Characterization and Modeling of Amino Epoxide Resins

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CHARACTERIZATION AND MODELING OF AMINE
EPOXIDE RESINS

A Thesis
Presented to the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

by

Maria Anastasia Argiriadi
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

Maria Argiriadi

Approved, August 1994

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W. Gary Hollis, Jr.
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This thesis characterizes the kinetic, electrical, and rheological behavior of three epoxide amine systems throughout cure. The investigation is explained in three chapters.

Chapter I reviews the characterization methods used in this analysis. Frequency Dependent Electromagnetic Sensing (FDEMS), Differential Scanning Calorimetry, and Rheology are explained in theory and in instrumentation.

Chapter II proposes and illustrates a possible chemical mechanism for epoxide amine reactions. It also specifically discusses three particular resins used in future composite processing.

Chapter III describes the FDEMS method of calibrating and monitoring the cure processing properties of each resin. After the calibration procedures are explained, the macromolecular quantities $\alpha$ and $\eta$ are predicted for several composite processing experiments using FDEMS dielectric sensor output. This analysis is conducted with three experimental resins.
CHARACTERIZATION AND MODELING OF EPOXIDE AMINE RESINS
Introduction

The objective of this investigation was to characterize the physical and chemical properties of three epoxide resin systems by monitoring their changing ionic and dipolar mobility through FDEMS (Frequency Dependent Electromagnetic Sensing). The experimental rheological and thermal behavior of each resin was correlated with the dielectric loss scaled to frequency ($\varepsilon'' \omega$) where $\omega$ equals $2 \pi \times \text{frequency}$. This characterization was performed by conducting a series of rheometric, calorimetric, and dielectric experiments under different temperature conditions.

Following the experimentation, models and calibrations were created to characterize each epoxy amine resin with respect to its ionic and dipolar mobility. One major focus in this study was to propose optimal kinetic models which contributed to the control of processing properties of the resin in composite fabrication. These theoretical kinetic models were devised on the basis of previous empirical equations and the characteristics of each resin's reaction mechanism.

After sufficient calibrations and kinetic equations were developed, several resin transfer molding and resin film
infusion experiments were examined. Through FDEMS and accurate calibrations, the molecular and physical states of the resins were monitored in situ during each processing experiment. This information helps to optimize the time and temperature schemes of future processing experiments. This ensures efficient resin infiltration, complete wet-out of the fiber preform and a desired degree of cure of the composite part.
Chapter I. Theory and Instrumentation

Introduction

Composites consist of high strength and high modulus fibers which are bonded to a polymer matrix. The resulting properties can not be achieved with either of the constituents acting alone. Fiber-reinforced composites present lower specific gravities, excellent strength-weight and modulus-weight ratios which make these materials superior to metallic substances. There are several different methods of processing these materials: autoclave curing, injection molding, resin film infusion (RFI), and resin transfer molding (RTM). The latter two are important in this investigation. These two processes serve as cost and waste efficient means for producing composite parts. Resin film infusion molding consists of a fiber fabric preform on top of a layer of resin. The part is then encapsulated in a polymeric film bag. While temperature is increased, vacuum and pressure are applied to the bagged part enabling the resin to flow into the preform during the early stages of the cure cycle. Resin transfer molding consists of a mold holding a dry fiber preform and a low viscosity resin which is pumped into the mold. A valve between the resin supply vessel and mold is opened and resin
is allowed to flow from the supply vessel into the mold. When the mold is full it is sealed, the temperature is increased, and the resin begins to cure. The design of the molds in both of these examples is important because the resin must saturate the preform in order to make a good part.13.

An optimum cure cycle depends on several factors such as resin cure kinetics and rheological profiles. Frequency Dependent Electromagnetic Sensing (FDEMS) is an excellent monitoring technique to characterize rheological and thermal properties of the resin. An advantage of FDEMS is that it can monitor the property changes in situ. This is accomplished by establishing a relationship between the dielectric sensor output ($\varepsilon'$ and $\varepsilon''$) and the resin's physical properties (viscosity and degree of cure). Once experimental FDEMS calibrations are formulated, properties can be predicted during any point of the RFI or RTM cure cycle.

**Capacitance and Permittivity**

Capacitance is the ratio of charge ($q$) on the plates of a capacitor to the potential difference that exists between them. Therefore:

$$C_o = \frac{q}{V} \text{ (coulombs/volt = farads)} \quad [1a]$$

When a dielectric material occupies the space between the
capacitance plates, the material undergoes polarization due to the electric field induced by the potential difference. This is seen below (Figure 1.1):

![Figure 1.1](image)

Therefore the edges of the dielectric material have localized charge (+ or - p) which is in contact with the plates. The resulting capacitance is:

\[ C = \frac{(q+p)}{v} \]  

[1b]

The relative permittivity, \( \varepsilon \), is defined as the ratio of the capacitor with material and the capacitor experiencing a vacuum:

\[ \varepsilon = \frac{C}{C_0} \]  

[1c]

Since \( C_0 \) is constant, fluctuations in capacitance are analogous to fluctuations in the dielectric constant \( \varepsilon \). In FDEMS experimentation the electric field between the plates changes sinusoidally. At lower frequencies complete
polarization can occur because the molecules can maintain their alignment. At higher frequencies the faster alternating current prevents the dipolar molecules from moving into alignment.

Theory and Instrumentation of FDEMS

A flat disposable DekDyne sensor, composed of two interdigitated comb electrodes, is used to measure the capacitance (C) and conductance (G) of the epoxy resin from the measured dielectric impedance. The relationship between impedance and capacitance/conductance is shown below:

\[ Z^{-1} = G + i\omega C \]  

[2]

In this investigation measurements were collected by using a Schlumberger-Solartron 1260 Impedance Gain-Phase Analyzer or a Hewlett-Packard 4192A LF Impedance Analyzer. Below is an illustration of the instrumentation (Figure 1.2).
Through acquisition software, the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ is calculated over the range of 5 hertz to 1 megahertz. The real component $\varepsilon'$ is the relative permittivity discussed earlier and the imaginary component $\varepsilon''$ is the dielectric loss factor which relates to the lost energy due to the time-dependent polarization and ionic conduction\textsuperscript{5,8,13}.

Using the electronic relationships $I = i2\pi f CV$ [3a] and $C = \varepsilon C_0$ [3b], the geometry independent complex permittivity can be calculated. The following derivations apply to a dielectric material in a parallel-plate capacitor when a resistor and capacitor are in parallel\textsuperscript{4}. When substituting [3b] into [3a],

$$I = i2\pi f C_0 \varepsilon'' V$$

$$I = i2\pi f (\varepsilon' + i\varepsilon'') C_0 V$$

$$I = i2\pi f C_0 (\varepsilon'' + i\varepsilon') V$$

$$I = i2\pi f C_0 \varepsilon'' V + i2\pi f C_0 \varepsilon' V \quad [4]$$

Substitution with Ohm's law, $V = I*Z$, where $Z$ is the impedance or the total resistance:

$$Z^{-1} = (2\pi f C_0 \varepsilon'' V + i2\pi f C_0 \varepsilon' V) / V \quad [5]$$

$$Z^{-1} = 2\pi f C_0 \varepsilon'' + i2\pi f C_0 \varepsilon' \quad [6]$$

Therefore, when setting [2] and [6] equal to each other:

$$2\pi f C_0 \varepsilon'' + i2\pi f C_0 \varepsilon' = G + i2\pi f C$$

or

$$0 = 2\pi f C_0 \varepsilon'' - G + i2\pi C_0 \varepsilon' - i2\pi f C \quad [7]$$

When separating the real and imaginary components the
following equations result:

\[ \varepsilon' = \frac{C(\omega)_{\text{material}}}{C_0} \quad \varepsilon'' = \frac{G(\omega)_{\text{material}}}{\omega C_0} \quad [8] \]

where \( \omega \) is equal to \( 2\pi \) frequency, and \( C_0 \) is equal to the air-replaceable capacitance. Both real and imaginary parts of \( \varepsilon' \) have dipolar and ionic components as seen below in [9a] and [9b]:

\[ \varepsilon' = \varepsilon'_d + \varepsilon'_i \quad [9a] \]
\[ \varepsilon'' = \varepsilon''_d + \varepsilon''_i \quad [9b] \]

The dipolar component originates from rotational diffusion of bound charge and molecular dipole moments. This signal is detected mostly at high frequencies and in highly viscous media. The frequency dependence of this dipolar component is given in the following Cole-Davidson function:

\[ \varepsilon(\omega)_d = (\varepsilon_x - \varepsilon_u) / (1 - i2\pif\tau)^\beta + \varepsilon_u \quad [10] \]

where \( \varepsilon_x \) and \( \varepsilon_u \) are the limiting low and high frequency values of \( \varepsilon_d \), \( \tau \) is the relaxation time that quantifies the rotational mobility of the dipoles, and \( \beta \) is the Cole-Davidson distribution parameter (\( 0 < \beta < 1 \)) which measures the distribution in the relaxation times.

The ionic component results from the translational diffusion of charge resulting in localized layers of charge near the electrodes. This component dominates at lower frequencies, lower viscosities, and high temperatures. Johnson
and Cole derived equations for the ionic contribution to $\varepsilon^*$

$$\varepsilon'_i = \varepsilon'_u + (\varepsilon_r - \varepsilon_u)/(1 + (2\pi f \tau)^2) \quad [11a]$$

$$\varepsilon''_i = \sigma_i / 2\pi f \varepsilon_0 + (\varepsilon_r - \varepsilon_u) 2\pi f \tau / (1 + (2\pi f \tau)^2) \quad [11b]$$

where $\varepsilon_0$ is the permittivity in a vacuum ($8.85 \times 10^{-14}$ Farads/cm) and $\sigma$ is the conductivity (ohms$^{-1}$ cm$^{-1}$) which is dependent on the cell and sample size.

The first term in equation [11b] represents the conductivity of the free ions translating through the medium. At lower frequencies the ions are able to align with the electric field. However the second term expresses the charge polarization effects which are minimal at frequencies below 10 Hertz, or highly fluid resin states. When rearranging equation [11b]:

$$\varepsilon''i 2\pi f = \sigma / \varepsilon_0 + \left[ (\varepsilon_r - \varepsilon_u)((2\pi f)^2\tau) \right] / \left[ 1 + (2\pi f\tau)^2 \right] \quad [12]$$

The second term becomes negligible when the first term is extremely large. Therefore at frequencies where:

$$\sigma / \varepsilon_0 >> \left[ (\varepsilon_r - \varepsilon)((2\pi f)^2\tau) \right] / \left[ 1 + (2\pi f\tau)^2 \right] \quad [13]$$

The ionic conductivity is related to the loss factor:

$$\varepsilon''i 2\pi f = \sigma / \varepsilon_0 \quad [14]$$

As seen above, the frequency dependence of $\varepsilon^* \omega$ ($\omega = 2\pi f$) can determine ionic mobility, $\sigma$, and the rotational mobility, $\tau$, which quantitatively relates to the reaction advancement and viscosity of the resin. Therefore, it is this frequency
dependent parameter that is used to monitor properties in situ during composite processing in this investigation. In order to relate \( \varepsilon'' \omega \) with degree of cure and viscosity, differential scanning calorimetry and rheological experimentation is correlated with FDEMS measurements through a time dependence.

