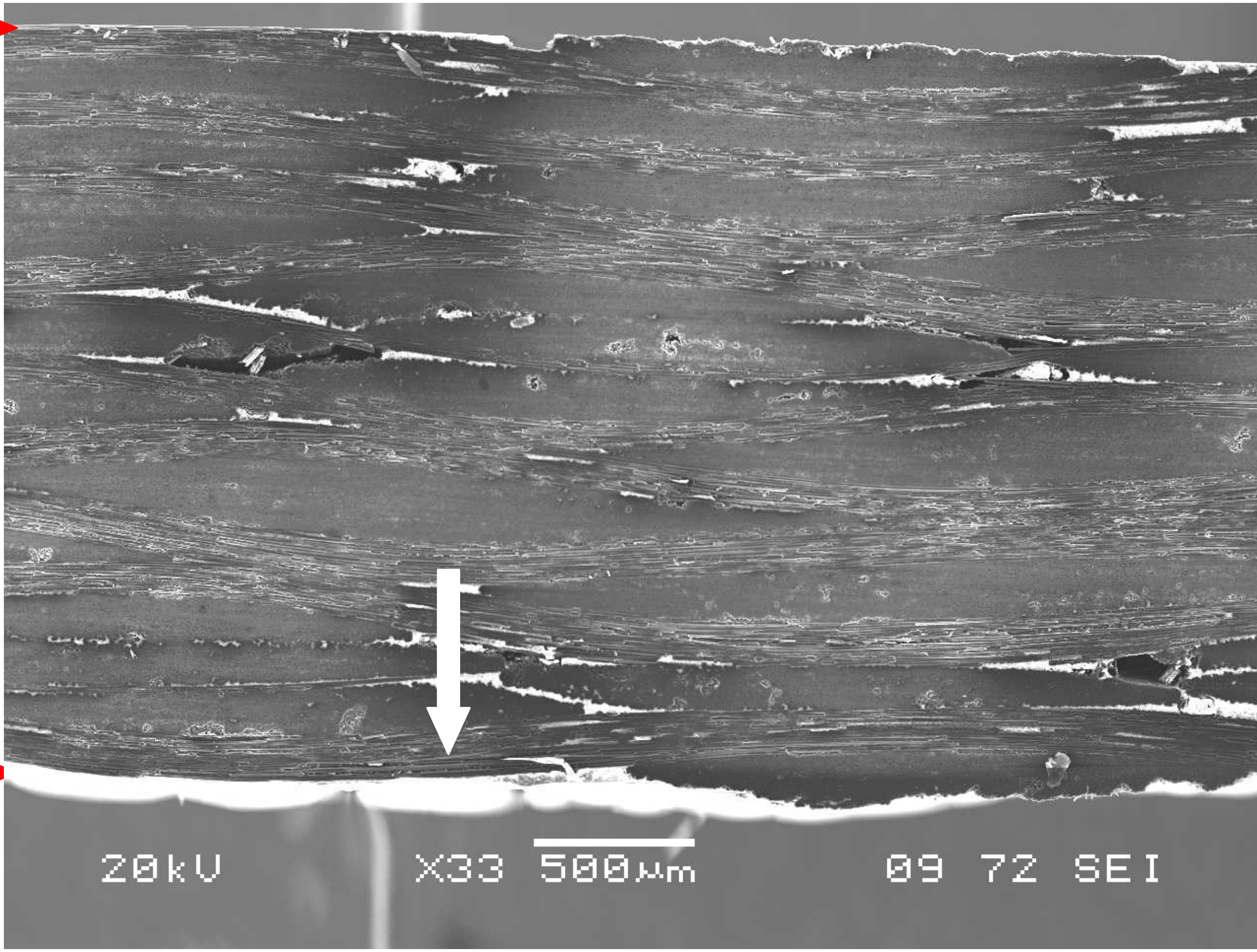




Tool face

Resin rich regions are overexposed due to charging

Bag face



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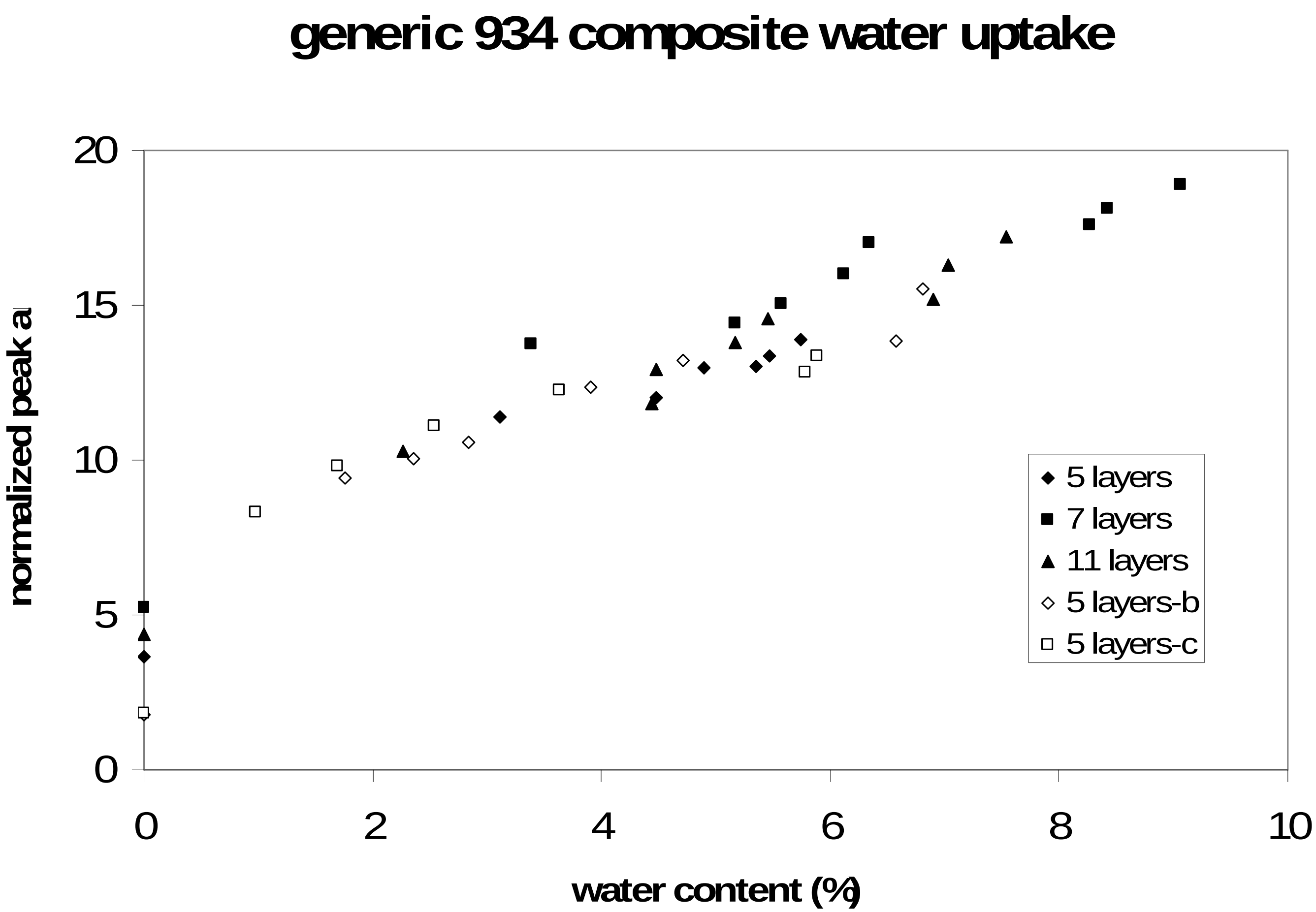
A plot of normalized water absorbance at 5215 cm^{-1} versus % water uptake measured at the bag face of a composite made using generic "934" resin and carbon fiber fabric



