Methods for the Evaluation of Carbon Based Composite Surfaces for Subsequent Adhesive Bonding

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The Joint Advanced Materials and Structures Center of Excellence

Water uptake, cure state and kinetic evaluation of candidate prepregs for composite repair

- **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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- **3. Spirit AeroSystems, Wichita, KS - contractor**
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FAA Technical Monitor

- **Curt Davies**

Other FAA Personnel Involved

- **Larry Ilcewicz**

Industry Participation

- **Spirit AeroSystems**

Topics

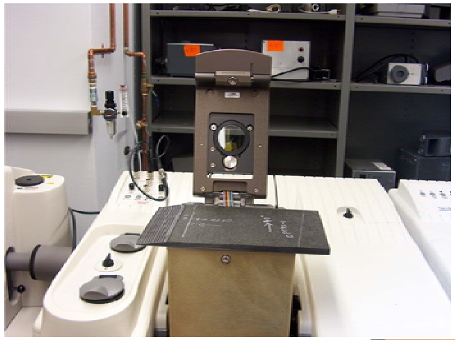
- **Diffuse Reflectance Near IR spectroscopy for composite surface water content**
- **Diffuse Reflectance Near IR spectroscopy for surface resin cure state**
- **Diffuse Reflectance Near IR spectroscopy for prepreg aging studies**
- **Contact angle measurement with mechanical testing**
- **Candidate repair prepreg analysis and cure**

Near IR studies

Background

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

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

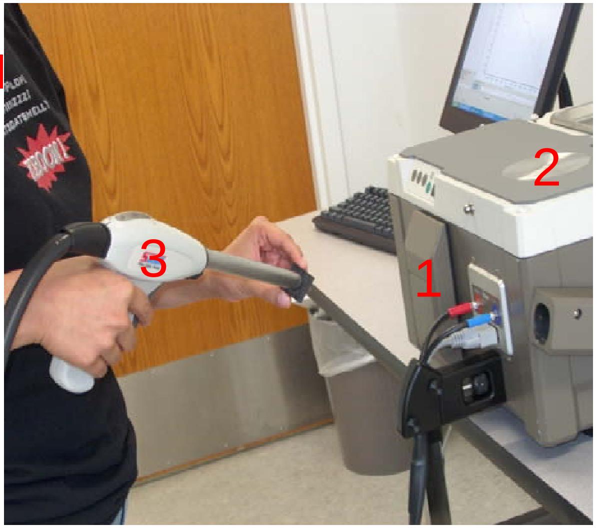


Antares II

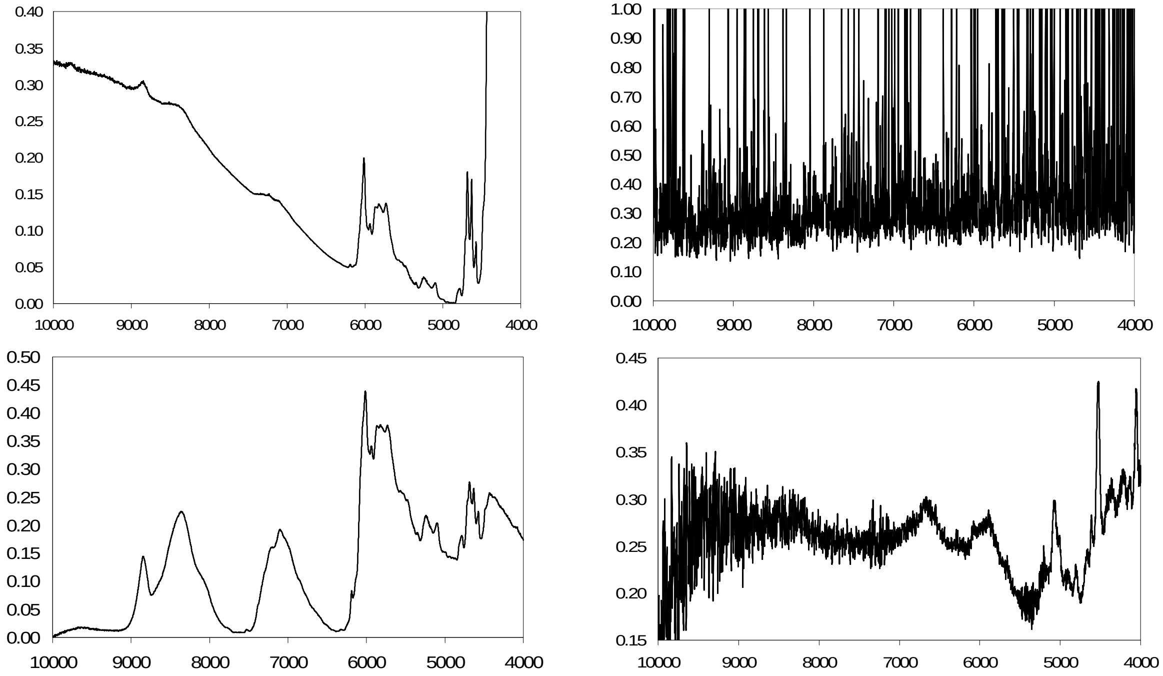
1. Transmission module

2. Integrating sphere reflectance module

3. Remote triggered diffuse reflectance module



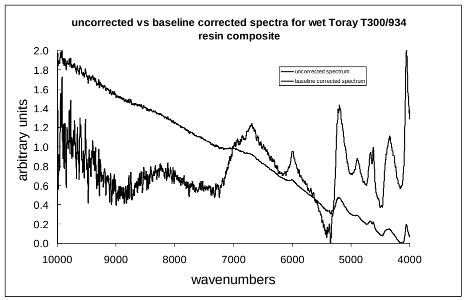
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

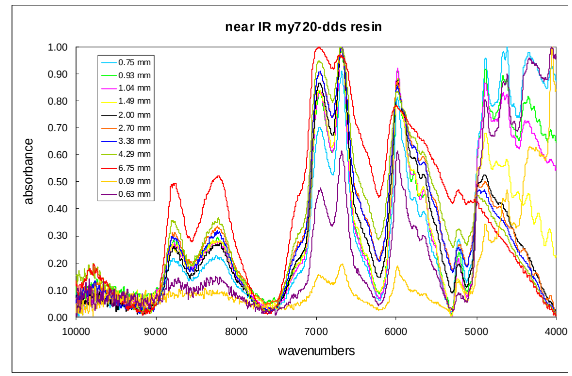


All x – wavenumbers (cm-1) All y – absorbance. Lomod thermoplastic elastomer (3.01mm thick), upper left – near IR spectrum in transmission, lower left - diffuse reflectance near IR spectrum obtained using the integrating sphere module. Uncured 934/T300 prepreg (1 layer), upper right – near IR spectrum in transmission, lower left - diffuse reflectance near IR spectrum obtained using the integrating sphere module.

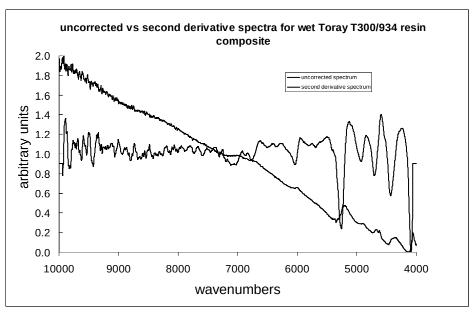
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

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

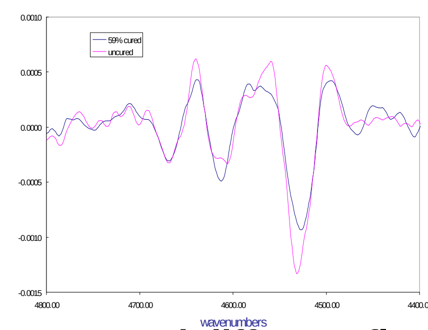




Chemometrics calibration curve – second derivative spectra are subjected to partial least squares analysis



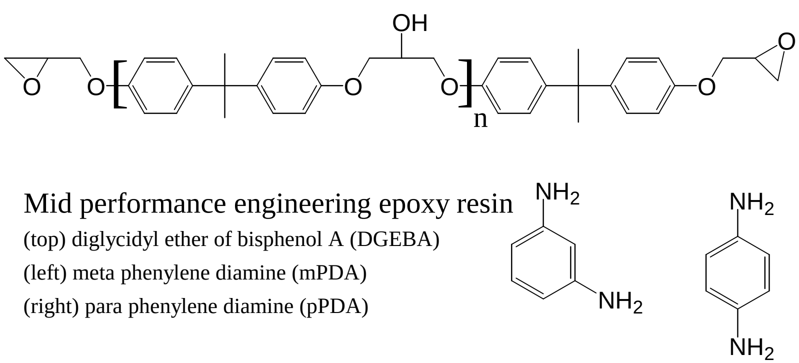
Second derivative spectra of curing T800/3900 prepr

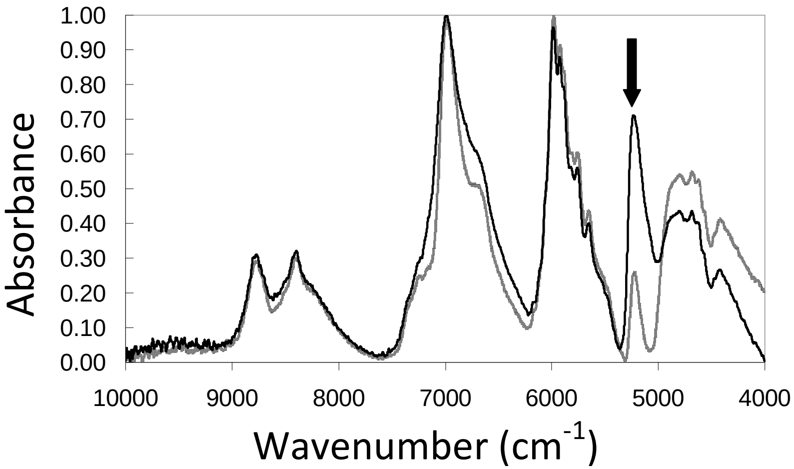


(Top left) Conventional diffuse reflectance and baseline corrected diffuse reflectance spectra of wet 934/T300 prepreg. (Top right) conventional diffuse reflectance spectra of MY720-DDS resin versus plaque thickness. (Bottom left) Conventional diffuse reflectance and second derivative spectrum of 934-T300 prepreg. (Bottom right) Second derivative spectrum of curing T800/3900 prepreg.

Near IR studies
Water uptake
and desorption

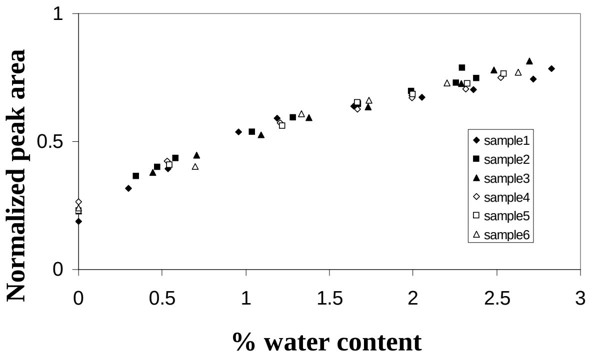
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

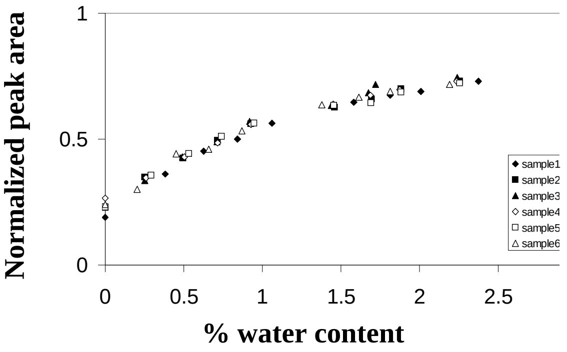


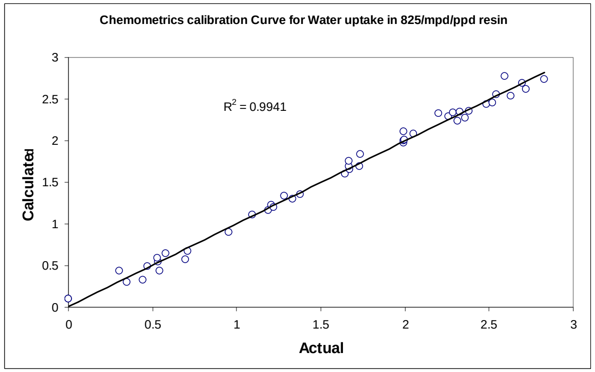


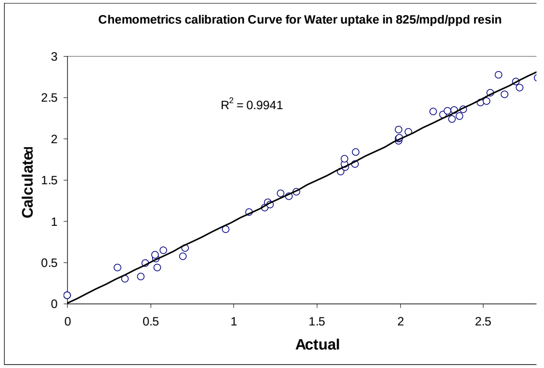
(Left) DGEBA/m&pPDA resin constituents. (Right) Near IR spectrum of the resin before (hatched line) and after (full line) exposure to water. The arow denotes the absorption band at 5215 cm^{-1} attributed to water in the resin

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



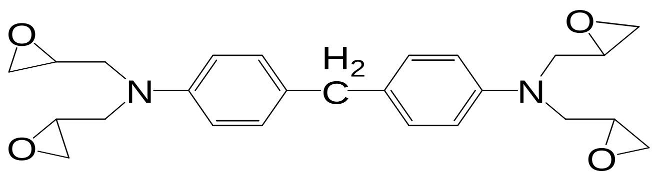


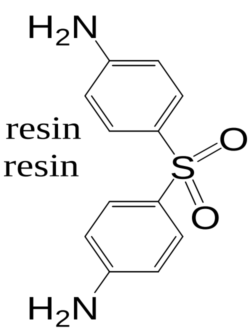




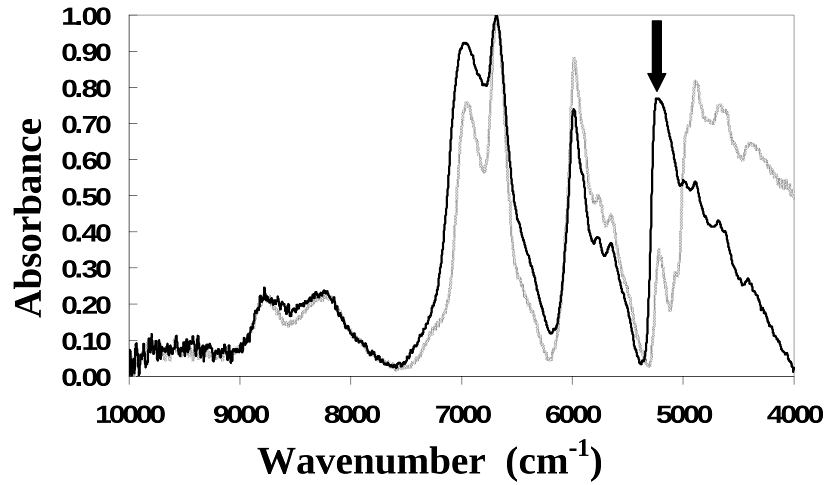
(Top left) Beeer plot of normalized absorbance at 5215 cm^{-1} versus water content during water uptake. (Top right) Similar plot but obtained during water desorption cycle. (Bottom left) Chemometrics calibration plot for water absorption. (Bottom right) Chemometrics calibration plot for water desorption