When examining a typical isothermal dielectric run of an epoxy-resin (Figure 1.3 below), each line represents an individual frequency.

![Figure 1.3](image)

Initially there is an overlapping band of frequencies. This illustrates that the ionic translational diffusion is the dominant physical process. With decreasing ionic mobility the
curves separate and illustrate that the rotational diffusion of bound charge and molecular dipole moment is dominant. As shown above, the noticeable peaks in the curve for the differing frequencies mark the dipolar diffusion peaks.

When relating this output to an amine-addition polymerization reaction, the sudden decrease in $\varepsilon''*\omega$ relates to a sudden decrease in mobility of ions suggesting a crosslinked network. Once oligomers are formed through an epoxide homopolymerization or a primary-amine addition, dipolar relaxations become frequency dependent.
Theory and Instrumentation of Differential Scanning Calorimetry

In order to measure the heat evolved in a curing reaction, experiments are performed in a Differential Scanning Calorimeter (DSC). The instrumentation monitors the rate of heat generation as a function of time. It is a technique which identifies glass transition temperatures, extent of polymerization and enthalpy of the reaction. As shown below (Figure 1.4) two calorimetric cells hold two sample pans, one experimental sample and one inert reference.

![Temperature sensors](image)

Aluminum pans are used to hold approximately 6 to 10 milligrams of epoxy resin. Holes are punched into each pan to allow release of any volatiles. Each of the individual cells contain a heating device which maintains equal temperatures in both pans, depending on whether the polymeric sample experiences an endo or exothermic reaction. The heat differential is plotted versus time or temperature.

The total heat generated to complete the polymeric cure

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(100% of cure) is equal to the area under either a dynamic or isothermal curve. It is expressed as:

\[ H_r = \int (dQ/dt) \, dt \]  
\[ H_{\text{total}} = H_{\text{residual}} + H_r \]

where \( H_r \) is the heat of reaction and \( (dQ/dt) \) equals the rate of heat of generation either in a dynamic test or isotherm. The degree of cure at any time \( t \) is defined as:

\[ \alpha_c(t) = H(t)/H_{\text{total}} \]

Therefore, the progression of the curing reaction can be monitored by observing alpha with respect to time or temperature.

In this investigation isothermal experiments were conducted at temperatures that were significant in the RFI or RTM processing cure cycles. After conducting an isothermal run for a particular sample, a reramp is conducted to obtain any residual heat that did not evolve during the isotherm. This residual heat is combined with the heat of reaction from the previous run to generate the total heat of reaction, \( H_{\text{total}} \) (equation [15b]). This information is integrated by a computer program which calculates the area under the isothermal curve in order to ascertain \( \alpha \) and \( d\alpha/dt \) (rate of cure).
Kinetics

Degree of cure, which is determined by experimental dynamic and isothermal DSC measurements, is used to design an ideal kinetic model to measure to the rate of the curing mechanism. Theoretical degree of cure can quantitatively project the amount of converted epoxide groups during a cure cycle.

The three experimental resins used in this investigation undergo epoxide amine reactions. There are several mechanisms, which will be illustrated, that are involved in the cure of the epoxy resins. Therefore, the rates of these individual mechanisms must be approximated.

To model the kinetics it was necessary to derive an equation expressing da/dt as a function of a and temperature. Statistical fits were conducted for each proposed model. Once strong theoretical models were generated, the degree of cure was correlated with the FDEMS dielectric response in order to monitor a throughout an entire RTM or RFI experiment.
Rheology describes two concepts (1) the relation between stress and strain which relate to deformational geometries and (2) the physical response a material displays under a given stress i.e. viscous flow$^{1,2}$. In this investigation rheology is used to elucidate the nature of the flow properties of each epoxy resin system in order to optimize composite processing.

There are three different stress relationships that render three deformational geometries. They are as follows:

(1) Extension deformation is where a material of a certain length and cross sectional area is deformed along the axis perpendicular to that area as shown below in Figure 1.5$^2$:

![Figure 1.5](image-url)
The following mathematical relationships represent stress and strain where the force applied changes unit length $L$ to $L'$ and area $A$ to $A'$. The resulting strain represents the changes in length divided by the unit length.

\[
\sigma = \frac{F}{A} = \text{stress} 
\]
\[
\epsilon = \frac{dL}{L} = \ln \frac{L'}{L} = \text{strain} 
\]

(2) Shear deformation is the stress and strain relationship used in rheometric measurements. It characterizes the stress that is applied tangent to the surface area of the material (Figure 1.6). This causes a displacement measured as $x^{1,2,14}$.

\[
\tau = \frac{F}{A} = \text{shear stress} 
\]
\[
\gamma = \frac{x}{L} = \text{shear strain} 
\]

Viscosity is expressed in terms of shear deformation due to internal friction which occurs when one layer of fluid is caused to move in relationship to another layer. A proportionality constant $\eta$ sets the relationship between the
stress and strain as shown below:

\[ \tau = \eta \ast \dot{\gamma} \]  \hspace{1cm} [19]

where \( \dot{\gamma} \) = rate of change of strain.

(3) Bulk deformation is classified as pressure applied to all surface areas which results in strain per unit volume denoted \( \delta V/V^2 \). 14

Viscoelasticity, which describes a material’s ability to resist flow or behave as an elastic, is a response to the stresses which are applied. If a material flows and deforms under stress, energy is released as heat. However if the material is an ideal elastic heat is not released. Energy is stored until the deformation is reversed upon removal of the stress. The elastic response is illustrated in the following equation which is quite similar to the viscosity shear stress and strain relationship. 2

\[ \tau = G \ast \gamma \]  \hspace{1cm} [20]

where \( G \) is the modulus of the material which relates to the material’s stiffness.

A polymeric resin’s response is a combination of viscous and elastic behavior (viscoelasticity). 5 Therefore \( G \) which denotes the modulus and \( \eta \) which denotes the viscosity constant are two important parameters that are monitored in this investigation.
Dynamic mechanical testing was conducted on each epoxy resin system. This is when a material is subjected to a sinusoidal strain in order to measure stress. If the material is an ideal elastic solid the stress and strain signals are in phase and have the same amplitude. However if the solid acts as ideal fluid then the stress and strain signals are out of phase by $90^\circ$. It is the material's viscoelastic behavior that results in a phase shift angle $\delta$. The angle $\delta$ lies between the in phase and out of phase extremes. The following diagram shows both shear strain and shear stress and the phase shift between these components (Figure 1.7). 

When conducting dynamic mechanical testing $G'$ is the elastic modulus parameter that represents the ability to store deformational energy. $G''$ is the viscosity modulus parameter which represents the ability of the polymeric material to
dissipate energy as heat. These two terms combine to generate the complex modulus which is the overall resistance to deformation. The following equations demonstrate how these moduli are calculated through the shear stress and strain relationship:

\[ G' = \frac{\tau'}{\gamma} = \frac{\tau''}{\gamma \cos \delta} \]  \[21a\]

\[ G'' = \frac{\tau''}{\gamma} = \frac{\tau''}{\gamma \sin \delta} \]  \[21b\]

where \(\delta\) is the phase shift angle between stress and strain, \(\tau'\) is the ratio of elastic stress, and \(\tau''\) is the ratio of viscous stress.

\[ G^* = \frac{\tau''}{\gamma} \quad \text{or} \quad G^* = G' + iG'' \]  \[21c\]

where \(G^*\) is equaled to the complex modulus

\[ \eta^* = \frac{G^*}{\omega} \]  \[21d\]

where \(\eta^*\) is the dynamic viscosity which represents the ability of a material to dissipate energy as a function of the shear rate. The variable \(\omega\) denotes the angular frequency.

In this investigation a parallel plate arrangement was used to conduct experimentation (Figure 1.8). A computer test center controls temperature, data collection, and manipulation using RECAP2 acquisition software. The computer sends signals to apply a deformational force upon the sample. The torque transducer measures the applied stress with respect to the strain and sends signals back to the computer to calculate the
desired moduli $G', G''$ and $\eta^{11}$.

When establishing a viscosity profile for a particular epoxy thermoset resin, it is important to identify the gelation point. This point measures the time at which the molecular weight of a resin goes to infinity or an infinite crosslinked network can be detected. The time at which the elastic and viscosity moduli reach equilibrium ($G' = G''$) marks the gelation point$^{16}$. Knowledge of this time and the trend of the dynamic viscosity of a particular resin system is needed to optimize composite processing. A low viscosity epoxy is desired when the resin is introduced into a preform or mold.
Sensor wetout (when each sensor is covered by resin) is dependent on the resin's ability to flow within the mold before gelation time. In order to become familiar with the flow properties of each experimental resin, isothermal holds and temperature sweeps were conducted. Values of $\eta$ were then correlated to FDEMS measurements to create a viscosity model.
Chapter I. References


Chapter II. Chemistry of Epoxy Research Resins

Introduction

An epoxy resin is defined as any molecule containing more than one alpha epoxy group in order to generate crosslinking. The extensive three dimensional crosslinking enables the resin to become a thermoset. Most epoxy resins are characterized as excellent adhesives to a variety of substrates and reinforcements. They display low shrinkage during cure and have outstanding thermal stability, chemical and solvent resistance properties. These properties make these resins ideal for fiber-reinforced composite processing.