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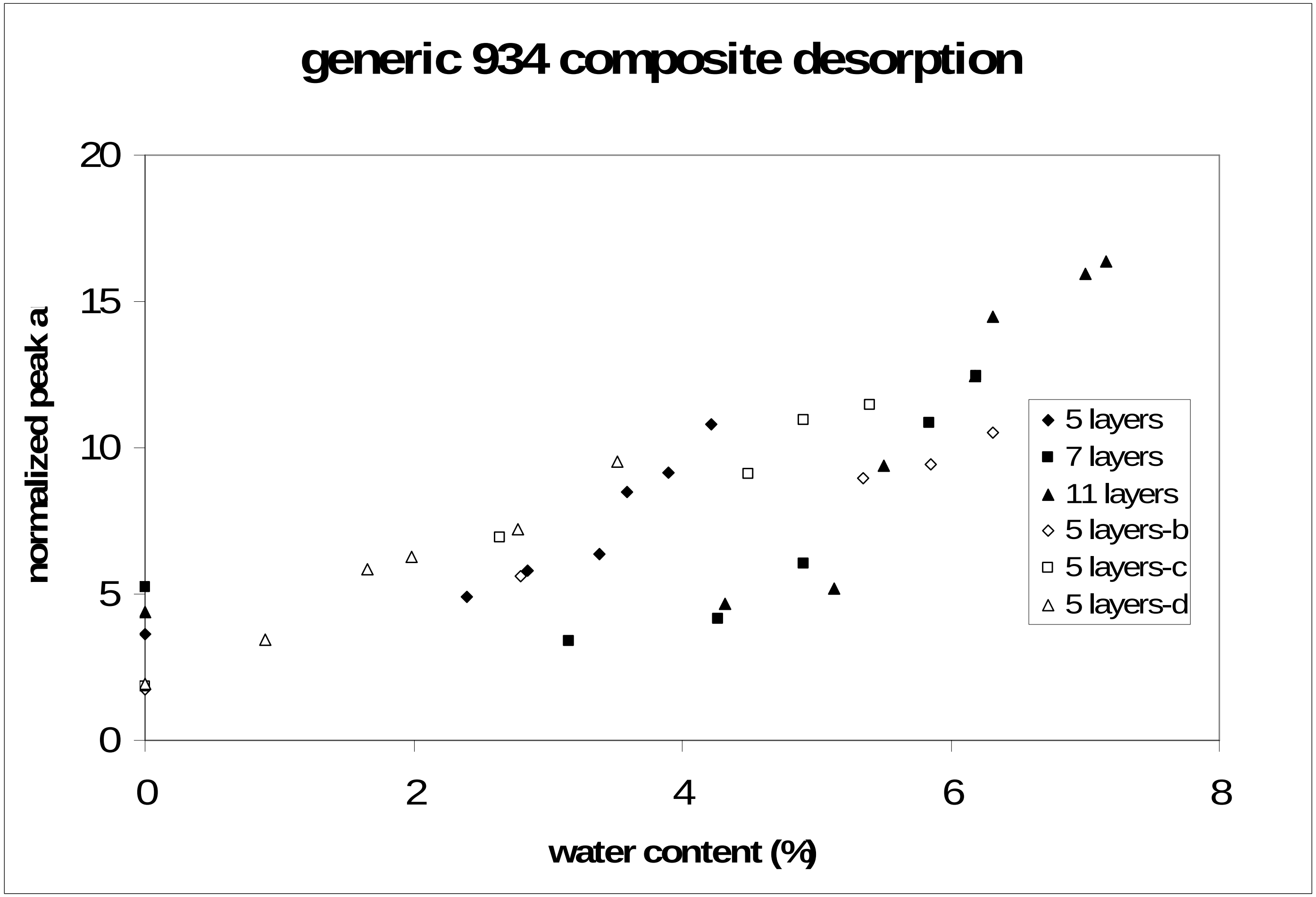

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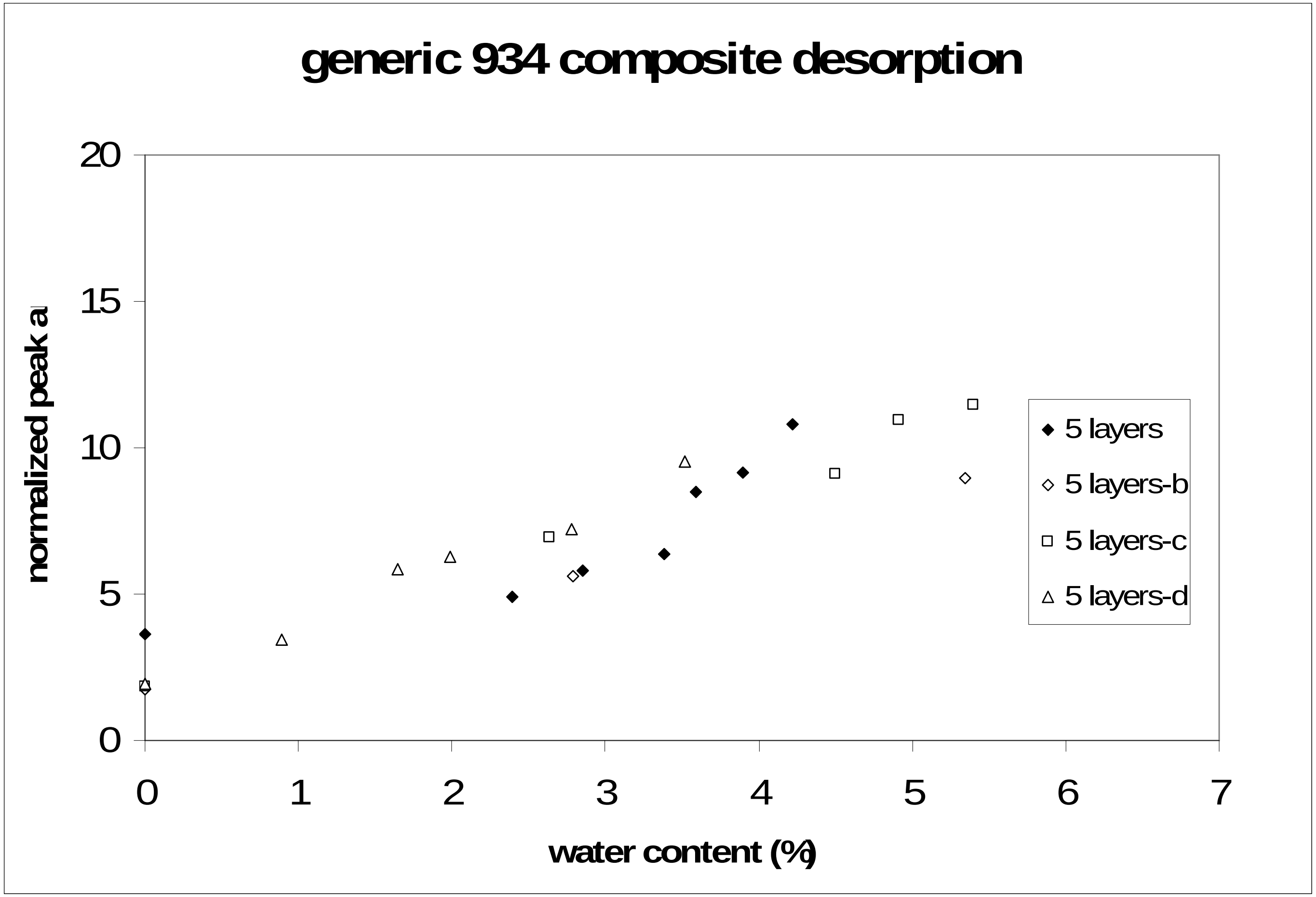
5 layers