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



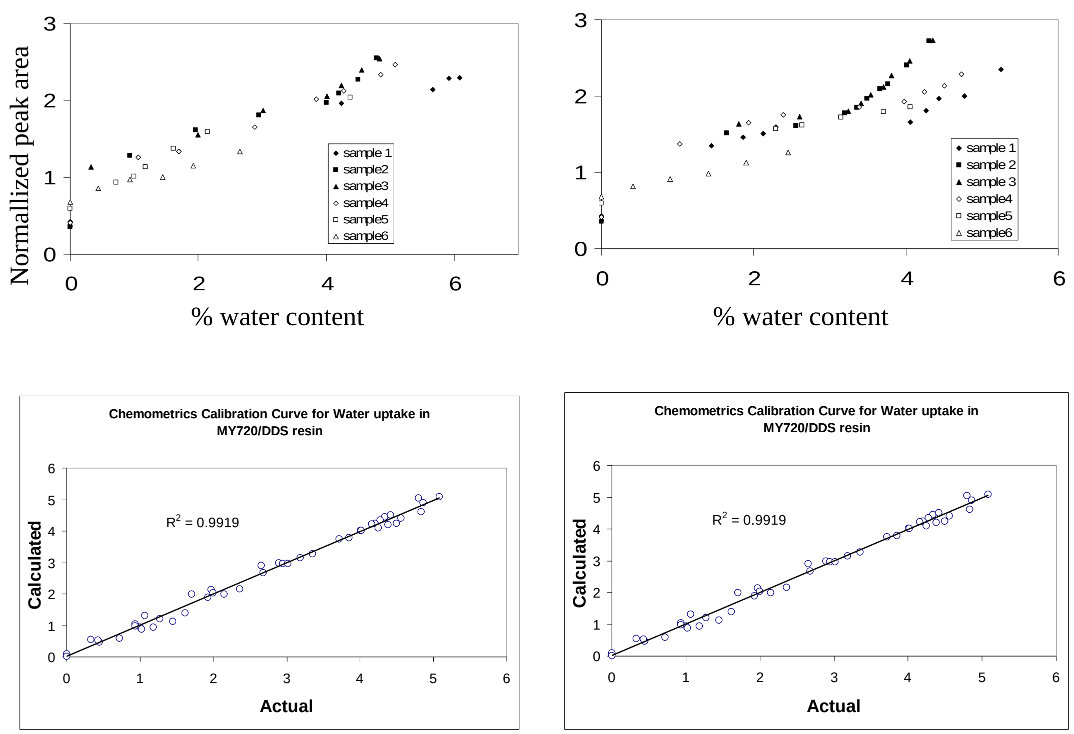


High performance epoxy resin
(top) TGDDM (MY720) resin
(right) DDS curative



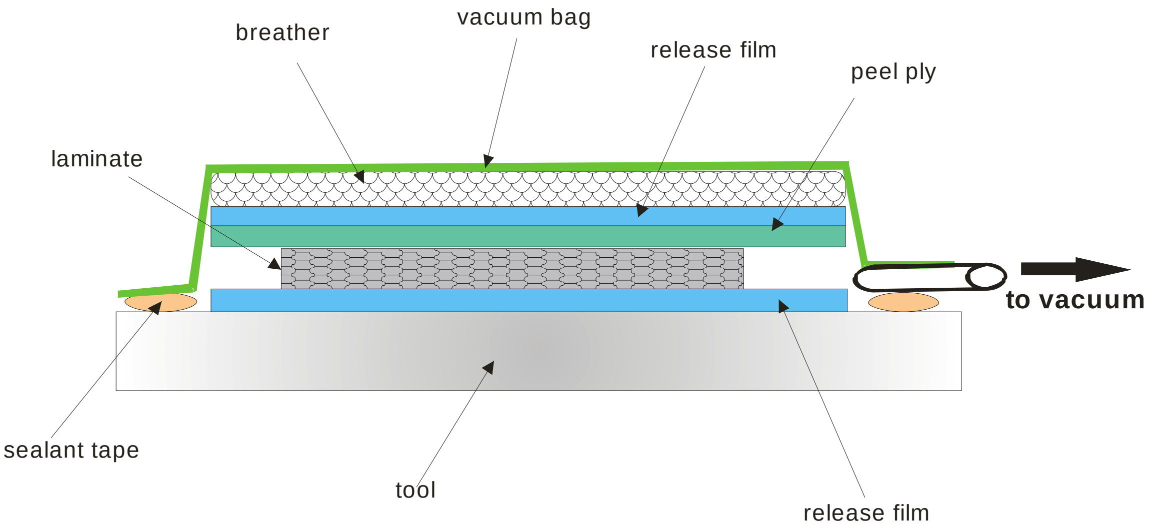
(Top left) MY720 and DDS resin constituents. (Top right) Near IR spectrum of the resin before (hatched line) and after (full line) exposure to water. The arow denotes the absorption band at 5215 cm^{-1} attributed to water in the resin

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



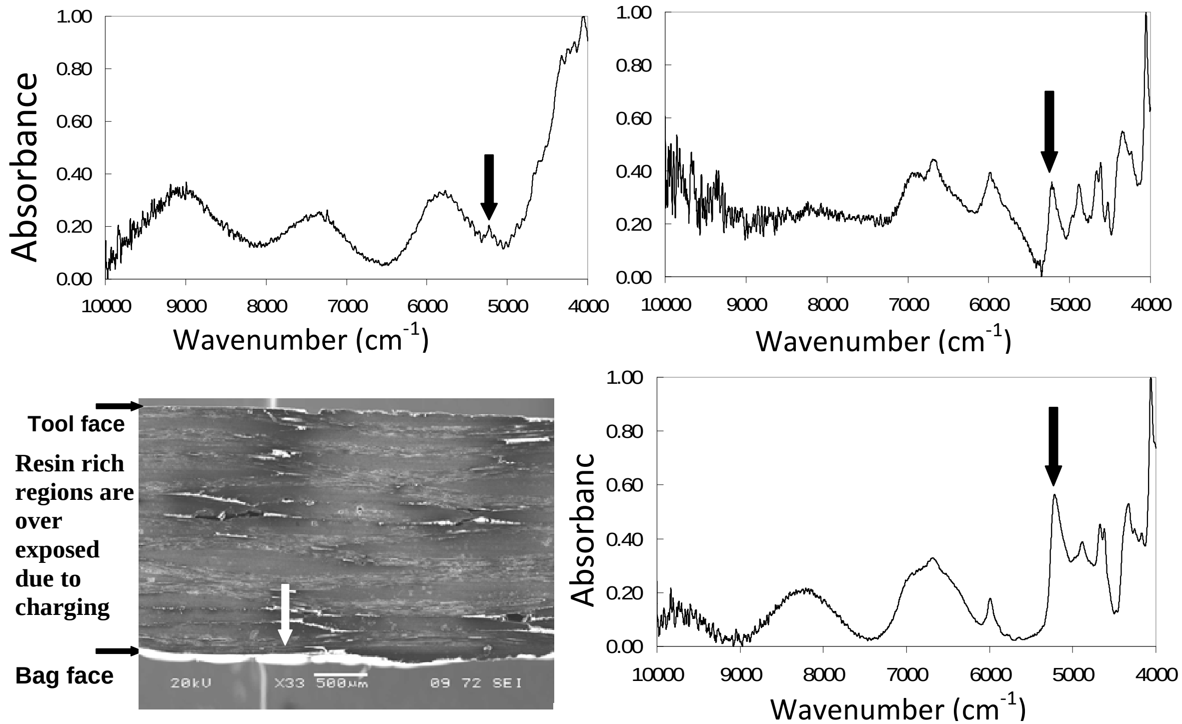
High performance MY720/DDS resin (Top left) Beer plot of normalized absorbance at 5215 cm^{-1} versus water content during water uptake. (Top right) Similar Beer plot but obtained during water desorption cycle. (Bottom left) Chemometrics plot for water absorption. (Bottom right) Chemometrics plot for water desorption.

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



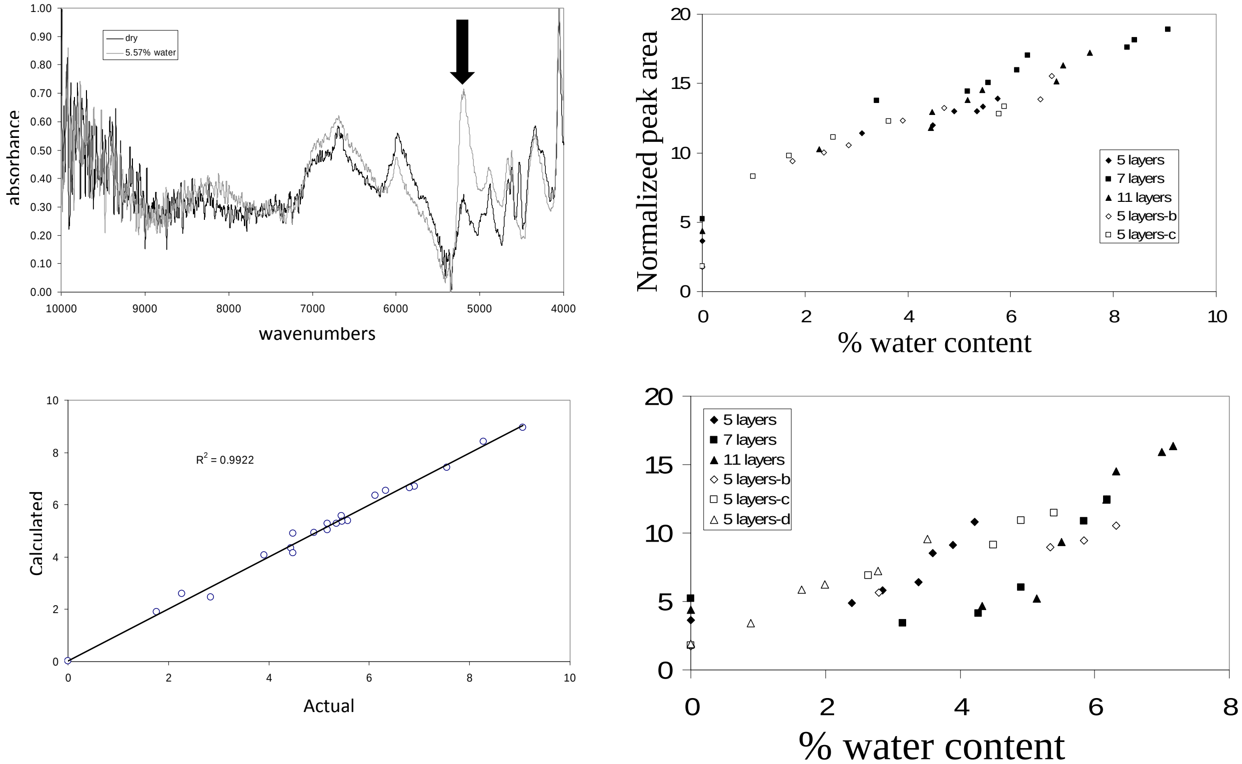
Sketch of vacuum bagging setup used to prepare small plaques of prepreg for testing purposes.

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



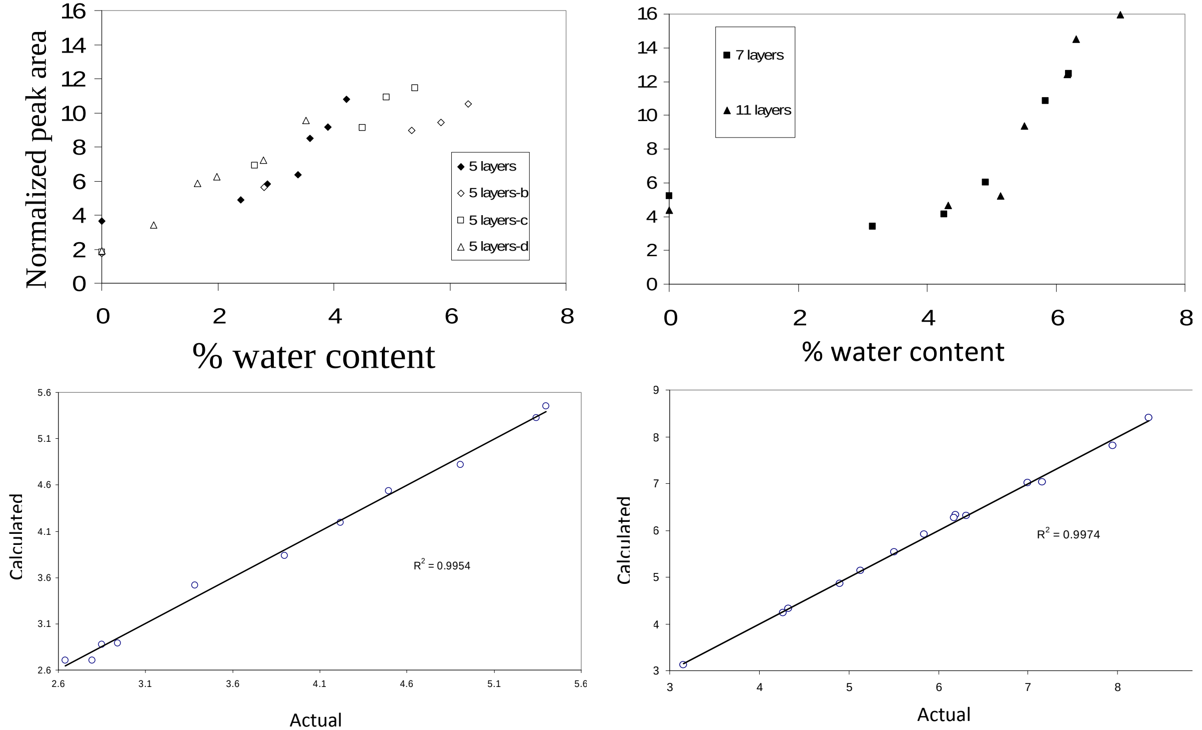
Near IR spectrum of (Top left) 934/T300 cured woven composite tool face, (Top right) Near IR spectrum of 934/T300 cured woven composite bag face, (Bottom left) SEM of cross section of uncoated 934/T300 cured woven composite bag face down with resin rich regions overexposed. (Bottom right) Diffuse reflectance near IR spectrum of cured T800/3900 composite bag face. Water at 5215 cm^{-1} is denoted by the arrows

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



934/T300 composite - plots of normalized 5215 cm^{-1} peak areas versus water content (Top left) Near IR spectrum of dry and wet composite with 5215 cm^{-1} peak arrowed (Top right) Normalized Beer plots during water absorption cycle (Bottom left) Chemometrics plot during water absorption cycle (Bottom right) Normalized Beer plots during water desorption cycle.

