CURE KINETICS AND SYNTHESIS OF SOME RESINS AND PREPREG SYSTEMS

A Dissertation by

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The following faculty members have examined the final copy of this dissertation for form and content, and recommended that it be accepted in partial fulfillment of the requirement for the degree of Doctor of Philosophy with a major in Chemistry.

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ABSTRACT

The research reported in this dissertation details the synthesis, characterization and cure kinetics of some resin and prepreg systems. The first chapter gives an introduction to the research presented in this thesis. A summary of epoxy and amine cure reactions that occur in epoxy resins and prepreg systems, the role of catalyst and studies on the cure kinetics with differential scanning calorimetry are presented. The synthesis of various phthalonitrile resins and their cure behavior is also discussed. The second chapter discusses the synthesis of control compounds and physical methods used in later chapters. The third chapter focuses on the cure kinetics of a high performance epoxy prepreg resin system based on DGEBA/TGDDM/DDS using differential scanning calorimetry. Three different sets of experiments were performed in dynamic, isothermal, and combined ramp and soak scanning to follow the cure kinetics in a multi-step cure cycle. The buildup of prepreg resin network structure during the cure cycle has been investigated using Dynamic Mechanical Analysis. Thermal Volatilization Analysis (TVA) and Sub-Ambient Thermal Volatilization Analysis (SATVA) experiments were conducted to fractionalize the condensable products released during curing of the prepreg system. The fourth chapter deals with the cure kinetics of a high performance epoxy prepreg resin system based on TGDDM/DDS with BF$_3$ catalyst with differential scanning calorimetry. As earlier, three different sets of experiments were conducted using dynamic, isothermal and combined ramp and soak scanning to follow the cure kinetics in a multi-step cure cycle. The gel point was measured using dynamic shear rheometry of the prepreg resin in isothermal mode. The fifth precursor. The cure profile was investigated on preconditioned resin with muffle furnace under ramp and also combined ramp and soak conditions. The thermal stability of
the precured resin was investigated with Thermomechanical analysis. Finally, TVA and SATVA experiments were conducted on uncured resin to characterize volatiles produced during cure.
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LIST OF ABBREVIATIONS

Put them in alphabetical order  fluoroboric acid

DGEBA  Diglycidylether of Bisphenol A
DDS  4,4’-Diaminodiphenyl Sulfone
DSC  Differential Scanning Calorimetry
FTIR  Fourier transform infra-red spectroscopy
NMR  Nuclear Magnetic Resonance Spectroscopy
DDM  diaminodiphenylmethane
Tg  Glass transition temperature
Ea  Activation Energy
TGDDM  N,N,N’,N’-tetraglycidyl-4,4’-diamino diphenyl methane
BF₃MEA/BFE  Boron trifluoride monoethylamine
α  alpha
β  beta
TGAP  Triglycidyl p-aminophenol
DMA  Dynamic Mechanical Analysis
TVA  Thermal Volatilization Analysis
SATVA  Sub-Ambient Thermal Volatilization Analysis
TMA  Thermomechanical Analysis
TGA  Thermogravimetric
α  degree of cure
αₚ  maximum achievable degree of cure
LIST OF ABBREVIATIONS (continued)

da\alpha/dt \quad \text{rate of cure}

T \quad \text{absolute temperature}

t \quad \text{time}

G' \quad \text{storage modulus}

G'' \quad \text{loss modulus}

G* \quad \text{complex modulus}

E \quad \text{modulus}

tan\delta \quad \text{mechanical loss factor}

BAPS \quad \text{bis[4-(4-aminophenoxy)phenyl]sulfone}

T800/3900 \quad \text{Thornell 800/3900 prepreg}

T300/934 \quad \text{Thornell 300/934 prepreg}

TLC \quad \text{Thin Layer Chromatography}

BPA \quad \text{Bisphenol A}

DFBP \quad \text{difluorbenzophenone}

DCB \quad 1,2 \text{ dicyano, 4-nitrobenzene}
CHAPTER 1
INTRODUCTION

1.1 Epoxy resin Chemistry

Epoxy resins have a wide range of applications including aerospace, automobile, construction, electronics, paints, adhesives and coatings. The rapid growth in the use of epoxy resins is due to basic properties such as low viscosity, quick and easy cure (from 5 to 150 °C depending on the curing agent), low shrinkage during cure, high adhesive strength, high mechanical properties, chemical resistance and versatility.[1] Epoxy resin can be defined as any molecule that contains two or more alpha epoxy groups which can be reacted to form a thermoset system.[2]

1.2 Curing Agents

The great utility of epoxy resins lies in the reactivity of the epoxy group with a large number of molecules upon which it transforms from thermoplastic liquid state to a tough, hard thermoset network without the evolution of by-products. The term curing means the process by which one or more reactants i.e., an epoxide and a curing agent (hardener, activator or catalyst) transform from a low-molecular weight material to a highly cross-linked network. This may involve only the epoxide or both the epoxide and the crosslinking/curing agent. These curing agents can be further divided into basic and acidic curing agents. The basic curing agents may include Lewis bases, inorganic bases, primary and secondary amines and amides. The acidic curing agents include Lewis acids, carboxylic acid anhydrides, poly-basic organic acids and phenols. Catalytically functioning curing agents do not participate in the network formation but promote the
reaction between the epoxy groups. These include tertiary amines and boron trifluoride complexes.\textsuperscript{[1,2]}

The mechanism of the epoxy-amine curing reactions has been widely analyzed. This takes place in three principal steps.

i. The reaction of the primary amine N-H with the epoxy group.

ii. The secondary amine N-H then reacts with another epoxy group

iii. Alternatively, an etherification reaction can take place between the hydroxyls formed during the above two steps and any of the unreacted epoxy groups. (This tends to not happen unless the curing agent is mixed with the epoxy in a stoichiometrically unbalanced fashion).

The rate constants for reactions with primary and secondary amines are different. The ratio of the rate constants i.e., primary to secondary amines, has a strong effect on the cure process. There is no good agreement from the literature on values of the two rate constants.\textsuperscript{[7]} The etherification reaction is dependent on temperature and the basicity of the diamine. It is also accepted that the cure reaction occurs by two mechanisms-one catalyzed by the hydroxyl groups initially present in the epoxy prepolymer and those generated during the reaction. The reactivities of some different aromatic amines with the diglycidylether of bisphenol A (DGEBA) were found to be in the order of 4,4’-methyleneedianiline (MDA) > 4,4’-methylenebis[2,6-diethylaniline(MDEA)] > 4,4’-diaminodiphenylsulphone(DDS) > 4,4’-methylenebis[3-chloro-2,6-diethylaniline] (MCDEA) . Hence, the relative reactivity ratio, r for the secondary amine and epoxy to the primary amine and epoxy \((r = K_2/K_1)\) increases with the basicity of the amine.\textsuperscript{[3,4,5]}
Jovan et al. studied the influence of substituents on the amine curing agent on the reaction kinetics of epoxy/amine model systems with phenylglycidyl ether (PGE) and aniline. It was found that electron donating groups like methoxy substituted in p-anisidine result in an increase in the relative reactivity ratio, $r = 0.549$, and lead to an activation energy ($E_a$) of 8.9 kcal/mole which is lower than that measured for aniline ($r = 0.399$, $E_a = 12.5$ kcal/mole). On the other hand, the electron withdrawing nitro group in p-nitroaniline decreases the $r$ value to 0.089 and increases the activation energy to 14.9 kcal/mole. This is attributed to the direct conjugation of the nitro with the amine group that reduces the basicity of the amine, and hence the reactivity of the amine with epoxy groups.\[^8\]

Etherification reactions are pronounced at higher temperatures and also increase with the initial ratio of epoxy/amine in the reaction mixture.\[^3,6\] The mechanism for epoxy-amine cure reactions is shown in figure 1.1 and for the epoxy-amine cure reactions catalyzed by protons, in figure 1.2.\[^7,8\]
Figure 1.1. Reactions of epoxies with amines and hydroxyls
Figure 1.2. Epoxy ring opening - catalysed by Hydrogen bond donor-acceptor
1.3. Thermodynamics of Cure

1.3.1. Heat of Polymerization

The heat of polymerization of an epoxy resin indicates the amount of heat given off during the cure reaction and is normally expressed in kilocalories or kilojoules per mole of epoxy. The heat given off, when the epoxide ring is opened by polymerization with another epoxide or with a hardener, can illuminate the nature of the cure reaction. During the polymerization reaction, the heat liberated is referred as an exotherm.\[1\] If a catalyst like boron trifluoride is present, the cure will start at room temperature without application of heat. As the temperature rises, curing takes place at a faster rate with an appreciable shorter cure time. If the cure temperature is too high, side reactions and degradation reactions are promoted and network integrity will be impaired. The epoxy amine cure will take place in two stages. In the first stage, the small molecules will combine to give larger linear units. During the second stage all these clusters are joined together to form a network.\[9\] The heat of evolution is proportional to the extent of consumption of epoxy groups in the epoxy resin or to the loss of curing agent.\[10\]

1.3.2. Degree of Cure

At the beginning of cure of an epoxy resin, before the molecules are crosslinked, the resin exists as a thermoplastic solid or liquid. As the cure proceeds, the cross linking becomes more extensive and the resin is transformed into a thermoset. The degree of cure can be referred to as the extent to which epoxy groups have been consumed and if present, the extent of consumption of the reactive groups in the curing agent. A perfectly cured system is one in which the degree of cross linking is sufficient to produce optimum physical properties for a particular application. Hence, during cure two basic concepts are
involved, namely conversion (i.e., disappearance of reactive groups) and cross-linking (which means coupling of molecules into a three dimensional network to form a thermoset of desired properties). Certain properties will also change by varying the cross-link density. Increasing the crosslink density is usually attained by selecting short chain difunctional molecules or by increasing the average functionality (f) of the reagents. Decreasing the crosslink density by selecting longer chain difunctional molecules, by adding monofunctional molecules, or by lowering \( f_{\text{average}} \) will improve toughness, increase the elongation to break, and decrease cure shrinkage.\[^{[1]}\]

There are a number of techniques for the analysis of state of cure of epoxy resin systems. These include Differential Scanning Calorimetry (DSC), infra-red (IR) spectroscopy, measurement of equilibrium swelling and measurement of glass transition temperature. C.L. Brett investigated the influence of degree of cure on the bonding performance of adhesive AY105 containing DGEBA and diaminodiphenylmethane (DDM). The state of cure was characterized in terms of the glass transition temperature and residual heat of reaction. It was found that under isothermal conditions, full bond strength was reached with 95% conversion at a glass transition temperature (Tg) of 95 °C.\[^{[11]}\] (Note that this is considerably lower than the Tg for 100% conversion which is above 130°C). Michelle, et al. investigated the cure of carbon/epoxy prepreg 8552 and concluded that lower heating rates such as 2.5 °C/min provide a cure which is more homogenous and controlled than that obtained at higher heating rates of 5 and 10 °C/min.\[^{[10]}\] Sourour, et al. investigated the cure reaction of DGEBA with m-phenylene diamine (m-PDA) and found that maximum cure can be obtained under isothermal conditions by curing the material above the ultimate glass transition temperature.\[^{[12]}\]
1.3.3. Glass Transition temperature:

As the temperature of the polymer is raised through its glass transition temperature, the nature of the polymer changes from a hard, glassy and brittle state to a softer and flexible rubbery state. This change is accompanied by changes in properties like refractive index, thermal conductivity, mechanical stiffness, moduli, heat capacity and volume expansion coefficient. The glass transition temperature of a cured epoxide reflects the extent and nature of its cross linking but not necessarily its thermal stability.\textsuperscript{[13]} It is also a useful index of degree of cure.\textsuperscript{[14]}

S. Tarifa, et al., investigated the Tg of epoxy resins based on DGEBA thermally cured with DDM. During the cure cycle Tg increases towards higher values and eventually reaches $T_{g\infty}$. Such a change is attributed to an increase in the extent of cure. An additional endotherm occurs at higher temperatures above $T_{g\infty}$ due to chemical degradation of the network. For heating rates of 1 and 3 $^\circ$C/min, $T_{g\infty}$ values change from 179.4 to 181.7 $^\circ$C.

The activation energy for the glass transition can be determined using the equation given by H. Kissinger.\textsuperscript{[15]}

\[
E_a = \frac{-k(\text{dln}(q/T_{g\infty}^2))}{\text{d}(1/T_{g\infty})} \tag{1.1}
\]

where

\begin{itemize}
  \item k is the Boltzman constant
  \item q is the critical heating rate
  \item and $T_{g\infty}$ is the classical ultimate glass transition temperature.
\end{itemize}
The effect of processing temperature and mechanical mixing on the Tg and activation energies was investigated by Ching for the TGDDM/DDS epoxy system. It was found that the apparent glass transition temperature of the uncured resin mixture \( (T_{g0}) \) increases from 8.5 °C to 18.9 °C at a fixed mixing speed of 200 rpm. The overall activation energy for cure ranges from 91–98 kJ/mole on increasing the mixing speed from 200-900 rpm. \( T_{g0} \) decreases from 16.2 to 8.3 °C on further increasing the mixing speed from 500-900 rpm. This was attributed to molecular chain scission of the oligomer and reduction in the average molecular weight at these higher mixing speeds.\(^{[16]}\)

John, et al., found that the Tg values and thermal stability of polymers arising from isothermal cure schedules are generally higher than those obtained from dynamic cure, for epoxy cured with modified imidazole curing agents. The reduced Tg under dynamic conditions was attributed to some decomposition when the system was cured to a final cure temperature appreciably above the ultimate Tg.\(^{[17]}\)

1.3.4. Diffusion Control of the Cure Reaction

If the cure reaction occurs in adiabatic or isothermal conditions and is above the glass transition temperature of the ultimately cured polymer, the reaction proceeds to completion. If the reaction occurs substantially below the maximum glass transition temperature of the fully reacted material, the reaction stops at an intermediate conversion as the resin undergoes pre gel point vitrification. After vitrification, the kinetics become diffusion controlled.\(^{[2]}\)

A model for the rate of cure under isothermal conditions is given by the equation.\(^{[18]}\)

\[
\frac{d\alpha}{dt} = \frac{d\alpha}{dt_{\text{chem}}} \cdot f_d(\alpha) \quad (1.2)
\]
where \( \frac{d\alpha}{dt} \) describes the chemically controlled kinetics. If the reaction is chemically controlled, \( f_d \) is unity.

Otherwise

\[
f_d(\alpha) = 2 \left( 1 + \exp\left(\alpha - \alpha_f \right) \right) - 1
\]

where \( b \) is an empirical parameter and \( \alpha_f \) is the final conversion at that temperature.

1.3.5. **Effect of catalyst on the cure of epoxy resins:**

Boron trifluoride monoethylamine (BF\(_3\)MEA) is sometimes added to epoxy resins to accelerate their cure at elevated temperatures (120 °C or higher).\(^{[19]}\) The cure reactions of epoxy resin based on tetruglycidyl-4,4''-diaminodiphenylmethane (TGDDM) with diaminodiphenylsulfone (DDS) in the presence and absence of boron trifluoride mono-ethylamine have been studied in the early stages of cure. George, et al., investigated the cure kinetics of aerospace resin containing TGDDM cured with DDS in the presence of boron trifluoride mono ethylamine used in a commercial carbon fiber epoxy prepreg Hercules AS3501.\(^{[20]}\) The cure kinetics were studied with techniques such as DSC and FTIR.

During the isothermal cure at 140 °C, in the presence of added catalyst, it is noticed from the plot of rate of reaction versus time, that autocatalysis is not occurring and the rate of production of hydroxyls is greatest in the initial stages of cure and decreases as cure proceeds. Fiber optic FT-IR spectroscopy showed a shift in the N-H bond stretching from 3280 cm\(^{-1}\) to 3230 cm\(^{-1}\) before cure which is due to weak bond formation between the oxygen of the epoxy group and the hydrogen of the amine BF\(_3\) complex (the catalyst). Hence, for the unanalyzed epoxy system, the primary amine
epoxide addition reaction exhibits autocatalysis where in the presence of 1% BF₃MEA catalyst, the autocatalysis is replaced by nᵗʰ order kinetics.⁻²⁰

Munns, et al., investigated the performance of cured epoxy resins with BF₃ catalyst. Dynamic mechanical experiments have been conducted on an epoxy system made with TGDDM and a polyglycidylether of Bisphenol A novalac that were cured with DDS in the presence of BF₃MEA catalyst. Changes in the α and β transitions have been noticed. The increase in the β transition is attributed to the additional amine reaction driven by the heat from the exothermal H⁺(BF₃.EtNH₂⁻) catalysed polymerization. The α transition that represents the Tg of the final network increases with increase in the concentration of the catalyst due to a higher degree of crosslinking.¹¹⁹,²¹

Boron trifluoride complexes with nitrogen and oxygen containing Lewis bases were made by R.E.Smith, et al., and added to epoxy resin consisting of TGDDM cured with DDS.²² All the boron trifluoride complexes are converted to fluoroboric acid (HBF₃OH) under normal epoxy cure conditions. The fluoroboric acid is the true catalyst for epoxy resin cure. Fluoroboric acid is produced from BF₃-Oxygen or BF₃-Nitrogen complexes. Under cure conditions from 140 °C to 160 °C boron trifluoride complexes are converted to fluoroboric acid which will catalyse the epoxy cure. Fluorine-19 NMR was used to identify the formation of different BF₃ complexes and FTIR was used to monitor the cure.²²

Barton studied the cure of TGDDM-DDS resin systems with added borontrifluoride-ethylamine (BFE) catalyst using DSC in isothermal mode.²³ It was noticed that upon the addition of catalyst there is a competition between the amine addition reaction and cationic polymerization reaction. With an increase in the
concentration of BFE the cationic polymerization reaction becomes more dominant and
the heat of reaction decreases. For isothermal cure temperatures 128.5 and 168.5 °C the
heats of reaction for isothermal area are 303.7 and 323.8 J/g and for residual cure they are
255.1 and 100.4 J/g, respectively which shows that cationic polymerization is more
dominant. The catalyzed cure reaction commences at a temperature about 80 °C lower
than that for the unanalyzed system but completion of the cure exotherm requires re-
scanning around 250 °C.

Harris and Temin proposed a reaction mechanism involving the adduct RNH₂BF₃ or
the salt produced by disproportionation (RNH₃⁺BF₄⁻). The oxonium ion can be
formed from a complex of adduct or salt and epoxide. The propagation reaction can
proceed by further reaction of oxonium ion with epoxide. The reaction mechanism is
illustrated in figure 1.3.

\[
2\text{RNH}_2\text{BF}_3 \xrightarrow{\triangle} \text{BF}_2\text{RNH}_2 + \text{RNH}_3\text{BF}_4^-
\]

![Reaction involving adduct or salt of BF₃ catalyst with epoxy](image)

**Figure 1.3.** Reaction involving adduct or salt of BF₃ catalyst with epoxy
Happer et al concluded from $^{19}$F and $^{11}$B NMR Spectroscopy studies that, on heating, Boron trifluoride-Ethylamine (BFE) is converted to $\text{BF}_3\cdot\text{NH}_3\cdot\text{C}_2\text{H}_5$.\footnote{23} Furthermore, BFE on reaction with water at 85 °C produces $\text{BF}_3(\text{OH})\cdot\text{NH}_3\cdot\text{C}_2\text{H}_5$. More active $\text{BF}_3$ species are deactivated during early stages of cure.

Smith, et al., using $^{19}$F NMR and FTIR concluded that BFE was hydrolyzed in a variety of solvents to acids such as $\text{HBF}_4$ and $\text{HBF}_3\text{OH}$ by traces of water. Hydrolysis was very rapid at 100 °C and above. FTIR studies showed that the $\text{HBF}_4$ is a more effective accelerator than BFE.

Eleno, et al., investigated the cure of commercially available prepreg resins such as Narmco 5208, Fiberite 934 and Hercules 3501, which use the TGDDM and DDS epoxy system.\footnote{24,25,26} Narmco 5208 does not have any catalyst. The latter two contain BF$_3$ catalyst mixed with and without acetone, respectively. It was found that the rate of consumption of epoxy is in the order of: acetone mixed TGDDM-DDS-BF$_3$ > non-acetone mixed TGDDM-DDS-BF$_3$ > TGDDM-DDS with no catalyst. It was noticed that in the prepreg Fiberite 934, BF$_3$-epoxy complexes constitute almost 30% of the catalytic species and are the predominant active catalytic species of the cure reaction.

The structures of some epoxy resins and amines are shown in figures 1.4 and 1.5, respectively.\footnote{7}
(a) Diglycidyl ether of bisphenol A (DGEBA)

(b) Triglycidyl p-aminophenol (TGAP)

(c) Tetruglycidyl-4,4'-diaminodiphenylmethane (TGDDM/MY720)

**Figure 1.4.** Some epoxy resin systems
Some common curing agents in epoxy cure reactions

(a) 4,4'-diaminodiphenylsulfone (DDS)

(b) 4,4'-diaminodiphenylmethane (DDM)

(c) meta-phenylenediamine (m-PDA)

(d) Isomers of dimethylthiotoluenediamine (DMTDA)

Figure 1.5. Some common curing agents in epoxy cure reactions
1.4. Thermal Analysis

Thermal analysis refers to a collection of experimental analytical techniques used to investigate changes in the properties of a material as a function of temperature.\(^{[27]}\) The advantages of thermal analysis over other analytical methods are

i. The sample can be studied over a wide temperature range using various temperature programs

ii. Almost any physical form of sample such as solid, liquid or gel can be accommodated

iii. Small amount of samples to the extent of 0.1 μg to 10 mg can be used

iv. The atmosphere in the vicinity of the sample can be standardized

v. Time for the experiments can range from several minutes to several hours.

Some of the thermal analysis techniques that are used during this study are:

Differential Scanning Calorimetry (DSC),

Dynamic Mechanical Analysis (DMA),

Thermal Volatilization Analysis (TVA) and

Thermomechanical Analysis (TMA).

1.4.1. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a thermoanalytical technique used to measure the heat flow to and from a material as a function of temperature.\(^{[28]}\) In this technique both the sample and the reference pans are maintained at the same temperature throughout the experiment. The difference in the amount of heat required to equalize the temperature of a sample and its reference is measured as an exotherm or endotherm. The result of a DSC experiment is a curve of heat flux versus temperature or time.\(^{[14]}\)
Exothermic or endothermic processes in the sample result in a positive or negative peak with respect to baseline. The exotherm measured during this study constitutes a negative peak. DSC curves are used to calculate the enthalpies of thermal transitions by integrating the corresponding endotherm or exotherm. The main advantages of this technique are sample size (on the order of milligrams) and the ability to quantify overall reaction kinetics with relative speed and ease. It also measures thermal transitions such as Tg (the glass transition temperature), which is associated with the degree of crosslinking or state of cure of a resin. DSC can be operated in two basic modes

i. Dynamic temperature scanning (ramp) and

ii. Isothermal scanning (soak).

Small samples are necessary to prevent excessive temperature differentials.

**The basic assumptions in DSC kinetics are**

i. the rate of kinetics process \( \frac{d\alpha}{dt} \) is proportional to the measured heat flow.

ii. the temperature gradient through the sample and the sample-reference temperature difference is small.

An exotherm generated by the DSC instrument is shown in figure 1.6.\(^{[29]}\) The integrated area between the curve and the baseline represents the total amount of heat associated with the reaction or transition. The total heat, \( Q_{total} \), associated with the reaction or transition is equal to the area in the DSC trace as shown in equation (4)

\[
Q_{total} = \int_{t_0}^{t_f} (dq/dt) \, dt
\]  

(1.4)
Where \( \frac{dq}{dt} \) is the heat flow, \( t_0 \) and \( t_f \) are the initial and final times for complete cure. The degree of cure, \( \alpha_t \), at an intermediate time \( t \) can be calculated by integrating the heat flow up to that time, \( t \) i.e., \( \Delta t \) with the following equation (5)

\[
\alpha_t = \frac{\int_{t_0}^{t} \frac{dq}{dt} \, dt}{Q_{\text{total}}} = \frac{\text{area } A}{\text{area } A + \text{area } B} \tag{1.5}
\]

The rate of cure \( \frac{d\alpha}{dt} \) can be calculated by differentiating the cumulative degree of cure with respect to time.

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**Figure 1.6.** A DSC exotherm in dynamic scanning mode. The area between the base line and the exotherm represents the amount of heat produced during the reaction.
1.4.2. Cure Kinetics

Computational aides have helped us model the cure kinetics of epoxy based materials. These models help us better understand the effect of processing conditions, raw material properties and equipment size on process behavior. It also leads to significant savings in the amount of experimental work required to determine optimum processing conditions. These models will also help in developing relationships between processing conditions, structure and properties of the final product. The mechanisms and kinetics of cure determine network morphology. This, in turn, dictates the physical and mechanical properties of the cured product. The most important aspect of the model is an accurate description of the cure kinetics.

A phenomenological model captures the main features of the reaction kinetics ignoring the details of how individual species react with each other. Mechanistic models, on the other hand, are obtained from balances of species involved in the reaction, and hence are better models for prediction and interpretation. However, phenomenological models are the most popular for these kinds of systems.

The general formula for rate of reaction according to a phenomenological model is

\[
\frac{d\alpha}{dt} = K f(\alpha) \tag{1.6}
\]

where \(\alpha\) is the fractional conversion of the reactive group (degree of cure), \(t\) is the reaction time, \(K\) is the reaction rate constant and \(f(\alpha)\) is some function of \(\alpha\).

Most commonly, \(K\) is considered to have an Arrhenius temperature dependence given by

\[
K = A \exp(-E_a/RT) \tag{1.7}
\]
Where A is the frequency factor, R is the universal gas constant (8.314 J/mol.K), \( E_a \) is the activation energy and T is the absolute temperature.

As the chemical reaction progresses, the reaction rate decreases and approaches zero as the reaction comes to completion. In the absence of vitrification, the degree of cure will reach unity at the completion of the reaction.

With these concepts, \( f(\alpha) \) can be taken as\[^{[39]}\]

\[
f(\alpha) = (1-\alpha)^n g(\alpha)
\]  
(1.8)

This equation includes an \( n^{th} \) order reaction model \((1-\alpha)^n\), with \( g(\alpha) = 1 + C\alpha \), where C is the autocatalysis intensity.

