Pre-Repair Surface Inspection and Post repair Evaluation of Cure State Using Near Infrared Spectroscopy

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

WICHITA STATE UNIVERSITY

CECAM center of excellence for composites and advanced materials

The Joint Advanced Materials and Structures Center of Excellence

Motivation and Key Issues

To help US Aero Space manufacturers of large composite parts produce and maintain a better product in a more cost effective manner

Objective

To remove some of the qualitative judgements that have to be made concerning composite repair and replace them with quantitative measurements

Approach

To adapt spectroscopic based technology for the analysis of cure state and water content in composites and to transfer this technology to industry

FAA Sponsored Project Information

Principal Investigators & Researchers

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FAA Technical Monitor

- Curt Davies

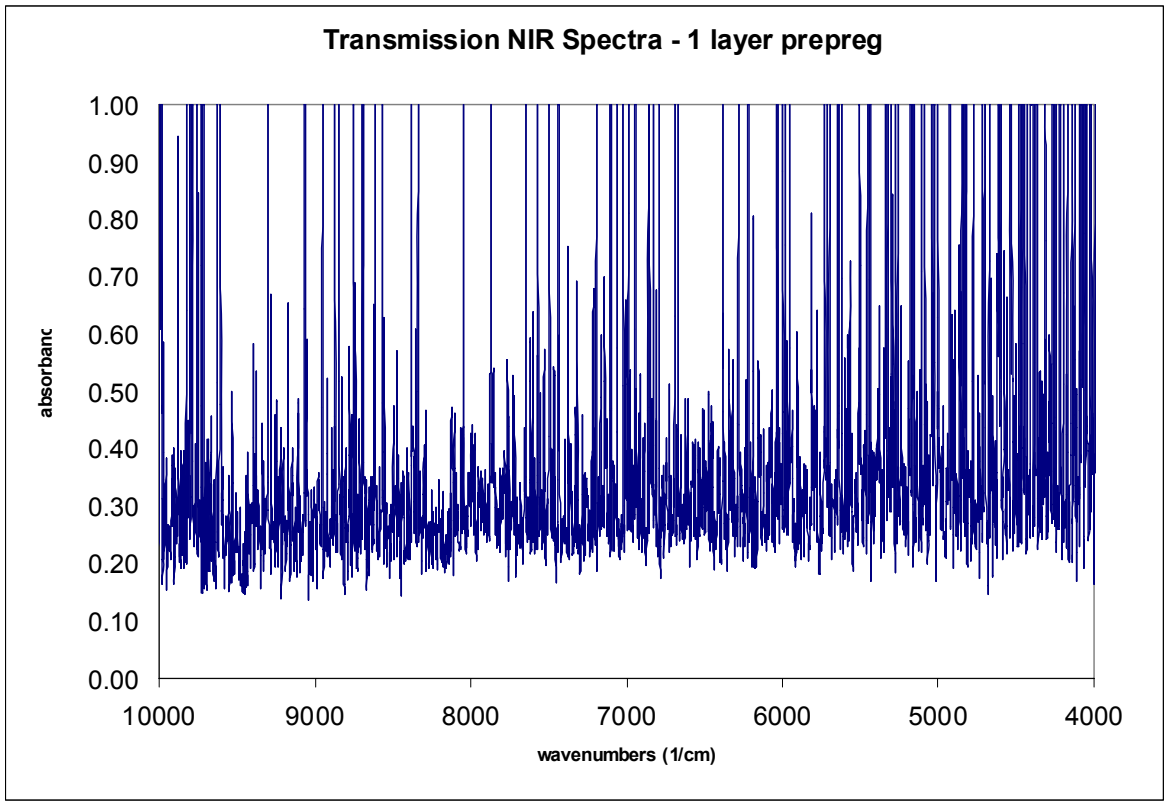
Other FAA Personnel Involved

- Larry Ilcewicz

Industry Participation

- Spirit AeroSystems

Unfortunately near IR spectroscopy of composites does not work in transmission



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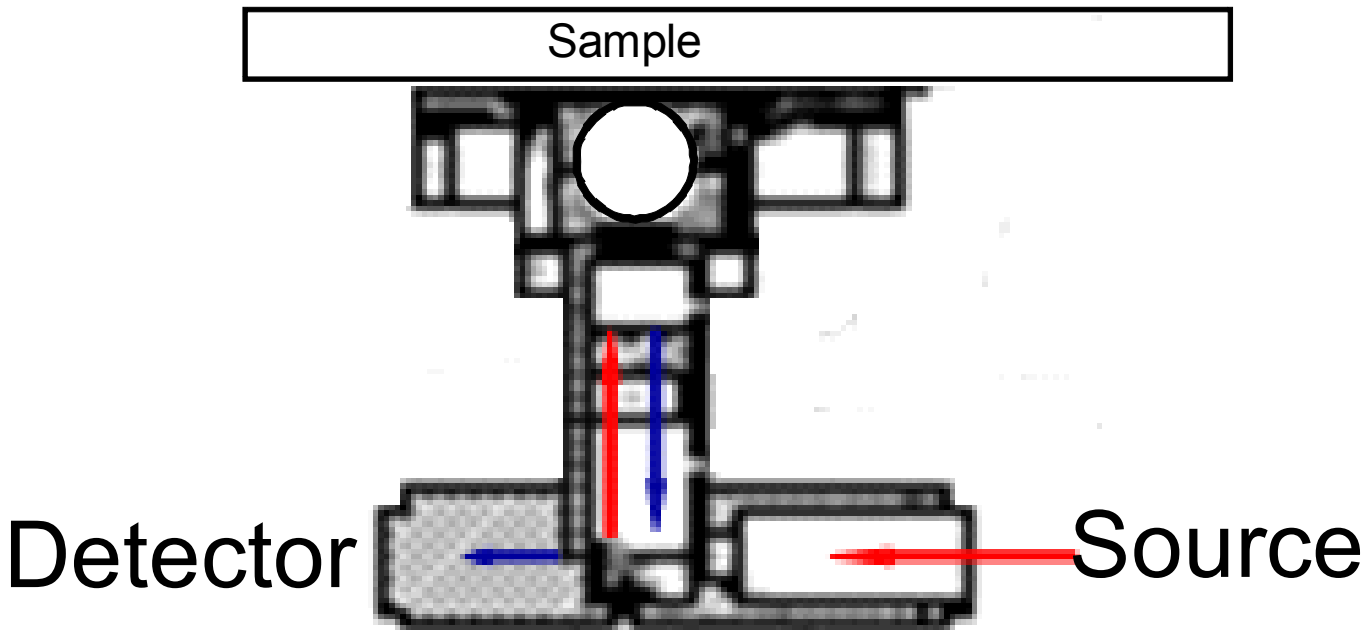
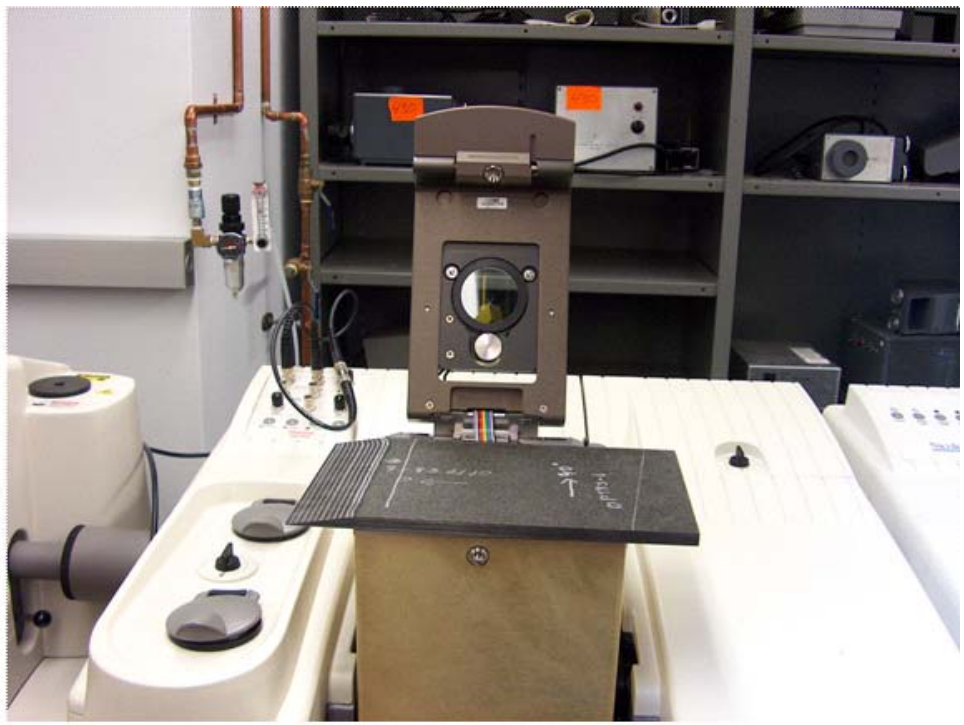
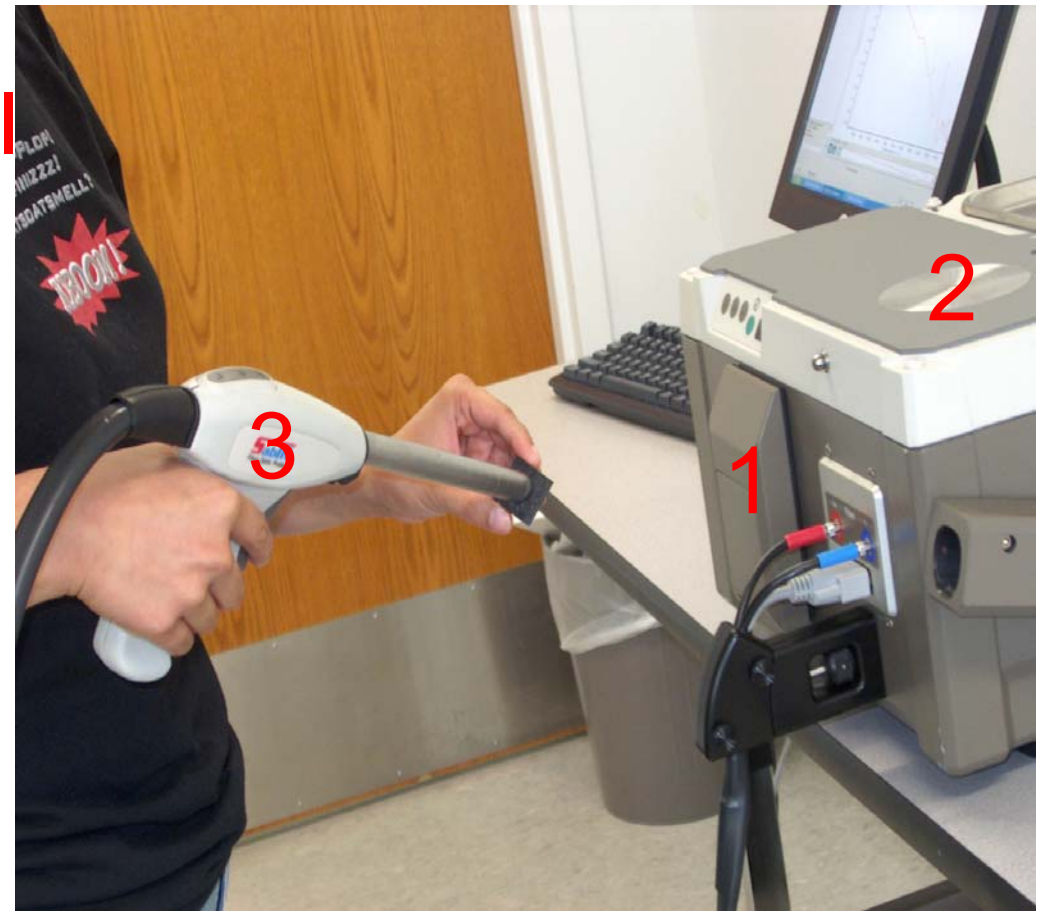


A composite sample is placed on top of the integrating sphere module for analysis

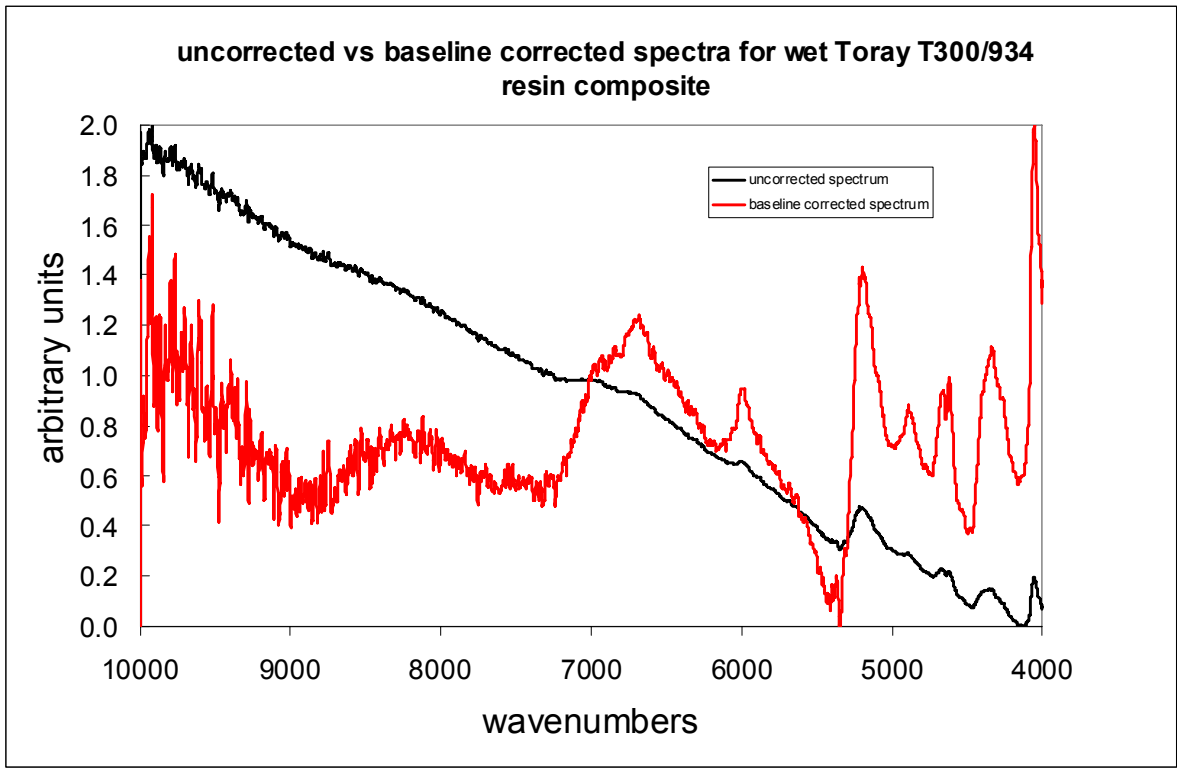


Antares II

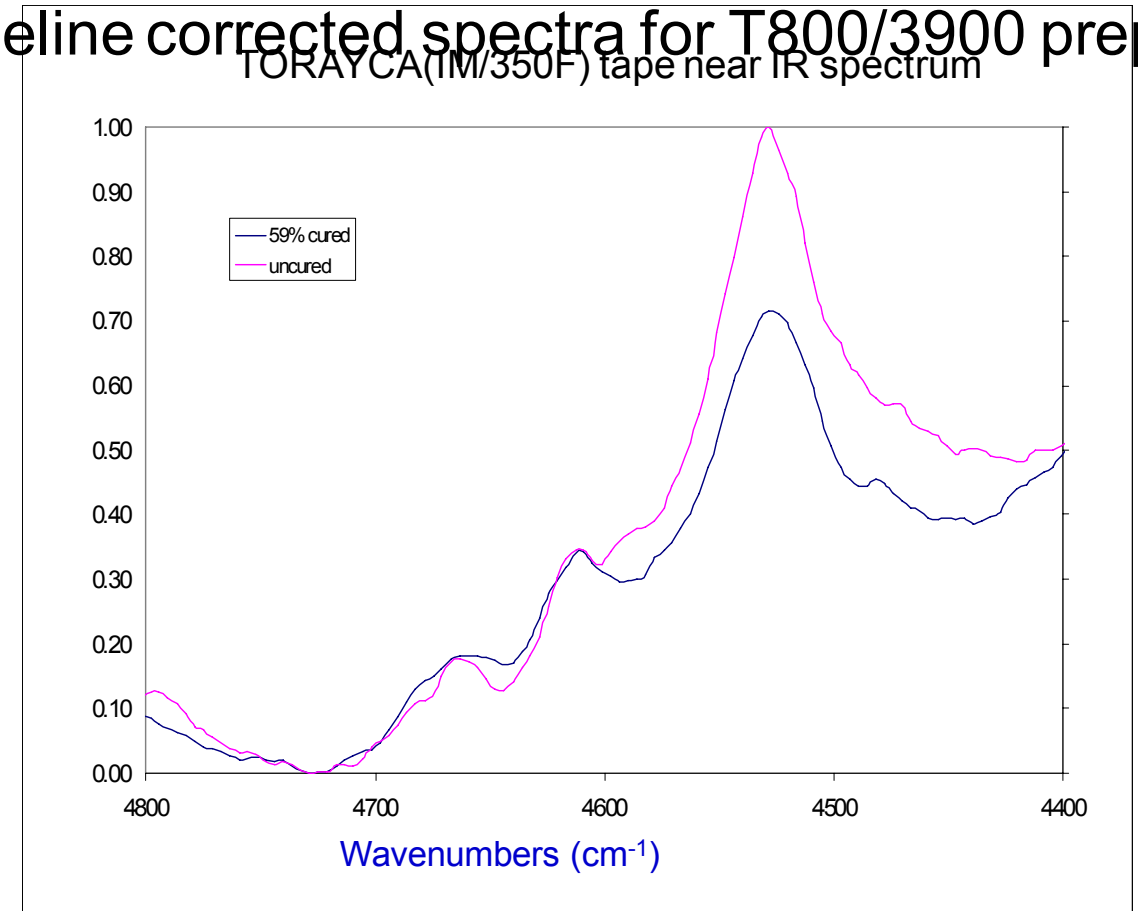
1. Transmission module
2. Integrating sphere reflectance module
3. Remote triggered diffuse reflectance module



Conventional calibration curve – peak area is ratioed to that of an invariant peak after baseline correction