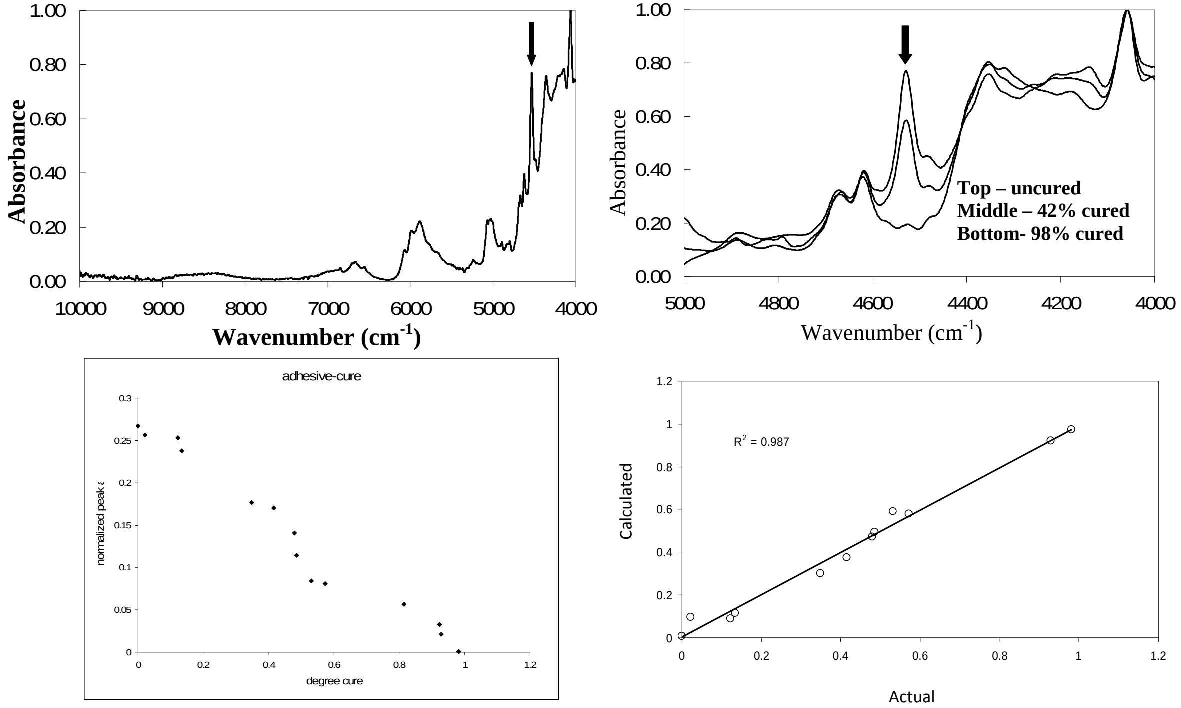
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



934/T300 composite - plots of normalized 5215 cm^{-1} peak areas versus water content during water desorption (Top left) Normalized Beer plot during water desorption cycle of 5 layer composite (Top right)) Normalized Beer plot during water desorption cycle of 7 and 11 layer composite (Bottom left) Normalized Chemometrics plot during water desorption from 5 layer composite (Bottom right) Normallized Chemometric plot during water desorption from 7 and 11 layer composite

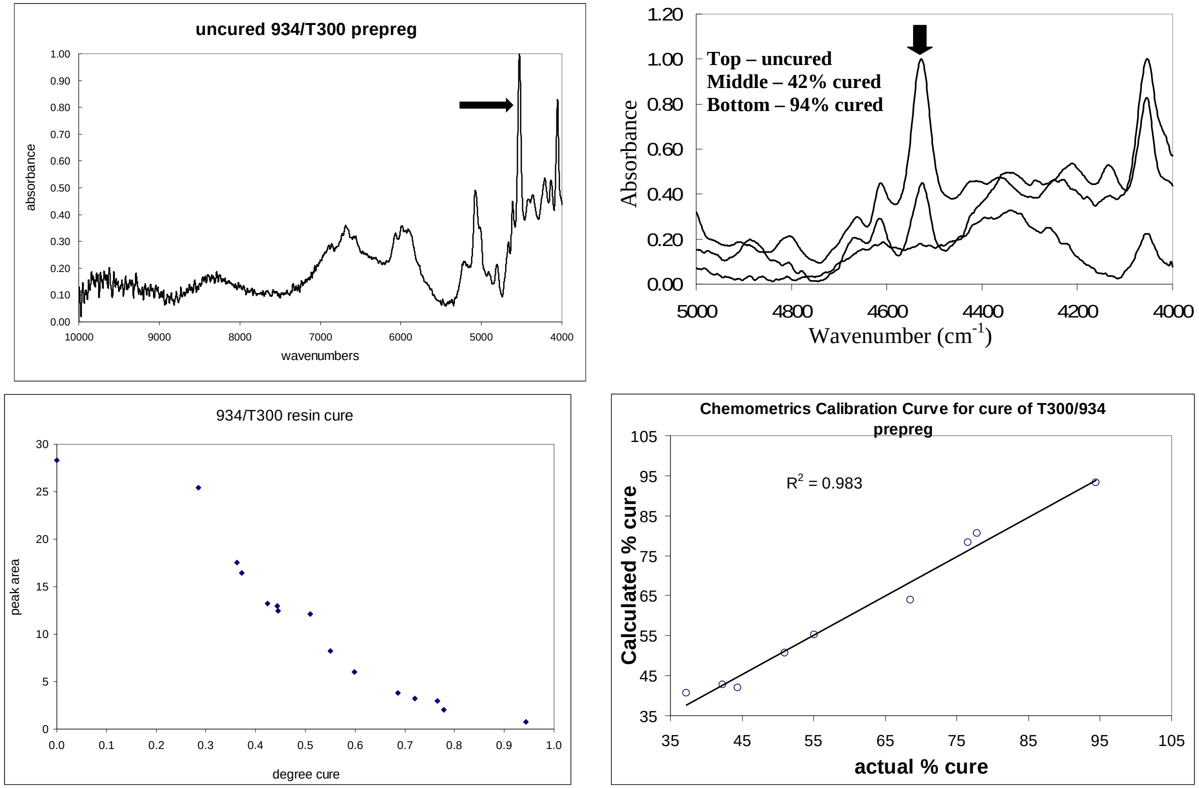
Near IR spectroscopy Resin and composite cure studies

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



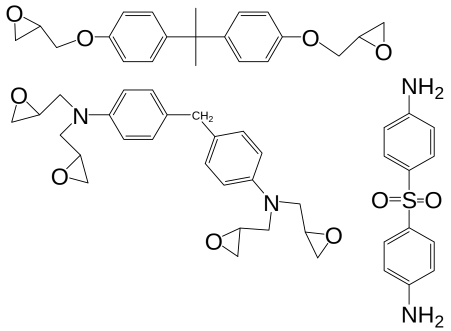
Fiberite FM377U aluminum filled adhesive cure. (Top left) Uncured Fiberite FM377U aluminum filled adhesive with 4530 cm^{-1} band annotated. (Top right) Stacked spectrum for curing adhesive (Bottom left) Fiberite Fm377U adhesive % cure by DSC versus (Beers law) normalized peak area at 4530 cm^{-1} (Bottom right) Chemometrics calibration curve for adhesive cure. The 4350 cm^{-1} peak is indicated by the arrow.

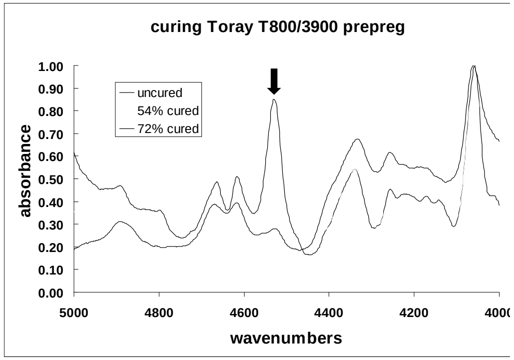
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

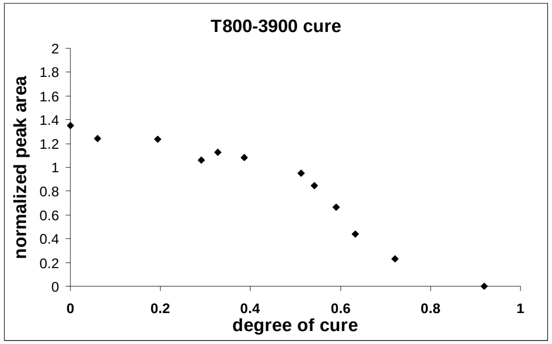


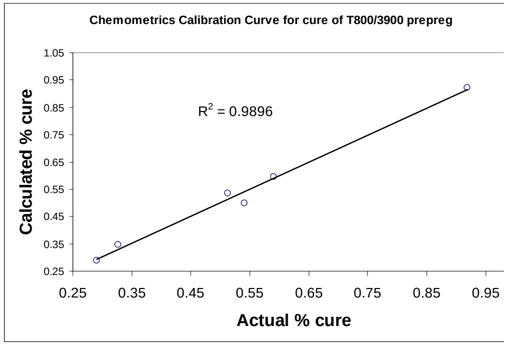
934/T300 prepreg cure. (Top left) Uncured 934/T300 prepreg with 4530 cm^{-1} band annotated. (Top right) Stacked spectrum for curing prepreg (Bottom left) 934/T300 prepreg % cure by DSC versus (Beers law) normalized peak area at 4530 cm-1 (Bottom right) Chemometrics calibration curve for prepreg cure. The 4350 cm^{-1} peak is indicated by the arrow.

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



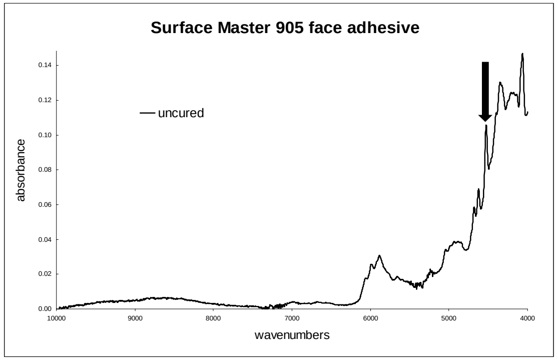


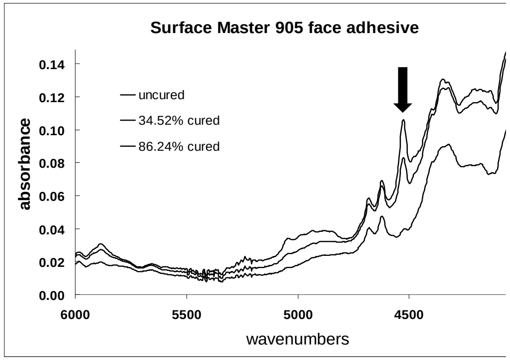


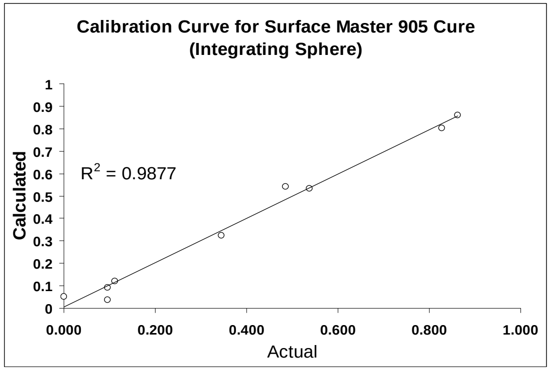


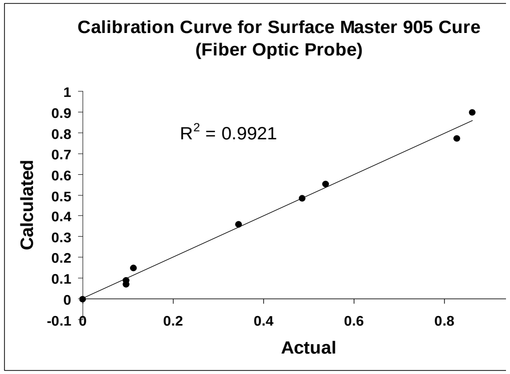
(top left) Components of T800/3900 prepreg. (top right) Spectra of curing prepreg. (bottom left) Beer plot of cure versus normalized peak area (bottom right) Chemometrics plot for the cure reaction. The 4350 cm^{-1} peak is indicated by the arrow.

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair





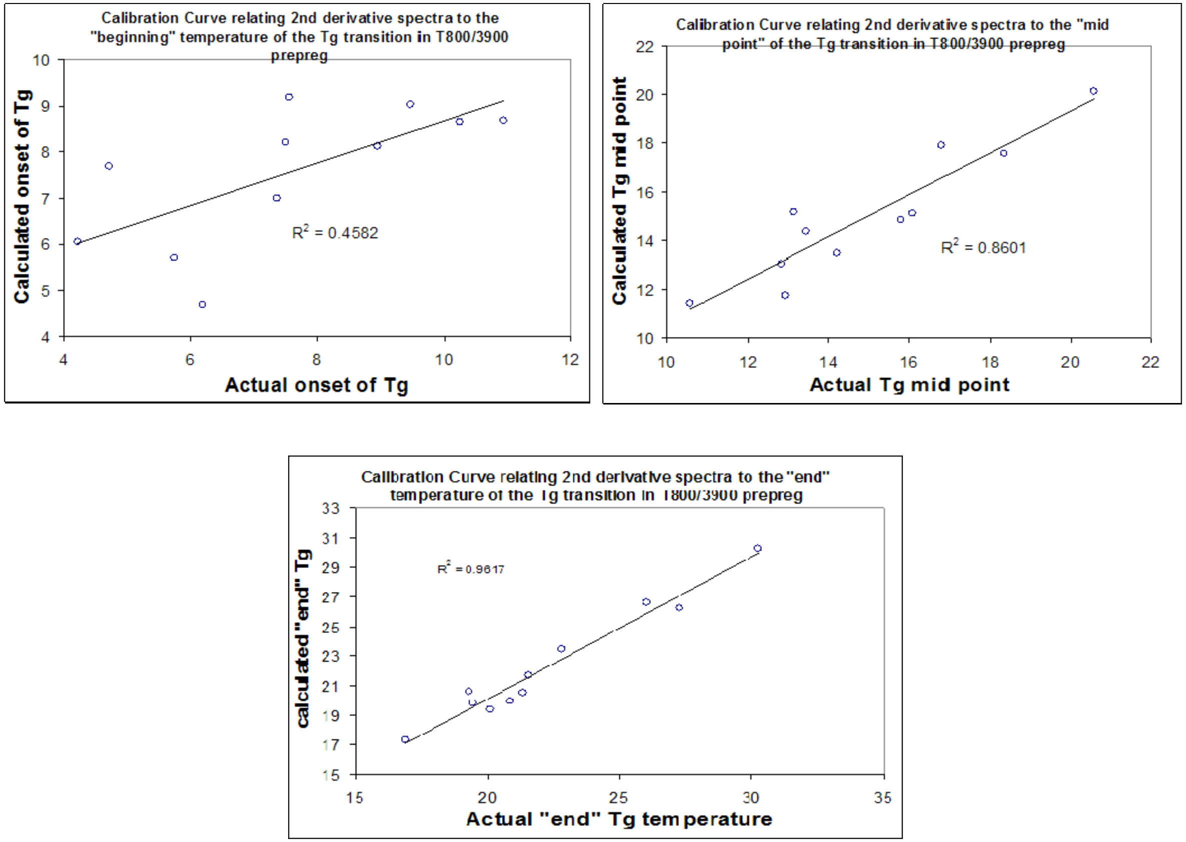




(top left and top right) Cure of Surface Master 905 face adhesive by near IR spectroscopy. A comparison of the performance of the diffuse reflectance probe (bottom left) and the integrating sphere probe (bottom right) during cure of the adhesive. The 4350 cm^{-1} peak is indicated by the arrow.