Alternatively, Bogetti and Gillespie\[^{[39]}\] combined K and \( f(\alpha) \) as

\[
d\alpha/dt = A \exp(-E_a/RT)(1-\alpha)^n \alpha^m
\]  
(1.9)

If the resin vitrifies before the completion of the reaction, the maximum achievable degree of cure (\( \alpha_f \)) will be less than unity and equation 8 becomes,

\[
f(\alpha) = g(\alpha)(\alpha_f-\alpha)^n
\]

Woo, et al.,\[^{[12]}\] made efforts to describe \( d\alpha/dt \) versus \( \alpha \) data with a modified Arrhenius type equation, and defined \( d\alpha/dt \) as

\[
\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \quad \text{for } \alpha \leq 0.3
\]  
(1.10)

\[
\frac{d\alpha}{dt} = K_3(1-\alpha) \quad \text{for } \alpha > 0.3
\]  
(1.11)

The constants \( K_1, K_2 \) and B were determined by a non-linear least curve fit to the \( d\alpha/dt \) versus \( \alpha \) data, using the Lavenberg-Marquardt algorithm. The value of \( K_3 \) was obtained by fitting a linear least square curve to \( d\alpha/dt \) versus \( \alpha \) at \( \alpha > 0.3 \).
Kamal, et al., developed a new kinetic model for unanalyzed epoxy-amine cure

\[
\frac{d\alpha}{dt} = K\alpha^m(\alpha_f - \alpha)^n \quad (1.12)
\]

where \(\alpha_f\) is the maximum degree of cure and \(m, n\) are fitting parameters independent of temperature. \(K\) is the rate constant and depends on temperature. If the reaction is catalyzed by the products of reaction, equation (12) can be recasted as

\[
\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_f - \alpha)^n \quad (1.13)
\]

where \(k_1\) is the rate constant for the reaction catalyzed by the groups initially present in the resin and \(k_2\) is the rate constant for the reaction catalyzed by the newly formed groups and represents the influence of reaction products on the rate of reaction.

Opalicki, et al., investigated the cure kinetics of carbon fiber reinforced TGDDM/DDS epoxy systems using DSC.\(^{[50]}\) It was concluded that carbon fibers exert only a small influence on the cure kinetics. This is supported by experimental results i.e. activation energy for the neat resin and prepreg are 82.0 and 72.7 kJ/mole and \(\ln K\) values are 16.20 and 13.60 respectively for the autocatalytic kinetic model.

Autocatalysis takes place at the early stages of cure and diffusion control at later stages of cure, making cure analysis complicated. Horie, et al., adapted a kinetic mechanism to account for diffusion control.\(^{[50]}\)

The overall rate constant was modified by taking into account the rate constant for diffusion controlled reaction. According to Havlicek and Dusek,\(^{[50]}\) the rate constant was modified to …
\[
\frac{1}{k_a(\alpha, T)} = \frac{1}{k_T(\alpha, T)} + \frac{1}{k_d(\alpha, T)}
\]  

(1.14)

where \(k_a\) is the overall rate constant, \(k_T\) is the rate constant for the chemically controlled reaction and \(k_d\) is the diffusion controlled rate constant.

Matejka, et al., studied network formation, on curing epoxy resin systems such as DGEBA and TGDDM with amines.\[^{51}\] It was concluded that the system with TGDDM undergoes cyclization which results in a delay of gelation and promotes cure to higher conversions, something not observed with DGEBA. The rate of network build up was studied for epoxy resin systems containing epoxies such as DGEBA, diglycidylaniline (DGA) and TGDDM cured with different amines such as Octane-1,8-diamine (OMDA), 4,4’-diaminodiphenyl methane (DDM) and 4,4’-diaminodiphenyl sulfone (DDS). It was found that the reactivity of amines are in order of OMDA>DDM>DDS while epoxides follow the order TGDDM>DGEBA>DGA.

The influence of the structure of both epoxies as well as curing agents on the cure kinetics was studied by Stutz, et al., by considering \(E_s\), the segmental activation energy.\[^{52}\] \(E_s\) is defined as the average minimum energy required to a give a chain enough mobility to allow for reaction. The \(E_s\) values for DGEBA and TGDDM vary from 0.3 to 0.8 kJ/mole This was attributed to the higher functionality of TGDDM over DGEBA.

The symmetry effect on network formation was illustrated by considering DGEBA cured with structural isomers of DDS. Segmental activation energy increases from 0.3 to 1 kJ/mol when symmetric 4,4’-DDS was replaced by its more unsymmetric 3,3’-DDS (as shown in figure 1.7). The amino groups in 3,3’-DDS are more basic than 4,4’-DDS leading to fast initial cure but slow at the end.
The effect of fortifiers such as PGEHA (a condensation product of phenyl glycidyl ether (PGE) and 4-hydroxy acetanilide (HA)), and VCDRC (a condensation product of vinyl cyclohexane diepoxide (VCD) and resorcinol (RC)) on the cure kinetics and thermal stability of resin systems with TGDDM cured with DDM/DDS was studied by Hitesh, et al., \cite{53}. It was found that the onset of curing of the base resin system (118 °C and 145 °C), complete cure temperature for the base resin system (215 °C and 270 °C) and temperature range over which the resin is cured for the base resin system (97 °C and 125 °C) are higher for the system cured with DDS than with DDM. This was attributed to the electron withdrawing sulfonyl group in 4,4’-DDS that lowers the reactivity of the

Figure 1.7.\cite{52} Symmetry effects in the thermoset cure kinetics.
DDS curative. The trends in cure of epoxy systems with fortifier depends on both the structure of the amine curing agent and the functionality on the fortifier.

The thermal stability and activation energy of degradation of the epoxy systems with and without fortifier (20 phr, parts per hundred of resin) are in the order of TGDDM-DDS > TGDDM-DDS-PGEHA > TGDDM-DDS-VCDRC > TGDDM-DDM > TGDDM-DDM-VCDRC > TGDDM-DDM-PGEHA. The high thermal stability of the systems with DDS was attributed to the greater heat resistance imparted by the sulfone group to the cured resin.\(^{(53)}\)

Portelli, et al., studied fluorine based epoxy resins as advanced composite matrix resins.\(^{[54]}\) It was concluded that the resins with fluorine in the back bone have both high Tg and extremely low sensitivity to moisture absorption. SP-500, a carbon fiber prepreg based on fluorine containing resin absorbs moisture 80% less than the TGDDM/DDS epoxy system.

1.4.3. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) is a technique that characterizes the mechanical response of a material by monitoring property changes (G*, G’, G”, η, …) with respect to temperature and / or frequency of operation.\(^{[55]}\)

Dynamic mechanical analysis involves the application to a material of an oscillating stress. From this method, the tendency to flow (viscosity) can be calculated from the phase lag and the stiffness (modulus) from sample recovery, as shown in figure 1.8(a). If the material is perfectly elastic, the deformation and hence the strain occur exactly in phase with the applied stress. If perfectly viscous, the strain will be exactly 90° out of phase. When some internal molecular motion is occurring in the same frequency
range as the implied stress, the material exhibits viscoelastic behavior and the strain response will lag behind the applied stress by some angle $\delta$. This phase lag results from the time necessary for molecular rearrangement and is associated with relaxation phenomena. The ratio of stress to strain is the Youngs modulus, $E$, a measurement of materials stiffness and is shown in figure1.8(b).[55]

The advantage of this method over others is that it gives information about major transitions as well as secondary and tertiary transitions which are not identifiable by other methods.

This technique is useful to observe viscoelastic response in polymers. It separates the dynamic modulus of the material into two distinct parts, i.e., elastic and viscous (or damping component). The elastic component ($G'$) describes the energy stored in the system whereas the viscous component ($G''$) describes the energy dissipated during the process. Measuring the mechanical loss factor ($\tan \delta = G''/G'$) as a function of temperature is useful when comparing the viscoelastic responses of different materials.

DMA can be used to analyze a wide variety of materials in different geometries. Samples can be tested in the form of bars, films, fibres and viscous liquids. The sample weight is typically between 1-2 gm. The dynamic mechanical analyzer (DMA) can provide valuable information about changes in molecular motion with temperature. Some of the applications of the DMA are measuring storage and loss modulus ($G'$ and $G''$), glass transition temperature ($T_g$), Sub Glass transition temperatures ($\beta$), degree of crystallinity, heat dissipation properties, etc.
Figure 1.8. (a) DMA supplies an oscillatory force, causing a sinusoidal stress applied to the sample and generates a sinusoidal strain. The lag between the stress and strain waves quantifies modulus, viscosity and damping. (b) The ratio of stress to strain is the modulus, \( E^* = E' + i E'' \) and \( \eta^* = E^*/\omega \), where \( E^* \) is the complex modulus and \( \eta^* \) is the complex viscosity\[55\]

The stress \( \sigma \) and strain \( \varepsilon \) can be expressed as a function of time as follows

\[
\sigma = \sigma_o \sin(\omega t + \delta) \tag{1.15}
\]

\[
\varepsilon = \varepsilon_o \sin \omega t, \text{ where } \varepsilon \text{ is the resultant strain from applied stress} \tag{1.16}
\]

Where \( \omega \) is the angular frequency and \( \delta \) is the phase angle. Then

\[
\sigma = \sigma_o \sin \omega t \cos \delta + \sigma_o \cos \omega t \sin \delta \tag{1.17}
\]

The stress can be considered to consist of two components, one in phase with the strain \((\sigma_o \cos \delta)\) and the other \(90^\circ\) out of phase \((\sigma_o \sin \delta)\). When these are divided by the strain, the modulus can be separated into in-phase (real) and out of phase (imaginary) components. These relationships are:

\[
\sigma = \varepsilon_o E' \sin \omega t + \varepsilon_o E'' \cos \omega t \tag{1.18}
\]

\[
E' = \frac{\sigma_o \cos \delta}{\varepsilon_o} \text{ and } E'' = \frac{\sigma_o \sin \delta}{\varepsilon_o}
\]
Where $E'$ is the real part of the modulus, and, $E''$ is the imaginary part. The complex representation for the modulus can be expressed as follows

$$E^* = E' + iE''$$  \hspace{1cm} (1.19)

$$\tan\delta = \frac{E''}{E'}$$  \hspace{1cm} (1.20)

The real part of the modulus ($E'$) is called the storage modulus. This is because it is related to the storage of energy as potential. The imaginary part is the loss modulus ($E''$) and is associated with the dissipation of energy as heat when the material is deformed.

$\tan\delta$ measures internal friction or damping and is the ratio of energy dissipation per cycle to the maximum potential energy stored during a cycle. The damping is also an indicator of how efficiently the material loses energy to molecular rearrangements and internal friction.

$\tan\delta = \frac{E''}{E'} = \frac{\eta''}{\eta'}$ where $\eta''$ is the energy loss portion of the viscosity and $\eta'$ is the storage portion and it is shown in figure 1.8(c).

DMA gives the values of viscosity and modulus at each point during a temperature scan allowing us to estimate kinetic behavior as a function of temperature. From this technique, we can determine the minimum viscosity during cure, the time to minimum viscosity, the time spent at minimum viscosity during cure, the onset of cure, and the gel point. The gel point is the cure state where the material changes from a viscous liquid to a viscoelastic solid. The viscosity starts to increase when the contribution due to cure of the material overtakes the softening of the material, when it is heated. As the viscosity increases, a crossover between $E'$ and $E''$ occurs and the gel
point is reached when $\tan \delta (E''/E') = 1$, when crosslinks have progressed to form an initial infinite network throughout the specimen. A reaction will cure completely without vitrification if the cure temperature is above the ultimate $T_g$ of the material. The significance of multi step cure is to drive reactions to completion and to extend the minimum viscosity range to allow greater control in forming or shaping of the material.

The simplest method of application of DMA is to hold the temperature constant and scan the material across the frequency range of interest. Sampling frequencies are often performed with a simultaneous temperature scan to speed up data collection, but the data may not be accurate as two variables are changing at the same time. Ideally, frequency scans should be done isothermally.

Ratna et al., investigated the gelation and vitrification of epoxy resins with different epoxy functionality viz. TGDDM, TGAP and DGEBA. There is an increase in viscosity with functionality. A higher viscosity in turn restricts chemical reaction which requires molecular mobility. Hence, TGDDM gels after TGAP and DGEBA.

Lopez et al. studied the time for gelation ($t_{gel}$) and the time for vitrification ($t_{vit}$) for three epoxy systems, viz,

- DGEBA/1,3-bisaminomethylcyclohexane (1,3-BAC),
- tetruglycidyl-4,4’-diaminodiphenylmethane (TGDDM) / 4-4’-diaminodiphenyl sulfone (DDS) and
- TGDDM/epoxynovolac (EPN)/DDS

at different isothermal temperatures using DMA. Gelation was determined as the onset of massive increase in storage modulus or by the peak of $\tan \delta$. Activation
energies for the cure of these systems were calculated from plots of $t_{gel}$ versus $T^{-1}$ and they are in good agreement with values obtained by DSC, for the above systems for the same isothermal runs. The time for gelation $t_{gel}$ can be obtained from DMA experiments. The degree of conversion at that particular time ($t_{gel}$) can be determined from DSC results (from the plots of conversion versus time). Hence, correlating the results from DMA and DSC, the conversion values at the gel point can be calculated.

The glass transition ($\alpha$) and other sub transitions ($\beta, \gamma, \delta$) can be noticed during a DMA scan as shown in figure 1.9.\textsuperscript{[55]} The area above Tg and below the melt is known as the rubbery plateau. The length of this area is dependent on the molecular weight between the entanglements and the modulus is proportional to either number of cross links or the chain length between entanglements.

Gelation, vitrification and tan $\delta$ can be noticed from figure 1.9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{DMA Transition.png}
\caption{Transitions that occur during DMA analysis of a cured resin.\textsuperscript{[55]}}
\end{figure}
1.4.4. Thermal Volatilization Analysis

Thermal Volatilization Analysis (TVA) is first described by McNeill. This is a method useful for the characterization of polymers and the study of thermal degradation processes. The products of polymer pyrolysis are of three kinds, i.e.,

i. involatile residue left behind in the sample boat

ii. high boiling oils and waxes on the walls of the vicor glass tube that holds the sample boat and

iii. volatiles in the form of gases and volatile liquids that pass to traps on the vacuum line (condensable or non-condensable)

The main concept behind TVA, i.e., in a continuously evacuated system, volatiles are lost from a heated sample to the cold surface of a trap on the vacuum line. During this process, the small pressure developed is measured by pirani gauge as the sample temperature is increased in a linear manner, thereby the thermograms are generated as plots of pressure vs time and temperature.
McNeill demonstrated that the degradation behavior represented by TVA and SATVA curves was also useful for fingerprint materials, polymer with additives and copolymers such as vinyl acetate – ethylene, vinyl acetate – styrene, vinyl acetate – vinyl chloride and polymer blends such as PVA-PVC, PVA-PMMA\textsuperscript{[62-65]}. Stevenson et. al studied the degradation of an acetylene terminated sulfone(ATS) resin.\textsuperscript{[66]} They successfully determined the mechanisms of degradation using TVA and SATVA. It was concluded that at lower temperatures, chain scissions are due to thermally weak linkages from sulfones. At higher temperatures, chain scissions are attributed to polyaromatic ring fusion.

Sub-Ambient Thermal Volatilization Analysis

Sub-Ambient Thermal Volatilization Analysis was conducted for all condensable volatiles collected during the TVA experiment.\textsuperscript{[61,66,67]} McNeill demonstrated the use of SATVA to study the volatile products of degradation of a copolymer of vinyl bromide(VB) and methyl methacrylate(MMA).\textsuperscript{[68]} Each product vaporizes according to volatility and is monitored in the trace SATVA. Three major products carbon dioxide, methyl bromide and MMA were identified by gas phase infrared spectroscopy.

1.4.5. Thermomechanical Analysis

Thermo Mechanical Analysis (TMA) was used primarily to determine dimensional changes in a sample while the sample is heated, cooled or held at fixed temperature under applied force. Two factors are paramount in the interpretation of a TMA experiment. The first is the onset of penetration which locates the temperature (s) at which the resin first softens and is analogous to the resin $T_g$. The second is the degree of penetration which is inversely proportional to the perfection of the network.
1.5. Phthalonitrile Resins

Polymer composites are envisaged to be the effective alternatives to concrete and steel due to their high strength to weight ratio and environmental stability\(^{[69]}\). These properties make them dominant materials in most of the high performance missiles and aircraft structures. However, in aerospace and construction industries the limiting factors for the application of polymeric composites are cost, high combustibility and limited high temperature application i.e, application window less than 200 °C.

Phthalonitrile polymers are under development as high-temperature polymers for a wide variety of applications such as composite materials, adhesives and electrical conductors.\(^{[69]}\) It is also established that mechanical properties and thermal and oxidative stability of phthalonitrile based composite materials are superior to many of the high temperature composites. Keller, et al., demonstrated that the phthalonitrile networks can be synthesized upon curing with aromatic diamine or phenolic (~1-3%) catalysts. These networks have high \(T_g\) values (\(\geq 300\)°C) and excellent thermooxidative stability and are useful for development of new composite materials for marine and aerospace applications.

Satya et al. studied the cure behavior and properties of three systems from the phthalonitrile monomers 4,4’-bis(3,4-dicyanophenoxy)biphenyl (BPh), 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (BAPh), 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane (6FPh) cured with an aromatic curing agent 1,3-bis(3-aminophenoxy)benzene (APB).\(^{[70]}\) The rate of polymerization of the three polymers are in the order of 6FPh>BPh>BAPh. This is attributed to the more electrophilic nitrile groups due to the presence of the electron withdrawing –C(CF\(_3\))\(_2\)-
linking unit relative to –C(CH₃)₂-linking unit in BAPh. The total heat release at 900 °C is 4.8, 2.1 and 1.5 kJ/g accordingly and weight losses from Thermogravimetric analysis (TGA) experiments at 650°C for the above three systems are 5.8, 4.9 and 2.5% which is an indication of their high thermal stability.

Satya, et al., investigated the cure reactions of an aromatic ether-containing monomer, 4,4′-bis-(3,4-dicyanophenoxy)biphenyl with different aromatic diamine curing agents to increase the processability of phthalonitrile based composites.\textsuperscript{[71]} 1,3-bis(3-aminophenoxy) benzene (m-PAB) curing agent was substituted with low volatile sulfone containing diamines bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) and bis[4-(3-aminophenoxy)phenyl]sulfone (m-BAPS). It has been established through IR studies that triazene rings formed during the cure process but the exact mechanism of the amine-phthalonitrile reaction is still unknown. Cure of phthalonitrile with BAPS is more advantageous than APB due to slow polymerization and thereby broad processing window. This is attributed to the lower basicity of the BAPS due to the electron withdrawing sulfone group compared to the electron donating phenoxy group of APB. Further the deactivation is more pronounced when the amine substitution is at para position. Thus, the p-BAPS is more advantageous than the m-BAPS. The $T_g$ of the thermoset with m-BAPS as curing agent is higher than the p-BAPS and is attributed to the low reactivity of the p-BAPS.

A variety of phthalonitrile monomers containing aromatic ether, thioether, imide and sulfone linkages between the terminal phthalonitrile units have been synthesized. The polymerization reaction can be initiated with different types of curing additives such as organic amines, strong organic acids, organic acid/amine salts, metallic salts and metals.
Teddy, et al., synthesized phthalonitrile monomers with terminal phthalonitrile units interconnected with sulfonyl linkages thereby varying the distance between the polymerization centers.\textsuperscript{[72,73]} The chemical and physical properties of the polymers depend on the flexibility in the interconnecting linkages and also on the bridging groups. Some of the bridging groups with best properties are those with aromatic, polar and flexible moieties such as phenoxy and sulfone groups.

Conventional epoxy based composites and adhesives have a maximum service limit of 200 °C but polyimide resins shows a limit of 300 °C.\textsuperscript{[74-78]} The disadvantage with polyimide systems is that they produce voids due to the evacuation of volatiles during polymerization. Hence, polyphthalocyanines with diether linkages were synthesized in which flexible linkages reduce brittleness and intractability.

Efforts were made to develop polymers from an easily processable, potentially low cost phthalonitrile monomer and converting them to conductive material.\textsuperscript{[81-84]} Materials with high conductivity can be obtained either by chemical doping of a linear conjugated system or by thermal treatment. In the first case, the conductivity varies with the amount of dopant. Conductivity by thermal treatment was achieved by Teddy, et al., by polymerizing diether-linked bisorthodinitrile monomers with amine curing agent at temperatures between the melting point of the monomers and thermal decomposition point for the polymers.\textsuperscript{[79,80]} It was found that conductivity of the resulting polymer is increased linearly as a function of polymerization temperature. The limiting factor is the water absorptivity which is about 5-10% of their weight. This objective was achieved by synthesizing perfluorinated phthalonitrile and thereby forming polythalocyanine resin.
This shows improved quality such as high water repellency and oxidative resistance due to fluorocarbon bridging chains.

Phthalonitrile polymer has been synthesized by Dawn, et al., from low melting phthalonitrile oligomer, 4,4’-bis(3,4-dicyanophenoxy)biphenyl which has multiple aryl ether linkages interconnecting the terminal phthalonitrile units, and an aromatic amine curing additive, 1,3-bis(3-aminophenoxy)benzene (m-APB). Flexible ether linkages were incorporated into the polymeric backbone to increase the processability without losing thermal, mechanical and flammability properties of the phthalonitriles. Low melting phthalonitrile oligomers are in need as processable resins for composite fabrication below 150 °C for marine applications. The low melting phthalonitrile polymers also have improved toughness which was attributed to the decrease in the cross-link density of the network arising from the flexible multiple aromatic ether linkages. The m-APB is a good curing additive as it has a low melting point around 109 °C and reacts with the oligomers at processing temperatures of 150-200 °C.

A multiple ether linked phthalonitrile was synthesized by Mathew, et al., which has a large processing window and low softening temperature. This bisphenol A based phthalonitrile resin was synthesized from excess of bisphenol A and 4,4’-difluorobenzophenone and capped with 4-nitrophthalonitrile. This phthalonitrile monomer with aromatic ether linkages was cured with p-BAPS (which has high thermal stability with initial processing temperature ~200 °C). This resin has desired properties such as a longer processing window (softening temperature around 75 °C, free-flow around 145 °C and polymerization temperature higher than 250 °C), enhanced processability, thermal and thermooxidative stability.
1.6. **Overview of the study**

This study is focused on the chemical characterization and cure kinetics of prepreg resins (an assembly of fibers impregnated with resin) T800/3900 and T300/934 which are used in the fabrication of load bearing composite structures for incorporation into the fuselage of next generation aircraft. These materials are cured to generate thermosets with desired properties needed for a particular application. It is also focused on the investigation of the thermal stability of easily processable phthalonitrile resin.

These prepreg resins are cured in the standard cure cycle in the autoclave. Sometimes materials with sub standards are generated due to application of improper or insufficient cure cycles. Sometimes, hot spots are generated in the parts leading to char the composite and degrade the prepreg resin resulting in complex and expensive repairs. It is found that hot spots are generated where there is a maximum rate of reaction and sufficient heat is produced to char the material. Hence, there is a need to revise the cure cycle that will minimize the char formation by minimizing the spike so that the rate maximum should occur at lower temperatures. Chemical analysis is also necessary to gain insight into the composition and reactivity.

Chemical characterization of the prepreg resins was carried out with thin layer chromatography, FTIR and NMR spectroscopy to identify the major components of the resin systems.

The cure profile of the prepreg resins T800/3900 and T300/934 was investigated using Differential Scanning Calorimetry(DSC). A series of experiments were conducted for both the prepregs under dynamic (ramp), isothermal (soak) and combined ramp and soak conditions. Under dynamic conditions, experiments were conducted over a range of
heating rates from 0.5 °C to 20 °C/min for both the prepreg resins. However, isothermal experiments were conducted from 120 to 180 °C for the resin T300/934 and for the resin T800/3900 ranging from 110 to 190 °C depending on their curing temperature range. Combined ramp and soak experiments for both the above resin systems were designed with a range of heating rates from 0.5 to 5 °C/min in the ramp part of the experiment combined with different isothermal temperatures starting from 140 °C to 180 °C for the resin T300/934 and from 160 °C to 190 °C for the resin T800/3900. These experiments were designed as a modification to the industrial cure cycles.

2D plots were generated for degree of cure and rate of cure as a function of time and temperature which helped in predicting the conversions at unknown variables. The Gel point for the prepreg resin T300/934 was predicted from the rheometric experiments. For the prepreg resin T800/3900, the mechanical properties such as build up of initial modulus and gel point were determined through DMA and the products of degradation were determined with TVA and SATVA. Gas phase IR and NMR techniques were applied to materials isolated by TVA and SATVA.

The conditioned Phthalonitrile resin was subjected to cure from 250 °C to ≤ 350 °C with heating rates 0.1,0.2 and 0.3 °C/min. The combined Ramp and Soak experiments were conducted by ramping the material from 250 to 300 and 350 °C at 0.3 °C/min and soaking at the final temperatures. The cured material was subjected to thermomechanical analysis (TMA) to determine its thermal stability. The bubble formation during conditioning of the material was elucidated with TVA and SATVA. The materials isolated during the above experiments were identified with Gas phase IR and NMR techniques.
CHAPTER 2

Materials and Physical Methods

This chapter presents a listing of all chemicals and solvents employed at various stages of research work. Further, a brief discussion of spectroscopic and thermal analysis techniques are also presented here.

2.1. Materials

Sheets of T800/3900 and T300/934 prepreg resins were received from the industry and refrigerated at -20 °C until use.

BisphenolA based resins (Epon 825, 834, 1001F, 1004F and 1009F) were obtained as research samples from Resolution Performance Products and stored at 0 °C until use.

Tetraglycidyldiaminodiphenyl methane (TGDDM) epoxy resin was received from Huntsman Advanced Materials.

DDS, Bisphenol-A, Potassium Carbonate, 4,4’-difluorobenzophenone, 4-nitrophthalimide, 4-nitrophthalamide and toluene were received from the Aldrich chemical company.

Dimethylformamide with molecular sieves, 4,4’-Bis(3-aminophenoxy)diphenyl sulfone, tetrahydrofuran, chloroform were received from Acros Organics.

Thionylchloride and 4-nitrophthalonitrile were received from Fluka Chemicals.

Solvents such as cyclohexane, ethylacetate, and isopropylalcohol were from Fisher Scientific Chemicals.

KBr (FTIR Grade) was received from the Alfa Aesar Company.
2.2. Synthesis of compounds

“Synthetic” 934 epoxy resin: Tetrabcuryldiaminodiphenyl methane (TGDDM/MY720) epoxy resin and diaminodiphenylsulfone (DDS) curative were weighed out in a mole ratio of 1.1 mole DDS to 1.0 mole TGDDM. The DDS was dissolved in minimum acetone and added to the TGDDM resin in a wide mouthed freeze dry flask to create a clear mixture. An oil bath was pre-heated to 120 °C and set aside. The freeze dry flask was attached to a good vacuum pump through a dry ice trap and pumped at room temperature until rising viscosity caused excessive foaming. The flask was then heated with pumping by dipping into the oil bath, then removing from the bath when bubbling became excessive. The flask was then heated at 120 °C for 10 min. The flask was then removed from the oil bath and quenched in an ice/water bath. The resin mixture is opaque at room temperature and clarifies at 140 °C. The acetone content in the resin mixture was then measured by proton NMR spectroscopy. By these means, we were able to prepare “synthetic” 934 resin.

