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

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center of excellence for composites and advanced materials

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Measurement of cure state of emerging resin systems prior to bonding

- **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 bonding and 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

- William T.K. Stevenson[1], Irish Alcalen[1], Daniel Lenz[1], Lamia Salah[2], John Tomblin[2],
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- **2. NIAR, Wichita State U.**

FAA Technical Monitor

- **Curt Davies**

Other FAA Personnel Involved

- **Larry Ilcewicz**

Industry Participation

- **Spirit AeroSystems**

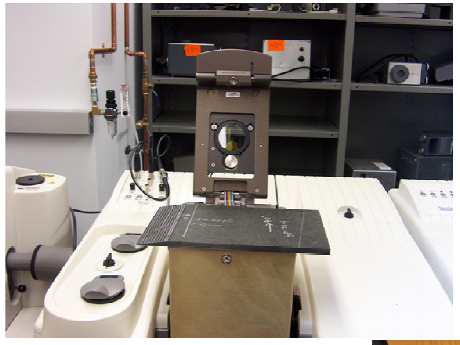
Topics

- **Diffuse Reflectance Near IR spectroscopy for polyimide cure state measurement**
- **Diffuse Reflectance Near IR spectroscopy for metal nanoparticle filled epoxy resin cure state measurement**

Near IR studies Background

Measurement of cure state of emerging resin systems prior to bonding

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

Measurement of cure state of emerging resin systems prior to bonding

The thermal stability of amine cured epoxy resin based composites is limited by the thermal stability of the amine-epoxy crosslink.

The thermal stability of anhydride cured epoxy resin based composites is limited by the thermal stability of the ester crosslink.

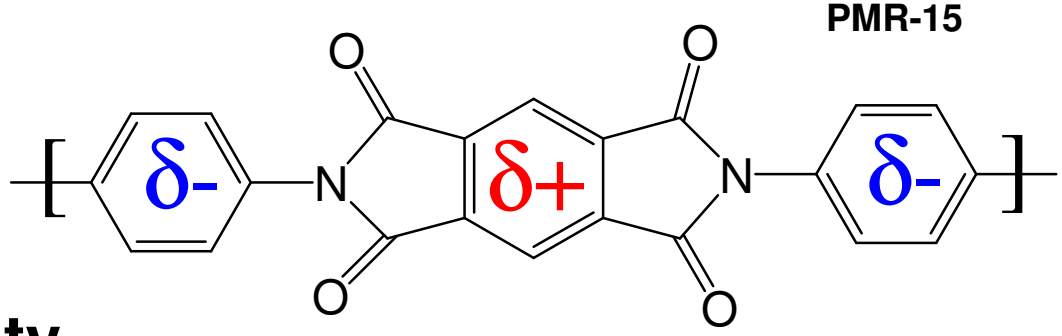
Neither are optimal choices for the construction of engine support mounts

Eventually, reinforced ceramic materials will fill this void

Until then, something better than epoxy resin must be developed for this application

