MINIMIZING UNCERTAINTY IN CURE MODELING FOR COMPOSITES MANUFACTURING

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Abstract

The degree of cure and temperature are consistent variables used in models to describe the state of material behaviour development for a thermoset during cure. Therefore, the validity of a cure kinetics model is an underlying concern when combining several material models to describe a part forming process, as is the case for process modeling. The goals of this work are to identify sources of uncertainty in the decision-making process from cure measurement by differential scanning calorimeter (DSC) to cure kinetics modeling, and to recommend practices for reducing uncertainty.

Variability of cure kinetics model predictions based on DSC measurements are investigated in this work by a study on the carbon-fiber-reinforced-plastic (CFRP) T800H/3900-2, an interlaboratory Round Robin comparison of cure studies on T800H/3900-2, and a literature review of cure models for Hexcel 8552. It is shown that variability between model predictions can be as large as 50% for some process conditions when uncertainty goes unchecked for decisions of instrument quality, material consistency, measurement quality, data reduction and modeling practices. The variability decreases to 10% when all of the above decisions are identical except for the data reduction and modeling practices.

In this work, recommendations are offered for the following practices: baseline selection, balancing heats of reaction, comparing data over an extensive temperature range (300 K), choosing appropriate models to describe a wide range of behaviour, testing model reliability, and visualization techniques for cure cycle selection. Specific insight is offered to the data reduction and analysis of thermoplastic-toughened systems which undergo phase separation during cure, as is the case for T800H/3900-2. The evidence of phase separation is a history-dependent Tg-α relationship. In the absence of a concise outline of best practices for cure measurement by DSC and modeling of complex materials, a list of guidelines based on the literature and the studies herein is proposed.
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<td><strong>A</strong></td>
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<td>Epoxide concentration</td>
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<td>$E_0$ initial epoxide concentration before reaction</td>
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<tr>
<td><strong>(HX)</strong></td>
<td>Any hydrogen-bond donor molecules</td>
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<td><strong>(HX)$_A$</strong></td>
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**Chemical Modeling Symbols**

$K, k$ Arrhenius equation
- $K_e, K_{eff}$ is the effective or overall rate equation (measured cure rate)
- $K_c$ is the chemically controlled rate equation
- $K_d$ is the diffusion controlled rate equation

$A$ Rate constant

$E$ Activation energy

$i = 1$ to $3$ Subscript to identify reactions of epoxy with primary amine, secondary amine, and the etherification reaction, respectively

$\phi$ Heating rate

$T_{peak}$ Temperature at the peak of the heat flow profile

$T_{final}$ Temperature at the end of the reaction in the heat flow profile, in this work a local minimum in heat flow

$\alpha_p$ Degree of cure at the peak of the heat flow profile

$\alpha_f$ Final degree of cure

$\dot{\alpha}$ Cure rate

$\alpha_f, \alpha_{max}$ Final degree of cure less than full cure (equations 2.56, 2.57)

**Tg-$\alpha$ Relationship Symbols**

$T_g$ Glass transition temperature

$T_{g0}$ Initial glass transition of the uncured material (or B-staged)

$T_{gi}$ Instantaneous glass transition temperature

$T_{gf}$ Final glass transition temperature, measured in the Cp signal on the cooldown from the maximum ramp temperature required to ensure that the full reaction heat flow profile is captured, and may or may not be equal to $T_{g\infty}$

$T_{g\infty}$ Glass transition of the fully cured material

$T_{g, gel}$ Temperature at which gelation occurs

$T_{\beta}$ Secondary softening temperature, in this work used to denote the glass transition temperature of a second phase
\( w \)  
Percent weight

\( k \)
Fitted constant, \( k = \frac{T_{g_1}}{T_{g_2}} \), equation 5.2 where \( T_{g_1} \) and \( T_{g_2} \) are glass transition temperatures for two phases

\( \frac{E_x}{E_m} \)
Ratio of lattice energies for the crosslinked polymer to uncrosslinked polymer

\( \frac{F_x}{F_m} \)
Ratio of segmental mobilities for the crosslinked polymer to uncrosslinked polymer

\( \lambda \)
\( = \frac{T_{g_0}}{T_{g_{\infty}}} \), a material constant in the DiBenedetto equation

\( \alpha_{\text{critical}} \)
Mid-point of the S-shape transition of equation 5.8

\( D \)
Multiplier in equation 5.8

\( F \)
Breadth of the transition from the copolymer \( T_g \) line to the epoxy \( T_g \) line in equation 5.8

**Diffusion Rate and Diffusion Factor Relationship Symbols**

\( C_1 \)
Material constant; may be equal to the universal WLF constant of 17.44

\( C_2 \)
Universal WLF constant of 56.1

\( A_d \)
Rate constant for diffusion

\( E_d \)
Activation energy for diffusion

\( R \)
Gas constant

\( b \)
Material constant

\( f_v \)
Free volume

\( V_f \)
Free volume

\( V \)
Total macroscopic volume

\( V_o \)
Volume occupied by molecules

\( a_f \)
Linear expansion coefficient for free volume (0.00048 /°C)

\( f_g \)
Free volume at \( T_g \) (2.5%, or 0.025)

\( C \)
Material constant, CPC equation

\( \tau \)
Relaxation time
\(a_T\)  
Time-temperature superposition factor

\(a_c\)  
\(= a_{c0} + a_{cT}T\), critical degree of cure, onset of diffusion for CPC equation

\(E_v^*\)  
Height of the potential barrier between equilibrium positions

\(v_f\)  
Average free volume per molecule

\(v_0\)  
Close-packed molecular volume

\(\gamma\)  
Numerical factor to correct for the overlap of free volume and lies between 0.5 and 1

\(D\)  
Diffusion coefficient according to the Einstein equation, 
\[D = \frac{kT}{6\pi\eta r^2},\]
equation B.20 in this work, where \(k\) is a rate constant, \(T\) is temperature, \(r\) is molecular radius, \(\eta\) is viscosity

\(a^*, V^*\)  
Material constant and an adjustable constant in equation B.28, respectively

\(V_{fc}\)  
Critical fractional free volume, equation B.29

**Physical Properties Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)</td>
<td>Modulus</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Stress</td>
</tr>
<tr>
<td>(v)</td>
<td>Poisson’s Ratio</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Viscosity</td>
</tr>
<tr>
<td>(K)</td>
<td>Fitting parameter for (Cp) relationship in Appendix E</td>
</tr>
<tr>
<td>(Cp)</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>(Cp_l)</td>
<td>Heat capacity of the liquid (rubbery) state</td>
</tr>
<tr>
<td>(Cp_g)</td>
<td>Heat capacity of the glassy state</td>
</tr>
<tr>
<td>(\Delta T_{c})</td>
<td>Difference between (T) and (T_g) at vitrification in Appendix E</td>
</tr>
<tr>
<td>(s, c)</td>
<td>Slope and constant for a linear relationship in Appendix E</td>
</tr>
</tbody>
</table>

**DSC/MDSC Measurement Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_s)</td>
<td>Temperature of the sample and container (assume it is uniform)</td>
</tr>
</tbody>
</table>
Nomenclature

$T_r$  
Temperature of the reference and container (assume it is uniform)

$T_p$  
Temperature of the energy source (programmed temperature)

$R$  
Thermal resistance path between the energy source and the sample and container

$\frac{dH}{dt}, \dot{H}$  
Measured heat flow

$\frac{dQ}{dt}, \dot{Q}$  
Heat flow produced or absorbed by a kinetic response or material transition

$C_{p_s}$  
Total heat capacity of the sample and container

$C_{p_r}$  
Total heat capacity of the reference and container

$T_0$  
Temperature measured by the Tzero™ thermocouple

$H_{Total}$  
The sum of all heat flow, total heat flow

$C_{p_{Total}}$  
Total heat flow ÷ Average heating rate, total specific heat

$C_{p_{Rev}}$  
Heat flow amplitude ÷ Heating rate amplitude, reversible specific heat

$C_{p_{NonRev}} = C_{p_{Total}} - C_{p_{Rev}}$, nonreversible specific heat

$H_{Rev} = C_{p_{Rev}}*(Average \, heating \, rate)$, reversible heat flow

$H_{NonRev} = H_{Total} - H_{Rev}$, nonreversible heat flow

$H, H_r, Q$  
Heat of reaction

$\dot{H}$  
Heat flow

$\dot{H}_{baseline}$  
Heat flow magnitude of the baseline under an area measurement. Baseline meaning the heat flow response of the instrument (may include empty pans)

$H_{Total}$  
Sum of reaction heats for a sequence of measurements/tests

$H_{Ultimate}$  
Heat evolved if full cure is achieved

$H_{iso}$  
Heat measured during an isothermal hold

$H_{Lost, \, Q_l}$  
Lost heat of reaction during temperature equilibration for an isothermal test

$H_{res}$  
Residual heat of reaction measured during a subsequent dynamic test

$m$  
Mass

$a, b$  
Constants for a straight line in equation 2.21
\( KCp \) \hspace{1cm} \text{MDSC calibration constant for specific heat}

\( T_m \) \hspace{1cm} \text{Melting temperature}

**Rasekh Equation Symbols**

- \( R \) \hspace{1cm} \text{Parameter defined in the Rasekh work as } R = \Delta T/(0.5 + Bi^{-1})
- \( \Delta T \) \hspace{1cm} \text{Temperature rise due to reaction heat}
- \( Bi \) \hspace{1cm} \text{Biot number (} hL/K \text{)}
- \( h \) \hspace{1cm} \text{Autoclave convection}
- \( L \) \hspace{1cm} \text{Composite half thickness}
- \( K \) \hspace{1cm} \text{Composite conductivity}
- \( H_r \) \hspace{1cm} \text{Resin heat of reaction}
- \( a \) \hspace{1cm} \text{Diffusivity}
- \( \rho_r, \rho_c \) \hspace{1cm} \text{Densities for resin and composite}
- \( V_r \) \hspace{1cm} \text{Resin volume fraction}
- \( Cp_c \) \hspace{1cm} \text{Composite specific heat}
Acknowledgements

Thank-you to my Heavenly Father for His provision and care throughout this process.

Thank-you to my supervisor, Dr. Anoush Poursartip, for his support and enthusiasm for this project and my growth as a researcher. It has been a privilege to be a member of the UBC Composites Group, and I thank my past and present group members for their technical and moral support. Thank-you to supervisory committee members Dr. Göran Fernlund and Dr. Warren Poole for their guidance at various stages throughout this work.

The Natural Sciences and Engineering Research Council of Canada (NSERC) and UBC Graduate Fellowship program provided funding for the project and my time as a PhD student. Thank-you to the Department of Materials Engineering for their administrative and facilities support, and to Dr. John Kadla for use of his lab’s thermogravimetric analyzer. Thank-you to The Boeing Company, in particular Dr. Karl Nelson, for supplying the material for this work (namely T800H/3900-2) and for technical advice. A special note of appreciation is due to the Round Robin participants and partners for their dedication to the study and pleasant cooperation throughout the process.

I have been blessed with many supportive people in my life throughout these years. I would like to thank my parents, Burton and Elizabeth Dykeman, sister Debbie Dykeman, and Aunt Audrey and Uncle Doug Embree (Ph.D.), for their constant encouragement. Also, thank-you to friends in Vancouver who have walked this road with me, notably Veronika Klaptocz, Tunji Osinubi, the congregation at Marineview Chapel and pastoral team Mark and Petra Anderson, friends from St. John’s College, housemates and friends at 3520 West 11th (Andrea Basler, Sabrina Crispo, Carly Huitema, Kang Wang), Melea Burns, Monica Danon-Schaffer, Voytek Klaptocz, Jacqueline Lynch, Ian Okabe, Jason Swanepoel, Erin Young, and fellow women in engineering and science (DAWEG, Jade Bridges, NEW@UBC, SCWIST). Finally, thank-you to friends from home, Miriam (McLaughlin) Crammond, Janice King, Elizabeth (Coates) MacIntosh, Christine (Haney) Makowichuk, who have stood by me over years and miles.
Dedication

To my grandmother
Mary Ann Allardice (Gibb) Dykeman

September 16, 1919, Arbroath, Scotland –
March 11, 2004, Jemseg, New Brunswick

“For his eye is on the sparrow,
and I know He watches me.”
– Civilla D. Martin, 1905 (Matthew 10:29-31)
Chapter 1. INTRODUCTION

1.1. IMPORTANCE OF RELIABLE CURE MEASUREMENT AND MODELING FOR PROCESS MODELING

Process modeling refers to the prediction of material behaviour during part manufacturing, and ultimately final part shape. For thermosetting materials the manufacturing process involves the application of a time-temperature-pressure-vacuum cycle, and the material properties influencing shape stability include rate of cure, volumetric cure shrinkage, viscosity, modulus, coefficient of thermal expansion, specific heat [Fernlund et al., 1999; Nelson et al., 2000; Curiel and Fernlund, 2004]. Each of these properties has the common state variables of degree of cure and temperature, and hence process model validity is very much dependent on the accuracy of measurements and models for cure rate. This thesis deals with the uncertainty of cure measurement and modeling for carbon-fibre-reinforced-plastics (CFRP’s), and the influence of uncertainties on process modeling validity.

Of particular interest to this work are materials of importance to the aerospace industry, namely CFRP’s Hexcel AS4/8552 and Toray T800H/3900-2 (AS4 and T800H designate the fiber type, 8552 and 3900-2 the resin). Due to proprietary restrictions, we do not know their exact applications in aerospace structures, but it is worth considering the extensive use of CFRP’s in the construction of commercial airplanes such as the Boeing 787 and Airbus A380. The Boeing 787 is constructed with as much as 50% FRP by weight, and the A380 with roughly 25% (including carbon fibre, glass fibre, aramid fibre, and hybrid reinforcement) which is being used in structures such as the fuselage (787 only), wing, wing box, vertical and horizontal stabilizers, trailing edge, landing gear, fairings, and for many non-structural interior fixtures [The Boeing Company, 2007b, 2007c; Federal Aviation Administration, 2007; Composites World, 2007]. The major advantages of using CFRP are a savings on fuel (lower costs for airlines and reduced emissions), a one step manufacturing process which reduces the number of parts (e.g. 787 fuselage made of CFRP reportedly eliminates 1,500 aluminum sheets and 40,000 - 50,000 fasteners), improved tension-loaded structures over aluminum (e.g. fuselage), and reductions to both the scheduled and nonroutine maintenance (reduced risk of corrosion and fatigue of composites compared with metal) [The Boeing Company, 2007b]. With a call on the commercial aerospace field to be emission free in 50 years by the International Air Transport Association (IATA, the global trade organization representing 250 airlines and 94% of the world's scheduled air traffic), the use of FRP’s will become increasingly
important [Constantineau, 2007]. Figures 1.1 (a) and (b) illustrate the use of FRP’s for the Boeing 787 and Airbus 380, respectively.

1.2. Issues for Experimentalists and Modellers Studying Cure Kinetics

The most popular method of cure measurement is by differential scanning calorimetry (DSC). Over 50 years have gone by since the advent of commercial DSC’s, and in that time instruments have become increasingly sophisticated and accessible to users with a range of expertise. Unlike other techniques for measuring cure, e.g. FTIR and NMR which are more precise in determining molecular structure, DSC is affordable and does not require an extensive chemistry background in order to interpret the heat flow signal. Supporting the practice of DSC’s for cure measurement is an extensive body of literature diverse in materials, instrumentation, and methodology for measurement and modeling.

The widespread use of DSC to produce cure kinetic models means that the quality of experiments and models in the literature ranges from poorly contrived polynomial fits based on a few isothermal tests, to highly developed mechanistic models by chemists and chemical engineers. The latter models often rely on information from secondary testing methods (e.g. FTIR to determine the ratio of reactants) which are not as readily available to all modellers. Furthermore, there are those establishing singular methodologies and now advancing to the automation of their unique process for widespread use [Vyazovkin, 2000; Skordos and Partridge, 2001; Flammersheim and Opfermann, 2002]. In parallel with these efforts is a call for open data sets and models [Calado and Advani, 2000]. A common source of consistent material evaluation and communication of cure kinetics for all users, novice and advanced, would help narrow the debate as to what model to use for a given material and application.

Missing from the literature is an evaluation system to qualify and quantify the goodness of measurements and applicability of models. What is needed is a measure of goodness to judge one’s own methodology for measurement and modeling, and assessment of the application of the model to process conditions of interest. Such a validation process would of course be necessary for accepting a model in any materials database, and should be useful for publication reviews. Fundamental to these goals is an understanding of the decision-making process throughout measuring and modeling, and the uncertainties that can arise as a result thereof. The remaining section in this Chapter outlines the studies undertaken in this work to address these issues.
1.3. **Scope and Overview of Thesis Work**

The goals of this thesis are to identify sources of uncertainty in the decision-making process (from cure measurement by DSC to cure kinetics modeling), and to recommend practices for minimizing uncertainty. This objective was met by: 1) reviewing the literature on best practices (Chapter 2); 2) exploring methodologies for cure model selection, fitting, and evaluation (Chapter 3); 3) measuring the cure behaviour of prepreg system T800H/3900-2 by DSC and proposing a cure model to describe the complexities of this system (Chapter 4 and 5); 4) an interlaboratory Round Robin designed to test variability in cure measurement and modeling practices (Chapter 4 and 5); and, 5) by combining the review and findings in a concise list of best practices for cure measurement and modeling (Chapter 6). The remainder of this section elaborates on the scope of each chapter.

At this time in the progress of cure kinetics, there is a wealth of choices surrounding the basic elements of the decision-making process, and there is sufficient information to conduct evaluations of measurement and model results for specific materials. Chapter 2 presents an overview of the knowledge of cure kinetics, measurement by DSC and data reduction, analysis and modeling practices in the literature. A comparison of models in the literature for Hexcel 8552 (or AS4/8552) revealed considerably different cure predictions for the same cure cycle. The results of this study are recorded in Chapter 3.

Two methodologies for cure model selection and fitting, and evaluation were explored in this work: 1) isoconversionals; and, 2) process maps. Visual methods are essential to understanding cure behaviour and checking for consistency in cure data and models. Isoconversionals refer to contours of constant degree of cure which are traditionally used to calculate Arrhenius kinetic parameters. In this work they have been used as a tool to collapse an extensive data set onto a single plot for comparison between test methods, mechanisms in different temperature and conversion zones, and for fitting the cure rate model. The process map tracks the progress of cure on a degree of cure versus temperature axis by following contours of constant time and heating rate. The advantage of this map over other techniques in the literature is the ability to move between isochronal and isorate contours such that any cure cycle can be traced. The process map also serves as a tool for cure cycle selection. These methods are described in Chapter 3 and used in Chapter 5 for the study of T800H/3900-2.

To evaluate the sources of uncertainty and best practices, a cure kinetics model for T800H/3900-2 was developed based on DSC measurements. Some of the specific issues explored were baseline selection,
Chapter 1: Introduction

balancing heats of reaction, determining differences between isothermal and dynamic tests over a wide range of experimental conditions, and model fitting techniques. An interlaboratory Round Robin study on cure measurement and modeling of T800H/3900-2 engaged the international community in the question of quality of the cure kinetics modeling process. Information about the material system, DSC measurement techniques, and Round Robin design are recorded in Chapter 4. The results and discussion for both of these studies are found in Chapter 5. Included are the models developed in this thesis and those by Round Robin participants. Chapter 6 presents a summary and conclusions regarding best practices for measurement and modeling as reviewed in this work. Future T800H/3900-2 and Round Robin work is also proposed.
Figure 1.1 (a) has been removed due to copyright restrictions. The information removed is a schematic of the Boeing 787 highlighting the use of FRP’s [Boeing Company, The, 2007, "Boeing 787 Parts," (http://seattlepi.nwsource.com/dayart/20070517/Boeing787parts0517_corr2.gif)].

Figure 1.1 (b) has been removed due to copyright restrictions. The information removed is a schematic of the Airbus A380 highlighting use of FRP’s [Composites World, July 2005, "Airbus Flies First A380, Confirms Production Delay," (http://www.compositesworld.com/hpc/issues/2005/July/899)].
Chapter 2. **Literature Review**

This chapter reviews the literature for testing and modeling cure kinetics using differential scanning calorimetry (DSC), with special emphasis on the practices for epoxy-amine reactions and process modeling for CFRP structures. The testing-to-modeling decision-making process has been divided throughout this work into the following categories: 1) material and instrumentation knowledge; 2) experimental parameters; 3) data reduction; 4) data analysis; and, 5) model development, or selection, and fitting. Additionally, the communication of material behaviour through visual techniques has been an important part of the accepted use of cure models and will be reviewed.

### 2.1. Cure Reactions and Behaviour During Processing for Thermoset-Based Materials

#### 2.1.1. Resin chemistry for epoxy resin with amine hardener

There are three basic reactions during an epoxide and amine reaction as illustrated in Figure 2.1: 1) epoxide and primary amine to form secondary amine; 2) epoxide and secondary amine to form tertiary amine; 3) epoxide reacting with hydroxyl or itself (homopolymerization) to form ether. The first two reactions are well established [Shecter et al., 1956; Horie, 1970]. Etherification is generally cited as a reaction when there is an excess of epoxy and when testing progresses to high temperatures [Simon, 1992]. Alternatively, Cole [1991] showed that etherification can also occur at low degrees of cure depending on the catalyst for the reaction.

Below is the scheme for the three reactions. The first four relations were mapped by Horie et al. [1970] based on the work by Schecter et al. [1956], and the fifth relationship was proposed by Cole [1991] based on work by Chiao [1990]. Cole’s description for the etherification reaction is considered in this work because to date it is the most encompassing of all the possible combinations of reactions to achieve ether during an epoxide-amine reaction.

\[
\begin{align*}
A_1 + E + (HX)_0 & \xrightarrow{k_1} A_2 + (HX)_0 \\
A_1 + E + (HX)_0 & \xrightarrow{k_2} A_2 + (HX)_0 \\
A_2 + E + (HX)_0 & \xrightarrow{k_3} A_3 + (HX)_0 \\
A_2 + E + (HX)_0 & \xrightarrow{k_4} A_3 + (HX)_0 \\
E + mH + nA_3 & \xrightarrow{k_5} ether + mH + nA_3
\end{align*}
\]
where $A_1$, $A_2$ and $A_3$ are primary, secondary, and tertiary amine, $E$ is epoxide, $(HX)$ can be any hydrogen-bond donor molecules, wherein typically $(HX)_0$ is described as either hydroxyl or impurity initially resident in the system, $(HX)_t$ is hydroxyl group formed in the amine-epoxide addition reaction at time $t$, and $k$ is the rate constant. Parenthesis are used to show that these groups participate in the reaction, but remain unchanged; they are catalysts. The concentration of hydroxyl groups changes during reaction: for every N-H bond consumed by epoxide, an O-H bond is formed. In the fifth equation, Cole has accounted for the catalysis by hydroxyl, tertiary amine, and homopolymerization to form ether linkages. The coefficient $m$ refers to the number of hydroxyl groups consumed, and $n$ refers to the number of tertiary amine groups acting as catalysts. The concentration of hydroxyl and tertiary amine is preserved after the reaction.