2.3. Physical Methods

Instrumentation

FT-IR Spectroscopy

A Thermo Nicolet Avatar FTIR spectrometer was used to obtain FT-IR spectra of the resin and reference materials as KBr discs and liquid films on sodium chloride salt plates. About 2 mg of the material was mixed with about 300 mg of KBr and mixed in a dentists ‘wiggle bug’ mixer then pressed at 20000 lb pressure to produce semi-transparent coherent discs for analysis. Otherwise, the components of the resin that are soluble in
organic solvents were dissolved then smeared onto a salt plate for analysis after evaporation of the solvent. The samples were subjected to a maximum of 128-256 scans to produce a good signal to noise ratio.

**Nuclear Magnetic Resonance Spectroscopy**

A Varian 300 MHz or a Varian 400 MHz NMR spectrometers was used to obtain solution proton and carbon-13 spectra. Samples were dissolved in appropriate deuterated solvent and were analyzed by \(^1\)H and \(^{13}\)C NMR Spectroscopy.

**Thin-Layer Chromatography**

Components of the resin were separated using thin layer chromatography using silica gel with fluorescent indicator. Samples around 200-300mg were dissolved in chloroform, centrifuged and filtered, and the supernatant liquid was painted across a preparative TLC plate. The plate was developed using a mobile phase consisting of a mixture of cyclohexane, ethylacetate and isopropyl alcohol in 6:3:1 ratio. The plate was turned 90ºC and redeveloped using the same solvent system. The material was finally removed using Tetrahydrofuran (THF). The two isolated fractions were analyzed by \(^1\)H NMR spectroscopy.

**Differential Scanning Calorimetry (DSC) and Data Analysis**

Thermal analysis of the resins was performed using a Perkin Elmer DSC6 instrument with proprietary software. Samples were cured in hermetically sealed aluminum pans. Sample sizes were about 20 mg to generate a sufficient exotherm for reliable measurement. The instrument was pre-set at a starting temperature of 30 ºC for all DSC runs.
Data analysis was performed using Microsoft Excel. Three dimensional plots with best fit surfaces were constructed where appropriate using Table Curve 3D version 4.0 for Windows (Systat Software).

**Dynamic Mechanical Analysis:**

Dynamic Mechanical Analysis tests were performed by AvPro, Inc., to investigate the buildup of prepreg resin network structure as well as properties during the cure cycle as a function of cure state and thermal history. The machine was operated at a fixed frequency less than 10 Hz. Storage modulus and loss modulus were calculated for T800/3900 prepreg resin as a function of time and temperature for ramp and soak experiments over a range of heating rates and using different soak temperatures such as 120 °C, 175 °C and 185 °C. Ramp and Soak experiments were conducted to develop a relationship between the build up of storage modulus with conversion obtained from DSC experiments. Experiments were also conducted to show how the build up of modulii is influenced by change in ramp rates and by the interruption of cure at low conversion.

**Thermal Volatilization Analysis:**

The prepreg resin was studied by Thermal Volatalization Analysis in a continuously evacuated system to identify the volatiles produced during the cure process of the prepreg resin T800/3900 and volatiles produced by the unconditioned Phthalonitrile resin which are root cause of bubbles during conditioning of the resin. A vacuum to an order of $10^{-4}$ Torr was achieved using a rotary oil vacuum pump in combination with a silicon oil diffusion pump and liquid nitrogen cold traps. A Sample was placed in a quartz crucible and heated in a vicor glass tube which was surrounded by a muffle furnace with a chromel-alumel thermocouple. The vicor glass tube was attached
to the vacuum line by an adapter with an internal cold finger, that was kept cold by a continuous flow of cold water to condense the ‘Cold Ring Fraction’ of degradation. A thermal insulation tape surrounding the vicor tube just above the oven to keep the outside of the tube hot. Copper cooling coils were placed around the vicor tube above thermal insulation which protects the greased adapter from freezing. A reproducible ramp of 3 °C/min was achieved from 20 °C to 350 °C by using an Omega Temperature Controller, CNI 8A22. The sample temperature was determined depending on the temperature of the furnace by means of a calibration experiment. The calibration curve for the apparatus was generated by simultaneous recording of sample and oven temperatures with two thermocouples. Volatiles produced during the process were recorded by a series of four Edward PRE 10K pirani gauges attached to the vacuum line at different points. Pirani gauge 1 was located next to the sample tube and it measures total volatile production. Pirani gauge 2 was situated next to a trap which was not brought into use during this study. Pirani gauge 3 was situated following a trap cooled to -196 °C with liquid nitrogen. The difference in the pressure between Pirani gauges 1 and 3 measures the production of room temperature liquids such as water and benzene and condensable gases such as carbon dioxide. Data acquisition was made through an Omega Data Acquisition, OMB-DAQ-56 data collection hardware – software package. The Data Acquisition unit was attached to a series of four PRE 10K pirani gauges as stated above to read the voltage - pressure, and to the muffle furnace and Sub- Ambient Thermal Volatilization Analysis (SATVA) to read the temperatures at which volatiles were produced during curing. The production of volatiles as a function of temperature and voltage was recorded
On completion of the experiment, the residue in the boat was weighed and the internal cold ring fraction was washed and collected with chloroform to collect the oligomeric fraction for subsequent gravimetric, IR and liquid NMR analysis.

**Sub-Ambient Thermal Volatilization Analysis**

Sub-Ambient Thermal Volatilization analysis was conducted for all condensable volatiles collected during the TVA experiment. Condensable volatiles were collected in the trap cooled to $-196^\circ C$ and were transferred into another trap surrounded by paraffin wax and cooled to $-196^\circ C$ with liquid nitrogen. The paraffin wax contains a thermocouple which was connected to the DAQ-56 data capture unit so that the trap temperature can be recorded as a function of time. The liquid nitrogen was removed from the trap and the paraffin wax was allowed to warm up slowly to about 10 $^\circ C$ in about 90 minutes. Gases evolved from the trap as it was warmed up were measured by Pirani gauge 3 and recorded by the DAQ-56 unit together with the trap temperature. These gases were finally condensed into a cold trap at $-196^\circ C$ and then distilled into a gas IR Cell for IR analysis. After completion of the gas IR analysis, the product mixture was condensed onto frozen d6 acetone for NMR analysis with more than 99% efficiency.

**Thermomechanical Analysis:**

Thermomechanical tests were performed by NIAR laboratories to investigate the softening temperature and degree of penetration of phthalonitrile resin. A TA QA 400 TMA instrument was used and the cured resin sample was subjected to a sharp probe with a load of 0.5 N under nitrogen atmosphere. The resin sample was cured previously
from 250 °C to an end temperature ≤ 350 °C at the heating rates 0.1, 0.2 and 0.3 °C/min under nitrogen atmosphere in a mould to generate parallel surfaces. Then the resin was heated in the TMA instrument to 500 °C at 10°C/min with a sharp probe on the sample.
3.1. Introduction

To properly study the cure behavior of the resin, it is necessary, first of all, to determine its chemical composition. Studies shows that many of the commercially available high performance epoxy based aviation resins contain N,N,N',N'-tetraglycidyl-4,4'-diamino diphenyl methane (TGDDM/MY720) and / or the diglycidyl ether of bisphenol A (DGEBA) as epoxy resin precursors and diamino diphenyl sulfone (DDS) as the curing agent. Identification of components was achieved by direct comparison of the characteristic peaks with that of NMR reference compounds, and simulated spectra using NMR modeling software (ACD™).

Manufacturing of large load bearing composite structures and repairs to parts in the aerospace industry involves curing of epoxy resins and adhesives as pre-impregnated composite materials in the autoclave. Repairs to the parts are conducted using prepreg bonded to the part using a high shear adhesive. The repair is then autoclaved. Both the resins and prepreg materials are shown to produce good product consistently but occasionally a substandard part is produced. Hence, there is a need to better optimize the cure cycle in the autoclave to fully cure both resin and adhesive while minimizing problems like char formation. Some cure takes place in the prepreg which is B-stage by the supplier.

An example of an autoclave cure cycle was produced in figure 3.1. The autoclave is heated from ambient temperature to 120 °C (250 °F) at a rate of 3 °C (5.4 °F) /min (step I) , and held there for 50 min to equalize temperatures throughout the autoclave
(step II). The autoclave is then heated to 175 °C (350 °F) at a rate of 3 °C (5.4 °F) /min (step III), and held there for 120 min (step IV). The entire cure cycle, excluding time required for loading and unloading the autoclave, and cool-down from 350 °F, takes a minimum of 4.5 hours.

Figure 3.1. An example of an autoclave cure cycle for epoxy based thermosets

To properly understand this industrial cure cycle, it is not sufficient to simply perform isolated ramped and isothermal cure experiments as is commonly undertaken in research and quality control laboratories. Rather, the two must be combined to fully follow the cure cycle in the industrial autoclave.
To begin with, should appreciable cure be achieved during segments I and II of the cure cycle, the problem would become intractable. Fortunately, it was simplified as negligible cure is usually achieved during segments I and II of the cure cycle. Thus, the entire cure cycle can be modeled around a single ramp and soak cycle. Three sets of experiments were designed to investigate the cure profile

i. Dynamic temperature scan (ramp) over a range of heating rates from 0.5 to 20 °C/min

ii. Isothermal temperature scan (soak) from 110 °C to 190 °C

iii. Combined both the ramp and soak segments to mimic the actual ramp and soak cure cycle.

3.2 Experimental Section

3.2.1 Materials

This is mentioned in chapter 2.3

3.2.2 FT-IR Spectroscopy

This is mentioned in chapter 2.3

3.2.3 Nuclear Magnetic Resonance Spectroscopy

This is mentioned in chapter 2.3

3.2.4 Thermal Analysis

Thermal analysis of the resin using a Perkin Elmer DSC6 instrument has been discussed in chapter 2.3

Dynamic Temperature Scanning (ramp) experiments were conducted by scanning from 30 °C to a maximum of 300 °C over various heating rates ranging from 0.5 to 20
ºC/min. The sample was cooled to 30 ºC and rescanned from 30 ºC to 300 ºC at 10 ºC/min to determine the ultimate glass transition temperature, Tg (Tg∞).

Isothermal scanning (soak) experiments were conducted from 110 ºC to 190 ºC in increments of 5 ºC. The sample was ramped quickly to the isothermal temperature at 50ºC/min, then soaked at that temperature until the signal returned to the baseline. The sample was cooled down to 30 ºC and rescanned to 300 ºC at 3 ºC/min to determine the intermediate Tg and residual exotherm. The sample was again cooled down to 30 ºC and scanned to 300 ºC at 10 ºC/min to determine the ultimate Tg (Tg∞).

Combined Ramp and Soak experiments were conducted in four steps. The sample was subjected to dynamic scanning from 30 ºC to an end cure temperature at heating rates ranging from 0.5 to 5 ºC/min. The sample was cooled down to 30 ºC and ramped quickly at 50ºC/min to the end temperature, then subjected to isothermal cure at that temperature until the signal returned to the base line. Then the sample was cooled down to 30 ºC and rescanned to 300 ºC at 3 ºC /min to determine intermediate Tg and residual cure. The sample was then cooled to 30 ºC and again scanned to 300 ºC at 10 ºC/min to determine the ultimate Tg. The isothermal scanning was conducted from 155 ºC to 190 ºC in increments of 5 ºC.

Data analysis and two dimensional plots were performed using Microsoft Excel and Origin 6.1 (Origin Lab Corporation). Three dimensional plots with best fit surfaces were generated using table curve®3D version 4.0 for Windows (Systat Software). One and two component Kamal fitting experiments were performed using the OriginLab™ graphing software.
3.2.5. Dynamic Mechanical Analysis

This is mentioned in chapter 2.3

3.2.6. Thermal Volatilization Analysis

This technique is discussed in chapter 2. Two TVA runs were made by ramping the sample (T800/3900 prepreg resin) at a heating rate of 3 °C/min from 20 °C to 267 °C and 350 °C.

Sub-Ambient Thermal Volatilization Analysis

This is mentioned in chapter 2.3

3.3 Results and Discussion

A combination of spectroscopic and separation techniques were employed to gain insight into the chemical composition of the resin in the prepreg. By combining the results obtained from proton Nuclear Magnetic Resonance Spectroscopy and Infrared Spectroscopy we were able to generate a semi-quantitative compositional analysis of the resin.
3.3.1. FT-IR Spectroscopy

Figure 3.2. FT-IR spectrum of T800/3900 pre-preg resin on a salt plate after solvent was allowed to evaporate. Resin was extracted from the pre-preg with chloroform.

Figure 3.2 shows the FT-IR spectrum of the extractable resin as a KBr disc. Absorbances were labeled according to common principles or by comparison with the Infrared spectra of reference compounds. The IR spectrum affirmed the presence of aromatic and saturated material. The presence of DDS curative was affirmed by the sulfone absorbances at 1143 cm\(^{-1}\) and 1104 cm\(^{-1}\). Unreacted epoxy was identified by the absorbance at 915 cm\(^{-1}\). The absence of carboxy terminated butadiene acrylonitrile (CTBN) rubber toughening additive was affirmed by the absence of its distinctive nitrile stretch at 2236 cm\(^{-1}\), weak carbonyl stretch at about 1720 cm\(^{-1}\) due to terminal carboxylic
acids in the material, substituted olefinic stretches at 1630-40 cm$^{-1}$, and out of plane bending modes at 967 cm$^{-1}$ and 911 cm$^{-1}$, respectively. The absence of dicyandiamide (DCDA) curative was confirmed by the absence of the very distinctive nitrile absorbances at 2206 cm$^{-1}$ and 2161 cm$^{-1}$ respectively and the weak out of plane bending absorption at 925 cm$^{-1}$. The absence of a strong absorbance in the carbonyl region of the spectrum affirms that the resin did not contain a significant level of polyvinylacetate (PVA) toughening agent. The absorbance at 1720 cm$^{-1}$ was attributed to carbonyl containing impurity.

3.3.2. Nuclear Magnetic Resonance Spectroscopy

A proton NMR spectrum of the material in chloroform extracted from the uncured prepreg resin was collected and signals were identified according to accepted principle and with reference, where appropriate, to the NMR spectra of reference compounds. Because signal intensity is directly proportional to the relative number of structural units, the proton NMR spectrum of an organic mixture is especially useful in compositional analysis if it contains identifiable non overlapped resonances that allow us to quantify the structural unit in the mixture. As we were able to identify a number of non-overlapped signals in this spectrum, we found this technique to yield more information, more rapidly, than any other method of structural investigation. The proton NMR spectrum of the resin in chloroform was produced in figure 3.3.
**Figure 3.3.** $^1$HNMR spectrum of material extracted from T800/3900 prepreg resin in CDCl$_3$.

**Figure 3.4.** Identification of TGDDM (MY720) epoxy resin in the prepreg in CDCl$_3$. (TGDDM: tetra glycidyl diamino diphenyl methane)
Figure 3.5. Identification of DDS curing agent in T800/3900 pre-preg resin in CDCl₃.
(DDS: diamino diphenyl sulfone)

Figure 3.6. Identification of DGEBA additive in T800/3900 pre-preg resin CDCl₃.
Using this technique, we were able to identify TGDDM resin as a component of the prepreg (figure 3.4), along with diaminodiphenyl sulfone (DDS) curing agent (figure 3.5) and diglycidyl ether of bisphenol A (DGEBA) epoxy resin (figure 3.6). The DGEBA resin was identified as monomer due to the results of carbon-13 NMR experiments which are discussed subsequently.

Acetone is the only low boiling point solvent that will dissolve DDS. DDS is dissolved in acetone and mixed into the prepreg. The complete absence of an NMR signal at 2.05ppm for acetone in the NMR spectrum of the resin suggest either that the DDS was added to the prepreg without added solvent or that all of the acetone has been removed.

13C Nuclear Magnetic Spectroscopy

13C NMR analysis of the resin was performed to identify any toughening agents in the prepreg. The carbon 13 NMR spectrum of an organic sample is inherently simpler and easier to interpret than the corresponding proton NMR spectrum. The carbon -13 NMR spectrum of the resin mixture extracted from T800/T3900 prepreg was examined in the light of prior experience, and compared to that of reference compounds, and simulated spectra using NMR modeling software (ACD\textsuperscript{tm}), with a view to identify and interpret “unknown” signals in the spectrum. The C-13 NMR spectrum of material from the resin is produced in figure 3.7.

Reference is made to specific carbons contained in specific reference compounds corresponding to components identified as present in T800/T3900 resin.

These reference compounds are drawn in figure 3.8. Compound “A” is the tetrafunctional epoxy resin TGDDM, often referred to as MY720 (TGDDM: tetra glycidyl diamino diphenyl methane). MY720 imparts a high Tg and stiffness to an epoxy resin.
Compound “B”, diaminodiphenyl sulfone or DDS is often incorporated into prepreg resin because it is a very inactive curing agent that imparts a long shelf life to the prepreg. When cured into an epoxy resin, DDS imparts stiffness and thermal stability to the resin. Compound “C“ is the diglycidyl ether of bisphenol A (DGEBA) monomer, while compound “D” is DGEBA dimer. DGEBA is synthesized as a mixture of monomer, dimer, and higher oligomers. The overall chain length is determined by the ratio of epichlorohydrin to bisphenol A in the reaction “pot”. Compound “D” is sketched as representative of DGEBA oligomers. A DGEBA based resin with a high oligomer content is often incorporated into a formulation in order to improve fracture toughness.

Signals in the C-13 NMR spectrum of material from T800/3900 prepreg resin were assigned as indicated in figures 3.9 -3.13

**Figure 3.7.** C-13 NMR spectrum of T800/3900 pre-preg resin in CDCl₃.
Figure 3.8. Reference compounds: Compound A - TGDDM, MY720 (TGDDM: tetra glycidyl diamino diphenyl methane), Compound B - dianodiphenyl sulfone or DDS, Compound C - diglycidyl ether of bisphenol A (DGEBA) monomer, Compound D - DGEBA dimer.
Figure 3.9. C-13 NMR spectrum of T800/3900 prepreg (60 - 20) ppm

Figure 3.10. C-13 NMR spectrum of T800/3900 prepreg (100 - 60) ppm
Figure 3.11. A comparison of C-13 NMR spectra in the range (75 – 65) ppm for, (top left) – Epon 825 DGEBA resin containing monomer only, (bottom left) – material C-13 NMR spectrum of T800/3900 prepreg extracted from T800/3900 prepreg, (right) – Epon 1004 resin containing a high proportion of oligomer

Figure 3.12. C-13 NMR Spectrum of T800/3900 prepreg (140-100) ppm
DGEBA has been identified as a component of the mixture. It, therefore, became necessary to gain some insight into the oligomer content in the DGEBA added to the prepreg. Fortunately, C-13 NMR spectroscopy is ideally suited to this type of analysis. Consider DGEBA dimer – D in figure 3.8. Carbons 4 and 43 at the ends of the molecule are indicated with green arrows. Carbon 23 in the bridging motif is indicated with the brown arrow.

Epon resin 825 (M ~ 340) is almost pure monomer. If it is left at room temperature, it will eventually partly crystallize. The carbon 13 NMR signal from the end carbons in Epon 825 resin is indicated by the green arrow (figure 3.11, top left). In contrast, Epon 1004F resin (M ~ 1800) contains a high oligomer content. The carbon 13 NMR signals from the bridging carbons are indicated by the brown arrow. The much weaker signal from the end carbons are indicated by the green arrow. The strongest signal in the spectrum at highest ppm is produced by other bridging carbons corresponding to C22, C23 and C25 in figure 3.8 – D.
Carbon 13 NMR signal strengths obtained in the normal acquisition are not directly proportional to carbon content for a variety of reasons, most importantly due to insufficient time between scans to allow the carbons to relax back to a Boltzman distribution. Nonetheless, the technique is semi quantitative when comparing carbons of similar type. The NMR spectrum in the (75 – 65) ppm range of material extracted from T800/3900 is reproduced in figure 3.12, bottom left. The almost complete absence of signal from the bridging carbon (figure 3.8, “D” – C23) indicates that the DGEBA added to the prepreg is almost pure monomer.

The red arrows in figure 3.13 and insert, point to where the carbonyl signal from polyvinyl acetate (PVAc) would be located if it were present in the mixture. Apparently, PVAc (or polymer containing vinyl acetate groups) is present in the mixture only in trace amounts if at all.

### 3.3.3. Compositional Analysis of Resin in the Prepreg

Examination of the prepreg has indicated that it contains a relatively simple mixture of resin and curative. A quantitative estimation of composition was made using proton NMR spectroscopy. The proton NMR spectrum of the resin mixture was re-acquired, except using d6 acetone to better dissolve the DDS curative. The delay between scans was extended from 0.5 sec to 15 sec to ensure that the proton pool had completely relaxed between scans. The proton NMR spectrum was reproduced in figure 3.14. With reference to figure 3.8, signals designated “A” in figure 3.14 correspond to protons on carbons 3, 5, 12, and 16 of DDS – in other words, 4 protons per molecule. Signals designated “B” in figure 3.14 correspond to the low field portion of the doublet of signals generated by protons on carbons 2, 9, 27, and 31 of MY720 resin – in other words, 4
proton equivalencies per molecule. (Signal splitting is due to coupling with the single proton on the adjacent carbon). The proton singlet designated “C” in Figure 3.14 corresponds to protons on carbons 13 and 14 of DGEBA monomer i.e, 6 proton equivalence per molecule.

An estimate of the composition of resin in T800/3900 prepreg was determined by integrating these signals. A compositional breakdown is made in Table 3.1. It is evident from the table, that the active N-H to (combined) epoxy group mole ratio is about 1.14 : 1. As is usual, the curative is present in excess of the amount required for stoicheometric reaction with the epoxy.

Table 3.1
Composition of resin in T800/3900

<table>
<thead>
<tr>
<th>Component</th>
<th>Integral</th>
<th>Relative mole ratio in prepreg mixture</th>
<th>Mass % in prepreg resin mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDS curative</td>
<td>A-1.56</td>
<td>0.39 Mole</td>
<td>16.7 mass %</td>
</tr>
<tr>
<td>MY720 resin</td>
<td>B-1.00</td>
<td>0.25 Mole</td>
<td>72.6 mass%</td>
</tr>
<tr>
<td>DGEBA monomer resin</td>
<td>C-1.10</td>
<td>0.183 Mole</td>
<td>10.7 mass%</td>
</tr>
</tbody>
</table>
**Figure 3.14.** Proton NMR spectrum in d6 acetone of resin in T800/3900 prepreg. Protons used to determine proportions of DDS, MY720, and DGEBA monomer are designated as “A”, “B”, and “C” respectively in the figure.
Figure 3.15 Structures of the major components of T800/3900 prepreg resin (a) TGDDM epoxy resin (b) DGEBA monomer (c) DDS curing agent
3.3.4. Dynamic Temperature Scanning

Programmed DSC experiments were performed in order to characterize the cure kinetics during the ramped portion of the cure cycle. The prepreg sample was ramped to an end temperature - usually 350 °C, at a predetermined heating rate. A representative programmed DSC trace of the T800/3900 prepreg, at a heating rate of 5 °C/min, is shown in the figure reproduced in figure 3.16. The cure reaction is well defined and ends at around 320 °C.

![Dynamic Temperature Scanning Diagram](image_url)

**Figure 3.16.** An exotherm generated from dynamic temperature scanning of T800/3900 prepreg resin @ 5 °C/min.
The DSC cell is then cooled to room temperature and re-heated to 300 °C at a standard heating rate of 10 °C/min as is shown in figure 3.17. The absence (always) of a residual exotherm in the second programmed segment affirmed that the cure reaction had been completed during the first segment. The degree of cure (α), and the rate of cure (dα/dt) were calculated from the first programmed segment. The ultimate glass transition temperature Tg was calculated from the second programmed segment.

![Temperature vs. Heat Flow](image)

**Figure 3.17.** Heat flow curve produced at 10 °C/min of T800/3900 epoxy prepreg resin precured under programmed conditions at 5 °C/min. Note the absence of any residual exotherm and the ultimate glass transition temperature (arrowed).

The degree of cure at a fixed point in this reaction was defined as the ratio of the partial area of the exotherm up to that point to the total area under the exotherm. A set of data points (time, temperature and degree of cure) for every heating rate was generated.
The degree of cure ($\alpha$) as a function of temperature was calculated over a range of heating rates from 0.5 °C/min to 20 °C/min. and results were plotted in figure 3.18. Each curve is an average over two experiments. If a significant difference between the two experiments was observed, the experiment was repeated. The cure reaction was shifted to ever higher temperatures at higher heating rates.

**Figure 3.18.** 2D plot of degree of cure ($\alpha$) of T800/3900 epoxy prepreg resin versus temperature for cure as a function of heating rate in dynamic heating experiments.

By differentiating the plot of the degree of cure versus time, rate of cure profiles were generated for the cure reaction as shown in figure 3.19.
By using these results and Table Curve 3D software, three dimensional plots of $\alpha$ and $d\alpha/dt$ as a function of heating rate and temperature were generated as shown in figures 3.20 and 3.21. We were able to generate best fit surfaces with corresponding best fit equations for $\alpha$ and $(d\alpha/dt)$ as a function of heating rate and temperature as shown in figure 3.20 and 3.21. By using these curves intermediate conversion and rate curves can be generated at intermediate linear heating rates and temperatures. If a non-linear ramp is applied so that the heating rate is a function of temperature, then $\alpha$ and $(d\alpha/dt)$ versus temperature or time can not be generated from the graph.

Figure 3.19. 2D plots of cure rate $(d\alpha/dt)$ of T800/3900 epoxy prepreg resin versus temperature, for resin cured over a range of heating rates
Figure 3.20. 3D plot of degree of cure (α) of T800/3900 epoxy prepreg under programmed conditions as a function of heating rate (dT/dt) and temperature (T).

Figure 3.21. 3D plot of rate of cure (dα/dt) of the T800/3900 epoxy prepreg under programmed conditions as a function of temperature (T) and heating rate (dT/dt).
The apparent activation energy \( (E_a) \) can be measured for a resin cure reaction as a function of the degree of cure \( (\alpha) \). This activation energy can yield insight into changes in the mechanism of cure. As the cure reaction proceeds, the reaction medium changes – it becomes more polar due to the creation of hydroxyl functionality, and becomes more viscous due to the buildup of oligomers and ultimately a gel fraction. The former accelerates cure, while the latter retards the cure reaction. Newly formed hydroxyl groups can act as catalyst in the ring opening of the epoxy ring by the amine group. As the viscosity of the resin builds up, it becomes more difficult for the functional groups to find each other, hence the apparent \( E_a \) increases. In such a case, the reaction is said to be diffusion controlled. A plot of \( E_a \) vs \( \alpha \) for the resin was constructed by using the information summarized in figures 3.18 and 3.19

The generic rate law equation for resin cure can be stated as

\[
d\alpha/dt = k \cdot F(\alpha)
\]  

(3.1)

where \( \alpha \) is the extent of cure, and \( k \) is the Arrhenius rate constant which is defined as

\[
k = A \cdot \exp\{-E_a/RT\}
\]  

(3.2)

with \( A \) as the pre-exponential shape factor, \( E_a \) as the activation energy, \( R \) as the gas constant, and \( T \) as the temperature in degrees Kelvin.

