APPLICATIONS OF DIFFUSE REFLECTANCE NEAR-INFRARED SPECTROSCOPY AND CURE KINETICS STUDY BY DIFFERENTIAL SCANNING CALORIMETRY TO SELECTED THERMOSETTING POLYMER-BASED SYSTEMS OF INTEREST IN THE AVIATION INDUSTRY

A Dissertation by

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APPLICATIONS OF DIFFUSE REFLECTANCE NEAR-INFRARED SPECTROSCOPY AND CURE KINETICS STUDY BY DIFFERENTIAL SCANNING CALORIMETRY TO SELECTED THERMOSETTING POLYMER-BASED SYSTEMS OF INTEREST IN THE AVIATION INDUSTRY

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DEDICATION

I dedicate this work to my advisor the late Dr. William T.K. Stevenson, my Mama and Papa, my husband Jason, my family and friends, and to the Lord God Almighty
ACKNOWLEDGEMENTS

I will always be eternally grateful to Dr. Bill Stevenson for all the things he has taught me not only about polymer chemistry but life in general. He was a great mentor and research advisor. He will be sorely missed.

I acknowledge the graduate and undergraduate students of the Stevenson research group for all the assistance they have extended to me in completing this work and for the wonderful company that made this academic journey fun and enjoyable.

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Lastly, I would like to express my gratitude to the US Federal Aviation Administration for funding this research.
ABSTRACT

Diffuse Reflectance Near-Infrared (near-IR) Spectroscopy combined with Partial Least Squares (PLS) regression was used to determine the moisture content and degree of cure in unfilled epoxy resins, carbon-reinforced epoxy resin and epoxy resin adhesives. PLS-generated calibration curves were consistently superior than the calibration curves based on Beer’s law. The same technique was also applied to polyimide-based prepregs to determine the degree of cure through the softening temperature, $T_s$. In both epoxy-based and polyimide-based systems, good correlations were established between the near-IR spectra and the properties of interest. The combination of the rapid, non-destructive technique coupled with a sophisticated chemometric software shows promise as a reliable technique that could be of great benefit to the aviation industry.

Another aspect of this study was the evaluation of an epoxy resin prepreg as a candidate material to be used in repair scenarios in the aviation industry. The prepreg was partially characterized using mid-IR and $^1$H NMR spectroscopies indicating that it contains diglycidyl ether of bisphenol-A (DGEBA) and diamino diphenyl sulfone (DDS) as a curing agent. Ramp and soak experiments using the Differential Scanning Calorimetry (DSC) were performed to study the cure kinetics. A recommended cure cycle was determined to be a combination of a dynamic heating to 150-155 °C at 2 °C/min and an isothermal heating at the end temperature for 20 minutes.
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<td>Cure</td>
<td>The hardening of a polymeric material through the cross-linking of polymer chains. Cure can be promoted by heat, addition of curing agents or irradiation.</td>
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<td>Hot spots</td>
<td>Excessive rise of temperature at local points during polymerization due to inefficient heat dissipation.</td>
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<td>Loss Modulus</td>
<td>In dynamic mechanical analysis (G’), the energy converted to heat during deformation. Also called the viscous modulus.</td>
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<td>Prepreg</td>
<td>Also known as pre-impregnated composite fibers. These composite fibers already contain resin matrix before curing as opposed to hot injection process.</td>
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<td>Runaway Cure</td>
<td>Process by which an exothermic reaction goes out of control. This is common in polymerization because of its high exothermicity and self-accelerating kinetics.</td>
</tr>
<tr>
<td>Storage Modulus</td>
<td>In dynamic mechanical analysis (G’’), the energy stored elastically during deformation. Also called the elastic modulus.</td>
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CHAPTER 1
INTRODUCTION

1.1 Thermosetting Polymers

There are two classes of polymers based on the organization of the chains and their response to temperature. Thermoplastic polymers are linear-chain polymers with little to no branching and have weak intermolecular forces between chains. Once synthesized, they can be softened, reshaped and will flow after the application of heat. Thermosetting polymers, on the other hand, form crosslinks when cured resulting in a three-dimensional network of covalent bonds. After curing, they may become hard and infusible or soft and rubbery. A thermoset will not flow after the application of heat unless the polymer networks are destroyed. Thermosets can swell in a good solvent but will not dissolve.\(^1\)

The irreversible polymer networks in a thermoset resin give rise to a combination of good electrical, mechanical and thermal properties. Thermosets have excellent heat, creep, UV, and chemical resistance.\(^2\)

1.1.1 Epoxy Resin Thermosets

The main structural feature in uncured epoxy resins is the presence of the epoxide group, a three membered ring with oxygen connected to two carbon atoms. The epoxy ring is very reactive due to instability caused by a high degree of ring strain within the structure. The backbones of epoxy resins could be aliphatic, cycloaliphatic or aromatic or a combination of the three. One of the most widely used epoxy resin is diglycidyl ether of
bisphenol-A (DGEBA). It is produced in the reaction between epichlorohydrin and bisphenol-A in the presence of a strong base. The secondary hydroxyl group present in the molecular chain gives this resin excellent adhesion. Figure 1.1 shows the structure of DGEBA.

![Figure 1.1 Structure of diglycidyl ether of bisphenol-A (DGEBA).](image)

All epoxy resins can self-polymerize with the addition of the right catalysts. But the majority of applications make use of coreactants, also called curing agents. (3) The final properties of the cured composite are enormously influenced by the choice of the curing agent. Amines, amides, anhydrides, acids and phenolics could be used as curing agents for epoxy resins. This wide selection of curing agents provides a broad spectrum of possibilities for improving the cured resin’s performance.

Cured epoxy resins have an excellent balance of mechanical, thermal, chemical and electrical properties. Their applications in the aviation industry involve both thermal and room temperature cure. A higher performance epoxy resin can be obtained by using a resin with higher functionality. The degree of crosslinking is then higher than that of the standard difunctional resin and consequently they possess better adhesive characteristics.
Multifunctionality arises as a result of $N$-glycidyl, $O$-glycidyl and $N$- and $O$-glycidyl groups in the resin structure. Figure 1.2 shows some examples of multifunctional epoxy resins.

![Triglycidyl isocyanurate (TGIC)](image1.png)

![N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM)](image2.png)

![Epoxy novalac (EN)](image3.png)

**Figure 1.2** Structures of some multifunctional epoxy resins.
1.1.2 Polyimides

Polyimides are a class of high performance polymers that have exceptional thermal, mechanical and physical properties. They have resistance to temperatures ranging between -270 to 740 °F for extended exposure times and up to 900 °F short-term for high-temperature specialty grades. Polyimides are thermooxidatively and dimensionally stable and retain a high degree of mechanical strength at temperatures beyond the degradation of many polymers and can have the highest resistance to temperature among any other unfilled polymers. These outstanding properties are attributed to the imide group (Figure 1.3) present within the backbone of the polymer.

\[
\text{Figure 1.3 Structure of the imide group}
\]

Several polyimides can be synthesized from a variety of monomers. However the best thermal and oxidative properties have been obtained when R and R’ are aromatic. The combination of the aromatic structure with the imide group results in a polymer with a very high glass transition temperature and a good oxidative stability.

The most common method of obtaining polyimides is a condensation of a tetracarboxylic acid dianhydride with an aromatic diamine (Figure 1.4)
Figure 1.4 General scheme for the formation of a polyimide through condensation.
The reaction produces a polyamic acid intermediate that undergoes ring closure after cyclohydration. Upon conversion to the imide, the polymer becomes insoluble and intractable.

1.2 Principles of Near Infrared Spectroscopy

The near-infrared region spans the interval between 12800 and 4000 cm\(^{-1}\) (780-2500 nm). The absorption bands in this region are the result of overtones and/or combination of bands originating in the mid-IR region of the spectrum. If we assume that these band energies are due to the harmonic molecular vibrations of a diatomic molecule, we can use Hooke’s law to estimate the fundamental frequencies:

\[
\nu = \frac{1}{2} \pi \sqrt{\frac{k}{\mu}}
\]

(Equation 1.1)

where \( \nu \) is the vibrational frequency

\( k \) is the classical force constant

\( \mu \) is the reduced mass of the two atoms

This works fairly well only for true diatomic molecules. Unfortunately, this approximation only gives the average or center frequency of the bond.\(^{(6)}\)

In reality, molecular vibrations are not perfect harmonic oscillators. Their energy levels therefore are not equidistant. This allows for transitions between nonadjacent energy levels and interactions between vibrations.\(^{(7)}\) The concept of an anharmonic oscillator allows for the more realistic calculations of the positions of the allowed
overtone transitions. The relationship between wavenumber and the vibrational energy of the bond is calculated from the Schrödinger equation

$$\tilde{\nu} = \left( \frac{\nu}{\nu + 1} \right) v_1 \nu - v_1 \nu + \nu^2 \right)$$

(Equation 1.2)

where $\nu$ is an integer number, i.e., 0,1,2,3,…, n

$x_1v_1$ is the unique anharmonicity constant for each bond

Equation 1.2 will yield estimates of band positions that are closer to the observed positions compared to those calculated using Equation 1.1. Workman states that the first overtone for a fundamental can be calculated as a 1% to 5% shift due to anharmonicity. Furthermore he illustrated the use of Equation 1.3 to estimate the position wherein the first overtone can be found for a fundamental absorption at about 2632 cm$^{-1}$ (~3800 nm)

$$\lambda = \left[ \frac{A}{\kappa} + \frac{\lambda}{\kappa} (0.01,0.02,...,0.05) \right]$$

(Equation 0.3)

$$\nu = \left[ \frac{3800}{2} + (3800 \times 0.01) \right] = 1938nm \text{ to } \nu = \left[ \frac{3800}{2} + (3800 \times 0.05) \right] = 2090nm$$

The first overtone is expected to occur somewhere between 1938 and 2090 nm (5160 and 4785 cm$^{-1}$) rather than at 1900 nm (5263 cm$^{-1}$) as calculated using a simple harmonic oscillator model.
As stated previously, the near-infrared spectra arise from molecular absorptions of overtone bands (12500 to 5555 cm\(^{-1}\)) and combination (5555 to 4000 cm\(^{-1}\)) bands from fundamental vibrational bands found in the mid-infrared region. Vibrational overtones occur when a molecule is excited from the ground state to a second or higher vibrational state. A transition from the ground state to the second vibrational state is called the first overtone, a transition from the ground state to the third excited state is known as the second overtone, and so on. The intensity of overtone bands decreases as the transition number increases. Combination bands occur when a single photon excites two or more molecular vibrations.

Only combinations and overtones involving higher-frequency fundamentals are strong near-IR absorbers, such as CH, OH, NH, C=O, and COOH.\(^{(9)}\) The overtone and combination bands are about 10-1000 times less intense than the fundamental bands of the mid-IR region. This makes it possible to work with relatively long pathlengths and analyze samples up to several centimeters in thickness.

1.2.1 Diffuse Reflectance and the Integrating Sphere

A major reason for the increased popularity of near-IR spectroscopy is the large number of samples that can be rapidly identified or analyzed with little or no sample preparation. Acquisition of high-quality spectra from non-homogeneous samples can be achieved by the use of diffuse reflectance spectroscopy.

Diffuse reflectance is based on the collection and analysis of light beam that has been reflected and scattered by a sample (Figure 1.5). The back reflected, diffusely scattered
light is then collected by the accessory and directed to the detector optics. Only the part of the beam that is scattered within a sample and returned to the surface is considered to have been subjected to diffuse reflection.\(^{(10)}\)

![Diagram of light reflection from smooth and rough surfaces](image)

**Figure 1.5** Light reflection from (a) smooth surface (specular reflectance) and (b) rough surface (diffuse reflectance)

Lambert was the first to attempt a mathematical description of diffuse reflection.\(^{(11)}\) He proposed that the remitted radiation flux \(I_r\), in an area \(f\) cm\(^2\), and solid angle \(\omega\) steradians (sr), is proportional to the cosine of the angle of incidence \(\alpha\) and the angle of observation \(\vartheta\), i.e.:

\[
\frac{dI_r}{df} = \frac{CS_0}{\pi} \cos \alpha \cos \vartheta = B \cos \vartheta
\]

(Equation 1.4)

where \(S_0\) is the irradiation intensity (W/cm\(^2\)) for normal incidence

- \(C\) is a fraction of the incident radiation flux which is remitted
- \(B\) is the radiation density or surface brightness (W/cm\(^2\) sr)
Equation 1.4 is known as the Lambert cosine law. Since an ideal diffuse reflector does not really exist, therefore deviations always occur from the Lambert cosine law. In general the law holds true only when both the angle of incidence \( \alpha \) and the angle of observation \( \vartheta \) are small.

Most theories that have been developed to describe the diffuse reflectance of radiation evolved from a general radiation transfer equation such as the one shown in Equation 1.5

\[
-\,dl = \kappa \rho \, ds
\]  

(Equation 1.5)

An equation such as this describes the change in intensity, \( dl \), of a beam of radiation of a given wavelength in a sample whose density is \( \rho \) and for which the pathlength is \( ds \). \( \kappa \) corresponds to the attenuation coefficient for the total radiation loss whether that loss is due to scattering or absorption.\(^{(11)}\) Various workers have attempted to derive a simplified solution to the radiation transfer equation. Kubelka and Munk\(^{(6)}\) came up with a two-constant equation that is experimentally testable and is the most widely accepted and used solution. The Kubelka-Munk equation is expressed as follows:

\[
f(R) = \left(1 - \frac{R^2}{2R}ight) = \frac{k}{s} = \frac{Ac}{s}
\]  

(Equation 1.6)

where \( R \) is the absolute reflectance

\( k \) is the molar absorption coefficient

\( s \) is the scattering coefficient
The Kubelka-Munk equation creates a linear relationship for spectral intensity relative to sample concentration. It assumes infinite sample dilution in a non-absorbing matrix, a constant scattering coefficient and an infinitely thick sample layer. Most near-IR software employ Kubelka-Munk conversions for diffuse reflectance spectra.