All three experimental resins discussed in this investigation possess curing mechanisms that have amine addition reactions. There are several classifications of amine curing agents: aliphatic, cycloaliphatic, and aromatic. All three resins react with aromatic amines. These curing agents have a useful storage life as opposed to aliphatics and cycloaliphatics. Their relatively small nucleophilic character and bulky nature increases the cure temperature and the room temperature viscosity. The concentration of this amine curing agent depends on the molecular weight of the amine, the number of active hydrogens in the amine, and the equivalent weight of
The following set of reactions display simplified versions of the amine epoxide curing mechanisms (Figure 2.1):

1. \( \text{NH}_2 + \text{CH}_2\text{CH}_2 + \rightarrow \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} \)
   - Primary amine
   - Epoxide
   - Secondary amine
   - Hydroxyl

2. \( \text{HO-CH}_2\text{CH}_2\text{NH} + \text{CH}_2\text{CH}_2 + \rightarrow \text{HO-CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OH} \)
   - Secondary amine
   - Epoxide
   - Tertiary amine
   - Hydroxyl

3. \( \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_2\text{CH}_2 + \rightarrow \text{NH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \)
   - Hydroxyl
   - Epoxide
   - Ether
   - Hydroxyl

4. \( \text{n CH}_2\text{CH}_2 + \rightarrow \text{n CH}_2\text{CH}_2\text{O} \)
   - Epoxide
   - Ether

Figure 2.1
As seen in these mechanisms, epoxide consumption is hydroxyl auto catalyzed after the primary amine reaction occurs. In reaction #3 an ether linkage occurs between an epoxide and a hydroxyl group. Reaction #4 is a homopolymerization which can occur due to the presence of impurities or specific catalysts (discussed later).

3501-6 Experimental Resin

3501-6 is an experimental resin produced by Hercules and was obtained from NASA Langley Research Center, Hampton, Virginia. This resin was used in three resin film infusion experiments at Northrop Research Center, California. 3501-6 contains the following components1,3:

(1) one major epoxide - tetraglycidyl 4,4' diaminodiphenyl methane (TGMDA or TGDDM) (Figure 2.2)

(2) two minor epoxides - (a) alicyclic diepoxy carboxylate
(b) epoxy cresol novolac
In order to demonstrate amine epoxide cure mechanisms, Hercules 3501-6 will be discussed in detail. When heating the 3501-6 resin system to a temperature of 177°C, epoxide consumption occurs predominantly by chain extension by ether linkages. There are three different reactions that determine the total rate of polymerization: the primary amine reaction, the secondary amine reaction, and the epoxide hydroxyl reaction. Examples of these postulated mechanisms are shown in Figure 2.4.
(i) secondary amine reaction

(ii) secondary hydroxyl reaction

(iii) epoxide hydroxyl reaction

Figure 2.4
The primary amine reaction has been determined to proceed a magnitude faster than the secondary hydroxyl and the epoxide hydroxyl reactions. Thus, it dominates the early stages of cure. When devising a kinetic model, all three of epoxide conversions shown above should be incorporated into a comprehensive kinetic equation.

The Lewis acid, boron trifluoride monoethylamine is an effective catalyst for the homopolymerization of 3501-6 epoxy resin system. It acts as a chain propagator where its Lewis acid properties coordinate with the epoxy functionality as shown below. The epoxy group solvates the catalysts, creating an oxonium ion which is then attacked by other epoxides (Figure 2.5a and 2.5b).

![Figure 2.5a and 2.5b](image)

This process continues until a highly three-dimensional crosslinked network is formed (Figure 2.6).
Increasing the concentration of this catalyst enhances the production of uniform networks with fewer defects, resulting in improved mechanical properties. This particular boron trifluoride derivative has negligible reactivity at room temperature but initiates homopolymerization at around 80°C-100°C.

In a paper presented by Roger J. Morgan and Eleno T. Mones, statistical probabilities were calculated to demonstrate that 75% of secondary and epoxide-hydroxyl reactions form rings. At later stages of cure, when viscosity reaches a maximum and diffusion restrictions are high, intramolecular crosslinking predominates over intermolecular crosslinking. This enables the resin to reach full cure.
Shell 1895 Research Resin

Shell 1895 resin-curing agent system contains two parts: (1) a mixture of three multifunctional epoxy additives and (2) an amine curing agent. For proprietary reasons, the exact structures of these three epoxy additives are not disclosed. The major multifunctional monomer is known to be a derivative of a newly introduced high performance resin called Epon HPT 1071, N,N,N',N'-tetraglycidyl-α,α'-bis(4-aminophenyl)-p-diisopropylbenzene (shown Figure 2.7)\textsuperscript{1,10}.

![Figure 2.7 Epon HPT resin 1071](image)

The structure is very similar to 3501-6's tetrafunctional epoxy resin. TGDDM and HPT 1071 are both products based upon epichlorohydrin and bisphenol A chemistry (Figure 2.8)\textsuperscript{9}:

![Figure 2.8 Epichlorohydrin](image)

The high aromatic content in these resins provides
thermal stability, backbone rigidity and increased crosslinking density\textsuperscript{1,6}.

The curing agent in the Shell 1895 system is 100% diethyl toluene diamine. The following is a proposed structure (Figure 2.9)\textsuperscript{10}:

![Figure 2.9](image)

This aromatic amine provides a longer pot life which is suitable for experimental testing and composite processing. It displays excellent chemical resistance and cures at elevated temperatures.

**PR500 Experimental Resin**

Unlike Shell 1895 and 3501-6, PR500 epoxy resin (Figure 2.10) is based on diglycidyl ether of fluorene bisphenol. The exact structures of the amine curatives and additives are not disclosed for proprietary reasons\textsuperscript{10,11}. Incorporation of the rigid groups shown below, gives desirable properties such as improved thermal stability, improved solubility, and an increased Tg with low crosslink density. This last
characteristic provides PR500 with higher ductility and decreased moisture intake. These enhanced properties are ideal for composite processing."
References for Chapter II


11. 3M Aerospace Materials Department, "Material Safety Data Sheet."

Chapter III. Processing and In situ Monitoring of Three Experimental Resins

Characterization of Hercules 3501-6 Experimental Resin

The Hercules 3501-6 resin system was characterized by its viscosity properties, degree of cure, and frequency dependent dielectric behavior. Through extensive experimentation, these properties were closely observed at three different isothermal temperatures: 121°C, 149°C, and 177°C.

Kinetic Analysis

The experimental degree of cure of Hercules 3501-6 was monitored by a Differential Scanning Calorimeter (DSC) at the three crucial temperatures. Polymeric samples, ranging from 6 to 10 mg, were placed in standard aluminum pans. The heat evolved from the milligram sample of 3501-6 was measured with respect to time. Each isothermal run was followed by a 50-300°C reramp of the same resin sample at 2°C/min. This was conducted to obtain any residual heat not released in the original isotherm. Figures 3.1a-3.1c and 3.2a-3.2c display these isothermal runs with their respective reramps. Heats of reaction were calculated through an integration program called PLOTHEAT.BAS which transforms raw heatflow, time, and
3.1a DSC Isothermal Cure of 3501-6 @ 121°C

3.2a DSC Temperature Ramp after a 121°C Isothermal Cure of 3501-6
3.1b  DSC Isothermal Cure of 3501-6 @ 149°C

3.2b  DSC Temperature Ramp after a 149°C Isothermal Cure of 3501-6
3.1c DSC Isothermal Cure of 3501-6

3.2c DSC Temperature Ramp after a 177°C Isothermal Cure of 3501-6
temperature data to heats of reaction, $\alpha$, and $d\alpha/dt$ with respect to time. The program is designed to integrate the area under the curve during the total run time. The degree of cure can be determined by the expression $\alpha = H/H_r$ where $H$ is the heat calculated at time $t$ and $H_r$ is the heat evolved from the entire reaction. The rate of cure $d\alpha/dt$ can be expressed by:

$$d\alpha/dt = (dQ/dt)/H_r$$

The following (regularly used) model equations were considered to fit the experimental DSC data.

1. $d\alpha/dt = k \times (1-\alpha)^n$
2. $d\alpha/dt = k \times (\alpha)^m \times (1-\alpha)^n$
3. $d\alpha/dt = (k_1 + k_2 \times \alpha^n) \times (1-\alpha)^n$

These three empirical kinetic equations given above are generally considered when choosing a mechanistic kinetic model for an amine epoxide system. Equation #3 is the Kamal equation which has been found to be successful when applied to most autocatalytic epoxy systems.

In amine-cured epoxies there are three main reactions: the primary and secondary amine reactions with the glycidyl ether and the etherification through a pendant hydroxyl group. The primary and secondary amine reactions are autocatalyzed by the presence of hydroxyl groups from water, the amines themselves, or impurities. The three equations given above can successfully represent this autocatalytic behavior for most amine epoxide systems.
resins.

In order to test these proposed equations, SYSTAT statistical software and BASIC computer fit programming were used to calculate possible parameters with a least square fit method. When attempting to use the equations given above for autocatalytic behavior of 3501-6, very large statistical losses resulted. The problem lay in the fact that Hercules 3501-6 is a complex mixture containing not only TGDDM and DDS, as discussed earlier, but also two other epoxies. This deviates from typical autocatalytic behavior because two extra rate constants need to be included in the comprehensive kinetic equation. In order to obtain a strong detailed kinetic model, Hercules 3501-6 was therefore treated as a complex curing resin. Complex curing behavior, as described by P. Chiu and A. Letton\textsuperscript{1} is displayed by a resin exhibiting more than one independent epoxy reaction occurring in the course of the cure. These three reactions dominate at different temperature settings, and therefore should have separate rate constants in the comprehensive kinetic equation. They performed a series of DSC ramps at 1.25K/min, 5.00K/min, and 20K/min (Figure 3.3)\textsuperscript{1}. They found three observable peaks, one characterizing a major reaction and two smaller peaks indicating secondary reactions. Furthermore, they evaluated
the complex curing behavior of 3501-6 by the following verified kinetic parameters:

[Table 3-1]

<table>
<thead>
<tr>
<th></th>
<th>ln A (1/sec)</th>
<th>E/R (K)</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major</td>
<td>17.37</td>
<td>11220</td>
<td>1.06</td>
<td>0.850</td>
</tr>
<tr>
<td>Medium</td>
<td>19.16</td>
<td>10250</td>
<td>1.17</td>
<td>0.095</td>
</tr>
<tr>
<td>Minor</td>
<td>46.22</td>
<td>20570</td>
<td>3.05</td>
<td>0.055</td>
</tr>
</tbody>
</table>

From the Arhenius equation \( \ln k = \ln A + \left( -\frac{E}{RT} \right) \), values of the rate constant for the major, medium, and minor independent reactions were determined at the temperatures 121°C, 149°C, and 177°C. This rate constant is used to determine \( \frac{da}{dt} \) through nth-order polynomial equation:

\[
\frac{da}{dt} = k (1-a)^n
\]

where \( N \) equals a reaction order parameter (listed above) for all independent reactions. The following table lists calculated values for rate constants \( k_1, k_2, \) and \( k_3 \) at the three critical temperatures.
DSC ramps at 1.25K/min, 5.00K/min, and 20K/min
Assuming that $\alpha$ is equaled to zero at time zero, $\frac{d\alpha}{dt}$ can be determined. For example, for the major reaction at 121°C or 354K:

$$
\frac{d\alpha}{dt} = \ln(\ln A + \frac{-E}{RT}) \times (1-\alpha)^n
$$

at $t(0)$:

$$
\frac{d\alpha}{dt} = \ln(17.37 + (-11220K/354K) \times (1-0)^{1.05})
$$

$$
\frac{d\alpha}{dt} = (0.00912) \times (1)
$$

$$
\frac{d\alpha}{dt} = 0.00912
$$

Through backcalculation the degree of cure, $\alpha$ can be determined:

$$\alpha(t_{n}) = \alpha(t_{n-1}) + d\alpha$$

The degree of cure was determined for each independent reaction of the complex cure. In order to calculate the total value of $\alpha$ the following expression was used:

$$
\frac{d\alpha}{dt} = c_1(\frac{d\alpha}{dt}) + c_2(\frac{d\alpha}{dt}) + c_3(\frac{d\alpha}{dt})
$$

where $c$ expresses a weight factor which varies according to the independent reaction\textsuperscript{1}. As demonstrated by this equation all reactions, medium, minor, and major contribute to the total degree of cure of the resin system. This theoretical kinetic fit is compared to experimental DSC data previously
discussed. When comparing experimental $\alpha$ with theoretical $\alpha$, an adequate fit is observed for 121°C and 177°C (Figures 3.4a and 3.4b). The theoretical kinetic reaction model was used to predict time and temperature dependence of the degree of cure in future correlations with viscosity and dielectric behavior.