Substituting the value of \( k \) from equation (2) in equation (1) and taking logarithms yields

\[
\ln\{d\alpha/dt\} = \ln\{A \cdot F(\alpha)\} - \{E_a / R\} \cdot \{1/T\}
\]  

(3.3)

This equation shows the rate of cure in terms of degree of cure and temperature. \( F(\alpha) \) is an empirical function that defines the relationship between cure rate and the concentrations and chemical environment of functional groups in the resin. \( F(\alpha) \)
is complicated and difficult to measure and it changes with $\alpha$. However, we can arrive at values of $E_a$ without determining $F(\alpha)$ by plotting $\ln(d\alpha/dt)$ Vs $(1/T)$ for a fixed value of $\alpha$, so that $\ln A$ and $\ln F(\alpha)$ can be made constants.

The apparent $E_a$ was determined from equation (3.3) at a fixed value of $\alpha$. $\ln(d\alpha/dt)$ and $T$ are measured at a fixed value of $\alpha$ at a defined heating rate. Therefore, the value of $\ln\{AF(\alpha)\}$ is made a constant. Data was collected for a range of fixed values of $\alpha$ at different heating rates. By plotting the value of $\ln(d\alpha/dt)$ as $y$ and $1/T$ as $x$ we generated linear graphs with a gradient equal to $-E_a/R$ and an intercept equal to $\ln\{AF(\alpha)\}$, from which $E_a$ was calculated for a fixed value of $\alpha$ as shown in figure 3.22. The plots for all measured $\alpha$ values can be found in the Appendix A. Good linearity was achieved in all the cases. The variation of $E_a$ with $\alpha$ is shown in figure 3.23.

**Figure 3.22** A plot of $\ln (d\alpha/dt)$ versus $1/T$ for T800/3900 epoxy prepreg resin, cured at a fixed degree of cure $\alpha = 0.60$. 
Figure 3.23. Plot of the apparent activation energy (Ea) of the T800/T3900 resin cure reaction as a function of the degree of cure (α) from dynamic temperature scanning.

The apparent activation energy for the cure of the resin increases as a function of α. The absence of a bump at the early stages of the cure shows that the resin does not contain a low temperature catalyst. A large increase in Ea in the final stages of cure is consistent with the massive increase of micro viscosity near the completion of the reaction, making the reaction diffusion controlled.
3.3.5. Isothermal Scanning

The prepreg resin was subjected to isothermal cure to understand the cure under soak segments of an autoclave cure cycle. The sample was ramped quickly to the soak temperature at a fast heating rate of 50 °C/min, then held at that isothermal temperature for a prolonged period of time until the exotherm could no longer be detected. A sample exotherm is illustrated in figure 3.24 for an experiment performed at 185 °C. The isothermal experiments were conducted over a range of temperatures from 110 °C to 190 °C in the increments of 5 °C. It was determined that very long times are required to achieve maximum possible cure at low temperatures. It was also determined that maximum possible cures at low temperatures were markedly less than would be required for a commercially viable autoclave cure cycle and that the maximum possible cures at higher temperatures were achieved at shorter times. However, such conversions may be achieved at unacceptably high initial rates of cure. At intermediate temperatures, the resin can vitrify and the cure reaction can be locked into a maximum intermediate cure state even after a prolonged exposure at that temperature. For this reason, the isothermal segment is followed by a programmed cure segment to measure the intermediate Tg attained after prolonged reaction at the isothermal temperature and residual exotherm produced thereafter as the resin cures to completion. This final cure is carried out from 30 to 300 °C @3 °C/min. as shown in figure 3.25. A second ramped segment verifying that the cure reaction has been completed and measuring the “ultimate” Tg of the resin, was performed from 30 to 300 °C@ 10 °C/min as shown in figure 3.26.
**Figure 3.24.** An exotherm produced from isothermal scanning of the resin at 185 °C after a rapid jump to that temperature from 30 °C.
Figure 3.25. Intermediate Tg and residual exotherm produced from the rescan of the resin partially cured at 185 °C. This rescan was done from 30 °C to 300°C @ 3 °C/min.
Figure 3.26. Ultimate Tg of the resin isothermally cured at 185 °C followed by dynamic temperature scanning at a heating rate of 3 °C/min from 30 °C to 300 °C to complete the cure, then followed by dynamic temperature scanning at a heating rate of 10 °C/min from 30 °C to 300 °C.

The total cure exotherm (total heat of reaction) was obtained by adding both the isothermal and the following ramped exotherms. The degree of cure(α) at time t under isothermal conditions was calculated as the partial area of the isothermal exotherm up to time t divided by the area of the total cure exotherm. By these means, the intermediate cure states of the prepreg as a function of time over a series of seventeen isothermal temperatures between 110 °C and 190 °C were calculated and plotted in figure 3.27.

Two dimensional plots of rate of conversion versus time for T800/3900 resin cured over a range of isothermal temperatures are reproduced in figure 3.28. It should be
noted that initial rates of cure for the resin cured isothermally at high temperatures are
very large. This could lead to temperature overshoot and possible carbonization of the
resin in an autoclave cure cycle. The probability of temperature overshoot will be reduced
if the soak temperature is achieved after a slow ramp to that temperature, which will be
discussed subsequently. For the product to be accepted, at least 95% conversion should
be achieved. The ultimate conversion versus isothermal cure temperature over a range of
curing temperatures was plotted in figure 3.29 from which it can be determined that 95%
cure can be achieved under isothermal condition at 176 °C (349 °F) after a minimum of
about 160 minutes at that temperature. A plot of the ultimate glass transition temperature
versus isothermal cure temperature was made as shown in figure 3.30 from which it was
concluded that the ultimate Tg was about 208 °C for an isothermal cure at 176 °C.
Figure 3.27. 2D plot of degree of cure ($\alpha$) versus time for T800/3900 prepreg throughout isothermal cure cycles over a range of temperatures after a rapid jump to that temperature.
Figure 3.28. 2D plot of rate of cure (dα/dt) as a function of time for T800/39000 prepreg throughout isothermal cure cycles over a range of temperatures after a rapid jump to that temperature
Figure 3.29. Plot of maximum achievable cure ($\alpha_{\text{max}}$) versus isothermal cure temperature ($^\circ\text{C}$)

Figure 3.30. Plot of maximum achievable Tg versus isothermal cure temperature ($^\circ\text{C}$)
By using the data from figures 3.27 and 3.28, both the degree of cure and rate of cure were plotted as a function of cure temperature and cure time as shown in figures 3.31 and 3.32 to interpolate the extent of cure as well as rate of cure at intermediate cure temperatures and cure times.

Figure 3.31. 3D plot of degree of cure ($\alpha$) as a function of time and isothermal cure temperature

Figure 3.32. 3D plot of rate of cure ($d\alpha/dt$) as a function of time and isothermal cure temperature
Apparent Activation Energies for cure under Isothermal Conditions

Activation energies for isothermal cure of T800/3900 prepreg resin was determined according to the Kamal kinetic scheme. Rates of cure were correlated with degree of cure, for example at 145 °C, as in figure 3.33. The plot of cure rate versus conversion is clearly that of an autocatalyzed reaction - i.e., increasing to a rate maximum then decreasing thereafter to zero as the resin vitrifies.

![Graph of rate of cure versus degree of cure at 145 °C](image)

**Figure 3.33.** Plot of rate of cure versus degree of cure for resin in T800/3900 prepreg at 145 °C

Isothermal data was fitted into the kinetic model of Kamal as defined below (equation 3.4). Fitting was done with Origin 6.1 software using the Levenberg-Marquardt minimization algorithm. A good correlation was obtained for the entire range of temperatures. The results are furnished in table 3.2

\[
\frac{d\alpha}{dt} = \mathbf{A}_i + k_2 \alpha^m \overline{\alpha} f - \bar{\alpha}^n
\]  

(3.4)

where,
\( \alpha \) is the degree of cure, \( \frac{d\alpha}{dt} \) is the rate of cure, \( \alpha_f \) is the maximum degree of cure at that cure temperature, \( k_1 \) is the rate constant for the reaction catalyzed by groups initially present in the resin and \( k_2 \) is the rate constant for the reaction catalyzed by newly formed groups and represents the influence of the reaction products on the rate of reaction.

Assuming \( k_1 \) and \( k_2 \) follow Arrhenius rate constant dependence, activation energies and pre-exponential factors can be calculated.

\[
\ln k_1 = -\frac{E_{a1}}{RT} + \ln A_1 \quad (3.5)
\]

\[
\ln k_2 = -\frac{E_{a2}}{RT} + \ln A_2 \quad (3.6)
\]

Values of \( \ln k_1 \) and \( \ln k_2 \) so obtained were plotted versus inverse temperature and corresponding values of \( E_{a1} \) and \( E_{a2} \) were obtained from the slope of the plot, which was equal to \( -\frac{E_a}{R} \). Results were shown in figures 3.34 and 3.35.

From the isothermal data for the curing at 145 °C, \( E_{a1} \) and \( E_{a2} \) were found to be 74.7 and 53.8 kJ/mole respectively (m and n are fitting parameters independent of temperature).
Figure 3.34. Plot of \( \ln(k_1) \) versus reciprocal temperature for T800/3900. The gradient of the best fit straight line is set to \(-E_a/R\).

\[ y = -8988.1x + 16.009 \]
\[ R^2 = 0.9777 \]

Figure 3.35. Plot of \( \ln(k_2) \) versus reciprocal temperature for T800/3900. The gradient of the best fit straight line is set to \(-E_a/R\).

\[ y = -6465.3x + 11.656 \]
\[ R^2 = 0.9747 \]
Plots of rate of cure vs degree of cure for temp from 110 to 190°C are reproduced in Appendix B.

**Table 3.2**

Kinetic parameters for the isothermal data fitted into equation (3.4)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Alpha, max</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>m</th>
<th>n</th>
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<tr>
<td>110</td>
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<td>0.798080</td>
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<td>160</td>
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<tr>
<td>165</td>
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<td>2.047070</td>
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<td>170</td>
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<tr>
<td>175</td>
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<td>1.227960</td>
</tr>
<tr>
<td>180</td>
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<td>0.077150</td>
<td>0.769670</td>
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<tr>
<td>185</td>
<td>0.972790</td>
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<td>0.070060</td>
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<tr>
<td>190</td>
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<td>0.029840</td>
<td>0.099820</td>
<td>0.757610</td>
<td>1.408970</td>
</tr>
</tbody>
</table>
3.3.6. Combined Ramp and Soak Experiments

In an industrial cure cycle, cure is usually accomplished by soaking the prepreg at a high temperature after a slow ramp to that temperature. In other words, by a ramp and soak temperature profile. Often, a four step ramp and soak cure cycle is used, as illustrated in figure 3.1.

The early low temperature ramp and soak segments are normally used to bring all parts and part locations to a similar temperature before beginning the high temperature ramp segment. Depending on the composition of the curing resin, the low temperature ramp and short soak segment can advance the resin cure. In a classical isothermal cure experiment, in which the sample is soaked at a defined temperature after a very rapid jump to that temperature, the sample is uncured at the beginning of the isothermal scan, so that $\alpha$ is at zero at $t_0$. As discussed in section 3.3.5, initial rates of cure for resin cured isothermally at high temperatures are very large. This could lead to temperature overshoot and possible carbonization of the resin in an autoclave cure cycle. The probability of temperature overshoot is much reduced if the soak temperature is achieved after a slow ramp to that temperature. In a ramp and soak experiment, the sample arrives at the soak temperature with a cure history, in other words, $\alpha$ at $t_0$ is not zero.

Combined ramp and soak experiments were done in four steps.

1. The sample was heated from a preset temperature of 30 °C to the isothermal cure temperature (160 °C to 190 °C in increments of 5 °C) over a range of heating rates (0.5 to 5 °C/min)
2. The sample was cooled to 30 °C and heated to the isothermal cure temperature @50 °C/min and held at the isothermal temperature until the exotherm was complete.

3. The sample was cooled to 30 °C and heated to 300 °C @3 °C/min to determine the intermediate Tg and the residual exotherm.

4. The sample was again cooled to 30 °C and heated to 300 °C @10 °C/min to determine the ultimate Tg.

The degree of cure and rate of cure were calculated as a function of time to follow the cure process of the resin during the ramp and soak experiment. It was found difficult to integrate the exotherm from the ramp part of the experiment. Hence, previously generated data from dynamic scanning was utilized here. The soak portion of the experiment is then computed. Finally, both segments are combined with the residual cure to describe the evolution of conversion and reaction rate as a function of time throughout the ramp and soak experiment.

The degree of cure and rate of cure for the isothermal portion of the ramp and soak experiment were calculated from step 2 of the experiment. This was done by dividing the partial area of the isothermal exotherm with the total area which comprises area from dynamic temperature scanning (step 1), from isothermal scanning (step 2) and from dynamic temperature scanning in the residual exotherm (step 3).

The development of conversion through a ramp portion of a ramp and soak cure cycle for T800/3900 prepreg, heated to a soak temperature of 170°C was illustrated in figure 3.36. The development of conversion through the soak portion of the cure cycle was illustrated in figure 3.37.
Accumulated errors occurred, due to dilution of the exotherm by the fiber content and variance in the fiber content. Having confidence in the estimation of $\alpha_{\text{max}}$ as measured after isothermal cure after a fast ramp to that temperature, the soak portion of the ramp and soak cure cycle was normalized to reach $\alpha_{\text{max}}$ as defined by the isothermal experiments. All such renormalized 2D plots of further cure of the prepreg resin over the isothermal portion of a ramp and soak cure cycle are furnished in Appendix C. A renormalized version of the data contained in figure 3.37 was plotted in figure 3.38. Finally, the ramp and soak segments are combined to produce a conversion master curve.

Figure 3.36. Development of conversion through the ramp segment of a ramp and soak cure cycle at 170 °C for resin in T800/3900 prepreg
Figure 3.37. Development of conversion through the soak segment of a ramp and soak cure cycle at 170 °C for resin in T800/3900 prepreg

Figure 3.38. Normalizing final conversion to an averaged value for the soak segment of a ramp and soak cure cycle to 170 °C for resin in T800/3900 prepreg
Similarly, corresponding curves were constructed for the rate of cure over the ramp and soak segments of the ramp and soak cure cycle to 170 °C as shown in figures 3.39 and 3.40. (All 2D plots of rate of cure throughout the soak segment of a ramp and soak cure cycle are furnished in Appendix D.) Segments were then combined to produce the master curve for a ramp and soak cure to 170 °C of the prepreg resin as shown in figure 3.41. Master curves for both conversion and rate of cure are produced in appendices E and F for ramp and soak cure over a range of temperatures from 160 °C to 190 °C.

It is observed that the proportion of cure that takes place during the ramp portion of the cure cycle increases at lower heating rates. At identical heating rates, the proportion of cure that takes place during the ramp portion of the cure cycle increases also as the end or soak temperature increases. The exotherm “spike” at short times after achieving the soak temperature decreases in size when soak temperatures are reached at lower heating rates.

The rate maxima for the cure process can be manipulated by changing heating rate and soak temperature. For example, if rate curves for heating at 1 °C/min are compared, it may be observed that raising the soak temperature progressively from 160 °C to 190 °C reveals a rate maximum achieved during the ramp segment at that heating rate. The “spike” in the rate curve that occurs immediately after achieving the soak temperature is not observed or is much diminished when a rate maximum is achieved during the ramp segment. For this reason, it is suggested that heating rates of 1 °C/min or less should be employed over the ramp segment above ~140 °C.
The choice of upper soak temperature is critical to a successful cure if the criterion for success is $\alpha > 0.95$ or > 95% cure. Based on this criterion, the upper soak temperature should be greater than 175 °C (347 °F) for resin in the T800/3900 prepreg polymerized in a ramp and soak cure cycle.

**Figure 3.39.** Rate of cure throughout the ramp segment of a ramp and soak cure cycle to 170 °C for resin in T800/3900 prepreg

**Figure 3.40.** Rate of cure throughout the soak segment of a ramp and soak cure cycle to 170 °C for resin in T800/3900 prepreg
Figure 3.41. Master curve for the progression of conversion (α) and cure rate (dα/dt) throughout a ramp and soak cure cycle to 170 °C for T800/3900 prepreg. Times to the left of the y axis correspond to the ramp segment of the cure cycle.
3.3.7. Dynamic Mechanical Analysis (DMA)

The gel point of the resin is the first appearance of an infinite network and the conversion beyond which all flow ceases. Vitrification corresponds to simple hardening of the resin material prior to gelation and does not require the formation of an infinite network.

The buildup of prepreg resin network structure during the cure cycle has been investigated using Dynamic Mechanical Analysis in an instrument first developed for the rubber industry. The determination of build up of prepreg resin network properties as a function of cure state and thermal history have always been hampered by difficulties in sample preparation. Incorporating the resin into the prepreg changes the resin. Even a supplier could not supply a neat resin mixture with properties identical to resin in the prepreg. Even extracting with solvent can never be used to remove the resin from the prepreg that is identical to the resin prior to extraction as the solvent can never be subsequently completely removed from the extract. Hence, a reliable method of removing resin from prepreg without altering the resin has not yet been developed. As such, normal parallel plate viscometers cannot be used to determine the viscosity buildup in the neat prepreg.

The sample configuration for this experiment (DMA) is as shown in figure 3.42. Layers of prepreg are pressed together at room temperature and cut into a disk shape. The disk is slipped into a high temperature Viton™ rubber "O" ring to prevent resin from running out of the prepreg as it is heated, and the whole assembly is sealed into high temperature plastic sheeting which was moulded under pressure to generate ridges that slip into complimentary ridges in the DMA machine platens. (In contrast, a normal
parallel plate DMA analyzer places the sample between parallel plates that sit in a circulating air oven). Because the DMA machine used here possesses heating elements built into the sample platens for rapid temperature equilibration, the sample need not be temperature equilibrated before each measurement. The instrument can be programmed to accept multiple ramp and soak segments and (for example) the buildup of complex modulus ($G^*$), storage modulus ($G'$), loss modulus ($G''$), and $\tan\delta$ ($= G''/G'$) can be recorded as a function of time at a low forced frequency normally less than 10 Hz.

This sample configuration cannot be used to determine the gel point of the prepreg resin (which for an unfilled system is normally thought to be achieved when $\tan\delta$ first reaches 1), because the fibers in the prepreg interfere with the analysis. Even so, the point of initial viscosity and storage modulus buildup is easily discerned. In addition, changes in resin viscosity and sample consolidation before the beginning of cure can also be determined. Passage of the sample glass transition temperature through the soak temperature due to network buildup results in a peak in the $\tan\delta$ curve. Return of the $\tan\delta$ curve to the baseline indicates that all structures in the resin in the prepreg have achieved a glass transition temperature above the soak temperature. The DMA experiments for T800/3900 prepreg resin were carried out by AvPro Inc., of Oklahoma.

![Figure 3.42. Sample configuration for the DMA experiment.](image-url)
Experiments were conducted to determine the network buildup in the resin by subjecting the resin to three different cure cycles comprising ramp and soak segments designed to test if multiple ramp segments can accelerate cure.

**Cure cycle #1** corresponds to a fast ramp to 185 °C followed by a soak at that temperature to complete cure.

**Cure cycle #2** corresponds to a fast ramp to 120 °C followed by a slower ramp through cure temperatures, followed by a soak at 185 °C to complete cure.

**Cure cycle #3** corresponds to a fast ramp to 120 °C, followed by a very slow ramp through the first part to the cure reaction (120-140 °C) to allow leading and lagging thermocouples to equalize without wasting time in the cure cycle, such as would be the case if an isothermal segment were introduced at 120 °C for that purpose. Having substantially equalized temperatures at 140 °C, the ramp rate is increased from 0.5 °C/min to the faster but still slow 1 °C/min, to reach soak temperatures, while minimizing the possibility of producing an exotherm spike.

The buildup of storage modulus during all three cure cycles is illustrated in figure 3.43 and loss modulus in figure 3.44.

<table>
<thead>
<tr>
<th>Table 3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cure cycles comprising ramp segments to test acceleration in cure</strong></td>
</tr>
<tr>
<td><strong>Cure Cycle</strong></td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>#2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Table 3.3

<table>
<thead>
<tr>
<th>#</th>
<th>Temperature Change</th>
<th>Rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>from 30°C to 120°C</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>from 120°C to 140°C</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>from 140°C to 185°C</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>to complete cure</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3.43. Comparison of buildup of G' versus time and temperature for T800/3900 prepreg heated to 185 °C at rates detailed in Table 3.3, then held at 185 °C. The x axis indicates run time, the left y axis references the buildup of G', while the right y axis references run temperature in °C.

Figure 3.44. Comparison of buildup of η' versus time and temperature for T800/3900 prepreg heated to 185 °C at rates detailed in Table 3.3, then held at 185 °C. The x axis indicates run time, the left y axis references the buildup of η', while the right y axis references run temperature in °C. (η' tracks G")
The buildup of storage modulus in T800/3900 prepreg during cure cycles detailed in Table 3.3, is summarized in Table 3.4.

**Table 3.4.**

Summary of results of measurement of G' through cure of T800/3900 prepreg subjected to cure cycles detailed in Table 3.2 and in figure 3.43

<table>
<thead>
<tr>
<th>Cure Cycle #</th>
<th>time to minimum modulus 300 KPa (min)</th>
<th>temp @ minimum modulus (°C)</th>
<th>time to initial modulus growth (min)</th>
<th>temp @ initial modulus growth (°C)</th>
<th>time to maximum rubber modulus @ 185 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>135</td>
<td>65</td>
<td>after about 6 min @ 185 °C</td>
<td>163 min, 104 min @ 185 °C</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>135</td>
<td>88</td>
<td>174 °C</td>
<td>203 min, 105 min @ 185 °C</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>132</td>
<td>104</td>
<td>167 °C</td>
<td>221 min, 99 min @ 185 °C</td>
</tr>
</tbody>
</table>

The times to minimum modulus (or viscosity) are summarized in column 2. These times differ because minimum modulus is achieved after 120 °C. The initial peak in the storage modulus makes sense only if it corresponds to sample consolidation. The temperature corresponding to the minimum modulus (column 3) is similar for all three cure cycles, even though it is higher than 120 °C, at which point the three cure cycles diverge. This is strong evidence that little or no cure takes place at low temperatures in T800/3900 prepreg up to and exceeding 120 °C. The time to initial modulus growth for all three cure cycles is summarized in column 4. As expected, the shortest time is recorded for the sample that reaches the soak temperature most rapidly (cycle #1) and vice versa.
For prepreg subjected to cure cycle #1, initial modulus growth is achieved only after the soak temperature is achieved. At slower heating rates (cure cycle 2 then 3), more cure is achieved during warm up and the temperature at which initial modulus growth is observed drops to lower temperatures. The time to reach the maximum rubber modulus at 185 °C (a somewhat subjective measurement) increases as the ramp rate to the soak temperature decreases.

It must be noted that the attainment of a maximum rubber modulus does not necessarily mean that the prepreg is fully cured. It does, however, mean the cure has progressed to a maximum allowed at that temperature.

The progression of η' in T800/3900 prepreg during cure cycles detailed in Table 3.3, is summarized in Table 3.5.

Table 3.5

Summary of results of measurement of η' through cure of T800/3900 prepreg subjected to cure cycles detailed in Table 3.3 and in figure 3.44.

<table>
<thead>
<tr>
<th>cure cycle #</th>
<th>Tg reaches after ≈</th>
<th>maximum Tg achievable at 185°C after ≈</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>103 min, 44 min @ 185 °C</td>
<td>156 min, 97 min @ 185 °C</td>
</tr>
<tr>
<td>2</td>
<td>131 min, 30 min @ 185 °C</td>
<td>200 min, 102 min @ 185 °C</td>
</tr>
<tr>
<td>3</td>
<td>151 min, 29 min @ 185 °C</td>
<td>210 min, 88 min @ 185 °C</td>
</tr>
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</table>

The resin glass transition temperature (Tg) is assumed to cross through the soak temperature at the loss maximum in the η' versus time curve. As is summarized in Table 3.5, column 2, this state is achieved at soak times that are inversely rated to the ramp rate.
The maximum achievable Tg at a soak temperature is assumed to be achieved when the loss peak drops back to a baseline. As is summarized in Table 3.5, column 3, this state is achieved at times that are inversely rated to the ramp rate.

Experiments were conducted to figure out whether the low temperature transitions observed in the G’ and η” curves for T800/3900 in figures 3.43 and 3.44 are artifacts of sample settling – consolidation or genuine transitions.

It was known that the cure of the resin was not advanced appreciably by heating to 110 °C. In theory, therefore, the prepreg could be cycled from room temperature to 110°C a few times before appreciable cure is observed. If a real thermal transition is occurring, it should be either reversible, or at least alter the material so that subsequent cycles through the temperature segment will register a difference in the material. Consolidation, if it occurs, will occur only one time. To test for consolidation, the following cure cycle was observed for T800/3900 prepreg.

i. Ramp from RT – 110°C @ 2.8 °C/min
ii. Cool to RT @ 2.8 °C/min
iii. Ramp from RT -120°C @ 2.8 °C/min

The results of this experiment were summarized in figure 3.45. The storage modulus drops from room temperature to 110 °C. As expected this drop in G’ is accompanied by a loss peak. Cooling the sample back down to room temperature simply reverses the transition. The room temperature storage modulus increases a little as the prepreg is cycled through the ramp segments and the loss peak shifts to higher temperatures indicating that the sample experiences a small amount of cure in this experiment. The anomalous low temperature peaks in some of the storage modulus curves are not repeated.
in these more careful experiments. Hence those in figures 3.43 and 3.44 are simple artifacts of sample preparation.

**Figure 3.45.** Progression of $G'$ and $\eta'$ as a function of time for T800/3900 prepreg cycled from room temperature to 110 °C, back to room temperature, then from room temperature to 120 °C.

Experiments were conducted to build a relationship between the change of storage modulus with conversion, as obtained from DSC experiments.

The initial buildup of shear storage modulus in a prepreg represents a point in the cure cycle after which the construct becomes more robust and better able to retain shape and is less likely to shift, slide apart, or warp. The experiment detailed in figure 3.43 contains results pertaining to the beginning of the buildup of shear storage modulus during a ramp and soak experiment from 120 °C to 185 °C @ 1°C/min, followed by a thermal soak at 185 °C (DMA cure cycle #2). The conversion curve for this thermal profile has been determined previously from ramp and soak experiments at a soak temperature of 185 °C.(Appendix-E). The match between those two curves was shown in
The storage modulus leaves the baseline only two minutes after the soak temperature is attained. The conversion at this time was 61%.