A major component of diffuse reflectance sampling systems is the integrating sphere. Integrating spheres are have highly reflective and diffuse walls that allows reflected light to enter in and bounce around before approaching the detector. The detector is usually part of the integrating sphere assembly.\(^{(12)}\) The main function of this device is spatially integrating the light that is reflected from a sample or the light flux.

It is desirable that the inner surface of the integrating sphere should evenly scatter the light that falls on its surface (Lambertian scatterer). In this case, the scattered light intensity is proportional to the cosine of the angle of observation. The infrared beam from the interferometer is directed through an entrance port onto the sample placed behind the sample port as illustrated in Figure 1.6. Samples can be directly touching the sphere or separated from the sphere by a thin, infrared transparent window. Large solid angles can be obtained by placing the detector adjacent to the integrating sphere. In order to improve the isotropy (non-directionality) of the detection, the detector is not directly in the line of sight of the sample. A small, also highly reflective and scattering baffle is placed in the sphere such that it blocks the first reflection of the sample from reaching the detector.\(^{(12)}\)

The integrating sphere is preferable when dealing with powders and rough surfaces because the effects of non-homogeneities are at a minimum. This is because the integrating sphere collects light from every angle.
1.2.2 Fiber Optic Probe Spectroscopy

The ability to obtain spectra from remote samples has made near-IR spectroscopy a rapid, nondestructive method that can be used not only in the laboratory but also in the process control, allowing the extraction of information without having to physically remove samples from the processing line. (13)

The principle of light fiber spectroscopy is based on the transfer of light from the spectrometer through a suitable device, the fiber optic cable, to the sample and back to the spectrometer after transmission of or reflection from the sample. Quartz glass shows excellent transmission characteristics for the near-IR region and is used as the basic material for optical fibers. (7) Generally, such a fiber consists of a quartz core, a coaxial...
quartz cladding and a protective polymer coating. The refractive index \( n_1 \) of the core is slightly higher than that of the cladding \( (n_2) \) so that light falling on the open end of the fiber with an angle of incidence \(< \theta_{\text{max}} \) will propagate in the core by total internal reflection at the core-cladding interface. The angle of incidence will then be \(< \alpha_{\text{min}} \), the critical angle of total internal reflection, and part of the light will be refracted into the cladding with a resulting loss of radiation. The attenuation \( A \) (db/km) is calculated from the intensity loss of a sample \( (I) \) versus a reference \( (I_0) \) when radiation propagates through a fiber of definite length \( L \) (in km).

\[
A = \frac{10}{L} \log \frac{I_0}{I}
\]

(Equation 1.7)

\textbf{Figure 1.7} (a) Principal scheme of a light fiber (b) propagation of radiation in a step-index fiber (c) refractive index profile in a step-index fiber. (Image from Siesler, H. (1991). Makromol. Chem., Macromol. Symp., 52, 113-129)
1.2.3 Chemometrics

Chemometrics is the application of mathematical or statistical methods to chemical data. The International Chemometrics Society (ICS) offers the following definition: “Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods.”

Chemometric research spans a wide area of different methods which can be applied in chemistry. There are techniques for collecting good data such as optimization of experimental parameters, design of experiments, calibration, signal processing and for getting information from these data such as statistics, pattern recognition, modeling, structure-property-relationship estimations. Chemometrics tries to build a bridge between the methods and their application in chemistry.

In spectroscopy, the application of chemometrics is most often in calibration. Calibration is achieved by using the spectra as multivariate descriptors to predict concentrations of constituents of interest using statistical approaches such as Multiple Linear Regression (MLR), Principal Component Analysis (PCA) and Partial Least Squares (PLS). The latter is most widely used by spectrometrists for quantitative analysis. The advantages of PLS include ability to model multiple dependent as well as multiple independent variables. It can handle multicollinearity in independent variables and is robust despite data noise and missing data. It creates independent latents directly on the basis of cross products involving response variables making for stronger predictions and allowing for reflective and formative latents.
1.3 Overview of this Study

This study is divided into four chapters, each one addressing issues involving thermosetting polymers employed in the aviation industry. The first chapter focuses on the use of Diffuse Reflectance Near-IR Spectroscopy to determine the moisture content in different commercial epoxy polymer based systems. The second chapter covers application of the same spectroscopic technique in the monitoring of the degree of cure of some epoxy resin prepregs and adhesives. The third chapter discusses the partial characterization and study of the cure kinetics of a carbon-fiber reinforced high performance epoxy resin used in the repair of epoxy-based composites in the aviation industry. The fourth chapter centers on the usage of Diffuse Reflectance Near-IR Spectroscopy in monitoring the degree of cure of polyimide based systems.
2.1 Introduction

Epoxy resins are widely used as matrices for structural composite materials, adhesives, and organic coatings due to their good mechanical properties. Multifunctional epoxy resins such as tetracyclidyl-4,4'-diamino diphenylmethane (TGDDM) are commonly used in the production of high performance fiber composites in the aviation industry. These thermosetting resins have high glass transition temperatures (T<sub>g</sub>), high tensile strength and modulus, and excellent chemical and thermal resistance.\(^{(16)}(17)\)

However, it is well known that absorption of moisture can heavily affect properties, such as plasticization,\(^{(18)}(19)\) lowering of glass transition temperature,\(^{(18)}(19)(20)\) and reduction of mechanical strength\(^{(20)}(21)\). In most applications, epoxy-based components have the potential of being exposed to humid environments or moist conditions. For example, a cured TGDDM/DDS resin system is found to absorb between 4.0 and 6.5 wt. % of water at equilibrium, reducing T<sub>g</sub> by as much as 20°C for every 1% of absorbed moisture.\(^{(20)}(22)(23)\) When water is absorbed at elevated temperatures and for prolonged periods of time hydrolysis leading to permanent damage of the structural network may develop, which can give rise to the formation of microcracks and lead to catastrophic failures.\(^{(16)}(24)\)
Common methods for determining moisture content in polymeric materials include Karl-Fischer titration, thermogravimetric analysis (TGA) and the loss-on-drying (LOD) method. These methods are all destructive and time-consuming and cannot be applied to on-site analyses.

Mid-IR spectroscopy has been employed to study water in polymer films. Techniques used in this region are attenuated total reflectance, specular reflectance, and transmission. By analyzing changes in the absorbance of the peak at 3550 cm\(^{-1}\) (OH group stretching), the diffusion of water in polymer films has been effectively studied. However, these techniques are only applicable to very thin films. The sample thickness cannot exceed 50 µm in order to remain within the absorbance range in which the Beer-Lambert law is valid.

The overtone and combination bands arising in the near-IR region are about one order of magnitude less intense than the corresponding fundamentals occurring in the mid-IR range. This makes it possible to use thicker samples, up to several millimeters thick, without losing the linearity in the absorbance. With the introduction of diffuse reflectance and chemometrics, near-IR spectroscopy has become a method that is both rapid and nondestructive with little to no sample preparation. With the use of light-fiber optics technology, determinations can be made without physically removing samples from the processing line.

An isolated water molecule has three modes of vibration: the symmetric stretch (\(v_1\)), the bend (\(v_2\)), and the antisymmetric stretch (\(v_3\)). These vibrations produce strong absorptions in the mid-IR region of the spectrum and appear at 3450-3700 cm\(^{-1}\), 1595-
1650 cm$^{-1}$, and 3550-3750 cm$^{-1}$, respectively. Bands observed in the near-infrared region arise from the $2\nu_1$ overtone which gives a peak at 6900 cm$^{-1}$ and the combination of $\nu_2$ and $\nu_3$ which shows up at 5160 cm$^{-1}$. Musto and coworkers$^{(27)}$ studied the diffusion of water in a tetrafunctional epoxy resin using near-infrared spectroscopy. The peak at 6900 cm$^{-1}$ was difficult to detect due to its superimposition on the much stronger $\nu_{\text{OH}}$ overtone due to the hydroxyl groups in the cured epoxy resin. The peak at 5160 cm$^{-1}$ was found to be more suitable for determination of the water content because it is well resolved, has sufficient intensity and more importantly, is free from interference by the epoxy resin matrix.

In the present study, partial least-squares (PLS) calibration models based on diffuse reflectance NIR spectra were produced in order to predict the moisture content in a variety of epoxy-based systems.

2.2 Experimental Section

2.2.1 Materials

Resin components were obtained as research samples (Epon 825), or purchased from Huntsman Materials Co. (MY720), or otherwise purchased from the Aldrich Chemical Co. Solvents, including deuterated solvents, were purchased from the Aldrich Chemical Co. and were used as received.
2.2.2 Sample Preparation

Sheets of epoxy resin for water uptake experiments were cured between steel plates coated with mold release agent and using 1/8\textsuperscript{th} inch or 1/16\textsuperscript{th} inch spacers, then cut to size.

(a) A “mid performance” epoxy resin was prepared by melting the curing agent (a 1:1 mole ratio mixture of metaphenylenediamine [mPDA] and paraphenylenediamine [pPDA]) into diglycidyl ether of bisphenol A epoxy resin (Epon 825) in a stoichiometrically balanced ratio. The mixture was degassed by vacuum suction, poured into the mold, and cured for 2 hours at 120°C then for 2 hours at 180°C.

(b) A “high performance” epoxy resin was prepared by dissolving the diaminodiphenylsulfone (DDS) curative into acetone then stirring the solution into TGDDM (MY720) epoxy resin at a ratio of 1.1 : 1 (active NH : epoxy functionality). The mixture was vacuum pumped at 120°C to remove acetone then poured into a mold and cured for 2 hours at 140°C followed by 2 hours at 200°C.

Small (2”X2”) plaques of carbon fiber reinforced composite for water uptake studies were prepared from (a) BMS8-297 prepreg containing generic 934 resin mix with woven T300 carbon fibers (b) T700/2510 plain weave carbon/epoxy prepreg , using a double vacuum bag layup procedure on a flat steel tool as shown in Figure 2.1. Vacuum was maintained throughout cure in a forced air oven for 2 hours at 120°C followed by 2 hours at 200°C.
Figure 2.1. Diagram of vacuum bagging set-up used to prepare small plaques prepreg for water-uptake experiments

2.2.3 Instrumentation

Early measurements were made using an integrating sphere diffuse reflectance module custom built for the Thermo Electron Nexus spectrometer with an InGaAs detector. Spectra were collected using OMNIC™ software. The spectra were obtained at 60 scans with a resolution of 8 cm$^{-1}$. Calibration curves were made using Beer’s Law.

Later measurements were recorded using a Thermo Scientific Antaris II FTNIR spectrometer (10000–4000cm$^{-1}$) using an InGaAs detector. Spectra were collected using OMNIC™ software. Spectra were accumulated from 16 scans collected at a resolution of 8 cm$^{-1}$. Spectra of each sample were collected in triplicate. TQ Analyst™ software package was used to build calibration curves using partial least squares regression method.
2.2.4 Water Uptake Experiments

Water was placed into glass jars with Teflon seals. Samples were then suspended in polypropylene funnels which had several small holes drilled into it and then placed in the glass jars. The water levels were adjusted so they are not directly in contact with the samples on the funnel. Figure 2.2 is a sketch of the sample set-up. The sealed jars were then placed in a forced air oven at 70°C (~160°F). Samples were weighed periodically and the moisture gain was determined gravimetrically using the equation

\[
\% \text{ water content} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100
\]

(Equation 2.1)

Diffuse reflectance spectra were also obtained after the samples were weighed.

Figure 2.2. Water uptake experiment set-up
2.2.5 Water Desorption Experiments

Wet samples were dried in a forced air oven at 40°C and weighed periodically. The percent water content was calculated using Equation 2.1. Diffuse reflectance spectra were recorded after every weighing.

2.2.6 Treatment of Data

Calibration curves based on Beer’s Law were built by taking the ratio of water peak area at 5160 cm\(^{-1}\) normalized to an invariant peak and then plotting it against the percent water content as measured gravimetrically.

New calibration curves were generated using the TQ Analyst™ software specifically by use of the Partial Least Squares (PLS) method. Numerous studies have employed PLS as a preferred calibration model.\(^{(9)(29)(30)(31)}\) The software solves the problem of complex samples, variable baselines and overlapping peaks by allowing us to work with second-derivative spectra and to use Savitsky-Golay smoothing filters. The PLS calibration technique examines specified region(s) of the spectra to determine which areas are varying statistically as a function of component concentration or in our case, percent moisture content.

2.3 Results and Discussions

Near Infrared spectroscopic measurements were performed using the diffuse reflectance technique. Recent advances in hardware and software have made this
technique easier to apply to opaque materials such as prepreg and heavily filled materials. Early measurements were made using an integrating sphere diffuse reflectance module custom built for the Thermo Electron Nexus spectrometer (Figure 2.3, top left). Sample preparation is negligible and good quality spectra can be obtained using 60 scans. The sample, for example, a composite plaque, is simply placed on the top platen for analysis (Figure 2.3, top right). Spectra are ratioed to a spectrum of gold film. Later measurements were made using a dedicated near IR spectrometer – the Thermo Electron Antaris II spectrometer illustrated in Figure 2.3 (bottom). The spectrometer contains a transmission module, an integrating sphere module and a remote triggered reflectance module.