Polyimide resin

PMR-15

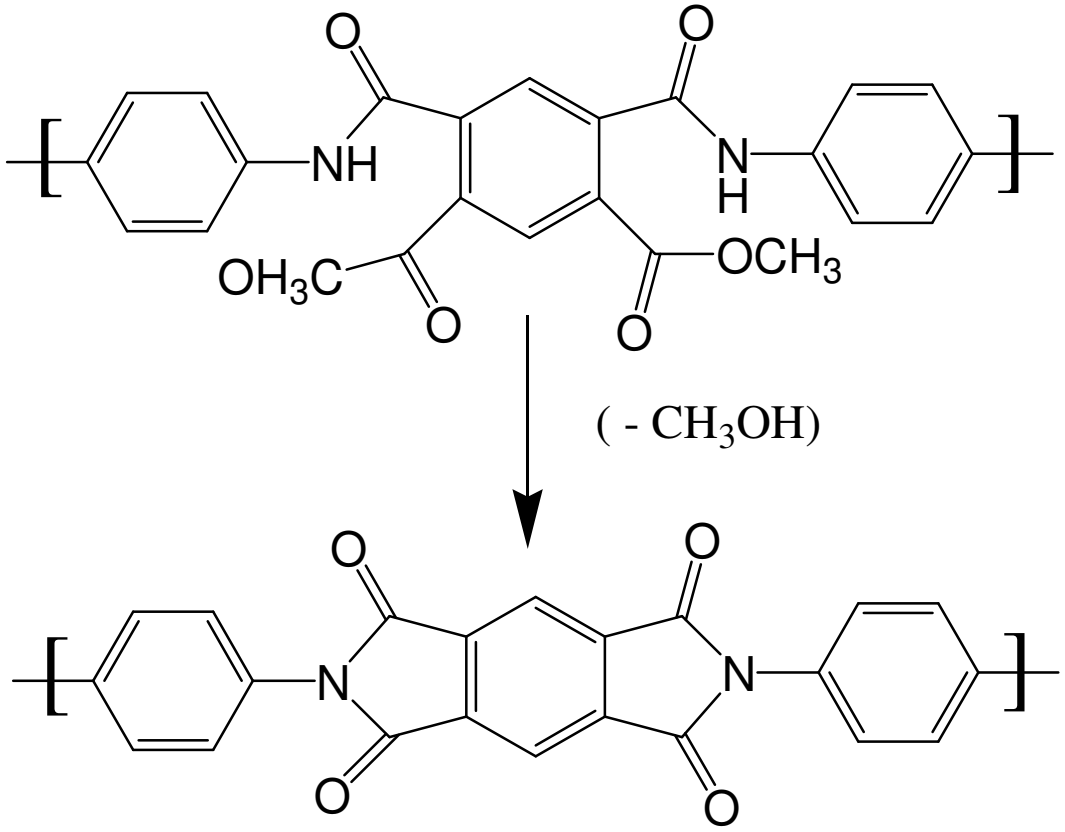


- Stiff, strong
- Good thermal stability
- More difficult to work with than epoxy resins
  - Fragile in the initial stages of cure
  - Volatile production
  - Complex cure cycles

Promoted by NASA for 20+ years

Integrated into defence systems but not much used in commercial aerospace

Polyimide cure



Measurement of cure state of emerging resin systems prior to bonding

Can we develop a reliable and simple way to track polyimide cure state on the shop floor?

- Polyimide cure cycles are daunting when compared with epoxy resin cure cycles
- Cure of polyimide is difficult to follow by ex. DSC, DMA
- Cure state was defined by softening temperature as measured by TMA
- The diffuse reflectance near IR spectrum was then collected and chemometrics was used to construct a calibration curve

Case study #1 A PI prepreg with known composition

Maverick Corporation, MVK-14 FreeForm Polyimide

Step 1. Ramp from 25℃ to 232℃ at 0.5℃/min

Step 2. Hold at 232℃ for 30 min

Step 3. Ramp from 232℃ to 266℃ in 120 min

Step 4. Hold at 266℃ for 380 min

Step 5. Ramp from 266℃ to 307℃ at 0.5℃/min

Step 6. Hold at 307℃ for 300 min

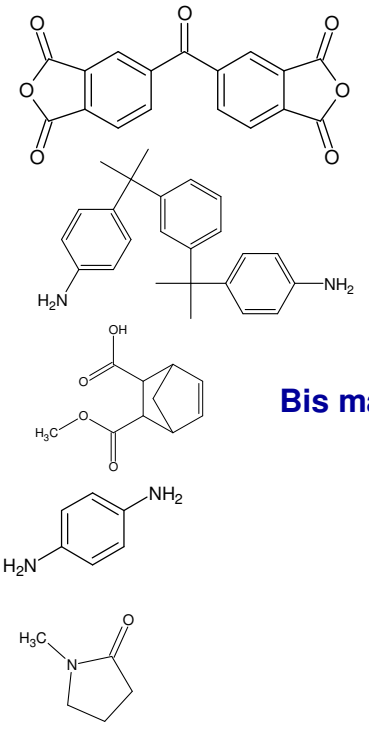
Substitute for PMR-15 with service limit 228°C

No MDA

Measurement of cure state of emerging resin systems prior to bonding

COMPONENTS: Polymer Ester Solution	CAS NO.	WEIGHT PERCENT
3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA)	2421-28-5	5 – 25
4,4'-[1,3-phenylene-bis-(1-methylethylidene)]bisaniline (BISM)	2687-27-6	5 - 15
Bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid monomethylester (NE)	36897-94-6	5 - 15
p-Phenylene Diamine (PPD)	106-50-3	0 – 15
Ethanol (EtOH)	64-17-5	10 – 45
1-Methyl-2-Pyrrolidinone (NMP)	872-50-4	0 – 5
Supplied on the following fabric: Carbon roving, tow, tape, or fabric	7440-44-0	45-75