However, in a second cure cycle which was ramped at 2.8 °C (= 5°F)/min to the lower temperature of 175 °C followed by a soak at that temperature. There was no exact data to compare at the same heating rate, however this was compared with DSC data for a ramp at 3 °C/min to 175 °C, followed by a soak at 175 °C. Beginning at 30 °C, the faster heating rate i.e, 3 °C/min will reach 175 °C after 48 min while the slower heating rate will take only 4 min longer to reach 175 °C, which hopefully is a negligible difference. The results of these DMA and DSC experiments are reproduced in figure 3.47. The storage modulus leaves the baseline at about 30% cure, almost exactly ½ of the corresponding conversion recorded in the previous figure 3.46. Obviously, the point of initial buildup of storage modulus is not related to something as simple as a gel point and contains elements of conversion and temperature which can oppose each other. Consider a ramped experiment to a very high temperature. At some point the cure reaction is energized. Dimers, then short oligomers, are formed. This buildup of molecular weight works to increase viscosity. However, the temperature is increasing also. This works to drop viscosity. Obviously, at very low conversions, temperature effects predominate. At higher conversions, the buildup of molecular weight becomes relatively more important.

We suspect that this initial buildup of shear storage modulus may be related in some instances to gelation and in some instances to vitrification of the resin in the composite. Vitrification is a function of both conversion and ambient temperature. From the above experiments it was concluded that
• If the prepreg is heated to soak temperature at a slow heating rate like 1 °C/min, the vitrification temperature of the resin may lag the cure temperature by only a small degree. When the ramp segment ends and the soak segment begins, the vitrification temperature quickly reaches the soak temperature and the shear storage modulus leaves the baseline, only a very short time after the soak temperature is attained as shown in figure 3.46 where the modulus begins to rise about 2 min after the attainment of the soak temperature.

• If the prepreg is heated to soak temperature at a fast heating rate like 2.8°C/min, the vitrification temperature of the resin may lag the cure temperature by a large degree. When the ramp segment ends and the soak segment begins, it takes a defined soak time for the vitrification temperature to reach the soak temperature and for the shear storage modulus to leave the baseline as shown in figure 3.47 where the modulus begins to rise about 10 min after the attainment of the soak temperature.

If this scenario is correct it becomes a very dangerous practice to equate the initial buildup of shear storage modulus or stiffness with a corresponding build up of composite strength, as the latter begins to develop only after the gel point when an infinite network forms.
Figure 3.46. Buildup of temperature (red), storage shear modulus (blue) and conversion (green) with time for a 1 °C/min ramp from 30 to 185 °C followed by a soak at that temperature.

Figure 3.47. Buildup of temperature (red), storage shear modulus (blue), and conversion (brown) with time for a ramp to 175 °C followed by a soak at that temperature. The DMA experiment is ramped at 2.8 °C/min to 175 °C. The DSC experiment is ramped at 3.0 °C/min to 175 °C.
DMA experiments were conducted to determine

i. the influence of final soak temperature on the buildup of shear modulii

ii. the influence of ramp rate on the build up of shear modulii when the final soak temperature is kept constant

iii. how tailoring the ramp rates to reach the soak temperature with a high conversion to minimize the exotherm spike influences the build up of shear modulus

iv. the build up of shear modulii in an interrupted cure at low conversions

i. The influence of final soak temperature on the buildup of shear modulii

Two experiments were conducted (13 and 15) with an initial ramp rate of 0.6 °C/min and a low soak temperature of 93 °C. In both experiments, the second ramp rate (0.6 °C/min) is the same. In the second experiment, the final soak temperature (185 °C) is raised over that used for the first experiment (168 °C). The results of runs are produced in figures 3.48 and 3.49 and the data was summarized in table 3.6.

The onset times for initial modulus buildup differ by only 1 min, illustrating the reproducibility of the technique. The loss maximum is achieved after achieving soak temperature in Run 13 and on the ramp segment of run 15. Times are very similar (run 13 – 317 min, run 15 – 319 min). The maximum shear storage modulus is attained in both instances at similar times, and appears to differ little between experiments, even though the ultimate crosslink density is different in both systems. The DMA technique is unable to determine if cure is complete under these conditions.
Table 3.6

Effect of upper soak temperature on buildup of physical properties in T800/3900 prepreg

<table>
<thead>
<tr>
<th>Run #</th>
<th>initial modulus growth (min, °C)</th>
<th>loss maximum (min, °C)</th>
<th>maximum modulus - subjective</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>271 min, 150 °C</td>
<td>317 min</td>
<td>385 min</td>
</tr>
<tr>
<td>(Figure 3.48)</td>
<td></td>
<td>15 min @ 168 °C</td>
<td>80 min@168 °C</td>
</tr>
<tr>
<td>15</td>
<td>270 min, 150 °C</td>
<td>319 min</td>
<td>380 min</td>
</tr>
<tr>
<td>(Figure 3.49)</td>
<td></td>
<td>179 °C on ramp</td>
<td>48 min@186 °C</td>
</tr>
</tbody>
</table>

Figure 3.48. AvPro run #13. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear loss modulus (grey), and tan(δ) (green)
The influence of ramp rate on the build up of shear moduli when the final soak temperature is kept constant

This was tested by constructing two 4 segment cure cycles containing identical soak segments but different ramp rates. In the first experiment (run 15) the first ramp is from 30 °C to 93 °C at 0.6 °C/min. The sample is then soaked at 93 °C for 60 minutes. The sample is subsequently ramped from 93 °C to 185 °C at 0.6 °C/min and soaked at 185 °C for four hours. In the second experiment (run 16) the first ramp is from 30 °C to 93 °C at 2.8 °C/min followed by soaking at 93 °C for 60 minutes. The sample is then ramped from 93 °C to 185 °C at 1.1 °C/min and soaked at 185 °C for four hours. The results are reproduced in figures 3.49 and 3.50 and data is summarized in table 3.7.

The initial buildup of storage modulus is related to conversion (in a complex fashion involving also ambient temperature), it comes as no surprise that the point of initial modulus growth occurs at a lower temperature in run 15 than in run 16, as more cure takes place in the slower ramp segments. The loss maximum occurs in the ramp segment of run 15 but in the upper soak segment of run 16 to support this assertion.

Figure 3.49. AvPro run #15. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear loss modulus (grey), and tan(δ) (green)
similar fashion, the maximum rubber modulus is achieved after only 48 min at the soak temperature in run 15 but after 75 min at the soak temperature in run 16. Similar principles appear to apply to the buildup of both conversion and mechanical properties, although it is probably best to establish a relationship between the two as along the lines of …

Mechanical properties = Function [conversion & measurement temperature]

<table>
<thead>
<tr>
<th>Run #</th>
<th>initial modulus growth (min, °C)</th>
<th>loss maximum (min, °C)</th>
<th>maximum modulus - subjective</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>270 min, 150 °C</td>
<td>319 min</td>
<td>380 min</td>
</tr>
<tr>
<td>(Figure 3.50)</td>
<td></td>
<td>179 °C on ramp</td>
<td>48 min@186 °C</td>
</tr>
<tr>
<td>16</td>
<td>153 min, 168 °C</td>
<td>181</td>
<td>250 min</td>
</tr>
<tr>
<td>(Figure 3.51)</td>
<td></td>
<td>9 min@185 °C</td>
<td>75 min@185 °C</td>
</tr>
</tbody>
</table>

Effect of ramp rates on buildup of physical properties in T800/3900 prepreg

**Figure 3.50.** AvPro run #16. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear los modulus (grey), and tan(δ) (green)
iii. How tailoring the ramp rates to reach the soak temperature with a high conversion to minimize the exotherm spike influences the build up of shear modulus

Three experiments (runs 11, 10 and 12) were conducted by tailoring the ramp rates to reach the soak temperature at high degree of cure. Run 11 was ramped from room temperature to 174 °C at 2.8 °C/min and soaked at 174 °C for 4 hours. Run 10 was conducted by ramping from room temperature to 54 °C at 2.8 °C/min, from 54 °C to 150 °C at 0.6 °C/min, from 150 °C to 166 °C at 0.2 °C/min, from 166 °C to 174 °C at 0.1 °C/min and finally soaked at 174 °C for 4 hours and a third run 12 was conducted by ramping from room temperature to 54 °C at 2.8 °C/min, from 54 °C to 150 °C at 0.6 °C/min, from 150 °C to 166 °C at 0.2 °C/min, from 166 °C to 185 °C at 0.1 °C/min and finally soaked at 185 °C for 4 hours.

Table 3.8

Effect of multiple decreasing ramp rates on buildup of physical properties in T800/3900 prepreg

<table>
<thead>
<tr>
<th>Run #</th>
<th>initial modulus growth (min, °C)</th>
<th>loss maximum (min, °C)</th>
<th>maximum modulus - subjective</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>62 min</td>
<td>94 min</td>
<td>165 min</td>
</tr>
<tr>
<td></td>
<td>(Figure 3.51) 7 min@175 °C</td>
<td>38 min@175 °C</td>
<td>109 min@175 °C</td>
</tr>
<tr>
<td>10</td>
<td>188 min, 153 °C</td>
<td>231 min</td>
<td>325 min</td>
</tr>
<tr>
<td></td>
<td>(Figure 3.52)</td>
<td>162 °C</td>
<td>173 °C</td>
</tr>
<tr>
<td>12</td>
<td>179 min, 151 °C</td>
<td>230 min</td>
<td>321 min</td>
</tr>
<tr>
<td></td>
<td>(Figure 3.53)</td>
<td>161 °C</td>
<td>172 °C</td>
</tr>
</tbody>
</table>

The influence of inserting multiple ramp segments with decreasing rates on the buildup of physical properties is summarized in Table 3.8. By comparing the results of runs # 10 and 12, the experiment can be seen to be very reproducible. As expected, the
insertion of ever decreasing ramp rates drops all physical milestones to lower temperatures. The maximum rubber modulus is observed in both instances to be achieved before the end of the last ramp segment.

**Figure 3.51.** AvPro run #11. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear loss modulus (grey), and tan(δ) (green)

**Figure 3.52.** AvPro run #10. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear loss modulus (grey), and tan(δ) (green)
iv. The build up of shear modulii in an interrupted cure at low conversions

An experiment (run 17) was conducted to investigate the build up of shear modulii on interruption of cure at low conversion. The sample was initially ramped from room temperature to 93 °C at 1.7 °C/min then soaked at that temperature for 60 minutes. Then the sample was cooled to 20 °C and ramped again to 177 °C at 1.7 °C/min and soaked for 4 hours.

It was concluded from the work done (in experiment i) that a dwell, even for 60 min, at 93°C will not lead to significant conversion. Even so, the small conversion achieved prior to cooling the sample to 20°C, produces a massive (and reversible) increase in stiffness of the prepreg close to room temperature. This partly cured prepreg will be very brittle and easily damaged. It is unclear whether or not cracks in the partly

Figure 3.53. AvPro run #12. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear loss modulus (grey), and tan(δ) (green)
cured resin (due to handling) would be repaired when the resin is reheated. The cooling and the reheating of the prepreg produce almost symmetrical loss peaks. At this fast heating rate the initial buildup of physical properties, upon reheating the prepreg, is not observed until 295 min into the run. At this exact point the soak segment begins. The loss maximum is achieved after 26 min at 175 °C. Maximum properties are developed after about 80 min at 175 °C. Results were shown in figure 3.54.

**Figure 3.54.** AvPro run #17. Shown are the variance with time of temperature (red), shear storage modulus (blue), shear los modulus (grey), and tan(δ) (green)
3.3.8. Thermal Volatilization Analysis / Sub-Ambient Thermal Volatilization Analysis

The identification of volatiles produced during cure of the resin in T800/3900 prepreg was successfully carried out through the use of Thermal Volatilization Analysis (TVA) and Sub-Ambient Thermal Volatilization Analysis (SATVA). During this process volatile fractions produced during cure and post cure under high vacuum conditions were trapped for subsequent analysis in the TVA/SATVA vacuum line. Two cure cycles were observed - from 20 °C to 267 °C and from 20 °C to 350 °C, both at a heating rate of 3 °C/min. The sample cure was carried out in this way so that the cure temperature is always higher than the interim glass transition temperature (Tg) of the sample. As such, volatiles are more easily lost into the vapor phase under high vacuum conditions

The TVA trace produced by a sample of resin in T800/3900 prepreg, weighing around 747mg and cured from 20 °C to 350 °C at 3 °C/min, was produced in figure 3.55. Significant amounts of volatiles were produced only above 267 °C. The SATVA separation of all condensable volatiles produced during cure from 20 °C to 350 °C at 3 °C/min, and collected on the vacuum line at -196 °C, is shown in figure 3.56. Only one significant broad peak was observed in the SATVA trace on warming the paraffin wax around the SATVA trap to 0 °C. The condensable volatiles produced during warming up of the SATVA trap were collected into a gas IR cell. The IR spectrum of the condensable volatiles is reproduced in figure 3.57. The condensable volatile product fraction was then distilled from the gas phase IR cell to a collection vessel containing d6 acetone. The 1-H NMR spectra produced by collecting those volatiles in d6 acetone is reproduced in figure 3.58. Both the gas IR and the proton NMR spectra identified the major product peak in the SATVA trace as water. The IR Spectrum of the Oligomeric [coldring] product
fraction is reproduced in figure 3.59 and the corresponding NMR Spectrum is produced in figure 3.60.

**Figure 3.55.** TVA trace of 747 mg of uncured T800/3900 Prepreg resin cured in the TVA experiment from 20 °C to 350 °C @ 3 °C/min. Significant amounts of volatiles are produced above 267 °C
Figure 3.56. SATVA trace of condensable volatiles produced from 747 mg of uncured T800/3900 prepreg resin cured in the TVA experiment from 20 °C to 350 °C @ 3 °C/min
Figure 3.57. IR Spectrum of condensable volatiles collected from the SATVA experiment following TVA of 747 mg uncured T80/3900 prepreg cured in the TVA experiment from 20 °C to 350 °C.
Figure 3.58. NMR Spectrum of condensable volatiles produced during the cure of 747 mg uncured T800/3900 prepreg cured in the TVA line from 20 °C to 350 °C @ 3 °C/min.

Figure 3.59. IR Spectrum of the cold ring fraction produced during the cure of 747 mg uncured T800/3900 prepreg cured in the TVA line from 20 °C to 350 °C @ 3 °C/min.
Figure 3.60. Proton NMR Spectrum of the cold ring product fraction from the curing of 747 mg of T800/3900 prepreg from 20 °C to 350 °C @ 3 °C/min

From the previous TVA experiment it is apparent that appreciable quantities of condensable volatiles are only produced above 267 °C. To confirm the lack of appreciable condensable volatile formation below 267 °C, a second TVA experiment was performed to that temperature. The results of this second experiment (from 20 °C to 267 °C @3 °C/min), as shown in Appendix. G, confirm that appreciable amounts of condensable volatiles are not produced from 20 °C to 267 °C in the TVA experiment. A summary of gravimetric analyses performed with both TVA experiments is reproduced in Table 3.9.

From examination of Table 3.9, it is noted that only a small proportion of sample mass lost during cure and post cure in the TVA experiment. More mass is lost on heating to 350 °C (post cure) than on heating to 267°C (cure) and is reflected in the condensable volatile emission curve that only records condensable volatile production after 267 °C.
Table 3.9

Summary of gravimetric analysis of the product fractions produced upon cure of T800/3900 prepreg in the TVA experiment to 267 and 350 °C

<table>
<thead>
<tr>
<th>TVA Run #</th>
<th>Sample Description</th>
<th>Weight, gm</th>
<th>% Residue</th>
<th>% CRF</th>
<th>% Volatiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T800/3900 Prepreg resin [20-350 °C @ 3 °C/min]</td>
<td>0.7471</td>
<td>94.4</td>
<td>3.1</td>
<td>2.6</td>
</tr>
<tr>
<td>2</td>
<td>T800/3900 Prepreg resin [20-267 °C @ 3 °C/min]</td>
<td>0.7499</td>
<td>97.3</td>
<td>1.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3.4. Summary

The major components of the epoxy in T800/3900 prepreg resin system were determined using spectroscopic analysis. The epoxy precursors were found to be DGEBA and TGDDM monomers, with DDS as curing agent. The plot of activation energy versus conversion for this resin cured under programmed conditions was monotonically increasing and consistent with plots of Ea vs α for resin that does not contain any low temperature catalyst. DDS amine based hardener is unreactive at room temperature, leading to long shelf lives for the frozen prepreg.

The cure kinetics of the prepreg resin was investigated using DSC. Three sets of experiments were conducted: dynamic temperature scanning, isothermal temperature scanning and combined dynamic temperature and isothermal temperature scanning (a ramp and soak cure cycle). As discussed previously for this prepreg, the dynamic temperature scanning experiments show that the cure reaction is shifted to higher temperatures with higher heating rates and that the reaction ends around 320 °C at a heating rate of 3 °C/min. DSC experiments conducted to high temperatures reveal that
post cure reactions can take place above 300 °C. As such, this class of resin (in the prepreg) should be cured below 300 °C using a lower heating rates in the ramp cycle to encourage low temperature cure. The ultimate glass transition temperature of the resin was found to be around 150.6 °C. As outlined previously, the apparent activation energy (Ea) increases monotonically with the degree of cure (α) due to the build up of resin viscosity. The absence of an early maximum in Ea Vs α curve at low degrees of cure shows that the resin does not contain a low temperature catalyst.

Isothermal DSC experiments were conducted from 110 °C to 190 °C in increments of 5 °C. It was found from the above experiments that the maximum degree of cure is a function of cure temperature. The intermediate glass transition temperature increases with increase in the isothermal cure temperature. The ultimate glass transition temperature of the resin was found to be around 223.8 °C which is higher than the one in dynamic temperature scanning, showing that the network formed under the isothermal conditions is different from the one formed under dynamic scanning conditions. As mentioned previously, the isothermal data could be broken down according to the two component kinetic model of Kamal. These Kamal parameters (k1, k2, Ea1, Ea2) were found to vary with isothermal cure temperature. From the values of k1 and k2 activation energies Ea1 and Ea2 were calculated.

A series of combined ramp and soak experiments were conducted and it was found that the ultimate extent of cure in the soak portion of the cure cycle at long times is not a function of the ramp rate to that temperature. (At longer times, conversions merge to a common value irrespective of the heating rate used in the previous ramp segment).
The cure at an intermediate temperature can be predicted from the combined ramp and soak plots if the initial degree of cure at the start of the soak cycle is known.

DMA experiments were conducted to characterize the cure profile of T800/3900 prepreg, and were found to give reproducible results. The onset of buildup of physical properties corresponds to a complex interplay between resin conversion and oven temperature. To some extent, principles observed in DSC experiments appear to cross over to these DMA experiments. For example, more cure at a slower heating rate leads to a lower onset temperature for the buildup of shear storage modulus, etc. The onset of buildup of shear modulus represents a transition of the prepreg from a soft material to a hard material but it should not be assumed that the material becomes strong at this point. Prepreg that has been partly cured then cooled becomes stiff. It is to be assumed that such material is fragile and should not be subjected to physical shock. Generic experiments on similar resin systems (not discussed here) show that reheating the partly cured prepreg, can re-soften the prepreg to release any built-up thermal or physical stress prior to final cure of the prepreg in the second cure cycle.

TVA and SATVA experiments were conducted from 20 °C to 267 °C and 350 °C @3 °C/min. The TVA experiments were followed by SATVA experiments that allowed us to fractionate the condensable products for subsequent spectroscopic analysis. The oligomeric “products” such as DGEBA, MY720 and DDS were collected as the coldring product fraction that is condensed onto the cooled degradation tube above the hot zone. Condensable volatiles such as water are collected after the SATVA experiment by distillation on the vacuum line.
Under these high vacuum conditions, only a small amount of volatiles ~ 3% were removed from these thin samples of prepreg: and within that mixture of volatiles, oligomers accounted for less than 66% and condensable volatiles (mostly water) as slightly more than 33%. *Much less material will be evolved from thick samples of prepreg cured under process conditions (rough vacuum) in an autoclave.*
CHAPTER 4

Thornell T300/934 Epoxy Resin Prepreg

1. Introduction

The need to determine the chemical composition of the prepreg resin and to revise its cure cycle has been discussed in chapter 3. An example of an autoclave cure cycle was reproduced in figure 3.1 and also discussed in chapter 3. Some cure takes place in the prepreg which is B-stage by the supplier.

To properly understand this industrial cure cycle, it is not sufficient to simply perform isolated ramped and isothermal cure experiments as is commonly undertaken in research and quality control laboratories. Rather, the two must be combined to fully follow the cure cycle in the industrial autoclave. As negligible cure is usually achieved during segments I and II of the cure cycle, the entire cure cycle can be modeled around a single ramp and soak cycle.

Three sets of experiments were designed to look into the cure profile

1. Dynamic temperature scan (ramp) over a range of heating rates from 0.5 to 20 °C/min
2. Isothermal temperature scan (soak) from 120 °C to 180 °C
3. Combining both the ramp and soak segments to mimic the actual ramp and soak cure cycle.

4.2 Experimental Section

4.2.1 Materials

The materials used are mentioned in chapter 2.3

4.2.2. FT-IR Spectroscopy

This is mentioned in chapter 2.3
4.2.3 Nuclear Magnetic Resonance Spectroscopy

This is mentioned in chapter 2.3

4.2.4 Thin-Layer Chromatography

This is mentioned in chapter 2.3

4.2.5. Thermal Analysis

Thermal analysis of the resin was performed using a Perkin Elmer DSC6 instrument and is discussed in chapter 2.3

Dynamic Temperature Scanning (ramp) experiments were conducted in the same way as discussed in chapter 3.

Isothermal scanning (soak) experiments were also conducted in the same way as discussed in chapter 3 but with isothermal temperature ranging from 120 °C to 180 °C.

Combined Ramp and Soak experiments were conducted in the same way as discussed in chapter 3 but with isothermal scanning ranging from 120 °C to 180 °C.

Data analysis and two dimensional plots were performed using Microsoft Excel and Origin™ 6.1 (Origin Lab Corporation). Three dimensional plots with best fit surfaces were generated using table curve®3D™ version 4.0 for Windows (Systat Software).

4.2.6. Dynamic Shear Rheometry

Dynamic shear rheometry experiments were conducted by Fluid Dynamics Inc, using a TS2R® rheometer to determine the gel point, in isothermal scanning mode with a fixed frequency. The sample was sandwiched between the shear plates of the rheometer and the build up of physical properties was measured under isothermal cure conditions. Dynamic shear rheometry experiments were done at 140 °C and 150 °C.
4.3. Results and discussion

A combination of spectroscopic and separation techniques were employed to gain insight into the chemical composition of the resin. Integrating the results obtained from proton Nuclear Magnetic Resonance Spectroscopy and Infrared Spectroscopy along with thin layer chromatography gave a semi-quantitative compositional analysis of the resin.

4.3.1. FT-IR Spectroscopy

Figure 4.1 shows the FT-IR Spectrum of T300/934 resin, extracted from prepreg, on a salt plate. The spectrum indicated the presence of aromatic and aliphatic compounds. The sulfone group of DDS was identified by the presence of absorbances at 1143 cm\(^{-1}\) and 1104 cm\(^{-1}\). The epoxy oxirane ring was identified by the absorbance at 915 cm\(^{-1}\). The absorbance at 1720 cm\(^{-1}\) was attributed to a carbonyl containing impurity.

Figure 4.1 FT-IR Spectrum of generic T300/934 prepreg resin on a salt plate from Chloroform
4.3.2. Nuclear Magnetic Resonance Spectroscopy

A proton NMR spectrum of the uncured T300/934 resin (extracted from prepreg) was collected and signals were identified according to accepted principles and with reference, where appropriate, to the NMR spectra of reference compounds. In proton NMR spectroscopy the signal intensity is directly proportional to the relative number of structural units. As such, the proton NMR spectrum of an organic mixture is especially useful in compositional analysis if it contains identifiable non overlapped resonances that allow us to quantify the structural units in the mixture. As we were able to identify a number of non-overlapped signals in this spectrum, we found this technique to yield more information, more rapidly, than any other method of structural investigation.

The proton NMR spectrum of a deuterated chloroform extract from the T300/934 prepreg resin is produced in figure 4.2, from which it is evident that the carbonyl group in the infrared spectrum of the resin is contained in acetone solvent. This may be attributed to the reason that DDS curative is relatively insoluble in MY720 resin and most other solvents but soluble in acetone, hence it is presumed that DDS is dissolved in acetone, then mixed into the MY720 resin and coated onto the fiber weave to form the prepreg.
Figure 4.2 Proton NMR spectrum of Generic T300/934 Resin from prepreg in deuterated chloroform
We were able to identify the epoxy component in the T300/934 resin as MY720 resin and the curative as diaminodiphenyl sulfone (DDS).

![Chemical structure of MY720 component]

**Figure 4.3** Identification of MY720 component from $^1$H NMR spectrum of Generic T300/934 resin in chloroform
Figure 4.4 Identification of diaminodiphenylsulfone (DDS) from 1-H NMR spectrum of Generic T300/934 resin in chloroform

The cure kinetics of the T800/934 resin in prepreg was compared with that of a synthetic 934 resin prepared by mixing MY720 resin with DDS curative in the same proportions using Differential Scanning Calorimetry (Figure 4.5).
It is obvious from the above DSC runs in figure 4.5 that there exists an anomalous low temperature polymerization of generic T300/934 resin, indicated by the arrow in figure 4.5. It is also apparent that the commercially available 934 prepreg resin is much more reactive than the synthetic version of the resin. This is consistent with a catalyzed polymerization. Boron trifluoride is a common catalyst in epoxy resin chemistry. It complexes with amines in the resin mixture and promotes low temperature polymerization. $^{11}$B and $^{19}$F NMR spectra, were conducted by colleagues of the department, showed the presence of BF$_3$.

Preliminary experiments in which BF$_3$ was mixed into “synthetic” 934 resin indicated that the catalyst content above 1% produced an unmanageably fast polymerization. Hence, the BF$_3$ level in 934 resin was assumed to be less than 1%.
4.3.3. Thin Layer Chromatography

A sketch of a TLC plate showing the separation of the major components of Generic T300/934 Prepreg Resin is shown in figure 4.6 which confirmed the presence of only two major components in T300/934 prepreg resin. Preparative TLC followed by NMR analysis allowed us to identify those components as MY720 resin and DDS curative. By running NMR spectra in deuterated acetone, we were able to ensure complete dissolution and transfer of the DDS curative into the NMR tube.

<table>
<thead>
<tr>
<th>Mobile Phase: cyclohexane:ethyl acetate:isopropyl alcohol (6:3:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetruglycidyldiaminodiphenyl methane (TGDDM-MY720), $R_f = 0.38$</td>
</tr>
<tr>
<td>Diphenyldiamino sulfone (DDS), $R_f = 0.13$</td>
</tr>
</tbody>
</table>

Figure 4.6 “Sketch” of the TLC plate showing the separation of the major components of Generic T300/934 Prepreg Resin.