**Viscosity Determination**

To measure the viscoelastic properties of Hercules 3501-6, rheological experiments were conducted with a Rheometrics RDA-700 Dynamic Analyzer. Isothermal holds were executed through a parallel plate arrangement. A sample of 3501-6 was placed between parallel plates resulting in a gap ranging from 0.6 to 0.8 millimeters. Three important variables were monitored, $G'$, $G''$, and $\eta$. $G'$ represents the elastic storage modulus which measures the ability to store deformational energy within the resin. $G''$ represents the loss modulus which measures the ability for resin to dissipate heat. When plotting $G'$ and $G''$ versus time a cross-over was observed. This indicates that the chemical gelation point has been reached. From the plots shown in figures 3.5b, 3.6b, 3.7b gelation points were estimated at the three crucial temperatures.

45
3.4a $\alpha$ versus time for theoretical and experimental $\alpha$ for 121°C

3.4b $\alpha$ versus time for theoretical and experimental $\alpha$ for 177°C
The crossover or gelation point indicates the point at which viscosity is no longer a measurable property due to the extensive crosslinking in the resin. Therefore all calibrations were calculated up until this point.

Viscosity or $\eta$ characterizes the resins resistance to flow measured in Poise (P). Figures 3.5a, 3.6a, 3.7a display the relationship between $\eta$ and time at the three chosen temperatures. As the temperature increases, the resin initially becomes fluid but later advances to a tough crosslinked solid. This causes $\eta$ to increase exponentially.

**FDEMS**

In addition to kinetic and rheometric investigations, in situ frequency dependent electromagnetic measurements were collected at several isothermal settings. In each dielectric experiment, kapton sensors were thinly coated with 3501-6 resin in a small tin sample pan. A thermocouple was housed on one side of the sensor in order to monitor the
3.5a  \( \eta \) versus Time for Isothermal Cure of 3501-6 @ 121°C

3.5b  \( G' \) and \( G'' \) versus Time Plot for Isothermal Cure 3501-6 @ 121°C
3.6a  η versus Time for Isothermal Cure of 3501-6 @ 149°C

3.6b  G' and G'' versus Time Plot for Isothermal Cure of 3501-6 @ 149°C
3.7a \( \eta \) versus Time for Isothermal Cure of 3501-6 @ 177°C

3.7b \( G' \) and \( G'' \) versus Time Plot for Isothermal Cure 3501-6 @ 177°C

50
impedance bridge were connected to the sensor. Each experiment generated a log ε"*ω versus time relationship. Through impedance measurements, physical properties such as degree of cure and viscosity were able to be monitored. The dielectric loss ε" relates to the ionic and rotational mobility of the dipole. This mobility parameter can be applied to α and η.

**Calibrations**

The first relationship that was examined was the time-based correlation between experimental η and theoretical α. These can be observed in Figures 3.8a and 3.8b. There is an initial linearity that is seen in this relationship. However, data points deviate when the gel point is reached. During and after gelation, viscosity escalates exponentially with small increments in α. These figures demonstrate that η increases at a faster rate in relation to α at both 121°C and 149°C.

The degree of cure and viscosity were later correlated to the magnitude of the frequency dependent dielectric measurement ε" (the dielectric loss). In order to use this monitoring technique, isothermal runs were conducted at 80°C, 100°C, 121°C, 149°C, and 177°C. As seen in Figures 3.9a-3.9e, there is an ionic band that spans each plot diagonally. This band of overlapping frequencies indicates that ionic
Calibration Plot 121°C 3501-6
alpha and vs log eta

3.8a \( \alpha \) versus log eta calibration for 121°C

Calibration Plot 149°C 3501-6
alpha vs. log eta

3.8b \( \alpha \) versus log eta calibration for 149°C
translational diffusion dominated at that point in time. From a wide range of eleven frequencies, 5 kilohertz was selected because it was deemed the best representative frequency for cure monitoring. Time zero was designated for both the dielectric and viscosity data at each critical temperature in order to assure thermal equilibrium in each experiment. The highest point in the ionic band marked t(0) for the FDEMS isotherm data. Therefore, the offset time for these calibrations ranged approximately from 5 to 10 minutes for each temperature. The rheometric t(0) was designated by drawing a smooth curve through beginning points due to initial scattering. The first consistent point on this smooth curve was considered time zero. Calibration plots were generated to show the relationship between log ε"*ω, the degree of cure, and viscosity at all three temperatures.

When establishing a correlation between viscosity and ε"*ω, an inverse linear relationship is observed. When comparing this calibration with an earlier calibration ('90-'91), the slopes remain consistent. This type of temperature independent calibration (Figure 3.10) is used to monitor viscosity during all stages of the RTM cure cycle.

However, the calibrations between ε"*ω and α are temperature dependent. Different calibration plots are used to
monitor different times in the cure cycle. These calibrations are displayed in figures 3.11a-3.11d.

A third type of correlation was generated for the 177°C isotherm. In order to monitor late stages of cure the slope method was used. This correlation illustrates the relationship between the normalized rate of change of ε" ((dε"/dt)/ε" at 5 kHz) and theoretical α. The rate of change was evaluated with a one point (Figure 3.12) and a five point (Figure 3.13) averaging method. The one point average was used in all subsequent calibrations and RFI correlations due to more constant data. As seen by the plot, α can be predicted in late stages of cure through monitoring the dielectric loss.

Simulated RTM ramp/hold/ramp/hold experiments

Three simulated RTM ramp/121°C hold/ramp/177° hold sequences were conducted rheometrically and dielectrically with two resin batches (two runs with newly received 6/2/94 and one run with batch received 4/93).
3.9a  FDEMS Isothermal Cure of 3501-6 @ 80°C

3.9b  FDEMS Isothermal Cure of 3501-6 @ 100°C
3.9c  FDEMS Isothermal Cure of 3501-6 @ 121°C

3.9d  FDEMS Isothermal Cure of 3501-6 @ 149°C
3.9e  FDEMS Isothermal Cure of 3501-6 @ 177ºC

3501-6 Calibration
$e''*\omega$ vs. eta

3.10  log $\eta$ versus log $e''*\omega$ Plot for 100ºC, 121ºC, 135ºC, and 149ºC Isothermal Data
3.11a  \( \alpha \) versus \( \log \epsilon^n \omega \) for 80°C Calibration

3.11b  \( \alpha \) versus \( \log \epsilon^n \omega \) for 100°C Calibration
3.11c $\alpha$ versus log $e^{**w}$ for 121°C Calibration

3.11d $\alpha$ versus log $e^{**w}$ for 149°C Calibration
3.12 Slope \( \frac{d\epsilon}{dt}/\epsilon \) \( \times \) \( \alpha \) versus Time for 177°C Calibration using Successive Points

3.13 Slope \( \frac{d\epsilon}{dt}/\epsilon \) \( \times \) \( \alpha \) versus Time for 177°C Calibration using Five Point Method
Figures 3.14a-f display the output from these runs. The temperature independent $\eta$ versus $\epsilon'^\omega$ calibration model was used to predict viscosity for the three dielectric runs. These predictions (Figures 3.15a-c) were compared to experimental rheometric results. The two minimums that are observed in the predicted and experimental values of $\eta$ occur during the two ramps. When temperature is incremented during the ramp, the initial flow increases due to increased kinetic activity. The three rheometric runs display consistent minimums at approximately 10 Poise and at approximately 20-30 Poise. This indicates that there are no observable differences between batches. These minimums compare to documented values (McDonnel Aircraft 15 January 1985 Figure 3.15d). When observing the predicted viscosities (Figures 3.15a-c) for the dielectric runs, the two old batch runs (ma051294 and ar061394) displayed much higher minimums. The new batch (ar060894) displayed predicted viscosities that matched the experimental minimums. This discrepancy in the dielectric backcalculation was probably due to experimental error, possibly in the FDEMS experimentation.
3.14a FDEMS ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with Old Resin on 5/12/94

3.14b Rheometer ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with Old Resin on 5/12/94
3.14c FDEMS ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with New Resin on 6/8/94

3.14d Rheometer ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with New Resin on 6/8/94
Data file: b: ar061394

3.14e FDEMS ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with Old Resin on 6/13/94

3.14f Rheometer ramp/hold at 121°C/ramp/hold at 177°C
Sequence Conducted with Old Resin on 6/13/94
Correlated Viscosity
for ma051294

Correlated Viscosity
for new rec'd resin 3501-6 ar060894

3.15a Backcalculated Viscosity for FDEMS run ma051294

3.15b Backcalculated Viscosity for FDEMS run ma060894

65
Correlated Viscosity
for old rec'd resin 3501-6 ar061394

![Graph showing correlated viscosity data with temperature and time on the axes.]