There are three stages during cure of an epoxy resin [Prime, 1997], Figure 2.2 a) and b). The first is the A-stage in which only monomers are present and the state is liquid. The B-stage is defined by initial formation of monomers into polymer chains. Covalent bond formation progresses until a point known as gelation is reached. Gelation is defined as the onset of a three-dimensional network created by crosslinks between the polymer chains, in that a molecule of infinite molecular weight is formed (occurs at roughly 50% conversion, Figure 2.2 b). As cure progresses after gelation, the glass transition temperature of the epoxy increases above the processing temperature reaching a glassy-elastic state and is vitrified. At vitrification the cure rate decreases dramatically. Full cure is reached when all of the epoxides have been consumed.

In a typical cure cycle, the onset of polymerization usually occurs during a heating segment. Heating the epoxy first increases the molecular chain mobility. However, by lengthening of the polymer chains and the formation of crosslinks between chains, motion is obstructed and viscosity begins to build. Viscosity build-up due to cross-linking becomes great enough to negate all decreases in viscosity due to heating and the third sub-stage of the B-stage is reached, gelation. At gelation the following material changes occur: 1) roughly 50% of crosslinking is complete between molecular chains such that a rigid network is formed; 2) the glass transition temperature increases with continued increase in the degree of cure; but, 3) the processing temperature is still well above the glass transition temperature and the high rate of stress decay continues; and, 4) modulus development begins as the network structure now behaves like a visco-elastic solid and can carry shear stress. In conjunction with covalent bond formation is the decrease of space between atoms and molecules, which also implies a decrease in space available for molecular movement or chain relaxation to preferential conformations. This space is better known as free volume. It is not known if free volume has a molecular composition and is rather thought of by some as voids in the
molecular configuration [Struik, 1978]. Therefore, it is described as an inverse measure of the degree of chain packing. With increased packing efficiency, mobility decreases, at first slowly, but later at an ever increasing rate until a critical degree of packing is reached and mobility steeply falls to zero [Struik, 1978]. Fundamentally, free volume \( V_f \) is the total macroscopic volume, \( V \), minus the volume occupied by molecules, \( V_o \),

\[
V_f = V - V_o(T)
\]

where the occupied volume has been described by Tant and Wilkes [1981] as the summation of volume within the Van der Waals radii and the volume associated with molecular vibration. Theoretically, the occupied volume will contract at a constant rate with decreasing temperature as predicted by its coefficient of thermal expansion (CTE). Figure 2.3 illustrates the general change in volume over the cure cycle, assuming the material is vitrified during the second isothermal hold such that the glass transition temperature is greater than the hold temperature (no change in specific volume slope on cooling).

With increased degree of cure, the free movement of chains is counteracted by network formation (crosslinking and secondary bond formation between chains) such that mobility is restricted (free volume and molecular vibrations decrease), stress builds-up at sites of chain restriction, and the relaxation times of molecules and chains increases. When a negligible rate of network mobility is reached and the glass transition temperature exceeds the process temperature, the epoxy has reached a glassy-elastic state and is vitrified. At this point the chain conformations and free volume are frozen in at the cure temperature. The onset of vitrification occurs approximately when the glass transition temperature is coincident with the isothermal cure temperature [Gillham, 1986]. Before vitrification, curing is controlled by chemical reactions with a relatively rapid rate of conversion. After vitrification, the chemical reactions are arrested and cure rate becomes controlled by diffusion. Diffusion refers to molecules moving slowly between network chains until they reach a free radical site for bonding. This is the fourth sub-stage in the B-stage. At this transition the modulus may increase by several orders of magnitude.

Figure 2.4 illustrates a time-temperature-transformation (TTT) diagram for thermoset materials, according to Enns and Gillham [1983]. Depending on the cure temperature, the thermoset will either go through gelation or vitrification first. If curing is performed above the ultimate glass transition temperature, \( T_{ge} \) (the glass transition of the fully cured material), only gelation will occur. If the cure temperature is below \( T_{ge} \) the polymer will first experience gelation and then vitrification. In a TTT diagram, the times to gelation and to vitrification are plotted as a function of the isothermal curing temperature. At temperatures below \( T_{go} \) (the glass transition of the monomer), the cure reaction is confined to the solid state and is very slow. Between \( T_{go} \) and \( T_{gel} \) (temperature at which gelation and vitrification occur at the
same time), the liquid resin will react until its glass transition temperature rises above the curing temperature, and vitrification arrests the curing. Between $T_{g,gel}$ and $T_{g,\infty}$, gelation precedes vitrification and a rubbery network is formed until $T_g$ rises above the curing temperature and the curing is stopped. Above $T_{g,\infty}$ the polymer remains in the rubbery state.

2.1.2. Material evolution for fiber-reinforced plastics

In comparison to thermoplastic matrix systems, thermosets inherently provide improved tensile strength and modulus, excellent chemical and solvent resistance, dimensional and thermal stability, good creep resistance, and excellent fatigue properties. A disadvantage compared to thermoplastics is their poor resistance to impact at room temperature, governed by brittleness of resin systems and low peel strength between layers to inhibit delamination. Various enhancements to the resin and prepreg system have been developed to improve the impact performance of thermosetting systems. Below is a list of solutions for improving toughness and some of their drawbacks [Odagiri et al., 1991; Kishi et al., 1995; Varley, 2007]:

1. Without altering the resin system or processability, inter-leaving, stitching, z pinning, and using thermoplastic fibres.
2. Adding tougheners (e.g. elastomers and thermoplastics) to the resin system. A sufficient quantity is needed to improve toughness which can challenge the ability to impregnate fibres in the resin system and decreases formability at room temperature.
3. Adding an independent film to the surface of the prepreg composed of a thermosetting resin and elastomer, or only a thermoplastic. An elastomeric material may compromise the thermal stability of the end-product. A thermoplastic film improves upon this aspect, but may fail in formability and solvent resistance.
4. An interlayer composed of resin and particles of elastomer or thermoplastic. Elastomer particle size is easily changed by curing conditions, and hence the impact resistance may be highly influenced by cure cycle. Again, elastomers have poor thermal resistance. Thermoplastic particles are also subject to poor thermal resistance and size control issues, but are an improvement over elastomers. Moreover, pre-formed polymer particles have shown an improvement in creep resistance, moisture resistance and processing over soluble thermoplastics.

This work is particularly interested in toughening by the fourth method since the material to be studied in subsequent chapters, T800H/3900-2, is an epoxy toughened by an interlayer of resin and localized, pre-formed thermoplastic particles (likely polyamide), as illustrated in Figure 2.5. Toughening by this method is dependent on the phase separation of the thermoplastic from the epoxy matrix during cure such
that the end product has the benefits of the high Tg of the epoxy, and the ductility of the thermoplastic. When the epoxy is uncured, the thermoplastic backbone should have high thermal stability and be miscible in the epoxy. As crosslinks are formed and the density of the system increases, the thermoplastic separates from the epoxy network and may exist in a co-continuous or a phase-inverted state (a thermoplastic rich phase). A high crosslink density is more beneficial to phase separation, and improved toughness, since the increase in molecular weight leads to incompatible miscibility which causes the separation (the opposite is true for rubber modifiers). Improved toughness is accomplished when the polymer particles have good adhesion to the epoxy matrix, the particles have high toughness and a lower modulus of elasticity than that of the resin. A higher molecular weight thermoplastic is also an advantage to improved toughness, but is limited by viscosity specifications for processing. More information about the toughening of thermosets can be found in the following reviews and articles: Kishi et al. [1995, 2005], Prime [1997], Hodgkin et al. [1998], Luo et al., [2001], Ratna [2003], Unnikrishnan and Thachil [2006], Varley [2007].

Specific to the nature of this work is the interest in the effects of an interlayer of thermoplastic particles on cure kinetics and diffusion. In general, thermoplastic modifiers modestly affect the chemical kinetics. Min et al. [1993] showed that a polysulfone modified epoxy system underwent more etherification and homopolymerization than an unmodified system due to the increase in viscosity with modifier addition which suppressed the amine reaction and left more unreacted epoxide for etherification and homopolymerization. Zucchi et al. [2005] for PS and PMMA modifiers measured a delay in the initial polymerization rate due to a dilution effect with the presence of the modifiers, but any shifts in the conversion curve were not greater than experimental error. Bonnet et al. [1999a] for an epoxy-amine system added polyetherimide (PEI) and polystyrene (PS) modifiers, respectively, and measured an increase in the rate of cure after phase separation, and a step increase in Tg. They linked the increase in both measurements to the epoxy-amine rich system present after phase separation, which was previously diluted with thermoplastic particles. Bonnet et al. developed two separate relationships for the Tg-α behaviour of the thermoplastic and thermoset. The higher values of Tg were designated as the thermoplastic phase since the PEI used had Tg = 210°C, and the lower values as the epoxy-amine phase which reportedly had a Tg,c = 177°C.

Phase separation has also been closely linked to viscosity effects. A decrease in viscosity has been measured when phase separation occurs at early stages of cure for epoxy resins with thermoplastic modifiers [Varley et al., 2007; Kim and Char, 2000]. Bonnet et al. [1999b] showed that this effect is true
for low quantities of modifier, but that viscosity may increase with higher modifier content (greater than roughly 30 wt%). Phase separation has also been linked with low system viscosity. Luo et al. [2001], for PEI modified epoxy, proposed that at higher temperature the cure occurs quickly and viscosity builds up sufficiently before phase separation can occur. This corresponds with findings by Varley et al. [2007] that the rate constant for secondary amine \((k_2)\) in Horie’s rate equation decreases with addition of PEI, particularly at high temperatures, and that the onset of vitrification occurs earlier at higher temperatures.

In summary, there are two conditions that promote phase separation of thermoplastic particles in thermosetting systems. The first is a high crosslink density since a difference in molecular weight drives phase separation for thermoplastic modifiers. Secondly, a lower system viscosity allows for the phase separation to occur, whereas a quick build-up of viscosity (such as cure at high temperatures) may delay phase separation. After phase separation, a decrease in viscosity and an increase in the reaction rate have been observed, as well as two Tg’s for the modifier and epoxy system, respectively.

2.2. **INSTRUMENTATION**

2.2.1. **Differential scanning calorimetry (DSC) technology**

Calorimeters measuring a difference in temperatures are documented in the literature as having their origins in the 18th Century for measuring phase transitions and chemical reactions [Hemminger and Hähne, 1984]. A device that measures the difference in temperature between a reactive sample and an inert reference was first named a Differential Thermal Analyzer (DTA), and is today also known as a Heat Flux DSC (HF DSC). The advantage of measuring the temperature difference is the increased sensitivity to the measurement of changes during reaction or phase transformation within an active sample. This is known as the Twin Principle, Figure 2.6. In turn, the temperature difference, the timing of the measurements, and the known thermal resistance through which the heat of reaction flows, serve as the basis for an indirect quantification of the heat of reaction. Calvet [1948] and Boersma [1955] both developed instruments based on quantitative data collection by placing the temperature sensors in the instrument itself instead of placing them inside the sample such that the density and thermal conductivity of the sample do not affect the area under the temperature-time curve. All currently marketed calorimeters based on this 'heat flux' principle follow either the Tian-Calvet design or that of Boersma (Tian developed a twin thermoelectric calorimeter based on the Peltier principle in 1923), the typical setup is illustrated in Figure 2.7. A second differential calorimeter type was developed at the same time as the DTA (Tian was one of its founders). This type is known as the Power Compensated Differential Scanning Calorimeter (PC DSC) because it measures heat flow (power) into or out of a test specimen and

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*Chapter 2: Literature Review*
provides a signal that is proportional to this measurement, general schematic in Figure 2.8. All DSC’s used in this work were of the heat flux-type DSC, and hence the next sections will deal specifically with this type.

### 2.2.2. Principles of DSC and modulated-DSC (MDSC)

To facilitate a discussion of the heat flux DSC operating principles in equation form, a simple diagram representing a single calorimeter cell will be referred to, Figure 2.9, where

- $T_s =$ temperature of the sample and container (assume it is uniform)
- $T_r =$ temperature of the reference and container (assume it is uniform)
- $T_p =$ temperature of the energy source (programmed temperature)
- $R =$ thermal resistance path between the energy source and the sample and container

\[
\frac{dH}{dt} = \text{measured heat flow}
\]

\[
\frac{dQ}{dt} = \text{heat flow produced or absorbed by a kinetic response or material transition}
\]

- $C_{p_s} =$ total heat capacity of the sample and container
- $C_{p_r} =$ total heat capacity of the reference and container

A first approximation [Gray 1968] of the heat flux DSC by heat transfer analysis combines the energy balance for a sample or reference cell with the rate of heat transfer from the cell to the surroundings,

\[
\frac{dH}{dt} = C_{p_s} \frac{dT_s}{dt} + \frac{dQ}{dt}
\]

\[
\frac{dQ}{dt} = \frac{T_p - T_s}{R}
\]

Substituting 2.4 into 2.3 gives a heat flow equation for an individual sample or reference holder,

\[
\frac{dH}{dt} = C_{p_s} \frac{dT_s}{dt} + \frac{T_p - T_s}{R}
\]

By notating equation 2.5 for both sample and reference holders, respectively, and subtracting the two equations, the resulting equation represents the measured difference in temperatures between the sample and the inert reference (note, $\frac{dH}{dt} = 0$ for the inert reference),
\[
\left( \frac{dH}{dt} \right) = -\frac{(T_f - T_r)}{R} + (C_p_f - C_p_r) \frac{dT_r}{dt} - C_p_r \frac{d(T_r - T_f)}{dt}
\]

where \(C_p_r\) is the specific heat of the reference container, and \(T_r\) is the temperature of the reference container, and the following assumptions are made:

1) \(R_s = R_r\) (instrument thermal resistance), and the effect of inequality makes no major difference to the analysis in any case;

2) \(C_p_s = C_p_r\) (instrument thermal capacitance);

3) \(dT_r/dt = dT_{r}'/dt = \) a constant value;

4) Only the thermal resistance between the furnace and sample is taken into account (no interaction between sample and reference sample);

5) No difference between mass or thickness of sample and reference sensors;

6) No heat exchange with the surroundings (heat leaks).

Figure 2.10 illustrates the graphical determination of \(R \frac{dH}{dt}\) from an experimental heat flux DSC curve, and the three terms in equation 2.6 have the following definitions:

Term I: is the principal DSC heat flow term continuously recorded by the instrument.

Term II: is the thermal capacitance imbalance term, and corrects the measured heat flow based on temperature difference for the change in system internal energy (sample). Term II represents the zero line displacement from the zero signal level, and represents the change in internal energy of the system when it deviates from the initial offset at steady state.

Term III: is the heating rate difference term, and corrects for the instrument thermal lag. At steady state, the instrument is at scanning equilibrium, term III and \(\frac{dH}{dt}\) are equal to zero and term I is equal and opposite to term II. Term III is the slope of the heat flow curve at any point of interest multiplied by the system thermal time constant, \(R C_p_r\) (units of time).

In recent years, a thermocouple has been added between the sample and reference sensor, first by TA Instruments and called Tzero™ technology, such that equation 2.6 is expanded to four terms to account for the thermal resistance imbalance between sample and resistance sensors, thermal capacitance imbalance, mass, and heating rate differences between the sample and reference sensors. The additional thermocouple between the sensors is accounted for by adding a term to equation 2.4 and designating the resistance and capacitance specific to the reference and sample sensors,
\[
\frac{dQ}{dt} = \frac{T_p - T_t}{R_s} + \frac{T_s - T_0}{R_t}
\]

where \(T_0\) is the temperature measured by the Tzero\textsuperscript{TM} thermocouple. Substituting 2.7 into 2.3, and subtracting heat flow equations for the sample and reference sensors, the expanded differential equation becomes

\[
\left( \frac{dH}{dt} \right) = -\frac{(T_s - T_t)}{R_s} + (T_s - T_0) \left( \frac{1}{R_s} - \frac{1}{R_t} \right) + (C_{p_s} - C_{p_r}) \frac{dT_s}{dt} - C_{p_r} \frac{d(T_s - T_t)}{dt}
\]

Recording two differential measurements has played an important role in achieving a flat instrument zeroline. Previously, the zeroline of the instrument (or baseline for an inert sample) would need to be subtracted from the measured heat flow signal using some reference zeroline performed at another time. Now the zeroline can be accounted for during measurement and is subtracted for each test by instrument software. To demonstrate the importance of a flat instrument zeroline, Figure 2.11 (a) shows the difference in zerolines for three instruments; the Perkin Elmer instruments are power compensated instruments and the TA Q1000 is a heat flux instrument based on equation 2.8. Although the instruments have different underlying heat flow equations, it is clear that the Perkin Elmer instruments have not fully accounted for all of the heat flow imbalances between the reference and sample furnaces. Figure 2.11 (b) shows the reaction heat flow for carbon-fibre-reinforced-plastic AS4/8552 (Hexcel) tested by each instrument at 10°C/min, with the instrument zeroline subtracted. There are considerable differences between these instruments in terms of reaction timing, definition of the reaction peaks, and magnitude of the heat flow at the end of the reaction. The reaction timing issue is beyond the scope of this discussion, but the other two discrepancies may be linked to the curvature of the instrument zeroline and perhaps consistency of the zeroline between tests.

Modulated DSC technology separates the two components of equation 2.3 (energy required to raise the temperature of the sensor and sample, and heat evolved or absorbed by the sample over time and temperature) into two unique signals, and hence kinetic events can be separated from non-kinetic events. The technology distinguishes between the two types of events by employing two simultaneous heating rates: 1) a linear heating rate that provides information similar to standard DSC; and, 2) a sinusoidal or modulated heating rate. The sinusoidal heating rate is programmed by the user choosing a modulation period (seconds), and a modulation temperature amplitude (± °C). For example, if we have a heating rate of 4°C/min ± 1°C per 60 seconds, 4°C/min is the average heating rate, ± 1°C is the modulation temperature amplitude, and 60 seconds is the period, Figure 2.12. Modulated temperature rate is the derivative of the modulated amplitude with time.
There are now three heat flows that can be extracted from the differential temperature response: total heat flow, reversing heat flow, and non-reversing heat flow. The total heat flow is calculated from the average value of the measured modulated heat flow, and is equivalent to standard DSC at the same average heating rate. A Fourier Transform analysis on the sine wave response continuously calculates the average heat flow every 0.1 seconds rather than using the simple average in order to enhance resolution. Taking this total heat flow and dividing it by the average heating rate yields the total heat capacity, $C_{p,\text{Total}}$. Alternatively, taking the actual modulating heat flow response and dividing it by the modulating heating rate yields the reversing component of the heat capacity, or $C_{p,\text{Rev}}$. The reversing heat flow is calculated by multiplying the reversing heat capacity by the average heating rate. Finally, the kinetic, or non-reversing, components are simply the total signals subtracted by the reversing signals. In summary,

Total Heat Flow: \[
\frac{dH_{\text{Total}}}{dt} = \text{average heat flow}
\]

Total $C_p$:
\[
C_{p,\text{Total}} = \frac{\text{TotalHeatFlow}}{\text{AverageHeatingRate}} K_{C_{p,\text{Total}}}
\]

where $K_{C_{p,\text{Total}}}$ is a proportional calibration constant for $C_{p,\text{Total}}$

Reversing $C_p$:
\[
C_{p,\text{Rev}} = \frac{\text{HeatFlowAmplitude}}{\text{HeatingRateAmplitude}} K_{C_{p,\text{Rev}}}
\]

where $K_{C_{p,\text{Rev}}}$ is a proportional calibration constant for $C_{p,\text{Total}}$

Reversing Heat Flow:
\[
\frac{dH_{\text{Rev}}}{dt} = C_{p,\text{Rev}} \cdot \text{AverageHeatingRate}
\]

Non-Reversing $C_p$:
\[
C_{p,\text{NonRev}} = C_{p,\text{Total}} - C_{p,\text{Rev}}
\]

Non-Reversing Heat Flow:
\[
\frac{dH_{\text{NonRev}}}{dt} = H_{\text{Total}} - H_{\text{Rev}}
\]

Contrary to the given names of the specific heat and heat flow components, MDSC does not measure the reversibility or non-reversibility of transitions. The term reversing was chosen because the true heat capacity is reversible. Heat capacity changes during a transition need not be reversible, and hence a change in the $C_{p,\text{Rev}}$ signal need not be a reversible transition. An example is the increase in $C_{p,\text{Rev}}$ associated with devitrification during a dynamic test, or conversely, the decrease in $C_{p,\text{Rev}}$ during vitrification. There is a shift in the signal to higher $C_p$’s, but this is not a reversible transition since cure is taking place during the transition. All $C_p$ changes occur in the reversing signal and MDSC does not classify processes as reversible or non-reversible.
For traditional DSC’s (i.e. non-modulated) a further baseline improvement is to subtract the effect of changing Cp from the heat flow signal. Subtraction of the changing Cp with cure and temperature is now performed automatically during modulated-DSC measurements, and would ideally yield a flat baseline between start and end points of a reaction, but depending on instrument zero-line and the onset of degradation kinetics during the reaction of interest, baseline selection continues to be open to interpretation. This will be discussed in the next section on data reduction and baselines.

The above explanations are slightly simplified from the true calculation details for the total and reversing components of the heat flow and heat capacity signals. In reality, the measured and calculated heat flows are done independently for the sample and reference and are further corrected for sensor and pan imbalances (mass, thermal conductivity, capacitance and resistance, and shape) before calculating the final heat flow or heat capacity signal. For further information on MDSC technology the reader is referred to TA Instruments literature, particularly the work of Thomas [2006].

2.3. EXPERIMENTAL DETERMINATION OF CURE KINETICS BY MDSC

Presently there are few formal standards for developing cure kinetics models based on DSC/MDSC experiments. Out of 11 standards agencies or associations found to address the use of plastics and composites, 40 standards were related to plastics and differential scanning calorimetry (including calibration standards), some of which are roughly duplicate between agencies. Of the 40 found, 6 standards deal specifically with cure kinetics measurement and modeling by DSC:

1. ASTM E698-99, Arrhenius Kinetic Constants for Thermally Unstable Materials;
2. ASTM E2041-01 Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt And Daniels Method;
3. ASTM E2070, Kinetic Parameters by Differential Scanning Calorimeter Using Isothermal Methods;
4. ASTM E2046-99 Reaction Induction Time by Thermal Analysis;
5. ASTM E2160-01 Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry; and,
Of these 6, only the first three listed deal directly with cure kinetics modeling. The first standard describes how to calculate activation energy from the peak temperatures of a series of dynamic tests without knowledge of the type of reaction, known as the Kissinger method. The second standard shows a model-fitting approach to determining the activation energy and the value of \( n \) for a single \( n \)th order reaction using one dynamic test. The third standard details how to use multiple isothermal experiments to determine activation energy and reaction order for a single mechanism (\( n \)th order, autocatalytic, or other). Baselines are assumed to be flat lines in the standards. These standards will be reviewed in more detail in this chapter, but it is sufficient to state that the standards are limited to simple systems and results. The other standards not discussed here include those for calibrating the instrument, measuring transition temperatures (e.g. \( T_g \)), measuring specific heat, measuring transitions for specific materials, and determining induction or oxidation times for specific materials.