4.3.4. Composition of generic T800/934 prepreg resin

Based on the TLC experiment followed by $^1$HNMR, we were able to arrive at an approximate compositional breakdown of T300/934 prepreg resin. The relative amounts of DDS and TGDDM were determined from non-overlapping peaks in the aromatic region of the $^1$HNMR spectrum of the resin in deuterated acetone. Integration of the aromatic protons assigned to DDS and TGDDM gave a mole ratio of 1.1 : 1. The
acetone content was determined by NMR spectroscopy. The fiber content was determined gravimetrically, as outlined in the Materials and Methods section. The relative masses of the major components were shown in Table 4.1 with structures in Figure 4.7.

Table 4.1

Approximate composition of T300/934 Prepreg Resin

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent Composition by Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Fiber</td>
<td>62.0 ± 0.4%</td>
</tr>
<tr>
<td>TGDDM (MY720 epoxy resin)</td>
<td>22 %</td>
</tr>
<tr>
<td>DDS (amine curative)</td>
<td>14 %</td>
</tr>
<tr>
<td>BF₃ (catalyst)</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>Acetone solvent</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>
Figure 4.7 Structures of the major components of T300/934 prepreg resin (a) TGDDM epoxy resin (b) DDS curing agent
4.3.5. Dynamic Temperature Scanning

Programmed DSC experiments were performed in order to characterize the cure kinetics during the ramped portion of the cure cycle. The prepreg sample is ramped to an end temperature usually 280°C, at a predetermined heating rate. A representative programmed DSC trace of the T800/934 prepreg, at a heating rate of 3 °C/min, is shown in the figure reproduced in figure 4.8. The cure reaction is well defined and ends at around 230 °C.

![DSC Trace](image)

**Figure 4.8** An exotherm generated from dynamic temperature scanning of T300/934 prepreg resin @ 3 °C/min. Temperature as x is plotted against heat flow as y.

The anomalous low temperature polymerization (arrowed) has been attributed to the presence of boron trifluoride catalyst in the resin system.
The DSC cell is then cooled to room temperature and re-heated to 300 °C at a standard heating rate of 10 °C/min as is shown in figure 4.9. The absence (always) of a residual exotherm in the second programmed segment affirmed that the cure reaction had been completed during the first segment. The degree of cure α, and rate of cure (da/dt) were calculated from the first programmed segment. The ultimate glass transition temperature Tg was calculated from the second programmed segment. Both were plotted as a function of temperature. In this experiment, Tg was measured for samples of T800/934 prepreg resin, that had been pre-cured into the DSC pan. It is more difficult to measure Tg for such samples than to measure Tg for pre-cured samples that have been crushed into the DSC pan. In the first instance, passage through Tg gives only a baseline slope change. In the second instance, passage through Tg relieves stress and marks the transition with a baseline translation.

![Figure 4.9 Heat flow curve produced at 10 °C/min of T300/934 epoxy prepreg resin precured under programmed conditions at 3 °C/min. Note the absence of any residual exotherm and the position of the ultimate glass temperature.](image)
The degree of cure at a fixed point in this reaction was defined as the ratio of the partial area of the exotherm up to that point to the total area. A set of data points of time, temperature, and degree of cure for every heating rate was generated. The degree of cure (\( \alpha \)), as a function of temperature over a range of heating rates from 0.5°C/min to 20°C/min., was calculated, and results were plotted in figure 4.10. Each curve is an average over two experiments. If a significant difference between the two experiments was observed, the experiment was repeated. The cure reaction was shifted to ever higher temperatures at higher heating rates. The low temperature catalyzed polymerization was clearly noticed at the lower heating rates, as a pronounced low temperature “tail” in the exotherm, otherwise sigmoidal conversion curves were the norm. By differentiating the cumulative cure profile, rate profiles were generated for the cure reaction under dynamic heating conditions which are shown in figure 4.11

**Figure 4.10** 2D plot of degree of cure (\( \alpha \)) of T300/934 epoxy prepreg resin versus temperature for cure as a function of heating rate in dynamic heating experiments.
Figure 4.11 2D plots of cure rate (da/dt) of T300/934 epoxy prepreg resin versus temperature, for resin cured over a range of heating rates.

By using these results and Table Curve 3D software, three dimensional plots of α and da/dt as function of heating rate and temperature were generated. We were able to generate best fit surfaces with corresponding best fit equations for α and (da/dt) as a function of heating rate and temperature as shown in figure 4.12 and 4.13. By using these curves, intermediate conversion and rate curves can be generated at intermediate linear heating rates and temperatures. If a non-linear ramp is applied, so that heating rate is a function of temperature, α and (da/dt) versus temperature or time can not be generated from the graph.
Figure 4.12. 3D plot of degree of cure ($\alpha$) of T300/934 epoxy prepreg under programmed conditions as a function of heating rate ($dT/dt$) and temperature ($T$).

Figure 4.13. 3D plot of rate of cure ($d\alpha/dt$) of the T300/934 epoxy prepreg under programmed conditions as a function of temperature ($T$) and heating rate ($dT/dt$).
On completion of the initial ramp segment at 3 °C/min, the T300/934 prepreg was reheated to 300 °C at a heating rate of 10 °C/min to check for any residual exotherm and to measure the resin glass transition temperature (Tg) after the first (cure) segment of the DSC experiment. In all instances, the prepreg was shown to be completely cured after the first (cure) segment of the DSC experiment. The Tg measured in the second segment, therefore, corresponded to the ultimate Tg of the cured resin. The ultimate Tg of the cured resin is plotted against the heating rate during cure in Figure 4.14. The 934 resin is shown to be cured to a similar structural end state, with Tg ~ 187 °C, irrespective of the heating rate employed during cure. The measured Tg is a function of heating rate during rescan. For this reason all the Tg were calculated at a constant heating rate of 10 °C/min.

Figure 4.14 Ultimate glass transition temperatures of T300/934 epoxy prepreg resin measured at a heating rate of 10 °C/min to 300 °C, after pre-curing over a range of heating rates to 280 °C.
Because all the cure reactions were always completed during the first ramp segment of the experiment, the heat flow during that segment was integrated and normalized to account for the inert fiber content in the prepreg, and the magnitude of the apparent exotherm was calculated as a function of heating rate, as shown in figure 4.15. The apparent exotherm increases from a heating rate of 0.5 °C/min through a heating rate of 1.5 °C/min and stabilized at higher heating rates. Even at the very highest heating rates (15-20 °C), the cure reaction is completed below 300 °C, so that it was presumed that there was no interference or superposition of post cure processes on the cure exotherm. By considering the heats of reaction generated at heating rates equal to and greater than 1.5 °C/min, the average heat of reaction was \( 453 \pm 25 \text{ J/g} \). This higher value of heat of reaction per gram of the resin is attributed to a higher final crosslink density of the resin which in turn translates into a higher functional group density in the resin.

A batch of synthetic T300/934 resin was prepared in the lab without BF₃ catalyst as mentioned in the earlier section. The heat of reaction of the commercial T300/934 prepreg resin with BF₃ catalyst after renormalization to account for fiber content, on curing under programmed conditions at a heating rate of 3 °C/min was measured to be 448 J/g while the measured heat of reaction of a synthetic batch of the resin under the same conditions of cure was measured to be 424 J/g of resin. The heat of reaction of the synthetic mix is, therefore, measured to be within about 5% of the heat of reaction of the commercial resin. This good agreement between the two values is strong circumstantial evidence for the generation of a similar end product in both instances.
Figure 4.15. Apparent exothermic heat of reaction per gram of Thornell T300/934 epoxy prepreg resin, renormalized to account for dilution by inactive fiber content, as determined by dynamic temperature scanning over a range of heating rates.

The procedure for calculation of activation energy has been discussed in chapter 3. The cure reaction can be influenced by the decomposition of catalyst and other residues that accelerate cure. A plot of $E_a$ vs $\alpha$ for the resin was constructed by using the information summarized in figures 4.10 and 4.11.

$E_a$ was calculated for a fixed value of $\alpha$, from the gradient of the graph, as shown in figure 4.16. The plots for all measured values of $\alpha$ can be found in Appendix H. Good linearity was achieved in all cases. The variation of $E_a$ and $A F(\alpha)$ with $\alpha$ is shown in figure 4.17.
Figure 4.16. A plot of ln (da/dt) versus 1/T for T300/934 epoxy prepreg resin, cured at a fixed degree of cure $\alpha = 0.15$.

\[ y = -10464x + 21.538 \]
\[ R^2 = 0.9899 \]

Figure 4.17. Plot of the apparent activation energy ($E_a$) and $A\cdot F(\alpha)$ for the cure of T300/934 epoxy prepreg resin under programmed conditions as a function of the degree of cure ($\alpha$).
In a normal cure reaction where the cure chemistry is similar throughout the entire process, a monotonically increasing apparent activation energy for cure will be observed with increasing $\alpha$. Increasing micro viscosity in the cure medium coupled with motional restraints due to covalent bond formation, makes it more difficult for functional groups to find one another and react. We have determined early cure in T300/934 resin from the plot of $E_a$ vs $\alpha$. We have determined that resin contains BF$_3$ that causes early cure. Therefore we assume that the BF$_3$ is responsible for early spike in the activation energy curve. $A\cdot F(\alpha)$ peaks during the early stages of conversion. $A\cdot F(\alpha)$ represents the concentration dependence and geometry of the reaction. It would seem that the early reaction undergoes a complex change in the presence of BF$_3$ which must be reclassified as a co-reagent and not a catalyst.

### 4.3.5. Isothermal Temperature Scanning

The cure reaction under isothermal conditions has been discussed in chapter 3. A sample exotherm is illustrated in figure 4.18 for an experiment performed at 135 $^\circ$C. The residual exotherm and intermediate Tg are shown in figure 4.19 and the ultimate” Tg of the resin is shown in figure 4.20.
Figure 4.18. Exotherm produced by soaking T300/934 prepreg resin at 135 °C after a rapid jump to that temperature.
Figure 4.19. Residual exotherm (vertical arrow) produced by a ramp cycle to 300 °C of the T300/934 prepreg at 3 °C/min, after an isothermal cure to completion at 135 °C. Also shown (horizontal arrow) is the ultimate intermediate Tg attained after isothermal cure to completion at 135 °C.
**Figure 4.20** Ultimate glass transition temperature of the fully cured T300/934 prepreg resin after isothermal cure at 180°C followed by a ramp from 30 °C to 300 °C at 3 °C/min to complete cure. The second ramp from 30 °C to 300 °C at 30 °C to 10 °C/min is used to measure the ultimate Tg of the resin system.
Plots of degree of cure versus time for isothermal cure temperatures from 120 to 180°C were made as per the procedure laid down in chapter 3 and plotted in figure 4.21. As expected, the cure reaction proceeds rapidly to complete conversion at 180°C and drops off at lower temperatures. The ultimate degree of cure after long times is a function of the isothermal cure temperature. The maximum degree of cure, as a function of isothermal curing temperature, was plotted in figure 4.22. The ultimate glass transition temperature of the T300/934 prepreg resin, achieved under the same conditions, is ~186°C (figure 4.14). It shows that complete conversion of the T300/934 prepreg resin requires a high isothermal soak temperature. Based on these results, it could be suggested that raising the final isothermal soak temperature in the commercial autoclave cure cycle from the existing 350°F to 360°F would produce a more fully cured product.
Figure 4.21. 2D plot of degree of cure (α) as a function of time for the T300/934 prepreg resin throughout isothermal cure over a range of temperatures
Figure 4.22. Intermediate maximum degree of cure ($\alpha_{\text{max}}$) of T300/934 prepreg resin, attained after prolonged soaking at an isothermal cure temperature after a rapid jump to that temperature.
Plots of reaction rate \((d\alpha/dt)\) vs time, as a function of cure temperature, for isothermal cure of the T300/934 prepreg resin, following a rapid jump to that temperature, are produced in figure 4.23. The magnitude of the initial spike in the rate of the cure reaction upon reaching the isothermal cure temperature increases with the isothermal cure temperature. This rate spike indicates the extent of heat evolution from the cure reaction. If this is high, it can cause localized charring. This has been found to occur during actual curing of parts made with this resin. Obviously, in order to reduce the possibility of overheating the resin, we must control this rate maximum.

The degree of cure \((\alpha)\) of the T300/934 prepreg resin was re-plotted as a function of both isothermal cure temperature and cure time, as shown in figure 4.24, to allow us to interpolate the extent of cure as a function of time and temperature. As outlined previously, we may fix one of the two variables - temperature and time, vary the other to calculate the degree of cure but both may not be changed at the same time. The cure rate \((d\alpha/dt)\) was re-plotted as a function of isothermal cure temperature and cure time as shown in figure 4.25 for the same reason, and with the same limitations.

The maximum intermediate glass transition temperature of the T300/934 prepreg resin, obtained after a prolonged isothermal cure were plotted as a function of the isothermal cure temperature as shown in figure 4.26. It was noticed that over most of the range of cure temperatures, the cure reaction proceeds until the intermediate glass transition temperature drifts to about 30°C above the cure temperature.

Due to an accumulation of experimental errors, we were unable to generate meaningful ultimate heats of reaction for the isothermal cure of T300/934 prepreg resin.
Figure 4.23 2D plot of rate of cure (dα/dt) as a function of time for the T300/934 prepreg resin throughout isothermal cure cycles over a range of temperatures.

Figure 4.24 3D plot of degree of cure (α) as a function of time and cure temperature for the T300/934 prepreg resin throughout isothermal cure cycles over a range of temperatures after a rapid jump to that temperature.
Figure 4.25. 3D plot of rate of cure ($d\alpha/dt$) as a function of time and cure temperature for the T300/934 prepreg resin throughout isothermal cure cycles over a range of temperatures after a rapid jump to that temperature.

The maximum intermediate glass transition temperature of the resin after prolonged isothermal heating, and measured during a 3 °C/min post-isothermal ramp, was plotted against curing temperature as shown in figure 4.26. This shows an increase in intermediate glass transition temperature with increase in cure temperature. By combining the data contained in figure 4.22 and figure 4.26, a plot of conversion versus intermediate glass transition temperature was generated (as shown in figure 4.27). The T300/934 prepreg resin builds up higher intermediate glass transition temperatures at lower degrees of conversion when compared to our in house synthetic epoxy resin system, i.e., for 85% conversion the intermediate glass transition temperature was around 173°C and this was attributed to a higher crosslink density at that conversion.
The ultimate glass transition temperatures are plotted as a function of isothermal cure temperature, and are shown in figure 4.28. Sources of error in these measurements include dilution of the transition by inert fiber content and difficulties in locating the transition in these stress free samples cured in situ in the DSC sample container.

As shown in figure 4.14 the ultimate Tg of the resin under these dynamic scanning conditions is insensitive to the curing rate. The ultimate Tg after isothermal cure and dynamic scanning to complete the cure reaction is also almost unaffected by the isothermal cure temperature. The ultimate Tg value from isothermal scanning is around 219±6 °C and is considerably higher than that measured from dynamic temperature scanning (around 187±4 °C). We can only surmise that cure under intermediate isothermal conditions promotes the primary amine reaction over the secondary amine reaction. This will retard the gel point conversion and lead to a more efficient cure and a higher ultimate glass transition.
Figure 4.26. Maximum intermediate glass transition temperature (Tg) of the T300/934 prepreg resin attained after prolonged isothermal heating, as measured during a 3 °C/min post-isothermal ramp to complete the cure reaction.
Figure 4.27. Plot of degree of cure correlated with intermediate glass transition temperature attained after prolonged isothermal curing of the 934 prepreg resin over a range of cure temperatures.
Figure 4.28. Ultimate glass transition temperatures of the 934 prepreg resin after prolonged isothermal cure over a range of temperatures, followed by a post cure ramp at 3 °C/min to 300 °C to complete the cure reaction. Ultimate Tg’s are determined by a second ramp at 10 °C/min to 300 °C.
4.3.7. Combined Ramp and Soak Experiments

Combined ramp and soak experiments were conducted as discussed in the chapter 3 but with the soak temperatures from 120 °C to 180 °C at 5°C increments. The degree of cure as a function of temperature during a programmed warm up to 160 °C over a range of heating rates is shown in figure 4.29

**Figure 4.29.** 2D plot of development of conversion ($\alpha$) in T300/934 prepreg resin as a function of temperature during programmed warm-up to 160 °C over a range of linear heating rates
Figure 4.30. 2D Plot, using raw data, of further development of conversion ($\alpha$) in T300/934 prepreg resin as a function of time during isothermal heating at 150 °C after ramping to that temperature over a range of linear heating rates.

Figure 4.31. Renormalized 2D plot of further development of conversion ($\alpha$) in T300/934 prepreg resin as a function of time during isothermal heating at 150 °C after ramping to that temperature over a range of linear heating rates.
The degree of cure and rate of cure for the isothermal portion of the ramp and soak experiment was calculated according to the procedure discussed in chapter 3.

A plot of the degree of cure as a function of time is shown in figure 4.30. A renormalized version of the data contained in figure 4.30 was plotted in figure 4.31. All such renormalized 2D plots of further cure of the T300/934 prepreg resin over the isothermal portion of a ramp and soak cure cycle are furnished in Appendix I.

A slower heating rate in step 1 leads to a higher initial conversion at the beginning of step 2. The conversion curves converge over long times which means that the ultimate conversion ($\alpha_\infty$) measured during an isothermal cure after ramping to that temperature over a range of heating rates is more a function of the isothermal cure temperature than the thermal history or initial degree of cure.

A three dimensional plot was made to yield a relationship between initial cure (as developed during the ramp segment), time at the isothermal soak temperature, and overall degree of cure; that can be used to interpolate the development of cure during isothermal heating of material that had been ramped to that temperature at a heating rate not studied by experiment. Such a plot for cure at 150 °C is reproduced in figure 4.32. All such three dimensional plots of $\alpha$ vs time and soak temperature throughout an isothermal cure over a range of temperatures from 120 °C to 180 °C, following a linear ramp to that soak temperature, are reproduced in Appendix J.
In similar fashion, the rate of cure \( (\text{d}\alpha/\text{d}t) \) of T300/934 prepreg resin for the ramp experiment was determined and plotted as shown in figure 4.33 for ramp and soak cure cycle. By simple differentiation, the conversion curves of figure 4.29 can be re-expressed as a set of rate curves figure 4.33 for reaction during the first linear ramp segment of the ramp and soak experiment.

**Combined Dynamic and Isothermal Scanning at 150 °C**

*Figure 4.32.* Renormalized 3D Plot of further development of conversion \( (\alpha) \) in T300/934 prepreg resin as a function of time during isothermal heating at 150 °C after ramping to that temperature over a range of linear heating rates
Figure 4.33. Plot of rate of reaction ($d\alpha/dt$) of T300/934 prepreg resin as a function of temperature during programmed warm-up to 160 °C over a range of linear heating rates.

Figure 4.34. 2D plot of reaction rate ($d\alpha/dt$) in T300/934 prepreg resin as a function of time during isothermal heating at 150 °C after ramping to that temperature over a range of linear heating rates.
Figure 4.3. 3D plot of reaction rate \((\frac{d\alpha}{dt})\) in 934 prepreg resin as a function of time during isothermal heating at 150 °C after ramping to that temperature over a range of linear heating rates.

By differentiating the raw, un-normalized conversion curves in figure 4.3, we were able to determine the rates of reaction for further conversion during the soak segment, for example, at 150 °C, as illustrated in figure 4.3. Two dimensional plots of \((\frac{d\alpha}{dt})\) vs time throughout an isothermal cure over a range of temperatures from 120°C to 180 °C, following a range of linear ramps to that soak temperature, are reproduced in Appendix K. The initial spike in the exotherm at the beginning of the soak segment at all temperatures can be much reduced by a sufficiently slow ramp to that temperature.

The rates of reaction for the soak portion were plotted as a function of initial degree of cure and time at the soak temperature. A best fit surface was obtained as shown in figure 4.35. for a soak at 150 °C. This allows us to to interpolate reaction rate curves produced after ramping at that temperature at any heating rate from 0 to 5 °C/min.
Three dimensional plots of \( \frac{d\alpha}{dt} \) vs time throughout an isothermal cure of T300/934 prepreg resin over a range of temperatures from 120 °C to 180 °C, following a linear ramp to that soak temperature, are reproduced in Appendix L.

To show the conversion process of the entire autoclave cure cycle, the ramp (normalized) and soak segments were combined. A plot of conversion versus time for T300/934 prepreg resin, ramped to 175 °C over a range of heating rates, is shown in figure 4.36. Times to the left of the y axis correspond to the ramp segment. Times to the right of the y axis correspond to the following soak segment. Significant cure is achieved during the ramped segment for heating rates below 2 °C/min. Two dimensional plots of conversion versus time for ramp and soak cure cycles to soak temperatures of 170 °C, 175 °C, and 180 °C are reproduced in Appendix M.

The pre-isothermal cure was somewhat less pronounced for cure cycles ending at 170 °C and somewhat more pronounced for cure cycles ending at 180 °C.
Figure 4.36. 2D plot, using raw data, of development of conversion in T300/934 prepreg resin throughout a programmed linear ramp to 175 °C followed by an isothermal soak at that temperature.
934 prepreg resin ramped to then held at 175°C

Figure 4.37. 2D plot, using raw data, of rate of cure (da/dt) of T300/934 prepreg resin throughout a programmed linear ramp to 175 °C followed by an isothermal soak at that temperature.
In order to show the reaction rate development throughout the entire autoclave cure cycle, ramp and soak segments were combined. A plot of rate versus time for 934 prepreg resin, ramped to 175 °C, over a range of heating rates, was shown in figure 4.37, from which it can be seen that the rate spike observed at the beginning of the isothermal segment is a strong function of previous heating rate. A heating rate of 1°C/min to 175°C is unique for the prepreg resin in that it produces a symmetrical low intensity exotherm that extends throughout the cure reaction with only a small observed autoacceleration at the beginning of the soak segment between 170 °C and 180 °C. Two dimensional plots of reaction rate versus time for ramp and soak cure cycles with soak temperatures of 170 °C, 175 °C, and 180 °C are reproduced in Appendix N. For cure cycles ending at 170°C, the rate maximum for heating at 1 °C/min is displaced marginally to the right of the time curve into the isothermal segment. For cure cycles ending at 180 °C, the rate maximum for heating at 1 °C/min is displaced marginally to the left of the time curve, both with reference to the 175 °C rate curve.
**Dynamic Shear Rheometry**

The gel point of a curing resin signals the first appearance of an infinite network, and the conversion beyond which all flow ceases. In order to measure the gel point conversion of the resin, we combined the results of DSC experiments with dynamic mechanical analyses (DMA) of the curing resin. In the DMA experiment, the resin was sandwiched between two circular flat platens. The assembly is placed in an oven and allowed to temperature equilibrate. Shear moduli are then obtained at a forced frequency. Due to the slow temperature equilibration, this type of instrument cannot be used to obtain measurements under programmed conditions with any efficiency. For this reason, we chose to measure the buildup of viscosity in the curing resin under isothermal conditions. In each instance, the gel point was assumed to have been reached when the storage ($G'$) and loss ($G''$) moduli become equal in magnitude. In order to minimize precure during temperature equilibration, data was collected at lower temperatures.

This technique did not produce a meaningful solution for the T300/934 prepreg resin. However, it gave some insight into the influence of added catalyst on the nature of the cure reaction. Initially, T300/934 prepreg was sandwiched between the shear plates of the rheometer, and the buildup of properties measured under isothermal cure conditions. Attempts were made to physically remove resin from the prepreg. These were all unsuccessful. Resin could be removed from the prepreg by dissolving in solvent, but becomes altered by the process. Hence, 934 resin was formulated in house, eventually settling on the method outlined in the "Materials and Methods" section. Attempts to formulate with added BF$_3$ catalyst proved unsuccessful as all the solvent could not be removed without some advancement of cure. As the ultimate heat of cure for both
materials was very similar, it was presumed to a first approximation, that although the synthetic resin may cure more slowly than the commercial version, the structural progression of cure would match that of the commercial resin and so the gel point conversion would be close to that for the commercial resin. As shall be made apparent, this assumption proved to be incorrect.

As the synthetic T300/934 resin cures more slowly than the commercial version, both conversion and rate progression were determined by DSC as a function of time at 140 °C and 150 °C – temperatures at which the rheometrics measurements were performed. The results were plotted in figures 4.38 and 4.39.

The synthetic resin was then cured under isothermal conditions at the same temperatures in the rheometer, and $G'$, $G''$, $G^*$, and $\tan \delta$ were determined as a function of time. The results for the experiment performed at 140 °C are shown in figure 4.40. The results of all of the viscometric experiments are furnished in Appendix O.
Figure 4.38 Degree of cure ($\alpha$) as a function of time for the isothermal cure of catalyst free synthetic “934 resin” at 140 °C and 150 °C.

Figure 4.39 Rate of cure ($d\alpha/dt$) as a function of time for the isothermal cure of catalyst free synthetic “934 resin” at 140 °C and 150 °C
Figure 4.40 Plot of the development of elastic modulus ($G'$), loss modulus ($G''$) and complex viscosity ($G^*$) during cure of catalyst free “934 resin” as a function of time measured under isothermal conditions at 140 °C.
Averaged plots of tanδ vs time were obtained for cure of the resin at 140 °C and 150 °C as shown in figure 4.4. Tanδ = 1 when the storage and loss shear moduli become equal. Using the conversion curve in figure 4.38, the average gel times for the above cures were translated into apparent gel points as shown in figure 4.42.

![Figure 4.41](image)

**Figure 4.41.** Plot of the development of tan delta versus time at 140 °C and 150 °C for curing catalyst free “934 resin”. The apparent gel point is reached when tanδ = 1
Figure 4.42. Apparent degree of cure for catalyst free “934 resin” at the gel point measured during isothermal cure at 140°C and at 150°C

By combining these results, the averaged gel point conversion for the synthetic resin was estimated as ≈ 0.56. In contrast, from theoretical considerations, the estimated gel point was 0.34 as measured according to the equation

$$P_c = \frac{[r(f_{we} - 1)(f_{wa} - 1)]^{-1/2}}{1} \quad ------(30)$$

Where, $P_c = \text{conversion of the deficient reagent at the gel point (in this instance, the epoxy resin resin)}$, $\approx \alpha_c$

$f_{wa} = \text{average functionality of the amine} = 4$

$f_{we} = \text{average functionality on the epoxy} = 4$

$r = \frac{Ne}{Na} = \text{ratio of epoxy functional groups to amine functional groups in resin}$, here, $r = 0.909$
However the above equation is completely valid only if all functional groups possess equal reactivity. Clearly, this condition is not met in the polymerization of amine groups, where the primary amine is more reactive than the secondary amine (that is, in addition, formed only after reaction of the primary amine). This will push P_{c} (or \alpha_{gel}) to a higher conversion. The basic epoxy–amine reaction is illustrated in figure 4.43.