Some of the strengths and limitations of near IR spectroscopy, with reference to materials of interest to the aviation industry, are illustrated in Figure 2.4. Transmission near IR spectroscopy is routinely applied to the analysis of unfilled plastics. For example, the non baseline corrected transmission near IR spectrum of Lomod™, a thermoplastic elastomer, in Figure 2.4 (a) shows rich detail. In contrast, the carbon fibers in an uncured single sheet of prepreg efficiently absorb all the energy from the near IR beam to produce a transmission spectrum devoid of information as shown in Figure 2.4 (b). The baseline corrected diffuse reflectance near IR spectrum of Lomod™ elastomer in Figure 2.4 (c) contains all the information present in the transmission spectrum. The baseline corrected diffuse reflectance spectrum of the uncured sheet of prepreg in Figure 2.4 (d) shows the peak due to water at 5160 cm\(^{-1}\).
ANTARIS II
A. Transmission Module
B. Integrating Sphere Reflectance Module
C. Remote-triggered Diffuse Reflectance Module

**Figure 2.3** (Top left) Nexus spectrometer with diffuse reflectance near IR module in sample compartment. The module contains the integrating sphere collection optics and IR detector (Top right) Composite plaque placed on top of module for spectrum acquisition. (Bottom) Antaris II near IR spectrometer, showing (a) transmission module (b) integrating sphere module and (c) remote diffuse reflectance module
Figure 2.4 All x – wavenumbers (cm\(^{-1}\)) All y – absorbance. (a) transmission near IR spectrum of Lomod elastomer (3.01mm thick), (b) transmission near IR spectrum of uncured 934/T300 (c) baseline corrected diffuse reflectance near IR spectrum of Lomod elastomer, (d) diffuse reflectance near IR spectrum of uncured 934/T300
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.

Figure 2.5. (Top) Diffuse reflectance and baseline corrected diffuse reflectance spectra of wet 934/T300 prepreg. (Bottom) diffuse reflectance and second derivative spectrum of 934-T300 prepreg.

Differences in the interpretation of transmission and diffuse reflectance near IR spectra are further illustrated in Figure 2.5. The diffuse reflectance near IR spectrum of carbon-filled prepreg (in this instance 934/T300 prepreg) is reproduced in Figure 2.5 (a). Note the pronounced baseline drift. The baseline corrected spectrum is reproduced in the same plot. The noise level in the baseline corrected spectrum below 7000 cm\(^{-1}\) is acceptable. Baseline correction is an accepted method of spectrum manipulation but can...
change band shape. A less intrusive method of removing baseline slope is to transform the absorption spectrum into the second derivative spectrum, as illustrated for T300/934 prepreg in Figure 2.5 (b).

**Figure 2.6** Baseline corrected diffuse reflectance spectra of MY720-DDS resin versus plaque thickness.

**Second derivative spectra of curing T800/3900 prepreg**
beam undergoes multiple reflections between the two faces of thinner samples, leading to higher apparent absorbances. However, this does not explain why the phenomenon becomes negligible above about 5000 cm\(^{-1}\). Of course, internal reflection is a function of wavelength. If this effect is due to multiple reflections of the beam in the film, it is unlikely that it will interfere with measurements performed on prepregs or cured composites. We have shown that carbon fibers absorb all incident near IR frequencies so the spectrum will be generated by energy backscattered from a single pass through the surface resin to the fibers.

2.3.1 Diffuse Reflectance Near-IR Measurement of Water in Unfilled Epoxy Resins

As a preliminary to the examination of prepreg and composite test pieces, water uptake in unfilled epoxy resin was measured. Two systems were selected for examination, a “medium performance” epoxy resin based on the diglycidyl ether of bisphenol A, and a “high performance” epoxy resin based on the use of N-(4-((4-(di(oxiran-2-yl)methyl)cyclohexa-1,4-dienyl)methyl)cyclohexa-1,4-dienyl)-N-(oxiran-2-yl)oxiran-2-amine, commonly referred to as MY720 resin.

The preparation of plaques of these resin systems are detailed in the Experimental section. Near IR spectra were obtained by averaging 60 scans with the integrating sphere attachment on the Nexus spectrometer. Structures in the mid performance epoxy resin are sketched in Figure 2.7. The epoxy resin used was Epon 825 where \(n \sim 0\). The baseline corrected near IR spectrum of “dry” and “wet” resin are reproduced in Figure 2.7. The
5160 cm\(^{-1}\) band, associated with the presence of water in the composite, is denoted by an arrow in the figure and is clearly visible.

**Mid performance engineering epoxy resin**
- (top) diglycidyl ether of bisphenol A (DGEBA)
- (left) meta phenylene diamine (mPDA)
- (right) para phenylene diamine (pPDA)

**Figure 2.7.** (Top) Medium performance engineering epoxy resin constituents. (Bottom) Near IR spectrum of the resin before and after exposure to water. The arrow denotes the absorption band at 5160 cm\(^{-1}\) attributed to water in the resin.
Beer’s law calibration curves were constructed for water absorption. In these calibration plots, the area under the 5160 cm\(^{-1}\) band is ratioed to the area of an absorbance that does not change with water content. Using this method, a good correlation could be obtained between gravimetrically determined water content during absorption (Figure 2.8 - top) and desorption (Figure 2.8 – bottom) cycles. Disadvantages of this method include the need to baseline correct spectra and the possibility that the invariant peak (Table 2.1) may not be entirely unaffected by water content in the resin. In an attempt to produce a better calibration curve, regions of second derivative spectra centered on the 5160 cm\(^{-1}\) band were subjected to partial least squares regression analysis and correlated with water content using the TQ Analyst™ software by Thermo-Fisher Scientific. The results of this analysis are reproduced as “goodness of fit” (actual vs. calculated water content) curves for water uptake (Figure 2.9 – top) and water desorption (Figure 2.9 – bottom). The chemometrics-generated calibration curves are easier to use than the Beer plots. The software scans a region of the second derivative spectrum of the unknown centered on 5160 cm\(^{-1}\), which then calculates the water content from the calibration curve. Due to the lack of spectral manipulation (baseline correction, peak ratioing), and high correlation coefficients (both above 0.99) the calibration curves generated using PLS are a more accurate predictor of water content in the resin.
Figure 2.8. Beer’s law calibration curve of normalized absorbance at 5160 cm$^{-1}$ versus water content in the resin during water uptake (Top) and desorption (Bottom) of mid-performance epoxy resin.
Figure 2.9 PLS generated calibration curve for water absorption (Top) and desorption (Bottom) of a mid-performance epoxy resin
The correlation coefficient for the Chemometrics analysis of water absorption in the mid performance epoxy resin (0.9941) is better than the correlation coefficient for water desorption (0.9889). This trend is echoed in plots for water added and desorbed from high performance resin and amplified in experiments using epoxy based composite.

Table 2.1. Invariant bands in the near IR diffuse reflectance spectrum used to ratio the water absorbance at 5160 cm\(^{-1}\) in Beer’s law calibration plots

<table>
<thead>
<tr>
<th>Material</th>
<th>Invariant band used for water uptake measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled resin containing DGEBA with mPDA and pPDA</td>
<td>6984 cm(^{-1})</td>
</tr>
<tr>
<td>Unfilled resin containing MY720 and DDS</td>
<td>6679 cm(^{-1})</td>
</tr>
<tr>
<td>T300/934 composite</td>
<td>4880 cm(^{-1})</td>
</tr>
<tr>
<td>T800/3900 composite</td>
<td>5995 cm(^{-1})</td>
</tr>
</tbody>
</table>

Structures in the high performance epoxy resin are sketched in Figure 2.10 (top). The epoxy resin used was MY720 with DDS curative. The baseline corrected near IR spectra of “dry” and “wet” cured resin are reproduced in Figure 2.10 (bottom). The 5160 cm\(^{-1}\) band, associated with the presence of water in the composite, is indicated by an arrow in the figure and is clearly visible.
Figure 2.10 (Top) High performance engineering epoxy resin constituents. (Bottom) Near IR spectrum of the resin before and after exposure to water. The arrow denotes the absorption band at 5160 cm\(^{-1}\) attributed to water in the resin.
Beer’s law calibration plots for water absorption and desorption are reproduced in Figure 2.11 (top and bottom) respectively. Both the magnitude of water uptake, and scatter in the plots, are greater than in corresponding plots for the “medium performance” epoxy resin, a consequence of a higher free volume content in the high performance epoxy resin than in the “mid performance” resin.

Corresponding chemometrics calibration plots for the absorption and desorption of water from the “high performance” epoxy resin are detailed in Figure 2.12. As expected, the correlation coefficient generated from the calibration curve for water absorption (0.9919) is higher than the corresponding correlation coefficient for water desorption in the resin (0.9882). In both instances, the Chemometrics analysis is superior to the Beer’s law plot analysis for this material.
Figure 2.11. Beer’s law calibration curve of normalized absorbance at 5160 cm\(^{-1}\) versus water content in the resin during water uptake (top) and desorption (bottom) of high performance epoxy resin
Figure 2.12 PLS generated calibration curve for water absorption (top) and desorption (bottom) of a high performance epoxy resin

R² = 0.991

R² = 0.988
2.3.2 Diffuse Reflectance Near-IR Measurement of Water in Epoxy Resin Based Prepreg and Composite

Composite plaques of cured T300/934 prepreg for water uptake and desorption were made by using the generic vacuum bagging setup illustrated in Figure 2.1. Plaques of T300/934 prepreg were vacuum bagged and cured in a forced air oven under vacuum.

The near IR spectra generated by these composite plaques are illustrated in Figure 2.13. The near IR diffuse reflectance spectrum of the “tool” face of dry T300/934 composite is reproduced in Figure 2.13 (Left). The near IR diffuse reflectance spectrum of the “bag” face of dry T300/934 composite is reproduced in Figure 2.13 (Right). The water absorbance at 5160 cm$^{-1}$ is noted with arrows. Clearly, the “bag” face spectrum contains more detail than the tool face spectrum. An SEM of a cross section through a plaque of T300/934 composite is reproduced in Figure 2.14 (bottom left). The picture was taken without prior carbon or gold coating so that resin rich nonconductive regions would be overexposed. From the SEM, it is clear that the bag face is richer in resin than the tool face, leading to a better quality near IR spectrum.
Figure 2.13. (Left) Near IR spectrum of 934/T300 cured woven composite tool (smooth) face, (Right) Near IR spectrum of 934/T300 cured woven composite bag (rough) face. 

Figure 2.14. SEM of cross section of uncoated 934/T300 cured woven composite bag face down with resin rich regions overexposed due to charging.
Some results of water absorption and desorption from cured T300/934 composite plaques are reproduced in Figure 2.15. A “dry” and a “wet” spectrum of cured T300/934 prepreg are shown with the water absorption indicated by the arrow.

**Figure 2.15.** Near IR spectrum of 934/T300 prepreg before and after exposure to moisture with 5160 cm⁻¹ peak indicated by the arrow.
A calibration curve based on Beer’s law for water absorption is reproduced in Figure 2.16 (top). A Chemometrics “goodness of fit” calibration curve generated from PLS regression for water absorption is reproduced in Figure 2.16 (bottom). Both the Beer’s law and Chemometrics calibration curves yield acceptable results for water absorption, with the Chemometrics calibration curve superior to the Beer’s law calibration curve. A Bee’s law calibration curve for water desorption from T300/934 composite, as reproduced in Figure 2.17, shows an unacceptably high scatter. However, some insight into the process can be generated if the thickness of the composite is considered a variable. A calibration curve based on Beer’s law is reproduced in Figure 2.18 (top) summarizing the results of four separate desorption experiments performed using 5 layer composites. Scatter is much reduced. Beer’s law type plot summarizing desorption experiments on seven and eleven layer composites are shown in Figure 2.18 (bottom). Scatter has not improved. Corresponding Chemometrics “goodness of fit” calibration curves generated from PLS regression analysis for 5 layer composites and 7/11 layer composites as shown in Figure 2.19.(top and bottom respectively), show a good (R > 0.98) correlation between the two sets of variables (the near IR spectrum and water content), during water desorption. Clearly, diffuse reflectance spectroscopy can be applied to these analyses if prior calibration experiments have been performed using composite test pieces of similar thickness
Figure 2.16. (Top) Beer’s law calibration curve of normalized absorbance at 5160 cm\(^{-1}\) versus water content in the resin during water uptake of 934/T300 prepreg. (Bottom) PLS generated calibration curve for water uptake of 934/T300
Figure 2.17. Beer’s law calibration curve of normalized desorption at 5160 cm\(^{-1}\) versus water content in the resin during water loss of 934/T300 prepreg.
Figure 2.18. Beer’s law calibration curve of normalized absorbance at 5160 cm\(^{-1}\) versus water content in the resin during water uptake (top) and desorption (bottom) of 5 layers 934/T300 prepreg.
Figure 2.19. PLS generated calibration curve for desorption of water of 5 layers 934/T300 prepreg (top) and 7/11 layers 934/T300 prepreg (bottom)
2.4 Conclusion

It has been determined that good quality diffuse reflectance near IR spectra can be obtained from cured epoxy resin and prepreg based on epoxy resin.

It has also been determined that second derivative diffuse reflectance near IR spectra of cured epoxy resin, and epoxy resin based carbon fiber reinforced composite, can be subjected to partial least squares analyses using a commercial Chemometrics software package, and that good quality calibration curves can be obtained that relate spectra to water content in the resin or prepreg.