Baseline corrected spectra for T800/3900 prepreg



Simple Beer's Law

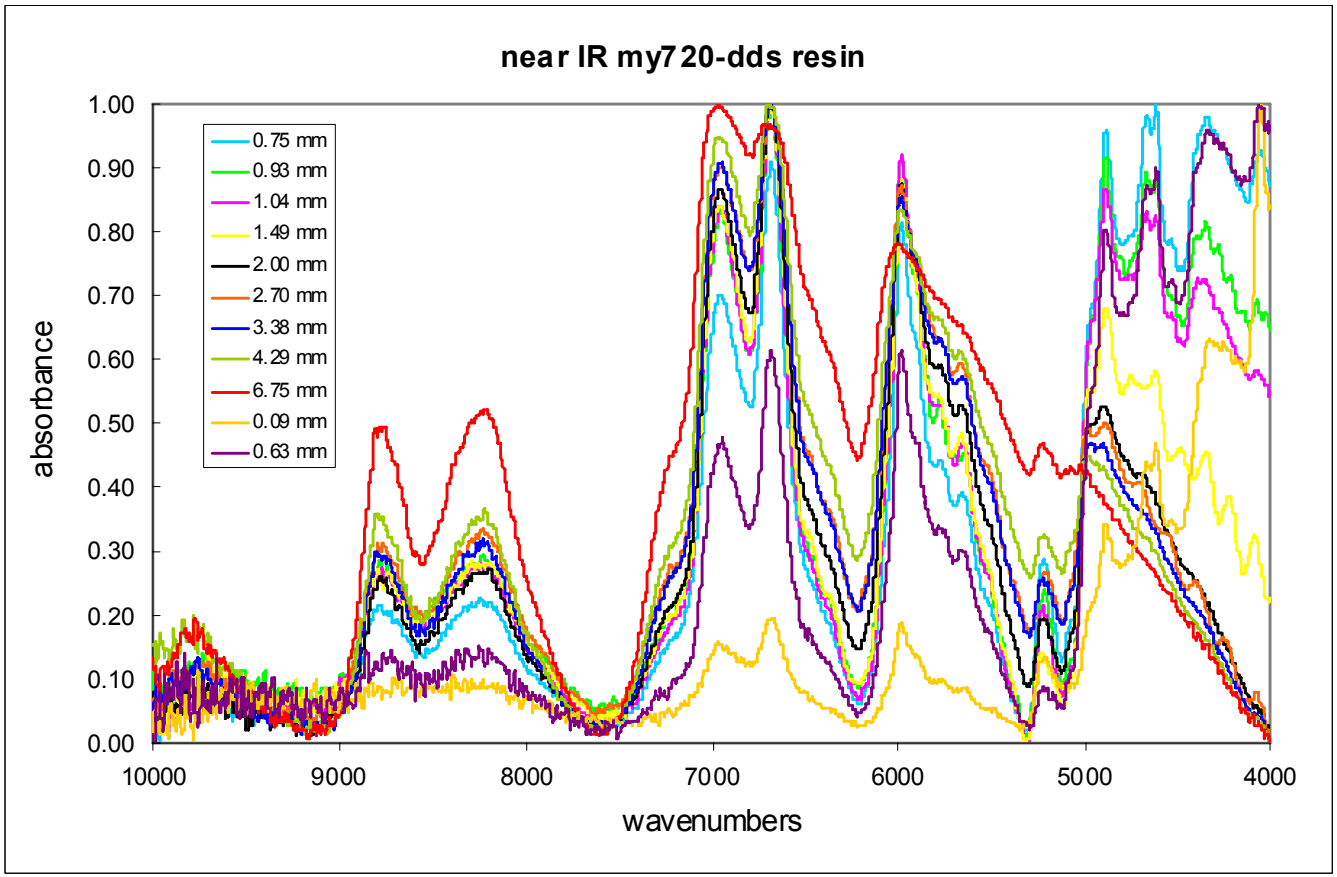
- $(A = e\,b\,c)$
- one unique peak used for analysis
- few standards required
- used when peaks don't overlap
- baselines must be stable
- sample matrix should be well understood
- accurate only in the range which the calibration curve is linear

However

A diffuse reflectance near IR spectrum of a resin is more complex than the transmission near IR spectrum of the same resin

For example

Absorptions at low wavenumbers in the near IR spectrum (5000-4000 cm^{-1}) are stronger for thinner samples than for thicker samples


near IR my720-dds resin
absorbance
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.75 mm
0.93 mm
1.04 mm
1.49 mm
2.00 mm
2.70 mm
3.38 mm
4.29 mm
6.75 mm
0.09 mm
0.63 mm
10000
9000
8000
7000
6000
5000
4000
wavenumbers

Chemometrics

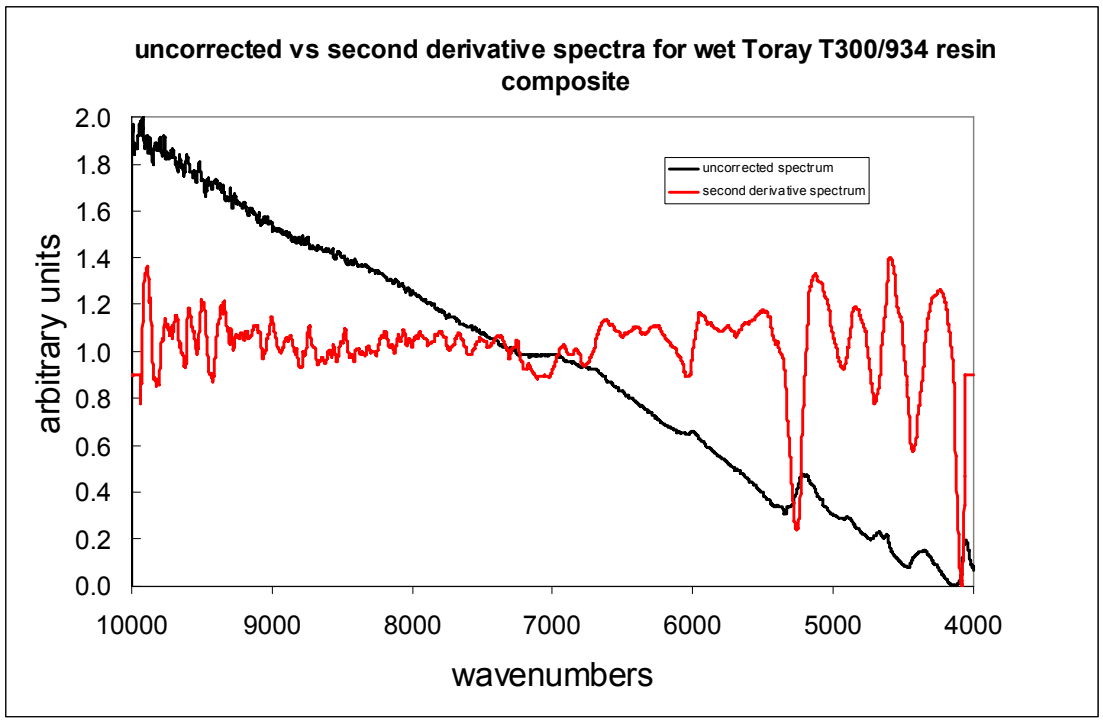
- International Chemometrics Society definition:

Chemometrics is the procedure of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods.

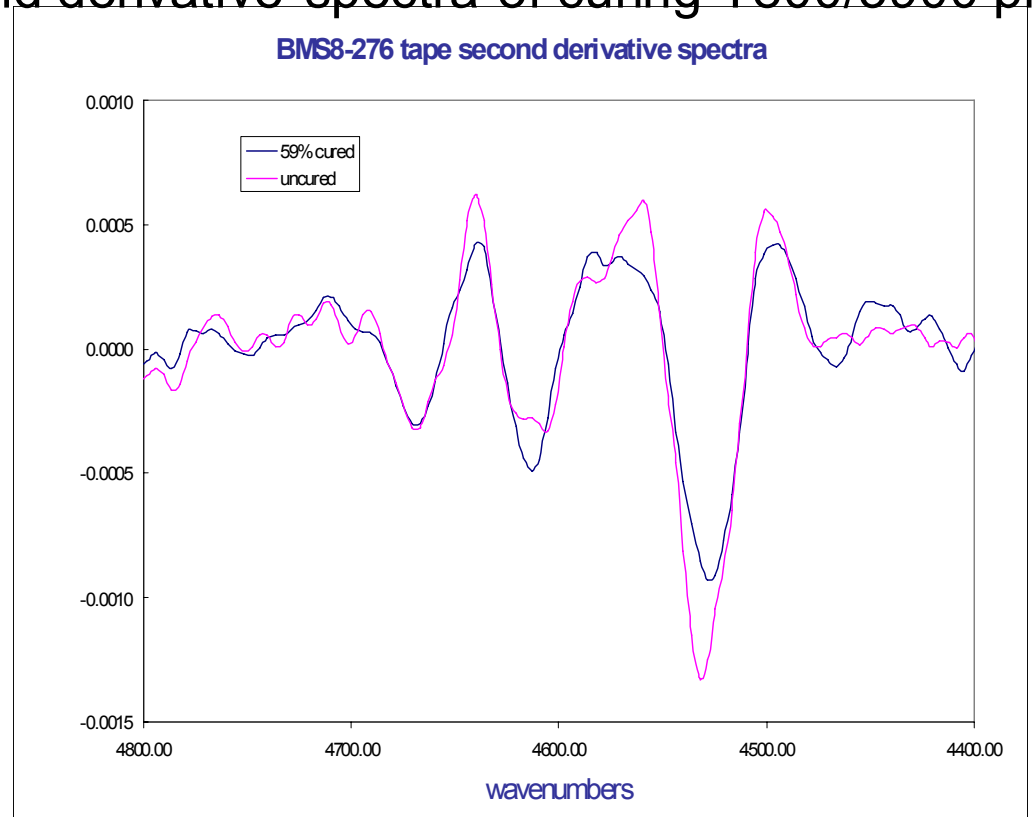
Partial Least Squares

- based on the partial least squares algorithm
- multiple region can be selected
- can be used when peaks overlap severely
- able to handle complex samples
- works well for relating sample properties other than concentration to spectra

Chemometrics calibration curve – second derivative spectra are subjected to partial least squares analysis



Second derivative spectra of curing T800/3900 prepreg



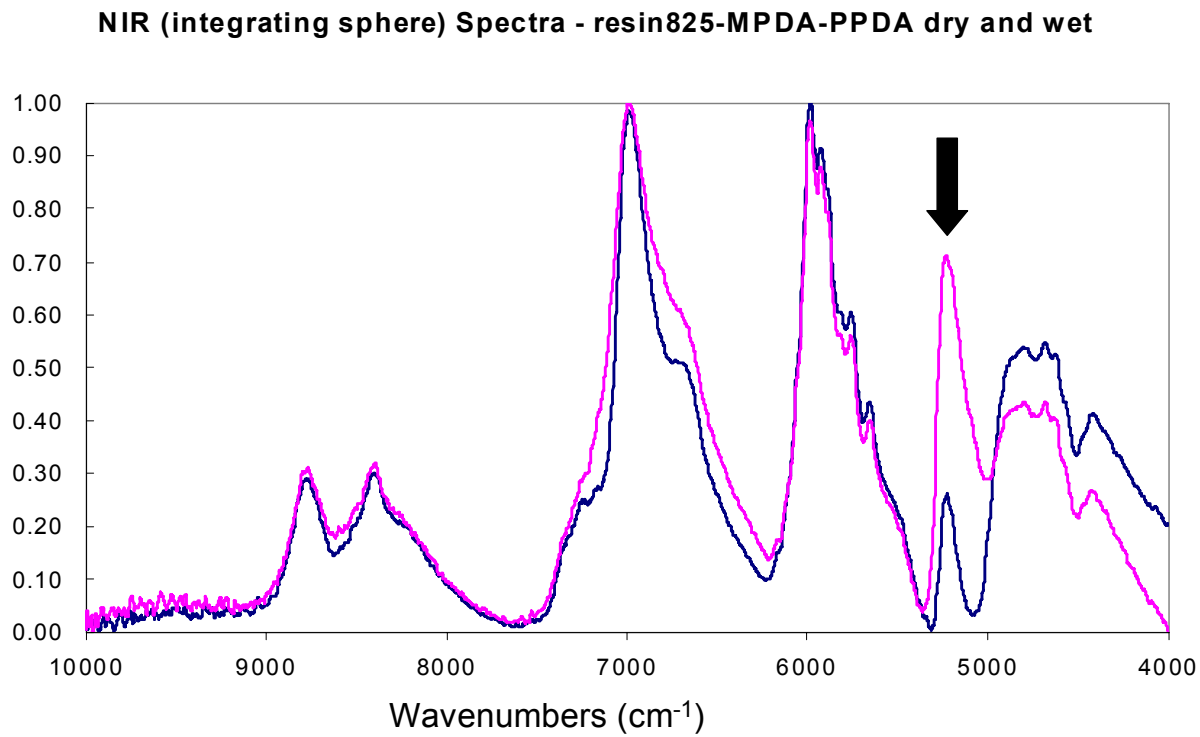
- **Goal #1**
- **To produce calibration curves relating near IR spectra to water content in epoxy resin based systems for water uptake and desorption in**
- **medium and high performance epoxy resins**

  and in
- **High performance adhesives and carbon fiber reinforced composites**

- **Background Info – water in composites**
- Combination stretching/deformation band @ 5215cm^{-1} due to $\nu_{assym} + \delta_{in\ plane}$

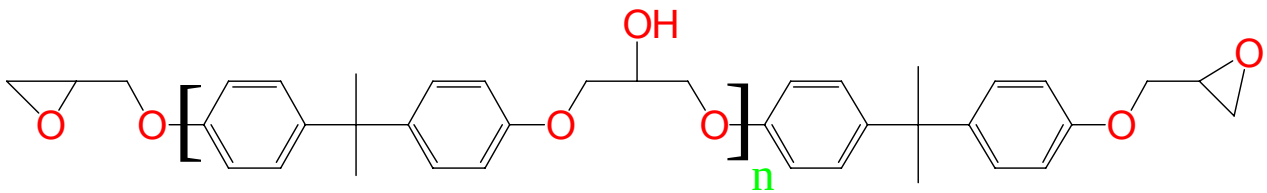
- Pro's
- Free of interference from resin hydroxyls
- Quantitative measure of water
- Con's
- Little info on state of water in resin

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



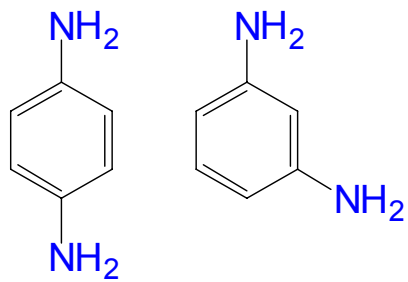
A stoicheometrically balanced mid performance epoxy resin