### 2.3.1. Measurements

Typical measurements gathered for cure kinetics analysis are heat flow and heats of reaction, \( T_g \)’s, and \( C_p \)’s, in both isothermal and dynamic modes. Specifically, the following parameters are of interest:

1) \( T_{g_0} \), the initial \( T_g \) of the uncured material (or B-staged), which is used in models of the \( T_g-\alpha \) relationship and to determine the storage and life-span of the material;

2) \( T_g \), the \( T_g \) for intermediate or partial degrees of cure, used to model the \( T_g-\alpha \) relationship which can be used in modeling both chemical and diffusion behaviour; typically, \( T-T_g \) is used to demonstrate how close the material state is to vitrification;

3) \( T_{g_\infty} \), the \( T_g \) for the fully cured material, is used in models of the \( T_g-\alpha \) relationship;

4) Peak temperatures of heat flow curves, used in determining Arrhenius rate constant;
5) Heat of reaction under isothermal and dynamic heat flow curves, taken as analogous to the heat evolved during reaction, and used to establish a normalized measure of reactant consumption for chemical and diffusion modeling;

6) Cp development during cure and temperature change, used in some definitions of diffusion.

Tg’s are measured during dynamic tests, as are peak temperatures. Heat of reaction, heat flow, and Cp are measured during both isothermal and dynamic tests. For each test mode there are some best practice guidelines established in the literature for obtaining the above mentioned measurements. These will be reviewed in this section.

There are two methods for starting isothermal DSC experiments: 1) drop the sample into the instrument, but this disrupts the temperature equilibrium and data is lost at the beginning of the reaction; or, 2) the sample can be heated at a fast rate to the isothermal temperature, wherein temperature equilibrium and knowledge of the cure on the heat-up create a loss of information. The cure rate is monitored until reaction completion at the elevated temperature. The limitations of this test exist at very small rates of heat generation when the instrument sensitivity may not be good enough to detect changes, and at high rates of heat generation if the instrument is not capable of establishing equilibrium relative to the reaction rate. For an nth order reaction where the maximum rate of heat evolution occurs at the beginning of the experiment, a loss of heat of reaction information may occur while the instrument is establishing temperature equilibrium. In practice, an upper bound for isothermal temperature selection is typically determined by the start of degradation reactions or the high temperature equilibration limitations of the instrument as discussed above. The lower temperatures are kept above the limit at which the heat flow signal is so low that it becomes distorted by instrument noise. The area calculations in general are a major source of uncertainty for the isothermal method due to baseline selection and instrument sensitivity. Nor can the isothermal method be easily applied to resolve heats of multiple reactions.

Dynamic tests are typically used to establish the ultimate heat of reaction for a system and to study the presence of multiple reactions. Cure kinetics analysis methods have been developed using only one test, two tests, and multiple tests, respectively. It is also through dynamic testing that Tg’s are measured, which is considered a more accurate measurement of cure development compared to heats of reaction. The dynamic tests would seem a logical choice over the isothermal tests from the standpoint of reduced measurement uncertainty and the capability of characterizing multi-reaction materials. However, isothermals have been favoured historically and there are several citations of how dynamics can give different model constants compared to isothermals. In a later section the differences between the cure kinetics stemming from the two test modes will be discussed.
Chapter 2: Literature Review

When the measured isothermal heat of reaction indicates incomplete cure, a dynamic test is commonly performed to capture the remaining heat of reaction (also known as a residual test). Authors have used the residuals exclusively to measure the degree of cure and Tg after progressively higher isothermal hold times [Wisanrakkit and Gillham, 1990; Simon and Gillham, 1992; Simon et al., 2000]. Profiles of degree of cure and Tg can then be plotted versus time for various isothermal temperatures. Alternatively, a heating ramp can be interrupted at progressively higher temperatures and dynamic residuals used to measure the degree of cure and Tg.

2.3.2. Data Reduction

Common to both types of testing, isothermal and dynamic, is the basic calculation that may be used for heat of reaction with time, $H$, degree of cure, $\alpha$, and cure rate, $\dot{\alpha}$. The heat of reaction evolved as a function of time is the integral of heat flow, $\frac{dH}{dt}$, with time,

$$ H(t) = \int_{0}^{t} \frac{dH}{dt} \, dt $$

2.14

When $t$ in the integral is equal to the time at which the heat flow stops and the reaction is over during an experiment, this is then the total heat of reaction for that experiment, $H_{\text{Total}}$. Degree of cure with time is calculated by dividing the incremental heat of reaction, $H(t)$, by the ultimate heat of reaction, $H_{\text{Ultimate}}$.

$$ \alpha = \frac{H(t)}{H_{\text{Ultimate}}} $$

2.15

The total isothermal heat of reaction is the addition of the heat measured during an isothermal hold until vitrification arrests the cure process, $H_{\text{iso}}$, plus the remaining or residual heat of reaction measured during a subsequent dynamic test, $H_{\text{res}}$. In general, the cure reaction during a dynamic test is driven to completion by increasing temperature, and hence the total heat of reaction is simply the ultimate heat of reaction, for dynamic tests.

2.3.2.1. Baselines

Area measurements and cure rate calculations require an appropriate baseline subtraction. The most traditional method of baseline selection for isothermals is to allow the heat flow to reach a point of negligible change, and draw a straight line from this magnitude to a matching magnitude at the start of the reaction, the straight dotted line in Figure 2.13 [Fava, 1968; Sourour and Kamal, 1976; Mijović, 1984;
The heat of reaction is then calculated by,

\[ H_{iso} = \int_0^t (\dot{H} - \dot{H}_{baseline}) \cdot dt \]  \hspace{1cm} (2.16)

where \( t_f \) is the end-of-reaction time, \( H \) is the heat of reaction (J), and \( \dot{H} \) is heat flow (W). Limitations in this method exist when the sample cures during sample/instrument equilibration at the isothermal temperature and inadequate sensitivity of the instrument to monitor low cure rates, both resulting in lost heat of reaction. Barton [1972] suggests that a way to quantify the amount of reaction occurring on the heat-up is to overlay the heat flow curve captured during the reaction with a second test on the fully cured sample which then becomes the baseline, the curved dotted line in Figure 2.13.

Cole [1991] accounts for the heat lost during heat-up by altering the degree of cure calculation to include an initial degree of cure, \( \alpha_0 \),

\[ \alpha(t) = \alpha_0 + \left( 1 - \frac{\alpha_0}{H_{Total}} \right) \dot{\alpha}(t) \]  \hspace{1cm} (2.18)

where \( \alpha(t) \) is the degree of cure with time, and \( H_{Total} \) is the total heat of reaction which is \( H_{iso} \) plus any residual heat of reaction, \( H_{res} \), captured with a subsequent dynamic test.

Another method to determine the position of a linear baseline, and the isothermal heat of reaction, is to rely on the heat of reaction magnitude measured by a dynamic test and the residual heat of reaction remaining after the isothermal test [Hubert et al., 2001], such that

\[ H_{isothermal} = H_{ultimate} - H_{residual} = \sum_{i=1}^{n-1} \frac{\dot{H}_{baseline} - \dot{H}}{m_{sample}} \cdot \Delta t \]  \hspace{1cm} (2.19)

and the baseline heat flow is solved for. This method was used because the isothermal times were deemed too short to reach a negligible cure rate, even though the isothermal times were 300 minutes. Antonucci et al. [2002], with concern for the heat lost during the first minute of testing, incorporated the choice of baseline into the fitting for the cure kinetics,

\[ \frac{dH}{dt} = \Delta H_{total} \cdot k(\alpha, T) + K \]  \hspace{1cm} (2.20)

where \( \Delta H_{total} \) is the heat released if the degree of cure of one is reached (equivalent in definition to \( H_{ultimate} \)), and \( K \) is the baseline. The authors clearly state that this baseline selection method has two assumptions: 1) only one reaction pattern is allowed; and, 2) the chemical conversion is proportional to the ratio between the current heat flow and \( \Delta H_{total} \).
There are four classical types of baselines discussed in the literature for dynamic tests [Barton, 1972], as illustrated in Figure 2.14 a) through d): a) the start and end reaction heat flow magnitudes are the same and a straight-line baseline connects the two; b) there is an apparent change in heat capacity during the reaction, evidenced by a difference between the heat flow magnitudes at the start and end of the reaction, and as a first approximation a sloping linear baseline is assumed; c) an improved approximation to the later case is a baseline proportional to the fractional conversion through the peak; and, d) a secondary exothermic process, e.g. thermal degradation, is the cause of the increase in heat flow magnitude at the apparent end of the reaction and is treated with a horizontal, linear baseline up to the end of the reaction, and vertical line drawn up to the end heat flow (an open-ended peak resulting in a cure rate greater than zero at the apparent end of cure).

Simon [1992] and Dupuy et al. [2000] found that a linear baseline (b) for a thermoset reaction inappropriately assigns a lower heat of reaction magnitude to a dynamic test followed by overestimated cure rates, as opposed to subtracting the effect of Cp on heat flow during dynamic cure (often approximated using a sigmoidal curve). Simon notes that evidence of underestimating residual heats of reaction (overestimating degrees of cure for partially cured tests) will be a continued increase in Tg at degree of cure of 1 on a Tg-α curve, even though residual heat of reaction is not being measured. Likewise, overestimating the residual heat of reaction by a flat baseline (a) will underestimate the final degree of cure and Tg∞ would be reached before a degree of cure of 1.

Sometimes even the subtraction of the changes in Cp from the heat flow signal does not match the starting and end heat flow magnitudes of a dynamic test, as is the case for the data curve in (d). This phenomenon was explored in Simon’s work [1992] and was attributed to etherification since it only appeared for a material with excess epoxy. The approach taken by Simon was to use a linear baseline and back-calculate the missing heat of reaction for the amine-epoxy reaction. A linear relationship was assumed between the actual and the underestimated heat of reaction values,

\[ \Delta H_{r, actual} = a \Delta H_{r, observed} + b \]  

Assuming that the shape of the actual Tg-x curve will be the same as the observed Tg-x curve, the curve was first shifted by a constant amount, \( b \), by acquiring a value for the missing heat of reaction that would cause the residual to be zero at the appropriate Tg∞ for the amine-epoxy reaction (3 cal/g, or 5 cal/g of reacting epoxy). Constant \( a \) was determined using the equation above and inputting values for \( b \), the actual total heat and observed total heat for the epoxy-rich system; \( a \) was found to be equal to 1.1. The actual \( \Delta H_r \) was taken to be the average value for the amine-rich and 1:1 mixtures, by dynamic testing. Solving this relationship in terms of degree of cure, and rearranging,
\[ \alpha_{\text{actual}} = 0.96 \alpha_{\text{observed}} \]

and hence the actual conversion is lower than the calculated conversion by 4%, for all isothermal tests, and applied linearly to all conversions. In order to employ this method, the user must know the amine-to-epoxy ratio, the \( T_{\text{g}} \), for the amine-epoxy reaction, knowledge that the etherification reaction is separate from the epoxy-amine reaction and as such can be measured independently. The biggest problem with applying this method to other materials may be the lack of knowledge of the reactant quantities, which is generally held as proprietary knowledge by the manufacturer. The other two factors can possibly be found by experimentation, but may prove difficult if the etherification is interacting with the epoxy-amine reaction.

Endotherms appear before the onset of dynamic reactions when moisture is released and when the material has been physically aged. Kessler and White [2002] showed how a cubic spline fit could be used to smooth out endotherms occurring immediately before the exothermic cure reaction; in their case it was used to eliminate the melt of water and the monomer. Wisanrakkit and Gillham [1990], Simon and Gillham [1992], and Simon et al. [2000] emphasized the need to run a preliminary dynamic test to pass through the endothermic process (or rather up to the maximum of the endothermic peak) in order to release the frozen-in/aged structure, followed by a fast quench to room temperature and a re-run of the dynamic test to capture the glass transition temperature and remaining heat of reaction. These methods eliminate the endothermic peak and improve interpretation of the reaction kickoff temperature and initial cure rates. Figure 2.15 shows an endotherm before a reaction exotherm, and a dotted line representing the desired correction to the heat flow curve either by erasing the effect by annealing, or by adding a cubic spline.

2.3.3. Analysis and modeling methods

2.3.3.1. Chemical models

There are two types of analysis used to obtain a kinetic model, fundamental and phenomenological. Fundamental, or mechanistic, models introduce molecular parameters of the monomer and of the growing macromolecules, for example, free volume and glass transition temperature, and generally track more than one reactant. The phenomenological, or empirical, models render an alternative to the fundamental model and are formulated to fit experimental results in terms of one reactant. Phenomenological models do not provide knowledge about the path of reaction since a complete understanding of curing chemistry is not needed, but are predominantly used because the parameters of mechanistic models prove difficult to
obtain and there is usually a lack of information on the molecular structure of a resin system due to proprietary restrictions. This work is primarily focused on phenomenological modeling.

The underlying assumption of phenomenological cure kinetics modeling using DSC is that the exothermic heat of reaction measured during cure is directly proportional to the number of epoxides reacted. The resin rate of heat generation term, \(dH/dt\), in its basic form is,

\[
\frac{dH}{dt} = H_R \frac{d\alpha}{dt}
\]

where \(H_R\) (J/g) is the heat of reaction released during cure, \(\frac{d\alpha}{dt}\) is the rate of reaction of reactant \(\alpha\), and \(\alpha\) is the fraction of a single reactant concentration depleted compared to its original concentration. The general phenomenological model can be represented by

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

where a function of \(\alpha\) describes the shape of a DSC heat flow curve and reflects the type of reaction (nth order, autocatalytic, or a combination of the two), and a temperature function is typically described by the Arrhenius rate constant \((K = Ae^{E/RT})\). Although equation 2.24 may also be used to include modelled diffusion behaviour, this section will only consider chemical dominated behaviour. An nth order reaction is characterized by having a maximum reaction rate at time \(t = 0\),

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

whereas an autocatalytic reaction attains a maximum reaction rate at 30-40% conversion,

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

Figure 2.16 shows the difference between these two reaction types.

The remainder of this section provides an overview of the models used in the literature for epoxy-amine reactions, and their development based on chemical reactions, or ease of model fitting. Recall the balance of reactants from Section 2.1,

\[
A_1 + E + (HX)_A \xrightarrow{k_i} A_2 + (HX)_A \\
A_1 + E + (HX)_0 \xrightarrow{k_i'} A_2 + (HX)_0 \\
A_2 + E + (HX)_A \xrightarrow{k_2} A_3 + (HX)_A \\
A_2 + E + (HX)_0 \xrightarrow{k_2'} A_3 + (HX)_0 \\
E + mH + nA_3 \xrightarrow{k_3} ether + mH + nA_3
\]
The accepted underlying model for epoxy-amine reactions (first four balances) was developed by Horie et al. [1970] without etherification,

\[ \frac{da}{dt} = (K_1 + K_2\alpha)(1 - \alpha)(B - \alpha) \]  \hspace{1cm} 2.27

where \( K_1 = \frac{1}{2} k_1'((HX)_0E_0 \) and corresponds to catalysis by unknown impurities (X) and hydroxyl (OH) initially present (or primary amine and epoxy reaction), \( K_2 = \frac{1}{2} k_2E_0^2 \) and corresponds to catalysis by hydroxyl groups formed in the reaction (secondary amine and epoxy reaction), and \( B = 2A_0/E_0 \) is the initial ratio of amine-to-epoxide equivalents. The ratio of reactivities for secondary amine to primary amine was found to be 0.5 in Horie’s work, and is widely accepted. The ratio was explained due to steric hindrance as the length of the molecule increases. When the availability of amine and epoxide bonds are stoichiometrically balanced, \( B = 1 \). Appendix A records the equations for the chemical balances which justify the Horie model.

Stemming from this underlying model, five trends in phenomenological modeling for epoxy-amine reactions can be drawn from the literature: 1. combining the two rate constants to a single effective rate constant; 2. allowing the reaction orders to vary as non-integers, and also functions of temperature and degree of cure; 3. decoupling the two reactions \( K_1 \) and \( K_2 \) such that their reaction orders are independent of one another; 4. adding multiple \( n^{th} \) order and autocatalytic models for improved fitting; and, 5. polynomial or other mathematical curve fits, which may maintain the physical concept of \( g(T) \) but not \( f(\alpha) \). Each trend will be reviewed here briefly.

Wisanrak kit and Gillham [1990] rearranged equation 2.27 to create an effective rate constant to fit cure data for a DGEBA/TMAB epoxy-amine system (DER 332 was the commercial epoxy)

\[ \frac{da}{dt} = k(b + \alpha)(1 - \alpha)(r - \alpha) \]  \hspace{1cm} 2.28

where \( k = \frac{1}{2} \frac{k_1'(HX)_0}{k_1E_0}, b = \frac{k_1'(HX)_0}{k_1E_0}, r = 2A_0/E_0 \). Note \( r \) is now exchanged for \( B \) in notation. Parameter \( b \) allowed for the second-order reaction that initially starts the cure, catalyzed by impurities (primary amine with epoxide reaction), and is essentially the ratio of \( K_1/K_2 \) as defined by Horie et al. [1970]. When the initial mixture of epoxide to amine is stoichiometric, \( r = 1 \), the equation reduces to \( \frac{da}{dt} = k(1 - \alpha)^2(\alpha + B) \). Opalički et al. [1996] used this model for Hexcel 8552, and Simon et al. [2000] for Hexcel 8551-7. Nam and Seferis [1993], for T800H/3900-2, used an effective rate constant by multiplying each reaction (primary and secondary amine) by empirically determined weighting factors,

\[ \frac{da}{dt} = K[y(1 - \alpha) + (1 - y)e^m](1 - \alpha)^n] \]  \hspace{1cm} 2.29

This model uses the concept of variable reaction orders (see next paragraph). The advantage of having only one rate constant is evident when the Rabinowitch approach for diffusion is used. This will be discussed in detail in the diffusion section (2.3.3.4)
Sourour and Kamal [1976] are credited as the first to show that reaction orders can be used as model fitting variables,

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n$$

2.30

Ryan and Dutta [1979] later used this model for a DGEBA epoxy system and varied $m$ and $n$ with temperature. This model implies a 1:1 amine-to-epoxy balance, and is likely the most commonly used model in the literature. A review by Calado and Advani [2000] included a summary table of 22 phenomenological models for epoxy-amine systems, 14 of which were of equation 2.30 form, 5 having $m$ and $n$ as functions of temperature. Alterations to reaction orders with temperature can also be found in the literature [Costa et al., 2005; Sun et al., 2002 (a) and (b), Rogers and Lee-Sullivan, 2003; Hojjati et al., 2000; Mijovic 1986].

Lee et al. [1982] are credited as the first to have separated the nth order and autocatalytic terms and used variable reaction orders to fit each term for Hercules (now Hexcel) 3501-6 prepreg,

$$\frac{d\alpha}{dt} = K_1 (1 - \alpha)^l + K_2\alpha^m(1 - \alpha)^n$$

2.31

Stemming from this work is the concept of having multiple reactions of either nth order or autocatalytic form. Buczek et al. [1999] suggested adding two nth order reactions to model Hexcel 8552,

$$\frac{d\alpha}{dt} = \sum \frac{d\alpha_i}{dt} = K_i(1 - \alpha_i)^n$$

2.32

while Rogers and Lee-Sullivan [2003] applied two autocatalytic terms with variable reaction orders for FM 300-U (a commercial, modified epoxy film). Sun et al. [2002b] applied two autocatalytic terms to model Hexcel 8552, and considered the summation of two reactions within the framework of each term

$$\frac{d\alpha_i}{dt} = \left( \frac{dT}{dt} \right)^{-1} K_i(\alpha_1 + \alpha_2)^m(1 - \alpha_1 - \alpha_2)^n$$

2.33

where $\alpha_1$ and $\alpha_2$ are two epoxy reactions. Barton [1980] coupled an nth order and two autocatalytic models for a commercial resin system, Shell Epikote 828.

Models can also be found that simply use a single autocatalytic or nth order model, typically with non-integer reaction orders. Hubert et al. [2001] and Ersoy et al. [2005] both used autocatalytic models for Hexcel 8552. Nth order models were used in early works by Prime [1970, 1973], Acitelli et al. [1971] and Prime and Sacher [1972] for DGEBA resins (namely DOW DER 332), and later works by Kenny et al. [1989] for a TGDDM system, and Woo and Seferis [1990] for a DGEBA system. These works
explored orders of reactions that were non-integers, and variable with respect to degree of cure and with respect to temperature.

There are also models which have little to no chemical foundation. Ng et al. [2002] used a cubic expression to fit data for Hexcel 8552, Cytec Fiberite 977-3 HM, and Hercules 3501-6 HM

$$\frac{d\alpha}{dt} = K_1\alpha^3 - K_2\alpha^2 + K_3\alpha + K_4\alpha$$  \hspace{1cm} 2.34

where $K_i$ is the Arrhenius equation. Um et al. [2002] for an epoxy-amine system created a model based on the addition of two mathematical functions, $\alpha = F_1(T) + F_2(T)$ where $F_1(T)$ was a sigmoidal function to express the primary amine and epoxy reaction, and $F_2(T)$ was a bell shaped curve for the secondary amine and epoxy reaction.

Trends in methodology for adding etherification reactions are much the same as those listed for epoxy-amine modeling, either relying on the fundamentals of chemical reactions or simply including an additional nth order or autocatalytic term to account for the reaction. The mechanistic approach by Cole [1991] is the most comprehensive in explaining the various mechanisms for etherification and will be reviewed here briefly. The model was based on observations by others (namely Chiao [1990]) that etherification can be catalyzed by tertiary amine, hydroxyl groups, or by itself (homooetherification). His model tracks both amine and epoxide consumption for the purpose of adequately accounting for the various combinations of catalysts,

$$\dot{\alpha} = B(K_1 + BK_2\beta)(1 - \beta)(1 - \alpha) + K_3(Y + \beta)^m (Z + \beta^2)^n (1 - \alpha)$$  \hspace{1cm} 2.35

where $\alpha$ and $\beta$ are the dimensionless parameters for consumption of epoxide and amine N-H bonds (primary plus secondary amine), respectively. $Y = H_0/2A_{10} = H_0/BE_0$ refers to the initial hydroxyl content (assumed to be negligible in Cole’s work), $Z$ is the ratio of tertiary amine to epoxide concentration initially present in the system, that is $Z = A_{30} = A_{10} = 2A_{30}/BE_0$. Coefficients $m$ and $n$ (not to be confused with the parameters $m$ and $n$ discussed for the epoxy-amine reactions) are orders of reaction which activate the etherification reaction mechanisms. When there is no etherification, the equation reduces to the Horie equation by setting $\beta = \alpha/B$. Cole outlined seven scenarios for etherification as shown in Table 2.1. Case 4 was estimated for the Narmco system (TGDDM MY 720, DGEBA SU-8, DDS HT 976) studied by Cole et al. [1991] having a $B = 0.6$ and $Z = 1.5$, which shows the onset of etherification at 0.1 degrees of cure during an isothermal hold of 180°C. For the case that etherification is not catalyzed by tertiary amine (Case 5, $m = n = 0$), the result is an nth order reaction for etherification with respect to epoxide consumption, and the equation for cure rate can be reduced to tracking only epoxide. If
etherification is catalyzed by tertiary amine, the reaction may start at low degrees of cure and temperatures.