Near IR spectroscopy Prepreg aging studies

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



Correlation of chemometrics plots of second derivative spectra with prepreg Tg for uncured but aged T800-3900 prepreg.

Surface analysis and repair of contaminated T800-3900 composite

- **T800-3900 composite is formed and scarfed**
- **Cleaned with acetone – lint free cloth**
- **Contaminated**
- **Cleaned with acetone – lint free cloth**
- **Surface free energy measured by contact angle analysis**
- **Repair made using ACG T800MTM-45 prepreg w Cytec FM300-2 adhesive, 32 plies w 7.7 msi stiffness**
- **Subjected to tensile testing**

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Contaminents

Skydrol

Paint stripper

Jet fuel

Perspiration

Water

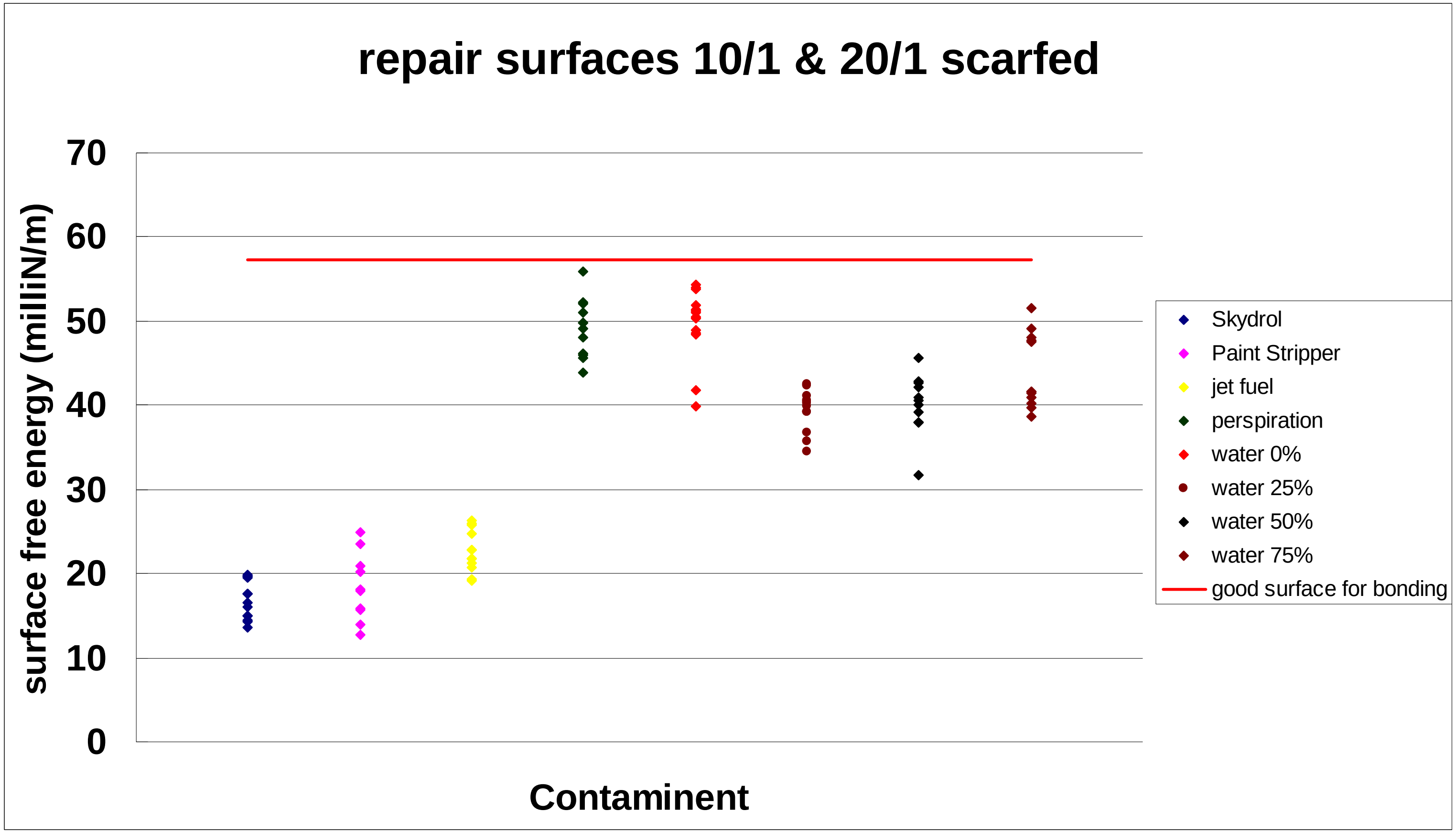
0%

25%

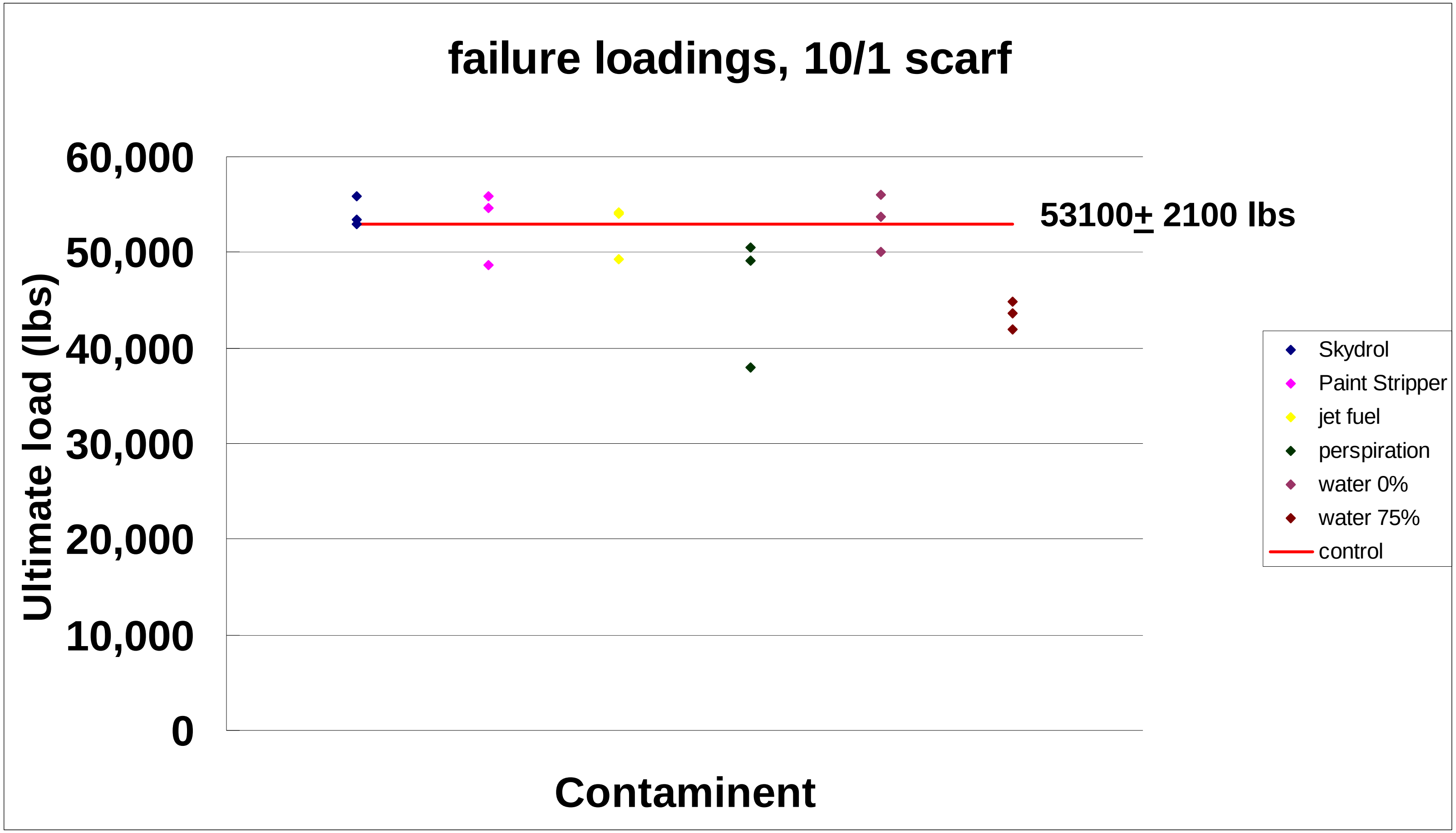
50%

75%

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair



Characterization and cure kinetics of T700-2510PW prepreg, a candidate material for the repair of epoxy based composites