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

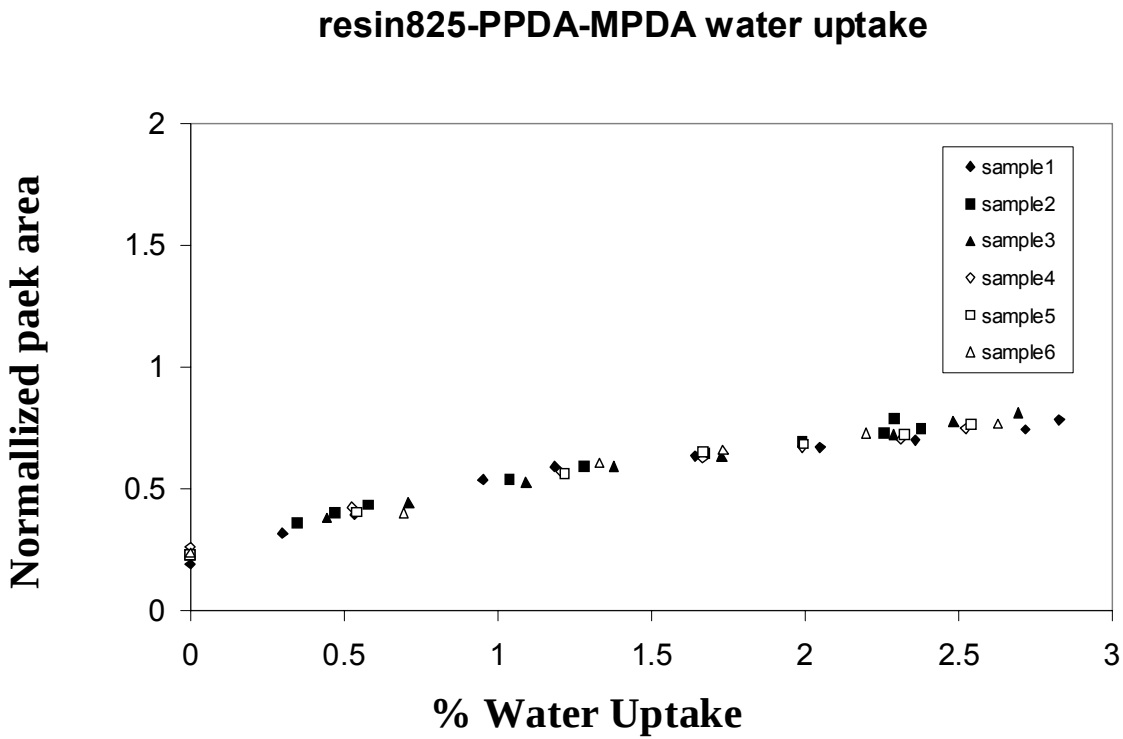


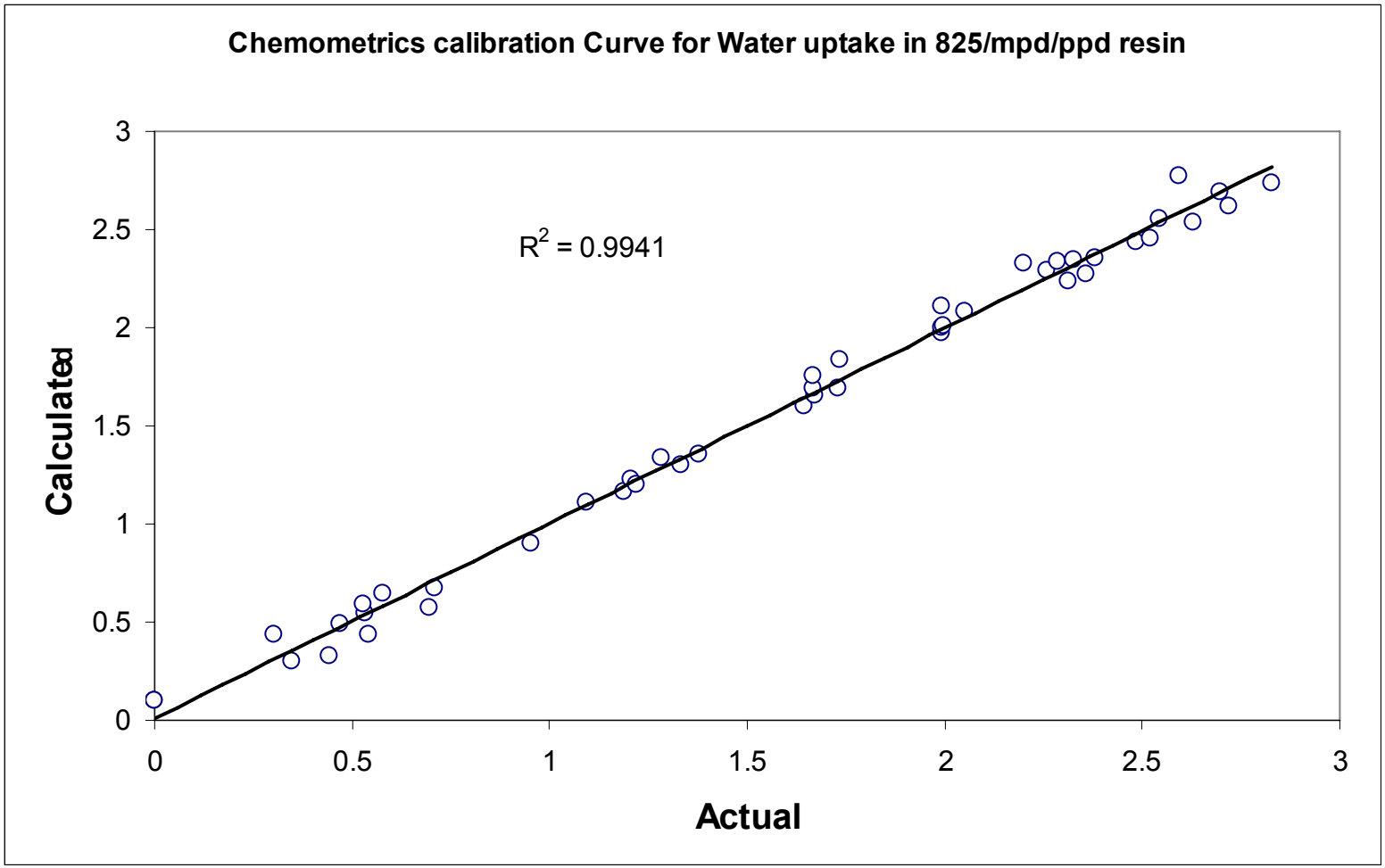
Epoxy Resin
Epon 825
n ~ 0

Curative - PPDA : MPDA
1:1 mole : mole

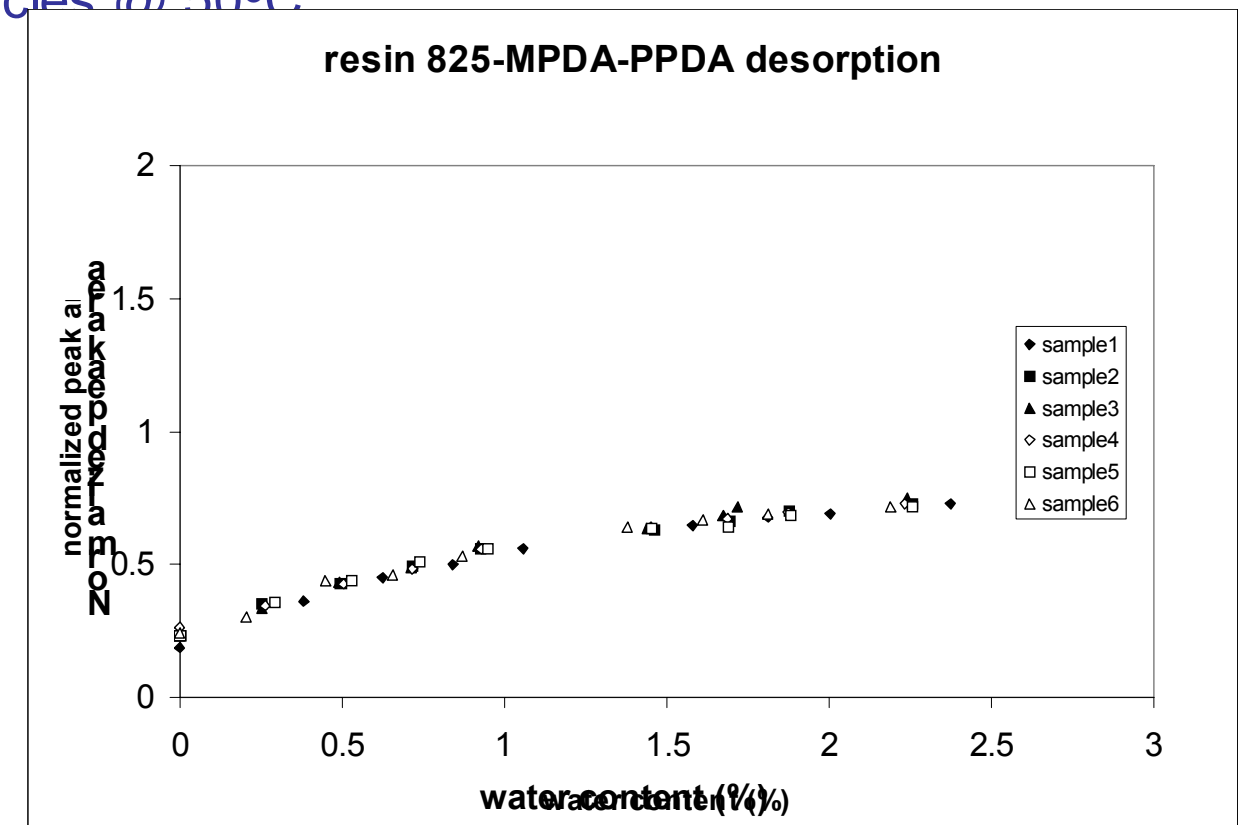


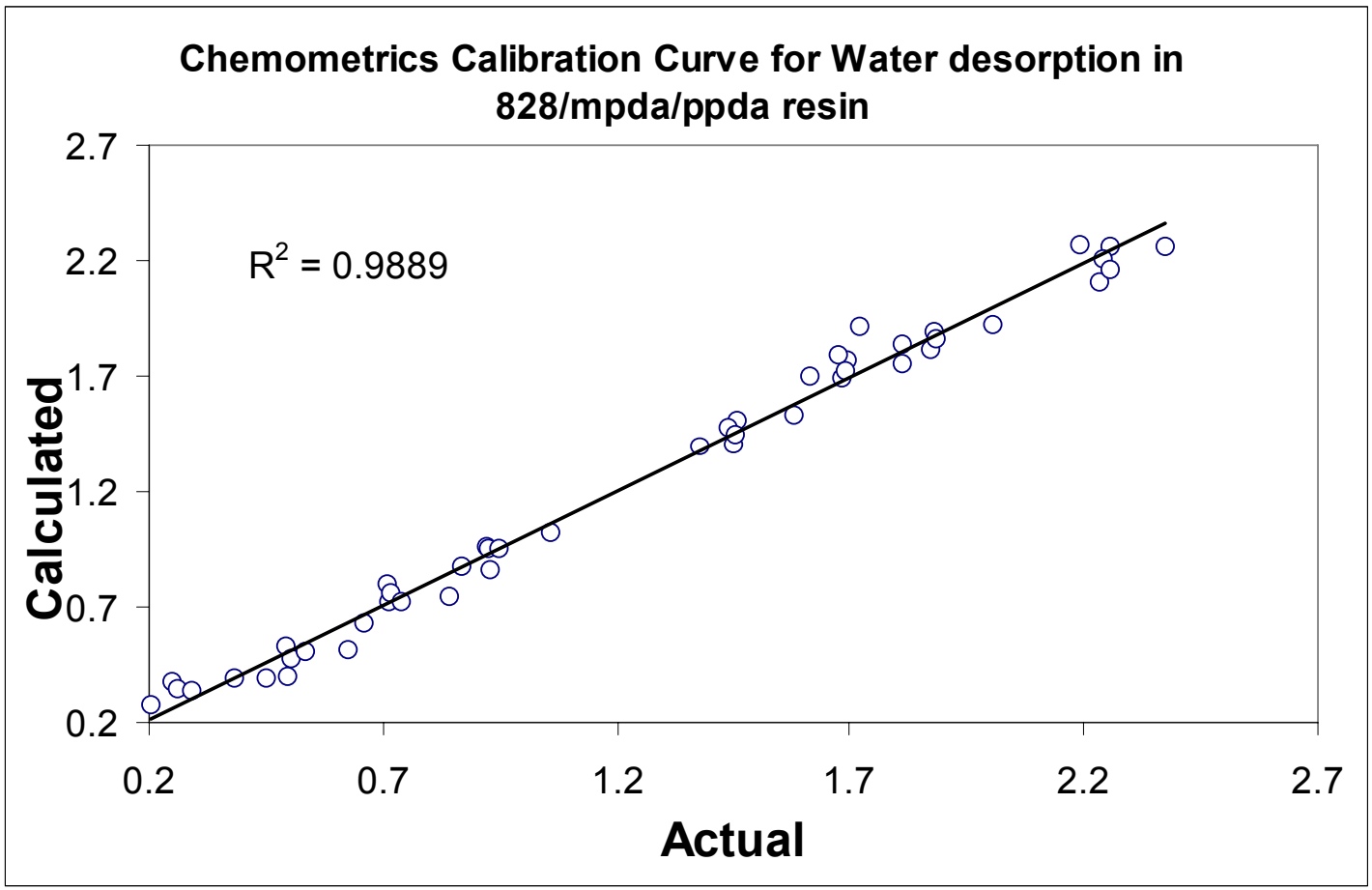
A plot of normalized water absorbance at 5215 cm^{-1} , versus % water uptake for a mid performance epoxy resin system



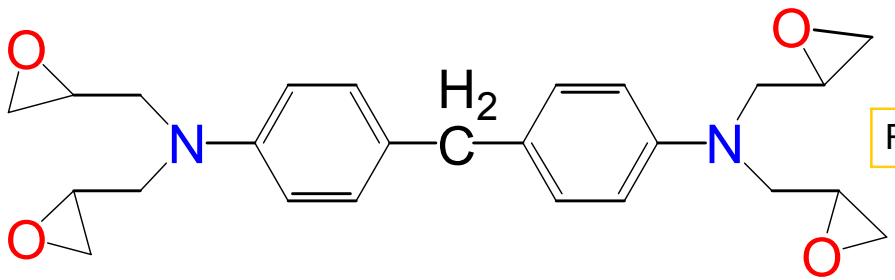

Chemometrics calibration Curve for Water uptake in 825/mpd/ppd resin
R2 = 0.9941
Calculated
Actual
0
0.5
1
1.5
2
2.5
3

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

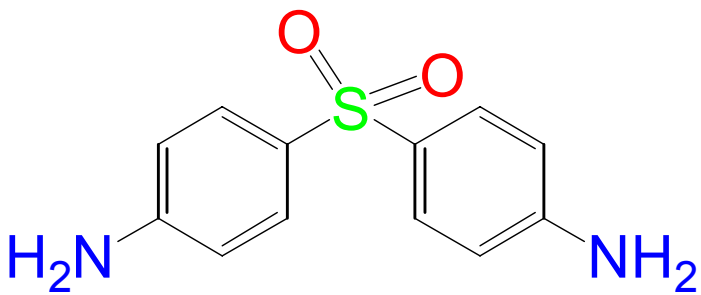



Chemometrics Calibration Curve for Water desorption in 828/mpda/ppda resin
R^2 = 0.9889
Calculated
Actual
2.7
2.2
1.7
1.2
0.7
0.2
0.2
0.7
1.2
1.7
2.2
2.7

Water in a high performance epoxy resin formulated to "mimic" 934 resin, with 1.1 to 1.0 mole/mole curative to resin



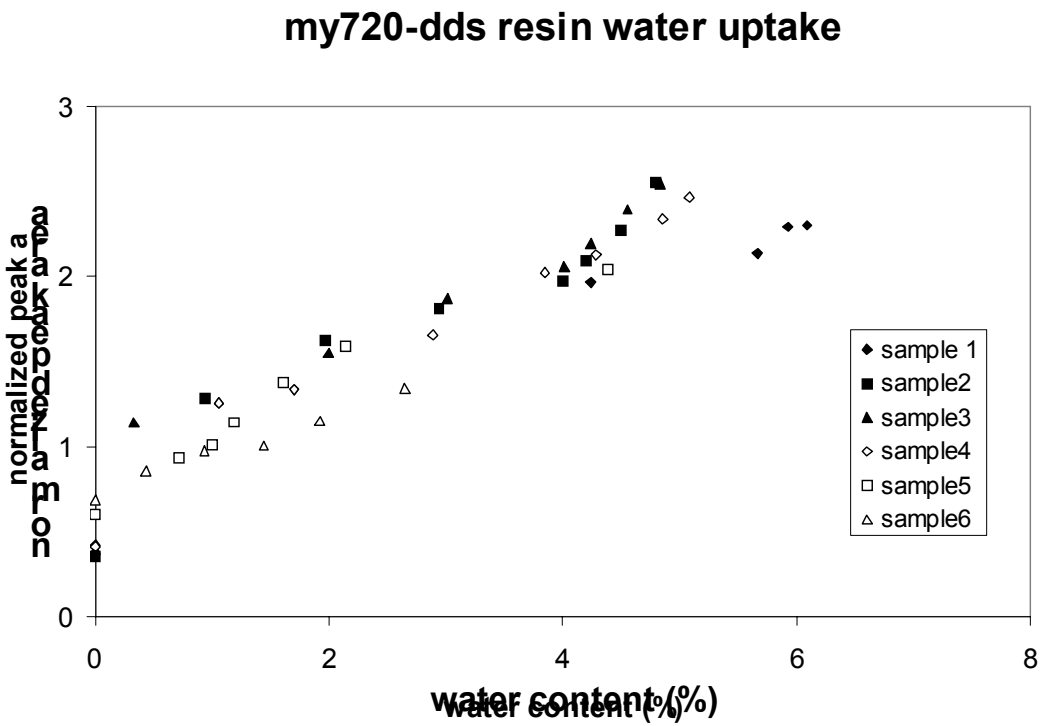
Resin – TGDDM (MY720)

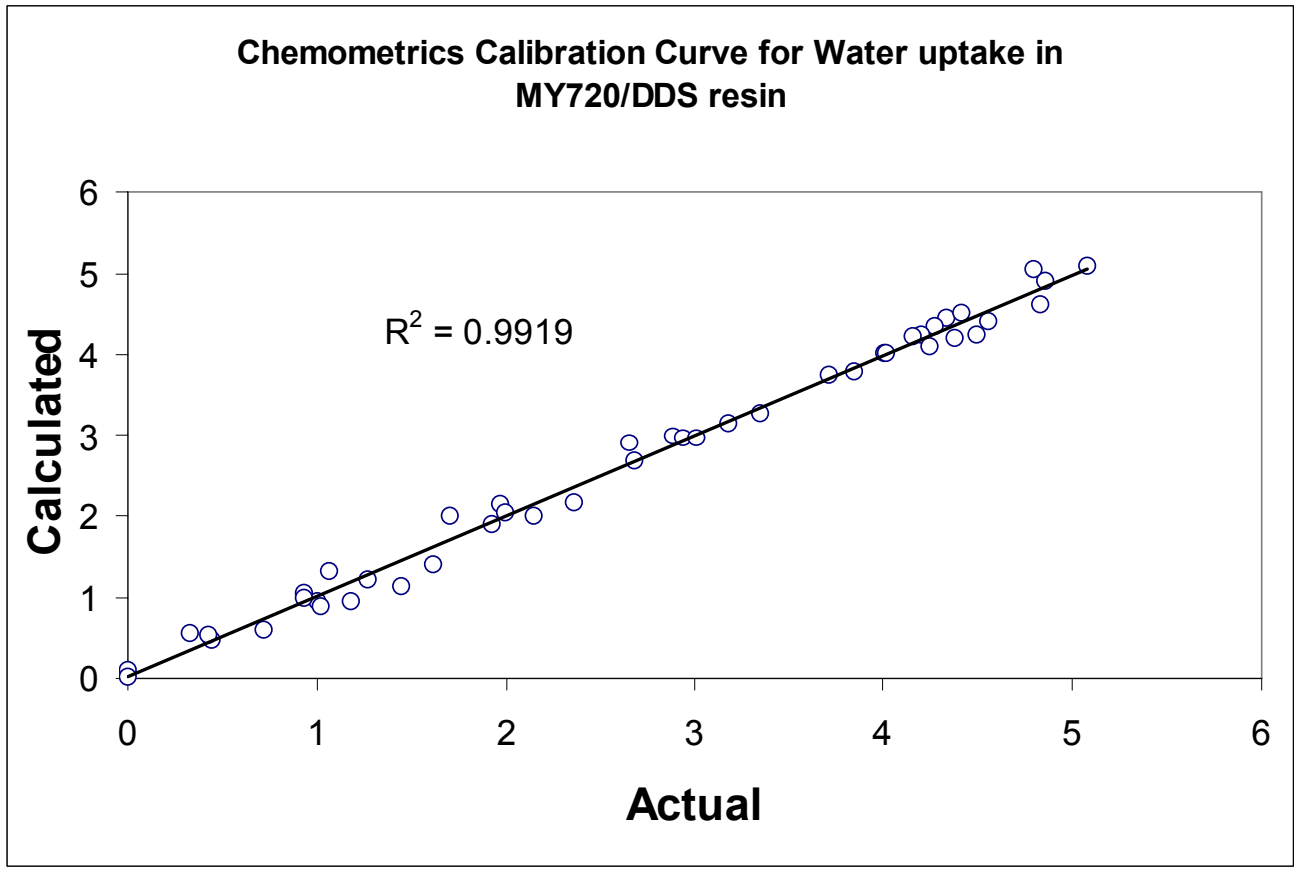


Curative - DDS

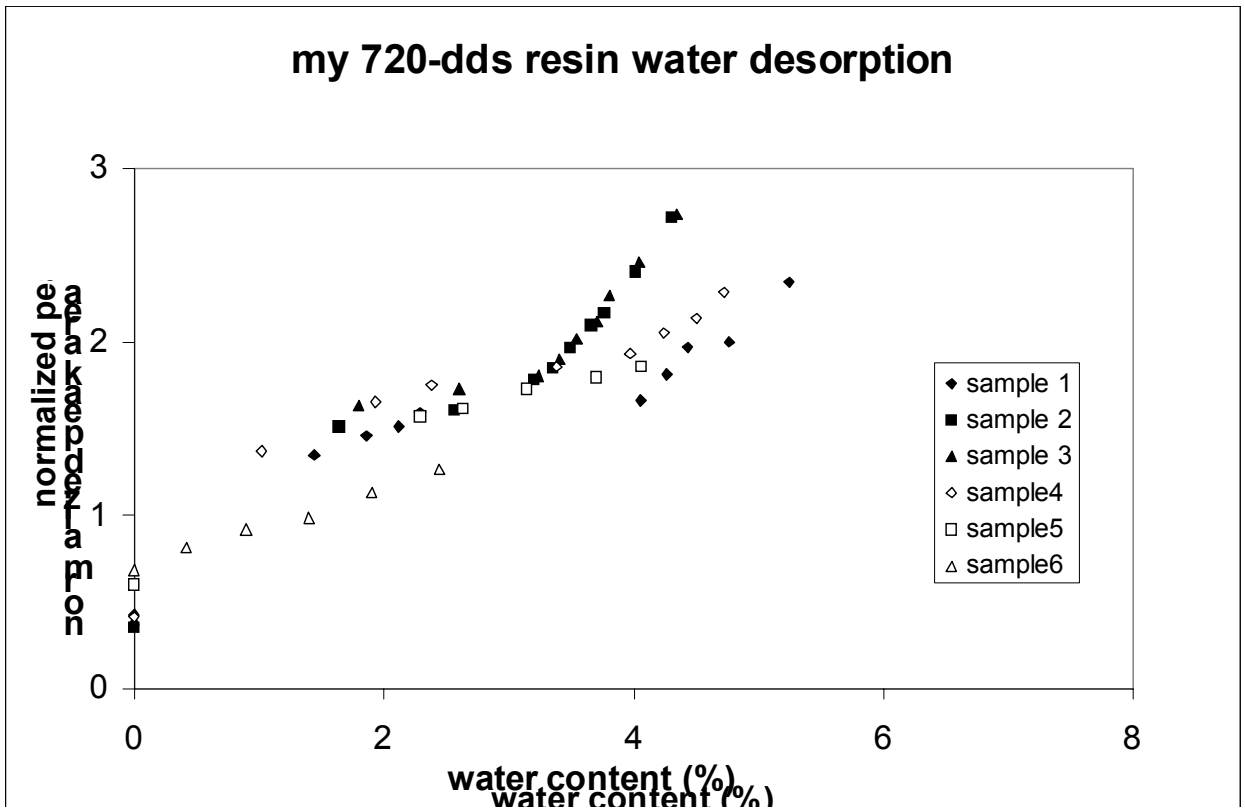
Resin cured between steel plates 2h at 140°C then 4h at 200°C