3.15c Backcalculated Viscosity for FDEMS run ma061394

3.15d McDonnel Aircraft Predicted Viscosity Values of 3501-6 for ramp/hold/ramp/hold Sequence
Correlation of $\alpha$ and $\eta$ with three RFI experiments

Hercules 3501-6 was the epoxy experimental resin used in three RFI experiments at Northrop B-2 Aircraft Facility on October 21, 1993, February 15, 1994 and April 12, 1994. A woven carbon fibered T stiffened panel was placed on top of a film of 3501-6 resin in an autoclave. No preheating was necessary in these RFI experiments. Through a film infusion effect, the resin was pulled and compacted into the T stiffened panel in the presence of a vacuum while the resin was liquified. A total of nine sensors were used in each experiment. Figures 3.16a-c display a 3-dimensional representation of all sensors on the preforms for the three experiments. Frequency dependent electromagnetic sensing was used to collect in situ measurements during the fabrication of the composite part. Dekdyne computer software stored impedance measurements during the Resin Film Infusion experiments and calculated the dielectric loss factor, $\varepsilon''$. Given the FDEMS measurements of the RFI, the value of $\varepsilon'' \times \omega$ was calculated by multiplying $\varepsilon''$ with $2\pi f$ (where $f$ equals frequency). Five kilohertz was chosen as the representative frequency as in the calibrations previously discussed. By extrapolating values of $\eta$ and $\alpha$ from the respective calibration plots, degree of cure and viscosity were monitored for each RFI experiment. In order to
3.16a Sensor Locations on T-stiffened Panel in Resin Film Infusion Run at Northrop 10/21/93
3.16b Sensor Locations on T-stiffened Panel in Resin Film Infusion Run at Northrop 2/15/94
3.16c Sensor Locations on Trapezoid-stiffened Panel in Resin Film Infusion Run at Northrop 4/12/94
backcalculate the viscosity, the log $\epsilon''*\omega$ versus log $\eta$ calibration was used. For backcalculating degree of cure, several temperature calibrations were used because $\alpha$ is a temperature dependent variable. For example, the 121°C calibration $\alpha$ versus $\epsilon''*\omega$ is used to predict degree of cure during the RFI 121°C hold and the 80°C and 100°C calibrations are used to determine points during the initial ramp.
October 21, 1993

A woven carbon-fiber T stiffened panel was used in a autoclave set for measuring K thermocouple millivoltages. This presented a problem for analysis because J type thermocouples were used to measure autoclave temperatures inside the bag on the preform. K type thermocouples were used to measure air temperatures outside the bag. When the K thermocouple temperature measurements were converted to J thermocouple readings, it was shown that the experiment did not reach the appropriate temperature holds.

The following table displays the sensor wetout times for dh102193:

[Table 3-4]

<table>
<thead>
<tr>
<th>sensor #</th>
<th>wetout time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94.0</td>
</tr>
<tr>
<td>2</td>
<td>32.0</td>
</tr>
<tr>
<td>3</td>
<td>36.0</td>
</tr>
<tr>
<td>4</td>
<td>27.0</td>
</tr>
<tr>
<td>5</td>
<td>45.0</td>
</tr>
<tr>
<td>6</td>
<td>110.0</td>
</tr>
<tr>
<td>7</td>
<td>disconnected</td>
</tr>
<tr>
<td>8</td>
<td>103.0</td>
</tr>
<tr>
<td>9</td>
<td>85.0</td>
</tr>
</tbody>
</table>
Sensor numbers 1, 4, 5, 6, 8 and 9 were analyzed for this run. FDEMS raw outputs are displayed in Figures 3.17a-f. The correlated degree of cure and correlated viscosity plots (Figures 3.18a-f and 3.19a-f) for each sensor display peculiarities because the preform failed to reach the desired temperature hold. The resin never reached full cure as displayed by each of the correlated degree of cure plots. When examining the predicted viscosity of this run, there are exaggerated minimums. Since the initial temperature hold was lower than the expected 121°C hold, the resin was less advanced entering the second ramp. The resin experienced more flow indicated by an exaggerated minimum. Viscosity is quenched at approximately 230 minutes for each sensor.
3.17a FDEMS Output of RFI Run at Northrop 10/21/93
Probe #1

3.17b FDEMS Output of RFI Run at Northrop 10/21/93
Probe #4
3.17c FDEMS Output of RFI Run at Northrop 10/21/93
Probe #5

3.17d FDEMS Output of RFI Run at Northrop 10/21/93
Probe #6
3.17e FDEMS Output of RFI Run at Northrop 10/21/93
Probe #8

3.17f FDEMS Output of RFI Run at Northrop 10/21/93
Probe #9
3.18a Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #1

3.19a Viscosity Correlation with RFI Experiment
dh102193.c Probe #1
3.18b Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #4

3.19b Viscosity Correlation with RFI Experiment
dh102193.c Probe #4
3501-6 dh102193.c Probe #5
Correlated Degree of Cure

3.18c Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #5

3501-6 dh102193.c Probe #5
Correlated Viscosity

3.19c Viscosity Correlation with RFI Experiment
dh102193.c Probe #5
3.18d Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #6

3.19d Viscosity Correlation with RFI Experiment
dh102193.c Probe #6
3.18 Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #8

3.19 Viscosity Correlation with RFI Experiment
dh102193.c Probe #8
3501-6 dh102193.c Probe #9
Correlated Degree of Cure

\[ \text{Alpha} \]

\[ \text{Temperature (C)} \]

\[ \text{Time} \]

3.18f Degree of Cure Correlation with RFI Experiment
dh102193.c Probe #9

3501-6 dh102193.c Probe #9
Correlated Viscosity

\[ \text{Eta} \]

\[ \text{Temperature (C)} \]

\[ \text{Time} \]

3.19f Viscosity Correlation with RFI Experiment
dh102193.c Probe #9
February 15, 1994

This RFI used a T stiffened panel in an autoclave. The thermocouples used for analysis (3, 4, 5, 6, 7, and 8) were J type and located on the preform inside the bag film. The autoclave time was adjusted to the actual FDEMS time in the data file. This was done to match thermocouple temperature data with dielectric data. The following table lists wetout times for the nine sensors according to the FDEMS and autoclave clocks:

[Table 3-5]

<table>
<thead>
<tr>
<th>sensor #</th>
<th>FDEMS time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.4</td>
</tr>
<tr>
<td>2</td>
<td>104.8</td>
</tr>
<tr>
<td>3</td>
<td>168.5</td>
</tr>
<tr>
<td>4</td>
<td>114.8</td>
</tr>
<tr>
<td>5</td>
<td>97.4</td>
</tr>
<tr>
<td>6</td>
<td>168.6</td>
</tr>
<tr>
<td>7</td>
<td>109.8</td>
</tr>
<tr>
<td>8</td>
<td>99.9</td>
</tr>
<tr>
<td>9</td>
<td>163.2</td>
</tr>
</tbody>
</table>

Similar wetout times result from similar sensor locations on the preform. Sensors #1, #3, #4, #6, and #9 were analyzed for this run. FDEMS raw output are displayed in Figures 3.20.
a–e. All of the sensors displayed similar rates of cure (Figures 3.21 a–e), except sensor #1 which was the first to wetout. When examining correlated viscosity Figures (3.22a–e), sensors #3 and #6 appear to have similar minimums during the 121–177°C ramp ranging 20 to 25 Poise. Sensors #4 and #9 have lower minimums ranging from 12 to 15 Poise. Sensor #1, which was the first to wetout and located on the lowest level of the preform, displayed the highest minimum.
3.20a FDEMS output for RFI run at Northrop 2/15/94
dh021594/1st continue/2nd continue Probe #1
85
3.20b FDEMS output for RFI run at Northrop 2/15/94
dh021594/1st continue/2nd continue Probe #3
3.20c FDEMS output for RFI run at Northrop 2/15/94
dh021594/1st continue/2nd continue Probe #4
3.20d FDEMS output for RFI run at Northrop 2/15/94
dh021594/1st continue/2nd continue Probe #6
3.20e PDEM output for RFI run at Northrop 2/15/94
3000 continue 2nd continue Probe #9
89
3.21a Degree of Cure Correlation with RFI Experiment
dh021594 Probe #1

3.22a Viscosity Correlation with RFI Experiment
dh021594 Probe #1
3.21b Degree of Cure Correlation with RFI Experiment
dh021594 Probe #3

3.22b Viscosity Correlation with RFI Experiment
dh021594 Probe #3
3.21c Degree of Cure Correlation with RFI Experiment
dh021594 Probe #4

3.22c Viscosity Correlation with RFI Experiment
dh021594 Probe #4
3.21d Degree of Cure Correlation with RFI Experiment
dh021594 Probe #6

3.22d Viscosity Correlation with RFI Experiment
dh021594 Probe #6
3.21e Degree of Cure Correlation with RFI Experiment
dh021594 Probe #9

3.22e Viscosity Correlation with RFI Experiment
dh021594 Probe #9
The April RFI (resin film infusion) experiment used a carbon woven trapezoid stiffened panel in an autoclave set for measuring J type thermocouples. All nine sensors were analyzed for this run. The following table lists the wetout times for each sensor:

<table>
<thead>
<tr>
<th>sensor #</th>
<th>wetout time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>76.0</td>
</tr>
<tr>
<td>2</td>
<td>42.0</td>
</tr>
<tr>
<td>3</td>
<td>88.0</td>
</tr>
<tr>
<td>4</td>
<td>83.0</td>
</tr>
<tr>
<td>5</td>
<td>64.0</td>
</tr>
<tr>
<td>6</td>
<td>169.0</td>
</tr>
<tr>
<td>7</td>
<td>70.0</td>
</tr>
<tr>
<td>8</td>
<td>88.0</td>
</tr>
<tr>
<td>9</td>
<td>180.0</td>
</tr>
</tbody>
</table>

Figures 3.23 a-i display the raw FDEMS output. All sensors demonstrate similar curves for the correlated degree of cure (Figures 3.24 a-i). When examining the backcalculated viscosity (Figures 3.25a-i), sensors 3, 5, 6, and 8 display the lowest minimums. Sensors 3, 6, and 8 are in the same region and on the same level of the preform. Sensor #5 is in
the same region, but is located on a different level. Sensors 1, 2, 7 (lowest level), 4, and 9 (highest level) all display higher minimums.
3.23a FDEMS Output of RFI Run at Northrop 4/12/94
Probe #1

3.23b FDEMS Output of RFI Run at Northrop 4/12/94
Probe #2
3.23c FDEMS Output of RFI Run at Northrop 4/12/94
Probe #3

3.23d FDEMS Output of RFI Run at Northrop 4/12/94
Probe #4
3.23e FDEMS Output of RFI Run at Northrop 4/12/94
Probe #5

3.23f FDEMS Output of RFI Run at Northrop 4/12/94
Probe #6
3.23g FDEMS Output of RFI Run at Northrop 4/12/94
Probe #7