Simon and Gillham [1992] developed a mechanistic model for the DER332/TMBA system and stated that etherification was not catalyzed by tertiary amine and modeled etherification as an autocatalytic reaction with respect to epoxy consumption. Alternatively, there are phenomenological models which add an nth order model [Lee et al., 1982; Barral et al., 1997] making the implicit assumption that etherification formation was only catalyzed by hydroxyl or was homopolymerized.

2.3.3.2. Solving for Arrhenius constants

Several methods have been developed to calculate the activation energy ($E$) and the pre-exponential, or frequency, factor ($A$) of the Arrhenius relationship for kinetics modeling. Current discussion in the literature for what method to choose is focused on whether or not the methods are dependent on prior knowledge of the $f(\alpha)$; that is, model fitting versus model free methodologies, respectively. Within these two classifications, the methods are designed around isothermal versus dynamic tests, area calculations versus peak temperature measurements, integral versus differential form, calculations at constant degrees of cure, and how many (or how few) tests are needed to find the Arrhenius model constants. Table 2.2 outlines the various methodologies developed for calculating Arrhenius constants for thermosetting materials, and their various classifications as listed above. The remainder of this section describes the methods.

1) Time-temperature superposition

The methodology of time-temperature superposition begins with a plot of degree of cure versus $\ln($time$)$ for the isothermals, Figure 2.17 (a), which is subsequently shifted along the time axis to create a single curve, Figure 2.17 (b), by multiplying the time of curves by a shift factor $t_2/t_1$ where $t_2$ is the curve to be shifted and $t_1$ is a stationary curve. Curves of higher temperatures are shifted to the right, or longer times, and curves of lower temperatures are shifted to the left, or shorter times. The relationship between the shift factor and activation energy is as follows,

$$\frac{t_2}{t_1} = \exp\left(\frac{E}{RT_1T_2} \left(\frac{T_1 - T_2}{T_1T_2}\right)\right)$$
The rate of cure, $\frac{d\alpha}{dt}$, is found by taking the derivative of the single curve. The rate constant, $A$, is model dependent for an nth order reaction, $(1-\alpha)^n$, and is found by plotting $\ln \frac{d\alpha}{dt}$ by $\ln (1-\alpha)$, where the line is straight when $n$ is chosen correctly, and the slope is $\ln A$. For autocatalytic reactions, Horie et al. [1970] and Sourour and Kamal [1976] plotted $(d\alpha / dt)/(1-\alpha)(B-\alpha)$ versus $\alpha$ and found that when the correct parameter values were used (in this case $B$) the slope up to the point of vitrification was linear and equal to the rate constant.

An extension of the TTS method was developed by Wisanrakkit and Gillham [1990], and has been subsequently used by Simon and Gillham [1992], and Simon and McKenna [2000]: isothermal contours of the progress of Tg were plotted and shifted with time to create a master curve. To track Tg with time, material was cured at various isothermal temperatures for progressive lengths of time, and a dynamic residual test was used to measure Tg and calculate the degree of cure. This method completely bypasses the need to evaluate isothermal baselines. The activation energy was measured independent of a model using a plot of the shift factors versus the reciprocal of temperature, but the pre-exponential factor was measured in terms of a model selected.

2) ASTM E2070, isothermal data

ASTM Standard E2070 [2000] outlines two model fitting methods for nth order and autocatalytic reactions, and one model free method, for isothermal data. For the model fitting approach using an nth order reaction, a plot of $f(\alpha)$ versus time for each temperature gives a straight line where the slope is $k$ given that for a first order reaction $-\ln (1-\alpha) = kt$, and a second order reaction $1/(1-\alpha)^2 = 1 + kt$. Activation energy is then determined from the slope of $\ln (k)$ versus $1/T$ isothermal, which should be a straight-line plot. Although this method can determine the activation energy, frequency factor and reaction order, the standard states that the application is over a small temperature range of roughly 10K (minimum of four temperatures within this range), and that it is not applicable to exothermic reactions when the thermal curves exhibit shoulders, discontinuities, or shifts in baseline. The standard also suggests that the rate and Arrhenius equations can be combined and cast in logarithmic form, and solved for by multiple linear regression analysis. For example, the autocatalytic equation in logarithmic form,

$$\ln[d\alpha / dt] = \ln[A] - E / RT + m \ln[\alpha] + n \ln[1 - \alpha]$$

2.37 resembles $z = a + bw + cx + dy$. 
Alternatively, ASTM E2070 offers a model free method for isothermal data. The integral of the rate equation for values of time to constant conversions can be applied across a series of isothermal temperatures,

\[
\ln[\Delta t] = \frac{E}{RT} + c
\]

where \(\Delta t\) is the time lapsed at isothermal temperatures up to a constant conversion or some other event of interest, and \(c\) is a constant which is actually a combination of the remaining terms, \(\ln(f(\alpha))\) and \(\ln A\), since they are both constant for a constant degree of cure. A plot of lapsed time versus the reciprocal of absolute temperature \((1/T)\) is linear with a slope equal to \(E/R\). Several contours of constant degree of cure can be plotted, known in the literature as isoconversionals. This method fits into the class of ‘model-free’ kinetics in terms of solving for \(E\) independently. The same restrictions apply to this alternative method as were described above, but with the additional statement that this method is to be used for determining the activation energy only. For a purely autocatalytic reaction, one approach is to take the time up to the cure rate peak (or to take the value of cure rate at this point) and plot it versus the reciprocal of temperature to find \(E\). If it is a simple reaction, the peak cure rate should occur at the same degree of cure (0.5) over the series of temperatures. Despite the restrictions outlined in the standard, this method has been used by authors Ramis and Salla [1995] over a 30°C range to explore the effect of inhibitors on cure of unsaturated polyester resin, and the values for \(c\) were used directly as the pre-exponential factor \((A)\). They also showed in their work that the activation energy of the inhibitor could be calculated by the isoconversional method.

3) ASTM E2041, dynamic data

Borchardt and Daniels [1957] developed a model-fitting methodology using a single dynamic test, described for an nth order reaction in ASTM E2041. A dynamic DSC scan is performed at a constant heating rate. The area under the curve is found incrementally with increasing time or temperature, and divided by the ultimate heat of reaction to find the degree of cure,

\[
\alpha = \frac{\int_0^t \frac{dH}{dt} dt}{H_R}
\]

and \(\frac{d\alpha}{dt}\) is found by dividing the incremental degree of cure by the change in time between increments.

The Arrhenius equation, \(k(T) = Ae^{-E/RT}\) is solved for in the following steps for an nth order reaction:

1) Taking the natural logarithm of the Arrhenius equation yields \(\ln k(T) = \ln A - E / RT\) which has the form of a straight line \(Y = mX + b\).
2) The cure rate for an nth order reaction is expressed as \( \frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \). Taking the natural logarithm of this equation yields \( \ln \frac{d\alpha}{dt} = \ln k(T) + n \ln(1 - \alpha) \). Find \( \ln[k(T)] \) by linearizing the nonlinear data by setting \( n = 1.0 \). Repeat for various temperatures.

3) Calculate values for \( \ln k(T) \) and plot them against \( 1/T \). Increase or decrease the value of \( n \) (or \( n \) and \( m \) for an autocatalytic reaction) until the plot yields a straight line. From this straight line the Y-intercept is \( \ln A \) and the slope is \(-E/RT\).

Figure 2.18 illustrates the curve fitting process that ensues to find an appropriate value for the reaction order to fit a straight line. This test method assumes \( n \) will be small, non-zero integers such as 1 or 2. Heating rates of less than 10K/min are recommended.

4) ASTM E698, dynamic data

ASTM E698 for unstable materials presents a model free approach to find the activation energy and pre-exponential factor by the following relationships,

\[
E \approx -2.19 R \left[ \frac{d \log_{10} \phi}{d (1/T_{\text{peak}})} \right] 
\]

\[
A = \frac{\phi E \exp^{E/RT}}{RT^2} 
\]

where \( \phi \) is the heating rate, and \( T_{\text{peak}} \) is the temperature at the peak of the heat flow profile. A best fit line through a plot of \( \log_{10} \phi \) versus \( 1/T_{\text{peak}} \) to find \( E \). This method recommends heating rates between 1 and 10K/min.

5) Isoconversional method, dynamic data

The isoconversional method has been developed for dynamic data on the basis of the differential form of the rate equation. Activation energy can be determined from the slope of a straight line from the plot of \( \text{Ln}[\text{Cure Rate}] \) versus the reciprocal of temperature as follows,

\[
\ln \dot{\alpha} = \ln[Af(\alpha)] - E/RT
\]

where \( f(\alpha) \) is a constant for a given degree of cure and becomes part of an effective term along with the rate constant when evaluating the intercept of the straight line. Activation energy is thus independent of the reaction model and only dependent on degree of cure, or the chemistry of the process is independent of temperature [Friedman, 1963]. Plots of \( \ln[d\alpha/dt] \) vs \( 1/T \) are known in the literature on decomposition as Friedman plots. Vyazovkin and Wight [1998] review this method’s broad use for solid state kinetics.
Although not standardized for the field of thermoset kinetics, this method is the general form of the Borchardt and Daniels’ model fitting method, and has been used throughout the history of dynamic testing. Prime’s review [1997] refers to this approach as the multiple-heating-rate method. Salla and Ramis [1996] have shown this method to be applicable to both isothermal and dynamic data, with the drawback that it cannot be applied at the beginning of the reaction when the reaction rate is nil.

6) Integrated equations, dynamic tests

In the same vein as the model free approaches using area measurements, integral approaches involving the tabulation of peak temperature from dynamic tests have been developed to relieve the analyst of area calculations affects by instrument insensitivity and baseline problems. The peak exotherm temperature, $T_p$, was found to vary predictably with heating rate, $\phi$, [Ozawa, 1970; Flynn and Wall, 1966] such that integration of the rate of conversion equation, including the rate constant, where $\frac{d\alpha}{dt} = \phi \frac{d\alpha}{dT}$, could be reduced to

$$\int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = A \int_{T_0}^{T_p} e^{-E/RT} dt = \frac{A}{\phi} \int_{T_0}^{T_p} e^{-E/RT} dT$$  \hspace{1cm} (2.43 a)

where $g(\alpha)$ is defined to account for dynamic cure. It was first approximated by Doyle [1961] and later formulated by Ozawa [1970] that the above relationship for a constant degree of cure could be reduced to,

$$\log \phi = \log \left[ \frac{AE}{g(\alpha)R} \right] - 2.315 - 0.4567 \frac{E}{RT}$$  \hspace{1cm} (2.43 b)

From this equation the activation energy can be determined directly from the slope of a plot of $\log(\phi)$ versus $1/T$. It was also observed by Horowitz and Metzger [1963], Prime [1973], and Peyser and Bascom [1974], that the extent of reaction up to the peak exotherm is constant and independent of temperature. Hence, the degree of cure up to the peak exotherm, $\alpha_p$, is a constant and the activation energy may be found by a difference method between two peaks at two heating rates,

$$E \approx -\frac{R}{0.4567} \frac{\Delta \log \phi}{\Delta(1/T_p)} = -\frac{R}{1.052} \frac{\Delta \ln \phi}{\Delta(1/T_p)}$$  \hspace{1cm} (2.44)

Kissinger [1957] derived an expression for the frequency factor for nth order reactions,

$$A = \frac{\phi E e^{E/RT_p}}{RT_p^2 [n(1-\alpha_p)^{n-1}]} \approx \frac{\phi E \exp[E/RT_p]}{RT_p^2}$$  \hspace{1cm} (2.45)

and a further equation for the frequency factor for autocatalyzed reactions can be approximated from [Prime 1981],
ASTM E 698 for thermally unstable materials suggests using Kissinger’s equation for an alternative to calculating \( E \). Both the Ozawa and Kissinger equations use isoconversionals, and the solutions for \( E \) can be categorized as model-free. Duswalt [1974] showed how methods using peak temperatures are advantageous for their application to materials expressing multiple reactions within a single dynamic temperature scan. Sun et al. [2002b] also showed that the integral method can be used to resolve the activation energies of a two-peak reaction, but proposed the rate constant to be dependent on heating rate.

Since very few commercial CFRP systems follow a single nth order or autocatalytic model, the model fitting approaches described in the standards are not often applicable. The isoconversional, model free methods have gained popularity in the literature, and it is well accepted that Arrhenius constants change with degree of cure due to changes in reaction mechanism, gelation, vitrification, and viscosity. Salla and Ramis [1996], on comparing several methods for calculating \( E \) and \( A \), determined that Ozawa’s method (equation 2.43) and the integral isoconversional form of the Arrhenius equation (equation 2.38) were in agreement for calculating \( E \). They also found that the differential isoconversional form (equation 2.42) when applied to both isothermals and dynamics were in agreement.

### 2.3.3.3. Differences between isothermal and dynamic cure

Differences between isothermal and dynamic cure kinetics has been an ongoing debate in the literature from the early days of kinetic modeling and commercial DSC’s (1960’s-70’s), to recent literature reviews [e.g. Calado and Advani, 2000]. The question specifically surrounds observations of higher activation energies calculated from dynamics compared to isothermals. Additionally, differences in chemical model parameters [Sun et al, 2002a, 2002b] and higher heats of reaction for dynamics [Prime, 1973; Salla and Ramis, 1996] have also been reported. Explanations for the differences have evolved from early proposals of corrections to the fundamental cure rate equation, to understanding sources of errors in data reduction and equations for solid state kinetics.

Prime [1970], Abolafia [1969] and Barrett [1967] showed epoxy resin activation energies for dynamic experiments that were 50-85% higher than for isothermal experiments when using techniques such as the Borchardt and Daniels method [1957]. Based on the work of MacCallum and Tanner [1970] who proposed that the cure rate equation should be a partial derivative
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\[ \frac{d\alpha}{dt} = \left( \frac{\partial \alpha}{\partial t} \right)_T + \left( \frac{\partial \alpha}{\partial T} \right)_T \frac{dT}{dt} \]  

where \( d\alpha/dt \) is the dynamic rate, \((d\alpha/dt)_T\) is the isothermal rate, and \(dT/dt\) the heating rate, Prime [1970] proposed a correction for dynamic cure rates

\[ \frac{d\alpha}{dt} = \left( 1 + \frac{E\Delta T}{RT^2} \right) \left( \frac{\partial \alpha}{\partial t} \right)_T \]  

which facilitated calculation of the same activation energy for dynamic experiments as found from isothermal experiments. However, the physical meaning of the partial derivative for constant time was discredited [Sestak and Kratochvil, 1973], and the differences in the measured activation energies were later attributed to differences in reaction mechanisms between low and high temperature cure (dynamics extending to higher temperatures than isothermals) [Riccardi et al., 1984]. Looking back at Prime’s work, this is a probable explanation since isothermal tests ranged from 23 to 160°C and the temperatures at the peak of dynamic heat flows for 5, 10 and 20°C/min ranged from 130, 148 and 170°C, respectively. Prime’s results also showed a higher activation energy for data after the peak than before. Likewise, Barrett and Abolafia, although not comparing their dynamic tests to isothermal findings explicitly, used high heating rates (4 to 32 °C/min) and measured activation energies greater than 100 kJ/mol (comparable to Prime’s values for dynamic tests). The high activation energies reported for dynamic tests in these early years of DSC testing were later found to coincide with the etherification reaction [Schneider et al., 1979; Apicella et al., 1984; Chiao, 1990; Cole, 1991; Sbirrazuoli et al., 2006]. In regard to the differences observed in heats of reaction, De Bakker et al. [1993] proposed that each reaction has its own enthalpy (83, 131 and 65 kJ/mol for epoxide reaction with primary amine, secondary amine and hydroxyl, respectively) and hence their dominance in temperature regions would result in different total heats of reaction. Salla and Ramis [1996] also explored the effect of various heat of reaction balances (e.g. \( H_{\text{Total}} < H_{\text{Ultimate}} \) versus \( H_{\text{Total}} = H_{\text{Ultimate}} \)) and concluded that changes in the definition of degree of cure did not notably alter the kinetic parameters (E, A). Given the historical layout of the debate, challenging the overlap of mechanisms between the two test modes (in temperature and degree of cure ranges) and accounting for heats of reaction appropriately should outweigh doubts to the underlying assumption that cure rate is a unique function of \( T \) and \( \alpha \).

Recent studies exploring Arrhenius parameters have focused on the validity of the kinetic analysis methods [Salla and Ramis, 1996; Cadenato et al., 2007; Sbirrazuoli et al., 1997; Vyazovkin and Wight, 1998, 1999], as developed for thermosetting reactions and those from other fields of solid state kinetics such as decomposition. Derivative and integral cure rate isoconversional methods (model free) have provided the most consistent solutions between isothermal and dynamic measurements, particularly when

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the value of $E$ varies greatly during the process. Unlike the equations by Ozawa and Kissinger or the Borchardt and Daniels single dynamic method, all of which give a single average result, the isoconversional methods calculate $E$ with respect to degree of cure. If a single mechanism exists, $E$ will not vary with degree of cure. If $E$ changes with degree of cure, the trends may provide information as to the underlying cure mechanisms of the reaction [Sbirrazzuoli et al, 1997; Vyazovkin and Sbirrazzuoli, 1999], although this must be viewed with caution as other processes can influence cure rate (e.g. vitrification, phase separation, inhibitors).

For purely kinetic studies, dynamic tests are still considered more reliable since their baselines, start and end points can be defined more easily. However, isothermal tests (or their residuals) are necessary for modeling diffusion. In general, cure models are not compared to both isothermal and dynamic data, although those pursuing advanced modeling programs assert that the two test modes should be used as complimentary data sources to cover the widest range of temperatures, degrees of cure, and material behaviour as possible [Flammersheim and Opfermann, 2002; Skordos and Partridge, 2001].

2.3.3.4. Diffusion models

With increasing cross-link density (concentration, viscosity), the Tg of the material also increases. Once the Tg reaches the cure temperature (or close to this point), the resin transitions from a rubbery to a glassy state, and the mobility of the reacting groups is restricted. This transition is known as vitrification, and the associated loss of mobility means that the reaction rate is no longer governed by chemical kinetics alone, but also by the rate at which available reaction sites at the ends of network chains can be occupied by molecules through diffusive chain and molecular movement. Diffusion is the process by which molecules spread from areas of high concentration to areas of low concentration.

There are currently three methods for adding a rate limiting diffusion term to the cure rate equation: 1) the Rabinowitch [1937] model which requires an expression for the diffusion rate based on free volume theory; 2) modifying the definition of the final degree of cure in the rate equation; and 3) use of a diffusion factor based on changes in Cp as measured by MDSC. The first two methods are of practical importance for this work as they are used exclusively in Chapter 5 to model T800H/3900-2. The third method is gaining interest among MDSC users at this time.

The widely accepted Rabinowitch model describes the chemical-to-diffusion-control phenomenon,
where \( K_e \) is the effective or overall rate constant (measured cure rate), \( K_c \) is the chemically controlled rate constant generally defined using the Arrhenius equation, and \( K_d(\alpha, T) \) is the diffusion rate constant, all with units of \((\text{sec})^{-1}\). \( K_d \) is solved for by rearranging the above equation, 

\[
\frac{1}{K_e(\alpha, T)} = \frac{1}{K_c(T)} + \frac{1}{K_d(\alpha, T)}
\]

or

\[
K_e = \frac{1}{f(\alpha)}
\]

for a single reaction. Diffusion kinetics has a temperature dependence typically described by the Arrhenius equation, and in addition has a limiting term dependent on the state of the material, \( f_d(T) \), since the rate of diffusion is governed by chain and molecular mobility. In the inverse form, the three rate constants become measures of time such that the total time scale for the reaction is equal to the time for chemically controlled reaction plus the time for diffusion. Hence, when the time for diffusion is small, the kinetics is dominated by chemical reactivity.

There are three prominent approaches in the literature for describing \( K_d(\alpha) \):

1. Williams, Landel and Ferry (WLF) equation [1955], modified by Wisanrakkit and Gillham [1990], referred to in this work as WLF-W;
2. Macedo and Litovitz equation [1965], modified by Simon and Gillham [1992], referred to in this work as ML-S;
3. Chern and Poehlein [1987] semi-empirical approach based on WLF, modified by Cole et al. [1991], referred to in this work as CP-C.

In each case, there are two components to the rate equation for diffusion: 1) a term describing the temperature dependence, originally of the Arrhenius form, but also applied as a constant; and, 2) a term to describe the state of the material, originally based on free volume theory, \( f_d(T) \) or \( f_d(T-Tg) \). In general, the following form is applicable to all three models,

\[
K_d = K_{do} \exp[f_d(T - Tg)]
\]

where \( K_d \) is the diffusion rate constant, \( K_{do} \) is a frequency factor, and \( f_d(T-Tg) \) is a function describing the free volume available for diffusion. Table 2.3 lists the three equations, how the temperature component is cited in the literature, meaning of parameters, and the modifications. The CP-C equation does not use \( Tg \) to describe the state of the material, but rather \( (\alpha - \alpha_c) \), which stems from the assumption that \( Tg \) and \( \alpha \) have a linear relationship. Appendix B details the generation of these three models from their root in the Doolittle equation [1951] for viscosity as a function of free volume. All three models can be found as equivalent given the appropriate substitutions for parameters are made.
A special case of combining the chemical and diffusion times was noted by Cole et al. [1991]. Assuming that the chemical reaction and diffusion have the same temperature dependence \( (K_c = K_d) \) allows the Rabinowitch equation to be rearranged such that diffusion can be described in a denominator applied to both reactions:

\[
\frac{1}{K_c(\alpha, T)} = \frac{1}{K_c(T)} + \frac{1}{K_c(T)f_d(\alpha)} \tag{2.52}
\]

\[
\frac{K_c}{K_e} = 1 + \frac{1}{f_d(\alpha)} = 1 + f_d(\alpha)^{-1} \tag{2.53}
\]

Commonly, \( f_d(\alpha) = \exp[f'(\alpha)] \), such that \( \frac{K_c}{K_e} = 1 + \exp[-f'(\alpha)] \). The inverse of this ratio becomes a diffusion factor, \( DF(\alpha,T) \),

\[
\frac{K_c}{K_e} = \frac{1}{1 + \exp[-f'(\alpha)]} \tag{2.54}
\]

and thereafter is applied to the cure rate equation as follows,

\[
\dot{\alpha} = \frac{K_{c1}f(\alpha) + K_{c2}f(\alpha)_2}{1 + \exp[-f'(\alpha)]} \tag{2.55}
\]

This method has been used to find the critical degrees of cure from the plot of \( K_c/K_e \) versus conversion for various isothermals. It was also a convenient method for ignoring the need to find the chemical rate constant when it is the combination of two equations for primary and secondary amine reacting with epoxy as in the equations derived by Horie et al. [1970], Sourour and Kamal [1976], Cole [1991]. The chemical rate constant is necessary to calculate \( K_d \) by the Rabinowitch equation.