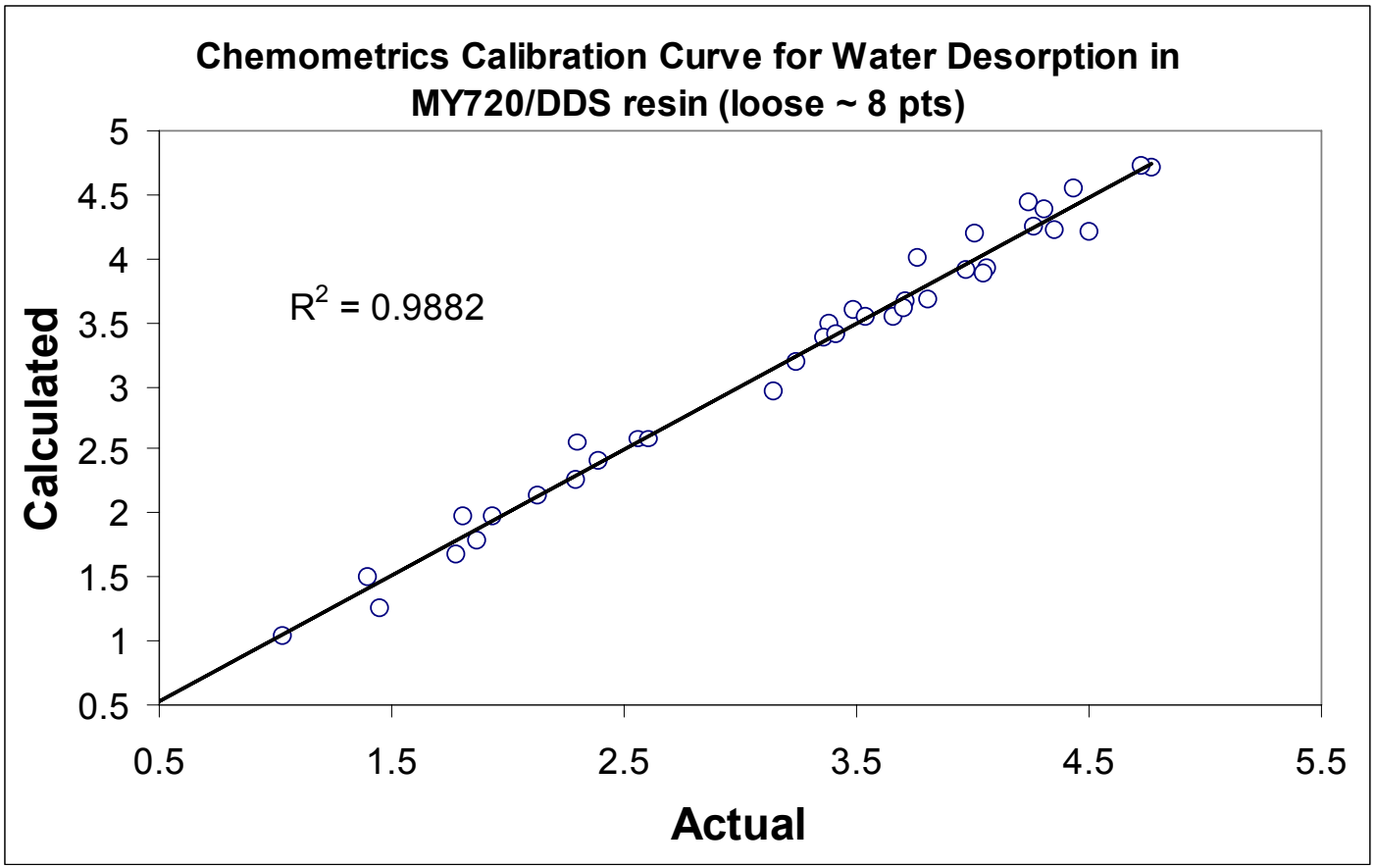
A plot of normalized water absorbance at 5215 cm-1 versus % water uptake for a high performance epoxy resin system




Chemometrics Calibration Curve for Water uptake in MY720/DDS resin
R^2 = 0.9919
Calculated
Actual
0
1
2
3
4
5
6

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



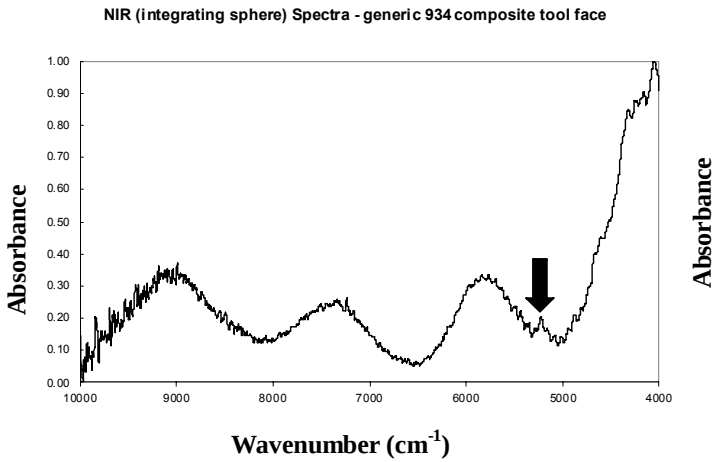

Chemometrics Calibration Curve for Water Desorption in MY720/DDS resin (loose ~ 8 pts)
R^2 = 0.9882
Calculated
Actual
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0.5
1.5
2.5
3.5
4.5
5.5

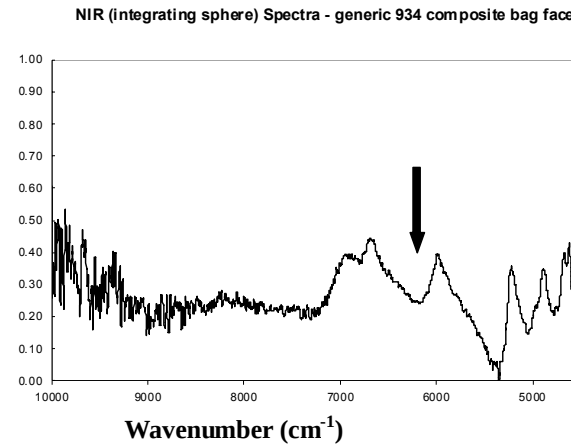
The near IR technique

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

- Does not work well on resin poor (tool) surfaces

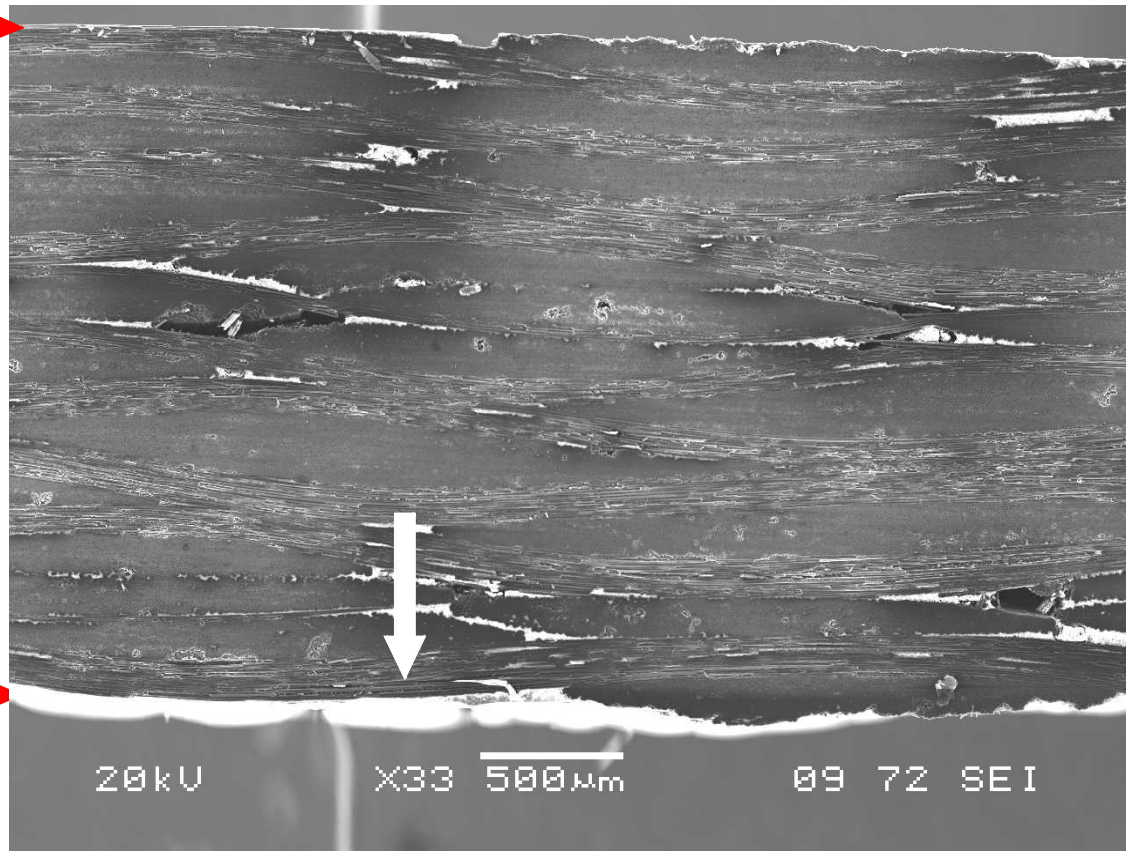
Near IR spectra of tool face (left) and bag face (right) of composite. “Bag face” spectra can be normalized





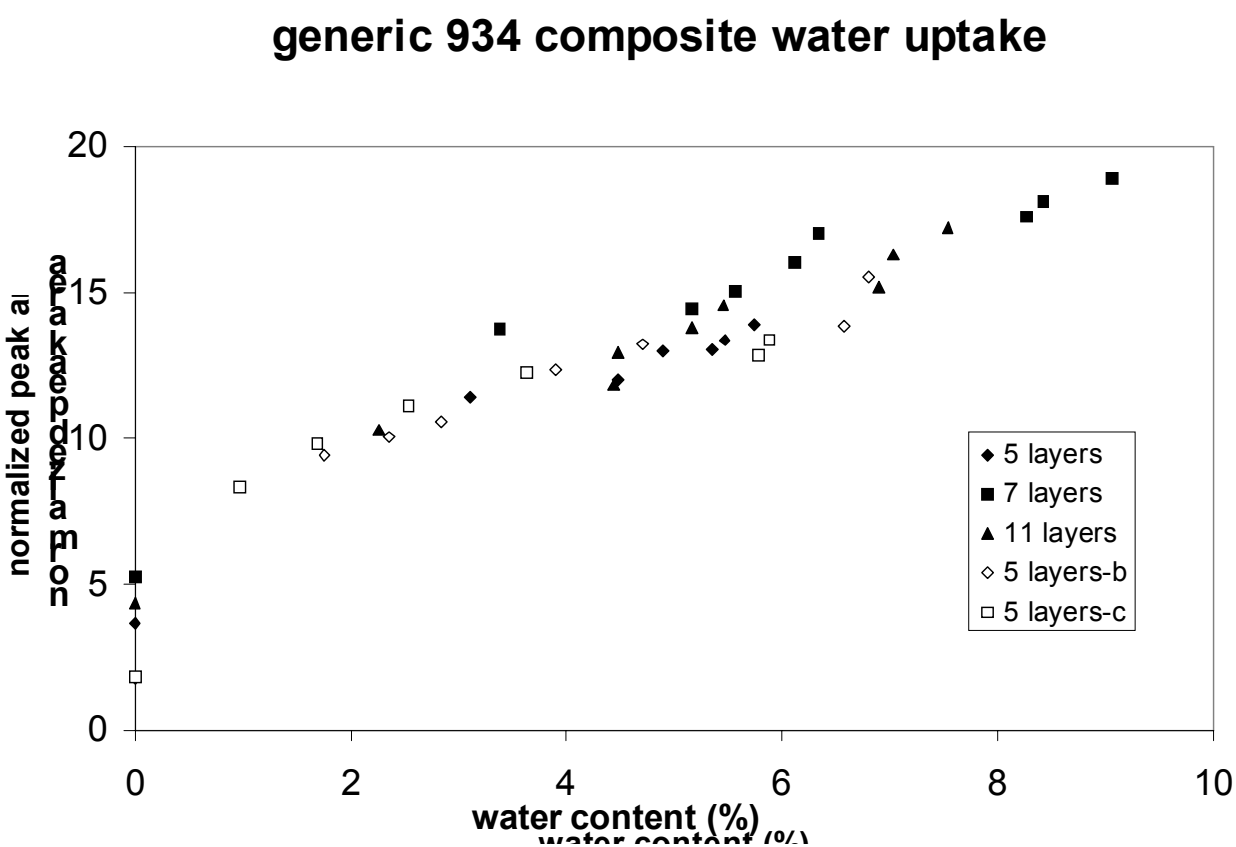
Tool face

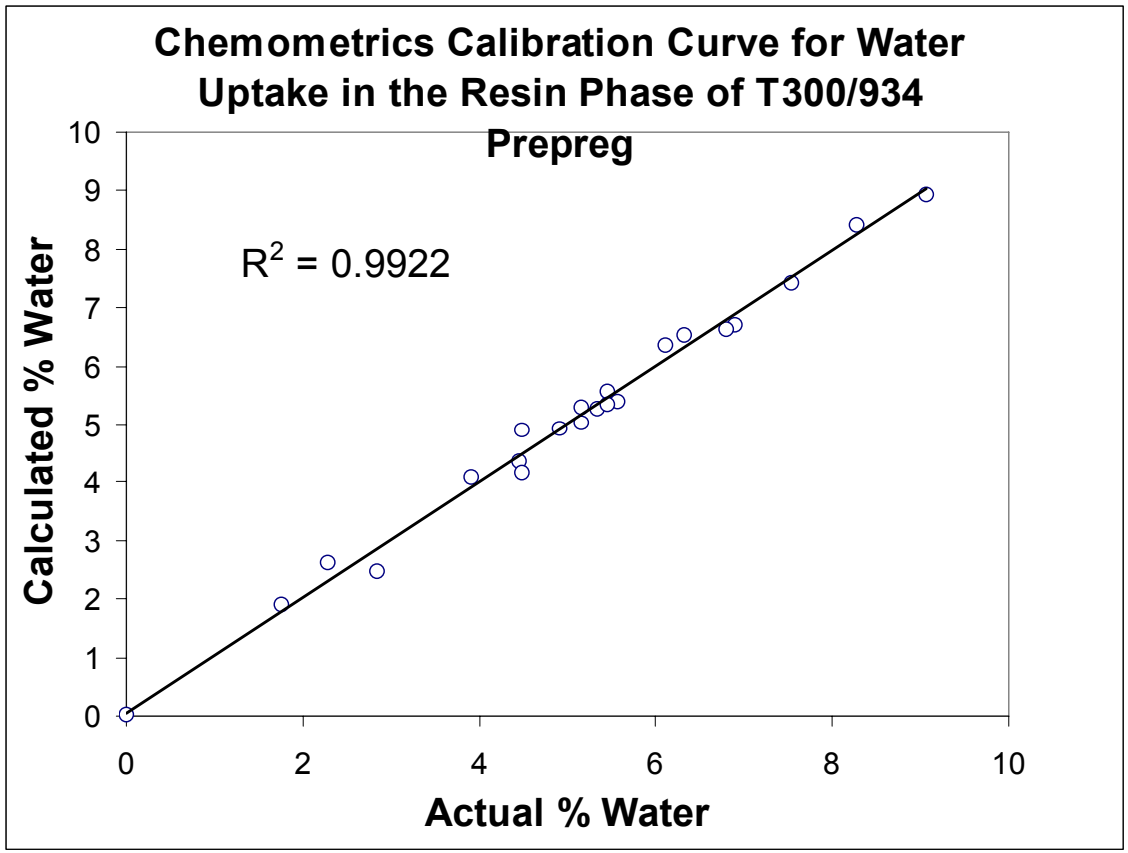
Resin rich regions are overexposed due to charging