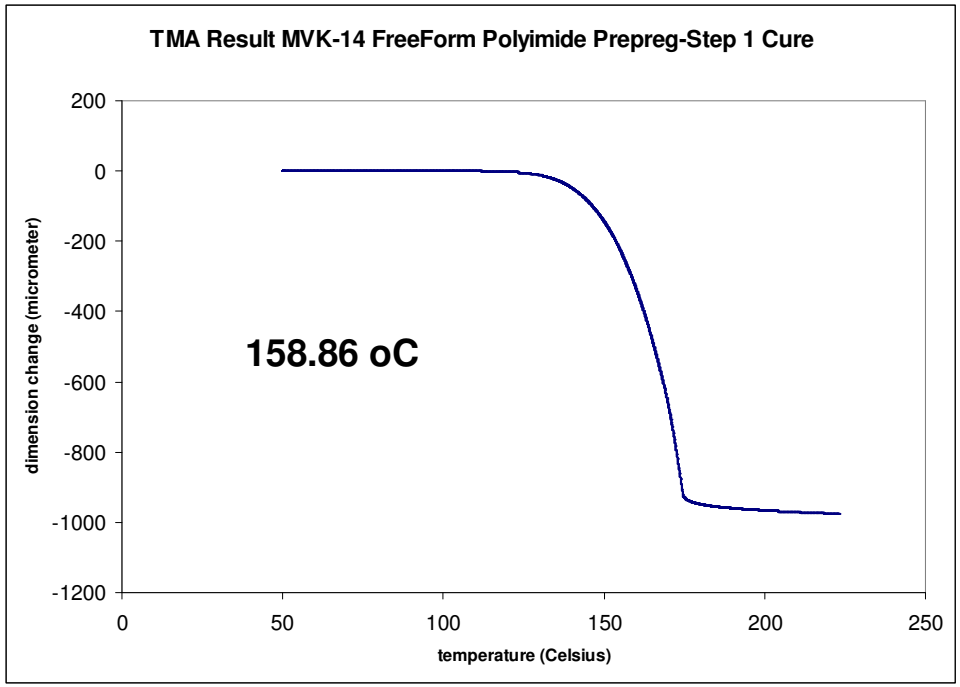
MVK-14



Bis maleimide

No MDA

TMA MVK-14



After

Step1 158.86oC

Step 2 163.54 oC

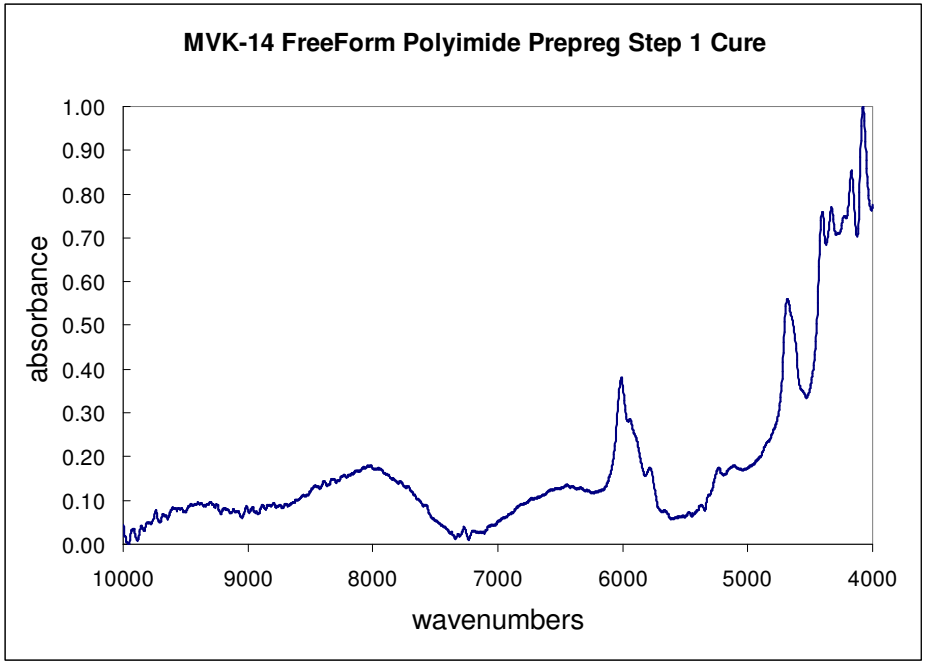
Step 3 204.45 oC

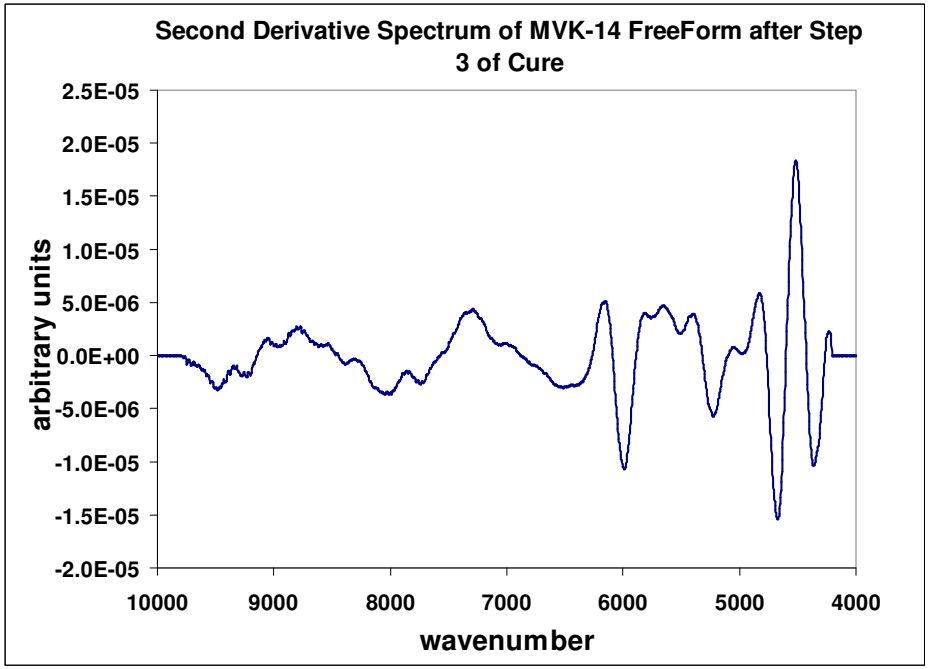
Step 4 264.81 oC

Step 5 266.95 oC

Step 6 289.72 oC

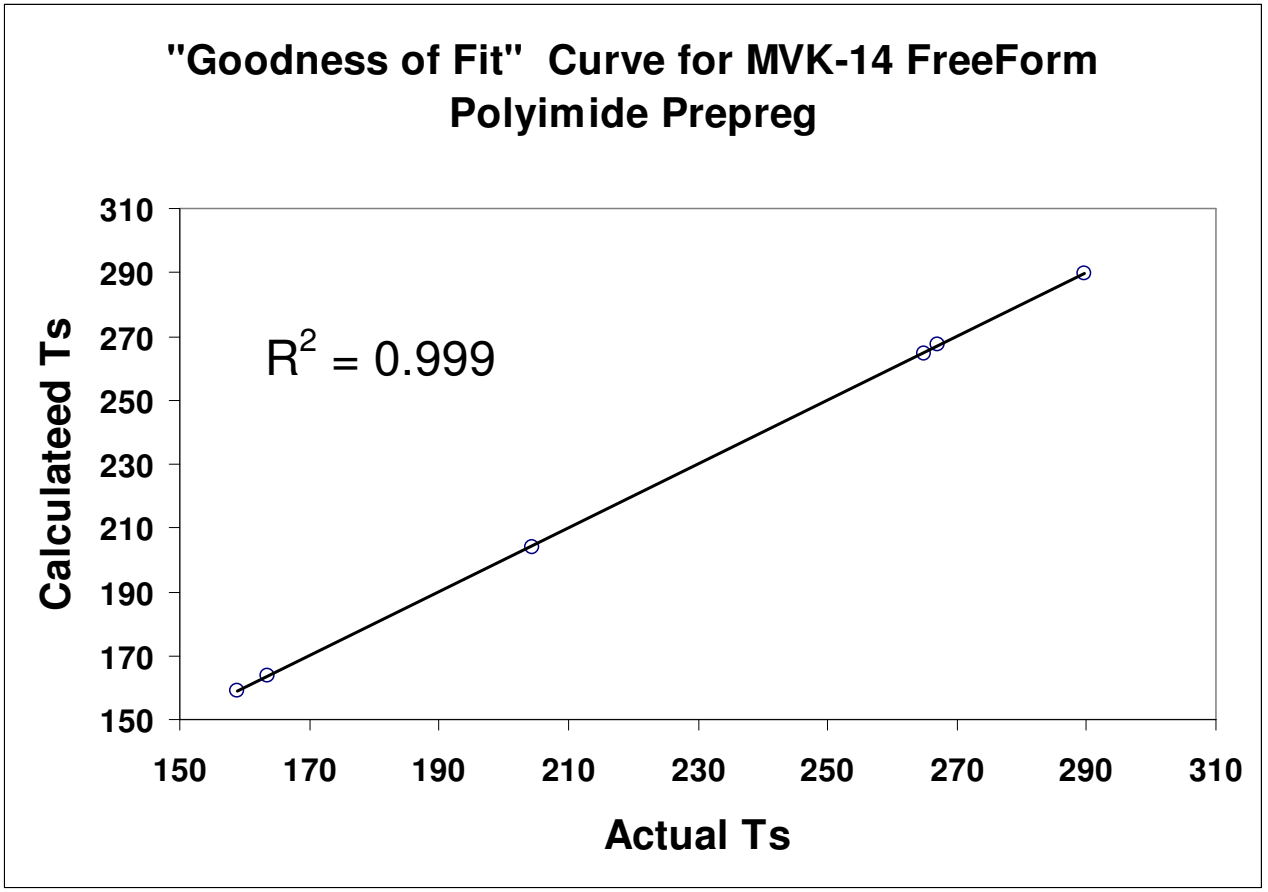
Measurement of cure state of emerging resin systems prior to bonding





Measurement of cure state of emerging resin systems prior to bonding

Strategy – use entire spectrum 10000 – 4000 cm^{-1} partial least squares analysis



Case study #2 PI prepreg supplied with less information

Ube Industries, PETI – 365APolyimide

Step 5. A ramp from 25℃ to 130℃ at 1℃/min

Step 1. Ramp from 25℃ to 260℃ in 210 min

Step 2. Hold at 260℃ for 60 min

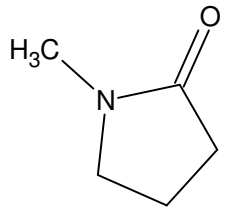
Step 3. Ramp from 260℃ to 371℃ in 60 min