Another method to account for diffusion modifies the definition of extent of cure in order to lower the reaction rate. Sbirrazzuoli and Vyazovkin [2002] used a relative degree of conversion instead of actual degree of cure,

\[
\alpha' = \frac{1}{H_T} \int_0^t \frac{dH}{dt} dt \tag{2.56}
\]

where \( H_T \) is the isothermal heat of reaction without the addition of a residual. The model for conversion is then \( f(\alpha) = (\alpha_T - \alpha)^n \), or \( f(\alpha) = \alpha^n(\alpha_T - \alpha)^n \). This method was also followed by Gonzalez-Romero and Cassilas [1989], using the DiBenedetto [1987] equation to describe the relationship between maximum conversion and temperature. Lee and Lee [1994] proposed that the degree of cure be normalized to the maximum value,
Work has been done by Van Assche and co-workers [1995, 1996, 1997, 2002] to show that a mobility factor, MF(\(\alpha, T\)), based on changes in heat capacity with temperature and cure can be used to describe vitrification and devitrification during cure

\[ MF(\alpha, T) = \frac{C_p(\alpha, T) - C_{p_g}(\alpha, T)}{C_{p_l}(\alpha, T) - C_{p_g}(\alpha, T)} \]

where \(C_p\) is the reversing heat capacity measured by MDSC, and subscripts \(g\) and \(l\) refer to glassy and liquid (or rubbery) states of the material. The intention was to apply the mobility factor to the cure rate equation in the same manner as the diffusion factor, where

\[ \begin{bmatrix} \frac{d\alpha}{dt}(\alpha, T) \end{bmatrix}_{\text{Measured}} = \begin{bmatrix} \frac{d\alpha}{dt}(\alpha, T) \end{bmatrix}_{\text{Chemical}} \cdot MF(\alpha, T) \]

assuming that diffusion control becomes dominant at the point of vitrification (\(T = T_g\)), the mobility factor reaching a value of 0.5 as does the diffusion factor. Meng and Simon [2005] reviewed this methodology and pointed out that this assumption does not necessarily hold as several works have shown that the point of vitrification is influenced by modulation period (frequency dependence), autoacceleration effects in free radical polymerization, enthalpy, relaxation phenomenon and cure conditions. At this time, the use of \(C_p\) models to predict diffusion behaviour is still under investigation and will be referred to future studies of reliable cure kinetics modeling, and in particular the cure modeling of material system T800H/3900-2. Although it is the current trend to present a model for \(C_p\) along with cure kinetics models, to the best of this author's knowledge there are no models asserting the use of a \(C_p\)-based diffusion factor.

The most popular relationship between \(T_g\) and degree of cure is the DiBenedetto equation [Nielsen, 1969; DiBenedetto, 1987]. The mechanistic form is as follows,

\[ T_g(\alpha) = T_{g_0} + \frac{[(E_x/E_m) - (F_x/F_m)]\alpha}{1 - [1 - (F_x/F_m)]\alpha} \cdot T_{g_0} \]

where \(E_x/E_m\) is the ratio of lattice energies for the crosslinked polymer to uncrosslinked polymer, and \(F_x/F_m\) is the ratio of segmental mobilities for the crosslinked polymer to uncrosslinked polymer. The modified form can be proved on the basis of the inverse rule of mixture and uses a fitting constant, \(\lambda = T_{g_0}/T_{g_c}\).
where subscripts 0 and ∞ refer to the uncured and cured states. When λ is equal to 1, the equation reduces to a linear relationship $T_g(\alpha) = T_{g0} + \alpha(T_{g\infty} - T_{g0})$ suggesting that the material is in the most condensed state at all degrees of cure. This equation does not take into account thermal history, and since $T_g$ is dependent on heating or cooling rate the relationship is associated with a specified temperature rate. Gillham [1986, 1997], Gan et al. [1989], Wisanrakkit and Gillham [1990], and Simon and Gillham [1992] found the $T_g$-$\alpha$ relationships for thermosetting materials to be unique with $\lambda$ less than 1. It is not uncommon to find relationships with $\lambda = 1$, as was chosen for simplicity by Chern and Poehlein [1987] in development of their diffusion factor, and will be shown in Chapter 3 for material 8552. The recent discovery that phase separated materials may exhibit blend versus separated $T_g$’s depending on cure history [Bonnet et al., 1999a] would suggest caution as to modeling an entire system by a unique relationship.

### 2.4. VISUAL PRESENTATION OF CURE MODEL BEHAVIOUR

There are two prominent visualization techniques in the polymer literature for displaying material properties: 1) material selection charts and mechanism maps by Ashby and colleagues; and, 2) the Time-Temperature-Transformation (TTT), Cure-Heating-Transformation (CHT), and the Conversion-Temperature-Property (T$_g$TP) diagrams by Gillham and colleagues. The former maps are based on post-process properties, whereas the later diagrams are used to describe the progress of cure and phase transformations with time and temperature. The purpose of all these diagrams/maps is to survey material properties and their relative changes during processing and with respect to other materials. Herein we will discuss the main attributes of each visualization technique.

The overall purpose of material selection maps is to survey values of design-limiting properties for a wide range of materials. A commonly used map is the modulus versus density map with guidelines of constant $E/\rho$, $E^{1/2}/\rho$, and $E^{1/3}/\rho$ for selection of materials of minimum weight, deflection-limited, design [Ashby, Materials Selection in Mechanical Design, 2nd Ed., 1999]. The charts effectively display distinctions between classes of materials (ceramics, metals, polymers, etc), and within a class (nylon, polyesters, HDPE, epoxies, etc.).

Mechanism maps survey the changes in material properties for a single material when it is subject to a process that induces small or large strain deformation. For example, modulus maps for amorphous
polymers based on fully polymerized material structure [Gilbert et al., 1986] plot the effects of small strain deformation when the polymer undergoes phase transitions due to viscoelastic parameters of time (stress relaxation) and temperature (dynamic loading). The modulus map, Figure 2.19, has axis of modulus and temperature (normalized by the glass transition temperature) with contours of constant frequency and is divided into regions for the glassy state, glass transition, rubbery state, viscous flow and decomposition. The diagram is constructed from approximate constitutive equations fitted to experimental data for each regime. The contours essentially relate the axis properties to another useful property such that by specifying any two properties the third can be read off the map. Similarly, a large strain deformation failure-mechanism map was developed by Ahmad and Ashby [1988]. The diagram plots normalized failure strength (σ/E) versus temperature (normalized to the glass transition temperature) with contours of constant strain rate and regimes of dominance between competing failure mechanisms in tension and compression: brittle fracture (crazing or shear-bandning), plasticity terminated by ductile fracture, cold-drawing, rubbery and viscous flow, purely elastic deformation, and effects of adiabatic heating on deformation. Parallel work has been done for large strain deformation mechanisms of metals and ceramics, e.g. wear mechanism maps.

Gillham [1986] developed the Time-Temperature-Transformation (TTT) diagram to visually track the time to gelation and the time to vitrification during an isothermal temperature hold, Figure 2.20. A TTT diagram plots the process input parameters of temperature versus log time where the temperature refers to both the isothermal cure temperature and glass transition temperature of the material. The plot may also contain contours of constant degree of cure and regimes of liquid, sol/gel rubber, gel rubber, sol glass, sol/gel glass, gel glass and char, separated by lines for gelation and vitrification/devitrification. The experimental work behind the diagram consists of a series of isothermal tests wherein a material is cured at elevated temperatures for progressive lengths of time. The glass transition data is subsequently measured by Differential Scanning Calorimetry (DSC) or Dynamic Mechanical Analysis (DMA) temperature ramp tests. A limitation of this diagram is that it can only be used for single isothermal holds, whereas in practical applications a cure cycle may consist of temperature ramps and more than one isothermal hold at different temperatures.

A separate Cure-Heating-Transformation (CHT) diagram was presented by Simon and Gillham [1994] to account for the progress of cure to gelation and vitrification during various temperature ramp magnitudes, Figure 2.21. The same axis is used as for the TTT diagrams. Like the TTT diagrams, the data to construct the CHT plot begins at only one initial degree of cure, and hence it is impossible to combine the TTT and CHT diagrams in their present state for any given cure cycle.
In addition to the TTT and CHT diagrams, Gillham [1997] proposes a Conversion-Temperature-Property (TgTP) diagram with the purpose of displaying changes in isothermal properties versus conversion, Figure 2.22. The underlying premise of this diagram is the relationship between macroscopic properties and molecular structure, given that a specific conversion represents a specific microstructure. The TgTP diagram uses the glass transition temperature as a measure of conversion based on the finding that there is a unique relationship between $T_g$ and $\alpha$ (e.g. DeBenedetto relationship). It is also suggested that the orthogonal axis be used to project values of the properties plotted. This diagram is also limited by the use of isothermal values only, and does not include a time factor such that conformational changes (relaxation phenomenon) are neglected, and property changes during a cure cycle cannot be tracked.

Adabbo and Williams [1982] proposed a conversion-temperature phase diagrams and considered an isothermal environment, constant heating rate, and adiabatic conditions, Figure 2.23. Their diagrams outlined the major transitions as proposed by Gillham and plotted a Tg-$\alpha$ curve. Their basic use of the chart was to show the extent of cure for a given temperature trajectory (dynamic or isothermal), the limit being vitrification at the Tg-$\alpha$ curve. Contours of constant time or heating rate were not applied to these charts.
**Table 2.1 Etherification cases [Cole, 1991]**

<table>
<thead>
<tr>
<th>Case</th>
<th>K₃ term</th>
<th>m</th>
<th>n</th>
<th>Z</th>
<th>Nature of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EH</td>
<td>1</td>
<td>0</td>
<td></td>
<td>Epoxide-hydroxyl, uncatalyzed</td>
</tr>
<tr>
<td>2</td>
<td>EH²</td>
<td>2</td>
<td>0</td>
<td></td>
<td>Epoxide-hydroxyl, catalyzed by hydroxyl</td>
</tr>
<tr>
<td>3</td>
<td>EHA₃</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>Epoxide-hydroxyl, catalyzed by all tertiary amine groups</td>
</tr>
<tr>
<td>4</td>
<td>EHA₃</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>Epoxide-hydroxyl, catalyzed only by tertiary amine groups formed in reaction</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>0</td>
<td>0</td>
<td></td>
<td>Homopolymerization, first order in epoxide</td>
</tr>
<tr>
<td>6</td>
<td>EA₃</td>
<td>0</td>
<td>1</td>
<td>1.5</td>
<td>Homopolymerization, catalyzed by all tertiary amine groups</td>
</tr>
<tr>
<td>7</td>
<td>EA₃</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>Homopolymerization, catalyzed only by tertiary amine groups formed in reaction</td>
</tr>
</tbody>
</table>

**Table 2.2 Methods for calculating Arrhenius constants (E, A)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Experiment</th>
<th>No. of Tests</th>
<th>Data Reduction Method</th>
<th>Modeling Arrhenius Constants</th>
<th>Isoconversional</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTS</td>
<td>Isothermals</td>
<td>Multiple</td>
<td>Area</td>
<td>Model-Free E</td>
<td>No</td>
</tr>
<tr>
<td>TTS (Wisanrakkit and Gillham)</td>
<td>Isothermal residuals</td>
<td>Multiple</td>
<td>Area, Tg</td>
<td>Model-Free E, Model-Fitted A</td>
<td>No</td>
</tr>
<tr>
<td>ASTM E2070</td>
<td>Isothermals</td>
<td>Multiple</td>
<td>Area</td>
<td>Model-Fitted E and A</td>
<td>No</td>
</tr>
<tr>
<td>Integral form ASTM E2070 Alternative Method</td>
<td>Isothermals</td>
<td>Multiple</td>
<td>Area</td>
<td>Model-Free E</td>
<td>Yes</td>
</tr>
<tr>
<td>ASTM E2041 (Borchardt and Daniels)</td>
<td>Dynamics</td>
<td>One Test</td>
<td>Area</td>
<td>Model-Fitted E and A</td>
<td>No</td>
</tr>
<tr>
<td>Differential Form (Friedmann)</td>
<td>Dynamics</td>
<td>Multiple</td>
<td>Area</td>
<td>Model-Free E, (A, Vyazovkin)</td>
<td>Yes</td>
</tr>
<tr>
<td>Differential Form (Barton)</td>
<td>Dynamics</td>
<td>Two Tests</td>
<td>Area</td>
<td>Model-Free E</td>
<td>Yes</td>
</tr>
<tr>
<td>ASTM E698</td>
<td>Dynamics</td>
<td>Multiple</td>
<td>Tpeak</td>
<td>Model-Free E and A</td>
<td>Yes</td>
</tr>
<tr>
<td>Integral Eqn.’s (Kessinger / Ozawa)</td>
<td>Dynamics</td>
<td>Multiple</td>
<td>T&lt;sub&gt;peak&lt;/sub&gt;</td>
<td>Model-Free E and A</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Table 2.3 Diffusion models and parameters

<table>
<thead>
<tr>
<th>$K_d$</th>
<th>Parameters</th>
<th>Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WLF-W:</strong></td>
<td>$C_1$ Material constant; may be equal to the universal WLF constant of 17.44</td>
<td>Absolute difference $</td>
</tr>
<tr>
<td>$K_d = \exp \left[ \frac{C_1(T - T_g)}{C_2 +</td>
<td>T - T_g</td>
<td>} \right]$</td>
</tr>
<tr>
<td><strong>ML-S:</strong></td>
<td>$A$ Rate constant</td>
<td>Use of Doolittle equation with WLF parameters to describe the state of free volume</td>
</tr>
<tr>
<td>$A = \exp \left[ -\frac{E_d}{RT} \right] \exp \left[ \frac{-b}{f_v} \right]$</td>
<td>$E_d$ Activation energy for diffusion</td>
<td></td>
</tr>
<tr>
<td>$f_v = a_f(T - T_g) + f_g$</td>
<td>$R$ Gas constant</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b$ Material constant</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$f_v$ Free volume</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_f$ Linear expansion coefficient for free volume (0.00048 /°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$f_g$ Free volume at Tg (2.5%, or 0.025)</td>
<td></td>
</tr>
<tr>
<td><strong>CP-C:</strong></td>
<td>$C$ Material constant</td>
<td>Temperature dependence of the critical degree of cure</td>
</tr>
<tr>
<td>$K_d = \exp [-C(\alpha - \alpha_c)]$</td>
<td>$\alpha$ Degree of cure</td>
<td></td>
</tr>
<tr>
<td>$\alpha_c = \alpha_{c,r} T - \alpha_{c,0}$</td>
<td>$\alpha_c$ Critical degree of cure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_{c,r}$ Rate of change of critical degree of cure with temperature, (°C⁻¹)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_{c,0}$ Initial critical degree of cure</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.1 Molecular schematic of (a) the epoxide-amine reactions and (b) etherification by reaction of epoxide and hydroxyl and (c) homopolymerization.
Figure 2.2 (a) Two-dimensional representation of a curing thermoset
Figure 2.2 (b) Degree of cure development during a temperature cycle: thin temperature line represents the programmed cure cycle, and thick temperature line represents the actual part temperature.

Figure 2.3 Free volume change during a two-hold cure cycle.
Figure 2.4 Time-temperature-transformation (TTT) diagram for a thermoset [adapted from Enns and Gillham, 1983]

Figure 2.5 Representation of CFRP and interlayer with thermoplastic particles before cure
Figure 2.6 Twin principle: (a) programmed heating rate, (b) thermal analysis, (c) differential thermal analysis

Figure 2.7 General heat flux set-up; S represents the sample cell/platform and R the reference cell/platform
Figure 2.8 Power compensation DSC by Perkin-Elmer Corp. [adapted from Höhne et al., 1996]: 1 heating wire, 2 resistance thermocouple

Figure 2.9 Thermal analysis cell schematic
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Figure 2.10  Graphical determination of dh/dt for a heat flux DSC curve  
[adapted from Gray, 1968]

Figure 2.11 (a)  Comparison of zerolines for three instruments
Chapter 2: Literature Review

Figure 2.11 (b) Exothermic heat of reaction recorded by three DSC’s

Figure 2.12 MDSC modulated temperature signal overlaid on the average heating rate
Figure 2.13  General isothermal baseline and example of accounting for heat lost during the ramp (curved, dashed line)

Figure 2.14 Four general dynamic baselines scenarios
[adapted from Barton, 1972]
Figure 2.15 Endotherm present due to moisture or physical ageing

Figure 2.16 Heat flow profiles of (a) nth order and (b) autocatalytic reactions
Chapter 2: Literature Review

Figure 2.17 (a) Time-Temperature-Superposition (TTS)

Figure 2.17 (b) Shifted to 170°C
Figure 2.18 ASTM E2041, Borchardt and Daniels [1957] reaction order fitting methodology [adapted from Prime, 1981]

Figure 2.19 Ashby modulus mechanism map [adapted from Gilbert et al., 1986]
Chapter 2: Literature Review

Figure 2.20 TTT diagram [adapted from Gillham, 1986]; thin grey lines are isoconversionals; thick s-shaped curve is the vitrification/devitrification transition; transition zones from liquid to glass

Figure 2.21 CHT diagram [adapted from Wisanrakkit and Gillham, 1991]: dashed lines are cure temperature isorate contours; solid, thin lines are $T_g$ isorate contours; solid, thick line is the vitrification/devitrification transition
Chapter 2: Literature Review

Figure 2.22  TgT property diagram showing zones of material states (liquid to glass) [adapted from Gillham, 1997]

Figure 2.23 Conversion-temperature phase diagram with a constant heating rate trajectory [adapted from Adabbo et al. 1982]
Chapter 3.  METHODOLOGY DEVELOPMENT

This Chapter describes the methods used in this work to analyze and understand the cure behaviour of an epoxy system (T800H/3900-2), and an inter-laboratory Round Robin study which investigated the sources of uncertainty in the measurement-to-modeling decision-making process. The first section details the model selection, fitting and validation process using isoconversionals. The second section presents the development of process maps for visualizing cure behaviour over a wide range of temperatures and conversion, and tracking arbitrary cure cycles. The third section records a comparison of cure models for a commercial epoxy system (Hexcel 8552) as found in the literature. This study was the motivation for the design of a Round Robin to study sources of uncertainty, also outlined in this final section.

3.1.  MODEL SELECTION, FITTING AND VALIDATION METHODOLOGY

3.1.1.  Model selection using cure rate isoconversionals

The concept of cure rate isoconversionals and their use for calculating activation energies and rate constants was discussed in Chapter 2. Cure rate isoconversionals refer to plotting a series of cure rate curves for constant degrees of cure over a range of temperatures. The cure rate is plotted on a natural logarithm scale, and the temperature axis is the inverse of the absolute temperature (K⁻¹) such that a straight line acquires the relationship

$$\ln \left[ \frac{d\alpha}{dt} \right] = -\frac{E}{RT} + \ln[A] + \ln[f(\alpha)]$$

where the slope is the activation energy divided by the universal gas constant, R, and the intercept is (Ln(A) + Ln(f(α))). In the present work, cure rate isoconversionals have been used as a visual tool for collapsing a broad range of data, both isothermal and dynamic, onto a single plot for phenomenological model fitting of chemical and diffusion behaviour. The natural logarithm scale used for cure rate allows comparison of data spanning a 300°C range, and hence changes in reaction mechanism and diffusion behaviour across temperature and degrees of cure is visually interpretable. This strategy also allows cure rates between isothermal and dynamics to be compared when their respective tests overlap the same temperature range. It was also found to be a useful format for presenting the goodness of model fit to data. This section will explore how cure rate isoconversionals can be used to develop phenomenological cure models from single to multiple reactions, and how to evaluate their goodness of fit to the data.
The characteristic isoconversional plots for nth order and autocatalytic behaviour are shown in Figure 3.1 (a) to (e), equations 2.25 and 2.26, respectively. For all four figures, \( E = 61.4 \text{ kJ/mol} \) and \( A = 9.8 \times 10^3 \text{ /sec} \). In Figure 3.1 (a) \( n = 1 \); (b) \( n = 3 \); (c) \( m = n = 1 \); (d) \( m = 1, n = 2 \); (e) \( m = 1, n = 0.5 \). Both isothermal (100 to 240°C in 10°C intervals) and dynamic (0.2 to 5°C/min) model points are shown on the isoconversionals, isothermal designated as squares, and dynamic as circles. The 0.2°C/min symbols are emphasized for clarity. The inset is an isothermal cure rate versus degree of cure profile for guidance.

The following general trends are evident in these plots:

(a) Maximum cure rate for an nth order reaction occurs at the start of the isothermal reaction and at roughly 0.6 for the dynamics, Figure 3.1 (a).

(b) An increase in the order of \( n \) decreases the cure rate faster as cure progresses, creating a greater spread between isoconversionals, and decreases the degree of cure at which the maximum cure rate occurs, Figure 3.1 (b).

(c) Maximum cure rate for an autocatalytic reaction occurs at roughly 0.5 degree of cure for both isothermals and dynamics, Figure 3.1 (c); minimum cure rate occur at lowest and highest degrees of cure, as the bell shape cure rate curve predicts.

(d) When \( n > m \), the peak cure rate occurs at low degrees of cure (below roughly 0.5) and the cure rate at high degrees of cure decreases for both isothermals and dynamics, Figure 3.1 (d).

(e) When \( m > n \), shifts the peak cure rate to higher degrees of cure (greater than roughly 0.5), for both isothermals and dynamics, Figure 3.1 (e).