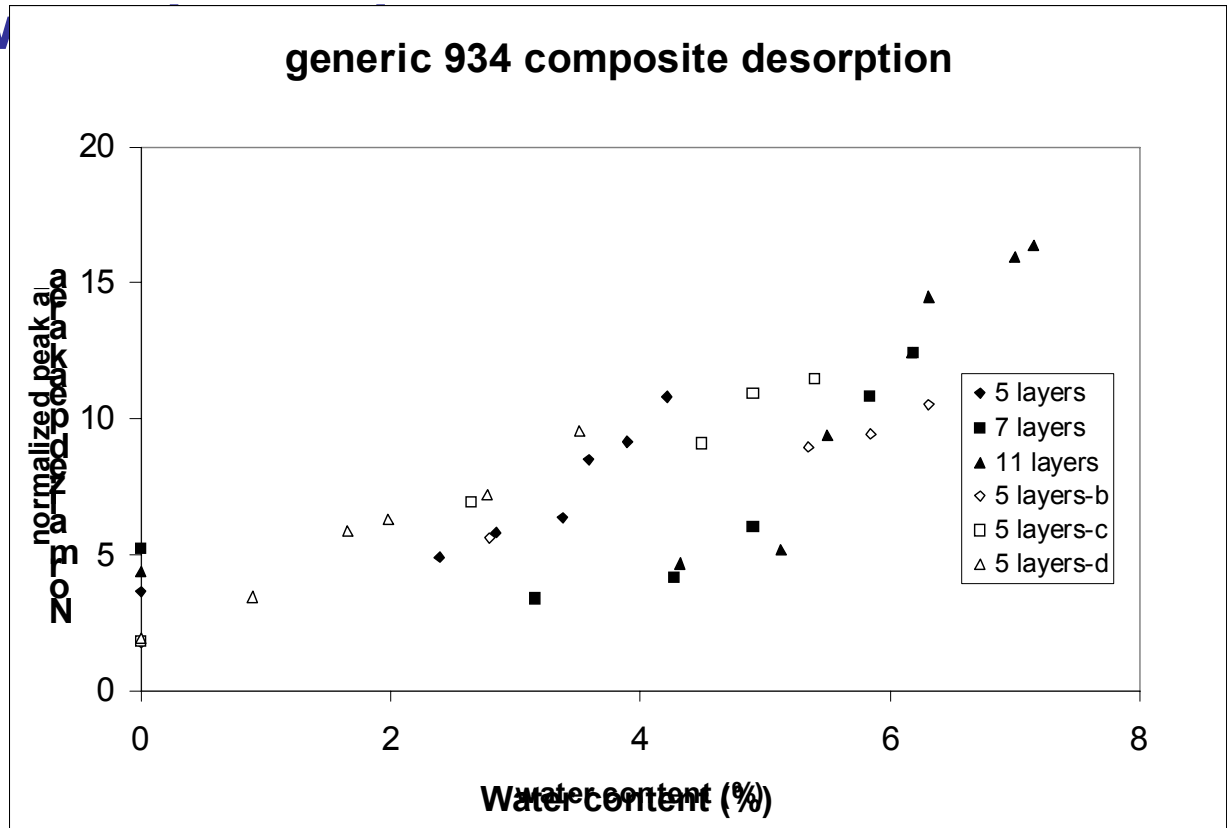
Bag face

A plot of normalized water absorbance at 5215 cm^{-1} versus % wa
us

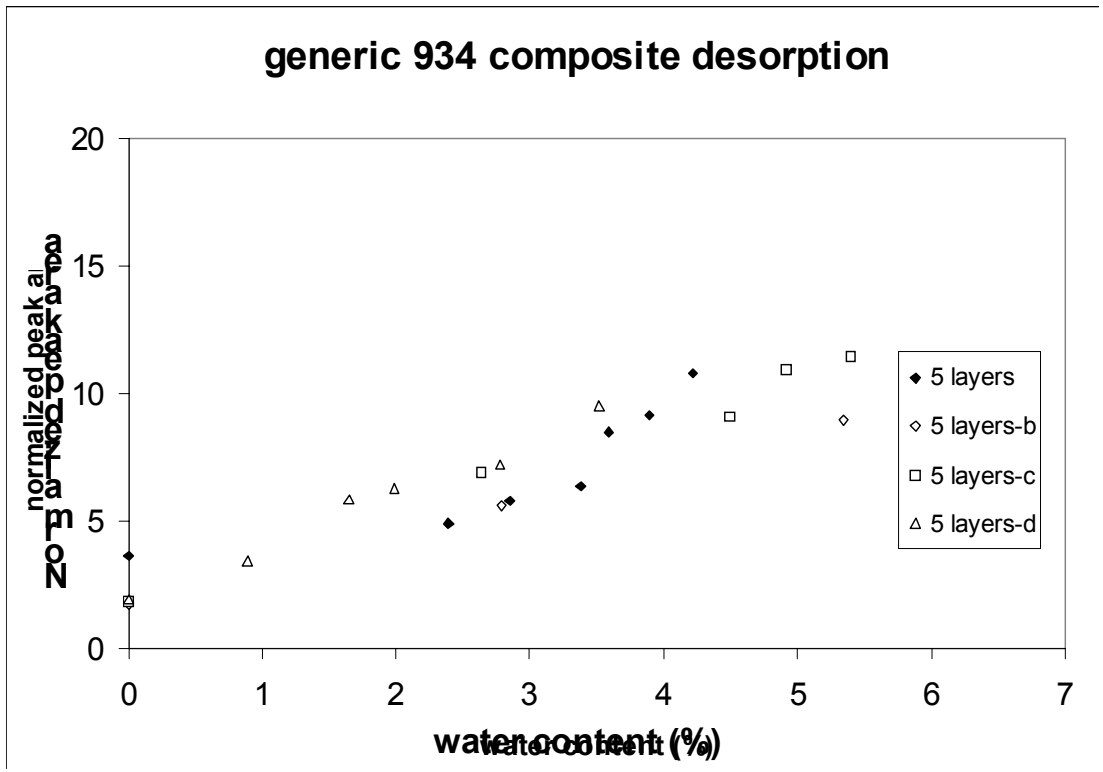


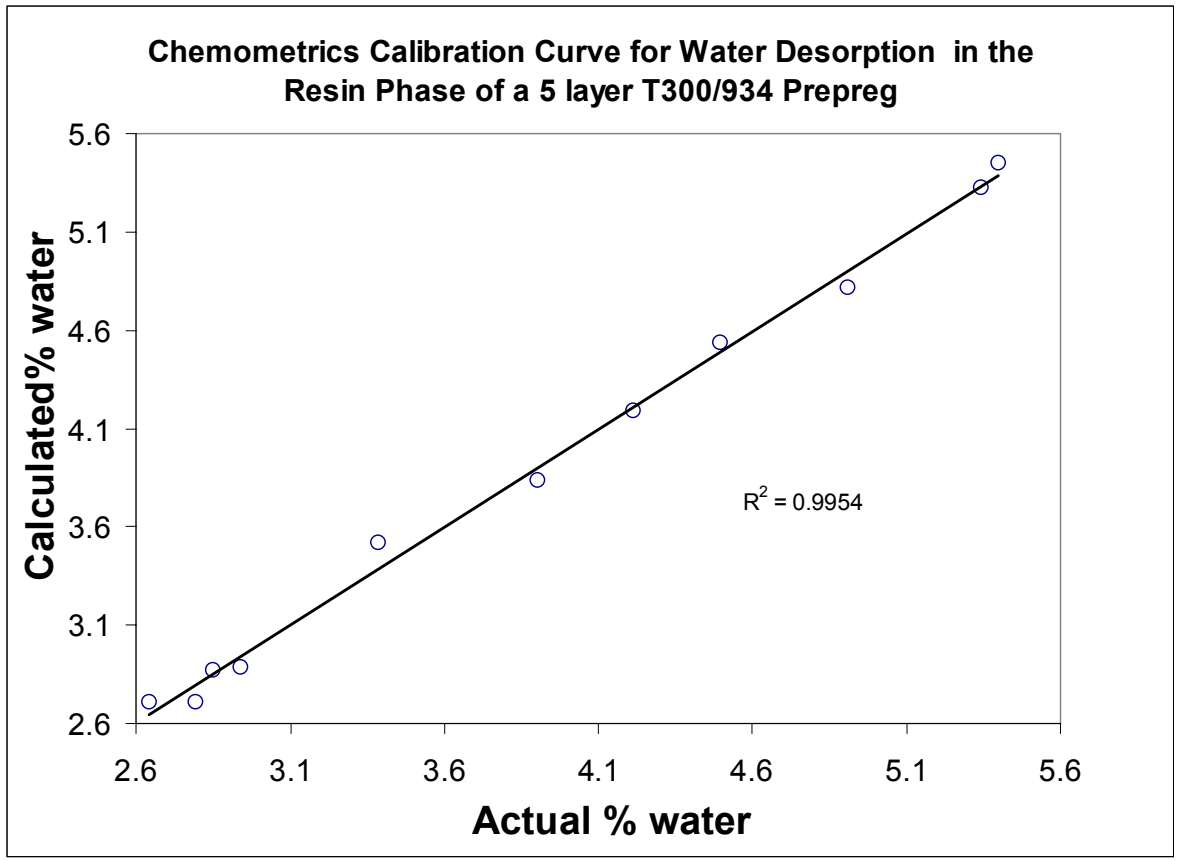

Chemometrics Calibration Curve for Water Uptake in the Resin Phase of T300/934 Prepreg
R2 = 0.9922
Calculated % Water
Actual % Water
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10

composite made using T300/934 prepreg,
w

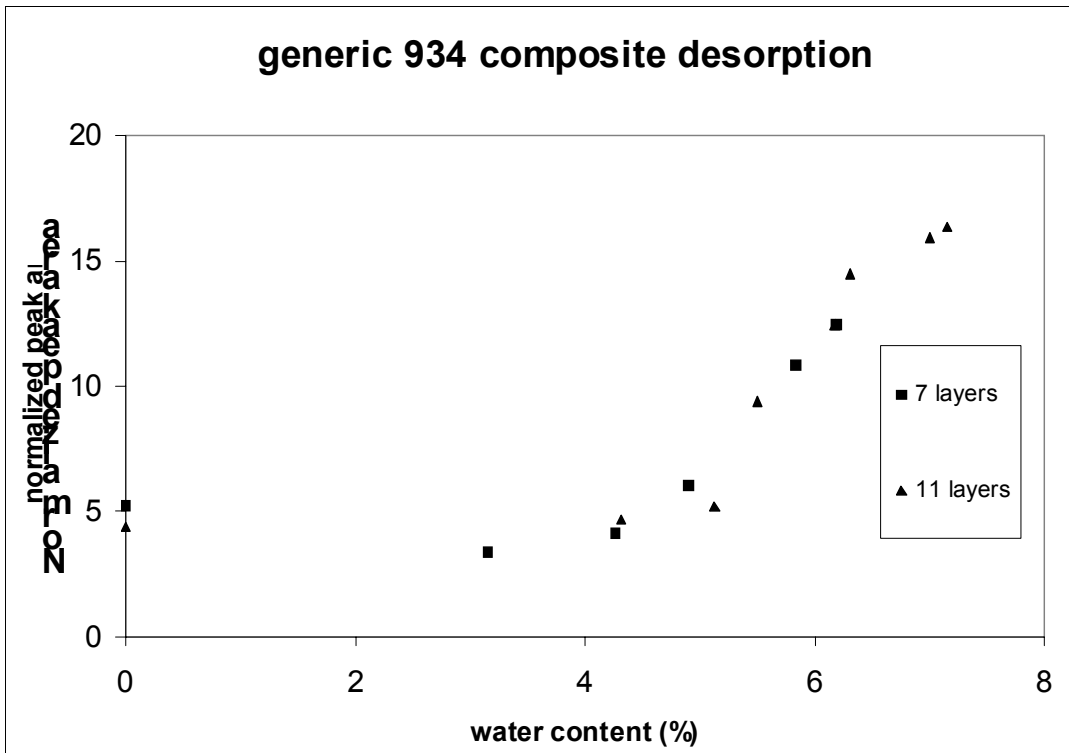


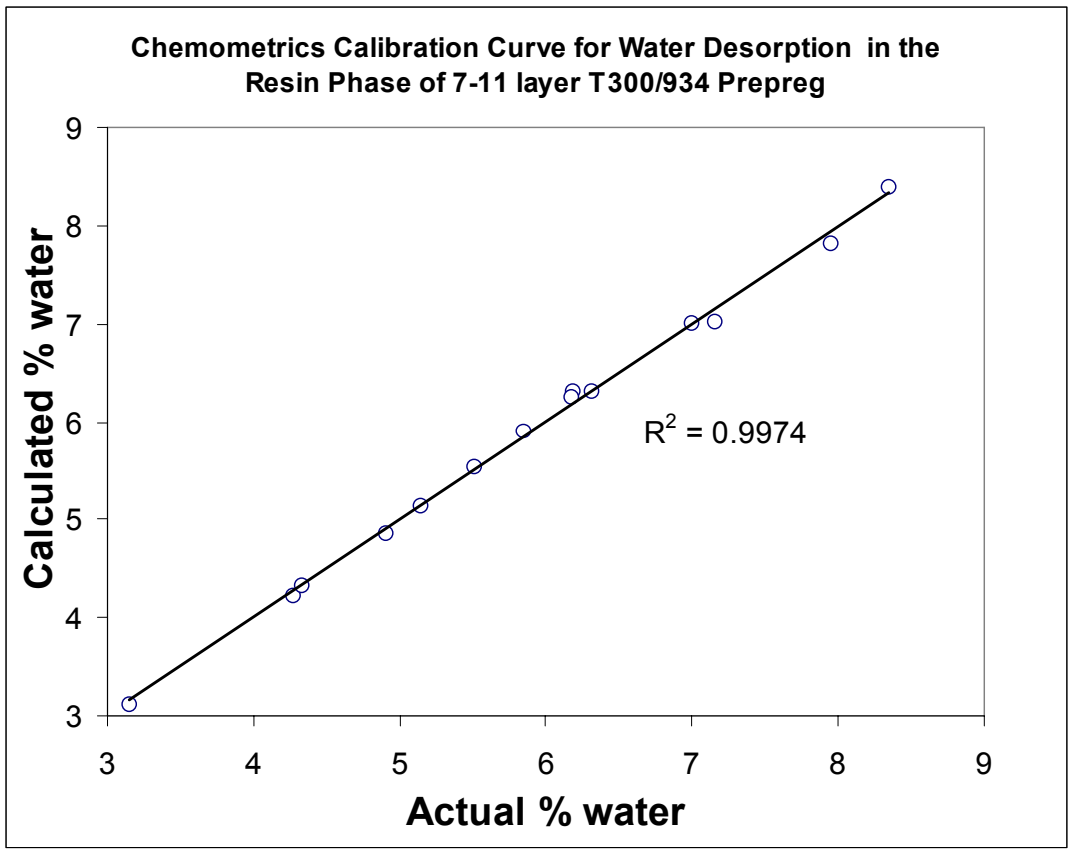
Desorption 5 layers

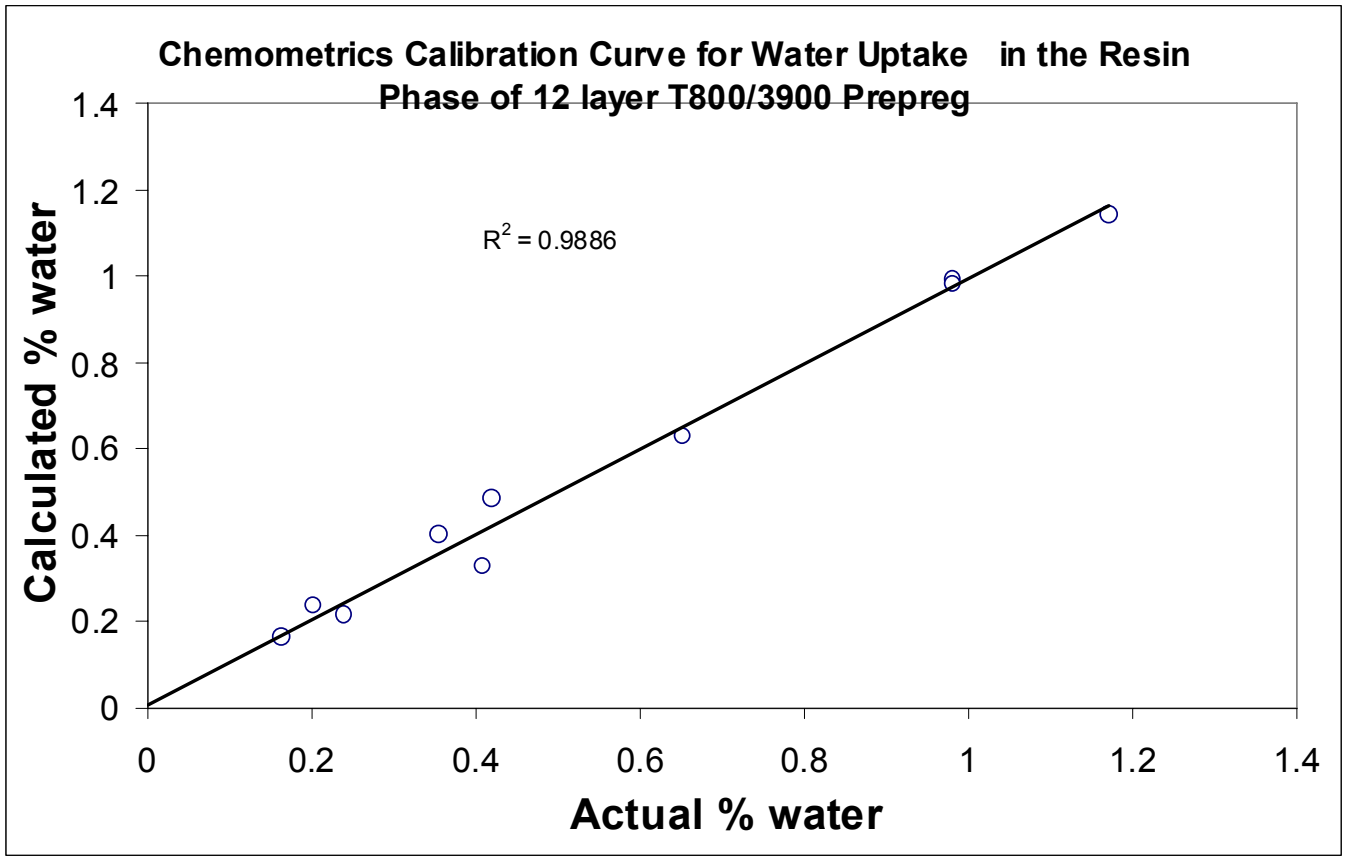


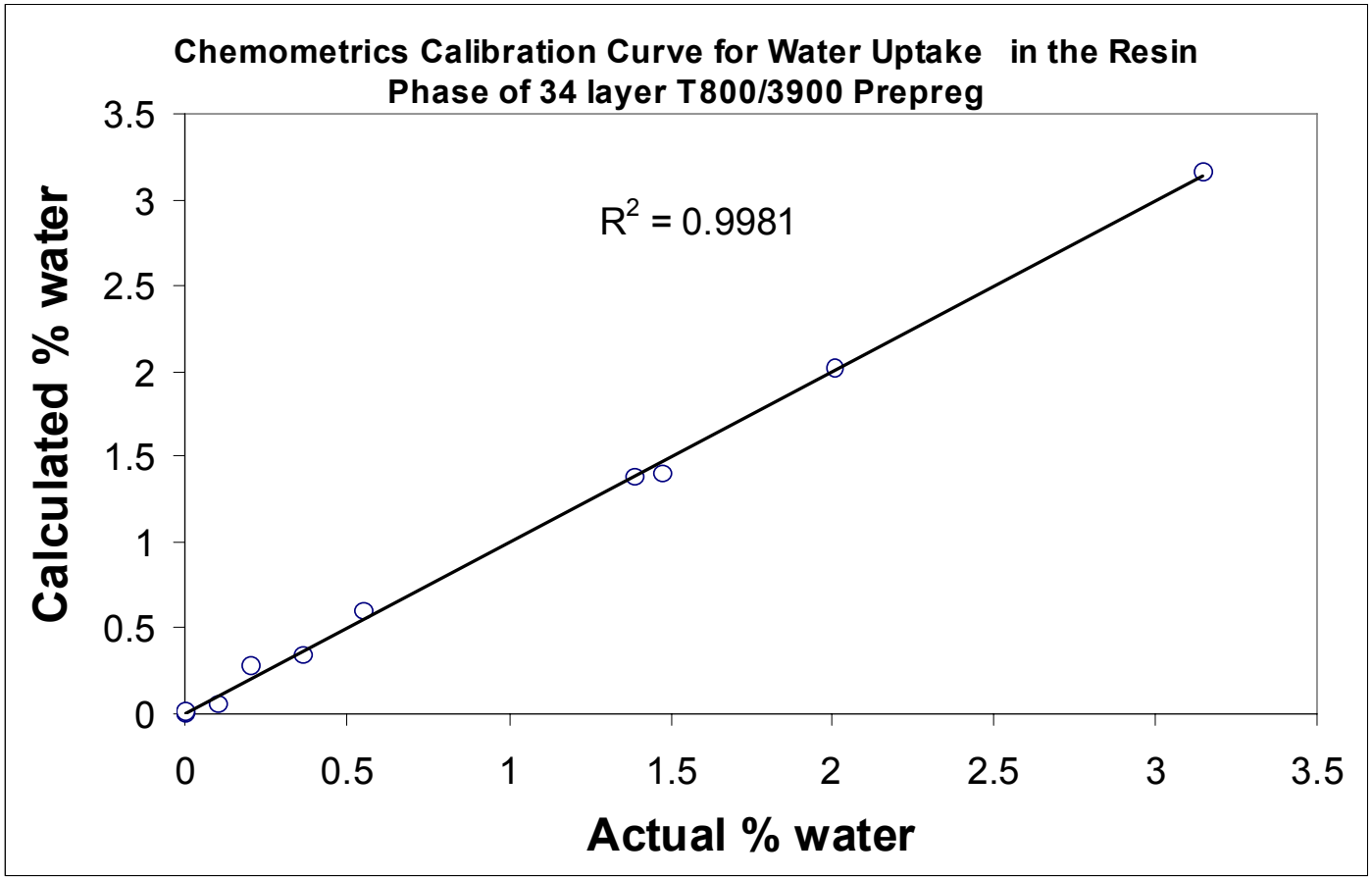

Chemometrics Calibration Curve for Water Desorption in the Resin Phase of a 5 layer T300/934 Prepreg
Calculated% water
Actual % water
5.6
5.1
4.6
4.1
3.6
3.1
2.6
2.6
3.1
3.6
4.1
4.6
5.1
5.6
R2 = 0.9954