3.23h FDEMS Output of RFI Run at Northrop 4/12/94
Probe #8
3.23i FDEMS Output of RFI Run at Northrop 4/12/94
Probe #9
3501-6 dh041294.bas Probe #1
Correlated Degree of Cure

- temp  • alpha

3.24a Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #1

3501-6 dh041294.bas Probe #1
Correlated Viscosity

- temp  ▼ eta

3.25a Viscosity Correlation with RFI Experiment
dh041294.bas Probe #1
3.24b Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #2

3.25b Viscosity Correlation with RFI Experiment
dh041294.bas Probe #2
3.24c Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #3

3.25c Viscosity Correlation with RFI Experiment
dh041294.bas Probe #3
Correlated Degree of Cure

\[\begin{align*}
\alpha & = \frac{t}{t_0} \\
T & = T_0 + \alpha t
\end{align*}\]

Correlated Viscosity

\[\begin{align*}
\eta & = \eta_0 \left(1 - \frac{T}{T_0}\right)
\end{align*}\]
Correlated Degree of Cure

- temp
- alpha

Correlated Viscosity

- temp
- eta

3.24e Degree of Cure Correlation with RFI Experiment

dh041294.bas Probe #5

3.25e Viscosity Correlation with RFI Experiment

dh041294.bas Probe #5
3501-6 dh041294.bas Probe #6
Correlated Degree of Cure

3.24f Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #6

3501-6 dh041294.bas Probe #6
Correlated Viscosity

3.25f Viscosity Correlation with RFI Experiment
dh041294.bas Probe #6
3501-6 dh041294.bas Probe #7
Correlated Degree of Cure

![Graph showing correlation between temperature and degree of cure.]

3.24g Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #7

3501-6 dh041294.bas Probe #7
Correlated Viscosity

![Graph showing correlation between temperature and viscosity.]

3.25g Viscosity Correlation with RFI Experiment
dh041294.bas Probe #7
3.24h Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #8

3.25h Viscosity Correlation with RFI Experiment
dh041294.bas Probe #8
3.24i Degree of Cure Correlation with RFI Experiment
dh041294.bas Probe #9

3.25i Viscosity Correlation with RFI Experiment
dh041294.bas Probe #9

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Characterizing PR500 for Resin Transfer Mold Applications

PR500 is a premixed, one-part epoxy containing catalyst which is used in resin transfer molding type processes. In order to monitor the chemical and physical properties of the resin during a Resin Transfer Mold (RTM) process, PR500 was characterized thermally, dielectrically, and rheometrically. After calibration curves were calculated viscosity and degree of cure profiles were conducted for two RTM experiments.

Kinetic Analysis

A Differential Scanning calorimeter (DSC) was again used to determine experimental values of $\alpha$ with respect to time. Measurements were conducted at five critical temperatures in RTM processing, 160°C, 170°C, 180°C, 190°C, and 200°C. 160°C was determined to be the lowest isotherm with an observable change in heat flow. As in 3501-6 experimentation, isotherms (Figures 3.26a-3.26e) were performed to generate integrated values of $\alpha$ and $\alpha/dt$. In searching for the optimal kinetic model for PR500, the equation:

$$\frac{d\alpha}{dt} = k \cdot \alpha^m (1-\alpha)^n$$

was first selected. Values of k (the rate constant), M, and N (overall reaction order constants) were calculated for the five critical temperatures. A least square fit analysis
3.26a DSC Isothermal Cure of PR500 @ 160°C

3.26b DSC Isothermal Cure of PR500 @ 170°C
3.26c DSC Isothermal Cure of PR500 @ 180°C

3.26d DSC Isothermal Cure of PR500 @ 190°C
3.26e DSC Isothermal Cure of PR500 @ 200°C
was used to generate these parameters through SYSTAT statistical software. In order to be precise with SYSTAT estimates, a program was devised to pinpoint accurate ranges for k, M, and N. The best kinetic fit resulted in the smallest squared total deviation between experimental and theoretical α. Optimal fits were created for each of the five temperatures.

A comprehensive model was developed for all temperatures using the following Arhenius equation:

\[ k = Ae^{-E/RT} \quad \text{or} \quad \ln(k) = (-B) \times 1/T + \ln(A) \]

where R is the ideal gas constant (1.987 cal/K-mol), A is the preexponential factor, and E is the activation energy. When plotting the relationship between the natural log of the rate constants and 1/T, an inverse linear relationship is observed. This is shown in Figure 3.27. When drawing the best fit line through these points, B (the slope) and A (the y-intercept) were determined. The values of A and B appear in the final comprehensive kinetic equation. New rate constants were backcalculated with these A and B using the Arhenius equation, and the values of M and N were averaged. The final equation is listed below with its calculated parameters.
3.27 Ln K versus 1/T for PR500

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final equation:
\[
\frac{da}{dt} = (8.407385 \times e^{\frac{-501204}{T}}) \times a^{0.33} \times (1-a)^{1.07}
\]

[Table 3-7]

<table>
<thead>
<tr>
<th>temp/filename</th>
<th>K</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>160C (prn15.dat)</td>
<td>0.042</td>
<td>0.33</td>
<td>1.07</td>
</tr>
<tr>
<td>170C (prn29.dat)</td>
<td>0.055</td>
<td>0.33</td>
<td>1.07</td>
</tr>
<tr>
<td>180C (prn17.dat)</td>
<td>0.070</td>
<td>0.33</td>
<td>1.07</td>
</tr>
<tr>
<td>190C (prn27.dat)</td>
<td>0.089</td>
<td>0.33</td>
<td>1.07</td>
</tr>
<tr>
<td>200C (prn21.dat)</td>
<td>0.110</td>
<td>0.33</td>
<td>1.07</td>
</tr>
</tbody>
</table>

This equation displays excellent fits with experimental data as shown in Figures 3.28a-3.28e.

Two other kinetic analyses were considered in order to describe PR500's autocatalytic behavior. An extra rate constant \( k_2 \) was proposed by Dr. Maussy from Georgia Tech which looks like the following:

\[
\frac{da}{dt} = (k_1 + k_2 \times a^n)(1-a)^n
\]

This equation mathematically accounts for a possible non-zero reaction rate at time zero. Therefore \( k_1 \) yields the initial reaction rate assuming \( a \) equals zero at time zero. Parameters were proposed with the following activation energies and preexponential factors:
for \( k_1 : E = 76 \text{ kJ/mol} \quad A = 7.7 \times 10^4 \)

for \( k_2 : E = 51 \text{ kJ/mol} \quad A = 1.1 \times 10^3 \)

[Table 3-8]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( M )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>3.07E-3</td>
<td>0.0464</td>
<td>0.70</td>
<td>1.10</td>
</tr>
<tr>
<td>180°C</td>
<td>7.80E-3</td>
<td>0.0870</td>
<td>0.70</td>
<td>1.10</td>
</tr>
<tr>
<td>200°C</td>
<td>0.0183</td>
<td>0.154</td>
<td>0.70</td>
<td>1.10</td>
</tr>
</tbody>
</table>

When comparing our experimental values with this proposed kinetic model, another excellent fit is observed for \( \alpha \) versus time (Figures 3.29a-3.29e).

A third and final kinetic model was proposed with respect to experimental data. A. C. Loos generated the following parameters:

[Table 3-9]

<table>
<thead>
<tr>
<th>( A_1 )</th>
<th>(-E_1/R)</th>
<th>( A_2 )</th>
<th>(-E_2/R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2259.287</td>
<td>-5247.800</td>
<td>2346048734</td>
<td>-10753.651</td>
</tr>
</tbody>
</table>

Rate constants were evaluated using these parameter values:
Illustrations 3.30a-3.30e exhibit the kinetic fit with experimental \( \alpha \). The reaction order constants for this equation remain the same for all temperatures:

\[
M = 1.1 \\
N = 1.43
\]

All three proposed models proved to be adequate. A. C. Loos' equation was used in calibration relationships with viscosity and dielectric measurements.
3.28a Theoretical and Experimental $\alpha$ versus Time at 160°C for three parameter fit

3.28b Theoretical and Experimental $\alpha$ versus Time at 170°C for three parameter fit
3.28c Theoretical and Experimental $\alpha$ versus Time at 180°C for three parameter fit

3.28d Theoretical and Experimental $\alpha$ versus Time at 190°C for three parameter fit
3.28e Theoretical and Experimental $\alpha$ versus Time at 200°C for three parameter fit

3.29a Theoretical fit, proposed by Dr. Maussy, of $\alpha$ versus Time at 160°C
3.29b Theoretical fit, proposed by Dr. Maussy, of $\alpha$ versus Time at 180°C

3.29c Theoretical fit, proposed by Dr. Maussy, of $\alpha$ versus Time at 200°C
3.30a Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 160°C

3.30b Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 170°C
Degree of Cure vs. Time

PR500 180°C Loos fit

3.30c Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 180°C

Alpha vs. Time

PR500 190°C Loos fit

3.30d Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 190°C
Degree of Cure vs. Time

PR500 200C Loos fit

3.30e Theoretical fit, proposed by Dr. Loos, of \( \alpha \) versus Time at 200°C
Viscosity and FDEMS Determination

In order to monitor physical properties of the resin transfer mold process, time based calibrations were developed as in 3501-6 characterization. Experimentation was conducted dielectrically and rheometrically as a function of time. In order to measure the viscoelastic properties of PR500, a Rheometric RDA-700 Dynamic Analyzer was used. These results are shown in Figures 3.31a-3.31h. Figures 3.31i-l display the FDEMS results.

The following table lists the gelation times at four temperatures:

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>80.0</td>
</tr>
<tr>
<td>170</td>
<td>55.4</td>
</tr>
<tr>
<td>180</td>
<td>41.0</td>
</tr>
<tr>
<td>190</td>
<td>30.0</td>
</tr>
</tbody>
</table>

When examining the ionic mobility at these four gelation times, log ε"*ω remains generally consistent with the exception of 160°C.