In the case where there are two reactions occurring at the same time, the above trends for individual reactions can be identified amid the more complex behaviour. For example, consider the addition of two reactions with \( A_1 = 9.8 \times 10^3 \text{ /sec} \), \( E_1 = 61.4 \text{ kJ/mol} \), \( A_2 = 6.34 \times 10^5 \text{ /sec} \), \( E_2 = 72.5 \text{ kJ/mol} \). Figure 3.2 shows the case when the first reaction of lower activation energy is an nth order equation of \( (m_1 = 0, n_1 = 1) \) and the second reaction is autocatalytic with \( n_2 = 1, m_2 = 1 \). The lower activation energy reaction (dominating at low temperatures) has its highest cure rate at low degrees of cure (slightly influenced by the autocatalytic reaction), and the second reaction has a maximum cure rate at 0.4 to 0.5 degree of cure, depending on its dominance over the first reaction. Consider now an additional autocatalytic equation with \( A_3 = 1.5 \times 10^9 \text{ /sec} \), \( E_3 = 101.6 \text{ kJ/mol} \), \( m_3 = 1 \) and \( n_3 = 2 \), Figure 3.3. Note the increase in slope at higher temperatures and the change of maximum cure rate occurring at 0.4 degree of cure at high temperatures, where the reaction dominates. Alternatively, a decrease in slope at low temperatures and high degrees of cure indicates diffusion, Figure 3.4.
3.1.2. Model fitting

As discussed in Chapter 2, calculation of the changes in activation energies with degree of cure and temperature (excluding any data affected by diffusion) can be used to interpret cure mechanisms. The mechanisms for epoxy reactions are well documented: epoxy with primary and secondary amine, etherification and homopolymerization (also discussed in Chapter 2). In the analysis of T800H/3900-2, the change in E with degree of cure and temperature fit into the known ranges for these reactions, Figure 3.5. Cole et al. [1991] provide a set of activation energies which are in good agreement with the literature on epoxy reaction mechanisms: epoxy-primary amine, 61.4 kJ/mol; epoxy-secondary amine, 72 kJ/mol; etherification, 101 kJ/mol. There is not a clearly defined transition between the epoxy-amine and etherification reactions, hence in Figure 5 they are shown to overlap at intermediate activation energies. From this knowledge the data in the isoconversional plot was divided into sections wherein the activation energies matched literature values, and as such were taken as an indication that the cure mechanism dominated, Figure 3.6. Based on identification of the mechanisms on the isoconversional chart, least squares was used to fit the data first to a model for epoxy-amine reactions (since the primary and secondary amine reactions are not readily separable), and then to the etherification reaction at high temperatures and degrees of cure. Isoconversional data showing a decrease at low temperatures was designated as diffusion and treated separately.

The cure rate isoconversional plot can also be used to check for differences in cure rate between isothermal and dynamic test modes. Figure 3.7 shows a case of data wherein the isothermals and dynamics do not overlap. This effect is particularly noticeable at low degrees of cure where cure should be dominated by the chemical reaction and not diffusion. As discussed in Chapter 2, the differences between isothermal and dynamic cure rates are closely linked with measurement and kinetic analysis compatibility between the two test modes. The effect shown in Figure 3.7 was found to be due to a baseline decision, as will be explained further in Chapter 5. This plot provides a quick assessment of this question, and reminds the analyst that the two test modes must overlap in temperature and degree of cure region for proper comparison.

3.1.3. Model validation

A typical model validation, or goodness of fit, tool is a plot of residuals (difference between data and model) versus an independent parameter. Residuals provides an immediate assessment of how close the model fits the data, and whether it over- or under-estimates the data. A cure rate isoconversional dataset can be used to check for goodness of model fit by plotting residual isoconversionals versus temperature.
In this work, residuals were divided by the data to show a measure of percent differences, or model error. This becomes a quick and simple visual tool for sharing the goodness of model fit with users, and identifies the limitations of the model. Figure 3.8 is an example of such a graph for isothermal data for T800H/3900-2; the model fit can be found in Section 5.2.6.

The next step in model validation is to test its predictions against data generated beyond the conditions of the data set used for modelling. This confirmation data should lie within the original data set upon which the model was fitted, and in regions outside of the original dataset which would be useful in practical applications (e.g. shelf life predictions). A logical solution for a cure kinetics model is to test intermediate points along a cure cycle [Ersoy et al., 2003] which would test predictions within the range of the original data set. Validating the model outside the dataset would include any isothermal temperatures not tested, e.g. room temperature cure is not usually modeled but can be measured to confirm the model.

3.2. PROCESS MAPS

This work draws from past visualization techniques for polymer processing (refer to Chapter 2) to suggest a novel mapping technique which is capable of tracking the polymerization and property development throughout the time-temperature stages of typical autoclave, hot press or oven processes. The result is a map that can be easily generated by any process model user without further material testing, needing only the available cure kinetics models and any material property models based on degree of cure and temperature, and a software spreadsheet package. The process map proposed uses axis of cure temperature versus degree of cure, similar to the T_gTP diagrams by Gillham [1997]. The map developed here will be referred to as the process map. The orthogonal axis is used to plot three types of contours: 1.) constant isothermal time; 2.) constant heating rate; and, 3.) constant material property values. The basis for this map is a model for cure rate that is dependent only on temperature and degree of cure. Material properties are in turn dependent on temperature and degree of cure, and hence employ the cure rate model. Ultimately, a user of the process map will be able to follow any combination of isothermal holds and temperature ramps to follow the progress of cure and material property development on a single map.

Predicting the degree of cure at an isothermal temperature is simply done by taking the integral of a cure rate equation. For the examples in this section, the cure model by Hubert et al. [2001] for Hexcel 8552
epoxy resin is used,

\[
\frac{d\alpha}{dt} = \frac{K\alpha^n(1-\alpha)^n}{1 + \exp C\left(\alpha - (\alpha_{c0} + \alpha_{CT}T)\right)}
\]

where \( K = A \exp\left(\frac{-E}{RT}\right) \) and values for parameters are: \( A = 1.53 \times 10^5 \) /sec, \( E = 66.5 \) kJ/mol, \( m = 0.813 \), \( n = 2.74 \), \( C = 43.1 \), \( \alpha_{c0} = -1.684 \), \( \alpha_{CT} = 5.475 \times 10^{-3} /K \). Figure 3.9 shows a series of constant time contours on a process map. A range of time contours from 600 seconds to a relatively long (but arbitrary) 5.3 hours is plotted in increments of 600 seconds. Note that in this plot the minimum plotted temperature is 100 °C for clarity since minimal reaction occurs before this temperature (unless held for very long times). Just as with the TTT diagram, we can overlay the vitrification or glass transition temperature curve, the gelation line, and any other zone of interest. Changes in rate of cure with temperature and degree of cure can be easily visualized on the process map: large distances between curves tells us that the cure rate is fast, and conversely small distances that the cure rate is slow, the lines becoming indistinguishable as diffusion, or mobility restriction, dominates over the cure reaction. By increasing the isothermal time, the blank space in the upper left corner of Figure 3.9 can be filled with constant time contours. In turn, to create more isothermal contours in the lower right corner of the plot, simply reduce the time increment between contours.

Figure 3.10 illustrates how the process map can be separated into the phases identified in the TTT and \( T_g TP \) diagrams [Gillham 1997]. The vitrification/devitrification line (DeBenedetto equation) divides the diagram between the monomer glass transition \( (T_{g0}) \) and ultimate glass transition \( (T_{g\infty}) \), and degrees of cure of 0 and 1. To the right of this line the material is in a glassy form (vitrified), and to the left in a rubbery form (devitrified or un-vitrified). The sol glass (or solid monomer) exists below the gel line, and at low temperatures; if the sol glass temperature is increased without cure beyond the gel line it becomes a liquid. Above the gelation line and before full cure, the material to the left of the vitrification/devitrification line is a sol/gel glass. If the temperature of the sol/gel glass is raised such that the material devitrifies before full cure is reached, the material becomes a sol/gel rubber. At full cure and at temperatures below \( T_{g\infty} \) the material is a gel glass, and above \( T_{g\infty} \) the material becomes a gel rubber.

Cure advancement during a temperature ramp can also be conceptualized on the process map by solving Equation 3.2 for a temperature that is changing with time from a fixed start temperature (e.g. room temperature) via the Arrhenius term. Figure 3.11 illustrates how a family of curves can be found at various heating rates for a constant initial degree of cure \( (\alpha_i = 0.001) \). This type of contour will be known
as *dynamic* contours. The isothermal and dynamic process maps can be overlaid on a single plot, Figure 3.12. The key behind moving between isothermal and dynamic contours is to remember that a specific microstructure is attributed to a given degree of cure, irrespective of the cure cycle path to achieve that microstructure. Here is an example for how to follow a single-ramp, single-hold cure cycle, Figure 3.13:

1. Start at $T = \text{room temperature}$, initial degree of cure $\sim 0$
2. Heat at 1 °F/min = 0.55 °C/min to 180 °C. On the $\alpha$-T map, we follow the first heating contour to 180 °C. The degree of cure after this heating ramp is 0.65.
3. We wish to hold at 180 °C for a time of 1 hour (3600 seconds). Since the isothermal contours are spaced 600 seconds apart, a 1-hour hold is equivalent to 6 contour lines. We plot our cure path by moving vertically to the sixth isothermal contour (ninth contour starting from zero time). The final degree of cure is 0.81.

The comparison of various heating rates with respect to the gel point in Figure 3.11 illustrates the importance of choosing the appropriate heating rate for a given material system. It is evident even from this plot that a slower heating rate allows time for the degree of cure to surpass gelation on the heat-up to the hold. It is well documented that mismatches between tool and part CTE’s cause the build-up of residual stresses if heating occurs past gelation, possibly leading to warpage. Choosing a heating rate of 1.65 °C/min would have been too fast for appreciable cure to occur before the isothermal hold at 180 °C.

Figure 3.13 is limited to plotting only single-ramp, single-hold cure cycles because there are no further dynamic contours to move to at the end of an isothermal hold. Alternatively, the heating rate can remain constant and the initial degree of cure, $\alpha_{n-1}$, can be varied to give a T-$\alpha$ map for a single ramp rate, with contours starting at various degrees of cure, as in Figure 3.14. Now any cure cycle using a constant ramp rate between numerous isothermal holds can be charted to follow the progress of cure at any point during the cycle. The procedure is to follow the appropriate contour as far as is appropriate, and then to move to the equivalent contour for the next stage, and so forth. An example of a multi-ramp, multi-hold cycle is shown on Figure 3.15 and described below with a heating rate of 3 °C/min:

1. Start at $T = \text{room temperature}$, initial degree of cure $\sim 0$
2. Heat at 3 °C/min to 140 °C. On the $\alpha$-T map, we follow the first heating contour to 140 °C. The degree of cure after this heating ramp is 0.04.
3. We wish to hold at 140 °C for a time of 1 hour (3600 seconds). Since the isothermal contours are spaced 600 seconds apart, a 1-hour hold is equivalent to 6 contour lines. We plot our cure path by moving vertically to the sixth isothermal contour (ninth contour starting from zero time). The degree of cure after this first isothermal hold is 0.07.
4. A second heating ramp is required to reach the cure temperature of 180 °C. The appropriate
heating ramp contour must pass through the degree of cure coordinate achieved at the end of the 140 °C isothermal hold. By inspection, it is clear that this point is equivalent to an isothermal hold of the material at 180 °C for 16.5 minutes (990 seconds), 1.65 contour lines.

5. The 180 °C isothermal hold lasts 140 minutes (8400 seconds). Simply follow a horizontal path to cover 14 contour lines. The final degree of cure is 0.83 for this particular material and cure cycle.

A limitation of Figure 3.15 occurs for the case when a very high ramp rate (practically instantaneous such that there is no cure advancement) is used to reach a high temperature followed by a lower ramp rate the same as the T-α map. Essentially the initial temperature becomes the elevated temperature in the Arrhenius and diffusion terms with zero initial degree of cure, equation 3.2. In the general case, a series of temperature ramp curves can be created with increasing initial temperature (T_{elevated}) at zero degree of cure as in Figure 3.16.

\[ \alpha_n = \alpha_0 + Ae^{-E/RT_{elevated}} \cdot f(\alpha) \cdot \Delta t \]  

3.3

This additional information becomes useful when considering the advancement of cure for many small-scale characterization tests using equipment such as a DSC or DMA that can achieve very fast heating rates.

Another advantage of the T-α map is that the contours of constant time can be changed to any constant property contour (e.g. viscosity), and the cure path (e.g. from Figure 3.13 or 3.15) can be overlaid to follow the build-up of that property during the process cycle. For example, this is a useful tool when selecting the appropriate cure cycle as not only the final degree of cure is important to know, but also when cure surpasses the gelation point during the cure cycle (as previously discussed), what cure rates avoid high exothermic reaction temperatures, and how long a material remains at low viscosity for the release of voids before cure build-up. One of the greatest influences of such matters in a cure cycle is the heating rate.

Figure 3.17 illustrates contours of constant cure rate, overlaid with the cure path of Figure 3.13. Cure rate contours start at 0.00003 /sec and increase by increments of 0.00002 /sec. Higher heating rates reach higher cure rates, particularly at elevated temperatures. Without information on the thermal boundary conditions of the process it is difficult to assess whether or not the exothermic reaction will cause excessive temperatures above the programmed cycle temperature, but indication of a high cure rate should trigger the need to validate the use of high heating rates to avoid an uncontrolled reaction or possible material degradation.
The same cure paths are overlaid onto a T-α map containing contours of constant viscosity in Figure 3.18. The contours increase by multiples of 2, ranging from 0.05 to 52428.8 Pa·sec. It is evident that a higher heating rate maximizes the time at low viscosities for the release of voids. This plot also illustrates the rate of viscosity build-up with cure, quickening as gelation is approached as represented by the decreasing distance between contours.

The following example will illustrate how the process map can be used to design an autoclave cure cycle for a common CFRP, Hexcel AS4/8552. Using the previous information mapped for the three heating rates, a cure cycle can be constructed which takes advantage of reasonable cure rates to control the reaction exotherm, maximizes time in the low viscosity region to remove volatiles and voids, minimizes processing time, and ensures that gelation does not occur during a heating ramp. To minimize process time, the fastest heating rate would be desirable, 3°C/min. A relationship developed by Rasekh et al. [2004] was used to determine the maximum allowable cure rate to avoid a temperature increase greater than 5°C,

\[
\frac{d\alpha}{dt} = \frac{1}{H_r} \left[ \frac{R \cdot a}{L^2} + \frac{dT}{dt} \right] \frac{\rho_r C_{p_r}}{\rho_c V_r}
\]  

where \( R \) is a parameter defined in the Rasekh work as \( R = \frac{\Delta T}{(0.5 + B_i^{-1})}, \) where \( \Delta T \) is the temperature rise due to reaction heat, \( B_i \) is the Biot number \( (hL/K) \), \( h \) is the autoclave convection, \( L \) is the composite half thickness, \( K \) is composite conductivity, \( H_r \) is the resin heat of reaction, \( a \) is the diffusivity, \( \rho_r \) and \( \rho_c \) are the densities for resin and composite, \( V_r \) is the resin volume fraction, and \( C_{p_r} \) is the composite specific heat. In this example it is assumed that the tool is very thin and hence does not contribute largely to the heat transfer analysis. The parameters used are recorded in Table 3.1, which resulted in a maximum cure rate of 0.00049 /sec for a part that is 54 ply thick (10.13 mm if a single ply is 0.1875 mm thick). Assume the viscosity should remain below 6.4 Pa·sec for at least 1 hour to remove sufficient volatiles and voids (in combination with applied pressure). Figure 3.19 shows the isothermal and heating rate contours (3°C/min) overlaid with the boundary conditions for cure rate and viscosity. Within these bounds a cure cycle 222 minutes long has been drawn to achieve the above stated conditions:

1. The low viscosity region begins at 116 °C, which would only allow 24.15 minutes in this region if there were no holds. An isothermal hold at 140 °C is added to make up for the remaining time required in the low viscosity zone. This intermediate temperature is selected because it is evident from the α-T map that higher temperatures will advance the cure beyond
the low viscosity zone such that the time in this zone will not meet the void removal requirement. Following only this logic, the intermediate hold time at 140 ºC should be 36 minutes.

2. The isothermal hold time at 140 ºC is lengthened to 45 minutes and a second isothermal hold is added at 163 ºC for 8 minutes to avoid going beyond the maximum allowable cure rate during further heating ramps.

3. The final isothermal temperature is selected to be 180 ºC for this example in order to achieve the highest degree of cure possible without the temperature ramp continuing beyond gelation or into the high cure rate zone. The duration should be at least 2 hours.

In the remainder of this work, the process map will be employed to demonstrate the capability of models (including any discontinuities in data they generate), and to compare material behaviour captured by different models for the same material.

### 3.3. **Motivation and Design for a Round Robin Study**

#### 3.3.1. Retrospective study of variability in the decision-making process for cure kinetic models proposed in the literature for 8552

Ten cure models were found in the literature for Hexcel 8552 (resin and prepreg), and five estimations of the Tg-α relationship. Hexcel (formerly Hercules) 8552 is a TGDDM epoxy matrix for use in primary aerospace structures, toughened with a DDS amine (tetruglycidyl-4,4’-dimainodiphenylmethane-4,4’-diaminodiphenyl sulfone). The matrix is also supplied with unidirectional or woven carbon or glass fibres. The studies on prepreg found in the literature had carbon fibres (designation AS4) at 35wt%. The Manufacturer’s Recommended Cure Cycle (MRCC) for the epoxy system differs slightly between product data sheets for United States and the European Union. The basic time-temperature schedule is recorded here:

1. US: Ramp at 1.8-3°C/min (3-5°F/min) to 107°C (225°F); EU: Ramp at 1-3°C/min (2-5°F/min) to 110°C (230°F).
2. US: Hold at 107°C for 30-60 minutes; EU: Hold at 110°C for 60 minutes.
3. US: Ramp at 1.8-3°C/min (3-5°F/min) to 177°C (350°F); EU: Ramp at 1-3°C/min (2-5°F/min) to 180°C (356°F).
Table 3.2 records the authors and year of publication, material (resin or prepreg), heat of reaction, experimental conditions, models and constants, and details about the model parameters. Of the ten models, two are only applicable to dynamics because of their heating rate dependent terms [Sun et al., 2002 (b); Costa et al., 2005]. As a first comparison, the predictions for all models are plotted for a 1.8°C/min ramp up to 177°C, Figure 3.20. The variability at the end of the ramp for degree of cure is 0.44 ± 0.26 (57.6%). Figure 3.21 (a), (b) and (c) illustrate the model predictions of degree of cure with time for the lower and upper bounds of the MRCC, 1, 1.8 and 3°C/min heating ramps, respectively. The two dynamic models are not included since they cannot accommodate isothermal holds. It is evident from this plot that no two models predict the same progression of cure, nor the same final degree of cure. Reasons for the differences between predictions stem from the components of various models, differences in experimental method, and possibly even measurement errors and differences between batches of material. Figure (c) shows the consequence of using the lowest rated heating rate. Gelation (roughly 0.5 degree of cure) occurred during a ramp which could have resulted in residual stress build-up. Figure 3.22 shows the Tg-α relationships in the literature. The variation between models was captured quantitatively by comparing several critical points along the MRCC: 1. the time to reach gelation at the MRCC’s cure temperature; this is a value that is given in some product data sheets; 2. the degree of cure and Tg at the start of the isothermal hold, which can be related to residual stress build-up if the gel point was passed during the ramp; 3. the maximum cure rate within the MRCC limits, which in turn was used to calculate the maximum allowable part thickness such that the temperature of the part does not increase beyond 5°C during autoclave processing; and, 4. the final degree of cure and Tg after the isothermal hold which reflect the strength of the material used for parts. The averages and standard deviations are reported below (models by Ng, Costa and Sun (b) were not used in these calculations):

1. Time to gelation at 177°C (estimated to be 0.5 degree of cure): 18.29 ± 6.97 min (38.1%)
2. Degree of cure before final hold:
   a. 1.8°C/min ramp: 0.50 ± 0.24 (46.7%); Tg at 0.5 degree of cure according to Figure 3.22 varies between 65 and 113 °C.
   b. 3°C/min ramp: 0.44 ± 0.22 (52.0%); Tg at 0.29 degree of cure according to Figure 3.22 varies between 48 and 96 °C.
3. Degree of cure after the final hold:
   a. 1.8°C/min ramp: 0.89 ± 0.08 (8.6%); Tg at 0.89 degree of cure according to Figure 3.22 varies between 176 and 213 °C.
   b. 3°C/min ramp: 0.89 ± 0.08 (8.6%).
The variability between predictions by these models is appreciable. Perhaps the error for the final degree of cure (not Tg) is within experimental limits, but all other errors are not acceptable. A brief discussion will be presented here to highlight probable explanations for the variation in model predictions.

The authors vary in their choice of temperature range, experimental program (isothermal or dynamic temperature scan), and type of measurement (heat of reaction or temperature at peak heat flow deflection). Sun et al. [2002b] and Costa et al. [2005] used dynamic experiments exclusively. Both groups used the peak temperatures as a means of monitoring the degree of cure rather than the area under a heat flow versus time curve (Ozawa’s method [1970]), and developed heating rate dependent terms such that the model is not useable during an isothermal hold. The rest of the models were derived from isothermal experiments and area measurements. No group compared both isothermal and dynamic experiments. The downside of using dynamics exclusively is that they do not describe diffusion behaviour (unless very low rates are used) and their potentially high temperature ranges may enter into different mechanisms than those which occur at low temperatures. The result is an overestimation of the cure rate at low temperatures and low degrees of cure, as observed for the Sun et al. (b) and Costa et al. models. The same error may occur if too much importance is placed on fitting very high isothermal temperatures; it is difficult to discern if this was the case for Sun et al. (a). The model by Ng et al. [2002] shows a severe lag in cure development. It is questionable whether or not the parameters reported for this model are correct. Details are not offered as to how they proved the cubic model to fit the 8552 data, but it is surmised that they were fitting the cure rate versus degree of cure data. The model used in works by Ersoy et al. [2005] also shows a delay in comparison to other models. This group used residuals and area measurements to develop their cure model. Unlike any other model in this review, the Ersoy 2005 work demonstrated the ruggedness of their model by testing intermediate points along the cure cycle for Tg and degree of cure, which showed their model timing to be accurate. However, their Tg development with degree of cure is shown to be considerably delayed compared to other models in Figure 3.22. The variation in the interpretation of cure rates at low temperatures and degrees of cure may also be due to instrumentation restrictions. Isothermal DSC methods are well known for their inaccuracies at the beginning of tests due to instrument sensitivity at low degrees of cure, and temperature equilibrium to achieve the ideal situation of subjecting the sample instantaneously to an elevated temperature; hence the attraction of dynamic methods.

With respect to the variation in final degree of cure and rate of approach to this value, Ersoy et al. [2005], Hubert et al. [2001] and Sun et al. [2002a] employed a denominator to account for the change from a
chemical to a diffusion dominated reaction at vitrification, and Opalicki et al. [1996] used the WLF equation. As discussed in Appendix B, both of these methods have the same origins.

In summary, there are several factors which may have contributed to the variability between models. These factors are difficult to test since authors provided limited information in some cases, and there is no consistent reporting scheme within the cure modeling community:

1. Material quality control. Batch-to-batch variability and possible changes to the chemistry (the findings span a decade). The state of the material before cure testing was not reported, and hence the history of the material is unknown.

2. Unknown instrument and measurement quality (no basis for comparison), and a wide variety of instruments used.

3. Data reduction decisions were not consistently reported. It is not always stated whether zerolines were removed, what the baselines were, or if $H_{\text{Total}}$ always equalled $H_{\text{Ultimate}}$.