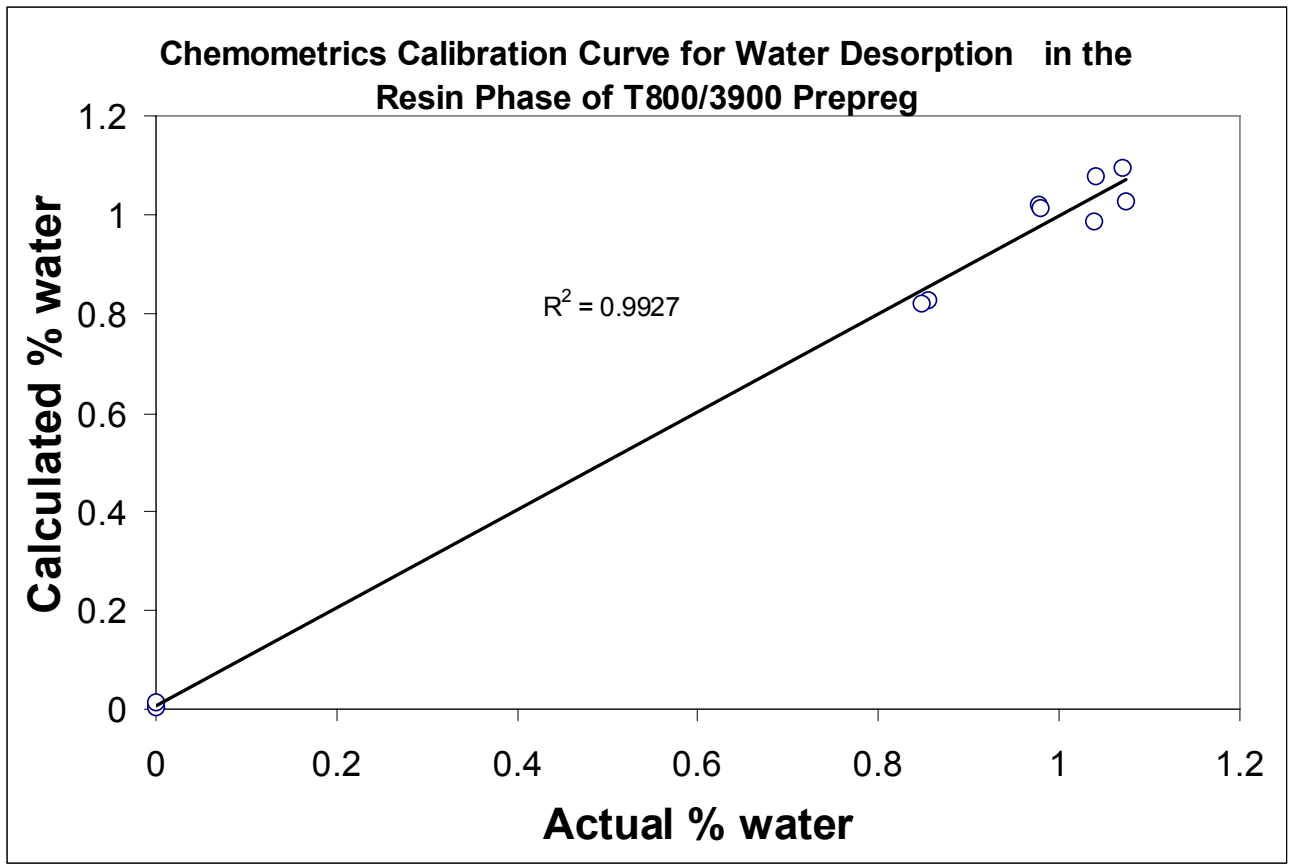
Desorption 7 & 11 layers




Chemometrics Calibration Curve for Water Desorption in the Resin Phase of 7-11 layer T300/934 Prepreg
Calculated % water
Actual % water
R2 = 0.9974
3
4
5
6
7
8
9


Chemometrics Calibration Curve for Water Uptake in the Resin Phase of 12 layer T800/3900 Prepreg
R^2 = 0.9886
Calculated % water
Actual % water
0
0.2
0.4
0.6
0.8
1
1.2
1.4


Chemometrics Calibration Curve for Water Uptake in the Resin Phase of 34 layer T800/3900 Prepreg
R^2 = 0.9981
Calculated % water
Actual % water
0
0.5
1
1.5
2
2.5
3
3.5

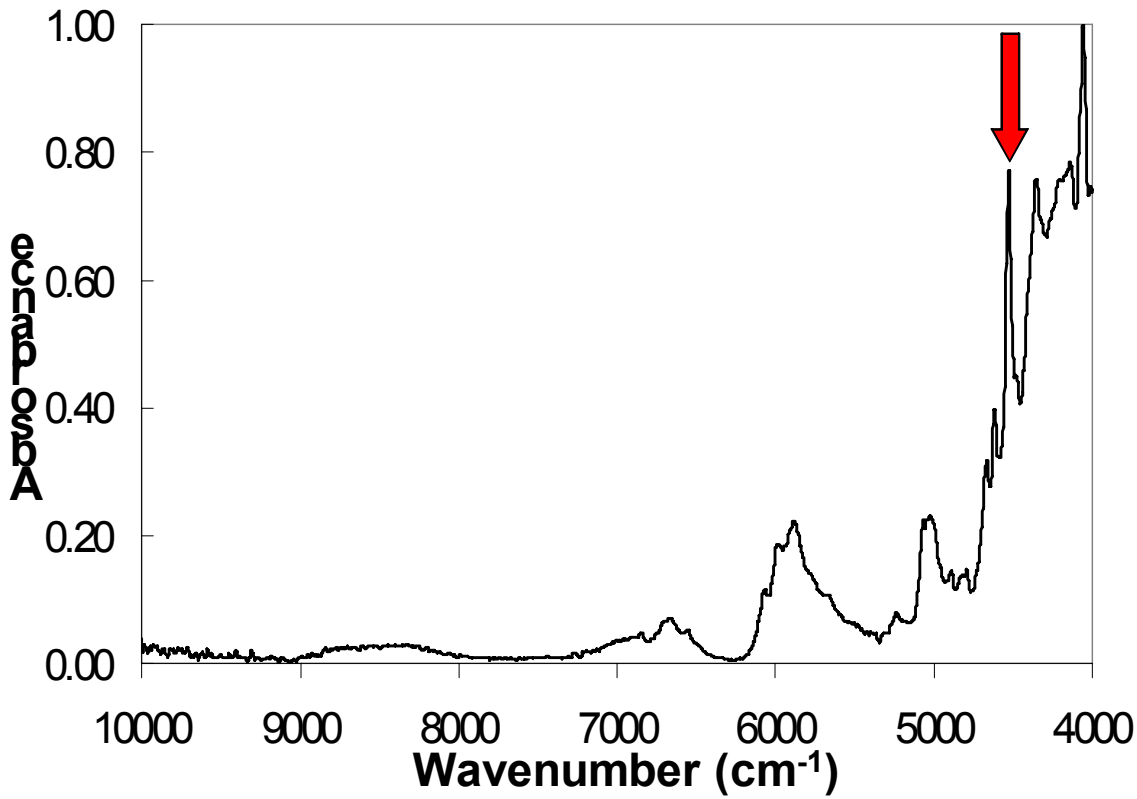

Chemometrics Calibration Curve for Water Desorption in the Resin Phase of T800/3900 Prepreg
Calculated % water
Actual % water
R2 = 0.9927
0
0.2
0.4
0.6
0.8
1
1.2

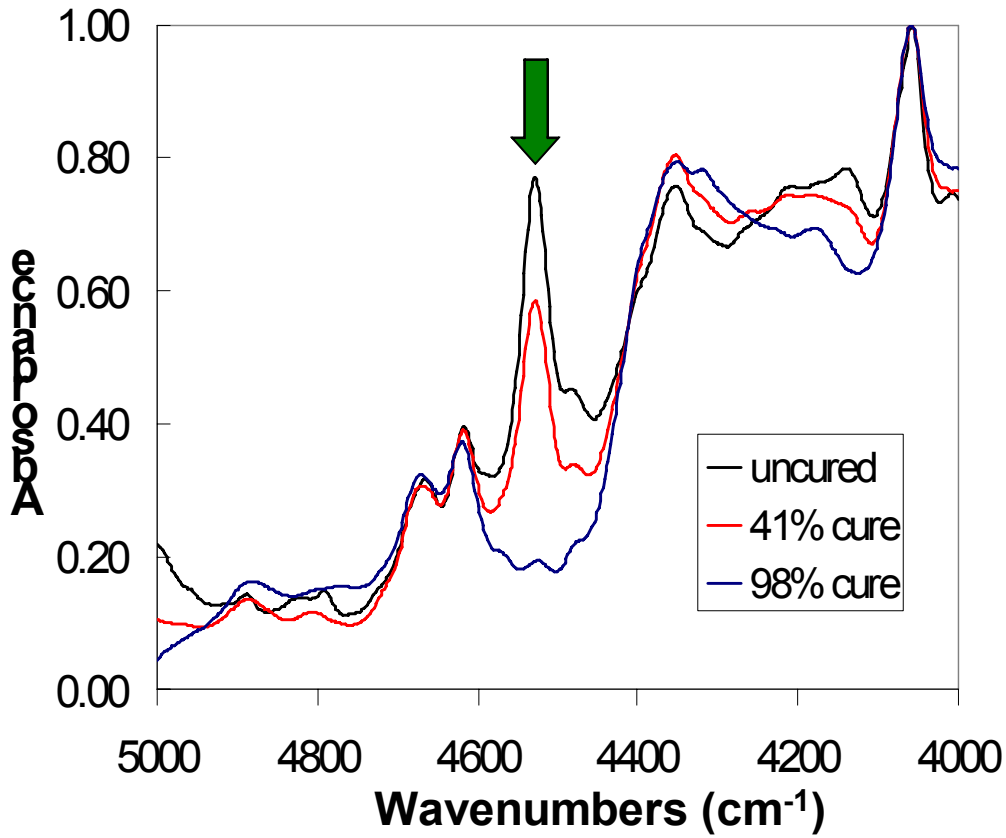
- **Goal #2**
- **To produce calibration curves relating near IR spectrum to cure state in epoxy based**
- **High performance adhesive systems**
- **High performance carbon fiber reinforced composite systems**

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

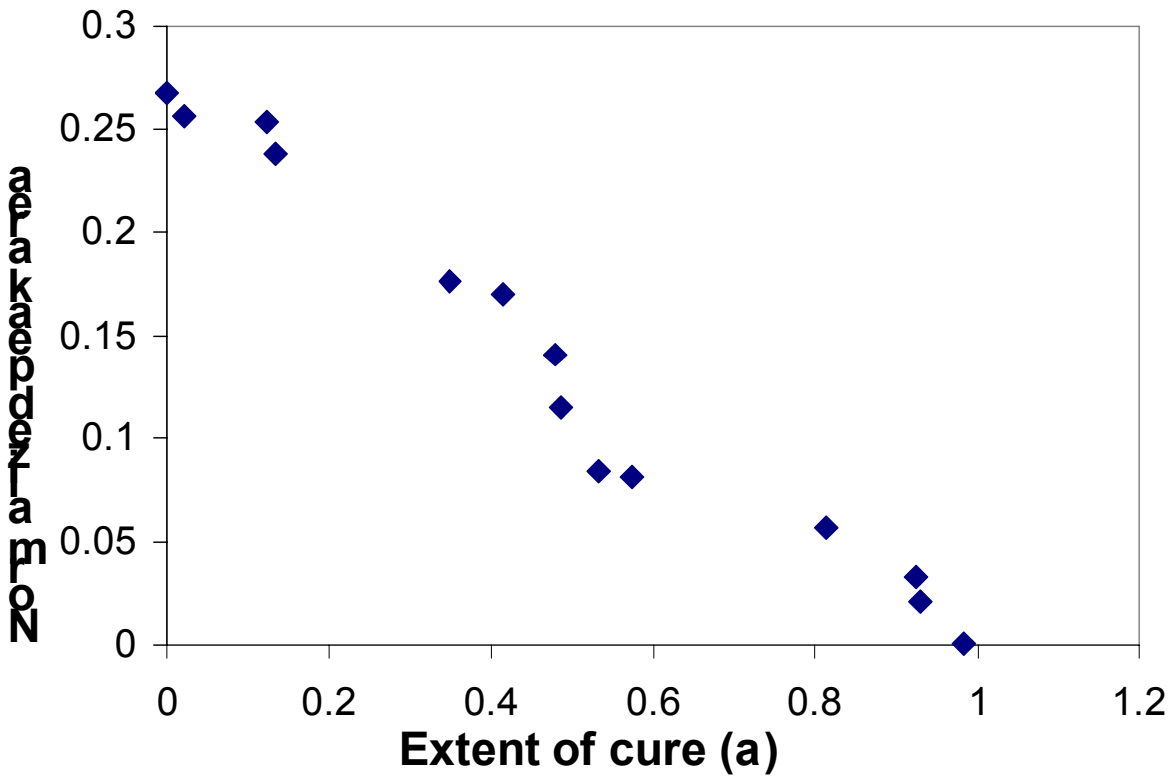
Background

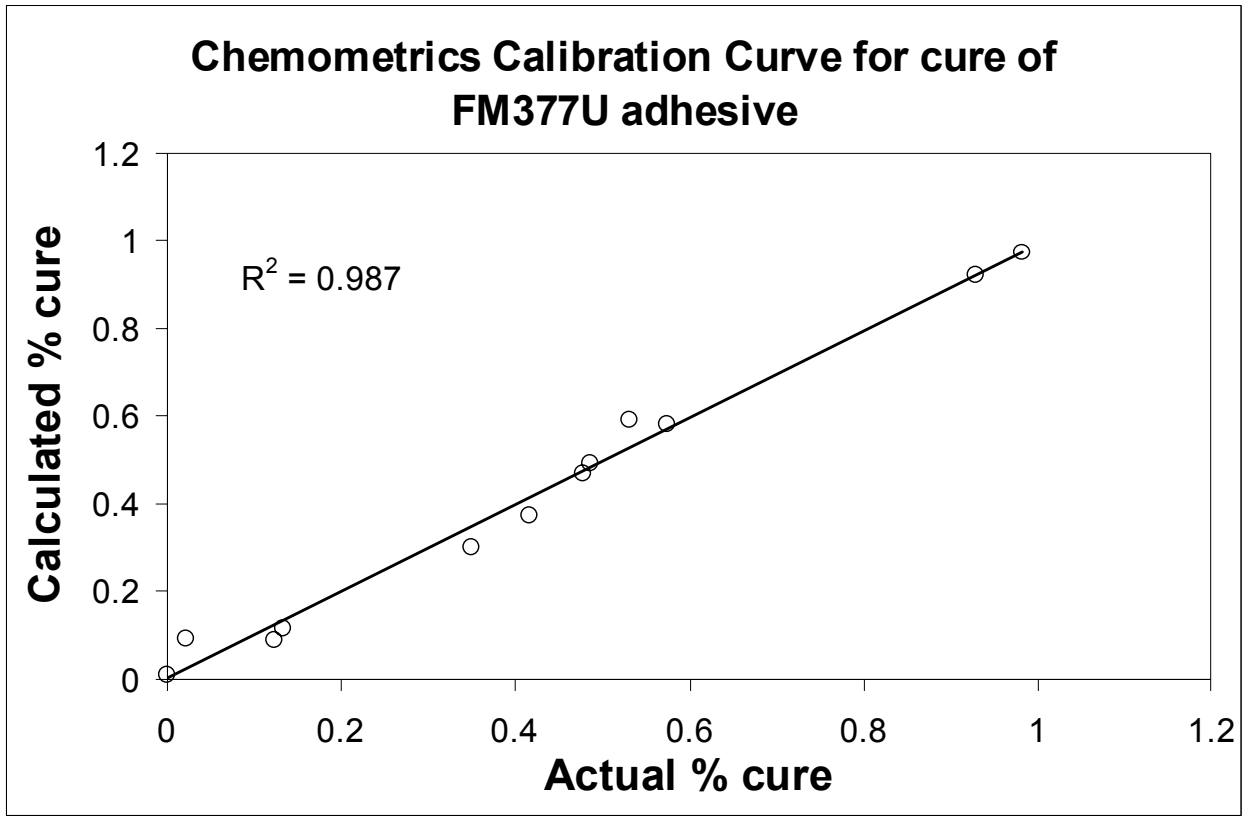
The epoxy group produces a strong and well defined combination band at ~ 4530 cm-1 due to $CH\nu_{assym}$ + ring $\delta_{in\ plane}$

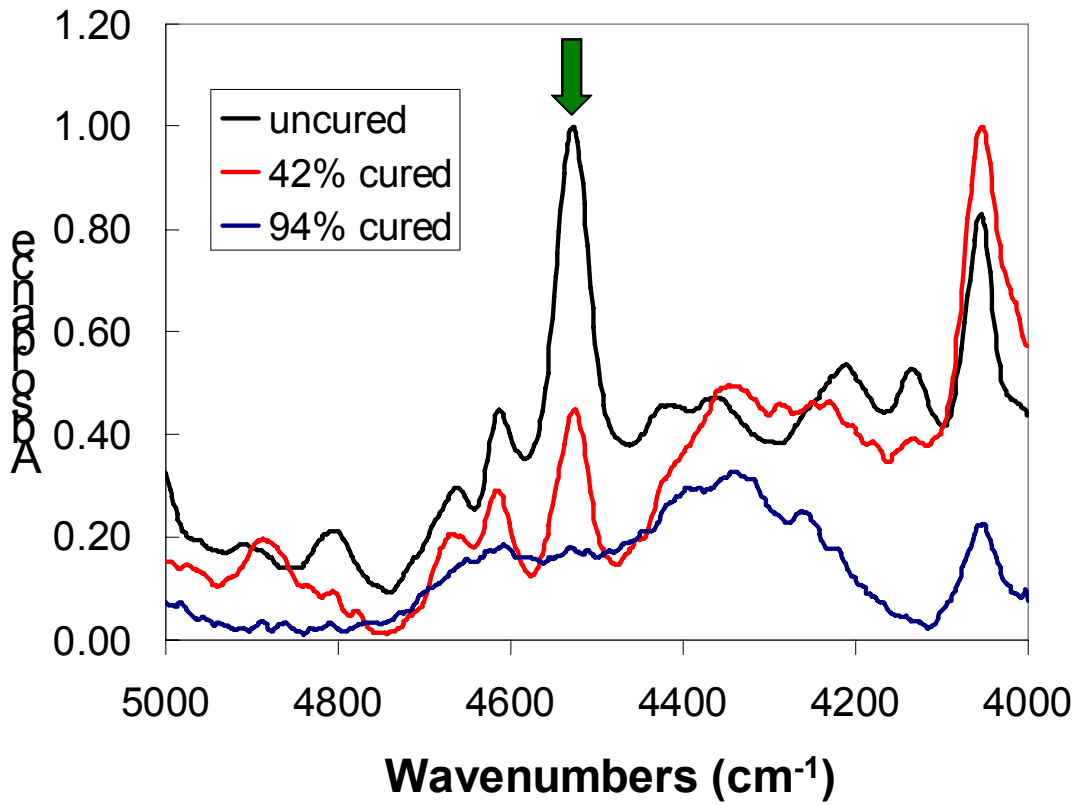

1.00
0.80
0.60
0.40
0.20
0.00
Absorbance
10000
9000
8000
7000
6000
5000
4000
Wavenumber (cm-1)