Step 4. Hold at 371℃ for 60 min

Measurement of cure state of emerging resin systems prior to bonding

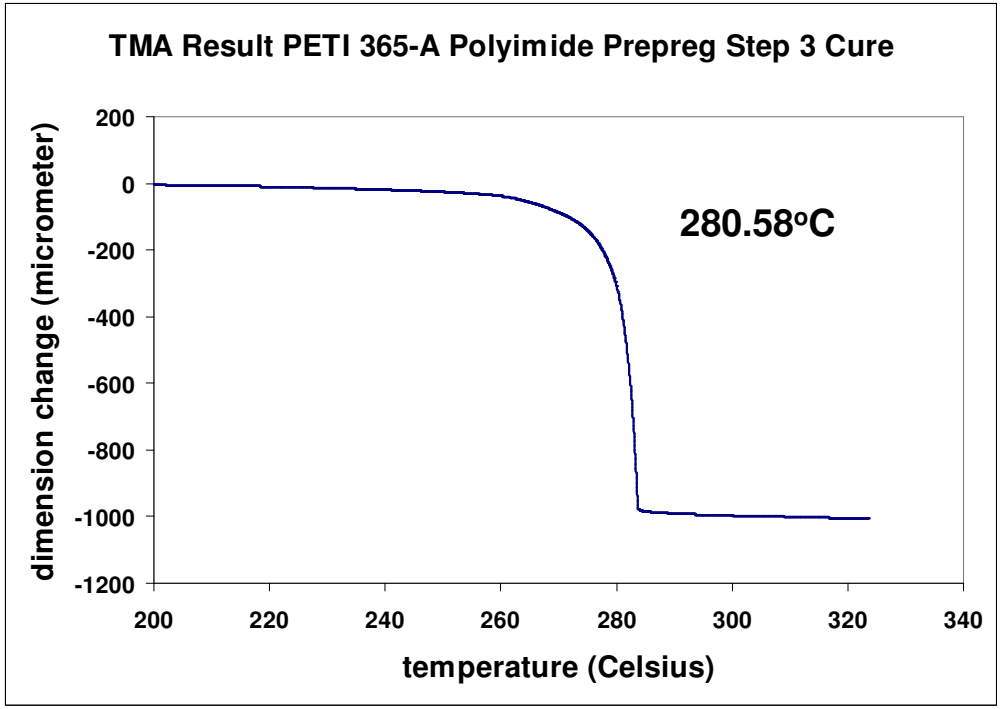
Chemical name	Chemical formula	wt%	CAS No.
Amide acid	confidential	30 ~ 40 wt%	Not registered
N-methyl-2-pyrrolidone (NMP)	$CH_3NC_4H_6O$	60 ~ 70 wt%	872-50-4

OSHA hazardous ingredients (29 CFR 1910. 1200) : NMP is hazardous ingredient.