4. Comparing both resin and prepreg. Opalicki et al. [1996] showed a change in timing between the two.

5. Chemical model accuracy. Models that cannot handle both dynamic and isothermal predictions will only have limited use. Whether or not a model attempts to predict the mechanisms laid out in the literature by authors such as Horie [1974] and Cole [1991] is another factor that will affect accuracy. Sun et al. [2002b], Buczek et al. [1999], Opalicki et al., and Antonucci et al. [2002] have used a two reaction model. Sun et al. and Antonucci et al. suggest an activation energy which is in the cited range for etherification. Model complexity is better observed by low dynamic tests. A 10°C/min heat flow profile will not show the temperature ranges of individual mechanisms, however, an isoconversional cure rate plot should still show the change in slope at high temperatures and degrees of cure.

### 3.3.2. Design of a Round Robin study to test sources of uncertainty in cure kinetics analysis

Sources of uncertainty in cure kinetics testing by DSC and modeling can be arranged into eight categories: 1) sample preparation; 2) equipment selection; 3) experimental design; 4) measurement; 5) data reduction; 6) data analysis; 7) model selection; and, 8) fitting the model to data. Within each category, a myriad of issues can arise to compromise the accuracy of measurements and models. A
Round Robin study was designed to isolate the major sources of uncertainty by asking participants to repetitively develop a model for the same material, wherein each round of the study eliminated one category of uncertainty. In the interest of time, two elimination stages were pursued after participants completed a first stage of generating their own data and models: 1) experimental design and measurements; 2) data reduction. The three stages of the Round Robin are outlined in Table 3.3.

### 3.3.2.1. Expectation of participants

Participants were asked to join the study based on their experience in cure kinetics analysis. Although the actual experimentalist need not have had extensive experience with cure kinetics measurement and modeling, it is expected that the knowledge of the laboratory will be at their disposal and that appropriate instrument calibration and experimental/data analysis procedures will be applied. The purpose is not to test the proficiency of a laboratory to produce reliable cure kinetics models, and as such the proficiency of participating laboratories was not identified at any time during the study, nor will be in the subsequent publication of study findings (i.e. data and model identification was and will be confidential in all publications and correspondence).

The following aspects of commitment were required of each laboratory coordinator, the details of which were based on the recommendations of ASTM E 691 for conducting interlaboratory studies, and were formalized in a statement to be signed and returned to the UBC Composites Laboratory as part of the agreement to participate in this Round Robin (see the section on Agreement forms in Appendix C):

i. Adherence to manufacturer's specifications for DSC calibration and operation;

ii. Attention to safe handling and proper storage of materials;

iii. Ensuring that all participants in the Round Robin are familiar with the testing and data analysis for cure kinetic model development. The importance of familiarization cannot be overemphasized. Many interlaboratory studies have turned out to be essentially worthless due to lack of familiarization [ASTM E691]. More than one person may participate in the study from each laboratory (e.g. one person to perform the testing, and another to perform the data analysis), but these participants must consistently perform the same task for the duration of the Round Robin;

iv. All testing and data analysis are performed with due diligence but not under irregular circumstances to the normal operation of the participating laboratory;

v. To return all data and reports as requested according to the study time-line;
vi. Any questions or errors regarding the procedure will be reported immediately to the Round Robin Coordinator.

### 3.3.2.2. Material quality control

The state of the material prior to testing at the location of each participant was requested in the form of its measured $T_g_0$. Material mailed to participants was tracked for ‘out-of-storage-time’ until arrival and storage in the participant’s freezer at -20°C. The material was sealed with desiccant in plastic bags for shipping, but was not packed in dry ice. A piece of the material was requested to be mailed back to the UBC laboratory as a second confirmation that the state of the material did not change during shipping. The shelf-life for T800H/3900-2 was unknown, but that reported for 8552 by Hexcel is a 10 day tack life at 21°C and 12 months at -18°C, from the date of manufacture. The Material Received Response Form is recorded in Appendix C. The findings are reported in Chapter 5 along with the Round Robin results.

### 3.3.2.3. Testing instrument quality

A set of tests was designed to determine the quality of participating instruments in terms of heat flow signal in terms of noise, repeatability and reproducibility. Three types of tests were requested: 1) five dynamic zero-line tests (heat flow measurement without samples or sample containers), and two isothermal zero-lines, to determine noise and the repeatability of the instrument heat flow signal; 2) three dynamic tests on standard materials, tin and indium, to determine reproducibility and calibration accuracy; and, 3) three dynamic tests on the CFRP system T800H/3900-2 to determine reproducibility of the signal across a broad temperature range. The descriptions of these tests and forms to report the findings are reported in Appendix C. The results of the instrument quality tests are reported in Chapter 5.

### 3.3.2.4. Guidelines for testing and reporting results

General guidelines for testing were suggested to participants, such as sample and test randomization and safety precautions. For each of participant analysis, a general format was proposed for the reporting of results. For stages 1 through 5, Appendix C details the guidelines sent to participants.
Table 3.1 Parameters and values used to calculate the maximum cure rate for a process map example

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoclave convection, h</td>
<td>100</td>
<td>W/m²</td>
</tr>
<tr>
<td>Composite conductivity, K</td>
<td>0.69</td>
<td>W/mK</td>
</tr>
<tr>
<td>Number of plies</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Ply thickness</td>
<td>0.1875</td>
<td>mm</td>
</tr>
<tr>
<td>Maximum allowable temperature increase due to reaction exotherm, ΔT</td>
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<td>K</td>
</tr>
<tr>
<td>Resin heat of reaction</td>
<td>550E3</td>
<td>J/kg</td>
</tr>
<tr>
<td>Composite specific heat, Cpₜ</td>
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<td>J/kgK</td>
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<td>Composite density, ρₜ</td>
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<td>Resin density, ρᵣ</td>
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<td>kg/m³</td>
</tr>
<tr>
<td>Resin volume fraction, Vᵣ</td>
<td>57.42</td>
<td>%</td>
</tr>
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</table>

Table 3.2 Literature review of models and parameters for Hexcel 8552

<table>
<thead>
<tr>
<th>Group / Model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hubert et al. 2001</td>
<td>( A = 1.53E5 ) /sec, ( E = 66500 ) J/mol, ( m = 0.813 ), ( n = 2.74 ) ( C = 43.1, a_{C0} = -1.684, a_{CT} = 0.00548 /K ) ( a_{gel} = 0.47 )</td>
</tr>
<tr>
<td>Ersoy et al. 2005</td>
<td>( A = 7E4 ) /sec, ( E = 65000 ) J/mol, ( m = 0.5 ), ( n = 1.5 ) ( C = 30, a_{C0} = -1.515, a_{CT} = 0.00517 /K ) ( T_g = 286\alpha - 78 ) (ºC) ( a_{gel} = 0.31 )</td>
</tr>
<tr>
<td>Player et al. 2000</td>
<td>A₁ = 1.27E5 /sec, E₁ = 63400 J/mol, m = 0.9, n = 2.1</td>
</tr>
<tr>
<td>Antonucci et al. 2002</td>
<td>A₁ = 84.6 /sec E₁ = 49800 J/mol ( A₂ = 119372 /sec, E₂ = 64707 J/mol ) ( A₃ = 2.45E24 /sec, E₃ = 262556 J/mol ) ( m₁ = 1, n₁ = 2.24, n₂ = 1.219 )</td>
</tr>
</tbody>
</table>

Table continued on next page
### Table 3.2 Continued

<table>
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<tr>
<th>Source</th>
<th>Prepreg: A1 = E1 = 8.06E5 /sec, E2 = 72722 J/mol</th>
<th>A2 = 1.25E4 /sec, E2 = 65639 J/mol, r = 1</th>
<th>( \ln k_d(T) = -77.8 /sec + 0.1536(K/sec)*T ), C1 = 9.66 /sec, C2 = 50 K</th>
<th>Resin: A1 = 1.09E6 /sec, E1 = 81984 J/mol</th>
<th>A2 = 175.9 /sec, E2 = 50225 J/mol</th>
<th>r = 1</th>
<th>( \ln k_d(T) = -78.09 /sec + 0.1585(K/sec)*T ), C1 = 10.33 /K/sec, C2 = 50 K</th>
<th>Tg = 267.36 + 232.12*( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opalicki et al. 1996</td>
<td></td>
<td></td>
<td>( \frac{d\alpha}{dt} = k(\alpha + B)(1-\alpha)(r-\alpha) )</td>
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<td></td>
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<tr>
<td></td>
<td>( \ln k_d(T) = \ln k_d(T_g) + \frac{C_1[T-T_g(\alpha)]}{C_2 + [T-T_g(\alpha)]} )</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sun et al. 2002 (a) I</td>
<td>A1 = 2416 /sec, E1 = 57300 J/mol</td>
<td>A2 = 0.6 /sec, E2 = 19600 J/mol</td>
<td>m = -0.0145/(K)*T + 7.61 , n = 150/(K)*T + -0.0095</td>
<td>C = 48.75, a( C_0 ) = -0.93, a( C_T ) = 0.0039 /K</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sun et al. 2002 (b) D</td>
<td></td>
<td>m1 = -0.288/(K)*T + 0.553, n1 = 2.603</td>
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<td></td>
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<td></td>
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<td>A1 = 1.52E9 /sec, E1 = 114770 J/mol</td>
<td>m2 = 0, n2 = -0.219/(K)*T + 0.779</td>
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<td>Sun et al. 2006</td>
<td>Tg0 = 1.4°C, Tg∞ = 231.5°C, ( \lambda ) = 0.64, a gel = 0.513</td>
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<tr>
<td>Ng et al. 2002</td>
<td>A1 = 1.67E+03 /sec, E1 = 5.09E+04 J/mol</td>
<td>A2 = 5.15E+03 /sec, E2 = 5.70E+04 J/mol</td>
<td>A3 = 1.04E+07 /sec, E3 = 9.07E+04 J/mol</td>
<td>A4 = 0, E4 = 0</td>
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<tr>
<td>Costa et al. 2005</td>
<td></td>
<td>n2 = -3.26/(K)*T +1.45</td>
<td></td>
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<td>Zukas and Ghiorse 2001</td>
<td></td>
<td>0-0.44 DOC: 159°C*( \alpha ) + 5</td>
<td>0.44-1 DOC 295°C*( \alpha ) - 52.8</td>
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<td>Bilyeu et al. 2002</td>
<td>Tg0 = 6°C</td>
<td>Tg gel = 86°C</td>
<td>Tgα = 248°C</td>
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### Table 3.3 Round Robin scheme for cure kinetics measurement and modeling

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I: Individual decision by each participant; C: Common decision for all participants
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Figure 3.1 (a) Cure rate isoconversionals, one nth order reaction 
(A = 9.0E3 /sec, E = 61.4 kJ/mol, n = 1), ■ isothermals, ● dynamics, 
0.2°C/min

Figure 3.1 (b) Cure rate isoconversionals, one nth order reaction 
(A = 9.0E3 /sec, E = 61.4 kJ/mol, n = 3), ■ isothermals, ● dynamics, 
0.2°C/min
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Figure 3.1 (c) Cure rate isoconversionals, one autocatalytic reaction
\( (A = 9.0 \times 10^3 \text{ /sec, } E = 61.4 \text{ kJ/mol, } m=1, n = 1) \), ■ isothermals, ● dynamics, ● 0.2°C/min

Figure 3.1 (d) Cure rate isoconversionals, one autocatalytic reaction
\( (A = 9.0 \times 10^3 \text{ /sec, } E = 61.4 \text{ kJ/mol, } m=1, n = 2) \), ■ isothermals, ● dynamics, ● 0.2°C/min
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Figure 3.1 (e) Cure rate isoconversionals, one autocatalytic reaction
(A = 9.8E3 /sec, E = 61.4 kJ/mol, m =1, n = 0.5), ■ isothermals, ● dynamics, ● 0.2°C/min

Figure 3.2 Cure rate isoconversionals, two reactions (A₁ = 9.8E3 /sec, E₁ = 61.4 kJ/mol, m₁ = 0, n₁ = 1, n₂ = 1, m₂ = 1), ■ isothermals, ● dynamics, ● 0.2°C/min
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Figure 3.3 Cure rate isoconversionals, three reactions ($A_1 = 9.8E3$ /sec, $E_1 = 61.4$ J/mol, $A_2 = 6.34E5$ /sec, $E_2 = 72.5$ kJ/mol, $A_3 = 1.5E9$ /sec, $E_3 = 101.6$ kJ/mol, $m_1 = 0$, $n_1 = 1$, $n_2 = 1$, $m_2 = 1$, $m_3 = 1$, $n_3 = 2$), ■ isothermals, ● dynamics, ● 0.2°C/min

Figure 3.4 Cure rate isoconversionals, diffusion at low temperatures and degrees of cure, ■ isothermals, ● dynamics, ● 0.2°C/min
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Figure 3.5 Activation energies calculated (no diffusion) by isoconversional method for T800H/3900-2 match values for mechanisms in literature

Figure 3.6 Designating mechanisms to temperature-degree of cure zones on the isoconversional plot for an epoxy system
Figure 3.7 Cure rate isoconversionals, differences between isothermal and dynamic cure rates

Figure 3.8 Percent difference between model and data
Figure 3.9 Step 1 of process map construction: constant time contours for 8552 [Hubert et al. 2001]; representative vitrification line

Figure 3.10 Thermoset phases identified on the T-α process map
Figure 3.11 Step 2 of process map construction: constant heating rate contours, 8552 [Hubert et al., 2001]

Figure 3.12 Overlay of constant time and heating rate contours, 8552 [Hubert et al., 2005]
Figure 3.13 Example 1: single ramp and single hold, 8552 [Hubert et al., 2001]

Figure 3.14 Step 3 of process map construction: constant heating rate contours for a single ramp rate, starting at various initial degrees of cure, 8552 [Hubert et al., 2001]
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Figure 3.15 Example 2: multiple ramp and multiple hold, 8552 [Hubert et al., 2001]

Figure 3.16 Step 4 of process map construction: heating rate contours starting from elevated temperatures, 8552 [Hubert et al., 2001]
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Figure 3.17 Cure path overlaid on contours of constant cure rate, 8552 [Hubert et al., 2001]

Figure 3.18 Cure path overlaid on contours of constant viscosity, 8552 [Hubert et al., 2001]
Figure 3.19 Example 3: cure cycle selection, 8552 [Hubert et al., 2001]

Figure 3.20 8552 model comparison: 1.8°C/min ramp to 177°C hold
Figure 3.21 (a) 8552 model comparison: 1°C/min ramps to 107 and 177°C holds

Figure 3.21 (b) 8552 model comparison: 1.8°C/min ramps to 107 and 177°C holds
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Figure 3.21 (c) 8552 model comparison: 3°C/min ramps to 107 and 177°C holds

Figure 3.22 8552 model comparison: 3°C/min ramps to 107 and 177°C holds
Chapter 4. MATERIAL AND EXPERIMENTAL PARAMETERS

4.1. 3900-2 RESIN AND T800H/3900-2 PREPREG MATERIAL INFORMATION

This section summarizes knowledge gleaned from patents and studies in the literature on the material studied in this work, T800H/3900-2. Two patents exist on the material, several papers on strength and toughness properties, and one previous study on cure kinetics. Due to propriety restrictions, the exact components (reacting and non-reacting), their percent weight and structure are unknown to the user. The history of the material as received for the present work is also noted in this section with information concerning changes with storage and out-time.

4.1.1. Resin chemistry and reactions during cure

A brief makeup and history has been collected from patents and journal articles and is included here and in the next section. In summary, T800H/3900-2 contains three components [Odagiri et al., 1991; Kishi et al., 1995]:

(A) Carbon fibres (T800H), 145 g/m² fiber areal weight

(B) Resin (3900-2) of a predominantly TGDDM (tetraglycidyl-4,4’-diaminodiphenylmethane) epoxy in combination with DDS (4,4’-Diaminodiphenyl sulfone) amine. The matrix is modified with a thermoplastic for improved toughness and is claimed to be a polyimide (additionally, a polyimide having a hexafluoropropane skeleton), or a block or graft copolymer having chain segments miscible with the thermosetting resin (specifically, a polyimide block copolymer comprising siloxane chain segments). The prepreg has 35 percent resin content by weight.

(C) There is an additional interlayer on the surface of the resin-fibre composite composed of resin (presumably the same as the matrix, but not clearly specified in the literature), with fine particles of amorphous polyamide

Tetraglycidyl-4,4’-diaminodiphenylmethane (TGDDM) is a tetra-functional epoxy, meaning that there are four epoxide molecules from which to create crosslinks with amine, Figure 4.1 (a). Correspondingly, the 4,4’-diaminodiphenyl sulfone (DDS) has two amine groups to react and create crosslinks, Figure 4.1 (b). The exact polyamide formulation is unknown. An early paper by Muraki et al. [1986] stated that an
amorphous polyamide with Tg of 150°C (TN-55 manufactured by Emser Werke) resulted in desired compression strength after impact (CAI) properties and a two phase structure of uniformly dispersed large particles which favoured a higher prepreg Tg than finely dispersed particles. Other candidates for second phase materials discussed in that paper included polyvinylformal, flexible polyamide, and high modulus thermoplastic, but the final selection was not revealed.

4.1.2. History of T800H/3900-2 prepreg

The development of T800H/3900-2 stems from Toray Composites America’s response to the aerospace industry’s demand for composites achieving higher strength, modulus and toughness in order to transition from their use in secondary airplane structures (fairings, cowlings, and radomes) to primary structures (wing box, fuselage), [Muraki et al., 1986; Odagiri et al., 1988]. To address toughness, a thermoplastic was added to the resin matrix and was denoted as the #3632 matrix system, for which the chemistry is unknown but the modifier was suggested to be either polyvinylformal, flexible polyamide, amorphous polyamide, polysulfone, or polyethersulfone [Muraki et al., 1986]. In 1988, Odagiri et al. publicized a new type 3900 series resin based on 3632 resin (identical curing reactivities), but the thermoplastic modifier technology was claimed to be improved and to have benefited impact and processing performance. The chemistry was not revealed, but in 1991 details were released in a conference proceeding to specify that the resin is a 177°C cureable TGDDM/DDS system, and the prepreg has 145 g/m² fiber areal weight and 35 wt% resin content by weight [Odagiri et al., 1991].

A U.S. patent was issued on behalf of Torayca by Odagiri et al. [1991] regarding a “thermoplastic-particulate interlayer toughening technology”, or heterogeneous interlayer. The interlayer technology developed by Toray consists of a base resin and fine thermoplastic particles placed on the surface of the prepreg to promote adherence between prepreg layers, Figure 4.2. The patent gives a broad range of material components suitable for the technology for the resin matrix, thermoplastic toughner, fibres and particles. Work on the T800H/3900 system by Nam and Seferis [1993] further states that the interlayer technology is used in this prepreg system and that the particles are an amorphous polyamide. Further clues to the chemistry of this prepreg system and interlayer technology are made in a patent by Kishi et al. [1995]. This patent was written to take into account the uncured and cured resin, but also claimed the following helpful information to add to our understanding of the prepreg system, in addition to what is stated above:

- 90% of the particles used in the interlayer should be localized in the region from the surface to a depth of 15% of the thickness of the prepreg.
- The thermoplastic in the matrix is claimed to be a polyimide (additionally, a polyimide having a hexafluoropropane skeleton), or a block or graft copolymer having chain segments miscible with the thermosetting resin (specifically, a polyimide block copolymer comprising siloxane chain segments).

- The content of thermoplastic resin in the thermoset resin is preferably 5-40% by weight, and more preferably 8-30% by weight with respect to the total components in the thermoset. This amount of thermoplastic will have a sufficient toughness-increasing effect while remaining easy to handle.

- The average thickness of the interlayer zone upon cure is 10-70µm and the distribution in the thickness of the interlayer zone is not more than 50 in terms of CV (standard deviation divided by the average thickness of interlayer zones, %).

- Fluctuation of the fabrication conditions such as heating rate, curing temperature and pressure do not affect the impact resistance.

As stated in the 1995 patent, the content of the thermoplastic resin in the element [B] may preferably be 5-40% by weight, more preferably 8-30% by weight with respect to the total components in the element [B]. If the content of the thermoplastic resin is within this range, toughness-increasing effect is sufficiently obtained while preventing the substantial deterioration of the ease of handling.

Okabe and Takeda [2002] published an evaluation of the interlaminar properties of the T800H/3900-2 prepreg system using an ultrasonic micro-spectrometer on the exposed interlaminar region. The interlaminar layer was assumed to be isotropic and found to have the following property ranges: Young’s modulus, $E = 3.5-4.8$ GPa; Poisson’s Ratio, $\nu = 0.24 - 0.42$; density, $\rho = 1.05-1.35$ (g/cm³); thickness = 12.5-17.5 µm. The average thickness of each ply was reported as 192 µm.

The manufacturer’s recommended cure cycle (MRCC) by Toray Composites [2001] is as follows (see Figure 4.3):

a. All temperatures based upon the lagging thermocouple embedded in the test laminate.

b. Apply full vacuum (23 in Hg minimum) to the vacuum bagged laminate(s) prior to initiating the cure cycle.

c. Place the bagged laminate(s) into the autoclave and connect the thermocouples to a temperature measuring device.

d. Close the autoclave door and initiate the cure cycle.
Chapter 4: Material and Experimental Parameters

e. Pressurize the autoclave to 20 psig and vent the bag to atmosphere. Increase pressure to 85-100 psig.

f. Initiate heating of the autoclave raising the laminate temperature to 355 ± 10°F (180°C) at a rate of 1 to 5°F/minute (0.56 to 2.8 °C/min). A heat-up rate of 0.3 to 5.0°F/minute (0.17 to 2.8 °C/min) is acceptable once the part reaches 335°F (168°C).

g. Dwell the laminate temperature at 355 ± 10°F (180°C) for a minimum of 130 ± 10 minutes.

h. After the 355 ± 10°F (180°C) dwell, lower the autoclave temperature at a rate not to exceed -5°F/minute (-2.8 °C/min).

i. When the laminate temperature is less than 140°F (60°C), the autoclave pressure may be reduced to ambient and then the doors may be opened.

j. Remove the vacuum bagged laminate(s) from the autoclave then debag and fabricate test specimen.