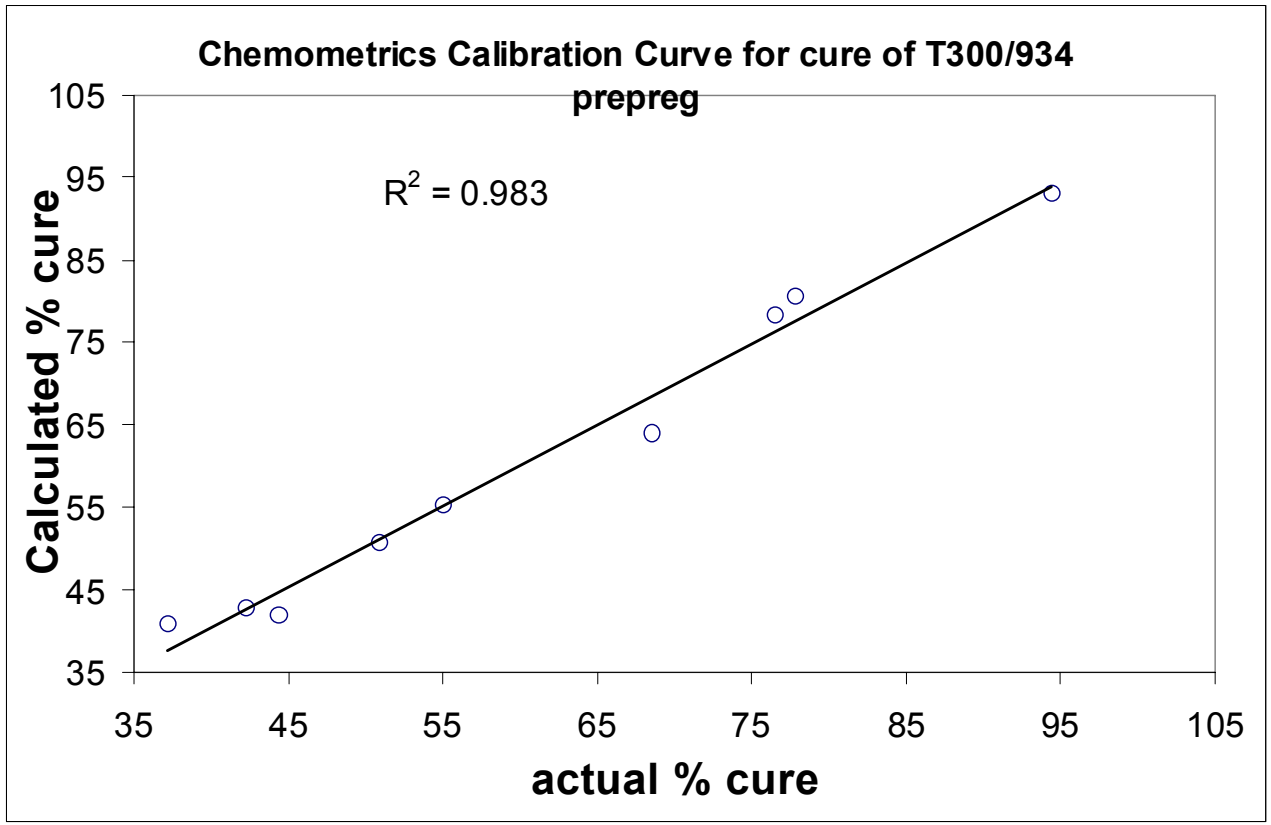

1.00
0.80
0.60
0.40
0.20
0.00
Absorbance
5000
4800
4600
4400
4200
4000
Wavenumbers (cm-1)
uncured
41% cure
98% cure

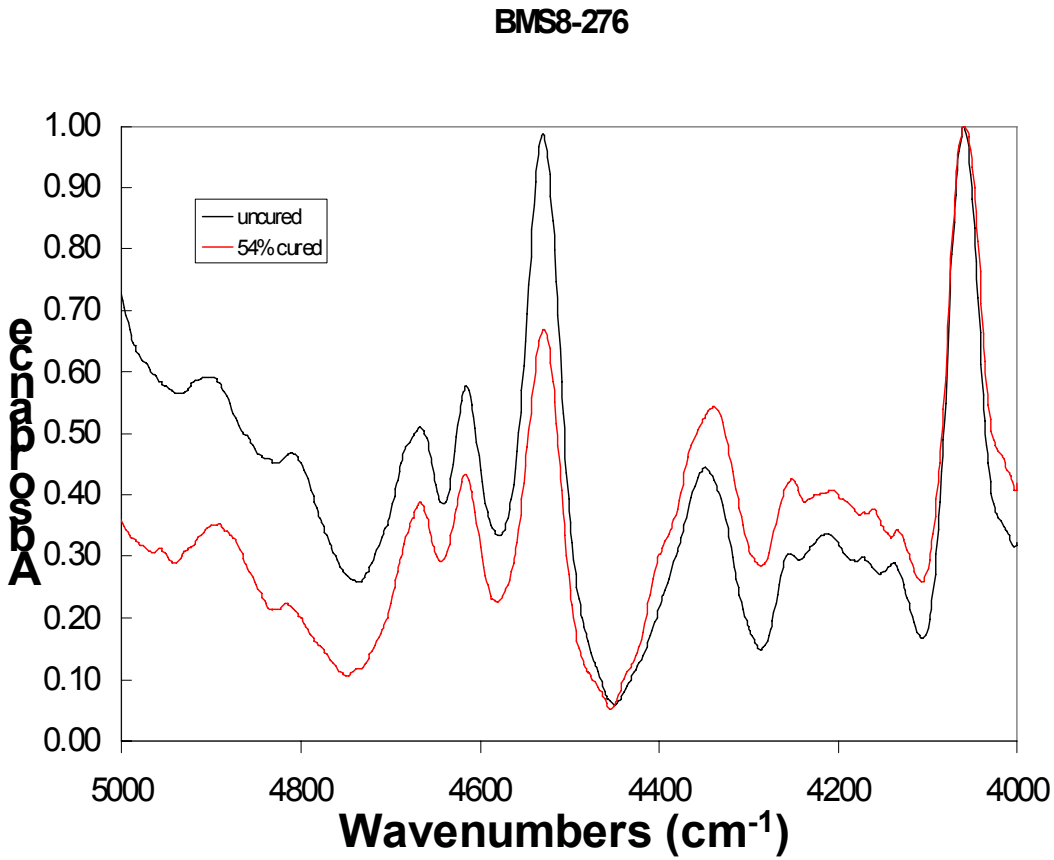
a vs normalized peak area for FM377U adhesive



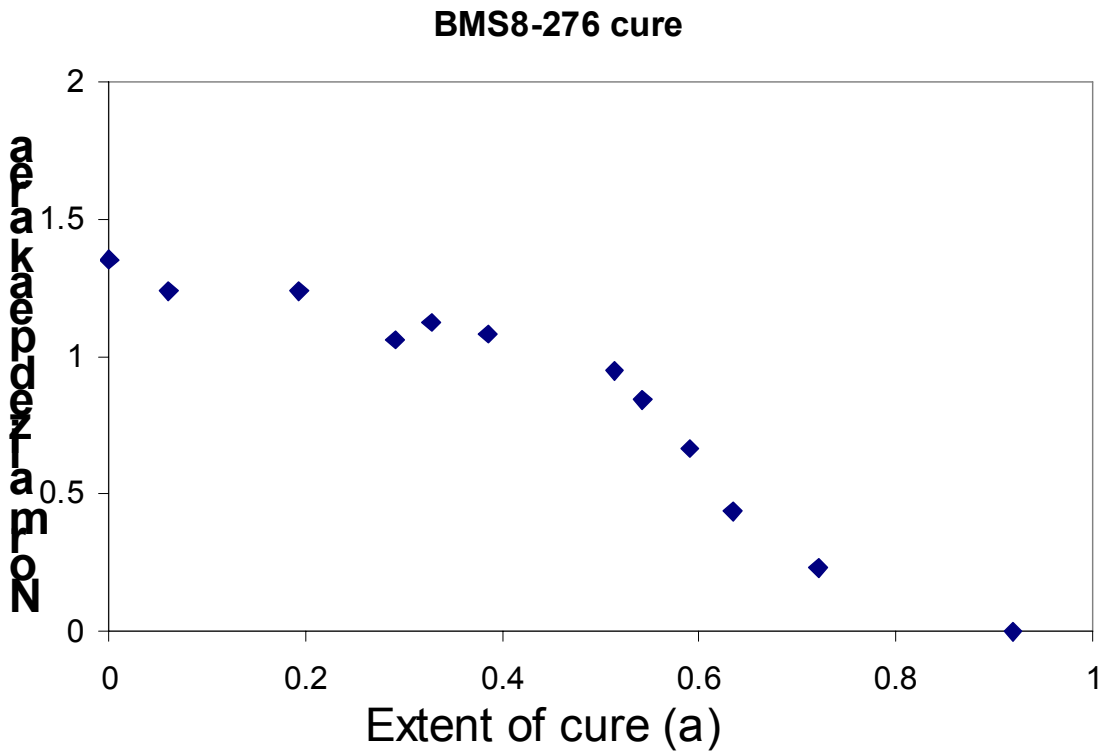

Chemometrics Calibration Curve for cure of FM377U adhesive
Calculated % cure
Actual % cure
R2 = 0.987
0
0.2
0.4
0.6
0.8
1
1.2

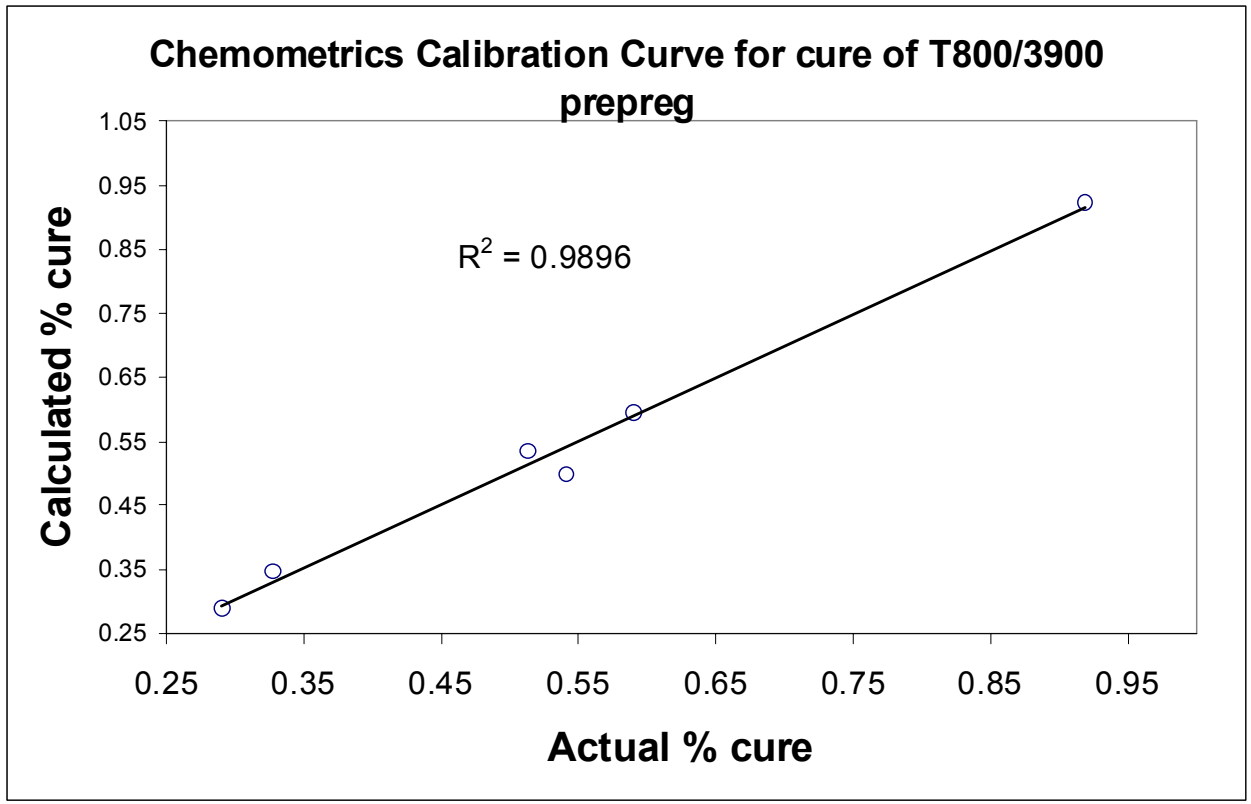

1.20
1.00
0.80
0.60
0.40
0.20
0.00
Absorbance
uncured
42% cured
94% cured
5000
4800
4600
4400
4200
4000
Wavenumbers (cm-1)


Chemometrics Calibration Curve for cure of T300/934 prepreg
R^2 = 0.983
Calculated % cure
105
95
85
75
65
55
45
35
35
45
55
65
75
85
95
105
actual % cure


BMS8-276
uncured
54% cured
Absorbance
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
5000
4800
4600
4400
4200
4000
Wavenumbers (cm-1)

a vs normalized peak area for TORAY T800/3900

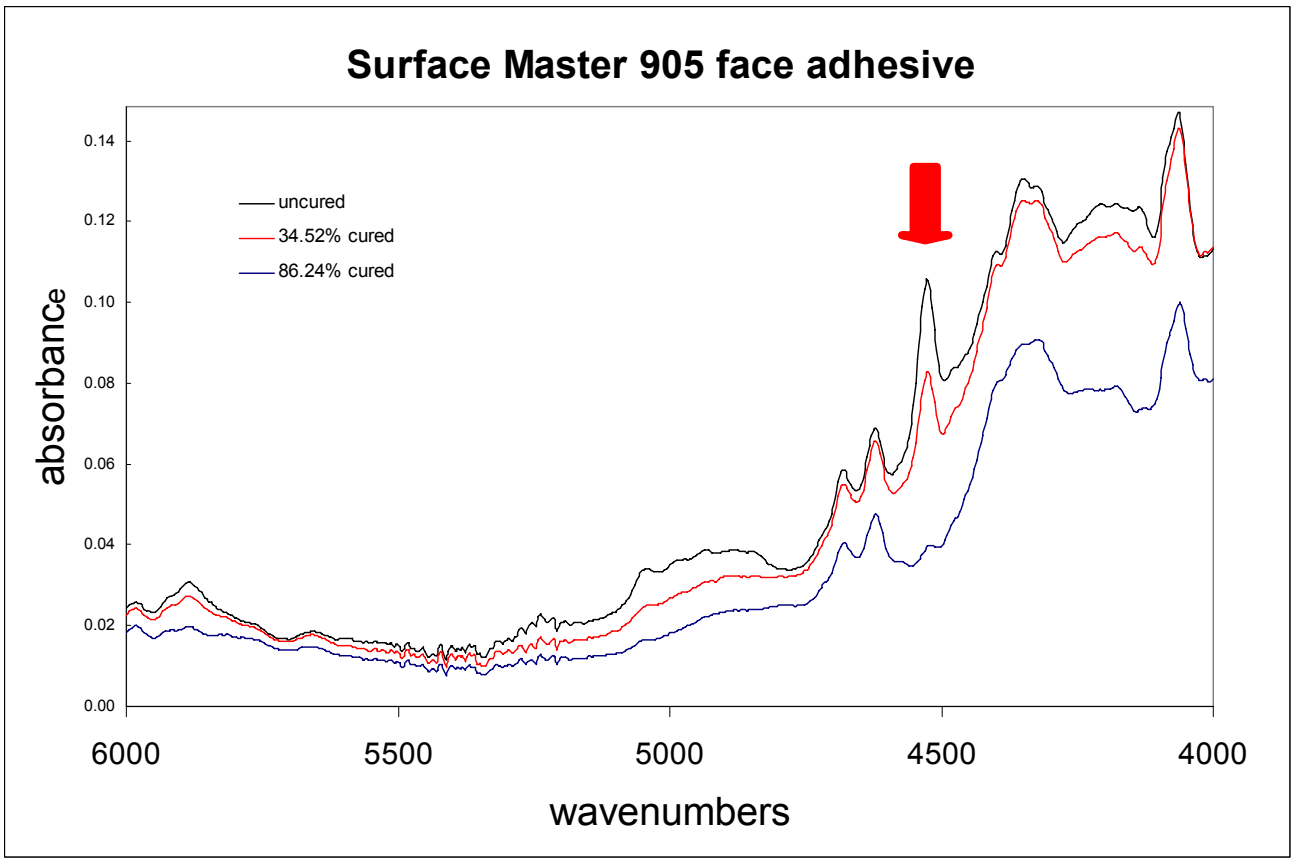


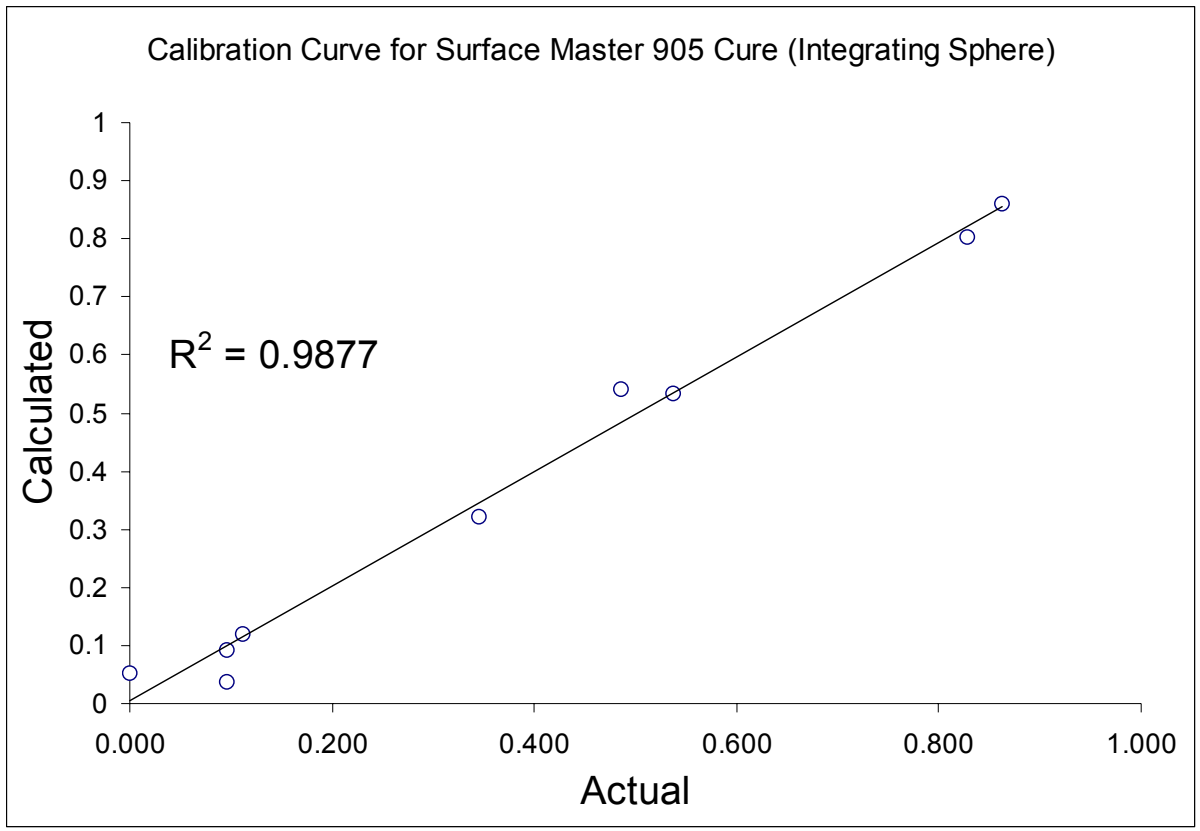

Chemometrics Calibration Curve for cure of T800/3900 prepreg
Calculated % cure
Actual % cure
R2 = 0.9896
1.05
0.95
0.85
0.75
0.65
0.55
0.45
0.35
0.25
0.25
0.35
0.45
0.55
0.65
0.75
0.85
0.95

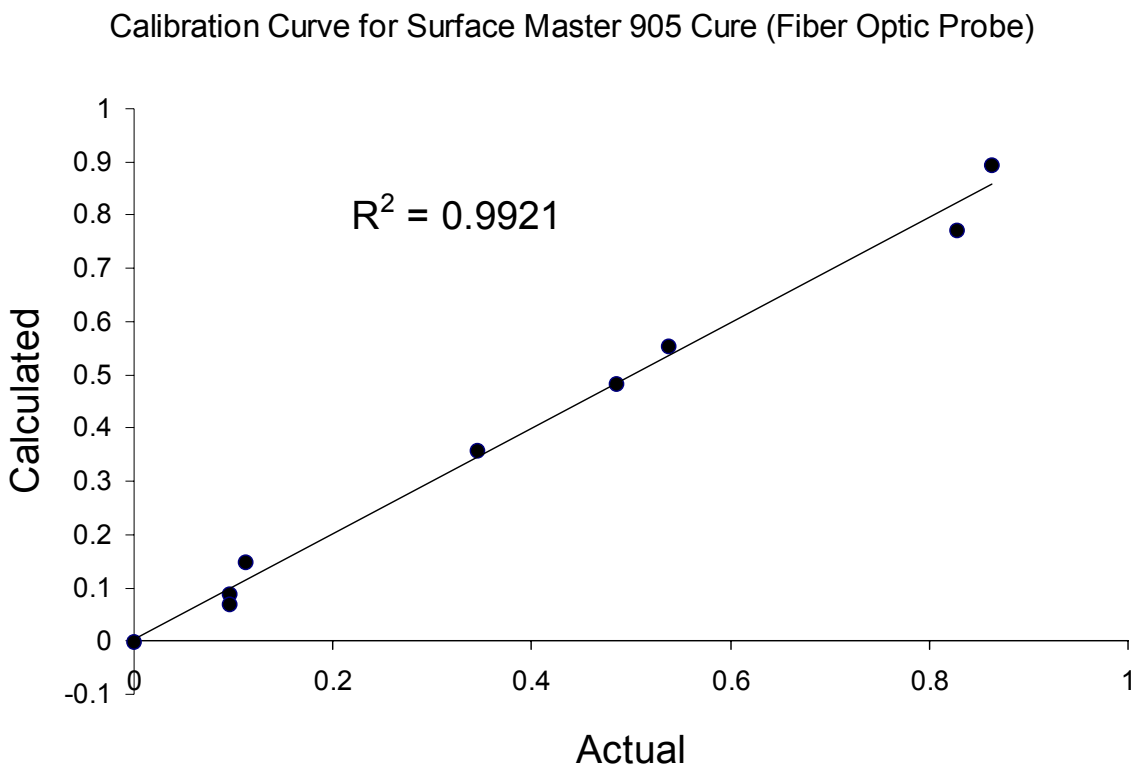
Can we apply this technique to OEM autoclave work?