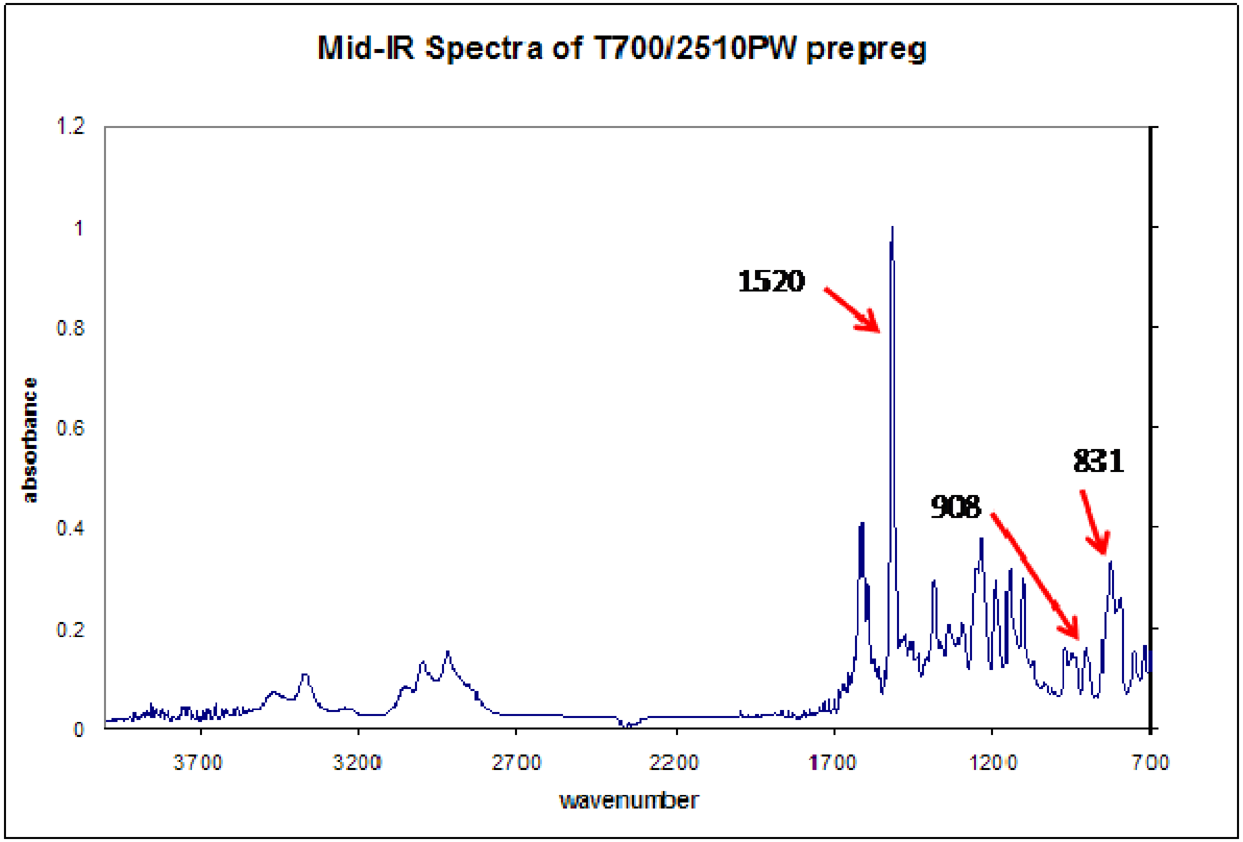
Structural analysis

Cure kinetics by DSC

- Ramped
- Isothermal
- Ramp and soak

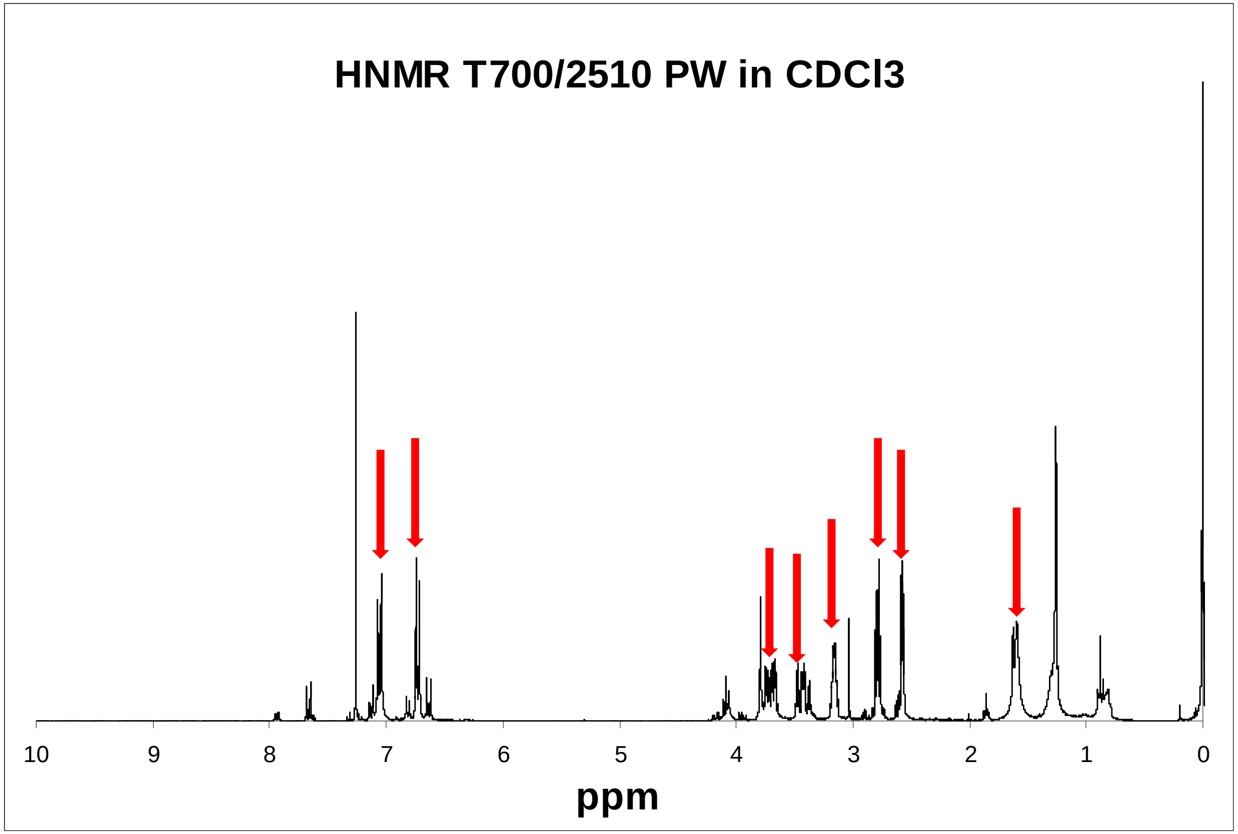
DMA

Mid infrared spectrum of resin extracted from T700-2510PW prepreg

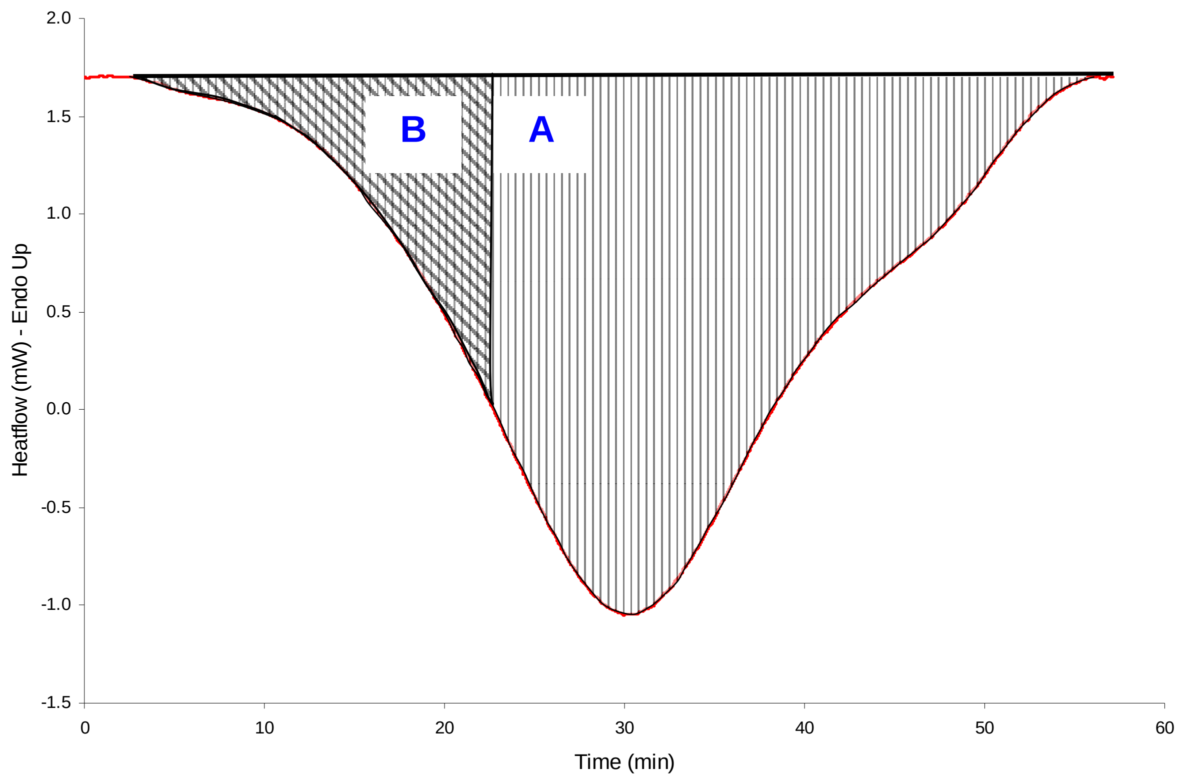


Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Proton NMR of T700-2510PW prepreg with DGEBA resonances arrowed



A Differential Scanning Calorimeter (DSC) Output



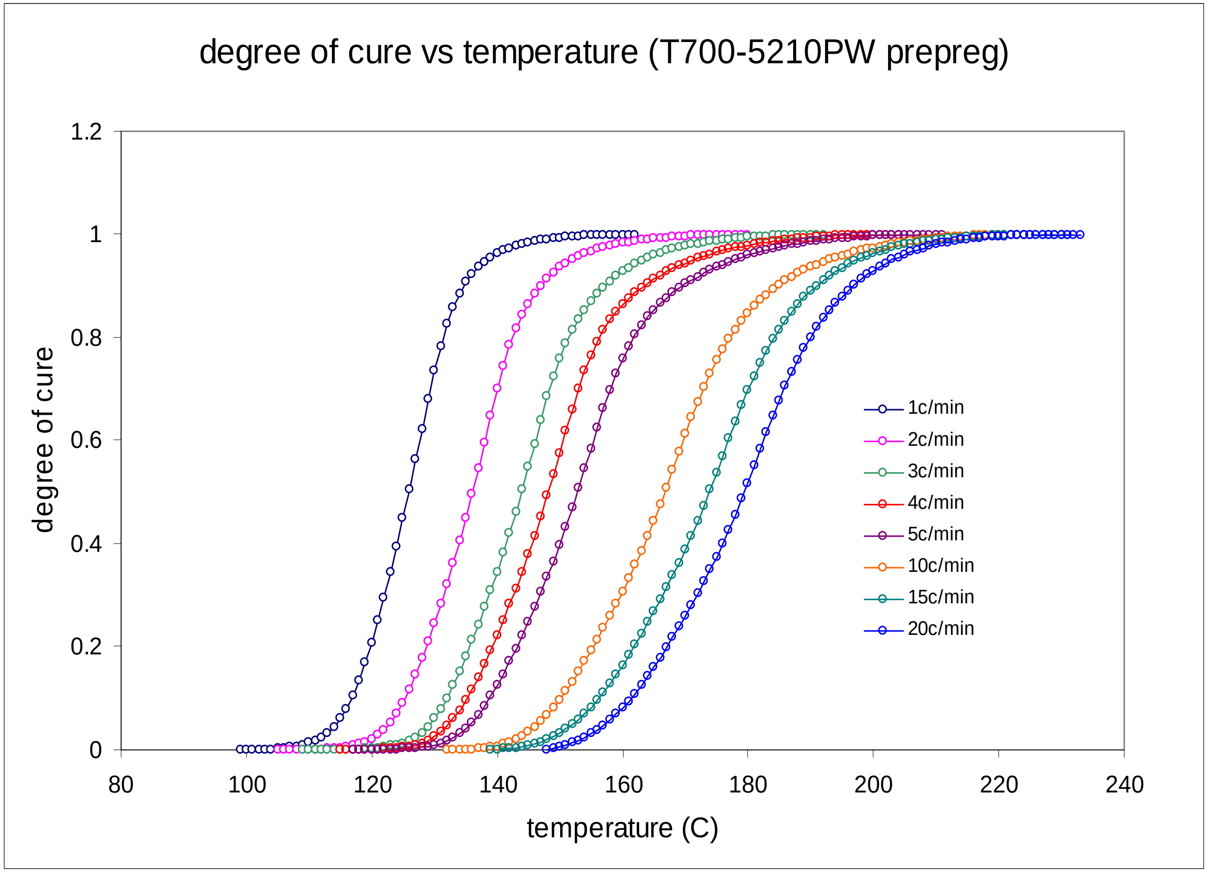
Degree of Cure at time t, $\alpha = \dfrac{B}{A+B}$

Flores, Gandikota,

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

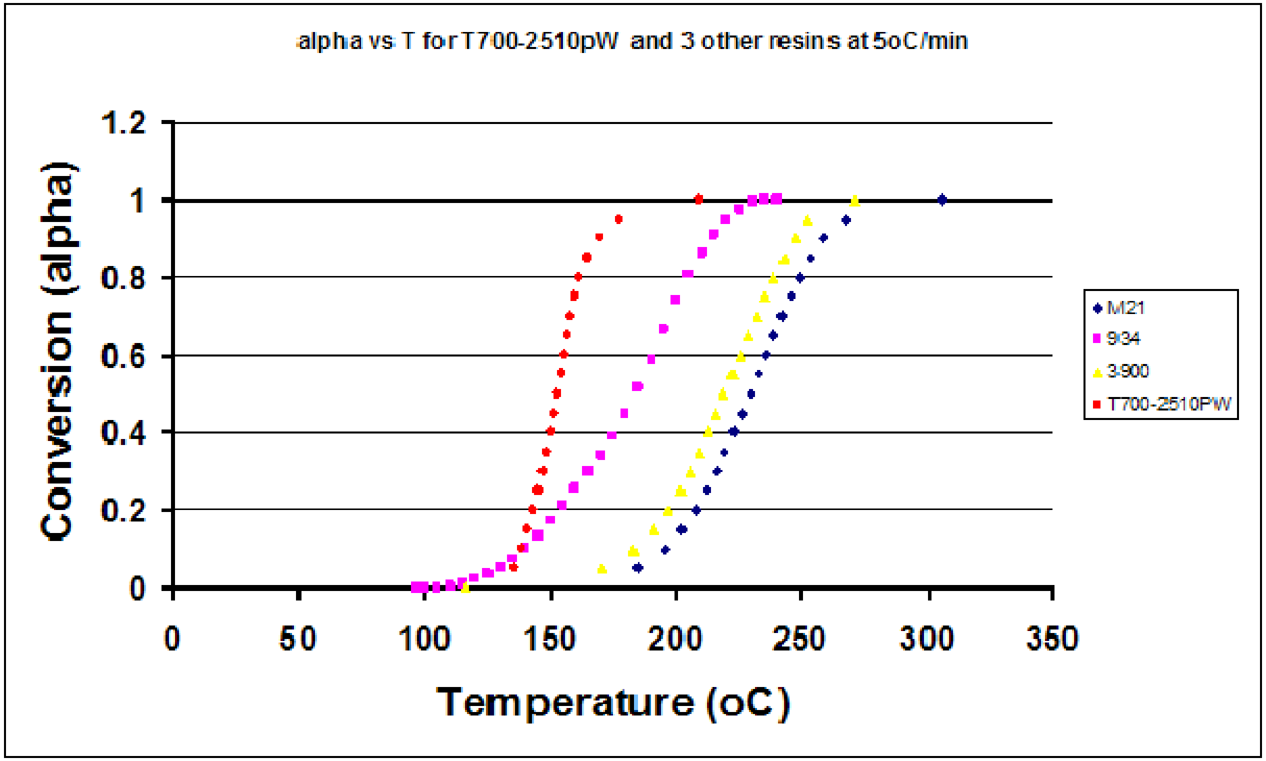
Cure of T700-2510PW Prepreg under Ramped conditions by DSC

Extent of cure



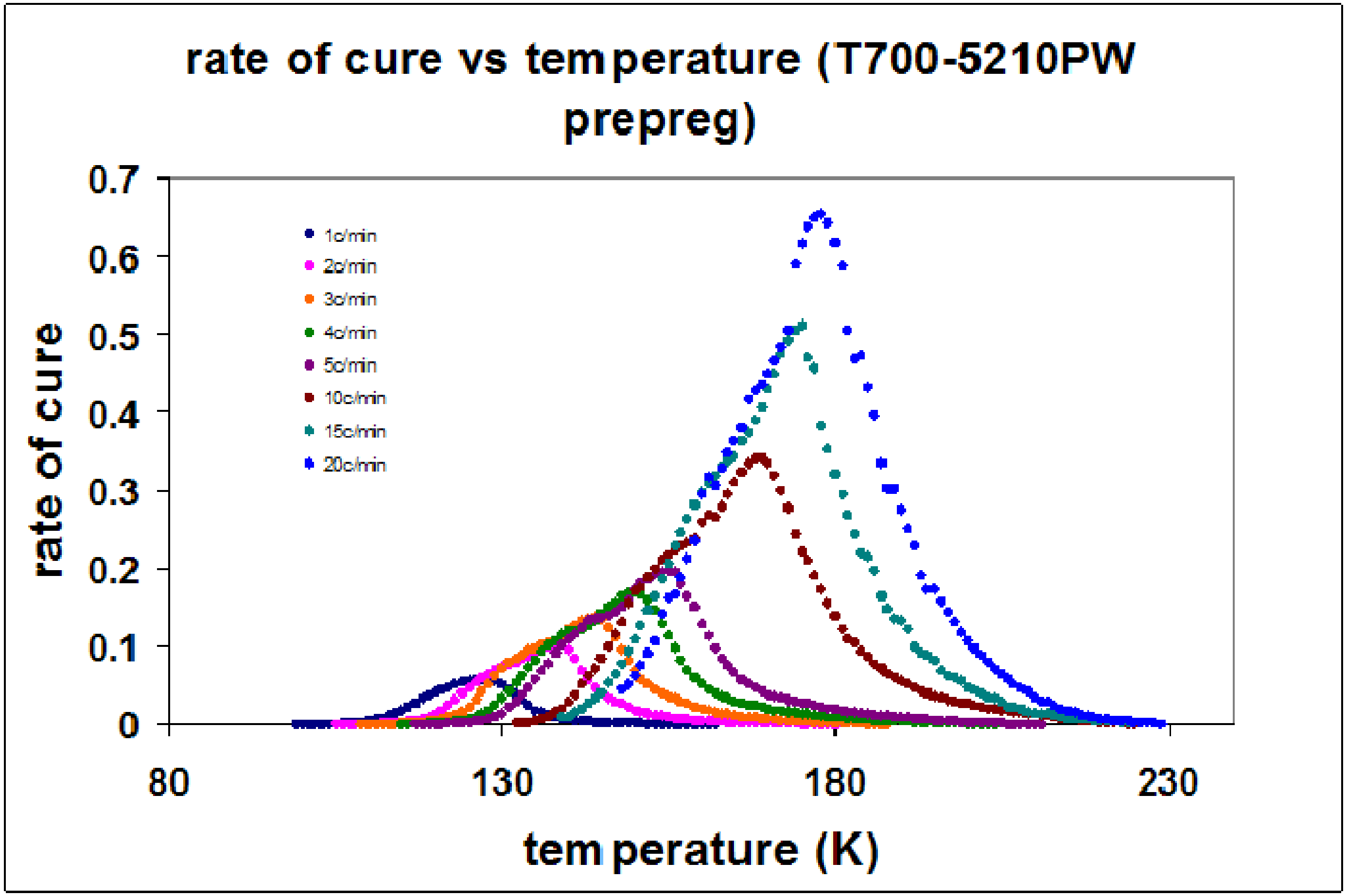
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Degree of cure (α) versus temperature (°C) for resin in T700-2510PW prepreg and resin in three other common high performance aviation prepregs, all cured under programmed conditions at 5°C/min,



Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Rate of cure (dα/dt) versus temperature (T) for T700-2510PW prepreg



Flynn Wall kinetics

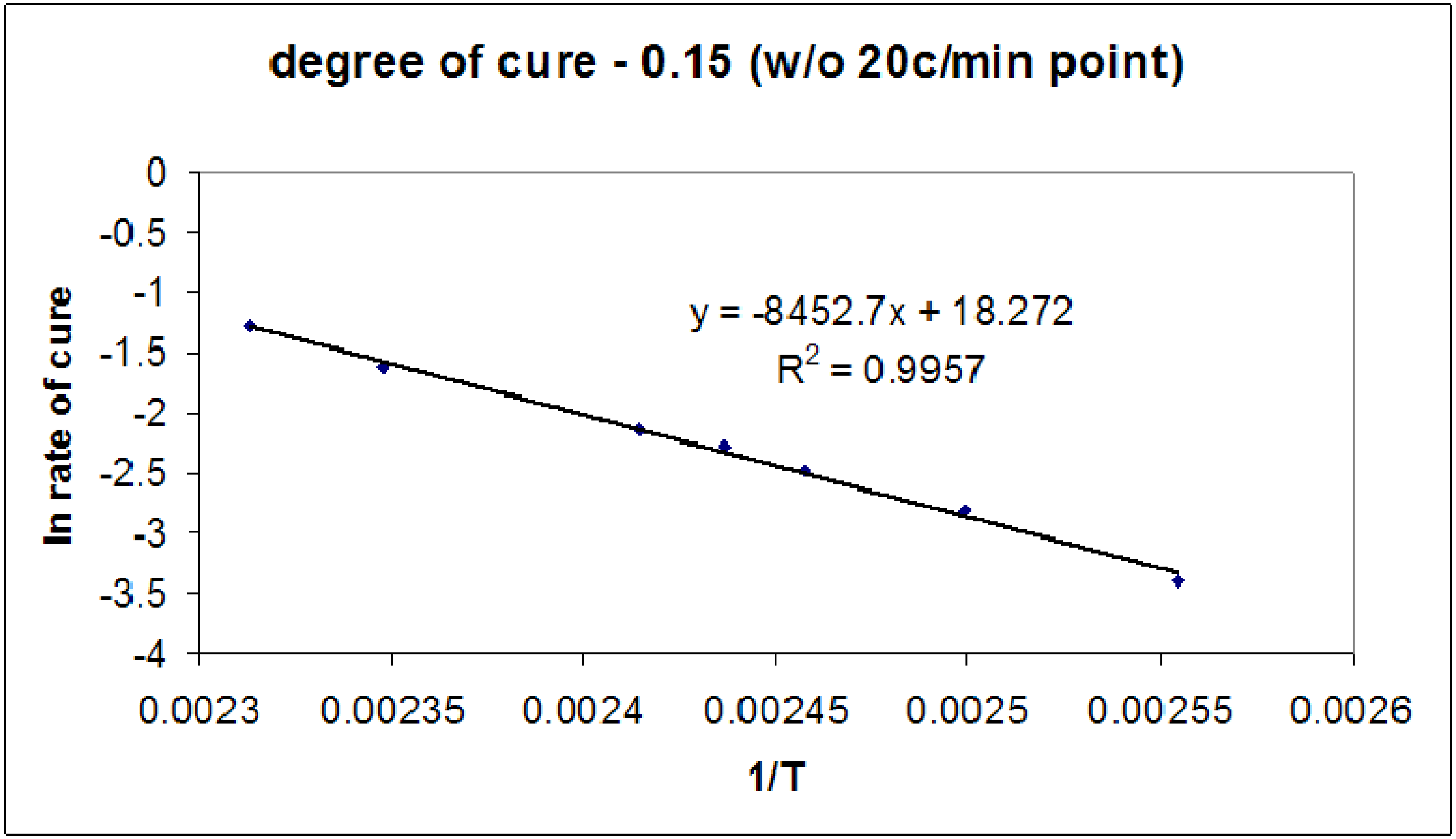
$$K = Ae^{\left(\frac{-E_a}{RT}\right)}$$

$$\frac{d\alpha}{dt} = K\left[f\left(\alpha\right)\right]$$

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + \ln\left[f\left(\alpha\right)\right] - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

m=Ea/R



JAMS

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

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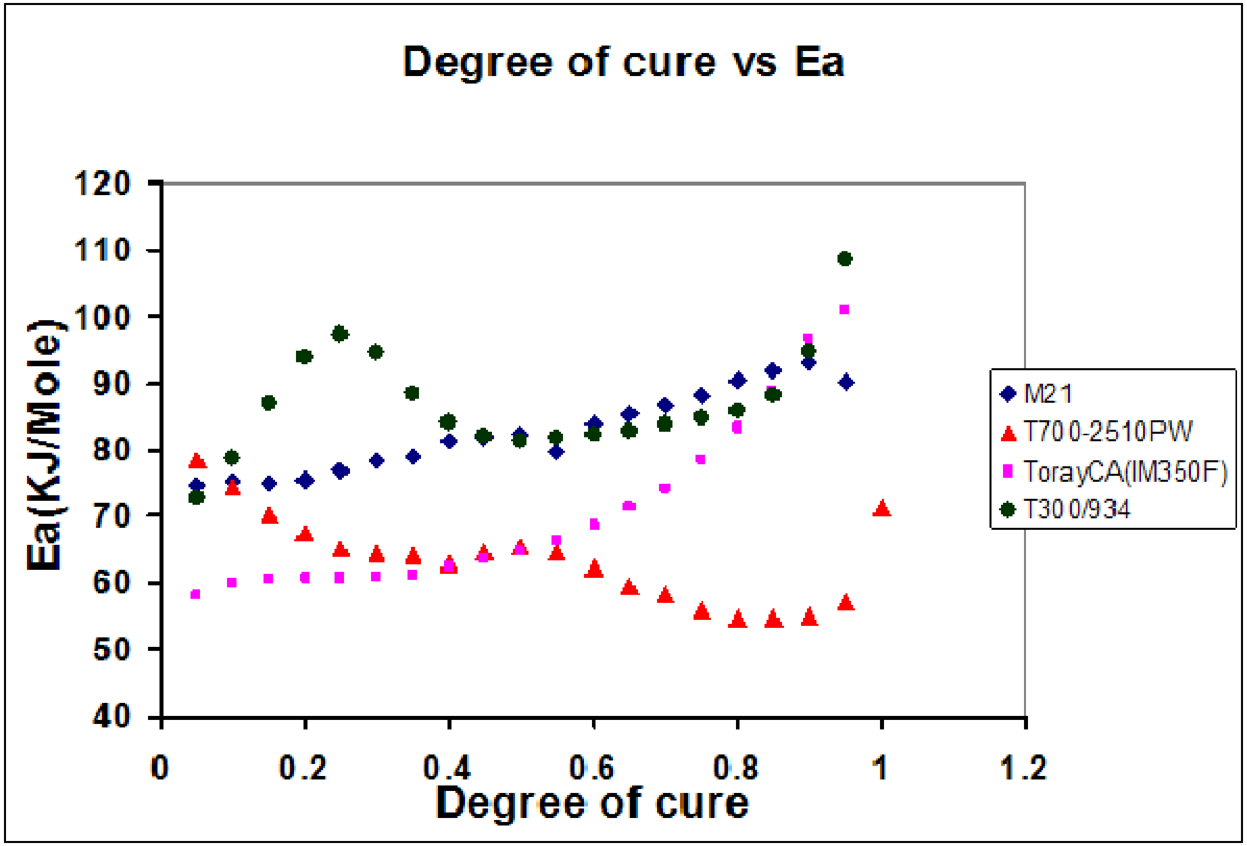
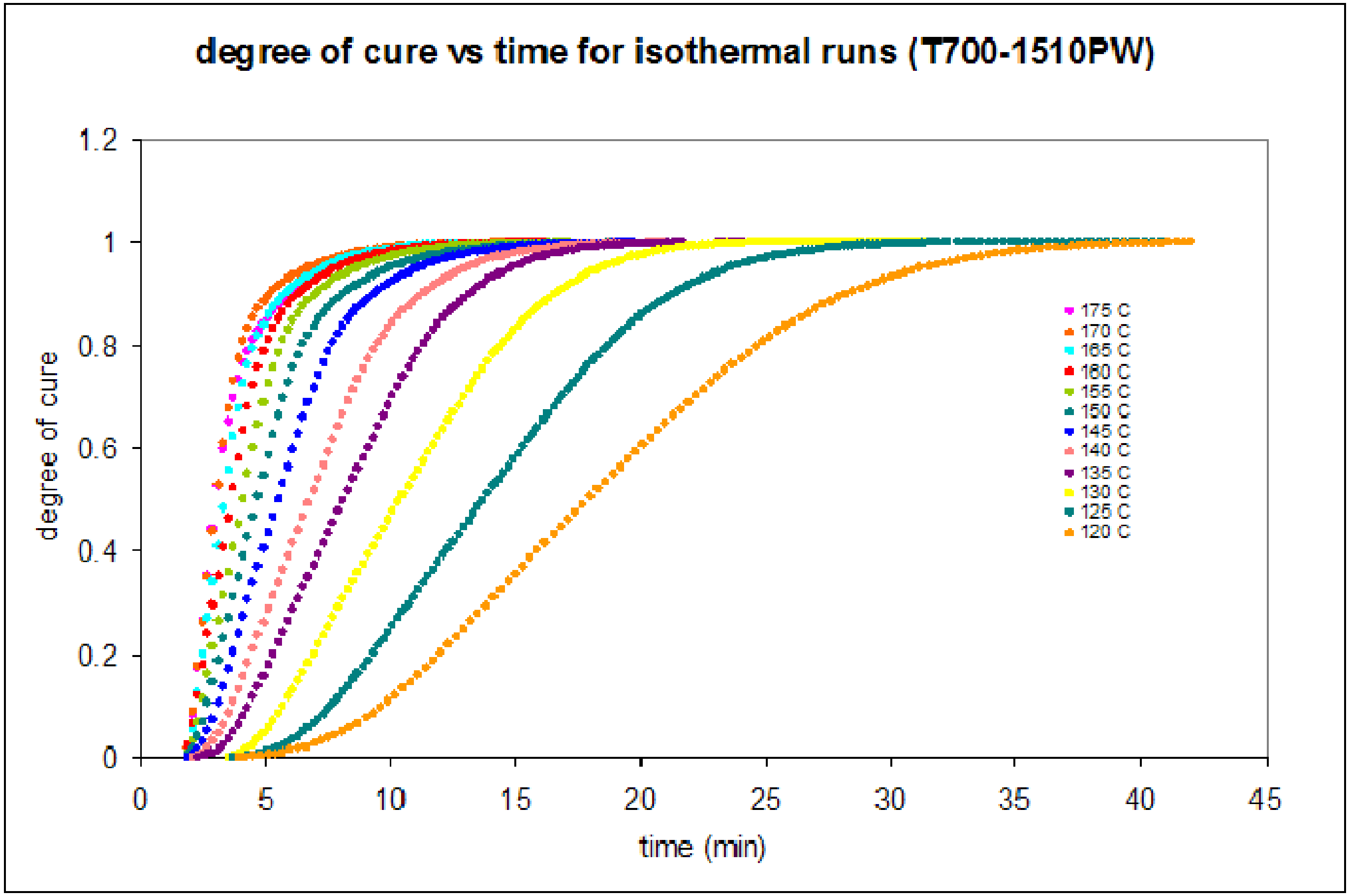
CECAM

Ea versus conversion (α) for resin in T700-2510PW prepreg, M21 pultrusion unitape, for resin in TORAYCA(IM350F) prepreg, and for resin in T300/934 prepreg



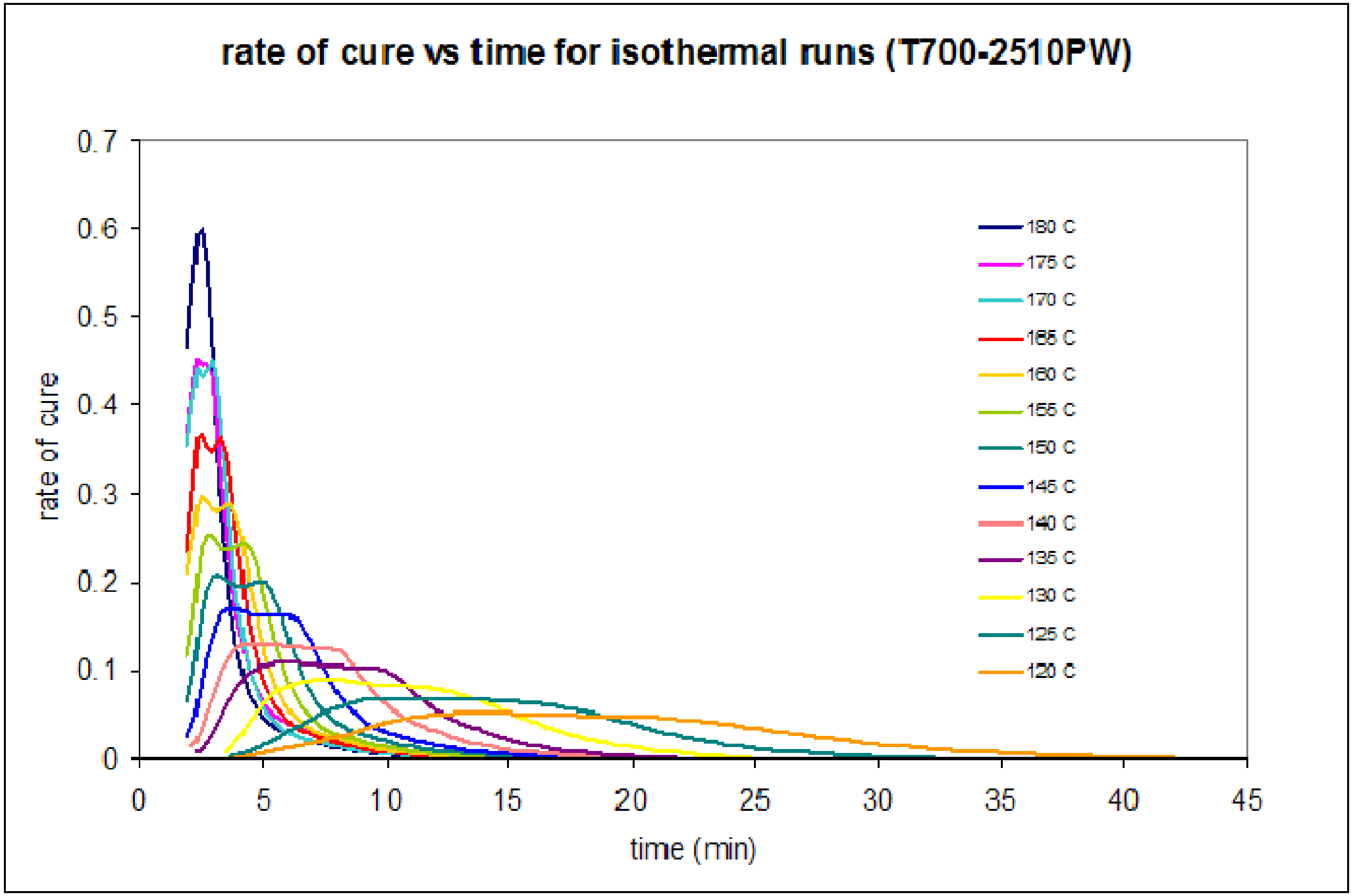
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Plot of conversion (α) versus time for cure, over a range of isothermal temperature of T700-2510PW prepeg



Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Plot of rate (dα/dt) versus time for cure, over a range of isothermal temperature of T700-2510PW prepeg



Kamal kinetic scheme for isothermal kinetics

$$d\alpha/dt = (K_1 + K_2\alpha^m)(\alpha_f - \alpha)^m$$

Where…

K_1 = rate constant for uncatalysed cure of resin

K_2 = rate constant for cure of resin catalysed by products

α = intermediate level of cure at isothermal temperature

α_f = ultimate level of cure at isothermal temperature

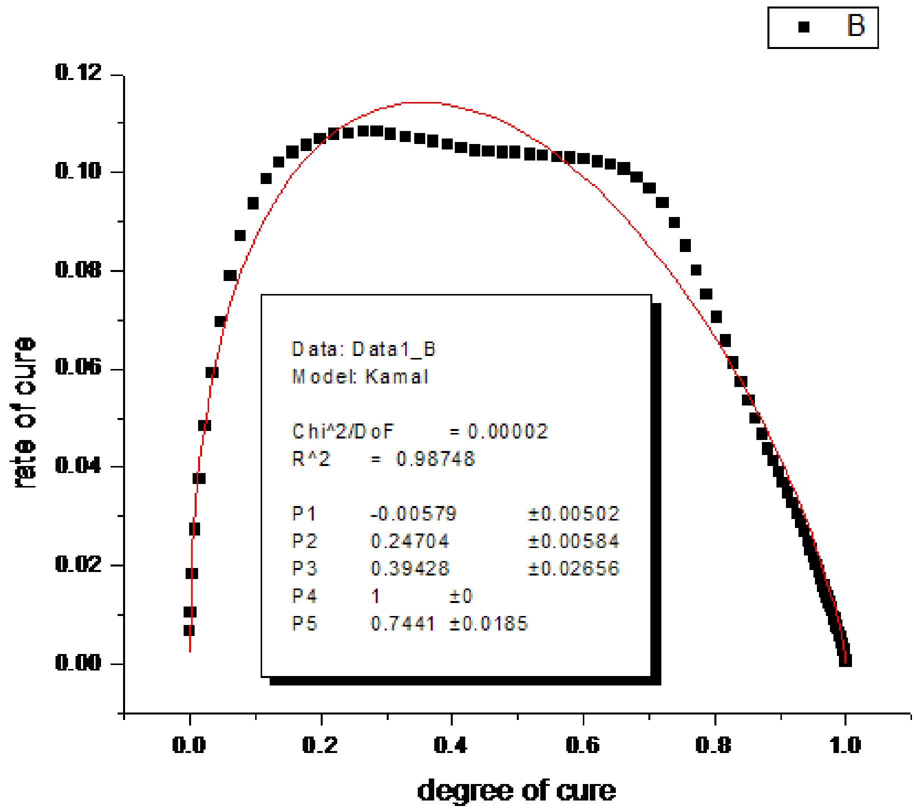
Isothermal experiments were performed from 120°C to 180°C in 5°C increments

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Plot of rate of cure versus degree of cure for resin in T700-2510PW prepreg at 140°C. Black squares – experimental data, red line – Kamal model prediction. The gradient of the best fit straight line is set to – Ea_1/R.

Poor fit to Kamal kinetics

External catalysis

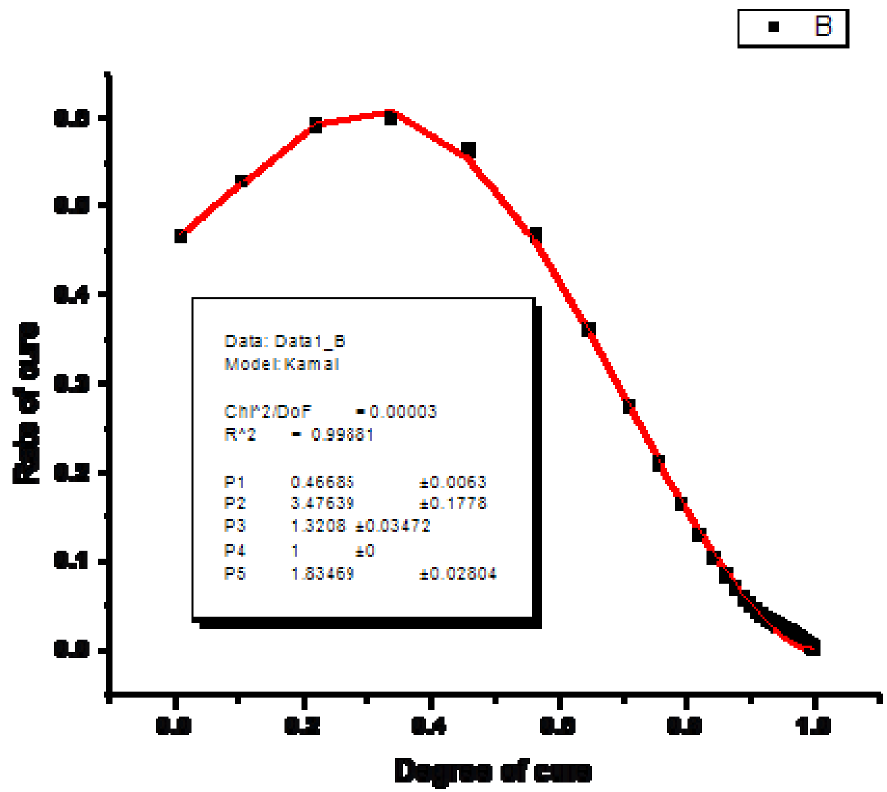


Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

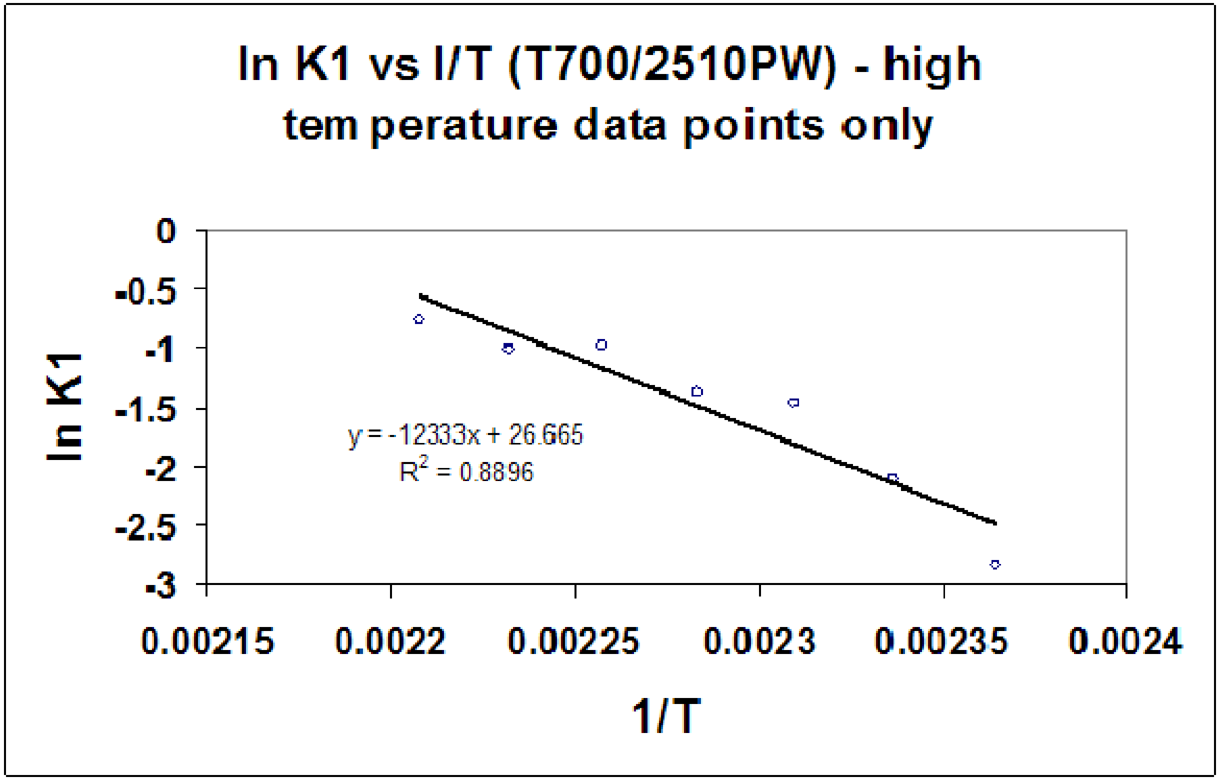
Plot of rate of cure versus degree of cure for resin in T700-2510PW prepreg at 180°C. Black squares – experimental data, red line – Kamal model prediction.

Good fit to Kamal kinetics

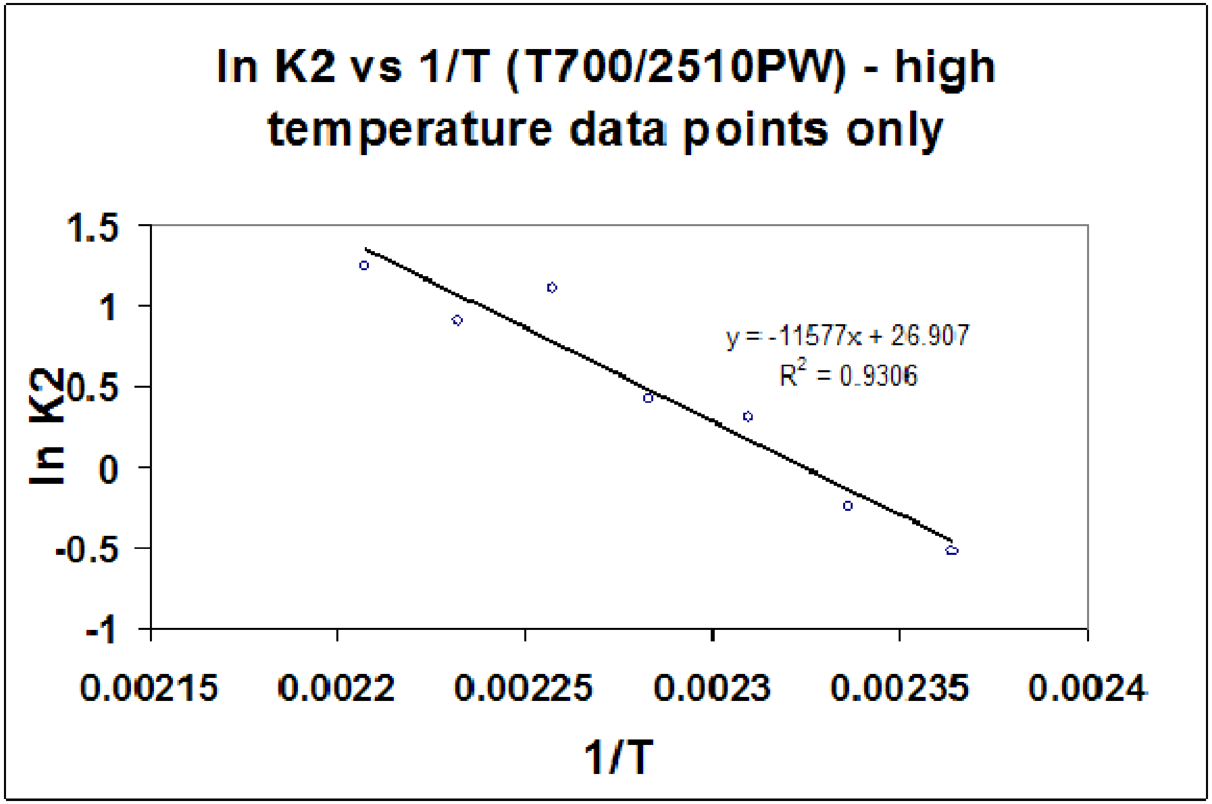
Relative effect of external catalysis is diminished



Plot of ln{K1} versus 1/T for T700-2510PW prepreg using data points collected at 150ºC or above. The gradient of the best fit straight line is set to –Ea_1/R.



Plot of ln{K2} versus 1/T for T700-2510PW prepreg using data points collected at 150ºC or above. The gradient of the best fit straight line is set to $-Ea_1/R$.



Values of Ea_1 and Ea_2 for T700-2510PW prepreg calculated according to the Kamal method.