M.G. Parthum and G.P. Johari proposed a direct relationship between the gelation time and the ionic mobility (dc conductivity or σ). This is proposed in the equation:
3.31a η versus Time for Isothermal Cure of PR500 @ 160°C

3.31b G' and G'' versus Time Plot for Isothermal Cure of PR500 @ 160°C
3.31c η versus Time for Isothermal Cure of PR500 @ 170°C

3.31d G' and G" versus Time Plot for Isothermal Cure of PR500 @ 170°C
3.31e $\eta$ versus Time for Isothermal Cure of PR500 @ 180°C

3.31f $G'$ and $G''$ versus Time Plot for Isothermal Cure of PR500 @ 180°C
3.31g $\eta$ versus Time for Isothermal Cure of PR500 @ 190°C

3.31h $G'$ and $G''$ versus Time Plot for Isothermal Cure of PR500 @ 190°C
3.31i FDEMS Isothermal Cure of PR500 @ 160°C

3.31j FDEMS Isothermal Cure of PR500 @ 170°C
\[ \sigma_o(t) = \sigma_o(t->0) \times [(t_{gel} - t)/t_{gel}]^x \]

Johari et al. used this equation through iterations and minimum mean square deviations in order to fit their conductivity data for a constant value of \( t_{gel} \). In order to test the validity of this equation values were generated for the parameters \( x \) and \( \sigma_o(t->0) \) for PR500. When taking the natural log of both sides of this equation,

\[ \ln \sigma_o(t) = \ln \sigma_o(t->0) + x \times \ln[(t_{gel} - t)/t_{gel}] \]

a plot of \( \ln \sigma_o \) versus \( \ln[(t_{gel} - t)/t_{gel}] \) can be made to estimate the values for \( x \) (given by the slope) and \( \sigma_o(t->0) \) (given by the intercept). The parameter \( \sigma_o \) can be calculated by the equation:

\[ \sigma_o = \varepsilon'' \times \omega \times \varepsilon_o \]

where \( \varepsilon_o \) is the permittivity of free space (8.8514 pF/m). Three temperatures were analyzed for PR500. When plotting \( \ln \sigma_o \) versus \( \ln[(t_{gel} - t)/t_{gel}] \), a linear relationship is not observed (Figures 3.32a-c). Therefore, the linear portion (Figures 3.32d-f) closest to gelation time was analyzed.
As seen above there is no trend that is observed in x or $\sigma_0(t\rightarrow0)$ as the temperature increases. This questions the validity of the Johari et al. and the proposed equation. Gelation is a macroscopic property. It is difficult to monitor the onset of gelation through the dielectric response because only microscopic motions are being monitored.
3.31k FDEMS Isothermal Cure of PR500 @ 180°C

3.31l FDEMS Isothermal Cure of PR500 @ 190°C
3.32a $\ln \left( \frac{(t_{\text{gel}}-t)/t_{\text{gel}}}{\sigma} \right)$ vs. $\ln \sigma$ for PR500 @ 170°C

3.32d Linear Portion closest to $t_{\text{gel}}$ from $\ln \left( \frac{(t_{\text{gel}}-t)/t_{\text{gel}}}{\sigma} \right)$ vs. $\ln \sigma$ for PR500 @ 170°C

slope = 0.16022
y-intercept = -24.3967
**Ln \([(t(gel)-t)/t(gel)]\) vs. sigma**

for 180°C isotherm PR500

**3.32b** \(\text{Ln } [(t_{gel}-t)/t_{gel}]\) vs. \(\text{ln } \sigma\) for PR500 @ 180°C

**Ln \([(t(gel)-t)/t(gel)]\) vs. sigma**

for 180°C isotherm PR500

**3.32e** Linear Portion Closest to \(t_{gel}\) from \(\text{Ln } [(t_{gel}-t)/t_{gel}]\) vs. \(\text{ln } \sigma\) for PR500 @ 180°C

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3.32c \( \ln \left[ \frac{(t_{gel} - t)/t_{gel}}{1} \right] \) vs. \( \ln \sigma \) for PR500 @ 190°C

3.32f Linear Portion Closest to \( t_{gel} \) from \( \ln \left[ \frac{(t_{gel} - t)/t_{gel}}{1} \right] \) vs. \( \ln \sigma \) for PR500 @ 190°C
Calibrations

Calibrations were conducted for 160°C, 170°C, 180°C, 190°C and 200°C at a frequency of 5kHz (chosen from the ionic band of each isothermal FDEMS output). As in 3501-6, calibrations were calculated up until the gelation time. Offset were considered due to temperature lag. The range of offset times was approximately 21 to 27 minutes for each of the five temperatures. Figures 3.33a-3.33c display calibrations of log ε"*ω versus viscosity and the theoretical degree of cure. Figure 3.34 illustrates the relationship between log ε"*ω and log η for all temperatures. A slope of approximately -1 is observed, demonstrating an inverse linear relationship between the decreasing ionic mobility and increasing viscosity.

For the high temperature cure at 180°C, another calibration plot was devised (Figure 3.35) using what is referred to as the slope method. Similar to the 177°C calibration of 3501-6, (dε"/dt)/ε" was calculated. The dielectric losses were taken at 50kHz. This is due to the 50kHz frequency remaining constant after the ionic band. This slope method is used to determine degree of cure at later stages of the RTM process.
PR500 160C isotherm
Alpha and Eta vs. log(e**w)

3.33a $\alpha$ and $\eta$ versus log $e^{**w}$ for 160°C Calibration

PR500 170C isotherm
Alpha and Eta vs. log(e**w)

3.33b $\alpha$ and $\eta$ versus log $e^{**w}$ for 170°C Calibration
3.33c α and η versus log ε"* ω for 180°C Calibration

3.34 log ε"* ω versus log η for 160°C, 170°C, 180°C
Isothermal Data
3.35 Slope \( (\Delta e''/\Delta t)/e'' \) and \( \alpha \) versus Time for 180°C Calibration using Five Point Method at 50 kHz
Using the calibrations described above, two experimental resin transfer mold processes were monitored. A pressure pot procedure was used for both experiments. A heated pressure pot warmed the resin to a desired temperature, followed by vacuum degassing to eliminate entrapped air during heating, mixing, and pouring. The resin was injected into a heated, closed mold preform containing layered graphite fiber sheets. A vacuum was drawn through the exit vent to help the injection process.

The first set of FDEMS figures (figure 3.36a-h) display the wetout files for runs dh121493 and dh121593 which were conducted at NASA Langley Research Center, Hampton, Virginia. A viscosity profile was conducted for these wetout files (Figures 3.36i-j). When observing these plots, the peaks illustrate the time of sensor wetout. Sensor 1 and 3 contain (a) and (b) peaks. These represent two different sensors 3a and 3b as shown on the FDEMS Sensor setup (Figure 3.37a-b). Once the sensor 3a wetout, the leads were disconnected and placed on 3b to measure its wetout. The second set of plots (Figure 3.38a-h) display the frequency dependent dielectric sensing of four sensors (1b, 2, 3b, 4) after wetout.
3.36a FDEMS wetout output for RTM run at NASA Langley
12/14/93 Probe #1

3.36b FDEMS wetout output for RTM run at NASA Langley
12/14/93 Probe #2
3.36c FDEMS wetout output for RTM run at NASA Langley 12/14/93 Probe #3

3.36d FDEMS wetout output for RTM run at NASA Langley 12/14/93 Probe #4
3.36e FDEMS wetout output for RTM run at NASA Langley
12/15/93 Probe #1

3.36f FDEMS wetout output for RTM run at NASA Langley
12/15/93 Probe #2

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3.36g FDEMS wetout output for RTM run at NASA Langley
12/15/93 Probe #3

3.36h FDEMS wetout output for RTM run at NASA Langley
12/15/93 Probe #4
Dh121493 Probe#2 Correlated Viscosity
PR500 wetout file

3.36i Viscosity Profile of Probe #2 during wetout
for RTM run 12/14/94

Dh121593 Probe#2 Correlated Viscosity
PR500 wetout file

3.36j Viscosity Profile of Probe #2 during wetout
for RTM run 12/15/94
3.37a  FDEMS sensor location for RTM run at NASA Langley 12/14/93

3.37b  FDEMS sensor location for RTM run at NASA Langley 12/15/93
3.38a FDEMS output for RTM run at NASA Langley  
12/14/93 Probe #1

3.38b FDEMS output for RTM run at NASA Langley  
12/14/93 Probe #2
3.38c FDEMS output for RTM run at NASA Langley 12/14/93 Probe #3

3.38d FDEMS output for RTM run at NASA Langley 12/14/93 Probe #4
Data file: b: dh121593.a

3.38e FDEMS output for RTM run at NASA Langley
12/15/93 Probe #1

Data file: b: dh121593.a

3.38f FDEMS output for RTM run at NASA Langley
12/15/93 Probe #2

152
3.38g FDEMS output for RTM run at NASA Langley 12/15/93 Probe #3

3.38h FDEMS output for RTM run at NASA Langley 12/15/93 Probe #4
Given the dielectric loss measurements from the FDEMS data, the value of $\varepsilon''*\omega$ was calculated by multiplying $\varepsilon''$ by $2\pi f$ (f equaling the frequency). Through the calibrations previously discussed, degree of cure and viscosity were predicted at different time points. In both experiments dh121493 and dh121593, there is a 177-178°C temperature hold. During the first 30 minutes of the run, values of $\alpha$ and $\eta$ were extrapolated corresponding to $\varepsilon''*\omega$ values from the 5kHz calibration plots for 160°C, 170°C, and 180°C. However, after approximately 30 minutes (when the frequencies separate from the ionic band), the slope ($d\varepsilon''/dt/\varepsilon''$) was calculated to correlate with respective values of $\alpha$ on the 180°C 50kHz calibration plots. Figures 3.39a-d and 3.40a-d display these correlations. Backcalculated viscosity was predicted from the temperature independent log $\eta$ versus $\varepsilon''*\omega$ calibration. Each sensor has an exponential increase in viscosity as seen in Figures 3.39e-h and Figures 3.40e-h.
Correlation of dh121493 Probe #1
PR500 Correlated Degree of Cure

3.39a Degree of Cure Correlation with RTM Experiment
dh121493 Probe #1

Correlation of dh121493 Probe #1
PR500 Correlated Viscosity

3.39e Viscosity Correlation with RTM Experiment
dh121493 Probe #1
Correlation of dh121493 Probe #2
PR500 Correlated Degree of Cure

3.39b Degree of Cure Correlation with RTM Experiment
dh121493 Probe #2

Correlation of dh121493 Probe #2
PR500 Correlated Viscosity

3.39f Viscosity Correlation with RTM Experiment
dh121493 Probe #2
Correlation of dh121493 Probe #3
PR500 Correlated Degree of Cure

Correlation of dh121493 Probe #3
PR500 Correlated Viscosity

3.39c Degree of Cure Correlation with RTM Experiment
dh121493 Probe #3

3.39g Viscosity Correlation with RTM Experiment
dh121493 Probe #3
Correlation of dh121493 Probe #4

PR500 Correlated Degree of Cure

3.39d Degree of Cure Correlation with RTM Experiment
dh121493 Probe #4

Correlation of dh121493 Probe #4

PR500 Correlated Viscosity

3.39h Viscosity Correlation with RTM Experiment
dh121493 Probe #4
3.40a Degree of Cure Correlation with RTM Experiment
dh121593 Probe #1

3.40e Viscosity Correlation with RTM Experiment
dh121593 Probe #1
Correlation of dh121593 Probe #2
PR500 Correlated Degree of Cure

3.40b Degree of Cure Correlation with RTM Experiment
dh121593 Probe #2

Correlation of dh121593 Probe #2
PR500 Correlated Viscosity

3.40f Viscosity Correlation with RTM Experiment
dh121593 Probe #2

160
Correlation of dh121593 Probe #3
PR500 Correlated Degree of Cure

- ▼ temp
- ● alpha

3.40c Degree of Cure Correlation with RTM Experiment
dh121593 Probe #3

Correlation of dh121593 Probe #3
PR500 Correlated Viscosity

- ▼ temp
- ● eta

3.40g Viscosity Correlation with RTM Experiment
dh121593 Probe #3
3.40d Degree of Cure Correlation with RTM Experiment
dh121593 Probe #4

Correlation of dh121593 Probe #4
PR500 Correlated Viscosity

3.40h Viscosity Correlation with RTM Experiment
dh121593 Probe #4
Characterization of Shell 1895 Experimental Resin

This epoxy resin system was characterized similarly to PR500 and 3501-6. Shell 1895 was analyzed dielectrically, rheometrically, and thermally in order to calibrate the resin through the time correlation method. One resin transfer mold experiment was monitored after calibrations were completed.