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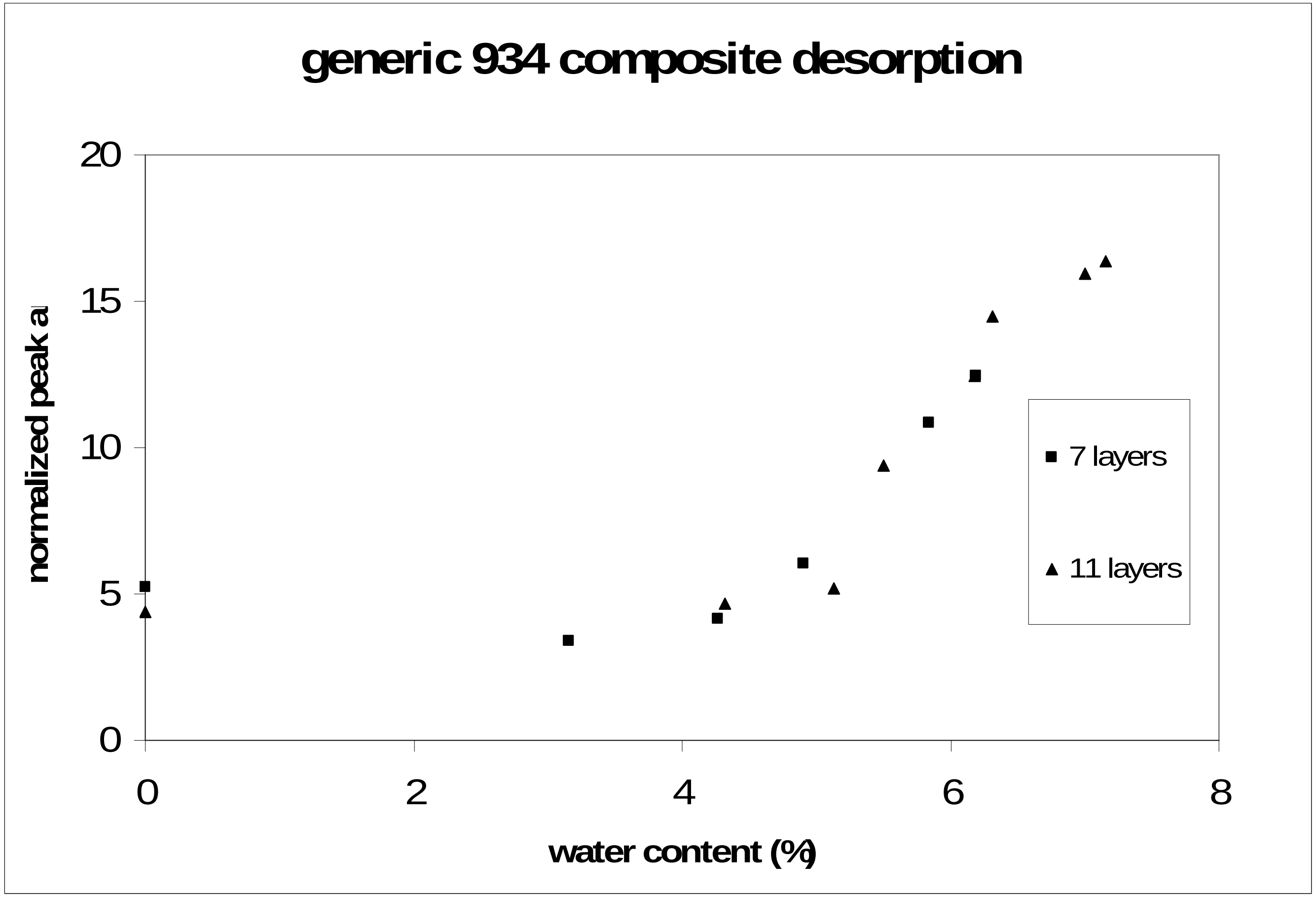
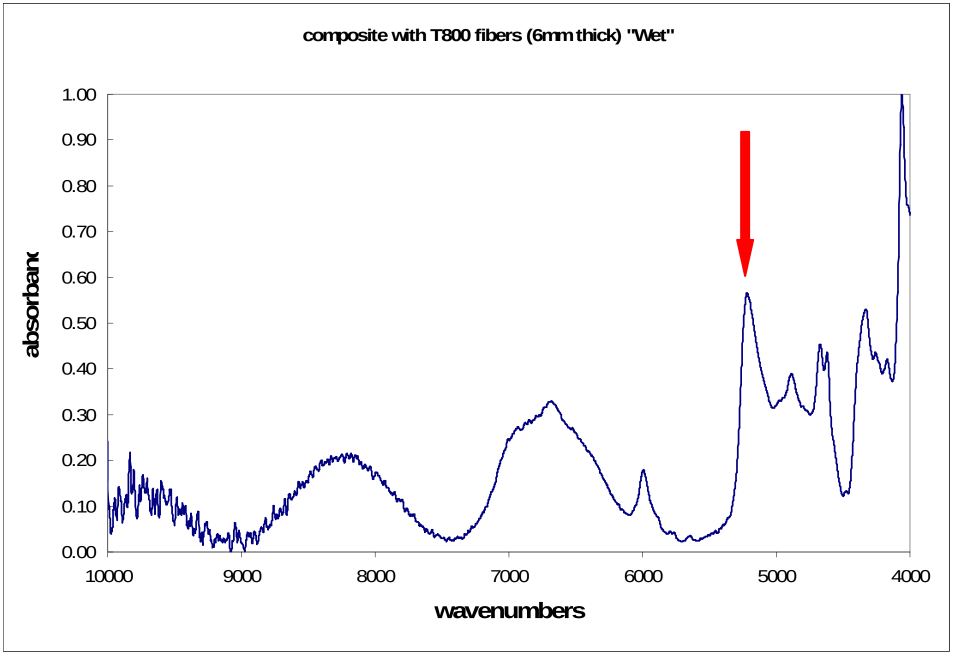
7 & 11 layers