Based on prior observations, it would appear that diffuse reflectance near IR spectroscopy, coupled to Chemometric analysis software, offers a useful alternative to more traditional methods employed by the aviation industry, for the analysis of the water content in epoxy resin based prepreg, composite, and adhesive. Moreover, near IR spectrometers are rugged and can be modified by the supplier to be usable under almost any set of conditions that would be encountered in original equipment manufacturing, facility shop floor, or aftermarket repair workshop.
CHAPTER 3

DETERMINATION OF CURE STATE OF EPOXY-BASED SYSTEMS BY NEAR-INFRARED SPECTROSCOPY

3.1 Introduction

In the past few decades, epoxy resins have found extensive use in many industrial applications, including high strength composite materials, adhesives, coatings and lacquers, and printed circuit boards. In most of these applications, the desired product properties are obtained following the formation of a highly cross-linked polymer network as a consequence of reactions between the epoxide and curing agent. Epoxy resins contain two or more epoxide rings per molecule. The epoxy groups react with curing agents in a ring-opening reaction to yield high-performance thermosetting plastics as shown in Figure 3.1. The curing process of the epoxy resin affects the chemical structure of the network and hence, its physicomechanical properties. When properly formulated and cured, they have excellent resistance to moisture and organic solvents, stable electrical characteristics under various environmental conditions, and an excellent adhesion to most materials. When reacted with curing agents, epoxies have very low shrinkage because no by-products are given off in their curing reaction. Determination of the state of cure advancement provides information on the nature and characteristics of polymerized materials. Several techniques have been used to follow the extent of epoxy resin cure: dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), high performance liquid chromatography (HPLC), size-exclusion chromatography, argentimetric titration, dielectric spectroscopy,
Raman spectroscopy\textsuperscript{(39)} and Fourier transform infrared spectroscopy (FTIR)\textsuperscript{(37,38,39,40)} (41,42,43).

\textbf{Figure 3.1.} General scheme for the epoxy-amine cure reaction

\begin{center}
\includegraphics[width=\textwidth]{reaction_scheme.png}
\end{center}
FTIR is by far the most utilized characterization method. This technique is not affected by the transition state and enables one to monitor the cure reaction throughout the epoxide conversion.\textsuperscript{(43)}

The functional groups involved in epoxy resin cure reactions all have strong characteristic absorptions in the mid-IR region. However the mid-IR spectra of epoxy resins and amine curing agents are very complex and have tendency for overlappings. Well-isolated primary amine, secondary amine, and hydroxyl group absorption bands are often not observed which leads to complications in obtaining quantitative analysis via infrared spectroscopy.\textsuperscript{(44)} Fortunately, the functional groups of interest in epoxy resin cure reactions have well isolated absorption bands in the near-infrared region of the spectrum. In epoxy resin systems, only CH, NH, and OH vibrations are active. As a consequence, near-IR absorption spectra are less complex than their counterparts in the mid-IR region.

The formation of products and disappearance of reactants were used to study several epoxy-amine crosslinking reactions using near-IR spectroscopy\textsuperscript{(45) (46) (47)} As curing takes places, functional groups such as the epoxy reactant at 4530 cm\textsuperscript{-1} and the NH of the primary amine crosslinking agent at approximately 6667 and 5000 cm\textsuperscript{-1} disappear. The appearance of certain functional groups were also observed as curing occurs such as the formation of the NH of a secondary amine band at 6667 cm\textsuperscript{-1} and the O-H as the oxirane ring is opened at around 7140 cm\textsuperscript{-1}. The secondary amine NH peak at 6667 cm\textsuperscript{-1} will eventually disappear as the tertiary amine is formed.\textsuperscript{(48)} The peak at 4530 cm\textsuperscript{-1} has successfully quantified epoxy resin cure reactions in previous literature.\textsuperscript{(43) (44)} This is a
well isolated intense absorption band due to terminal epoxide groups and indicates the concentration of epoxy reactants. \(^{(44)}\)

The integrity of a composite “patch” on a composite part is a strong function of how well the patch has been cured onto the part. If the degree of cure is too low, a repair will be deficient in mechanical properties. The same may be applied to the original manufacture of the part. Currently, a sample must be removed for DSC or other analysis, if the cure state is to be ascertained.

The utility of diffuse reflectance near IR spectroscopy as a tool for the on-site measurement of epoxy cure state will be evaluated for neat epoxy resin, epoxy based prepreg and composite, and heavily filled epoxy based adhesive.

### 3.2 Experimental Section

#### 3.2.1 Materials

All prepregs and adhesives were obtained as research samples from the National Institute for Aviation Research (NIAR) at Wichita State University.

#### 3.2.2 Sample Preparation

Plaques of BMS8-276 prepreg tape containing T800 carbon fibers and 3900 resin for resin cure studies were cured using standard vacuum bagging techniques.

Plaques of BMS8-297 woven prepreg containing generic 934 resin and T300 carbon fibers were sandwiched between release film then cured between aluminum blocks.

Sheets of Fiberite FM377U aluminum filled adhesive and Surface Master 905 are protected with a layer of treated paper on one side and a layer of polymer on the other.
The paper was removed and two sheets of adhesive were pressed together. The adhesive was then sandwiched between release film then placed between aluminum blocks prior to cure. The release film was removed. The polymer layers were retained and used to protect material during handling, then removed immediately prior to the experiment.

All materials were cured to an intermediate state in a forced air oven. The extent of cure in both instances was measured by DSC and correlated with the near IR spectrum of the prepreg or adhesive, obtained after removal of the protective polymer film and/or the release film where appropriate, as discussed subsequently in the text.

3.2.3 Instrumentation

Early measurements were made using an integrating sphere diffuse reflectance module custom built for the Thermo Electron Nexus spectrometer with an InGaAs detector. Spectra were collected using OMNIC™ software. Spectra were obtained from 60 scans with a resolution of 8 cm\(^{-1}\). Calibration curves were made using Beer’s Law.

Later measurements were recorded using a Thermo Scientific Antaris II FTNIR spectrometer (10000-4000cm\(^{-1}\)) using an InGaAs detector. Spectra were collected using OMNIC™ software. Spectra were accumulated from 16 scans collected at a resolution of 8 cm\(^{-1}\). Spectra of each sample were collected in triplicate. TQ Analyst™ software package was used to build calibration curves using partial least squares regression method.

The cure state of partly cured resin, adhesive, or prepreg was determined using a Perkin Elmer DSC6 or a ThermoElectron 2000Q DSC. The heat of complete reaction (dQ\(_o\) J/g) of uncured material was determined by programmed heating in the DSC. The
exotherm from partly cured material (dQ_p J/g) was determined in the same way. The %
cure was determined as [dQ_p*100]/dQ_o.

3.3 Results and Discussions

3.3.1. Diffuse Reflectance Near-IR Measurement of Cure in Epoxy Resin Based
Prepreg Systems

prepreg (b) stacked spectrum for curing prepreg (c) 934/T300 prepreg % cure by DSC
versus (Beer’s law) normalized peak area at 4530 cm^{-1} (d) PLS generated calibration
curve for prepreg cure. The 4350 cm^{-1} peak is indicated by the arrow.
The near IR spectrum of uncured 934/T300 prepreg is reproduced in Figure 3.2 (a). The epoxy band at 4530 cm\(^{-1}\) is clearly visible. The loss of epoxy absorbance with cure is illustrated in Figure 3.2 (b). A Beer’s law plot of cure state (% cure by DSC) versus normalized band intensity is reproduced in Figure 3.2 (c) while the results of a partial least squares Chemometrics “goodness of fit” plot of the second derivative of the epoxy absorbance versus cure state is reproduced in Figure 3.2 (d) with R > 0.98. Clearly, diffuse reflectance near IR spectroscopy is able to follow the cure of 934/T300 prepreg.

Prepreg based on 3900 epoxy resin and T800 carbon fibers has met with considerable commercial success. The prepreg is slow curing and catalyst free. After cure, it attains good fatigue and crack resistance coupled to a high modulus and T\(_g\). A partial compositional breakdown of the prepreg was made using spectroscopic techniques of analysis.\(^{(49)}\) With reference to Figure 3.3 (a), the prepreg was shown to contain DDS curative, MY720 resin, and DGEBA monomer. The resin is assumed to also contain a toughening agent that has so far resisted identification.
The diminution of the epoxy absorbance band at 4350 cm\(^{-1}\) with cure is illustrated in Figure 3.3 (b). The Beer’s law calibration plot for the cure reaction (Figure 3.3c) is constructed by plotting the normalized epoxy peak area versus the extent of cure by DSC. Clearly, either the “invariant” band against which the epoxy peak is normalized is not truly invariant, or the spectrum is complicated by overlapping absorbances.
The Chemometrics “goodness of fit” calibration curve (Figure 3.3d) gives a better fit to the data, with R > 0.98. Clearly, diffuse reflectance near IR analysis coupled to chemometric data processing is sufficient to calibrate for cure of T800/3900 prepreg.

3.3.2 Diffuse Reflectance Near-IR Measurement of Cure in Epoxy Resin Based High Performance Adhesives

Fiberite FM377U adhesive is a highly filled aluminum containing adhesive that does not lend itself to analysis by transmission near IR spectroscopy without time-consuming sample preparation. The near IR spectrum of uncured FM377U adhesive is reproduced in Figure 3.4 (a). Changes in the spectrum with cure are illustrated in Figure 3.4 (b). The Beer’s law plot in Figure 3.4 (c) relating spectrum to cure reveals less spectral interference than the corresponding plot for T800/3900 prepreg. The Chemometrics “goodness of fit” calibration curve for Fiberite FM377U adhesive, reproduced in Figure 3.4 (d), reveals a good correlation (R > 0.98) between the two variables of near IR diffuse reflectance spectrum and cure state.
Figure 3.4. Fiberite FM377U aluminum filled adhesive cure. (a) Near IR spectrum of uncured FM377U adhesive. (b) Stacked spectrum for curing adhesive (c) FM377U adhesive % cure by DSC versus (Beers law) normalized peak area at 4530 cm\(^{-1}\) (d) PLS generated calibration curve for adhesive cure. The 4350 cm\(^{-1}\) peak is indicated by the arrow.

Surface Master 905 is a high performance adhesive that is often used as a “face adhesive”. The adhesive is cured onto the surface of composite and sanded down prior to application of paint. Clearly, the proper cure of a “face adhesive” is essential if the sanding and subsequent painting processes are to proceed without complication. A “face adhesive” is also uniquely exposed on the surface of the composite, and, therefore, suited to this type of spectroscopic analysis. The near IR spectrum of Surface Master 905 “face adhesive” is reproduced in Figure 3.5 (a). Changes in the spectrum with cure are
illustrated in Figure 3.5 (b). Chemometrics calibration plots for the cure reaction are reproduced for spectra obtained using the integrating sphere attachment on the Nexus spectrometer (Figure 3.5c), and obtained using the remote triggered fiber optic reflection probe on the Antares II spectrometer (Figure 3.5d). Both calibration curves are illustrated. The surface cure calibration curve (R² = 0.9877) is reproduced for spectra obtained using the integrating sphere attachment on the Nexus spectrometer (Figure 3.5c), and obtained using the remote triggered fiber optic reflection probe on the Antares II spectrometer (Figure 3.5d). Both calibration curves are illustrated.

**Figure 3.5.** Cure of Surface Master 905 face adhesive. (a) Near IR spectrum of uncured Surface Master 905 adhesive. (b) Stacked spectra for curing adhesive. A comparison of the performance of the diffuse reflectance probe (c) and the integrating sphere probe (d) during cure of the adhesive. The 4350 cm⁻¹ peak is indicated by the arrow.
3.3.3 Prepreg Aging by Near IR Spectroscopy

Prepreg (and adhesive) is received by the parts manufacturer as a one component system with curing agent(s) added to the formulation. As a result, the material must be stored under refrigeration to minimize the advancement of cure with storage and prior to usage. The supplier defines a change in property beyond which the raw material is assumed to be defective. Usually, techniques such as DSC (relatively straightforward) or HPLC (more involved) are used to define whether or not the material is within performance specifications. For example, T800/3900 prepreg is assumed to be “out of specification” when the glass transition temperature of the uncured resin matrix exceeds 10°C at a DSC heating rate of 10°C/min. Usually, this corresponds to a reduction of “tack and drape” to where the prepreg cannot be properly shaped at room temperature.

Examination by DSC usually consists of removing material from the roll then transporting to the QC laboratory for analysis. The technique of diffuse reflectance near IR spectroscopy was applied to an analysis of the aging of T800/3900 prepreg to see if it could be applied to material “on the roll”. In theory, the glass transition temperature of a material at a defined heating rate is measured as a single temperature corresponding to the transition from a glass to an elastomer. In reality, the $T_g$ transition of uncured T800/3900 prepreg proceeds over a defined temperature range and possesses a low beginning temperature, a mid point, and a higher end temperature. The $T_g$ is assumed to correspond to the low temperature beginning of the transition.
Figure 3.6. PLS generated plots correlating the second derivative spectra with prepreg T_g for uncured but aged T800-3900 prepreg. (a) Correlation of spectra with the low temperature beginning of the transition. (b) Correlation of spectra with the mid point of the transition. (c) Correlation of spectra with the high temperature end of the transition.