Kinetic Analysis

The Differential Calorimeter was again used to analyze the kinetic behavior of the resin during polymerization. Measurements were collected at temperature holds of 90°C, 121°C, 135°C, 149°C, and 177°C (Figures 3.41a-e). In order to characterize this resin's kinetic mechanism, parameters were estimated to fit experimental DSC data to a proposed model (as in PR500 and 3501-6). Three equations were considered in characterizing this high performance system:

1. \( \frac{d\alpha}{dt} = k*(1-\alpha)^n \)
2. \( \frac{d\alpha}{dt} = k*\alpha^n*(1-\alpha)^n \)
3. \( \frac{d\alpha}{dt} = (k1+k2*\alpha^n)*(1-\alpha)^n \)

As described in the kinetic analysis of PR500, a statistical least square fit analysis was conducted to accurately calculate the parameters of the equations given
3.41a DSC Isothermal Cure of Shell 1895 @ 90°C

3.41b DSC Isothermal Cure of Shell 1895 @ 121°C
3.41c DSC Isothermal Cure of Shell 1895 @ 135°C

3.41d DSC Isothermal Cure of Shell 1895 @ 149°C

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3.41e DSC Isothermal Cure of Shell 1895 @ 177°C
above. The second order polynomial fit (2) appeared as the best fit. The final comprehensive kinetic equation was determined to be:

\[
\frac{da}{dt} = 2.24 \times 10^9 e^{-9541/T} \alpha^{-7.1} (1-\alpha)^{2.3}
\]

In order to verify the accuracy of this equation, \( \alpha \) versus time plots were compared between experimental and new theoretical data. As shown by Figures 3.42a-d, the chosen kinetic equation was an excellent fit.

Another kinetic model was developed by A. C. Loos to predict degree of cure for a newer batch of resin. The equations are as follows:

\[
\begin{align*}
\frac{da}{dt} & = (\frac{H_T}{H_u})(\frac{dB}{dt}) \\
\frac{dB}{dt} & = (k_1+k_2*BM)(1-B)^N \\
H_T/H_u & = 0.0033874T - 0.521654 \text{ if } T<450K \\
H_T/H_u & = 1 \text{ if } T \geq 450K \\
M & = 1.4597-247.12(1/T) \quad k_1 = 76496e^{(-8640/T)} \\
N & = 4.2432-1313.79(1/T) \quad k_2 = 39140e^{(-7076/T)}
\end{align*}
\]

Degree of cure was calculated for this model for selected temperatures 121°C, 135°C, 149°C, 177°C. The theoretical values agree nicely with experimental values in the beginning stages of cure (Figures 3.43a-d). However, there are deviations at maximum degree of cure due to the factor \( H_u/H_T \). This kinetic model was chosen to predict both time and temperature dependence of \( \alpha \) in future calibrations.
3.42a Theoretical and Experimental $\alpha$ versus Time at $121^\circ$C for three parameter fit

3.42b Theoretical and Experimental $\alpha$ versus Time at $135^\circ$C for three parameter fit
3.42c Theoretical and Experimental $\alpha$ versus Time at $149^\circ$C for three parameter fit

3.42d Theoretical and Experimental $\alpha$ versus Time at $177^\circ$C for three parameter fit
3.43a Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 121°C

3.43b Theoretical fit, proposed by Dr. Loos, of $\alpha$ versus Time at 135°C
3.43c Theoretical fit, proposed by Dr. Loos, of α versus Time at 149°C

3.43d Theoretical fit, proposed by Dr. Loos, of α versus Time at 177°C
Calibrations

FDEMS and rheometric isotherms (similar to PR500 and 3501-6 investigations) were conducted at 90°C, 121°C, 135°C, 149°C and 177°C (Figures 3.44a-j). The degree of cure and η were both time correlated to the magnitude of the FDEMS measurement ε", the dielectric loss. 125 Hz displayed constant dielectric data in the ionic band and was chosen as the representative frequency in subsequent calibrations. An initial time zero was selected for the dielectric and rheometric data. A correction factor was considered in determining this initial time. The highest point in the ionic peak was marked as the onset of the reaction or T(0) for the dielectric data. T(0) was designated for the rheometric data by drawing a smooth curve between points due to their initial scattering. The first consistent point was considered T(0). Calibrations were generated for 90°C, 121°C, 135°C, and 149°C which display η and the degree of cure versus ε"*ω (Figures 3.45a-d). At the high temperature 177°C, the slope method was used again creating a relationship between the normalized rate of change of ε", (dε"/dt)/ε" at 5Hz and theoretical α backcalculated with Loos’ kinetic model. These two variables were plotted versus time (Figure 3.46). The successive point and five point averaging method were used for this resin. The
five point calibration was used for future correlations due to more consistent points.
Data file: B:sw052093

3.44b FDEMS Isothermal Cure of Shell 1895 @ 90°C

3.44a η versus Time for Isothermal Cure of Shell 1895 @ 90°C
3.44d FDEMS Isothermal Cure of Shell 1895 @ 121°C

3.44c η versus Time for Isothermal Cure of Shell 1895 @ 121°C
3.44f FDEMS Isothermal Cure of Shell 1895 @ 135°C

3.44e η versus Time for Isothermal Cure of Shell 1895 @ 135°C
3.44h FDEMS Isothermal Cure of Shell 1895 @ 149°C

3.44g η versus Time for Isothermal Cure of Shell 1895 @ 149°C
Data file: yw71591

3.44j FDEMS Isothermal Cure of Shell 1895 @ 177°C

3.44i η versus Time for Isothermal Cure of Shell 1895 @ 177°C
Alpha and Eta vs. $\varepsilon^{\ast \omega}$

90°C Calibration Plot

$\alpha$ versus log $\varepsilon^{\ast \omega}$ for 90°C Calibration

Alpha and Eta vs. $\varepsilon^{\ast \omega}$

121°C Calibration Plot

$\alpha$ versus log $\varepsilon^{\ast \omega}$ for 121°C Calibration
Alpha and Eta vs. $\epsilon''^* w$
135°C Calibration Plot

3.45c $\alpha$ versus log $\epsilon''^* \omega$ for 135°C Calibration

Alpha and Eta vs. $\epsilon''^* w$
149°C Calibration Plot

3.45d $\alpha$ versus log $\epsilon''^* \omega$ for 149°C Calibration
Shell 1895 177C Isotherm (5kHz)

\( \frac{d\varepsilon}{dt} / \varepsilon \) and \( \alpha \) vs. time

3.46 Slope \( \frac{d\varepsilon}{dt} / \varepsilon \) and \( \alpha \) versus Time for 177°C Calibration using Five Point Averaging
Correlation of alpha and eta with an RTM experiment

The degree of cure and viscosity were monitored for one resin transfer mold experiment conducted at NASA Langley Research Center on April 23, 1993. Only sensor #3 was analyzed. Its FDEMS raw output is shown in Figure 3.47. As in previous correlations, values of $\eta$ and $\alpha$ were extrapolated from the appropriate calibration plots. Correlated degree of cure and viscosity are displayed in Figures 3.48 and 3.49. As seen before, viscosity experiences a minimum during the ramp and then quenches due to extensive crosslinking. During the 177°C hold, viscosity is no longer monitored. However the long time degree of cure is correlated until it approaches a theoretical maximum of 1.
3.47 FDEMS output for RTM run at NASA Langley
4/23/93  Probe #3
3.48 Degree of Cure Correlation with RTM Experiment
dh042393 Probe #3

3.49 Viscosity Correlation with RTM Experiment
dh042393 Probe #3
References for Chapter III


Conclusions

In this investigation, Frequency Dependent Electromagnetic Sensing proved to be an excellent technique to monitor the molecular and physical properties of amine-epoxy resins in composite fabrication. It was effective in detecting reaction onset, point of maximum flow, resin location, extent of reaction, and reaction completion.

Through characterization of each epoxy resin system, successful calibrations were developed to integrate viscosity, degree of cure, and the dielectric loss. This information was applied in order to effectively predict the processing properties during several RTM and RFI experiments. When observing the relationship between the ionic mobility and viscosity, a temperature dependence was not present. However, when establishing a relationship between ionic mobility and degree of cure a temperature dependence was elucidated.

One other major conclusion of this study concerned the varying kinetic models proposed for each resin system. All amine cured epoxies undergo autocatalytic behavior. Therefore, most systems follow Kamal's empirical rate equation. In this investigation Hercules 3501-6 was viewed as a complex curing resin with three epoxy additives. This resulted in three separate rate constants for three separate reactions in the
final comprehensive kinetic equation.

After characterizations and correlations of RTM and RFI experiments were completed, the information delivered by this study provided feedback to optimize future experimentation.
VITA

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Maria Anastasia Argiriadi was born in Brooklyn, New York, April 26, 1971. She attended and graduated from Pelham Memorial High School as valedictorian in June 1989. She earned a Bachelors of Science degree in Chemistry at the College of William and Mary in Williamsburg, Virginia. Afterwards, she enrolled in the Chemistry Graduate Program at the College of William and Mary and fulfilled requirements in August 1994. In the fall of 1994, she will be attending the University of Pennsylvania with a graduate fellowship in pursuit of her Doctorate in Chemistry.