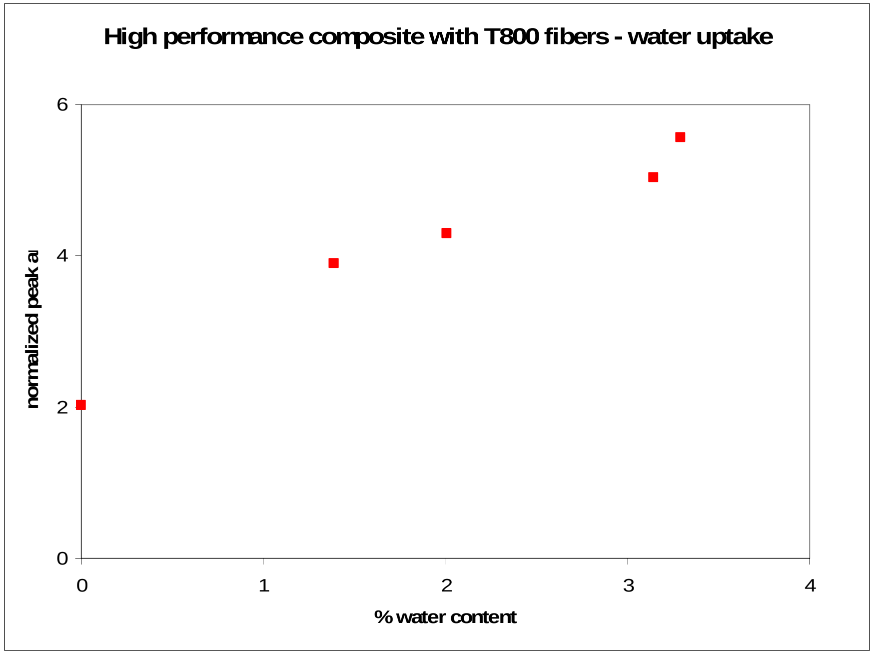


Conclusions

- Scatter during absorption of water by the composite < scatter during water loss
- Hysteresis during fast water loss due to concentration gradient imposed by fiber layers.
- At similar overall water content measured during a fast desorption cycle, the thicker composites contain less water at the surface and produce a smaller absorption

High performance composite with Toray T-800 fibers





Current near IR projects

Resin and adhesive cure state by diffuse reflectance (integrating sphere) near IR spectroscopy