Samples of T800/3900 prepreg were “aged” at low temperatures in a forced air oven. The DSC experiment was then performed at a heating rate of 10°C/min and the diffuse reflectance near IR spectrum was obtained. Linkage between the two variables – the measured T_g and the second derivative of the epoxy absorbance - was then tested using Chemometrics software with a partial least squares algorithm.

Correlation of the spectrum with the low beginning temperature of the T_g transition is made in Figure 3.6 (a), with the midpoint of the transition in Figure 3.6 (b), and with the
high end of the transition in Figure 3.6 (c). Clearly, the near IR spectrum does not correlate with either the beginning or the midpoint of the transition. However, a fair to good correlation can be made between the measured end point of the $T_g$ transition and the diffuse reflectance near IR spectrum with $R > 0.96$. As such, the use of near IR spectroscopy could afford a more convenient avenue for the determination of T800/3900 stored prepreg viability if the specifications could be rewritten in terms of the end point of the $T_g$ transition by DSC at a heating rate of $10^°C/min$.

3.4 Conclusions

It has been determined that good quality diffuse reflectance near IR spectra can be obtained from cured and uncured prepregs based on epoxy resin and highly filled adhesives based on epoxy resin.

Using the TQ Analyst software, second derivative diffuse reflectance near IR spectra can be subjected to partial least square analysis. Good quality calibration curves can be obtained that link second derivative spectra to cure state and glass transition temperature in the epoxy resin, curing epoxy based prepreg, and heavily filled epoxy based adhesive.

Diffuse reflectance near IR spectroscopy coupled to good Chemometric software poses a valuable tool for the on-site measurement of epoxy cure state for neat epoxy resin, epoxy based prepreg and composite, and heavily filled epoxy based adhesive.
CHAPTER 4

PARTIAL CHARACTERIZATION AND CURE KINETICS STUDY OF A CARBON-FIBER REINFORCED HIGH PERFORMANCE EPOXY RESIN

4.1 Introduction

A field repair of an epoxy resin based carbon fiber composite will proceed somewhat as follows. The offending volume will be removed from the part and the edges will be scarfed according to specifications. A layer of high shear adhesive will be laid down followed by layers of prepreg cut so as to replace the volume of removed material. The ensemble will then be vacuum bagged and cured under digitally controlled heating blankets. A candidate repair prepreg must be able to be cured at low temperatures not exceeding 250 °F without overheating due to the resin exotherm. This study was initiated to evaluate a candidate prepreg system for repair purposes, the T700/2510PW prepreg system. Essentially, this evaluation consisted of a qualitative structural analysis of the resin followed by a reasonably in depth analysis of the cure kinetics. Throughout, it was found sufficient to model the cure kinetics around the Arrhenius model. The extent of cure and rate of cure was followed by Differential Scanning Calorimetry (DSC). In some cases, cure was followed also by Dynamic Mechanical Analysis or DMA. Analyses of cure kinetics were performed under programmed conditions, followed by analysis of the cure kinetics performed under isothermal heating conditions, and finally, combining the two to determine the cure kinetics accompanying a ramp and soak cycle used in most instances of repair.
4.2 Experimental Section

4.2.1 Materials

T700/2510PW prepreg tapes were provided by the National Institute for Aviation Research (NIAR) at Wichita State University. Solvents, including deuterated solvents, were purchased from the Aldrich Chemical Co. and were used as received.

4.2.2 Instrumentation

A ThermoNicolet Avatar FT-IR spectrometer was used to obtain FT-IR spectra of the prepregs resin extracted into chloroform and then deposited on a NaCl salt plate.

$^1$H NMR spectra of the resin dissolved in deuterated chloroform were obtained using a Varian Inova 400 MHz or a Varian Mercury 300 MHz FT-NMR spectrometer.

All dynamic, isothermal and combined ramp and soak studies were performed using TA Instruments Q2000 DSC.

Dynamic Mechanical Analysis (DMA) was performed by Advance Processing Technology (Norman, OK) using an Alpha Technologies ATD 2000 rheometer.

4.3 Results and Discussion

4.3.1 Structural analysis

A qualitative structural analysis of the prepreg resin was performed in order to give basic structural parameters for the resin. The resin was extracted from the prepreg using
deuterated chloroform solvent. Infrared (IR) and proton Nuclear Magnetic Resonance (HNMR) spectra were obtained of the extract.

A mid-IR spectrum of the extract is reproduced in Figure 4.1. Aromatic C-H stretching was observed close to and above 3000 cm$^{-1}$. The standard aromatic ring breathing absorption at 1600 cm$^{-1}$ is present. Saturated material is also present. (C-H stretching below 3000 cm$^{-1}$ and bending at 1520 cm$^{-1}$) The complex stretching pattern between 3700 cm$^{-1}$ and 3200 cm$^{-1}$ has been linked in previous work$^{(49)}$ to amine N-H stretching vibrations. The complete absence of anhydride absorption at about 1800 cm$^{-1}$ is strong evidence against the material being an anhydride cured resin. A weak epoxy stretch was observed at 908 cm$^{-1}$. The fingerprint absorption at 831 cm$^{-1}$ supports the presence of para disubstituted benzene. A proton NMR spectrum of the extract is reproduced in Figure 4.2. The resonances identified by arrows support the presence of bisphenol A structural units and glycidyl ether epoxy resin functionality.

The spectral analysis shows the prepreg resin to be a diglycidyl ether of bisphenol A (DGEBA) based epoxy resin with an aromatic amine curing agent. The presence of catalyst cannot be determined from these analyses. The presence or absence of catalyst is approached from a kinetics viewpoint by looking for deviations from normal aromatic amine cured epoxy resin chemistry.
Figure 4.1. Mid-infrared spectrum of resin extracted from T700/2510PW prepgs.

Figure 4.2. $^1$H NMR of T700/2510PW resin in deuterated chloroform with DGEBA resonances indicated by arrows.
4.3.2 Differential Scanning Calorimetry (DSC)

The technique of Differential Scanning Calorimetry (DSC) has been applied to resin cure studies for many years. Essentially, the resin or prepreg is added to a DSC sample pan. The pan is hermetically sealed to protect the oven assembly from vapors from the curing resin. The weighed sample is added to the DSC oven and a cure cycle containing programmed or isothermal segments is applied to the sample. If the resin is not 100% cured by the end of the experiment, auxiliary experiments must be performed to complete the analysis.

A typical DSC exotherm is pictured in Figure 4.3. The apparent extent of cure (\(\alpha\)) at any time (\(t\)) may be calculated. If the time in question is represented by the arrow, then:

\[
\alpha_t = \frac{A}{A + B}
\]

This only works if the final cure state coincides with \(\alpha = 1.00\) and on the basic assumption of DSC, that the rate of reaction is proportional to the measured heat flow.\(^{(50)}\)

The amount of heat associated with the reaction can be determined by integrating the area between the baseline and the curve. The total heat, \(Q_t\), associated with the reaction is equal to the area in the exotherm:

\[
Q_t = \int_{t_0}^{t_f} \left( \frac{dq}{dt} \right) dt
\]

where \((dq/dt)\) is the heat flow and \(t_f\) is the time at which the DSC output goes back to the baseline.
The degree of cure $\alpha_t$ at an intermediate time can be calculated by integrating the heat flow up to that time $t$.

$$\alpha_t = \frac{\int_0^t \left( \frac{dq}{dt} \right) dt}{Q_t} = \frac{A}{A+B}$$

![Figure 4.3. A Differential Scanning Calorimeter (DSC) output with degree of cure $\alpha = A/(A+B)$](image)

Conversely, if the integral $\alpha_t$ versus time curve has been established, the rate of cure $(d\alpha/dt)$ can be recovered by differentiating said integral at time $t$. The general formula \(^{(51)}\) for the rate of reaction is:

$$\frac{d\alpha}{dt} = k \, f(\alpha)$$
where \( k \) is an Arrhenius rate constant \( [k = Ae^{-\frac{E_a}{RT}}] \) and \( f(\alpha) \) is some function of conversion as determined by experiment.

### 4.3.2.1 Programmed Cure

In programmed cure studies, the sample is heated at a linear rate to some predetermined end temperature, selected so that the resin has been completely cured by the end of the experiment. A programmed segment of this type would approximate the ramp segment in an autoclave cure. The sample is usually cooled to room temperature and re-ramped at 10°C/min to determine the ultimate \( T_g \) of the resin component. Therefore the end temperature of the first ramp segment should be high enough to complete cure but not high enough to begin degrading the resin network.

Programmed heating experiments of this type were performed, times were converted to temperatures, and the data was normalized to produce a plot of \( \alpha_T \) versus temperature, as reproduced in Figure 4.4. As expected, the cure reaction is shifted to higher temperatures at higher heating rates.

To give an idea of the relative reactivity of T700/2510PW prepreg resin, the degree of cure of this resin at a fixed heating rate of 5°C/min was plotted against that of other well-known resin systems, as reproduced in Figure 4.5. M21 unitape contains glycidyl ether and \( \beta \)-amino epoxy functionality, most probably arising from the inclusion of DGEBF resin with MY720 epoxy resin. Diamino diphenyl sulfone curative (DDS) was also detected. Prepreg 3900 contains MY720, DGEBA, and DDS curative, along with some
trace components. Neither M21 nor 3900 contain catalyst. Resin (934) is a BF$_3$ catalyzed mixture of MY720 and DDS. The T700/2510PW prepreg is more active than even the 934 resin, and cure is completed at 200°C at a heating rate of 5°C/min. Normally, heating rates closer to 1°C/min are used in heat blanket cure experiments and so the apparent conversion curve would be shifted to even lower temperatures at that lower heating rate. T700/2510PW prepreg, therefore, appears to be a good candidate for epoxy resin based

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**Figure 4.4.** Cure of T700/2510PW prepreg under Ramped conditions by DSC. Degree of cure versus temperature (°C)

The cumulative cures versus temperature curves in Figure 4.4 were differentiated to yield cure rate versus temperature curves depicted in Figure 4.6. As expected, the rate of cure curves are magnified and pushed to higher temperatures at higher heating rates.
However, it must always be remembered that the cure reaction is at lower heating rates is spread out over a longer time interval. Our possession of rate of cure data now allows us to apply Flynn-Wall\(^{(52)}\) kinetics to the cure reaction in order to determine if the apparent activation energy \((E_a)\) for cure is low or high and the extent to which \(E_a\) is a function of \(\alpha\), the cure state. If we assume that

\[
\frac{d\alpha}{dt} = k f(\alpha)
\]

where \(k\) is an Arrhenius rate constant \([k = A e^{-\frac{E_a}{RT}}]\) and \(f(\alpha)\) is some function of conversion then,

\[
\ln\left\{\frac{d\alpha}{dt}\right\} = \ln\{k f(\alpha)\}
\]

\[
\ln\left\{\frac{d\alpha}{dt}\right\} = \ln\{Af(\alpha)\} - \frac{E_a}{RT}
\]

The apparent activation energy \((E_a)\) was determined as follows. A value of \(\alpha\) is chosen (e.g. \(\alpha = 0.15\) or 15% conversion) and all programmed experiments are accessed to determine the temperature at which \(\alpha = 0.15\) at that heating rate. The temperature corresponding to \(\alpha = 0.15\) and the value of \(d\alpha/dT\) at that temperature are established. The values of \(d\alpha/dT\) are then converted to corresponding values of \(d\alpha/dt\). A plot is then established of \(\ln\{d\alpha/dt\}\) as \(y\) versus \((1/T)\) as \(x\). The apparent activation energy \(E_a\) is determined from the slope which is equal to \(E_a/R\)
Figure 4.5. Degree of cure ($\alpha$) versus temperature ($^\circ$C) for resin in T700/2510PW prepreg and resin in three other common high performance aviation prepregs, all cured under programmed conditions at 5$^\circ$C/min.

Figure 4.6. Rate of cure $\frac{d\alpha}{dt}$ versus temperature ($T$) for T700/2510PW prepreg.
An example of this method as applied to a sample cured to a level of 15% is illustrated in Figure 4.7. A good data fit is obtained (see $R^2 = 0.9957$), and the apparent activation energy is obtained from the slope of the graph, as detailed in the preceding list of actions. Other data sets were plotted with similar high $R^2$ values. The apparent activation energy of the epoxy cure reaction (E\(_a\)) is detailed in Figure 4.8 for T700/2510PW prepreg along with some other resin systems included for comparison.

The apparent activation energy for cure of M21 pultrusion unitape and for resin in TORAYCA(IM350F) prepreg increases monotonically with degree of cure, as is proper for a non-catalyzed resin system. The apparent activation energy for cure of T300/934 prepreg passes through a maximum at a low cure state and increases monotonically thereafter. If BF\(_3\) were a classical catalyst, this could not happen. In fact, the apparent activation energy should dip to a minimum during catalyzed cure. The apparent maximum in E\(_a\) is accompanied by a profound maximum in “A”, the pre-exponential factor of the Arrhenius relationship. This is strong circumstantial evidence that BF\(_3\) is not a classical catalyst, in that it not only changes the rate of cure, but also changes the base mechanism of cure. The resin in T700/2510PW prepreg also produces a curve of E\(_a\) vs $\alpha$ that achieves a maximum at an intermediate cure state. The maximum is less profound than that achieved with 934 resin and is achieved at a higher degree of cure ($\alpha \sim 55\%$), before increasing monotonically to 100% cure. We know that T700/2510PW prepreg cures more quickly than T300/934 prepreg, presumably because the curing agent is other than DDS which is known as one of the least active curing agents in common usage.
Figure 4.7. Sample plot of $\ln${cure rate} versus $1/T$ to determine apparent activation energy ($E_a$) for cure.