**Figure 4.43.** Reaction of an aromatic primary amine with two successive epoxy groups. The bigger the rate constant (K_{1}), the faster the reaction. K_{1} > K_{2}. 
If Pc is fixed at 0.56, \( r \) at 0.909, and \( f_{we} \) at 4, and if the equation is rearranged to find “\( f_{wa} \)”, then \( f_{wa} \) is driven to 2.17 from 4, in other words, as if the DDS has functioned almost as a difunctional curative. This can be explained in terms of the relative magnitudes of \( K_1 \) and \( K_2 \). Irrespective of the nature of the cure cycle, \( K_1 > K_2 \) always. If the cure is accelerated by the addition of catalyst, both \( K_1 \) and \( K_2 \) are enhanced. In addition, the relative difference between the two becomes less significant and Pc becomes reduced towards the theoretical value of 0.34. If the amine curative becomes less active, both \( K_1 \) and \( K_2 \) will be reduced. In addition, the relative difference in magnitude between the two will become accentuated, in other words \( K_1 \gg K_2 \) and the DDS will function as an effective difunctional chain extender almost until all the primary amines have been used up, at which point, secondary amines begin to react to form crosslinks. This, in effect, will postpone gelation until a higher conversion. Therefore, even though the final product is similar for reaction with and without catalyst, we cannot assume that the gel point conversion of the “synthetic” 934 mix is similar to that of the T300/934 prepreg resin with added BF\(_3\) catalyst. Unfortunately, we cannot fix the gel point conversion for the cure of T300/934 prepreg resin. It is entirely possible also that the gel point conversion for this commercial prepreg may vary somewhat from batch to batch with the level of BF\(_3\) catalyst in the material.
4.4. Summary

The major components of the epoxy resin system in T300/934 prepreg were determined using the techniques of chromatography and spectroscopy. The epoxy precursor was found to be TGDDM with DDS as the curing agent. This amine curing agent is relatively unreactive at ambient temperatures, giving the resin a long shell life. The resin also contained BF$_3$ catalyst, which complexes with amines in the resin and promotes low temperature cure.

The cure kinetics of the resin was investigated using DSC. Three sets of experiments were performed with DSC: dynamic temperature scanning, isothermal scanning and combined dynamic temperature and isothermal scanning. In dynamic temperature experiments, the cure reaction shifted to higher temperatures with faster heating rates (10-20 °C). The cure reaction ends around 230 °C. As the resin degrades around 300°C, the resin should be cured at lower temperatures using lower heating rates. The apparent heat of reaction increases with increase in heating rate. The average heat of reaction of the resin was calculated as $453 \pm 25$ J/g of prepreg resin. The ultimate glass transition temperature of the resin was around $187 \pm 4$ °C irrespective of the heating rate employed during cure. The apparent activation energy of the resin was found to vary with degree of cure, and increases with increase in degree of cure due to the build up of resin viscosity. A low temperature maximum in the $E_a$ vs alpha curve was attributed to low temperature catalysis by BF$_3$.

Isothermal experiments were then performed from 120 °C to 180 °C. It was found that the maximum degree of isothermal cure is a function of isothermal curing temperature. There is significant amount of ultimate cure of this resin even at low
temperatures, for example, around 64% at 130 °C. Cure proceeds rapidly to complete conversion at higher temperatures such as 180 °C. The maximum intermediate glass transition temperature increases with increase in curing temperature. The ultimate glass transition temperature measured for isothermal experiments was around 219 ± 6 °C and was considerably higher than that measured from dynamic temperature scanning. The cure under intermediate isothermal conditions promotes the primary amine reaction over the secondary amine reaction. This will retard the gel point conversion and lead to a more efficient cure and a higher ultimate glass transition.

A series of combined ramp and soak experiments were conducted and it was found that the ultimate extent of cure in the soak portion of the cure cycle at any intermediate time and temperature is not a function of cure history or initial degree of cure. At longer times, conversions merge to a common value irrespective of the heating rate used in the previous ramp segment. The final cure at an intermediate temperature can be predicted if the initial degree of cure at the start of the soak is known. This can also be predicted with the help of three dimensional surface fitting software. These plots are useful in predicting the values of degree of cure, rate of cure at intermediate times and initial degrees of cure at a given soak temperature. Hence, this model is helpful in predicting the degree of cure and rate of cure at any point of the combined ramp and soak cycle.

Dynamic shear rheometry of the prepreg did not allow us to estimate the gel point of the resin. Hence, experiments were held with formulated “synthetic” 934 resin made with DDS and TGDDM and without catalyst. The gel point for the synthetic resin was determined to occur at 56% conversion under isothermal conditions. Since the catalyst
influences the time for gelation in an epoxy resin cure, we could not calculate the gel point in commercial prepreg and presumed that it will vary depending on the level of BF$_3$ catalyst in the material.
CHAPTER 5

Processable Phthalonitrile Resin Containing Bisphenol A
and Benzophenone building Blocks

1. Introduction

High-temperature polymers in a variety of composites are of importance for aerospace applications due to their high strength and reduction in weight. The development of high-temperature polymers resulted from the incorporation of thermally stable aromatic and heteroaromatic rings within the backbone of a polymeric system. Phthalonitrile resins have been investigated as a high temperature substitute for epoxy resins.

Phthalonitrile resin was synthesized based on Bisphenol-A as precursor. Flexible aromatic ether linkages were incorporated between the phthalonitrile end units to lower the softening temperature of the resin. A three step synthetic scheme was developed to synthesize the precursor 4-nitrophthalonitrile, starting with phthalimide, due to the high cost of starting materials and intermediates. Each step utilized inexpensive reagents to produce the intermediates including 4-nitrophthalonitrile in good yield and high purity. This program of work was instigated to study an easily processable phthalonitrile resin system for use at 600 °F.

Phthalonitrile resin systems have been developed by Keller, et al., at the Navy research labs (Bethesda, MD). It is the purpose of this thrust to duplicate the synthesis of this resin system to determine feasibility of synthesis and to investigate the cure profile of this resin system. The current cure cycles are extremely complex. This investigation was also instigated to establish rationals for simpler cure cycles.
TMA experiments were conducted for the conditioned phthalonitrile samples

i. cured under ramp conditions from 250 to 350 °C @ heating rates of 0.1, 0.2 and 0.3 °C/min

ii. cured under combined ramp and soak conditions i.e, ramped from 250 to 300°C and 350°C @ a heating rate of 0.3°C/min and soaked at those temperatures.

5.2. Experimental Section

5.2.1. Materials

The materials used are mentioned in chapter 2.

5.2.2. Synthesis of aromatic ether linked phthalonitrile

Synthesis of 4-nitrophthalimide precursor

Phthalimide (30 g, 0.204 mol) was added to a 320 mL mixture of concentrated H$_2$SO$_4$ and 70% HNO$_3$ (6:1 v/v) at 0-10 °C. The solution was allowed to slowly warm to room temperature and held for 4 hours. The solution was added to ice water and stirred. The 4-nitrophthalimide was crystallized and precipitated out of ice water. The product was collected by vacuum filtration, washed with ice cold water and air dried overnight. Yield 31.5g (80%); m.p.199 °C (by DSC)

Synthesis of 4-nitrophthalamide precursor

4-nitrophthalamide (57.9 g, 0.300 mol) was added to NH$_4$OH (33%, 200 mL) with stirring. A yellow suspension was formed which was allowed to react at room temperature for 24 hours. A yellow precipitate, 4-nitrophthalamide was collected by vacuum filtration, washed with ice cold water and air dried overnight. Yield 60.1g(95%); m.p. 199 °C (by DSC)
Synthesis of 4-nitrophthalonitrile precursor

SOCl₂ (83.5mL, 1.144 mol) was added dropwise to DMF (200mL) under nitrogen purge that had been cooled to 0-5 °C. The 4-nitrophthalamide (60.1 g, 0.286 mol) was then added. The solution was allowed to slowly warm to room temperature and react for 18 hours under a nitrogen purge. The solution was then added to ice water to crystallize and precipitate the product. The 4-nitrophthalonitrile was collected by vacuum filtration, washed with ice cold water, and allowed to air dry overnight. Yield 45.2 g (92%); m.p.141 °C (by DSC)

Synthesis of aromatic ether linked phthalonitrile product

To a 100 mL, three-necked flask fitted with a thermometer, a Dean-Stark trap with a condenser and a nitrogen inlet, 10.0 g of Bisphenol A (43.8 mmol), 4.78 g of 4,4’-difluorobenzophenone (21.9 mmol), 9.07 g of powdered anhydrous K₂CO₃ (65.7 mmol), toluene (10 mL) and N,N-dimethylformamide (DMF 50mL) were added. The resulting mixture was degassed with argon at ambient temperature. The Dean-Stark trap was filled with toluene. The mixture was refluxed at 135-145 °C under an argon atmosphere for 12-18 hours or until no more water was collected in the Dean-Stark trap. The toluene was distilled off and the reaction mixture was cooled to 50 °C. 4-nitrophthalonitrile (7.60 g, 43.9 mmol) was added in one portion. The reaction mixture was heated to 80 °C for 6-8 hours. The reaction mixture was cooled to ambient temperature and poured into a 5% aqueous KOH solution which results in the formation of a solid. The solid was broken up and collected into a Buchner funnel. The white solid was dissolved in chloroform (200mL) and washed with 200mL of a 5% aqueous KOH solution, with 200 mL of
distilled water, with 200mL of aqueous HCl solution and finally with 200mL of water until neutral. The solid was vacuum dried to yield the final product (~18.2 g, 94%).

5.2.3. FT-IR Spectroscopy

This is discussed in chapter 2.3

5.2.4. NMR Spectroscopy

This is mentioned in chapter 2.3

5.2.5. Thermal Analysis – Differential Scanning Calorimetry

The procedure is mentioned in chapter 2. Dynamic Temperature Scanning (ramp) experiments were conducted in the DSC by scanning from 30 °C to 400 °C at a heating rate of 3 °C/min to find the melting points.

Sample curing for TMA experiments

The muffle furnace ‘Eurotherm 847 controller’ was used to conduct the ramp experiments from 250 °C to ≤ 350 °C at heating rates of 0.1, 0.2, 0.3 °C/min and combined ramp and soak experiments by ramping from 250 to 300 °C or 350 °C and soaking at those temperatures of the conditioned phthalonitrile resin.

5.2.6. Thermomechanical Analysis

This is mentioned in chapter 2.3

Curing experiments were performed by raising the uncured resin from 250°C to an end temperature (≤ 350 °C) using heating rates of 0.1, 0.2, 0.3 °C/min in a muffle furnace under nitrogen gas with the sample in a mould designed to generate parallel top and bottom surfaces. The cured resin was then cooled to room temperature. The resin was then ramped at 10 °C/min to 500 °C in the TMA apparatus with a sharp probe on the
The very slow cure of this resin ensures that further cure in the TMA apparatus is negligible.

Combined Ramp and Soak experiments were conducted by subjecting the uncured resin to ramping from 250 °C to an end temperature of 300 °C or 350 °C. The sample was then soaked at that temperature. The resin was then cooled and ramped at 10 °C/min to 500 °C in the TMA apparatus. The penetration profile was recorded as a function of oven temperature.

Two factors are paramount in the interpretation of a TMA experiment. The first is the onset of penetration. This locates the temperature(s) at which the resin first softens and is analogous to the resin Tg (glass transition temperature). The second is the ultimate degree of penetration which is inversely proportional to the perfection of the network.

5.2.8. Thermal Volatalization Analysis

The resin mass was subjected to extensive conditioning for 4 hours at 250 °C under vacuum to remove bubbles before cure. To investigate the origin of these bubbles the resin mass was subjected to Thermal Volatilization Analysis in a continuously evacuated system. This technique has been discussed in chapter 3.
5.3 Results and Discussion

5.3.1. Synthesis of aromatic ether linked phthalonitrile

The schematic representation for the synthesis of 4-nitrophthalonitrile is shown in figure 5.1.

Figure 5.1. Scheme for the synthesis of 4-Nitrophthalonitrile

The formation of 4-nitrophthalimide involves the electrophilic aromatic substitution of the nitro group onto the phthalimide with sulfuric acid and nitric acid. The two acids are mixed in a volumetric ratio of 6:1. H$_2$SO$_4$ was cooled to ice bath temperature and HNO$_3$ was then added to avoid an exotherm. The reaction mixture was allowed to warm to room temperature and react for four hours. (The solution turns to orange yellow color) The temperature was then increased to ~50 °C and the solution was kept at ~50 °C for one hour. The solution was then cooled to room temperature and allowed to react for four hours at room temperature. The solution was added slowly to ice water on stirring. The product 4-nitrophthalimide was collected by vacuum filtration,
washed with ice water and allowed to dry overnight. The product was obtained in good yield (80%).

A proton NMR spectrum of 4-nitrophthalimide was collected. The signals were identified according to accepted principles and with reference spectra from ACD software. The formation of the product 4-nitrophthalimide was confirmed and the $^1$H NMR spectrum of the product was shown in figure 5.2.

At 8.05 ppm, proton a, doublet of doublets was observed. This doublet is at the farthest upfield, indicating that the proton is meta to the strong electron withdrawing nitro group. It has an integration value equal to 1. This proton is at position 6 on the aromatic ring of 4-nitrophthalimide. Proton c is observed at 8.4 ppm with an integration value of 1 and a very small splitting of the peak indicates that proton c does not have any neighboring protons in either of its ortho positions. This concludes that the nitration occurred at the 4 position and that proton c is located at the 3 position.

The proton b appears as a doublet of doublets with the largest splitting. This indicates that proton b is located ortho to the nitro group and there is a proton in ortho position and another proton in meta position relative to the position of proton b.

Proton d appears as a singlet at 11.9 ppm and has an integration value equal of 1. This position indicates the deshielding by electron withdrawing group. These results are consistent with the molecular structure of 4-nitrophalimide.
Synthesis of 4-Nitrophthalamide

4-Nitrophthalamide (57.9 g, 0.300 mol) was added to NH₄OH (33%, 200 mL) with stirring. A yellow suspension was formed. It was allowed to react at room temperature for 24 hours. Then it was vacuum filtered and washed with ice cold water. The product was dried overnight. The product 4-nitrophthalamide was confirmed by the identification of the signals from the proton NMR spectrum according to accepted
principles as well as with spectrum produced by ACD software. The $^1$H NMR spectrum of the 4-nitrophthalamide was shown in figure 5.3.

The $^1$H NMR spectrum of 4-nitrophthalamide was compared with that of 4-nitrophthalimide to confirm the formation of amide. The imide protons have completely disappeared. Protons a, b, c are more shielded due to the opening of the five membered ring and occurred at upfield. All these protons have an integration values equal to 1. Proton d has an integration value equal to 2. Protons e and f with integration value of 1. They have different chemical shift values indicating that protons e and f are chemically different. We can not explain this effect with confidence. The integration ratio of protons a, b, c, d, e and f was 1:1:1:2:1:1 and are consistent with the structure of 4-nitrophthalamide.
Synthesis of 4-Nitrophthalonitrile

Thionylchloride and dry DMF (as solvent) were added to 4-nitrophthalamide and it was dehydrated to 4-nitrophthalonitrile. This solution was then added to ice water to crystallize the product. The product, 4-nitrophthalonitrile, was dried overnight and the proton NMR spectrum was collected. The proton NMR spectrum of 4-nitrophthalonitrile is shown in figure 5.4 and is in a good agreement with the proton NMR spectrum of commercially purchased 4-nitrophthalonitrile (shown in figure 5.5)
The $^1$H NMR spectrum of 4-nitrophthalonitrile was compared with that of 4-nitrophthalamide. Protons a,b,c occurred further downfield when converted to 4-nitrophthalonitrile. Proton c is further deshielded than the other protons and occurs at 9.05 ppm. The amide protons completely disappeared and this confirms the conversion of 4-nitrophthalamide to 4-nitrophthalonitrile.

Figure 5.4. $^1$H NMR Spectra of 4-Nitrophthalonitrile (synthesized) in DMSO
Figure 5.5. $^1\text{H}$ NMR Spectrum of 4-nitrophthalonitrile (Purchased) in DMSO
Synthesis of aromatic ether linked phthalonitrile

The synthetic pathway for the aromatic ether linked phthalonitrile was shown in figure 5.6.

**Figure 5.6.** Synthetic pathway for the aromatic ether linked polymer
Bisphenol A (BPA) is coupled to difluorobenzophenone (BP or DFBP) to form the adduct BP-DiBPA. The intermediate is then end capped with 1,2 dicyano, 4-nitrobenzene (DCB) to form the final adduct, BP-DiBPA-DiDCB. A twofold excess of BPA is added to the DFBP under basic conditions to displace the fluorines and couple the two species. Water, so produced, is removed using a Dean Stark trap. Basic conditions are maintained and DCB is added. The phenolate anions displace the nitrates to produce a final product that is purified by acidic and basic extractions. Synthesis conditions are reproduced in section 5.2.2. and in figure 5.6. This would be termed a “one pot” synthesis of the resin.

**Resin cure Profile**

The resin cure profile is summarized in figure 5.7. The resin mass is preheated at 250 °C for 4 hours under vacuum to complete the bubble forming reaction. The resin is then pulverized and solid BAPS (see figure 5.7) is ground into the resin mass. These two are melted together for a few minutes to complete the mixing process. The final resin cure reaction is then completed in a programmable muffle furnace at 250-350 °C under nitrogen.
Grind solid BAPS into Product, melt together 200 °C/5 min

Intermediate that will cure without bubble formation

Heat 4 h at 250 °C with pumping < 0.1 mm Hg Pressure

Cure to thermoset at 250-350 °C

**Figure 5.7.** Resin cure process
5.3.2. FT-IR Spectroscopy

An infrared spectrum of the phthalonitrile resin is reproduced in figure 5.8. The nitrile band is located at 2233 cm\(^{-1}\) and is indicated by the red arrow. The methyl band is located between 2800 and 3000 cm\(^{-1}\) and is bordered by the green arrows. The methyl band remains invariant throughout the polymerization.

![Infrared spectrum of uncured phthalonitrile resin.](image)

Figure 5.8. Infrared spectrum of uncured phthalonitrile resin.

The cure process involves conversion of nitriles to (it is thought) the cyclotrimerized product (figure 5.9). As such, the nitrile content in the resin should be diminished with cure. The nitrile region of uncured, partly cured, and fully cured phthalonitrile resin is reproduced in figure 5.10.
Figure 5.9. Formation of the cyclotrimerized product

Figure 5.10. The intensity of the nitrile absorption band versus cure state for phthalonitrile resin.

2233 cm$^{-1}$
Infrared analysis of the Cure State

The cure state versus final cure temperature (°C) is shown in figure 5.11 for the three ramp experiments conducted for the conditioned nitrile resin in the muffle furnace from 250 °C to an end temperature (≤ 350 °C) at heating rates 0.1, 0.2, 0.3 °C/min. The cure is measured by the loss of nitriles which is the ratio of the area under nitrile peak to the area under invariant methyl peak. It is noticed that a faster heating rate requires a higher end temperature to achieve the same loss of nitriles. It is also noticed that 100% removal of nitriles is never achieved, and indeed is not required for good performance.

Figure 5.11. Degree of cure, as measured by loss of nitrile absorbance, versus end temperature of cure in °C.
5.3.3. Thermal Analysis

**Differential Scanning Calorimetry**

The melting point of the intermediates and the product 4-nitrophthalonitrile is determined using Pyris 6 DSC on ramping the samples from 30°C to 400°C. The sample exotherm of melting is produced in figure 5.12.

![Melting Point of 4-Nitrophthalonitrile](image)

**Figure 5.12.** Sample exotherm from DSC scan for the melting of 4-nitrophthalonitrile

5.3.4. Thermomechanical Analysis (TMA)

**Dynamic Scanning Experiments**

TMA tests were conducted for the conditioned phthalonitrile sample mass as discussed in section 5.3.2. TMA analyses at 10°C/min were performed on resin samples that had been previously conditioned, mixed with 2% BAPS, and partly cured from 250
°C to higher end temperatures (≤ 350 °C) at 0.1 °C/min (Figure 5.13), 0.2 °C/min (Figure 5.14), and 0.3 °C/min (Figure 5.15) in the muffle furnace. Extents of cure are determined by IR spectroscopy as previously defined. Resin previously cured at a lower heating rate to a fixed end temperature is more fully cured than resin precured at a faster heating rate to the same fixed end temperature. Not only the extent of cure but also the temperature profile under which cure is achieved appears to affect performance in the TMA experiment. For example, resin cured to 49% loss of nitriles at 0.1 °C/min produces a lower onset temperature and a higher degree of penetration than resin cured to a lesser consumption of nitriles (but cured to a higher end temperature).

![TMA: Polyphththalonitrile with 2% mBAPS (0.1 C/min)](image)

**Figure 5.13.** TMA of phthalonitrile resin precured from 250 °C to a higher end temperature at a heating rate of 0.1 °C/min
Figure 5.14. TMA of phthalonitrile resin precured from 250 °C to a higher end temperature at a heating rate of 0.2 °C/min

Figure 5.15. TMA of phthalonitrile resin precured from 250 °C to a higher end temperature at a heating rate of 0.3 °C/min
The resin softening temperature in the TMA experiment was plotted against the upper end temperature of cure, for resin cured at 0.1 °C/min, as shown in figure 5.16. The degree of tip penetration after softening was plotted against the upper end temperature of cure, for resin cured at 0.1 °C/min, as shown in figure 5.17. At this heating rate, it is observed that a profound and critical change occurs in the network after exposure to temperatures in excess of 300 °C. The onset of softening and the degree of penetration afterwards, both improve dramatically after previous exposure of the resin to 300 °C.

![TMA: Polyphthalonitrile with 2% mBAPS (0.1 C/min)](image)

**Figure 5.16.** Resin softening temperature in the TMA experiment plotted against the upper end temperature of cure, for resin cured at 0.1 °C/min
Figure 5.17. Degree of tip penetration after softening plotted against the upper end temperature of cure, for resin cured at 0.1 °C/min

The resin softening temperature in the TMA experiment was plotted against the upper end temperature of cure, for resin pre-cured at all three heating rates (0.1, 0.2, 0.3 °C/min), as shown in figure 5.18. The degree of tip penetration after softening was plotted against the upper end temperature of cure, for resin pre-cured at all three heating rates (0.1, 0.2, 0.3 °C/min) as shown in figure 5.19.
Figure 5.18. Resin softening temperature in the TMA experiment plotted against the upper end temperature of cure, for resin cured at all three heating rates.

Figure 5.19. Degree of penetration in the TMA experiment, after the onset of softening, plotted against the upper end temperature of cure, for resin cured at all three heating rates.
Combined Ramp and soak experiments were conducted to cure the resin with end temperatures of 300 °C and 350 °C. Resin was cured to 300 °C at a heating rate of 0.3 °C/min then soaked at that temperature. Then it was subjected to the TMA experiment. The results of TMA experiments are shown in figure 5.20. It can be seen that a prolonged 13 h at 300 °C is required to raise the softening temperature above 200 °C.

![TMA: Polyphthalonitrile with 2% mBAPS (combined ramp and soak at 300 C)](image)

**Figure 5.20.** TMA of phthalonitrile resin pre-cured by ramp and soak experiments to 300 °C at a heating rate of 0.3 °C/min.

The resin was then ramped to an end temperature of 350 °C at a heating rate of 0.3 °C/min and then soaked at that temperature. It was noticed that raising the cure end temperature to 350 °C produces a profound change in the performance of the resin in the TMA experiment. When the soak temperature is raised to 350 °C, resin properties build up rapidly during soak. After as little as 1h at 350 °C, low temperature softening and penetration of the resin is completely eliminated. In fact, the resin is seen to expand without penetration until the onset of degradation temperatures around 500 °C. The results are shown in figure 5.21.
Figure 5.21. TMA of phthalonitrile resin pre-cured by ramp and soak experiments to 350 °C at a heating rate of 0.3 °C/min.

The onset softening temperature (by TMA) and the degree of cure (from nitrile indexes) are plotted as a function of soak temperature at 350 °C in figure 5.22. It is noted that full properties are achieved after only 1h at 350 °C. However, nitriles continue to be consumed throughout this temperature interval. The degree of penetration thereafter is plotted (with degree of cure) in figure 5.23. The degree of penetration undergoes the same profound change and diminution after 1h at 350 °C. A recommended conservative cure cycle for this resin, therefore, would be ramping from 250 °C to 350 °C at 0.3 °C/min followed by soak for 2hours at 350 °C.
Figure 5.22. The onset softening temperature (by TMA) and the degree of cure (from nitrile indexes) plotted as a function of soak temperature at 350 °C after heating to that temperature at 0.3 °C/min.

Figure 5.23. The degree of penetration after the onset softening temperature (by TMA) and the degree of cure (from nitrile indexes) plotted as a function of soak temperature at 350 °C after heating to that temperature at 0.3 °C/min.
5.3.6. Thermal Volatalization Analysis

The need for an extensive conditioning of the resin mass to remove “bubbles” prior to resin cure (4h @ 250°C with pumping) will add to the cost of the resin. The origin of these bubbles has been determined using thermal volatalization analysis technique. The TVA technique has been described in chapter 3. The TVA technique was used to analyze volatile products emitted by the resin system. Phthalonitrile resin (unconditioned) was added to a quartz crucible and positioned in the TVA degradation tube. The degradation tube was added to the oven head assembly and pumped to $10^{-3}$ torr. Two experiments were performed, a ramp to 300 °C @ 3 °C/min and a ramp to 500 °C @ 3 °C/min, both using approximately 250 mg of material. Volatiles emitted by the sample were detected using electronic Pirani pressure gauges as a milliV signal. The oven temperature was recorded as a mV thermocouple output and corrected to a true sample temperature. A OMB - DAQ – 56 data logger digitized both sets of signals and fed them to a spreadsheet. At the end of the TVA experiment, volatiles collected at -196 °C on the vacuum line were separated using the SATVA experiment and analyzed using gas phase spectroscopy. The TVA experiment to 500 °C is shown in figure 5.24. It is to be noted that the TVA sample thickness is very small. This, coupled to the very good vacuum achieved, will result in volatiles being removed at lower temperatures than from thicker samples under a rougher vacuum, as would be experienced during normal cure of the resin.
Figure 5.24. TVA of 250 mg phthalonitrile resin from room temperature i.e, 20 °C to 500 °C @ 3 °C/min. Pirani 1 measures the total volatile flux. Pirani 4 measures volatiles uncondensed at -196 °C (noncondensable gas production) in the vacuum line.

The bubble forming reaction, characterized by the production of volatiles below 300 °C, produces only condensable gases. Therefore, we can remove from consideration, the loss of oxygen from decomposing peroxide impurities or carbon monoxide from decomposing carbonate impurities, left over from synthesis. Both condensable and noncondensable volatiles are produced above 450 °C in small amounts. The high temperature peak in volatile production is a simple consequence of shutting the oven off at 500 °C. The low temperature volatiles were condensed in the SATVA trap and subjected to separation as the trap warmed to room temperature (figure 5.25).
SATVA trap is surrounded by paraffin wax so that the warm up occurs over a 2h period. The SATVA separation reveals a major (>95%) component, and a minor component (5%) in the product mixture. The volatility of the major component is that of a low boiling point solvent.