Preliminary results presented here

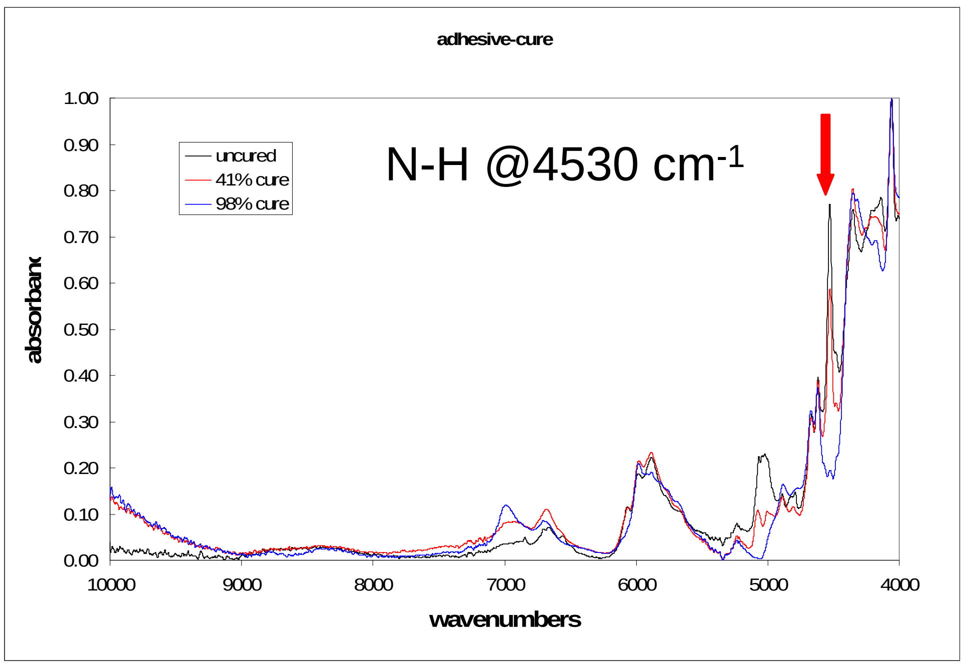
Adhesive water uptake studies

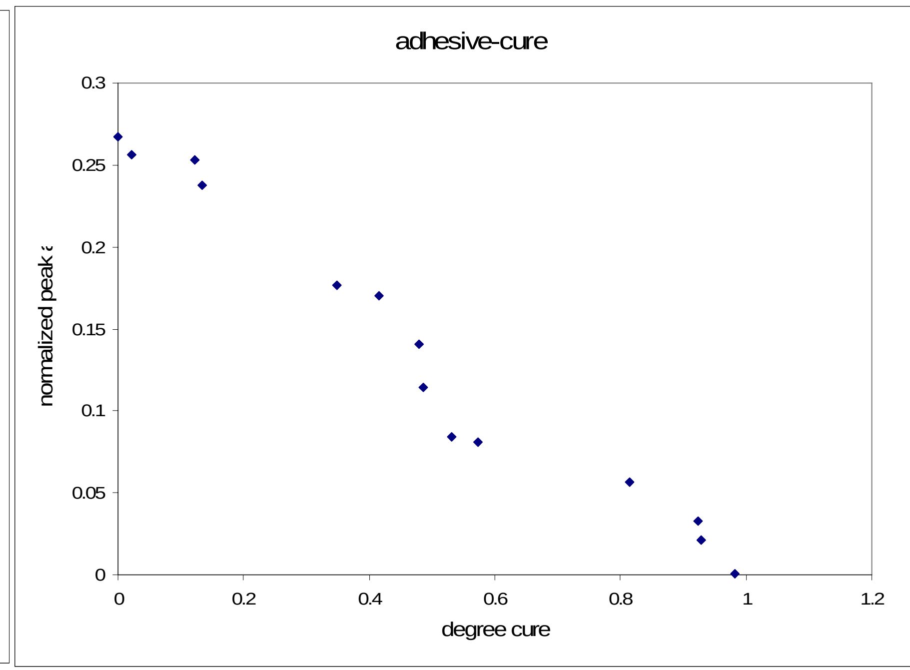
In progress

Composition of a filled high shear adhesive

Component	Analysis	Mass%
Aluminum Filler	Gravimetry	34 %
DGEBA epoxy resin with n = 0.4	Prep. TLC & ^{1}H NMR	35 %
TGDDM – MY720 epoxy resin	Prep. TLC & ^{1}H NMR	15 %
DDS amine curative	Prep. TLC & ^{1}H NMR	10 %
dicyandiamide (DCDA) amine curative	Mid IR	< 1%
CTBN rubber	Prep. TLC, ^{1}H NMR, mid IR	< 5 %

Filled High Shear Adhesive cure state by near IR spectroscopy





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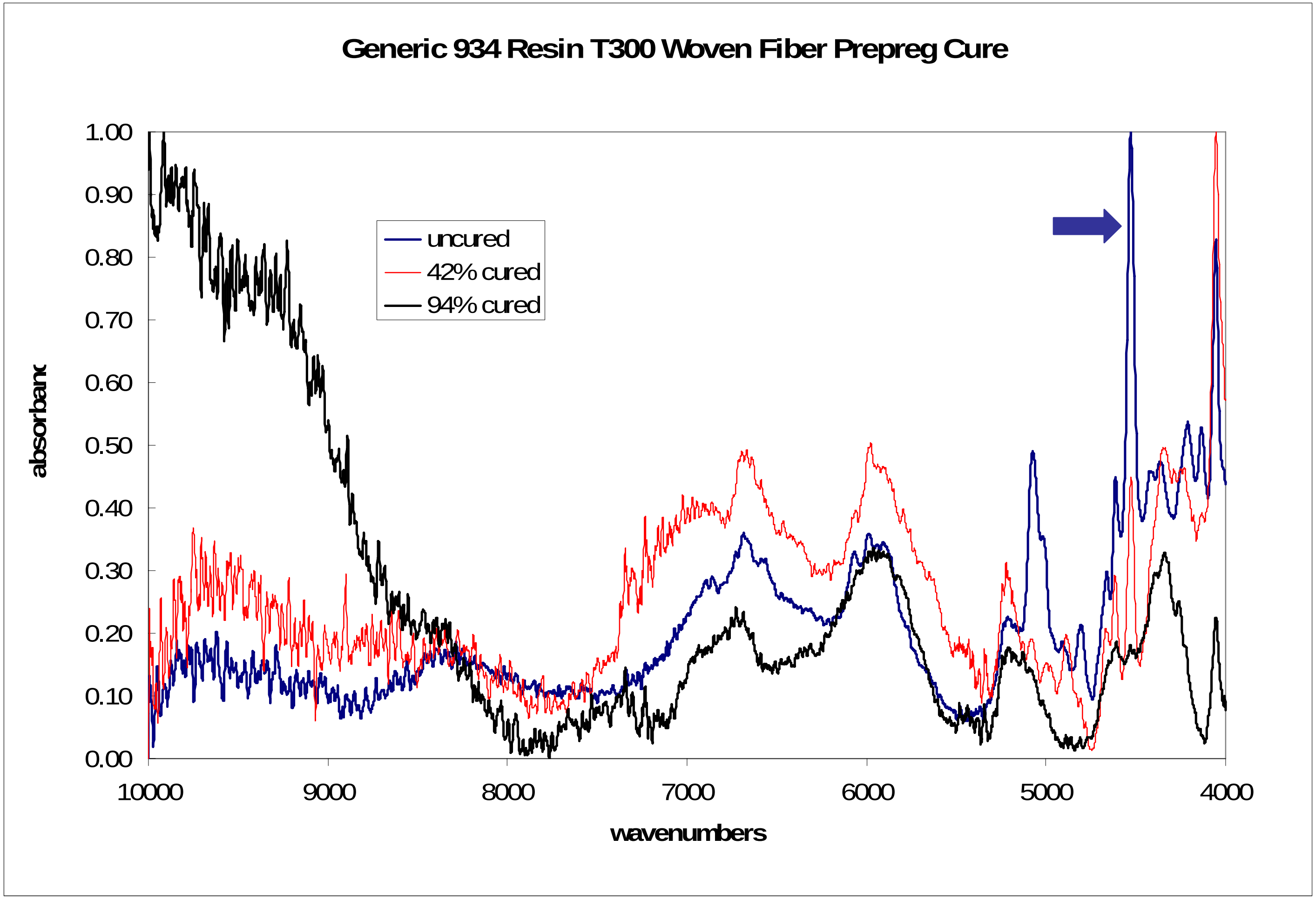
934 resin *w* T300 woven fibers prepreg - cure state

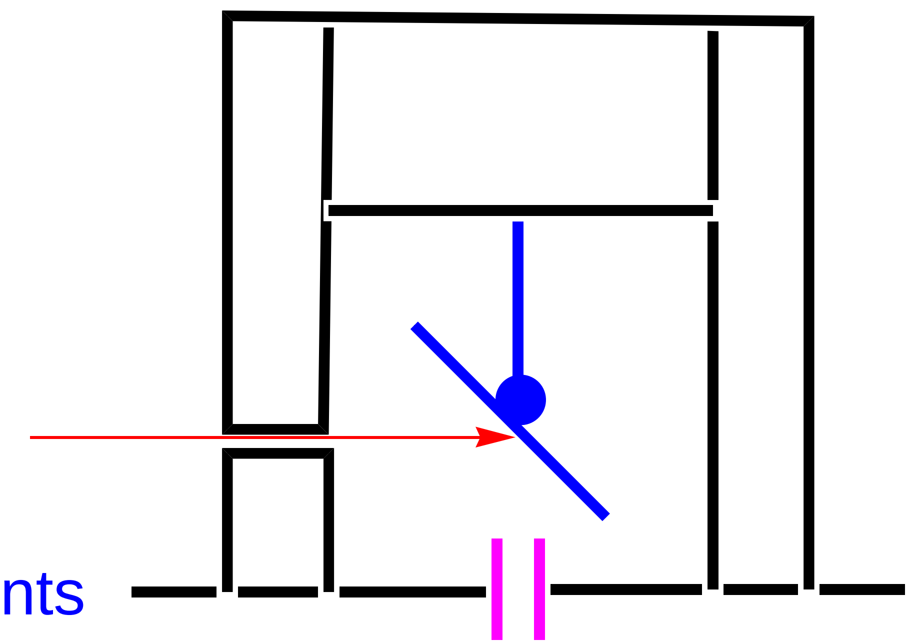


Laser Desorption – Mass Spectroscopy Experiment

Sample holder

Laser beam

MS siphon tube



Surface contaminants → Ion fragments

Phase I (Dec 2005) goals

To have a working LD-MS system in place to analyze surface treated composite samples

Progress

Completed – laser has been purchased, sample stage has been built and "debugged". System works.