Figure 4.8. $E_a$ versus conversion ($\alpha$) for resin in T700/2510PW prepreg, M21 pultrusion unitape, for resin in TORAYCA (IM350F) prepreg, and for resin in T300/934 prepreg
4.3.2.2 Isothermal Cure

The progress of resin cure under isothermal conditions (approximating the “soak” segment of a ramp and soak cure cycle) was determined by DSC. The raw heat flow data were manipulated and recast into a curve of $\alpha$ versus time as reproduced in Figure 4.9. From Figure 4.9, it may be observed that cure progresses more quickly at higher temperatures. It may also be observed that complete cure may be achieved (after a sufficiently long time) at temperatures as low as 120°C. Rate curves for the cure reaction are obtained (Figure 4.10) by differentiating the data in Figure 4.9. At the highest temperatures (ca. 180°C), the rate of reaction achieves the classic shape for epoxy resin cure. The rate is initially slow then increases to a maximum due to catalysis by products of reaction. At intermediate temperatures (~160°C), however, an unusual effect is observed, that of a double rate maximum. At even lower temperatures, the double rate maximum devolves into a rate plateau that extends over a prolonged time interval. This is the strongest evidence yet collated for an externally catalyzed or promoted reaction.

The Kamal (53) kinetic scheme was applied to this isothermal data in order to determine activation energies for uncatalyzed resin cure ($E_{a1}$ from $k_1$) and for resin cure catalyzed by products of the reaction ($E_{a2}$ from $k_2$).
Figure 4.9. Plot of conversion ($\alpha$) versus time for cure, over a range of isothermal temperature of T700/2510PW prepreg

The Kamal kinetic argument may be summarized as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_f - \alpha)^n$$

where

- $k_1$ is the rate constant for uncatalyzed cure of resin
- $k_2$ is the rate constant for cure of resin catalyzed by products
- $\alpha$ is the intermediate level of cure at isothermal temperature
- $\alpha_f$ is the ultimate level of cure at isothermal temperature
The Kamal model has been found to successfully describe cure kinetics of Araldite LY-566\(^{(54)}\) and Cytec Fiberite 976\(^{(55)}\) epoxy resins as well as unsaturated polyester resins.\(^{(56)}\)

In this study Kamal kinetics was applied to isothermal experiments performed from 120\(^{\circ}\)C to 180\(^{\circ}\)C in 5\(^{\circ}\)C increments. Deviations from Kamal kinetics constitute strong circumstantial evidence for external catalysis or promotion of the cure reaction. Curve fitting was performed using the Origin\(^{\text{TM}}\) curve fitting program. The degree of fit of experimental data points to the Kamal equation was plotted as a function of degree of cure. Three examples of “goodness of fit” curve modeling are reproduced below.
The agreement between the Kamal model and experimental data points at a high isothermal cure temperature (180°C) is illustrated in Figure 4.11. As expected from examination of the unmanipulated rate curves in Figure 4.10, data generated from the model with optimized parameters overlaps the raw data. At an intermediate temperature for example 140°C, the degree of fit is poorer as shown in Figure 4.12 (remember the double rate maximum in the rate curve of Figure 4.10).
Figure 4.12. 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 $-\frac{E_a}{R}$. (Poor fit to Kamal kinetics at intermediate temperatures due to external catalysis)

Interestingly, the degree of fit at low temperatures, for example, at 120°C (Figure 5.13) appears to improve over that obtained at intermediate temperatures (compare the $R^2$ values annotated on the figures [$R^2@180°C > R^2@120°C > R^2@140°C$]). This must not be misconstrued as a return to good curve fitting at low temperatures. Rather, the apparently improved fit is more likely to result from the two rate maxima (@ 140°C) merging into a plateau that approximates a single broad rate maximum.
Figure 4.13. Plot of rate of cure versus degree of cure for resin in T700/2510PW prepreg at 120°C. Black squares – experimental data, red line – Kamal model prediction. The gradient of the best fit straight line is set to $-E_{a1}/R$. (Poor fit to Kamal kinetics at low temperatures due to external catalysis)

Kamal kinetics are followed at higher temperatures and not at lower temperatures. Attempts to determine corresponding activation energies were, therefore, confined to interpretation of higher temperature experiments. Each fitting experiment produces values of $k_1$ and $k_2$ at that temperature. If $\ln\{k_i\}$ at temperature $T$ is plotted versus $1/T$, the corresponding activation energy may be recovered from the gradient of the plot. Plots for $E_{a1}$ and $E_{a2}$, constructed using data garnered at temperatures greater than or equal to 150°C, are reproduced in Figures 5.14 and 5.15 with results summarized in Table 4.1 along with data from other prepregs added for comparison.
Figure 4.14. Plot of $\ln k_1$ versus $1/T$ for T700/2510PW prepreg using data points collected at $150^\circ C$ or above. The gradient of the best fit straight line is set to $-E_{a1}/R$.

Figure 4.15. Plot of $\ln k_2$ versus $1/T$ for T700/2510PW prepreg using data points collected at $150^\circ C$ or above. The gradient of the best fit straight line is set to $-E_{a1}/R$. 
Table 4.1. Values of $E_{a1}$ and $E_{a2}$ for T700/2510PW and other prepregs calculated according to the Kamal method.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{a1}$ (kJ/mol)</th>
<th>$E_{a2}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T300/934</td>
<td>53.8 (2 parameters)</td>
<td>± ~0</td>
</tr>
<tr>
<td></td>
<td>64.3 (1 parameter)</td>
<td></td>
</tr>
<tr>
<td>TORAYCA(IM350F)</td>
<td>74.7</td>
<td>53.8</td>
</tr>
<tr>
<td>T700/2510PW</td>
<td>102.5</td>
<td>96.3</td>
</tr>
</tbody>
</table>

The presence of BF$_3$ in T300/934 prepreg accelerates initial cure such that the data is best described as externally catalyzed with no measureable internal catalysis, resulting in $E_{a2}$ $\sim 0$ kJ/mol. The activation energy ($E_{a1}$) for T300/934 prepreg may be thought of as the activation energy of cure with an external promoter. T700/2510PW prepreg cures more quickly than T300/934 prepreg. Even so, we are able to recover two activation energies for the former. We may relate this to the action of the external catalyst or promoter in the former, which only “kicks in” during mid cure, thus allowing for both activation energies to be recovered from the kinetic analysis. We know that T700/2510PW prepreg cures much more quickly than TORAYCA(IM350F) prepreg. However, the activation energies for cure of the former are greater than the activation energies for cure of the latter. The activation energy for cure is not the only determining parameter for cure rate. The overall order of reaction from the reaction mechanism is also important. The higher activation energies measured for the T700/2510PW prepreg (versus the TORAYCA(IM350F) prepreg), measure the greater temperature dependence of cure in T700/2510PW prepreg.
4.3.2.3 Combined ramp and soak experiments

Combined ramp and soak experiments were performed with T700/2510PW prepreg using a method developed previously. The experiment is immensely labor intensive which possibly explains that such analyses are confined to our research group. The experiment is summarized in Table 4.2. We have determined from numerous experiments that is not possible to reconstruct the kinetics of a ramp and soak experiment by simply duplicating the experiment in the DSC apparatus then normalizing the data. Consider the initial ramp section of the experiment. If we simply ramp to an intermediate temperature and switch to a soak segment, the data cannot be separated for analysis. Instead, we must utilize results of previous programmed experiments.

The cure and rate data for a complete programmed experiment at a set heating rate to a very high end temperature (thus ensuring complete cure) are examined and the kinetics of programmed cure to an intermediate end temperature (the ramp segment) are extracted from the complete programmed experiment. In order to condition the sample for the succeeding soak segment, it is first heated to the soak temperature at the predetermined programmed rate so that the extent of cure at $t_0$ (the beginning of the soak segment) is achieved. It is rapidly cooled to room temperature then rapidly reheated to the soak temperature and data are collected for the isothermal segment of the experiment. This separation of the ramp and soak segments allows us to establish baseline conditions for the soak segment. The cumulative cure and corresponding rate of cure for the soak segment is then determined.
After the rate of cure at the soak temperature drops to ~ 0, the sample is rapidly cooled to room temperature. The sample is then ramped at 3°C/min to a high end temperature to determine whether or not the sample contains any residual cure, and if so, how much. If residual cure ~ 0, the ramp and soak segments are combined to produce the ramp and soak experiments reproduced below. If residual cure after the ramp and soak segments is greater than zero, the experiment is renormalized to account for this residual cure. The ramp and soak segments are then combined to produce the ramp and soak experiments reproduced below. Random error cannot be eliminated from these experiments.

**Table 4.2.** Data collection in ramp – soak experiments.

<table>
<thead>
<tr>
<th>Experiment Step</th>
<th>Data obtained during ramp</th>
<th>Data obtained at soak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramp from room temperature to soak temperature</td>
<td>Heat of reaction to soak temperature during ramp segment = ( \Delta H_{(Trs)} )</td>
<td>Heat of reaction at soak temperature = ( \Delta H_{(Ts)} )</td>
</tr>
<tr>
<td>Fast cool to room temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fast re-heat to soak temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isothermal at soak temperature</td>
<td>Heat of reaction to intermediate time = ( \Delta H_{(t_i)} )</td>
<td>Ultimate isothermal heat of reaction = ( \Delta H_{(t_\infty)} )</td>
</tr>
<tr>
<td>Fast cool to room temperature</td>
<td>Residual heat of reaction = ( \Delta H_{(r)} )</td>
<td></td>
</tr>
</tbody>
</table>
The calculations of the extent of reactions in each step are shown below.

Extent of reaction to an intermediate (i) cure temperature during the first ramp cycle:

\[ \alpha = \Delta H_{(TRS)} + \Delta H_{(t\infty)} + \Delta H_{(r)} \]

Extent of reaction to soak temperature:

\[ \alpha = \frac{\Delta H_{TRS}}{\Delta H_{(TRS)} + \Delta H_{(t\infty)} + \Delta H_{(r)}} \]

Extent of reaction at intermediate soak time (tj):

\[ \alpha = \frac{\Delta H_{(TRS)} + \Delta H_{(tj)}}{\Delta H_{(TRS)} + \Delta H_{(t\infty)} + \Delta H_{(r)}} \]

Ultimate extent of reaction after soaking to long times:

\[ \alpha = \frac{\Delta H_{(TRS)} + \Delta H_{(t\infty)}}{\Delta H_{(TRS)} + \Delta H_{(t\infty)} + \Delta H_{(r)}} \]

The ramp and soak kinetics experiment can provide crucial information to the manufacturer. For example, it is of great importance to avoid “hot spots” in the curing part. We have observed over many systems hot spots are generally not encountered during the ramp segment of the cure process. We have found that the danger of generating a “hot spot” with runaway cure is greatest at the end of the ramp segment, just as the sample begins isothermal cure. Overall, it is generally wise to expose the part to a ramp segment during which significant cure is generated. Obviously, the ramp segment should also be sufficiently short that the overall cure cycle is economically viable.
Ramp and soak experiments were performed on the T700/2510PW prepreg with programmed segments at 1, 2, 3, 4, 5, 10, 15, and 20°C/min and with soak temperatures ranging from 125°C to 155°C in 5°C increments. Some ramp and soak experiments are illustrated below. The intersection of the x and y axes (t=0) corresponds to the end of the ramp segment and the beginning of the soak segment. The ramp segment is set before t=0 while the soak segment is set after t=0. The cumulative conversion curves for a soak temperature of 125°C are reproduced in Figure 4.16. The corresponding rate curves for a soak temperature of 125°C are reproduced in Figure 4.17. From the cumulative conversion curves (Figure 4.16), it may be concluded that significant conversion during the ramp segment is observed only when the heating rate is set at 1°C/min or lower. From the rate curves (Figure 4.17) it is observed that the autocatalytic shape of the rate curves during the isothermal segment (rate increasing to a maximum then decreasing thereafter) is completely removed when the previous ramp rate is 1°C/min or less (rate starts at a maximum level then drops off thereafter).
Figure 4.16. Ramp and soak of T700/2510PW prepreg to 125°C over a range of heating rates. Conversion (\(\alpha\)) versus time

Figure 4.17. Ramp and soak of T700/2510PW prepreg to 125°C over a range of heating rates. Rate of reaction (\(d\alpha/dt\)) versus time
Figure 4.18. Ramp and soak of T700/2510PW prepreg to 155°C over a range of heating rates. Conversion (α) versus time

If we now focus on cumulative conversion curves (Figure 4.18) and rate curves (Figure 4.19) for ramped then isothermal cure at 155°C, a modified picture emerges. At a soak temperature of 155°C, significant cure is observed during the ramped segment at all heating rates except the very highest. If we next focus on the rate curves (Figure 4.19) it may be observed that completely contained exotherms are produced during the ramp segment at heating rates of 2°C/min and 1°C/min (or lower). The exotherm “spike” observed just after attainment of the soak temperature is completely removed at previous heating rates of 3°C/min or lower.
Overall, it may be concluded that a good compromise cure cycle, minimizing both reaction rates and reaction time, may be constructed by heating to 150°C or 155°C at 2°C/min followed by a 20 min soak at that temperature.