Tg 365 °C, low melt viscosity, reduced void formation

TMA PETI 365-A



After

Step 5 57.48°C

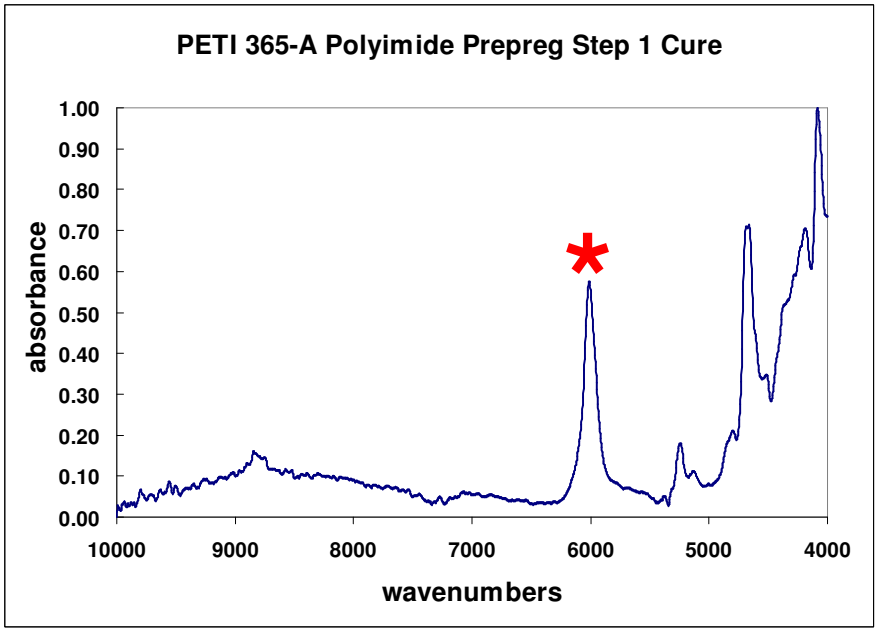
Step1 246.78°C

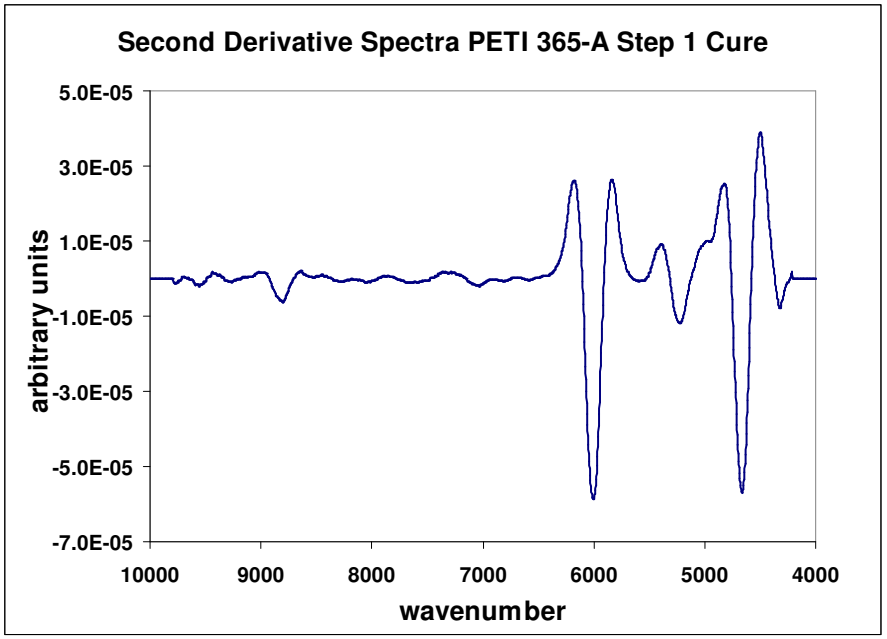
Step 2 270.89°C

Step 3 280.58°C

Step 4 321.56°C

Measurement of cure state of emerging resin systems prior to bonding

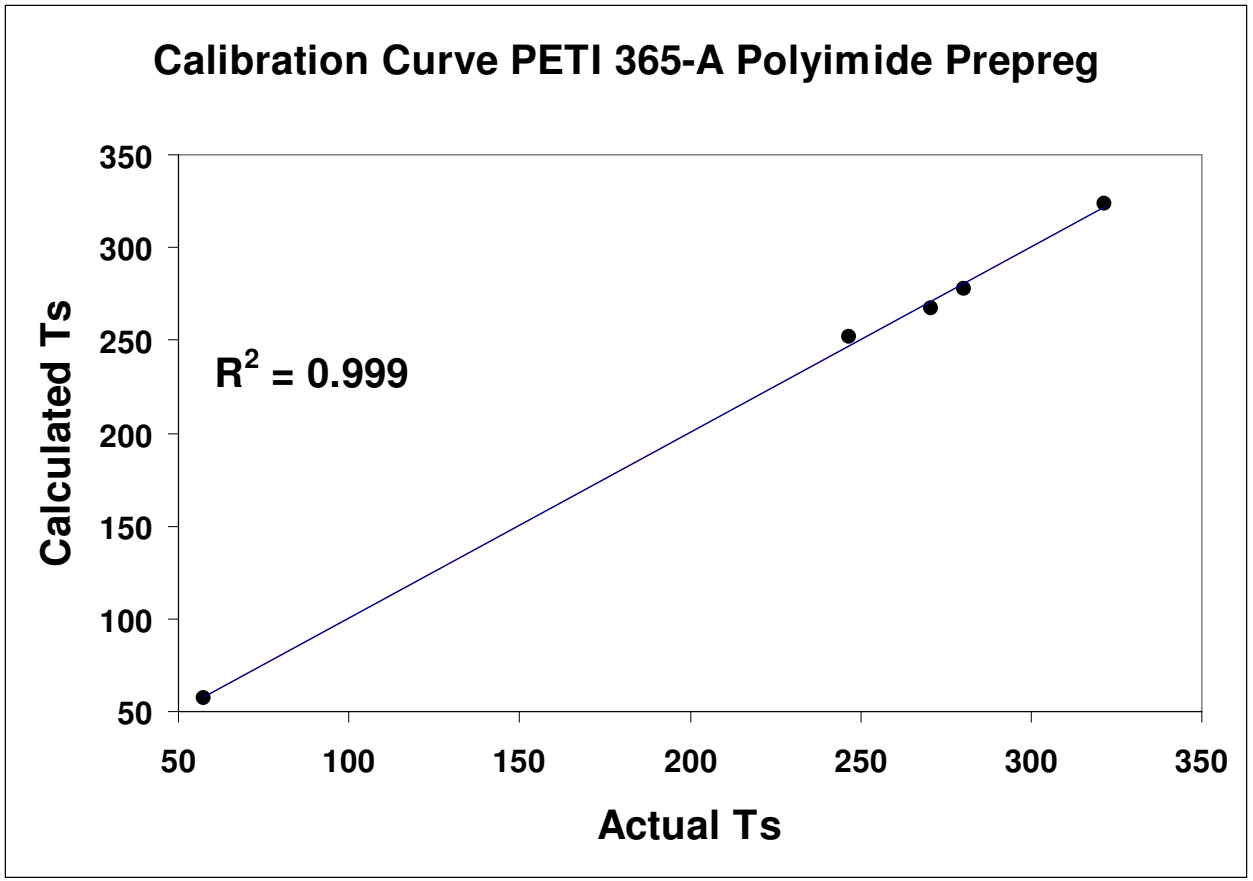




Measurement of cure state of emerging resin systems prior to bonding

Strategy –

use 6345 – 5509 cm^{-1} partial least squares analysis



Nickel nanoparticle filled epoxy resin for lightning strike protection

Until conductive carbon nanotubes can be made sufficiently cheaply to fill this niche, other systems must be investigated