Commenced work on Phase II

Development of spectral database for analysis of unknowns

Phase III (2006-07) goals

To integrate this technique into the joint FAA/NIAR scarf repair project to characterize "conditioned" scarfed repair surfaces made from high performance composite prior to repair layup for hydraulic fluid and jet fuel at the scarfed surface

Progress: To commence this summer

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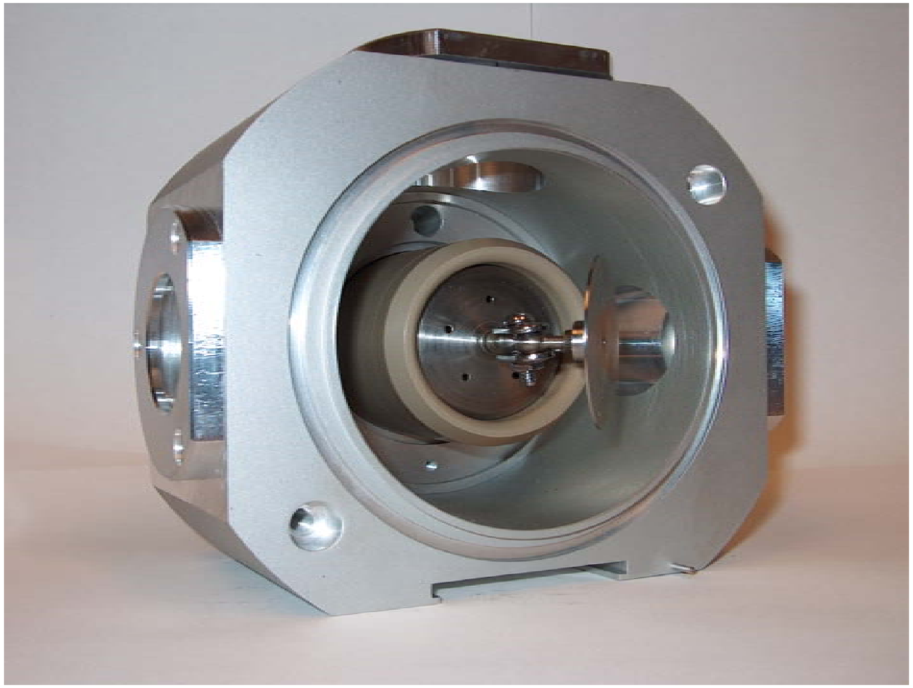

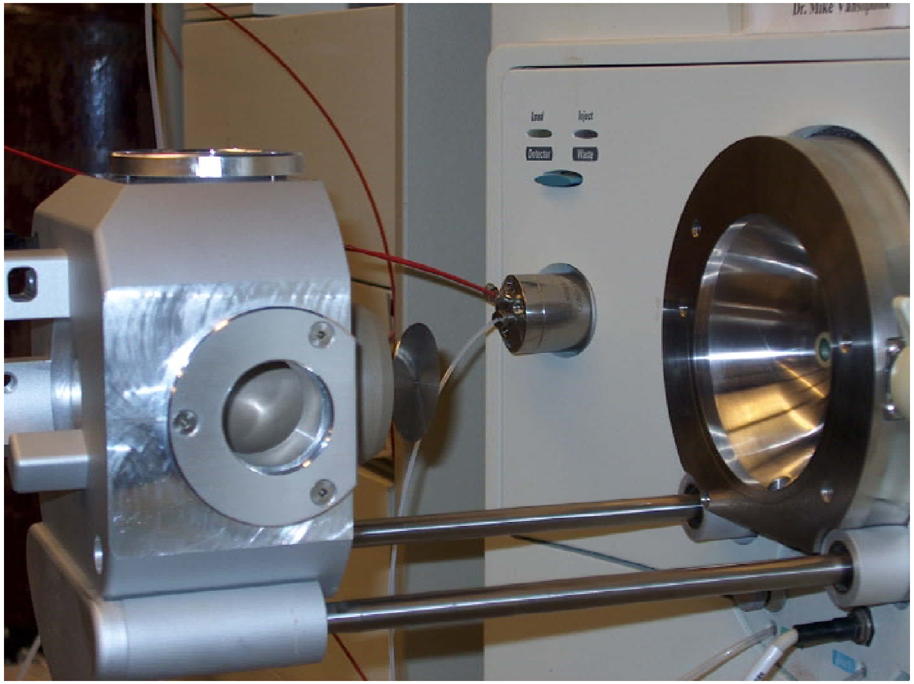

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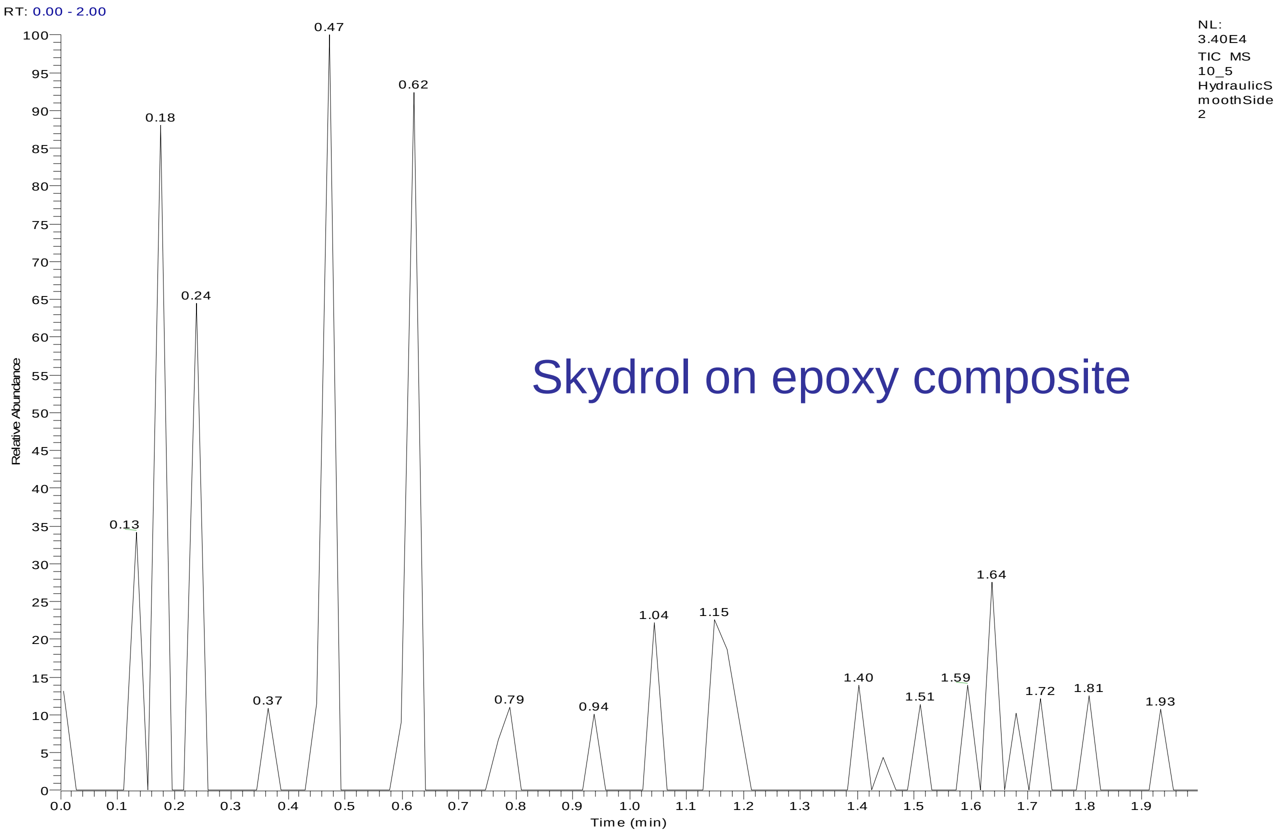
Material is removed from the surface in “bursts” We can focus on any burst or integrate the mass spectrum over the entire time interval. Molecular damage is minimal & parent ions can be identified