Figure 4.19. Ramp and soak of T700/2510PW prepreg to 155°C over a range of heating rates. Rate of reaction (dα/dt) versus time

4.3.3 Dynamic Mechanical Analysis (DMA) Study of T700/2510PW prepreg cure

In order to complete an analysis of T700/2510PW prepreg cure, it is necessary to perform Dynamic Mechanical Analysis (DMA) experiments in order to determine how the shear modulus or viscosity builds up over the cure cycle. This has far reaching
consequences for the fabricator. For example, in the early stages of cure, the resin is liquid and layers of prepreg can literally shift position if not secured in place, usually through a combination of compressive forces brought about by vacuum bagging and excess pressure in the autoclave. In a repair scenario, vacuum bagging is possible, but the application of autoclave pressure is often not an option. In these instances (for example, during a heat blanket cure) it is essential to determine the viscosity profile for the resin prepreg.

The examination of mechanical properties as a function of cure state is not a straightforward proposition. For example, we have never been able to remove resin from the prepreg without altering the resin in some way (for example, by adding solvent). Therefore, we may not remove resin and examine it in a simple shear rheometer to this end.

A DMA sample for this experiment is prepared as follows. A set of plies (~12 max) are assembled. If woven, they are stacked in no particular sequence, if linear they are layed up in a 90° stacking sequence. The layers of prepreg are compressed then cut with a circular die into the configuration pictured in Figure 4.20. The prepreg assembly is heat-sealed into a mylar capsule with indentations in the mylar to mesh with complimentary depressions in the top and bottom platens of the DMA instrument.

Experiments were performed using an encapsulation rheometer, originally developed for the elastomer market. The top and bottom platens contain the driving oscillatory motor, the load cell, and heating elements. As such, very good temperature control is achieved and measurements can be made under programmed heating conditions –
something not possible with more conventional parallel plate or cone and plate rheometers.

![Sample configuration for the DMA experiment](image)

**Figure 4.20.** Sample configuration for the DMA experiment

Dynamic Mechanical Analysis (DMA) of T700/2510PW prepreg was performed over a range of cure cycles, as detailed in Table 4.3. The single most important piece of information to be gleaned from these experiments is the initial time/temperature associated with the first dramatic upswing of sample viscosity or storage modulus. Before this point, the part is inherently fragile and layers of prepreg may slide over each other to reform the geometry of the part during cure. This phenomenon is especially important during a heat blanket cure where external autoclave pressure is not available. It is tempting to equate this initial buildup of physical properties with the resin gel point. However, although we are convinced that this point of initial property buildup is associated with the gel point, equating the two is not possible. The classical gel point is normally considered to occur when the shear storage and loss moduli are equal, i.e. when
\[ \tan \delta = \frac{G''}{G'} = 1. \] In these experiments, however, \( \tan \delta \) never equals 1 due to the presence of the fibers which add to the apparent viscosity/shear modulus at all times.

**Table 4.3.** Cure cycles used in DMA experiments.

<table>
<thead>
<tr>
<th>Cure cycle</th>
<th>Initial buildup of physical properties</th>
<th>100% cure achieved at</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1(^\circ)C/min to 155(^\circ)C &amp; hold for 120 min</td>
<td>125(^\circ)C on ramp segment</td>
</tr>
<tr>
<td>#2</td>
<td>2(^\circ)C/min to 155(^\circ)C &amp; hold for 120 min</td>
<td>134(^\circ)C on ramp segment</td>
</tr>
<tr>
<td>#3</td>
<td>1(^\circ)C/min to 165(^\circ)C &amp; hold for 120 min</td>
<td>125(^\circ)C on ramp segment</td>
</tr>
<tr>
<td>#4</td>
<td>2(^\circ)C/min to 165(^\circ)C &amp; hold for 120 min</td>
<td>134(^\circ)C on ramp segment</td>
</tr>
<tr>
<td>#5</td>
<td>1(^\circ)C/min to 175(^\circ)C &amp; hold for 120 min</td>
<td>125(^\circ)C on ramp segment</td>
</tr>
<tr>
<td>#6</td>
<td>2(^\circ)C/min to 175(^\circ)C &amp; hold for 120 min</td>
<td>135(^\circ)C on ramp segment</td>
</tr>
</tbody>
</table>
The results of these DMA experiments are summarized in Table 4.3. It may be observed from cure cycle #1 (Table 4.3 column 2 and Figure 4.21) that the point of initial increase of shear modulus (defined by the red arrow in Figure 4.21) is observed to occur during the 1°C/min ramp segment of this cure cycle. We know that T700/2510PW prepreg is completely cured shortly after reaching 155°C at a heating rate of 1°C/min. (see Figure 4.18) Resin cure is assumed to be completed when the shear loss modulus (the blue line) returns to the baseline shortly after attainment of the 155°C soak temperature. The plateau in $G'$ thereafter, becomes an estimate of the rubber shear modulus of the fully cured resin at 155°C.
Figure 4.22. DMA of uncured T700/2510PW prepreg from room temperature to 175°C at 2°C/min then held at 175°C for 120 min.

In contrast, a cure cycle of 2°C/min to 175°C was modeled followed by an isothermal segment at that temperature (Figure 4.22, Table 4.3 cure cycle #6) the resin will be completely cure by the end of the programmed cycle. Even so, the point of initial property buildup (the red arrow in Figure 4.22) is shifted to a higher temperature (135°C) due to the higher heating rate on the ramp segment. The rubber shear modulus was measured over the soak temperature as ~6.6 MPa at a soak temperature of 155°C (Figure 4.21) and ~6.0 MPa at a soak temperature of 175°C. This is more likely due to the temperature difference than to any changes in the material.
4.4 Conclusions

Resin in pre-cured prepreg may be chemically analyzed without too great a difficulty, yielding clues into how best to cure the resin in the composite. Kinetics experiments may be used to determine whether or not the resin cure is catalyzed.

Ramp and soak DSC experiments may be combined to yield valuable insight into resin cure in a ramp and soak autoclave cure cycle. Examination of ramp and soak cure cycles allows one to put together a cure cycle that will yield a complete cure of the resin with a minimum probability of formation of “hot spots” that can lead to char formation and rejection of the part.

DMA experiments can be used to determine a “pseudo” gel point in the resin, before which the part is very fragile, and after which the part is more physically robust.

Overall, it may be concluded that a good compromise cure cycle for T70/2510PW prepreg, minimizing both reaction rates and reaction time, may be constructed by heating to 150°C or 155°C at 2°C/min followed by a 20 min soak at that temperature.

By comparing the results of DSC and DMA experiments, the point of massive initial increase of composite viscosity/modulus, the “pseudo” gel point, can be equated to ~40-45 % conversion of the resin in T700/2510PW prepreg to cured composite.
5.1 Introduction

The engine mount assembly for many modern jetliners is constructed of carbon fiber reinforced epoxy resin composite, epoxy based adhesive and aluminum honeycomb. The mount assembly is protected from hot air leakage from the engine by a thermal blanket. The thermal stability of amine cured epoxy resin based composites is limited by the thermal stability of the amine-epoxy crosslink (Figure 5.1 in red).\(^{(57)}\)

![Figure 5.1](image-url) (Synthesis of epoxy crosslink (in red) by reaction of an aromatic primary amine with two glycidyl ether epoxy residues.)

Figures caption: Figure 5.1. Synthesis of epoxy crosslink (in red) by reaction of an aromatic primary amine with two glycidyl ether epoxy residues.
In contrast, 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. Polyimide resin systems constitute perhaps the best epoxy resin substitute currently available.

A representative much studied polyimide resin (PMR-15)\(^{(58)}\) is sketched in Figure 5.2 (top). The resin is obviously intrinsically stiff with bond rotations requiring bond breakage and reformation. The physical properties of many polyimide resin systems are enhanced through \(\pi\) stacking.\(^{(59)}\) As illustrated, regions of the polyimide chain are successively electron rich then poor. Polyimide chains in PMR-15 resin stack as illustrated in Figure 5.2 (bottom). This reduces free volume and therefore increases stiffness and softening temperature.

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**Figure 5.2.** (top) PMR polyimide resin. (bottom) \(\pi\) stacking
Polyimide cure is varied but centers on the reaction of an aromatic anhydride with an aromatic amine to form an aromatic amide intermediate at close to room temperature. This aromatic amide is processable with or without a solvent and is incorporated into a fiber reinforced prepreg. At much higher temperatures the amide acid is cyclized into the imide and the prepreg is cured into a fiber reinforced composite.

![Chemical structure](image)

**Figure 5.3.** Conversion of the amic acid intermediate to the imide linkage

A version of this second reaction is shown in Figure 5.3. Normally, water is produced as a co-product of imide formation. The water can phase separate to create a void content in the composite. Of interest is the replacement of the carboxylic acid intermediate with a methyl ester derivative. The methanol co-product thus obtained is more soluble in the cross linked matrix at high temperatures and does not phase separate to form void space, as does water.
We suspect that the amic acid to imide transformation is not exclusively an intramolecular process. Intermolecular condensation, such as is sketched in Figure 5.4, would help to account for the complete intractability of the final imide product.

![Suspected intermolecular imide formation](image)

**Figure 5.4.** Suspected intermolecular imide formation

Once thermally cured, polyimides have an excellent combination of properties that include high glass transition temperature, high toughness, high strength, moderate modulus, and good moisture and solvent resistance.\(^{60}\) They can withstand thermal degradation up to 560°C in the absence of oxygen.\(^{61}\) An essential prerequisite to obtaining the desired final properties is determination of the degree of cure. Methods previously used include Fourier-transform IR (FTIR) spectroscopy,\(^{62}\)\(^{63}\) X-ray
diffraction, \cite{64} FT-Raman spectroscopy, \cite{65} \cite{66} and fluorescence spectroscopy \cite{61}. These methods are destructive and time-consuming and therefore not ideal for on-site analysis.

This study utilized diffuse reflectance NIR to predict the degree of cure for polyimide resins.

5.2 Experimental Section

5.2.1 Materials

Experiments were confined to two commercially available materials, MVK-14 Freeform™ Polyimide Prepreg (resin - Maverick Corporation, prepreg – Renegade Materials), and PETI-365A Polyimide Prepreg (UBI Industries). A very useful summary of the composition and performance of these two resin systems has been published. \cite{67}

MVK-14 Freeform™ Polyimide is seen as a straightforward replacement for PMR-15 polyimide, without the methylene dianiline (MDA) component – a known carcinogen. It has been reported to have a service temperature of 288°C. The composition of MVK-14 Freeform™ Polyimide is summarized in Table 5.1.

PETI-365A Polyimide prepreg is considered as another “drop in” replacement for PMR-15 resin. PETI-365A polyimide is basically an acetylene terminated amic acid oligomer with an ultimate $T_g$ of 365°C. Acetylene terminated (AT) resin cure chemistry and stability was studied extensively by the US Air Force in the 1980’s – 90’s. \cite{67} AT cure proceeds smoothly in the absence of catalyst above 300°C with no volatile emission. If catalyst is added, the cure temperature can be brought down considerably. The
The composition of PETI-365A polyimide resin is summarized in Table 5.2.

**Table 5.1. Composition of MVK-14 Freeform™ Polyimide Prepreg**

<table>
<thead>
<tr>
<th>COMPONENTS: Polymer Ester Solution</th>
<th>CAS NO.</th>
<th>WEIGHT PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA)</td>
<td>2421-28-5</td>
<td>5 – 25</td>
</tr>
<tr>
<td>4,4’-[1,3-phenylene-bis-(1-methylethylidene)]bisaniline (BISM)</td>
<td>2687-27-6</td>
<td>5 - 15</td>
</tr>
<tr>
<td>Bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid monomethylester (NE)</td>
<td>36897-94-6</td>
<td>5 - 15</td>
</tr>
<tr>
<td>p-Phenylenediamine (PPD)</td>
<td>106-50-3</td>
<td>0 – 15</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>64-17-5</td>
<td>10 – 45</td>
</tr>
<tr>
<td>1-Methyl-2-Pyrrolidinone (NMP)</td>
<td>872-50-4</td>
<td>0 – 5</td>
</tr>
</tbody>
</table>

**Supplied on the following fabric:**
Carbon roving, tow, tape, or fabric

<table>
<thead>
<tr>
<th>CAS NO.</th>
<th>WEIGHT PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>7440-44-0</td>
<td>45-75</td>
</tr>
</tbody>
</table>

![Compound images](1)
Table 5.2. Composition of PETI – 365A Polyimide Prepreg

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>CHEMICAL FORMULA</th>
<th>CAS NO.</th>
<th>WEIGHT PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Amide” acid$^7$</td>
<td>confidential</td>
<td>Not registered</td>
<td>30 - 40</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone (NMP)$^8$</td>
<td>CH$_3$NC$_4$H$_6$O</td>
<td>872-50-4</td>
<td>60 - 70</td>
</tr>
</tbody>
</table>

5.2.2 Cure Cycles

Supplier suggested cure cycles for MVK-14 polyimide prepreg and PETI 365-A polyimide prepreg are reproduced in Tables 5.3 and 5.4. Upon examination of these cure cycles, it becomes apparent that polyimide resin cure cycles are more complex than corresponding amine cured epoxy resin cure cycles.
Table 5.3. MVK-14 Freeform™ cure cycle

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ramp from 25°C to 232°C at 0.5°C/min</td>
</tr>
<tr>
<td>2</td>
<td>Hold at 232°C for 30 min</td>
</tr>
<tr>
<td>3</td>
<td>Ramp from 232°C to 266°C in 120 min</td>
</tr>
<tr>
<td>4</td>
<td>Hold at 266°C for 380 min</td>
</tr>
<tr>
<td>5</td>
<td>Ramp from 266°C to 307°C at 0.5°C/min</td>
</tr>
<tr>
<td>6</td>
<td>Hold at 307°C for 300 min</td>
</tr>
</tbody>
</table>

Table 5.4. PETI-356A cure cycle

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ramp from 25°C to 260°C in 210 min *</td>
</tr>
<tr>
<td>3</td>
<td>Hold at 260°C for 60 min</td>
</tr>
<tr>
<td>4</td>
<td>Ramp from 260°C to 371°C in 60 min</td>
</tr>
<tr>
<td>5</td>
<td>Hold at 371°C for 60 min</td>
</tr>
</tbody>
</table>

*Midway Step 1 is a ramp from 25°C to 130°C at 1°C/min
5.2.3 Instrumentation

Near-infrared measurements were recorded using a Thermo Scientific Antaris II FTNIR spectrometer (10000-4000 cm\(^{-1}\)) using an InGaAs detector. Spectra were collected using OMNIC™ software. Spectra were accumulated from 16 scans collected at a resolution of 8 cm\(^{-1}\). Spectra of each sample were collected in triplicate. TQ Analyst™ software package was used to build calibration curves using partial least squares regression method.