Nickel nanoparticles have shown promise

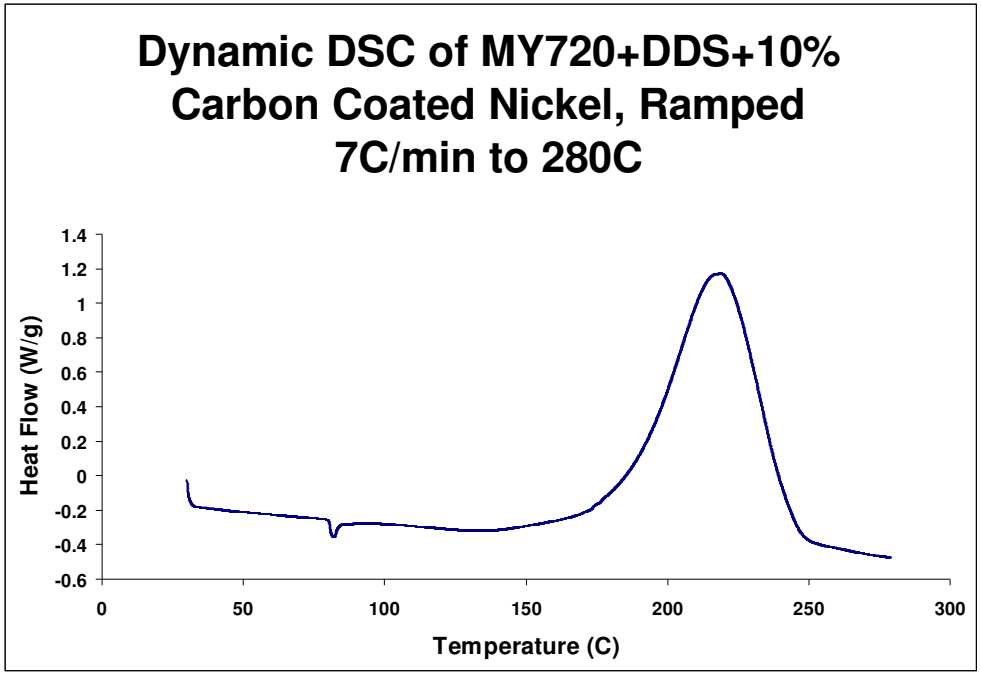
3 systems

- **Nickel**
- **Oxidized "passivated" nickel**
- **Carbon coated nickel**

Can we use near IR spectroscopy to follow the cure of nickel nanoparticle filled epoxy resin?

Measurement of cure state of emerging resin systems prior to bonding

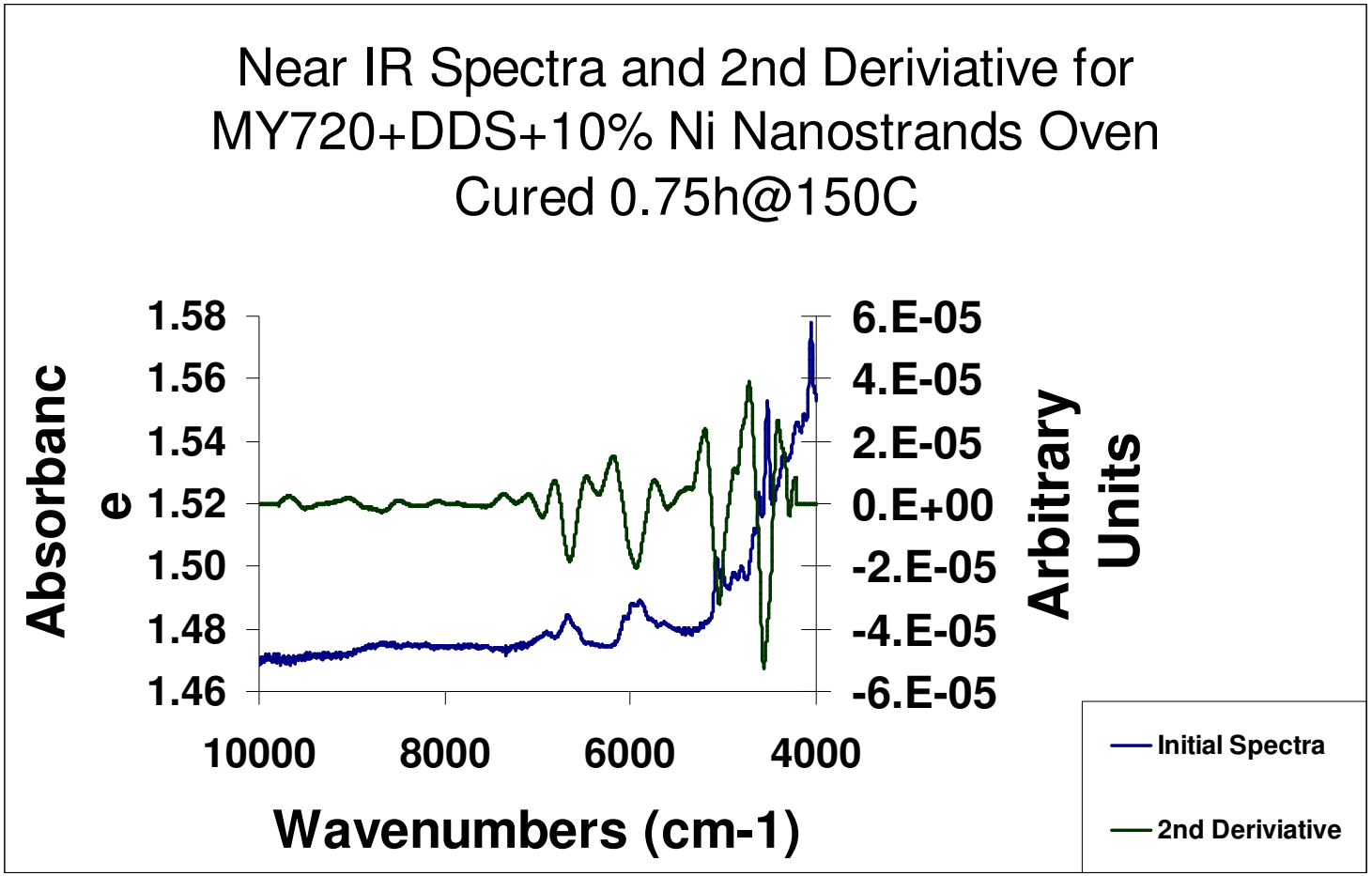
Material is cured in a forced air oven. Extent of cure is determined by DSC using the residual exotherm