	All Kj/mole	
System	**Ea_1**	**Ea_2**
T300/934	53.8 (2 parameter)	$\pm \sim 0$
	64.3 (1 parameter)	
TORAYCA(IM350F)	74.7	53.8
T700-2510PW	102.5	96.3

Combined ramp and soak experiments were performed using T700-2510PW prepreg using a method developed previously. The experiment is summarized below

Ramp from room temperature to soak temperature	Heat of reaction to intermediate temperature = ΔH(Ti)	Heat of reaction to soak temperature = ΔH(Ts)
Fast cool to room temperature		
Fast re-heat to soak temperature		
Isothermal at soak temperature	Heat of reaction to intermediate time = ΔH(ti)	Ultimate isothermal heat of reaction = ΔH(t∞)
Fast cool to room temperature		
Ramp to 300oC @ 3^{o}C/min for residual cure	Heat of reaction =ΔH(r)	

Examples

Extent of reaction to an intermediate cure temperature during the first ramp cycle

$$\alpha = \Delta H(Ti) / (\Delta H(Ts) + \Delta H(t\infty) + \Delta H(r))$$

Extent of reaction to soak temperature

$$\alpha = \Delta H(Ts) / (\Delta H(Ts) + \Delta H(t\infty) + \Delta H(r))$$

Extent of reaction at intermediate soak time

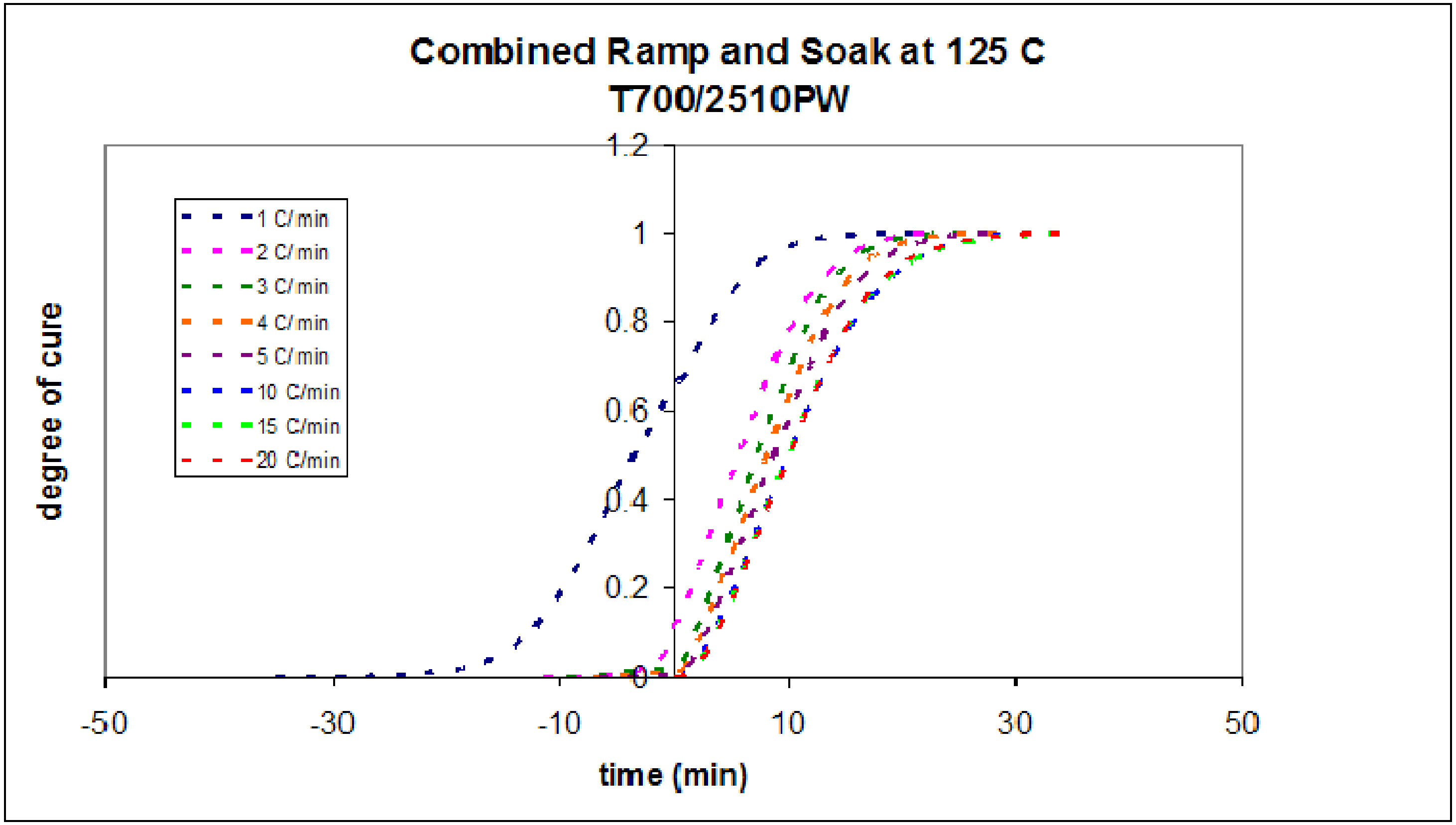
$$\alpha = (\Delta H(Ts) + \Delta H(ti)) / (\Delta H(Ts) + \Delta H(t\infty) + \Delta H(r))$$

Ultimate extent of reaction after soaking to long times

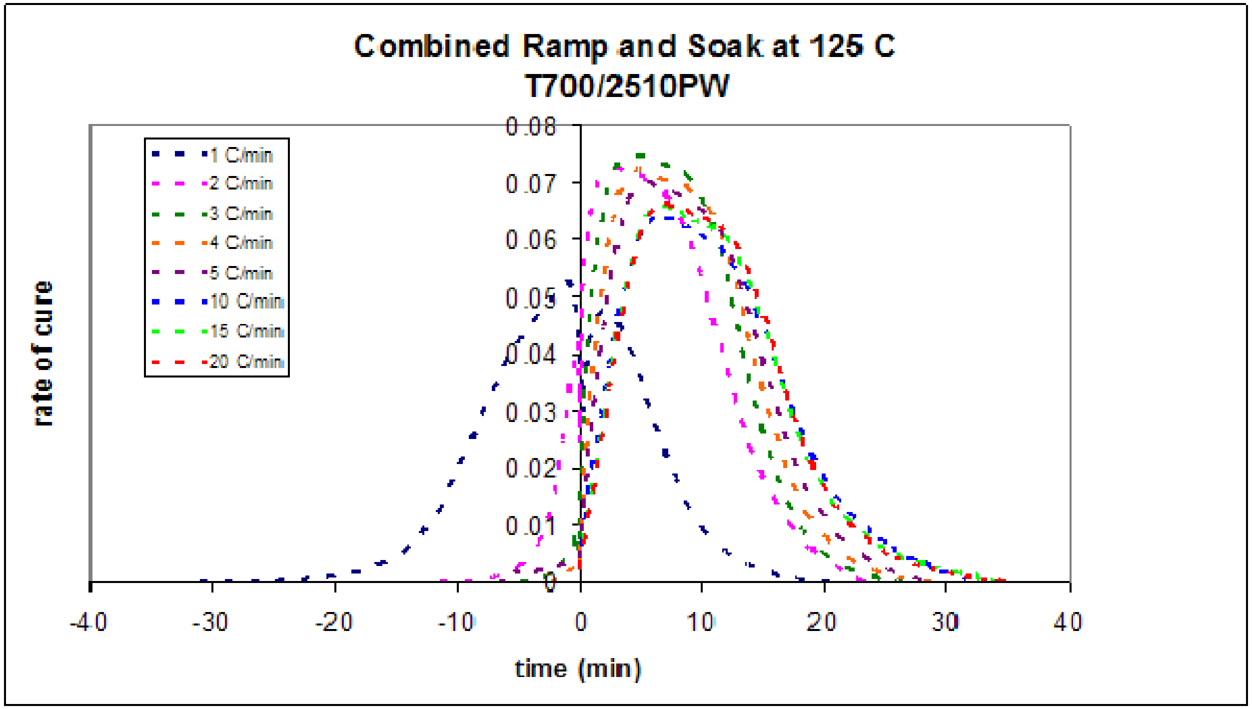
$$\alpha = (\Delta H(Ts) + \Delta H(t\infty)) / (\Delta H(Ts) + \Delta H(t\infty) + \Delta H(r))$$

Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

Ramp and soak of T700-2510PW prepreg to 125°C over a range of heating rates. Conversion (α) versus time



Ramp and soak of T700-2510PW prepreg to 125^{o}C over a range of heating rates. Rate of reaction (dα/dt) versus time



Ramp and soak experiments were performed at 125, 130, 135, 140, 145, 150, and 155^{o}C

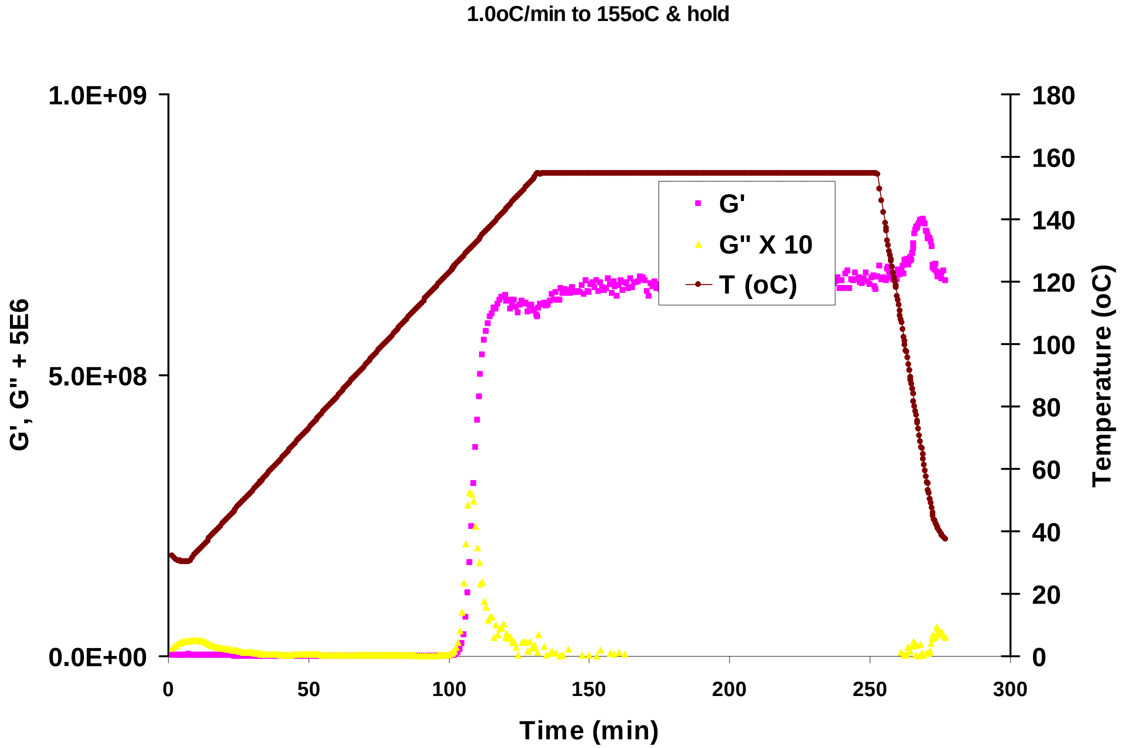
it may be concluded that a good compromise cure cycle, minimizing both reaction rates and reaction time, may be constructed by heating to 150^{o}C at 2^{o}C/min followed by a 20 min soak at that temperature.

Sample configuration for the DMA experiment

(Alpha Technologies ATD 2000 encapsulation rheometer)

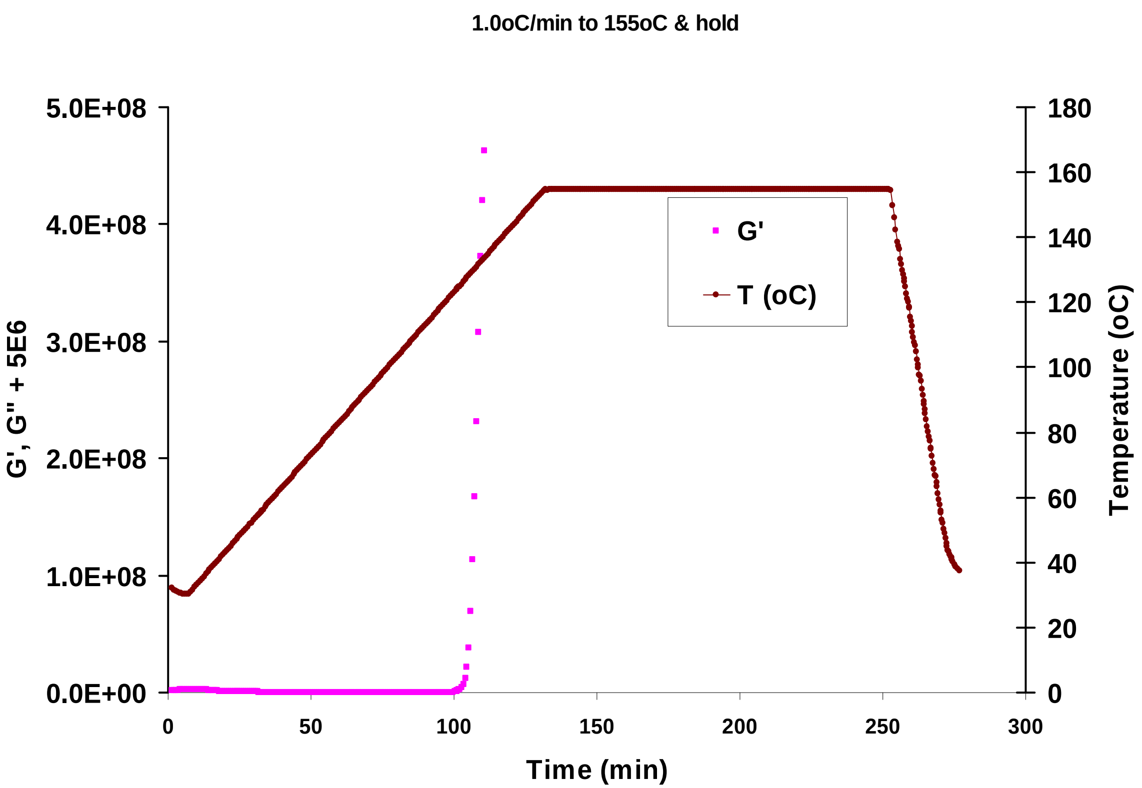
Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

DMA of uncured T700-2510PW prepreg from room temperature to 155°C @ 1°C/min then held at 155°C for 120 min. Temperature (°C), G', and G" are plotted as a function of time



Water uptake, cure state, surface free energy analysis, and kinetic evaluation of candidate prepregs for composite repair

DMA of uncured T700-2510PW prepreg from room temperature to 155°C @ 1°C/min then held at 155°C for 120 min. Temperature (°C), and G', are plotted as a function of time.



Cure cycle	Initial buildup of physical properties	100% cure achieved at
1^{o}C/min to 155^{o}C & hold for 120 min	125^{o}C on ramp segment	147^{o}C on ramp segment
2^{o}C/min to 155^{o}C & hold for 120 min	134^{o}C on ramp segment	6 min at 155^{o}C soak temperature
1^{o}C/min to 165^{o}C & hold for 120 min	125^{o}C on ramp segment	147^{o}C on ramp segment
2^{o}C/min to 165^{o}C & hold for 120 min	134^{o}C on ramp segment	6 min at 165^{o}C soak temperature
1^{o}C/min to 175^{o}C & hold for 120 min	125^{o}C on ramp segment	152^{o}C on ramp segment
2^{o}C/min to 175^{o}C & hold for 120 min	135^{o}C on ramp segment	165^{o}C on ramp segment

By comparing the results of DSC and DMA experiments, the gel point can be approximated at 40-45 % conversion of T70/2510PW prepreg.

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**

Water uptake, cure state and kinetic evaluation of candidate prepregs for composite repair

Water uptake, cure state and kinetic evaluation of candidate prepregs for composite repair