The cure states of partly cured polyimide prepregs were determined using a TA Instruments Q2000 DSC.

Thermomechanical measurements were taken using a Q400 TMA (TA Instruments) courtesy of the National Institute of Aviation Research at Wichita State University.

5.3 Results and Discussions

5.3.1 Differential Scanning Calorimetry (DSC)

The immediate goal of this work is to test the applicability of diffuse reflectance near IR spectroscopy as a tool to track polyimide cure state on the shop floor. Many polyimide cure cycles are daunting when compared to high performance epoxy resin cure cycles. As a preliminary to this work, some DSC experiments were performed to see if this more widely used technique is able to determine polyimide cure state. MVK-14 cure will constitute a mix of amic acid to imide cyclization and free radical based maleimide cure. PETI-365A cure will also constitute a mix of amic acid to imide cyclization. \(^{(68)}\)
with free radical acetylene polymerization. The free radical acetylene polymerization of PETI-365A resin will occur at a higher temperature than the free radical based bismaleimide rearrangement/crosslinking of MVK-14 resin, hence the higher end temperatures in the cure cycles detailed in Table 5.3.

Prepreg (uncured or cured to the end of a cure “step”, as defined in Table 5.3) was added to a DSC pan and subjected to a ramped DSC experiment from room temperature to 400°C at 3°C/min. DSC traces for uncured prepreg are reproduced in Figure 5.5. In both instances, a pronounced endotherm is observed at temperatures exceeding 150°C. Exotherms which should accompany the bismaleimide and the acetylene terminated cure reaction were not observed. The origin of this endotherm is unclear. It was postulated that this may accompany the imidization reaction. However, if such was the case, polyimide cure would occur over a small temperature range, could be made to involve only a short ramped cure profile, and would be as simple to implement as epoxy resin cure. In point of fact, the endotherms represented in Figure 5.5 resemble simple crystalline melting endotherms of resin components micronized into the mixture without complete dissolution.
Figure 5.5. DSC traces for MVK-14 and PETI-365A prepreg heated from room temperature to 400°C at 3°C/min. The quoted temperatures correspond to the onset of the DSC endotherm in both instances.
Initially, it was postulated that this endotherm could be used to track the cure state of the prepreg. However, such was not found to be the case. DSC traces performed on partly and completely cured PETI-365A prepreg are reproduced in Figure 5.6. After Step 1 has been completed, the melting endotherm increases in temperature from 192°C to 253°C. The endotherm disappears after Steps 2 and 3. A baseline shift reminiscent of a T_g transition is observed, but only after Step 2 (* in Figure 5.6, top right). A small “melting” endotherm reappears after Step 4 of the cure.
5.3.2 Thermal Mechanical Analysis (TMA)

As an alternative to using “conversion to chemical product” as a measure of cure state, we decided to link cure state to a physical property of the material. Thermal Mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA) were evaluated. DMA was excluded because partly cured polyimide is very brittle and does not easily survive manipulation and shaping. TMA, on the other hand, proved to be a reliable and reproducible tool to measure softening temperature ($T_s$). The technique is illustrated in Figure 5.7 for MVK-14 based prepreg and in Figure 5.8 for PETI-365A prepreg.

![Figure 5.7. Results of TMA experiments performed on MVK-14 prepreg subjected to prior heating consistent with the six cure steps.](image)

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>158.86</td>
</tr>
<tr>
<td>2</td>
<td>163.54</td>
</tr>
<tr>
<td>3</td>
<td>204.45</td>
</tr>
<tr>
<td>4</td>
<td>264.81</td>
</tr>
<tr>
<td>5</td>
<td>266.95</td>
</tr>
<tr>
<td>6</td>
<td>289.72</td>
</tr>
</tbody>
</table>
Figure 5.8. Results of TMA experiments performed on PETI-365A prepreg subjected to prior heating consistent with the five cure steps.

5.3.3 Diffuse Reflectance Near IR Spectroscopy

Having determined a numerical measure for cure state in both prepregs ($T_s$), we determined to see if a correlation could be made between $T_s$ and the near IR spectrum. The benefits of such an analysis are many. In contrast to epoxy resin cure, polyimide cure cycles are complex and difficult to optimize. A simple nondestructive test that will unambiguously define cure state will accelerate the testing and ultimately lead to a faster adoption of an optimized candidate by the fabricator.

Both prepregs were subjected to analysis by diffuse reflectance near IR spectroscopy over a range of cure states. Differing methods of data analysis were adopted for both sets of data.
Figure 5.9. A near IR spectrum and a second derivative spectrum chosen at random from the library of spectra accumulated for PETI-365A prepreg over a range of cure states.
Figure 5.10. A near IR spectrum and a second derivative spectrum chosen at random from the library of spectra accumulated for MVK-14 prepreg over a range of cure states.
A representative diffuse reflectance near IR spectrum and a second derivative spectrum for PETI-365A prepreg is illustrated in Figure 5.9 and for MVK-14 prepreg in Figure 5.10.

The level of success of Chemometrics based software, as applied to the analysis and correlation of near IR spectra is directly dependent upon picking an absorbance window that changes in a meaningful fashion with the property under investigation, in this instance – $T_s$. After some preliminary investigations, different approaches were taken for the two systems under investigation. With the PETI-365A prepreg it was decided to correlate $T_s$ with the prominent absorbance at $6020 \text{ cm}^{-1}$ (spectral range of $5509 \text{ cm}^{-1}$ to $6345 \text{ cm}^{-1}$) labeled with the red asterisk in Figure 5.9. With MVK-14 prepreg, it was decided to correlate $T_s$ with the entire near IR spectrum from $4000 \text{ cm}^{-1}$ to $10000 \text{ cm}^{-1}$. This means that the software will scan the whole region for any statistical variation in the spectra in relation to the $T_s$ values. In both instances, spectra were correlated using a partial least squares analysis.

The results of analyses performed on PETI-365A prepreg and on MVK-14 prepreg are reproduced in Figure 5.10 (left and right, respectively). In both instances, $R^2$ values exceeding 0.99 were obtained. As such, it was determined that the near IR method of determining polyimide cure state was a success.
Figure 5.11. PLS calibration curves for the correlation of diffuse reflectance near IR spectra with cure state for MVK-14 Freeform and PETI 365-A prepgs
5.4 Conclusions

It has been determined that diffuse reflectance near IR spectroscopy coupled with chemometric data analysis can be successfully applied to a determination of polyimide cure state as defined by a physical property such as $T_s$ measured by TMA without having to remove the prepreg from the shop floor. It is expected that an application of this technique in the developmental stages of resin use will significantly reduce the time required to bring these “new” polyimide prepregs to production.
CHAPTER 6

CONCLUSIONS

More aircraft structures are built with mostly composite parts, such an example is the Boeing 787 Dreamliner which has a 100% composite shell. This has reaffirmed the need to further refine techniques used in the analyses of thermosetting polymers used in the aviation industry.

The introduction of the integrating sphere and fiber optic technology have allowed for the use of diffuse reflectance near-infrared spectroscopy as a useful technique for the analysis of selected thermosetting polymers that are of interest in the aerospace industry. A key step in the successful implementation of these near-IR analyses is the use of chemometric methods, in the case of this study partial least squares (PLS) method was employed. It was shown that PLS generated calibration curves have significantly better correlation coefficients than simple Beer’s law plots. This study has shown examples wherein the use of diffuse reflectance near-IR spectroscopy can aid in composite manufacture and repair through nondestructive in situ measurement of the cure state and the surface water content in epoxy resin systems. The same technique was also applied to the determination of the cure state of polyimide resins. The combination of improved collection optics and sophisticated chemometric software has made diffuse reflectance near-IR spectroscopy a versatile method that can be employed in the aviation industry. It can definitely compete with the more time-consuming and destructive conventional methods that are currently being utilized.

This study also looked at an epoxy prepreg system as a candidate material for aviation parts repair. The resin system has been partially characterized using mid-IR and $^1$H NMR
spectroscopy. Structural analyses indicate that the resin contains DGEBA and DDS curing agent. The cure kinetics were studied in-depth with the aid of differential scanning calorimetry (DSC). DMA experiments were also employed to determine a gel point in the resin which essentially indicates at which point the material is fragile or robust. A good compromise cycle for this prepreg is proposed to be a combination of a ramp segment of 2°C/min to 150°C or 155°C and then a hold at that temperature for 20 minutes.
REFERENCES
REFERENCES


APPENDICES
APPENDIX A

Calculation of the Apparent Energy of Activation of Cure

Plots of ln(dα/dt) versus 1/T for the film adhesive from dynamic temperature experiments. Each plot is for a fixed value of α. Apparent activation energies are calculated from the slope of the graphs.

degree of cure - 0.05

\[
y = -9421.4x + 20.524
\]

\[
R^2 = 0.9914
\]

degree of cure - 0.10

\[
y = -6565.7x + 18.675
\]

\[
R^2 = 0.9978
\]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.15

\[ y = -8452.7x + 18.272 \]
\[ R^2 = 0.9957 \]

degree of cure - 0.20

\[ y = -8137.1x + 17.523 \]
\[ R^2 = 0.9964 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.25

\[ y = -7851.8x + 16.822 \]
\[ R^2 = 0.9968 \]

degree of cure - 0.30

\[ y = -7764.6x + 16.599 \]
\[ R^2 = 0.9971 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.35

\[
y = -7719.4x + 16.488 \\
R^2 = 0.9972
\]

degree of cure - 0.40

\[
y = -7578.7x + 16.151 \\
R^2 = 0.9978
\]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.45

\[ y = -7777.9x + 16.644 \]
\[ R^2 = 0.9976 \]

degree of cure - 0.50

\[ y = -7872.5x + 16.865 \]
\[ R^2 = 0.9964 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.55

\[
y = -7775.4x + 16.606 \\
R^2 = 0.997
\]

degree of cure - 0.60

\[
y = -7479.3x + 15.85 \\
R^2 = 0.9967
\]
Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.65

\[ y = -7461.8x + 15.713 \]
\[ R^2 = 0.9985 \]

degree of cure - 0.70

\[ y = -7288.4x + 15.168 \]
\[ R^2 = 0.9974 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.75

\[ y = -6632.7x + 13.381 \]
\[ R^2 = 0.9969 \]

degree of cure - 0.80

\[ y = -6129.8x + 11.883 \]
\[ R^2 = 0.9958 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.85

\[ y = -5889.3x + 10.991 \]
\[ R^2 = 0.9957 \]

degree of cure - 0.90

\[ y = -6332.6x + 11.349 \]
\[ R^2 = 0.9945 \]
APPENDIX A (continued)

Calculation of the Apparent Energy of Activation of Cure

degree of cure - 0.95

\[
y = -6537.5x + 10.776
R^2 = 0.9942
\]

degree of cure - 1.0

\[
y = -9471.7x + 14.856
R^2 = 0.9921
\]
APPENDIX B

Plots of the degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiments over a range of heating rates up to soak temperatures of 125 °C to 155 °C, followed by isothermal scan at that temperature. Data to the right of the y-axis correspond to the soak segment (step 2) while those to the left correspond to the ramp 1 segment (step 1).
Combined Ramp and Soak at 130°C

Combined Ramp and Soak at 135°C
APPENDIX B (continued)
APPENDIX C

2D plots of the rate of cure as a function of time for the combined ramp and soak experiments over a range of heating rates up to soak temperatures of 125 °C to 155 °C, followed by isothermal scanning at that temperature. Data to the right of the y-axis correspond to the soak segment (step 2) while those to the left correspond to the ramp 1 segment (step 1).
APPENDIX C (continued)

Combined Ramp and Soak at 135°C

Combined Ramp and Soak at 140°C
APPENDIX C (continued)

Combined Ramp and Soak at 145°C

Combined Ramp and Soak at 150°C
APPENDIX C (continued)

Combined Ramp and Soak at 155°C

![Graph showing rate of cure over time for different ramp rates.](image)
APPENDIX D

Plots of TMA results for MVK-14 Freeform™ polyimide prepreg subjected to prior curing consistent with the six cure steps in Table 5.3. The plot for TMA results after Step 1 cure is found in Figure 5.7
APPENDIX D (continued)

TMA Result MVK-14 FreeForm™ - Step 6 Cured

Dimension change (micrometer) vs. temperature (Celsius)
Plots of TMA results for PETI 365-A polyimide prepreg subjected to prior curing consistent with the five cure steps in Table 5.4. The plot for TMA results after Step 3 cure is found in Figure 5.8.