Example

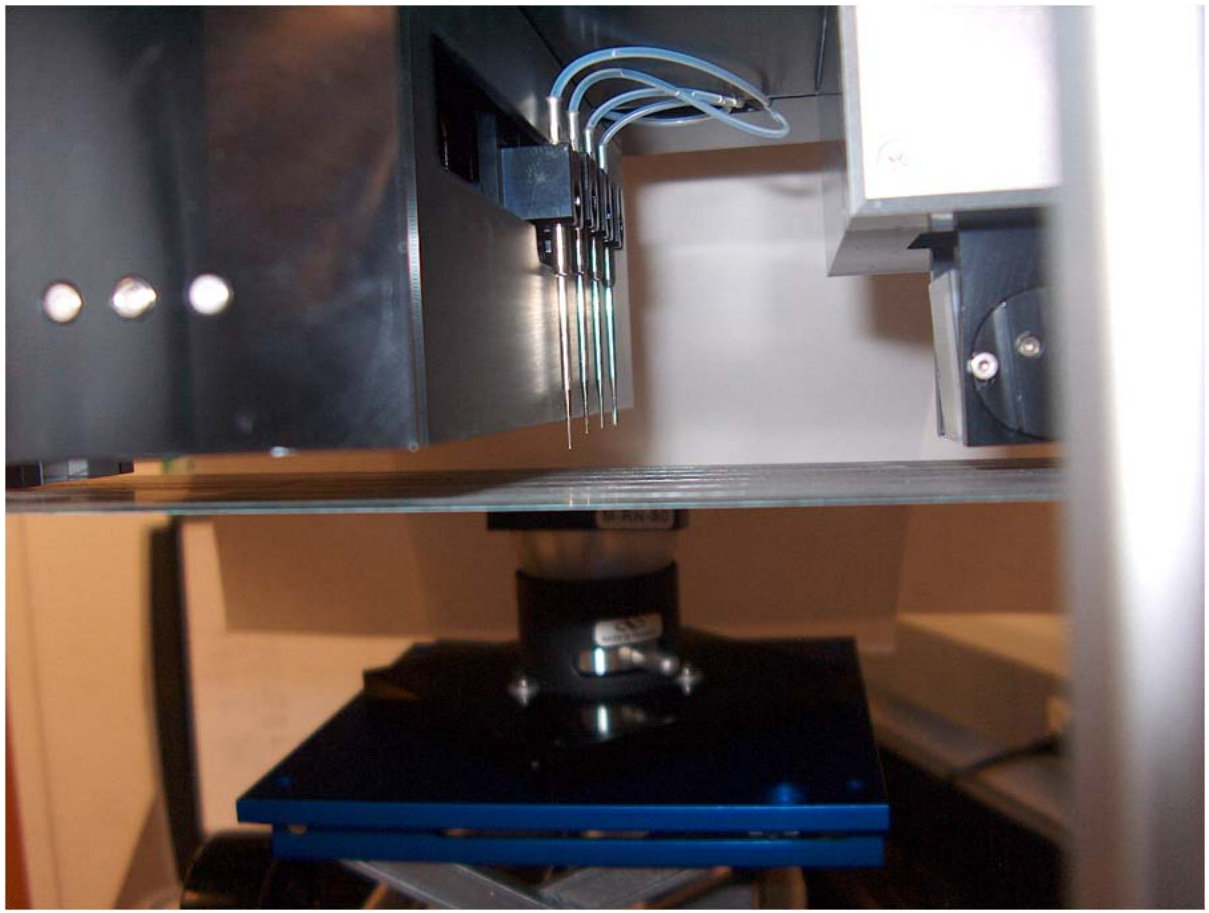
- An autoclave run was interrupted due to power failure
- Is the part properly cured?
- Can we use this technique to measure cure in face adhesive?

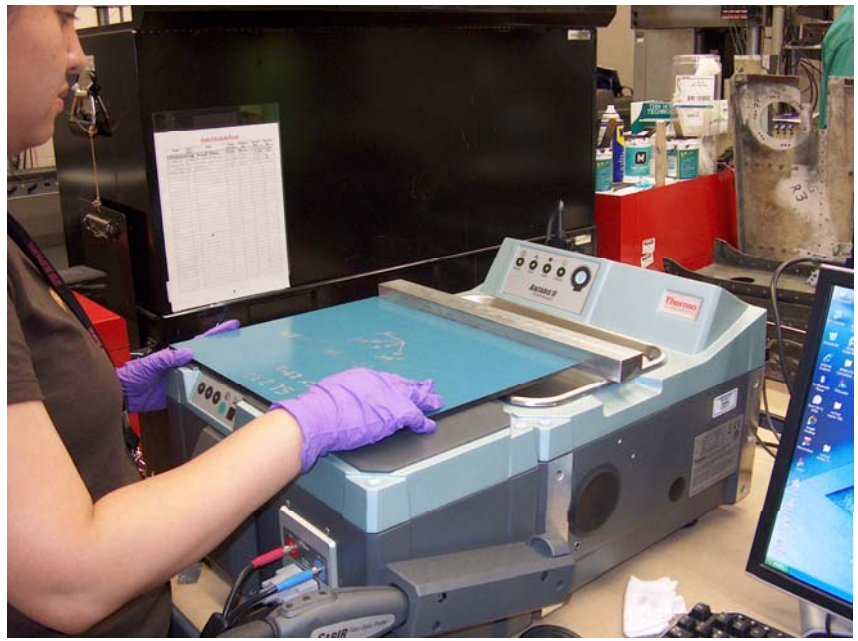

Surface Master 905 face adhesive
absorbance
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
uncured
34.52% cured
86.24% cured
6000
5500
5000
4500
4000
wavenumbers


Calibration Curve for Surface Master 905 Cure (Integrating Sphere)
Calculated
Actual
R^2 = 0.9877
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0.000
0.200
0.400
0.600
0.800
1.000


Calibration Curve for Surface Master 905 Cure (Fiber Optic Probe)
R2 = 0.9921
Calculated
Actual
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
0.2
0.4
0.6
0.8
1

Participation in FAA/NIST/NIAR scarf repair project



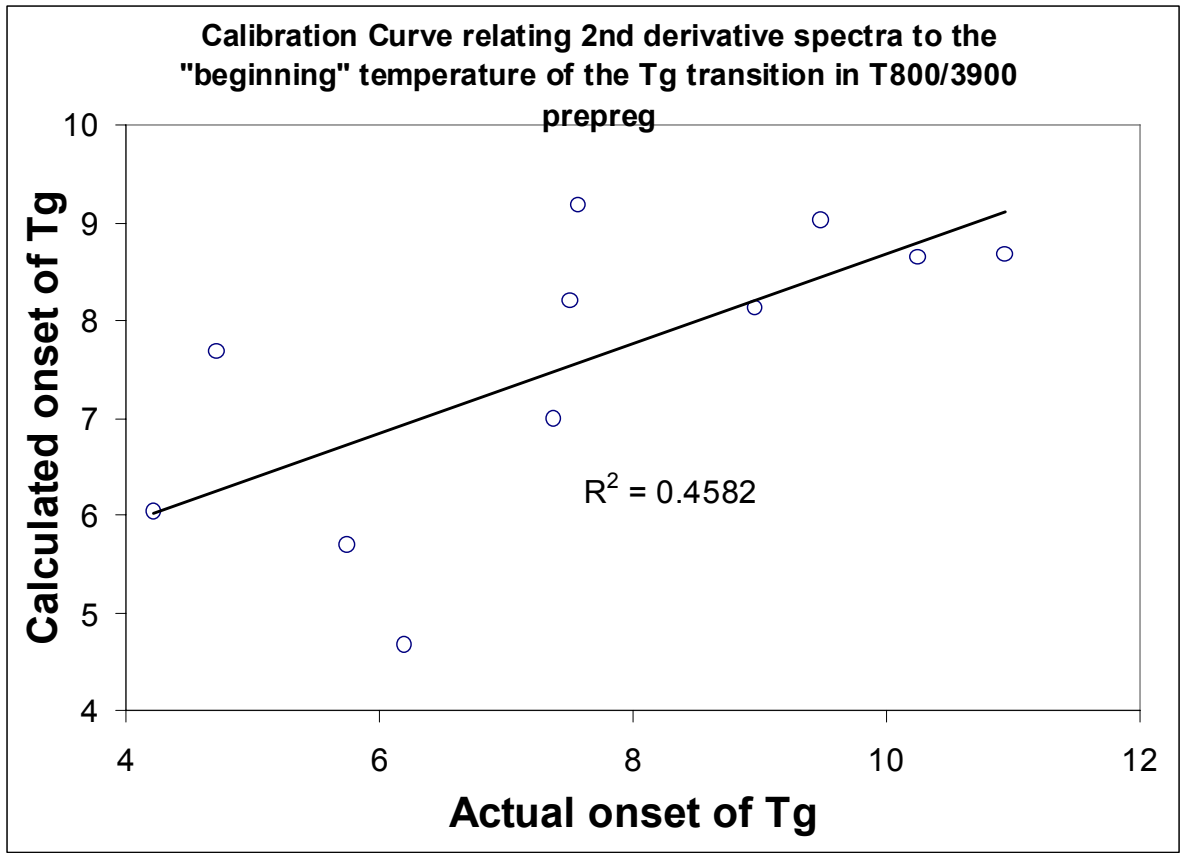


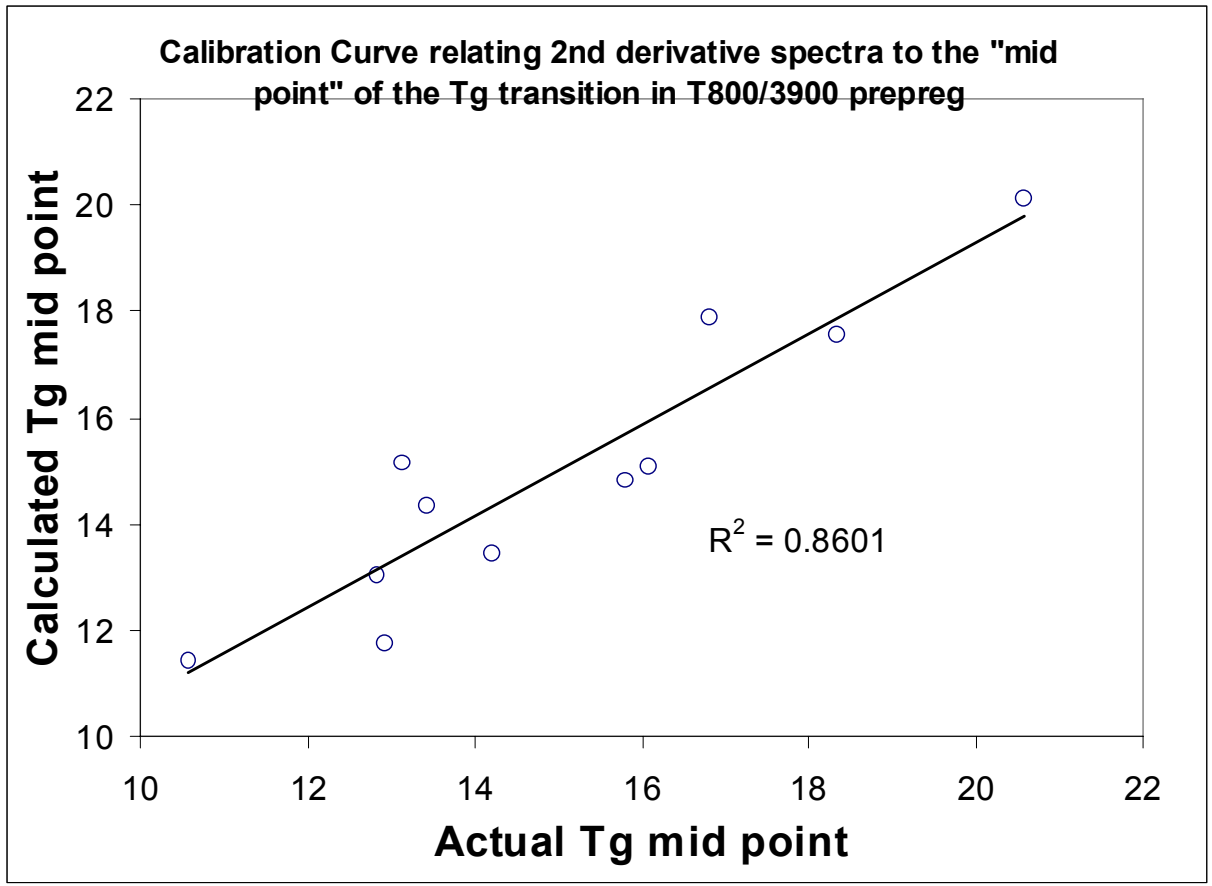
Sidebar….

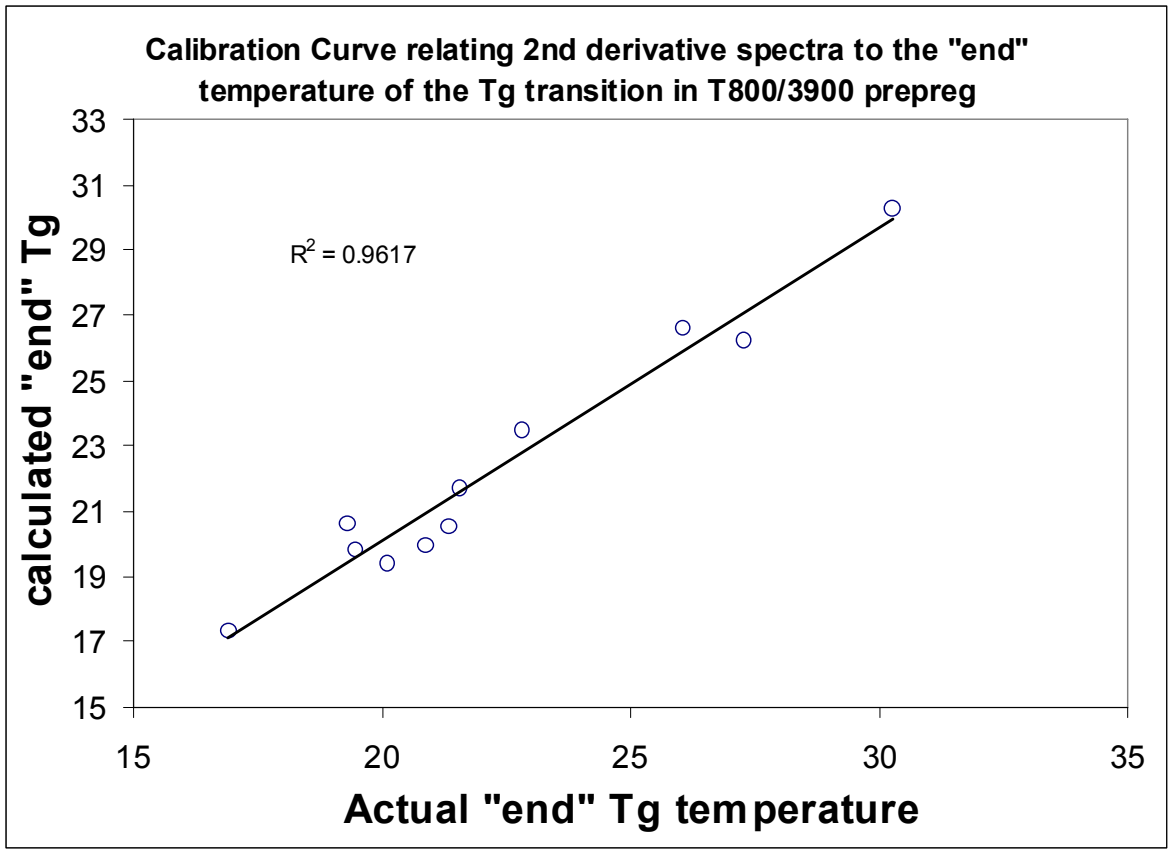
In order for this technique to be adopted by the aerospace industry, a case must be made for the purchase of equipment.
If utility can be established in other areas, a QC department can make a stronger case for such a purchase.
For example - can near IR spectroscopy be used to determine if uncured prepreg is within specifications?

Example

It has been established that T800/3900 prepreg is "out of spec" if the onset of the glass transition of the uncured prepreg is higher than 10°C
Can diffuse reflectance near IR spectroscopy be used to make this determination?


Calibration Curve relating 2nd derivative spectra to the "beginning" temperature of the Tg transition in T800/3900 prepreg
Calculated onset of Tg
Actual onset of Tg
R2 = 0.4582
10
9
8
7
6
5
4
4
6
8
10
12


Calibration Curve relating 2nd derivative spectra to the "mid point" of the Tg transition in T800/3900 prepreg
Calculated Tg mid point
Actual Tg mid point
R2 = 0.8601
10
12
14
16
18
20
22


Calibration Curve relating 2nd derivative spectra to the "end" temperature of the Tg transition in T800/3900 prepreg
calculated "end" Tg
Actual "end" Tg temperature
R2 = 0.9617
33
31
29
27
25
23
21
19
17
15
15
20
25
30
35

Conclusions

It would appear that near IR diffuse reflectance spectroscopy could be used as a rapid nondestructive "on the roll" technique for the acceptance/rejection of uncured prepreg, if the specification was rewritten to use the upper or end temperature of the glass transition of the uncured prepreg at a heating rate of 10°C/min

A Look Forward

Benefit to Aviation

- **Ability to accept/reject prepreg and adhesive "on the role"**
- **On site numerical based identification of water in composite**
- **Quantitative on site measurement of adhesive and composite cure**

Future needs

- **Low cost extension to develop new applications, complete FAA – NIAR scarf repair project, and complete technology transfer to Spirit AeroSystems (Doug Lewis) and other companies**