**Figure 5.25.** SATVA separation of condensable volatiles collected on the vacuum line between room temperature and 300 °C in the preceding TVA experiment.

Condensable volatiles were transferred to a gas phase IR cell for analysis. The IR spectrum of this product fraction is produced in figure 5.26.
Figure 5.26. Gas phase IR spectrum of condensable volatiles released from phthalonitrile resin during a ramped heating experiment from room temperature to 300 °C.

This IR spectrum is identical to that produced by pure gas phase chloroform. This was confirmed by proton NMR spectroscopy (not shown). The condensable volatile fraction constituted about 5% of the sample mass. About 47% of the sample simply evaporated from the hot zone and condensed onto the cold finger above the oven. This material was identical to the original monomer.

In another TVA experiment (not shown), pre-conditioned resin (4h @ 250 °C with pumping) did not produce low temperature volatiles below 300 °C. In other words, all the chloroform solvent had been removed by the conditioning process.
5.4. Summary

A multiple aromatic ether linked phthalonitrile resin was synthesized with a flexible spacer between reactive end groups. (The 4-nitrophthalonitrile precursor for the above reaction had previously been synthesized using an inexpensive synthetic scheme).

The conditioned phthalonitrile mass was cured with 2% BAPS in the muffle furnace. The sample was subjected to ramping at different heating rates from 0.1, 0.2 and 0.3 °C/min from 250 °C to an end temperature ≤ 350 °C. The precured sample was then subjected to TMA analysis from room temperature to 500 °C @ 10 °C/min. It was concluded that resin previously cured at a lower heating rate to a fixed end temperature is more fully cured than resin precured at a faster heating rate to the same fixed end temperature. For the same extent of loss of nitrile groups, the faster heating rates require a higher end temperature than the lower heating rates.

Combined ramp and soak experiments were carried out on the resin mass in the muffle furnace by ramping at a heating rate of 0.3 °C/min from 250 °C to an end temperature of 300 °C and 350 °C then soaking at that temperature. It was revealed that the degree of penetration undergoes a profound change and diminution after 1h at 350 °C.

A recommended conservative cure cycle for this resin could be ramping at 0.3 °C/min from 250 °C to 350 °C followed by soak for two hours at 350 °C.

TVA and SATVA experiments with the preconditioned resin mass revealed that bubble formation is due to removal of the last solvent added to the resin prior to cure.
CHAPTER 6
SUMMARY

T800/3900 Epoxy prepreg resin

The work presented in this dissertation has made an attempt to revise the cure cycles that take place in industrial autoclave. Work was also done to investigate the cure profile of phthalonitrile resin. Prior to developing methods and revising cure cycles, the major components of epoxy prepreg resin systems were identified using spectroscopic analysis. The epoxy prepreg system T800/3900 was found to consist of DGEBA and TGDDM with DDS as curing agent. DDS is relatively unreactive at ambient conditions giving a long shelf life. The cure kinetics of the prepreg resin system T800/3900 was investigated using DSC. Three sets of experiments were conducted using dynamic, isothermal and combined dynamic and isothermal temperature scanning.

In the dynamic temperature scanning experiments, the cure reaction shifted to higher temperatures with higher heating rates and the reaction ends around 320 °C at a heating rate of 3 °C/min. As postcure reactions take place above 300 °C, this resin should be cured below 300 °C with lower heating rates. The plot of activation energy vs cure gives an insight into the cure mechanism. The activation energy monotonically increased with conversion due to build up of resin viscosity. The absence of an early maximum in the plot of Ea vs α at low degrees of cure indicates that it does not contain any low temperature catalyst. The ultimate glass transition temperature of the resin was found to be around 150.6 °C.

Isothermal DSC experiments were conducted from 110 °C to 190 °C in increments of 5 °C. It is found that the maximum degree of cure is a function of cure
temperature. The intermediate glass transition temperature increases with increase in the isothermal cure temperature. The ultimate glass transition temperature of the resin was found to be around 223.8 °C which is higher than the one produced by dynamic temperature scanning showing that the network formed under isothermal conditions is different from the one formed from cure under dynamic temperature scanning. The isothermal data was found to be consistent with the two component model of Kamal. The Kamal parameters $k_1$ and $k_2$ were found to vary with isothermal cure temperature. From the values of $k_1$ and $k_2$ activation energies $E_{a1}$ and $E_{a2}$ were calculated.

A series of combined ramp and soak experiments were conducted and it was found that the ultimate extent of cure of the T800/3900 epoxy resin prepreg in the soak portion of the cure cycle at long times is not a function of the ramp rate to that temperature. (At longer times, conversions merge to a common value irrespective of the heating rate used in the previous ramp segment). The cure at an intermediate temperature can be predicted from the combined ramp and soak plots if the initial degree of cure at the start of the soak cycle is known.

DMA experiments were conducted to characterize the cure profile of T800/3900 prepreg, and were found to give reproducible results. The onset of buildup of physical properties corresponds to a complex interplay between resin conversion and oven temperature. To some extent, principles observed in DSC experiments appear to cross over to these DMA experiments. For example, more cure at a slower heating rate leads to a lower onset temperature for the buildup of shear storage modulus, etc.

TVA and SATVA experiments were conducted from 20 °C to 267 °C and 350 °C @ 3°C/min. The TVA experiments were followed by SATVA experiments to fractionate
the condensable products for subsequent spectroscopic analysis. The oligomeric “products” such as DGEBA, MY720 and DDS were collected as the coldring product fraction. Condensable volatiles such as water are collected after the SATVA experiment by distillation on the vacuum line. Under these high vacuum conditions, only a small amount of volatiles (~ 3%) were removed from these thin samples of prepreg; and within that mixture of volatiles (3%), oligomers accounted for less than 66% and condensable volatiles (mostly water) as slightly more than 33%. Much less material will be evolved from thick samples of prepreg cured under process conditions (rough vacuum) in an autoclave.

**T800/934 Epoxy prepreg resin**

The major components of the epoxy resin system in T800/934 prepreg resin were determined using the techniques of chromatography and spectroscopy. The epoxy precursor was found to be TGDDM with DDS as the curing agent. This amine curing agent is relatively unreactive at ambient temperatures, giving the resin a long shell life. The cure kinetics of the prepreg resin system T800/934 was determined with DSC. It also contained BF₃ catalyst which complexes with amines in the resin and promotes low temperature cure. As discussed earlier, three sets of experiments were conducted in dynamic, isothermal and combined dynamic and isothermal temperature scanning modes.

In dynamic temperature scanning the cure reaction shifted to higher temperatures with higher heating rates. The cure reaction ends around 230°C. As the epoxy resin degrades around 300°C this resin system should be cured at lower temperatures using lower heating rates. The ultimate glass transition temperature was found to be around 187°C ± 4°C. The apparent heat of reaction during programmed cure increases with
increasing heating rate and it was found to be $453 \pm 25$ J/g of prepreg resin. The apparent activation energy of cure of the resin was found to increase with an increase in the degree of cure due to build up of resin viscosity. A low temperature maximum in the $E_a$ vs $\alpha$ curve was attributed to low temperature catalysis by BF$_3$ in the resin.

Isothermal experiments were then performed from 120$^\circ$C to 180$^\circ$C in increments of 5 $^\circ$C. The maximum degree of cure is a function of isothermal temperature. The maximum intermediate glass transition temperature increases with increase in curing temperature. The ultimate glass transition temperature for isothermal cure of T300/934 prepreg resin was found to be around $219 \pm 6$ $^\circ$C and was considerably higher than that measured from dynamic temperature scanning. The cure under intermediate isothermal conditions promotes the primary amine reaction over the secondary amine reaction. This will retard the gel point conversion and lead to a more efficient cure and a higher ultimate glass transition.

A series of combined ramp and soak experiments were conducted and it was found that the ultimate extent of cure in the soak portion of the cure cycle at any intermediate time is not a function cure history or initial degree of cure. At longer times, conversions merge to a common value irrespective of the heating rate used in the previous ramp segment. The cure at an intermediate temperature can be predicted if the initial degree of cure at the start of the soak is known. This can also be predicted with the help of three dimensional surface fitting software. These plots are useful in predicting the values of degree of cure, rate of cure at intermediate times and initial degrees of cure at a given soak temperature. Hence, this model is helpful in predicting the degree of cure and rate of cure at any point of the combined ramp and soak cycle.
The gel point of the resin in the prepreg could not be found with dynamic shear rheometry. Hence, experiments were conducted with formulated synthetic 934 resin made with TGDDM and DDS but without catalyst. The gel point for the “synthetic” resin occurs at 56% conversion under isothermal conditions. Since the catalyst influences the time for gelation in an epoxy resin cure, gel point in commercial prepreg could not be calculated. However it varies depending on the level BF3 catalyst in the material.

**Phthalonitrile resin**

A multiple aromatic ether linked phthalonitrile resin was synthesized with a flexible spacer between reactive end groups. The conditioned phthalonitrile mass was cured with 2% BAPS in the muffle furnace. Then it was subjected to ramping at heating rates of 0.1, 0.2 and 0.3 °C/min from 250°C to an end temperature ≤ 350 °C. The precured sample was then subjected to TMA analysis from room temperature to 500 °C @ 10°C/min. It was revealed that the resin previously cured at a lower heating rate to a fixed end temperature is more fully cured than resin precured at a faster heating rate to the same fixed end temperature.

Combined ramp and soak experiments were carried out on the resin mass in the muffle furnace by ramping at a heating rate of 0.3 °C/min from 250 °C to an end temperature of 300 °C and 350 °C then soaking at that temperature. It was concluded that the degree of penetration undergoes a profound change and diminution after 1h at 350 °C. A recommended conservative cure cycle for this resin would be **ramping at 0.3 °C/min from 250 °C to 350 °C followed by soak for 2h at 350 °C.**

TVA and SATVA experiments with the preconditioned resin mass revealed that bubble formation is due to removal of the last solvent in the resin prior to cure.
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APPENDICES
APPENDIX A

Calculation of Apparent Activation Energy for Cure of T800/3900 prepreg under programmed conditions in the DSC apparatus

### Degree of Cure = 0.05

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<tr>
<th>(1/T \text{ (K)})</th>
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<td>0.0020</td>
<td>-1.0</td>
</tr>
<tr>
<td>0.0022</td>
<td>-2.0</td>
</tr>
<tr>
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<td>-3.0</td>
</tr>
<tr>
<td>0.0025</td>
<td>-4.0</td>
</tr>
<tr>
<td>0.0026</td>
<td>-5.0</td>
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\[ y = -7031.9x + 11.398 \]
\[ R^2 = 0.9936 \]

### Degree of Cure = 0.10

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</tr>
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<td>-1.0</td>
</tr>
<tr>
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</tr>
<tr>
<td>0.0024</td>
<td>-5.0</td>
</tr>
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</table>

\[ y = -7222.5x + 12.192 \]
\[ R^2 = 0.9955 \]
APPENDIX A (continued)

**Degree of Cure = 0.15**

\[ y = -7.286x + 12.435 \]
\[ R^2 = 0.9362 \]

**Degree of Cure = 0.20**

\[ y = -7.999x + 12.519 \]
\[ R^2 = 0.9957 \]

**Degree of Cure = 0.25**

\[ y = -7.318x + 12.579 \]
\[ R^2 = 0.9971 \]
APPENDIX A (continued)

Degree of Cure = 0.30

\[ y = -7337.8x + 12,614 \]
\[ R^2 = 0.9974 \]

Degree of Cure = 0.35

\[ y = -7384.9x + 12,686 \]
\[ R^2 = 0.9975 \]

Degree of Cure = 0.40

\[ y = -7519x + 12,921 \]
\[ R^2 = 0.9979 \]
APPENDIX A (continued)

Degree of Cure = 0.60

\[ y = -8264.2x + 14.068 \]
\[ R^2 = 0.9981 \]

Degree of Cure = 0.65

\[ y = -3587.6x + 14.503 \]
\[ R^2 = 0.998 \]

Degree of Cure = 0.70

\[ y = -8919.3x + 15.082 \]
\[ R^2 = 0.9977 \]
APPENDIX A (continued)

**Degree of Cure = 0.75**

\[ y = -9430.4x + 15.922 \]
\[ R^2 = 0.9973 \]

**Degree of Cure = 0.80**

\[ y = -10015x + 16.869 \]
\[ R^2 = 0.9969 \]

**Degree of Cure = 0.85**

\[ y = -10707x + 17.974 \]
\[ R^2 = 0.9955 \]
APPENDIX A (continued)

Degree of Cure = 0.90

\[ y = -11629x + 19.438 \]
\[ R^2 = 0.9921 \]

Degree of Cure = 0.95

\[ y = -12148x + 19.65 \]
\[ R^2 = 0.9931 \]
APPENDIX B

Rate of Cure Vs Degree of Cure at various temperatures for T800/3900 prepreg under isothermal conditions in the DSC apparatus

Rate of Cure vs Degree of Cure at 120°C

Rate of Cure vs Degree of Cure at 125°C
APPENDIX B (continued)

Rate of Cure vs Degree of Cure at 130°C

Rate of Cure vs Degree of Cure at 135°C

Rate of Cure vs Degree of Cure at 140°C
APPENDIX B (continued)

Rate of Cure vs Degree of Cure at 145°C

Rate of Cure vs Degree of Cure at 150°C

Rate of Cure vs Degree of Cure at 155°C
Rate of Cure vs Degree of Cure at 160°C

Rate of Cure vs Degree of Cure at 170°C

Rate of Cure vs Degree of Cure at 175°C
APPENDIX B (continued)

Rate of Cure vs Degree of Cure at 180°C

Rate of Cure vs Degree of Cure at 185°C

Rate of Cure vs Degree of Cure at 190°C
APPENDIX C

Degree of Cure Vs Time of T800/3900 prepreg under isothermal conditions after a slow ramp to that temperature

2D plot of the degree of cure (α) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 155 ºC after a slow ramp to that temperature.

2D plot of the degree of cure (α) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 160 ºC after a slow ramp to that temperature.
2D plot of the degree of cure ($\alpha$) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 165 °C after a slow ramp to that temperature.

2D plot of the degree of cure ($\alpha$) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 170 °C after a slow ramp to that temperature.
APPENDIX C (continued)

2D plot of the degree of cure (α) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 175 ºC after a slow ramp to that temperature

2D plot of the degree of cure (α) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 180 ºC after a slow ramp to that temperature
2D plot of the degree of cure ($\alpha$) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 185 ºC after a slow ramp to that temperature.

2D plot of the degree of cure ($\alpha$) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 190 ºC after a slow ramp to that temperature.
APPENDIX D

Rate of Cure Vs Time of T800/3900 prepreg under isothermal conditions after a slow ramp to that temperature

2D plot of the rate of cure (dα) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 155 ºC after a slow ramp to that temperature

2D plot of the rate of cure (dα) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 160 ºC after a slow ramp to that temperature
APPENDIX D (continued)

2D plot of the rate of cure (da) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 165 °C after a slow ramp to that temperature

2D plot of the rate of cure (da) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 170 °C after a slow ramp to that temperature

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APPENDIX D (continued)

2D plot of the rate of cure (da) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 175 °C after a slow ramp to that temperature

2D plot of the rate of cure (da) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 180 °C after a slow ramp to that temperature
APPENDIX D (continued)

2D plot of the rate of cure (dα) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 185 °C after a slow ramp to that temperature

2D plot of the rate of cure (dα) versus time for the prepreg resin T800/3900 cured under Isothermal conditions at 190 °C after a slow ramp to that temperature
APPENDIX E

Degree of Cure vs Time of T800/3900 prepreg under combined ramp and soak conditions

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 160 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX E (continued)

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 165 °C.

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 170 °C.
APPENDIX E (continued)

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 175 °C.

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 180 °C.
APPENDIX E (continued)

2D Plot of degree of cure (α) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 185 °C

2D Plot of degree of cure (α) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 190 °C
APPENDIX F

Rate of Cure Vs Time of T800/3900 prepreg under combined ramp and soak conditions

2D Plot of rate of cure ($d\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 160 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX F (continued)

2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 165 °C

2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 170 °C

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APPENDIX F (continued)

2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 175 °C

2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 180 °C
2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 185 °C

2D Plot of rate of cure (dα) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 190 °C
APPENDIX G

TVA and SATVA traces and related spectra of T800/3900 prepreg resin

TVA trace of prepreg resin T800/3900 during curing from 20 to 267 °C @ 3 °C/min
APPENDIX G (continued)

SATVA trace of Prepreg resin T800/3900 during curing from 20 to 267 °C @ 3 °C/min.
Gas Phase IR Spectrum of the volatiles from SATVA during curing from 20 to 267 °C @ 3 °C/min
APPENDIX G (continued)

NMR Spectra of Volatiles of Prepreg resin T800/3900 during curing from 20 to 267 °C @ 3 °C/min
IR Spectra of cold ring fraction of prepreg resin T800/3900 during curing from 20 to 267 °C @ 3 °C/min
APPENDIX G (continued)

$^1$H NMR Spectra of CRF of Prepreg resin T800/3900 during curing from 20 to 267 °C @ 3 °C/min
APPENDIX H

Calculation of Apparent Activation Energy for Cure of T300/934 prepreg under programmed conditions in the DSC apparatus

Plots of ln(dα/dt) versus 1/T for the T300/934 prepreg resin from dynamic temperature experiments. Each plot is for a fixed value of α. Apparent activation energies are calculated from the slope of the graphs.

For Degree of Cure = 0.05:
- Equation: \( y = -8763.1x + 17.502 \)
- \( R^2 = 0.9886 \)

For Degree of Cure = 0.10:
- Equation: \( y = -9459.4x + 19.296 \)
- \( R^2 = 0.9894 \)
APPENDIX H (continued)

Degree of Cure = 0.15

\[ y = -10464x + 21.538 \]

\[ R^2 = 0.9899 \]

Degree of Cure = 0.20

\[ y = -11274x + 23.184 \]

\[ R^2 = 0.9881 \]

Degree of Cure = 0.25

\[ y = -11690x + 23.825 \]

\[ R^2 = 0.9863 \]
APPENDIX H (continued)

Degree of Cure = 0.30

\[ y = -11359x + 22.764 \]
\[ R^2 = 0.9827 \]

Degree of Cure = 0.35

\[ y = -10634x + 20.918 \]
\[ R^2 = 0.9847 \]

Degree of Cure = 0.40

\[ y = -10111x + 19.622 \]
\[ R^2 = 0.9896 \]
Degree of Cure = 0.45

\[ y = -9867.3x + 18.99 \]
\[ R^2 = 0.9919 \]

Degree of Cure = 0.50

\[ y = -9798.5x + 18.75 \]
\[ R^2 = 0.9923 \]

Degree of Cure = 0.55

\[ y = -9833.3x + 18.728 \]
\[ R^2 = 0.9917 \]
Degree of Cure = 0.95

\[ y = -13043x + 22.565 \]

\[ R^2 = 0.959 \]
APPENDIX I

Degree of Cure Vs Time of T800/3900 prepreg under isothermal conditions in the DSC apparatus

Normalized 2D plot of the degree of cure ($\alpha$) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 120 °C after a slow ramp to that temperature.

Normalized 2D plot of the degree of cure ($\alpha$) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 140 °C after a slow ramp to that temperature.
APPENDIX I (continued)

Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 145 °C after a slow ramp to that temperature

Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 150 °C after a slow ramp to that temperature
Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 155 °C after a slow ramp to that temperature.

Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 160 °C after a slow ramp to that temperature.
Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 165 ºC after a slow ramp to that temperature

Normalized 2D plot of the degree of cure (α) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 170 ºC after a slow ramp to that temperature
APPENDIX I (continued)

Normalized 2D plot of the degree of cure ($\alpha$) versus time for the T300/934 prepreg resin cured under Isothermal conditions at 175 ºC after a slow ramp to that temperature

Normalized 2D plot of the degree of cure ($\alpha$) versus time for the 934 prepreg resin cured under Isothermal conditions at 180 ºC after a slow ramp to that temperature
APPENDIX J

3D Plots of degree of cure Vs time and initial degree of cure of T300/934 prepreg under isothermal conditions in the DSC apparatus

3D plot of the degree of cure ($\alpha$) versus time and initial degree of cure for the prepreg resin cured under isothermal conditions at 120 °C and 140 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 120 °C

Combined Dynamic and Isothermal Scanning at 140 °C
APPENDIX J (continued)

3D plot of the degree of cure ($\alpha$) versus time and initial degree of cure for the prepreg resin cured under isothermal conditions at 145 °C and 150 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

*Combined Dynamic and Isothermal Scanning at 145 C*

*Combined Dynamic and Isothermal Scanning at 150 C*
APPENDIX J (continued)

3D plot of the degree of cure ($\alpha$) versus time and initial degree of cure for the prepreg resin cured under isothermal conditions at 155 ºC and 160 ºC after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment.

Combined Dynamic and Isothermal Scanning at 155 C

Combined Dynamic and Isothermal Scanning at 160 C
APPENDIX J (continued)

3D plot of the degree of cure ($\alpha$) versus time and initial degree of cure for the prepreg resin cured under isothermal conditions at 165 ºC and 170 ºC after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 165 C

Combined Dynamic and Isothermal Scanning at 170 C
APPENDIX J (continued)

3D plot of the degree of cure ($\alpha$) versus time and initial degree of cure for the prepreg resin cured under isothermal conditions at 175 ºC and 180 ºC after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 175 C

![3D plot for 175 C](image)

Combined Dynamic and Isothermal Scanning at 180 C

![3D plot for 180 C](image)
APPENDIX K

Rate of Cure Vs Time of T300/934 prepreg under isothermal conditions after a slow ramp to that temperature

2D Plot of rate of cure (\(d\alpha/dt\)) Vs time for T300/934 prepreg resin under isothermal conditions at 120 °C after a slow ramp to that temperature

2D Plot of rate of cure (\(d\alpha/dt\)) Vs time for T300/934 prepreg resin under isothermal conditions at 140 °C after a slow ramp to that temperature
APPENDIX K (continued)

**Combined Ramp and Soak at 145°C**

2D Plot of rate of cure ($\frac{d\alpha}{dt}$) Vs time for T300/934 prepreg resin under isothermal conditions at 145°C after a slow ramp to that temperature.

**Combined Ramp and Soak at 150°C**

2D Plot of rate of cure ($\frac{d\alpha}{dt}$) Vs time for 934 prepreg resin under isothermal conditions at 150°C after a slow ramp to that temperature.
APPENDIX K (continued)

2D Plot of rate of cure (dα/dt) Vs time for T300/934 prepreg resin under isothermal conditions at 155 °C after a slow ramp to that temperature

2D Plot of rate of cure (dα/dt) Vs time for 934 prepreg resin under isothermal conditions at 160 °C after a slow ramp to that temperature
APPENDIX K (continued)

2D Plot of rate of cure \( \frac{d\alpha}{dt} \) Vs time for T300/934 prepreg resin under isothermal conditions at 165 °C after a slow ramp to that temperature

2D Plot of rate of cure \( \frac{d\alpha}{dt} \) Vs time for T300/934 prepreg resin under isothermal conditions at 170 °C after a slow ramp to that temperature
APPENDIX K (continued)

2D Plot of rate of cure (dα/dt) Vs time for T300/934 prepreg resin under isothermal conditions at 175 °C after a slow ramp to that temperature

2D Plot of rate of cure (dα/dt) Vs time for T300/934 prepreg resin under isothermal conditions at 180 °C after a slow ramp to that temperature
APPENDIX L

3D Plots of degree of cure Vs time and initial degree of cure of T800/3900 prepreg under isothermal conditions in the DSC apparatus

3D Plot of rate of cure ($\frac{da}{dt}$) Vs time and initial degree of cure for 934 prepreg resin under isothermal conditions at 120 °C and 140 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 120 °C
APPENDIX L (continued)

3D Plot of rate of cure (\(\frac{d\alpha}{dt}\)) Vs time and initial degree of cure for 934 prepreg resin under isothermal conditions at 145 °C and 150 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 145 °C

Combined Dynamic and Isothermal Scanning at 150 °C
APPENDIX L (continued)

3D Plot of rate of cure (\(\frac{d\alpha}{dt}\)) Vs time and initial degree of cure for 934 prepreg resin under isothermal conditions at 155 °C and 160 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 155 C

Combined Dynamic and Isothermal Scanning at 160 C
APPENDIX L (continued)

3D Plot of rate of cure ($\frac{d\alpha}{dt}$) Vs time and initial degree of cure for 934 prepreg resin under isothermal conditions at 165 °C and 170 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)
APPENDIX L (continued)

3D Plot of rate of cure (da/dt) Vs time and initial degree of cure for 934 prepreg resin under isothermal conditions at 175 °C and 180 °C after a slow ramp to that temperature (initial degree of cure from step 1 of the combined ramp and soak experiment)

Combined Dynamic and Isothermal Scanning at 175 C

Combined Dynamic and Isothermal Scanning at 180 C
APPENDIX M

Degree of Cure Vs Time of T300/934 prepreg under combined ramp and soak conditions

2D Plot of degree of cure (α) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 170 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX M (continued)

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 175 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
934 prepreg resin ramped to then held at 180 °C

2D Plot of degree of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 180 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX N

Rate of Cure Vs Time of T300/934 prepreg under combined ramp and soak conditions

934 prepreg resin ramped to then held at 170 °C

2D Plot of rate of cure (α) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 170 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
934 prepreg resin ramped to then held at 175 °C

2D Plot of rate of cure ($\alpha$) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 175 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX N (continued)

934 prepreg resin ramped to then held at 180 °C

2D Plot of rate of cure (α) as a function of time for the combined ramp and soak experiment over a range of heating rates up to a soak temperature of 180 °C. Data to the left of the y-axis corresponds to the ramp part of the experiment while that on the right side corresponds to soak part.
APPENDIX O

Plots of development of storage, loss and complex modulus as a function of time under isothermal conditions

Plots of development of storage modulus ($G'$), loss modulus ($G''$) and complex modulus ($G^*$) for the T300/934 prepreg resin as a function of time during isothermal cure at 140 ºC and 150 ºC.

(a) 140 C, Trial 1
Gel Time: 4593 sec
$\alpha_{gel} = 0.54$
(a) 140 C, Trial 2
Gel Time: 4642 sec
$\alpha_{gel} = 0.55$

\( G'(\text{Pa}) \)
\( G''(\text{Pa}) \)
\( G^*(\text{Pa-s}) \)
(b) 150 C, Trial 1
Gel Time: 2989 sec
\( \alpha_{gel} = 0.56 \)
(b) 150 C, Trial 2
Gel Time: 3121 sec
$\alpha_{gel} = 0.59$