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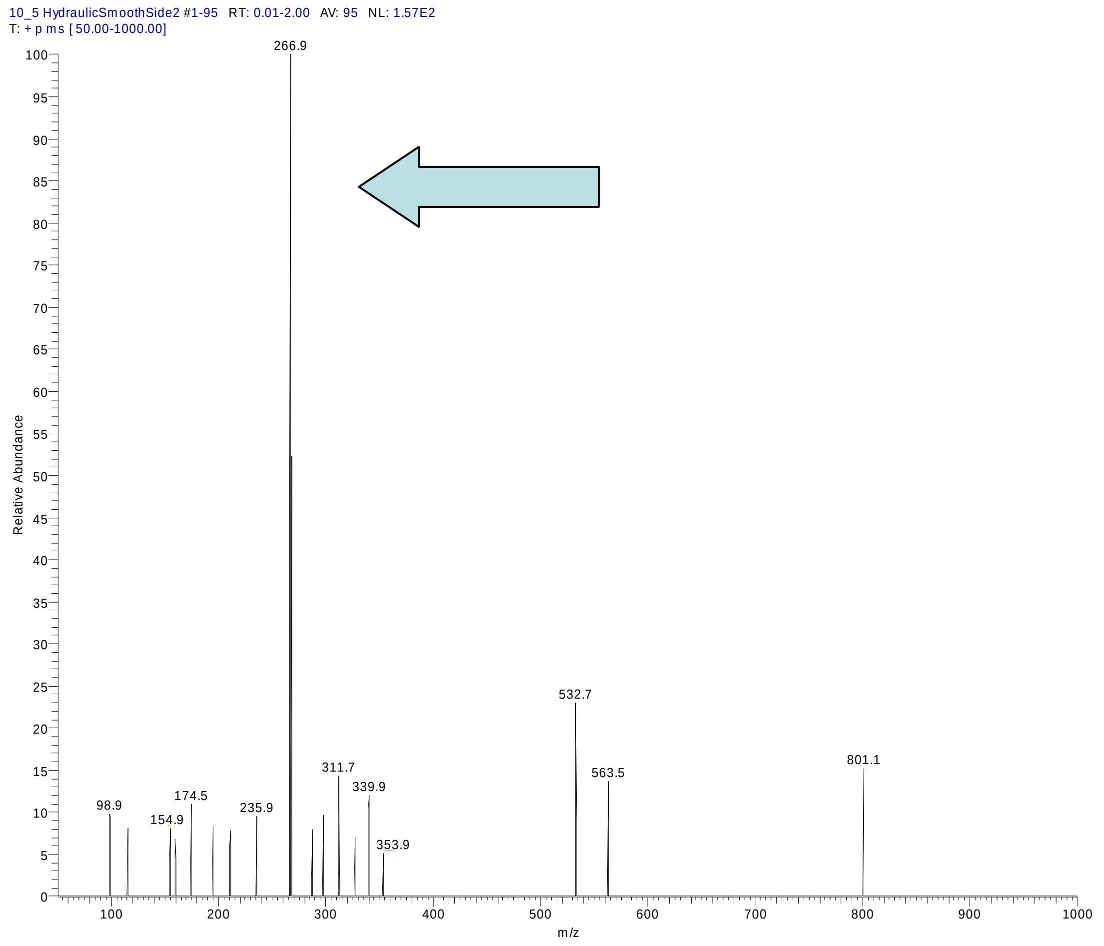
Time averaged spectrum with tributyl phosphate (TBP) M266 arrowed



Spectra can be integrated into the NIST library using NIST MS search program (Version 1.7) tool to produce a library of LD-MS spectra to compare with and help recognize unknowns

Proof of concept

- Acquire spectrum of skydrol on composite
- Add to NIST library
- Reacquire as "unknown" on composite, search library for best fit, and re-identify Skydrol as most probable species