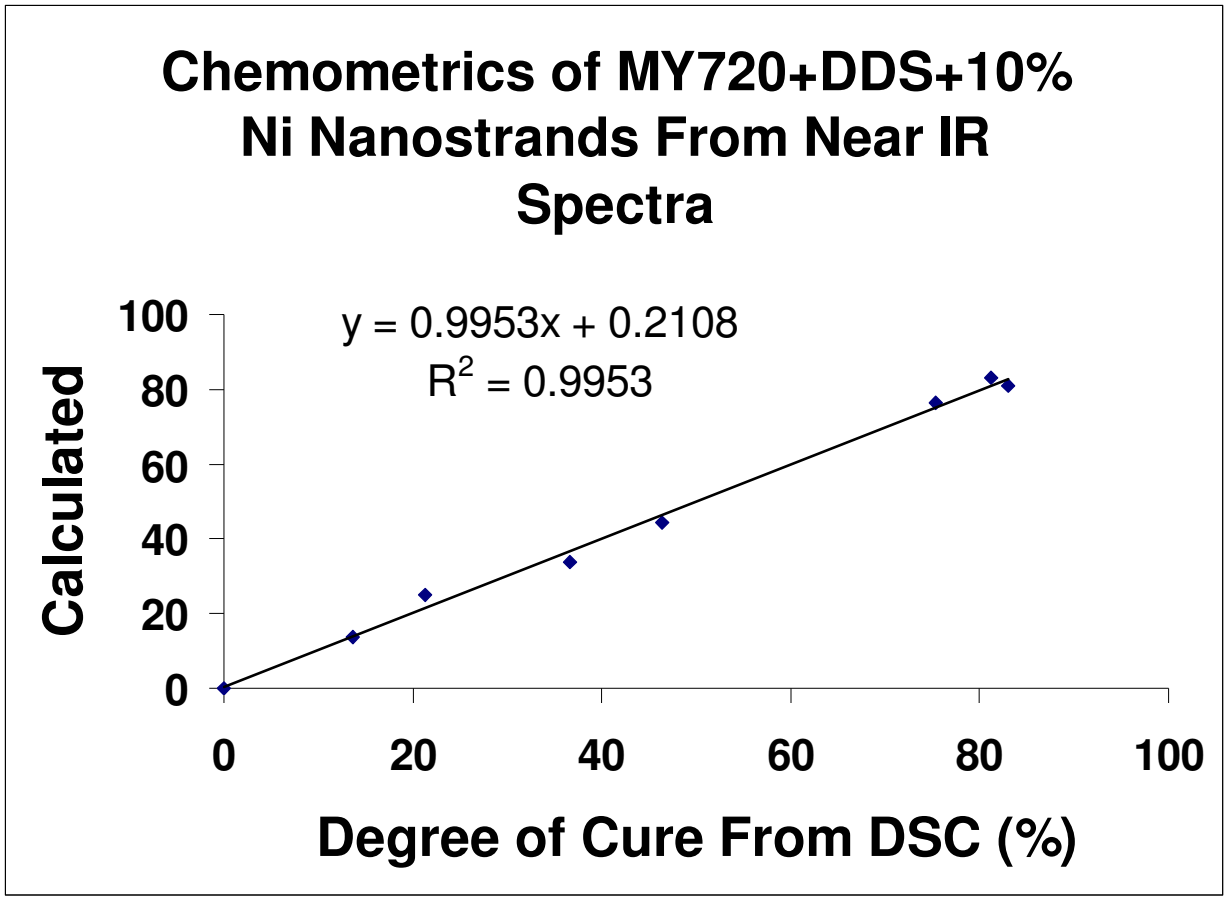
Measurement of cure state of emerging resin systems prior to bonding

Cure was followed using second derivative near IR spectroscopy from 10000 – 4000 cm-1

on silica support



Measurement of cure state of emerging resin systems prior to bonding



Conclusions

The utility of near IR spectroscopy in helping the aviation industry characterize carbon filled epoxy based composites prior to bonding has been previously determined. We have now shown that this technique may be applied to the characterization of other intractable materials such as, for example, polyimide based composites and nanoparticle filled epoxy based composites prior to bonding

A Look Forward

- Benefit to Aviation
- **Ability to incorporate new materials into common usage**
- **Quantitative on site measurement of composite cure prior to bonding**

- Future needs
- **Extension to develop new applications, and complete technology transfer to Spirit AeroSystems**

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