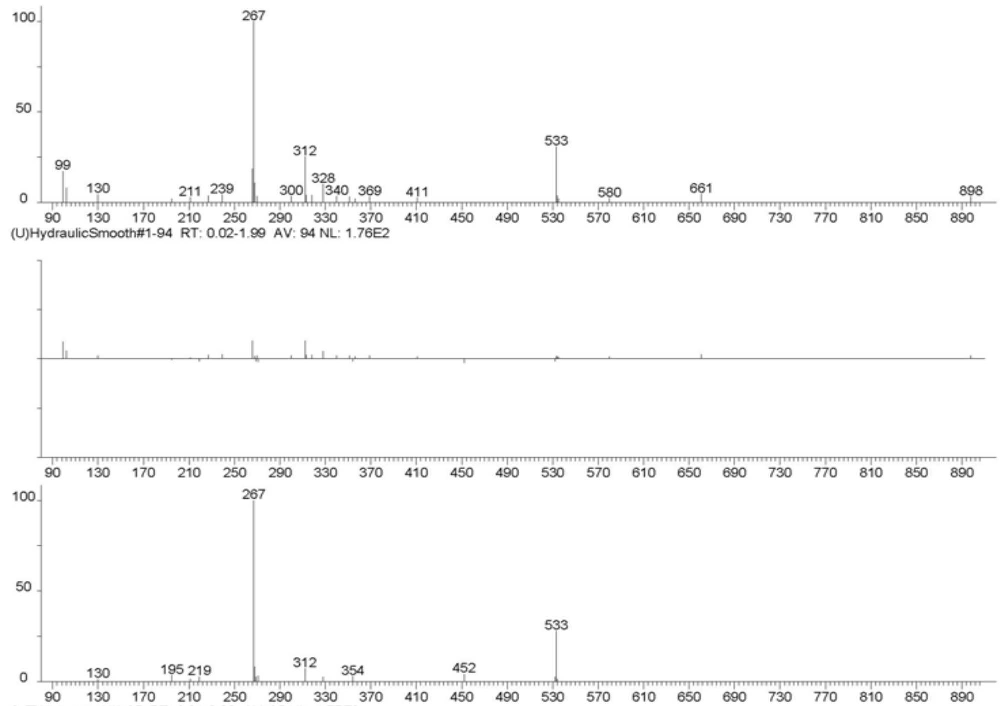
HydraulicSmooth#1-94 RT: 0.02-1.99 AV: 94 NL: 1.76E2
Formula:
MW: NA CAS#: NA NIST#: NA ID#: 8 DB: faa
Comment: T: + p ms [50.00-1000.00]
27 Masses and Abundances

99	173	195	21	239	44	268	108	312	254	328	102	356	21	533	309	580	23
102	82	211	28	266	185	270	36	313	40	340	34	369	32	534	39	661	46
130	45	227	38	267	999	300	34	318	41	351	31	411	25	535	20	898	33

No synonyms

Best fit
from database

“Unknown”



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1 611 663R 98.0P (U) HydraulicSmooth#1-94 RT: 0.02-1.99 AV: 94 NL: 1.76E2

2 306 422R 0.98P (U) hexa-ethyleneglycol#1-446 RT: 0.01-3.99 AV: 446 NL: 4.00E2

3 286 315R 0.44P (U) Sulfisoxazole

4 273 278R 0.28P (U) Adenosine

5 240 302R 0.07P (U) 3-Methylcholanthrene

6 232 307R 0.05P (U) Methanone, bis[4-(dimethylamino)phenyl]-

7 224 277R 0.04P (U) Ergotamine Tartrate

8 214 251R 0.02P (U) Benzenamine, 4,4'-methylenebis[2-chloro-

9 204 232R 0.02P (U) Octadecanoic acid, methyl ester

10 188 192R 0.01P (U) Propyl Gallate

11 152 178R 0.00P (U) Squalane

12 137 156R 0.00P (U) Stannane, (acetyloxy)triphenyl-

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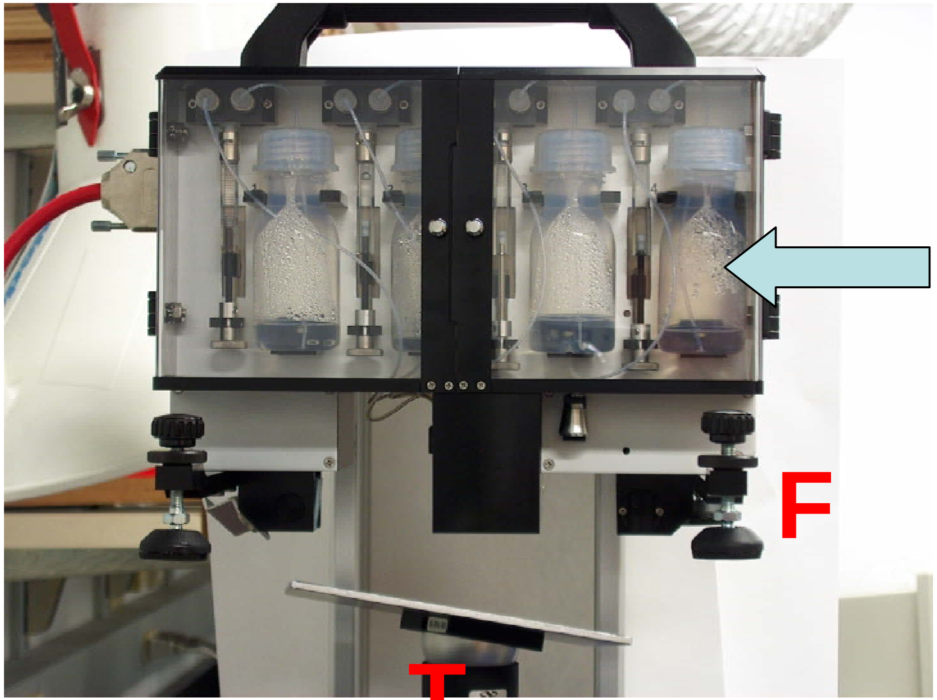
Surface free energy by contact angle measurement

H carry handle
F feet
B solvent bottle
T tilting stage



Phase I (Dec 2005) goals

To have a working automated portable multi-solvent contact angle measuring device in place to analyze surface treated composite samples as supplied by NIAR and Spirit Aerosystems beginning

Progress

Completed- Device has been fabricated and delivered (FDS PCA 100M-4). Sample mount has been modified to handle wedge shaped surfaces. Contact angle measurements have been made on scarfed surfaces ground into sheets of high performance composite.

Phase II (2006-07) goals

To integrate this technique into the joint FAA/NIAR scarf repair project to characterize "conditioned" scarfed repair surfaces made from high performance composite prior to repair layup for surface free energy at the scarfed surface

Progress: To commence this summer

Methods for the Evaluation of the Fitness of Fiber Reinforced Composite Surfaces for Subsequent Adhesive Bonding

Selected results

SURFACE	FLUID	CONTACT ANGLE (water)	SURFACE ENERGY - EOS (mN/m)
rough	none	59.2	48.28
smooth	none	65.3	44.57
wedge	none	47.5	55.16
smooth	deicing fluid	49.5	54.05
wedge	deicing fluid	45.5	56.29
rough	skydrol (hydraulic fluid)	47.2	55.33
smooth	skydrol (hydraulic fluid)	60	47.80
wedge	skydrol (hydraulic fluid)	66.5	43.83

rough	JP-8	37.5	60.66
smooth	JP-8	53.4	51.74
wedge	JP-8	45.3	56.41
	saltwater	no measurable contact angle, liquid simply spreads on contact	

A Look Forward

Benefit to Aviation

LD-MS: An analytical tool to provide surface analysis at atmospheric pressure of composite and metal surfaces contaminated with volatile organics

Contact angle device: A robust, portable, user friendly version of a device that can be mounted on a cart or robotic arm to contribute to a go/no go answer to the bonding question

Near IR diffuse reflectance: A device that can be mounted on a hand held grip to determine moisture content and surface cure state in a composite part

NIST repair project : Design of repair methodologies for thick composite parts in the field