4.1.3. History of material used in this work

The prepreg was manufactured on January 25th, 2004, batch number AB040108, roll number B1-401-128-4-1, and was received from The Boeing Company on October 29th, 2004. It was stored in a -20°C freezer and was tested over 3 years. For every MDSC test performed on this batch the $T_{g_0}$ was measured to ensure that the material had not advanced excessively. $T_{g_0}$ describes the state of the uncured resin, or as received prepreg (prepreg is generally B-staged to some low degree of cure for sufficient resistance to flow and handling ease). Figure 4.4 shows the change in $T_{g_0}$ over a two and a half year period. There are two trends evident in this Figure: 1) in January of 2005, February 2006, and April 2007, new pieces from the original received prepreg were cut for testing, after which point each piece of material experienced a decrease in $T_{g_0}$ of 3°C over the test period (e.g. seven months); 2) the $T_{g_0}$ of received prepreg which is not in regular use, but is resting in the freezer, also decreases with time by roughly 2°C over the total period. The most likely cause is moisture absorption which causes plasticization. Plasticization means that a molecule (e.g. water) nonbonding with the main structure (epoxy) exists interstitially, opening the structure and creating a softer material. The more the material is removed and replaced in the freezer, the more opportunity there is for condensation to build-up on the material surface and to be absorbed. As a consequence of this knowledge, two notes must be made for further data reduction and analysis: 1) the water absorbed may cause an endotherm before the reaction starts, complicating the baseline selection, and hence should be removed without starting the cure reaction; and, 2) $T_{g_0}$ chosen for modeling should...
be the non-plasticized value. Given this negative trend in $T_{g0}$, it is assumed that there is negligible cure during freezer storage. Later $T_{g0}$ measurements on uncured samples after a drying scan to 75°C confirm this assumption as the initial $T_{g0}$ value between 8 and 10°C can be achieved.

4.2. MDSC EXPERIMENTAL SET-UP

4.2.1. TA Q1000 MDSC

The instrument model used for cure experiments was a TA Instruments Q1000 MDSC\textsuperscript{TM} with a refrigerated cooling system, commissioned at UBC in December 2004, Figure 4.5. Three major components are shown in this photo: a) the DSC cell; b) insulated lid and automated arm; and, c) the autosampler arm and sample tray. Nitrogen gas was used to purge the cell at a rate of 50 ml/min. This instrument can be classified as a heat flux, disk-type DSC. Figure 4.6 shows cross-sections of the inside of the calorimeter cell, sample and reference platforms (or disks), and the automated lid system. Beneath the surface of the platforms is a thin, flat sensor machined from a single piece of constantan and braised to the silver heating block. The chromel/constantan thermocouple between the platforms is used to calculate heat flow between the platforms such that a flat baseline can be achieved (see description of Tzero\textsuperscript{TM} technology in Section 2.2.2). This thermocouple is also used to control furnace temperature. An insulated lid consisting of two silver lids and a dome-shaped heat shield covers the cell. For this particular model, opening and closing of the lid is automated. The sample and reference platforms are surrounded by a silver furnace having high thermal conductivity, and Platinel\textsuperscript{TM} windings Figure 4.7. To cool the furnace, an array of 54 symmetrically-arranged, high conductivity, nickel cooling rods connect the silver furnace and the cooling ring. The cooling ring is kept at -90°C when nitrogen is used. The automated sampling system, Figure 4.8, can hold up 50 samples to be loaded into the cell by an automated arm at the start of each test, and replaced back to the sample tray at the end of a test.

4.2.1.1. Instrument specifications

The Q1000 MDSC model has the following specifications:

1) Temperature accuracy to ± 0.1°C
2) Temperature precision to ± 0.05°C
3) Temperature range with nitrogen -90 to 550°C
4) Calorimetric precision for indium standards ±1%
Chapter 4: Material and Experimental Parameters

5) Sensitivity 1 µW
6) Baseline curvature <50 µW
7) Baseline reproducibility 10 µW
8) Heating rates from 0.01 to 200ºC/min
9) 40 mm³ sample volume for a non-hermetic standard aluminum pan

All specifications except for baseline curvature can be found in the promotional portfolio for the Q1000 instrument. The magnitude for baseline curvature was found in a presentation on Quantifying DSC Performance, provided by TA Instruments.

4.2.1.2. Calibration

Calibrations performed before testing include: 1) cell resistance and capacitance (otherwise known as the TZero™ calibration); 2) cell constant and temperature; and, 3) reversing and total specific heat. Eight calibrations were performed throughout the data collection for this study. This section includes a description of each of the calibrations, and reports the values for each calibration period and the consistency between calibrations.

The cell resistance and capacitance calibration is a misnomer, rather it is the measurement of the \( R_s, R_r, C_{ps}, \) and \( C_{pr} \) values for the four term heat flow equation (see Introduction for details),

\[
\left( \frac{dH}{dt} \right) = -\left( \frac{T_r - T_s}{R_r} \right) + \left( T_r - T_0 \right) \left( \frac{1}{R_s} - \frac{1}{R_r} \right) + \left( C_{ps} - C_{pr} \right) \frac{dT_r}{dt} - C_{pr} \frac{d(T_r - T_s)}{dt}
\]

The test to determine the parameters consisted of running a 10ºC/min dynamic between -90 and 400ºC, first for an empty cell (zeroline) and a second heating ramp test with sapphire specimens placed on each sensor, sample and reference. The sample and reference values for resistance and capacitance were compared by the instrument software, respectively, and the differences between the sample and reference measurements accounted for over the range of temperatures. The measured thermal imbalances assist in flattening the zeroline. There are no published specifications for baseline drift from zero heatflow, but for the instrument used in this work the expected performance is 10µW drift and <50µW in curvature. The drift and curvature of the baseline will be discussed with reference to the measurement of a standard sample of sapphire.
The cell constant and temperature calibration was performed using an indium sample supplied by TA Instruments (reference melting endotherm of 28.71 ± 0.08 J/g, and a melting temperature of 156.61 ± 0.02 °C), crimped in a standard aluminum pan. The enthalpy calibration (cell constant) and temperature calibration are ratios of the theoretical melting values (above) and the measured values. The variation in cell constants over eight calibrations was found to be 1.0303 ± 0.0364, maximum 1.1015 and minimum 0.9864 (a TA representative suggested a value between 0.90 and 1.20 with nitrogen, no literature value found), and measured melting temperature 158.04 ± 0.06 °C. The MDSC software allows for up to five standards to be entered for the temperature calibration, but only one point was found to be necessary. An error in the temperature calibration was found when using three standards and will be discussed in the next section.

The Cp reversing and total signals were calibrated using a sapphire specimen crimped between an aluminum pan and lid (non-hermetic), identical pan and lid on the reference sensor. A dynamic test was run between -50°C and 350°C at 5°C/min (±0.5°C every 100 seconds), and the value of Cp compared to the ASTM E1269 standard values. The calibration constant, KCp, for heat capacity is calculated by dividing the theoretical Cp at 146.85°C by the experimental Cp, at the same temperature. The average KCp reversing over eight calibrations was 0.9901 ± 0.0410, and KCp total was 1.0026 ± 0.0438 (TA specifies a value between 0.90 to 1.10 in their on-line help files). A concern for the Cp calibration is that the shape of the measured Cp curve is not the same as the theoretical curve, such that a small value chosen for KCp will underestimate the magnitude of Cp at other temperatures. Figure 4.9 shows the change in KCp (a) total and (b) reversing, over a 300°C range for eight calibrations. Zero-line flatness at most changes by 2.5% from the value at 156°C. For the material studied in this work, T800H/3900-2, an error of 2.5% in the height of the reversing heat flow signal will only amount to an error of 0.40% in the heat of reaction for a 5°C/min test. Tg transitions around 220°C occur over a 15 to 20°C temperature range, and hence a small inaccuracy of 1% or less would be expected, which means an error in Cp change during the transition of 1E-3 J/g°C. These inaccuracies are very small.

4.2.1.3. Temperature calibration error

A depression in the reversing Cp signal between 150 and 220 °C was found due to using a three-point temperature calibration. Tests on a sapphire sample were performed with and without the two additional temperature calibration points (Tin and Lead) and show that this is the cause of the depression, Figure 4.10 (reversing Cp results). A chart of the measured melting temperatures and the theoretical melting
temperatures of three standards (Indium, Tin, Lead) shows a linear relationship with equation 
1.0027*Tm(standard) + 0.6038 (R² = 0.9999), Figure 4.11.

In the on-line help documentation provided by TA, the following statements can be found about how a multi-point calibration is applied and is an improvement over a single-point calibration:

A multiple-point calibration is more accurate than a one-point calibration. A single-point calibration shifts the sample temperature by a constant amount. A two- or more-point calibration shifts the temperature by a constant amount below the first point, uses a smooth curve through the calibration points and maintains a constant temperature shift after the last point.

Most likely what occurred, referring to Figure 4.11, was that a constant offset was applied before 156°C (Tm for indium) and then a parabolic function was applied inaccurately above this temperature. The Cp signal is a function of the heating rate and modulation, and hence any error in temperature calibration will affect this measurement and furthermore the nonreversing signal. The implication of this artefact is that it caused the heat of reaction measured in this temperature zone to be at least 5 J/g lower compared to tests after the correction to the temperature calibration. Another compounding issue is the Tg measured which was found to be in error by -3 to -4 °C for Tg’s less than 156°C, and +4 to +5 °C for Tg’s reaching 200°C (comparing tests before and after recalibration). Given the complexity of the material system studied in this work, T800H/3900-2, the decision was made to repeat experiments using a single-point temperature calibration. TA Instruments is aware of the problem, and to date has not offered a reason for the error.

4.2.2. Material sample size and preparation

Material sample size is traditionally kept small for DSC experiments, e.g. 1 to 2mg of reactive sample is recommended by ASTM Standard E 2160. This guideline was set to avoid ‘runaway’ reactions, i.e. accumulating heat of reaction in the sample that raises the sample temperature beyond the control of the instrument. In the case of prepreg, 1 to 2 mg of reactive sample requires a sample four times this size since mass fraction of resin is roughly 25 to 30% of the total mass. A sample size of 5 to 6 mg yielded large variability in heat of reaction measurement from dynamic tests, and hence a study was undertaken to examine the effect of sample size on heat of reaction repeatability.

Upon visual inspection of the prepreg material, random striations of dark, shiny regions and lighter, dull regions, were noted across the width of the sheet in the fibre direction, Figure 4.12. The shiny regions on the prepreg measured 0.5 to 1 cm in width perpendicular to the fibres, and 6 to 10 mm in length parallel to
the fibres. A sample cut to fit an MDSC pan of 0.67 cm diameter can be taken from an entirely shiny region, or entirely dull region. A sample size of 1 to 1.5 cm perpendicular to fibres by 0.5 cm parallel to fibres, 12 to 18 mg, was found to reliably reproduce nominal heats of reaction as opposed to low values (if sample taken entirely from the dull region) or high values (if sample taken entirely from the shiny region). The sample was fit into the MDSC pan by layering it in 0.5 by 0.5 cm strips. Tests in this work were prepared as 3-ply samples and had an average mass of 16.74 ± 1.48 mg. The pan is made of aluminum (exact grade is unknown), and crimped with a tool designed by TA Instruments. Tongues and gloves were used during sample preparation to avoid contaminating the sample or pan, and for personal safety. Sample pans did not show any signs of deformation after testing, did not leak, and mass was retained.

4.2.3. Dynamic tests and experimental parameters

Dynamic tests were performed at 11 heating rates. Average heating rates chosen were: 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 8, and 10°C/min. Each average heating rate test was performed 3 times, with exception of the 0.2 and 0.5 °C/min tests which were only tested once. Recall the MRCC recommends heating rates between 0.56 and 2.8°C/min, and 0.17°C/min between 168°C and 180°C. Measurements for ultimate heat of reaction typically use 2, 5 or 10°C/min, although in this author’s experience the use of high heating rates such as 10°C/min may include a degradation exotherm depending on the material system. In addition to tests heated to the end of the cure reaction, tests were interrupted at various intermediate temperatures during cure for rates of 0.5, 1, 1.5 and 4°C/min. Table 4.1 records the final temperature for all dynamic tests at each heating rate. For 8 and 10 °C/min tests, the maximum temperature to capture the ultimate heat of reaction was raised to 310°C in order to capture the full reaction due to the fact that the calculated nonreversing signal stops 1.5 cycles (or 2 minutes in this work) before the final temperature is reached as instrument controls prepare for the next segment in the method. For a 4°C/min heating rate, the maximum programmed temperature needs to be 8°C higher than the minimum heat flow at the supposed end of the reaction, and hence a final temperature of 275°C is programmed. Opposing this decision to raise the maximum temperature is the knowledge that degradation will decrease the final Tg measured on the cool down if the temperature is raised too high. This discussion is particularly worthy of the note for those who rely on determining the final glass transition from a cooling curve. Based on TA Instruments recommendations for experiments, a period of 60 seconds and an amplitude ± ¼ °C the magnitude of the heating rate was used to ensure a reasonable length of time for glass transition measurements.
Since plastics are viscoelastic in nature, transition temperatures will be heating rate sensitive, for example, increasing heating rate will raise the Tg. Hence, it is desirable to measure all Tg transitions at the same heating rate: Tg₀, Tgᵢ, Tgᵢ, or Tgᵢ∞. This choice becomes even more important when considering what heating rate to use for capturing residual heats of reaction after partial cure tests (e.g. isothermal tests, interrupted dynamics or isothermal tests). Tgᵢ is measured in the Cp signal on the cool down from the maximum ramp temperature required to ensure that the full reaction heat flow profile is captured. A dynamic of 4°C/min (± 1°C over a 60 second period) was found to be the maximum heating rate before which degradation would lower the final glass transition temperature (Tgᵢ) of the fully cured material. Higher heating rates required higher maximum temperatures to capture the total heat of reaction and entered degradation, lowering Tgᵢ. It was further found that a 4°C/min test should not be ramped beyond 280°C, a temperature just high enough to capture the full heat of reaction, but not entering degradation. Figure 4.13 shows Tgᵢ’s measured for fully cured samples (200°C isothermal cure), cooled at 2 and 10°C/min from various final temperatures. The 2°C/min tests show degradation effects at 280°C, and the 10°C/min tests at 290°C. A Tgᵢ for 4°C/min cooling ramp from a maximum temperature of 280°C after a 200°C cure showed no degradation effects.

The following method was programmed for dynamic tests, with changes made to the modulation amplitude and average heating rate, and the maximum temperature in Segment 6:

Segment 1: Equilibrate at 30°C  
Segment 2: Modulate at ±1°C per 60 seconds  
Segment 3: Ramp to -40°C at 4°C/min  
Segment 4: Equilibrate at -40°C  
Segment 5: Modulate at ±1°C per 60 seconds  
Segment 6: Ramp to 275°C at 4°C/min  
Segment 7: Modulate at ±1°C per 60 seconds  
Segment 8: Ramp to 30°C at 4°C/min

Segments 2 and 3 measure the uncured Tg of the material, Tg₀. Segments 5 and 6 measure the heat of reaction. Segments 7 and 8 measure the final Tgᵢ. For interrupted tests, the maximum temperature of Segment is lowered and the remaining segments are as follows:

Segment 7: Equilibrate at 30°C  
Segment 8: Modulate at ±1°C per 60 seconds  
Segment 9: Ramp to 275°C at 4°C/min  
Segment 10: Ramp to 30°C at 4°C/min

where Segment 7 was a fast quench to room temperature (for example, 2 minutes to cool 90°C and 3 minutes to cool 130°C from 190°C) Segment 8 and 9 captured the residual heat of reaction and the Tg of partially cured material (designated Tgᵢ for intermediate), and Segment 10 measured the Tgᵢ.
4.2.4. Isothermal tests and experimental parameters

Eleven isothermal temperatures were selected between 130 and 230°C, at 10°C intervals, to capture the breadth of cure temperatures observed in dynamic cure. For each temperature, five tests were held for long times to reach a state of negligible change in the heat flow signal. This is decidedly more repeats than performed for the dynamics because of the large variability observed in heat of reaction measurements and heat flow profiles. The length of times required to achieve a negligible heat flow were found by trial and error. The times for 160 and 170 °C were longer due to results of lower heats of reaction at these temperatures compared to other isothermals. These aspects of variability and unbalanced heats of reaction will be discussed in depth in the data reduction section of this chapter. Partial cure tests were performed in the MDSC for the isothermal temperatures of 150 to 200°C. Table 4.2 records the hold times for the various temperatures.

Isothermal holds were also tested by MDSC for 90 to 120°C, but were not used extensively in later analysis because of difficult baseline interpretation. Oven tests were also performed for 70 and 80°C, for 48, 24 hours, respectively. Room temperature tests were also performed over a 90 day period and will be discussed in the next section.

Dynamic tests to capture the residual heat of reaction were performed for each isothermal test. A dynamic test of 4°C/min average heating rate with ± 1°C/min modulation amplitude, 60 second period, was chosen as discussed in the previous section.

To reach isothermal temperatures, a ramp of 100 °C/min was used for three reasons: 1) the limit of the machine is 200°C/min, but within the span of temperatures tested the instrument will not reach such a high heating rate; 2) a ramp will attempt to measure the heat flow whereas an equilibrium segment will not; an equilibrium segment will take time at the hold temperature and will miss cure information; 3) the modulation segment also takes time to establish and hence is constantly adjusting itself during the ramp to the hold, rather than starting after equilibrium has been reached; and, 4) as opposed to dropping the sample in the heated cell, the procedure is automated (dropping a sample would be difficult with the machine since the lid is mechanically opened and closed rather than manually). For an example of how the instrument controls temperature as a heating ramp of 100°C approaches a 180°C isothermal hold, a ramp starting at 40°C requires 1 minute to reach 120°C, another minute to reach 176°C, and another minute to reach 180°C. In this example, the 100°C/min heating rate was reached between 55 and 83°C.
The method used to determine the lost heat of reaction during the ramp to the hold temperature will be discussed in Chapter 5.1.2.3.

To allow for the measurement of heat capacity during cure, quasi-isothermal tests were performed with a modulation period of 60 seconds and ± 1°C amplitude. Since the average heating rate is zero, calculations for non-reversing heat flow are not applicable, and the resulting total heat flow is of interest for further data reduction. The parameter magnitudes were suggested by [Van Mele et al., 2004] because 1/60 Hz as a modulation frequency was found to best coordinate the calculations of the diffusion and mobility factors (as discussed in Chapter 2.3.3.4). Temperatures were chosen such that they were in the range of dynamic cure. Lower isothermal temperatures are typically limited by distortion of the heat flow signal by instrument noise, and the upper temperature by either degradation or the instrument cannot equilibrate the sample temperature and measure the heat of reaction quickly enough at the elevated temperature. These limitations will be tested in the data reduction section.

The following method is programmed for isothermal tests (residual dynamic included), changes made to the isothermal hold parameters in Segments 6 and 7,

- Segment 1: Equilibrate at 30°C
- Segment 2: Modulate at ±1°C per 60 seconds
- Segment 3: Ramp to -40°C at 4°C/min
- Segment 4: Equilibrate at -40°C
- Segment 5: Modulate at ±1°C per 60 seconds
- Segment 6: Ramp to 180°C at 100°C/min
- Segment 7: Hold for 240 minutes
- Segment 8: Equilibrate at 30°C
- Segment 9: Modulate at ±1°C per 60 seconds
- Segment 10: Ramp to 275°C at 4°C/min
- Segment 11: Ramp to 30°C at 4°C/min

Segments 2 and 3 measure the uncured Tg of the material, Tg₀. Segment 6 is a fast ramp to the isothermal hold temperature. Note that the rate decreases as the isothermal temperature is approached due to the PID controls of the instrument. Segment 7 measures the heat of reaction. Segment 10 measures the Tgᵢ of the isothermal cure and the residual heat of reaction. Segment 11 measures Tg∞. The above method was programmed for partial cure tests.

Simon [1992] recommends removal of endotherms that may exist before the onset of cure during a residual in order to achieve the correct residual heat of reaction and heat flow profile. This technique requires manually stopping the test once the endotherm peak has been reached, rapidly quenching and
rerunning the residual heating ramp. This is a tedious process for an operator and it was found in this work that the measured heat of reaction and Tg do not change with removal of the endotherm, only the shape of the nonreversing heat flow profile. For the majority of this work endotherms were not removed for ease of data collection. However, a series of residuals with endotherms removed was produced for analysis and modeling. These findings are discussed in Chapter 5.1.2.1.

4.3. MONITORING ROOM TEMPERATURE CURE

Room temperature cure, or aging, was held for a 90 day period. A piece of fresh prepreg from the original received quantity was cut into 26 pieces. Each piece was bagged and labelled with a day between 3 and 90. The individual bags were then doubled bagged with desiccant pouches and stored in a dark container at room temperature. Room temperature was monitored periodically, a total of 87 days, and was between 24 and 25 °C. Upon the designated day, a bag was removed and a 4°C/min (± 1°C per 60 second period) dynamic test to 275°C was performed on the sample. The cooling ramp was also recorded.

4.4. ROUND ROBIN DESIGN

A Round Robin study was designed to isolate the sources of measurement and modeling variability incurred during the development of cure kinetic models by different laboratories for the same material. Three stages were completed for this study as outlined in Table 4.3. Prior to starting the Round Robin, participants were asked to report their instrument’s performance with respect to calibration, zeroline flatness, signal noise, and accuracy of heat flow measurement according to standard samples. The tests developed for this preliminary stage were adapted from a DSC practitioners guide written by G.W.H. Höhne et al. [1996].

The material system used in the Round Robin study was T800H/3900-2 provided by The Boeing Company. This system had not previously been studied by any of the participants. The material was shipped to each laboratory within four days and was refrigerated immediately and tested for changes to the uncured glass transition temperature, Tg0. The Tg0 values measured by each lab did not change from that measured by the UBC lab; therefore, the material did not advance in cure during shipping to individual laboratories. For one participant the Tg0 was found to advance during the study, and material
from the UBC lab was resent to that participant. Tests at 2 and 5°C/min were also requested from each participant to be able to compare a similar experiment for all participants.

In Stage 1, participants used their own methods for sample preparation, experimental design, analysis and modeling to develop a cure kinetics model for the system. All sample preparations met appropriate standards for the instruments used. In Stage 2, participants were sent a data set produced at UBC and asked to perform data reduction (e.g. baselines, temperature transitions) and modeling. Table 4.4 records the isothermal test temperatures and hold times, dynamic heating rates and final temperatures. Isothermal holds were modulated at ± 1°C per 60 seconds and was accompanied by a residual and subsequent cooling ramp at 4°C/min (± 1°C per 60 seconds). Dynamic tests included used modulation of ± ¼ °C of the average heating rate magnitude over a period of 60 seconds.

After the data had been submitted to participants it was found that isothermal tests at 170-190°C had not been held long enough to measure the final decrease in heat flow as the reaction slowed to a negligible rate (ideally returning to the baseline at the reaction onset). The result was underestimated heats of reaction and overestimate cure rates for these temperatures. The final temperatures for the dynamic tests vary (Table 4.4). Non-integer heating rates were performed after the integer heating rates, and it was thought that the final temperature needed to be higher to collect all of the heat of reaction – this decision was later found to be in error when degradation was studied.

The same test methods as outlined in sections 4.2.3 and 4.2.4 were used to develop the Round Robin data set. Participants were left with the option of what data to analyze. A record of the instantaneous Tg’s (Tg’s) for the isothermals were also included. The Round Robin data was generated with the temperature calibration error, and hence was not used for further work in this thesis.

In Stage 3, the same data set as Stage 2 was provided and baselines were added, along with Tg and peak temperatures. The baseline chosen for dynamics was a straight line between the onset of the reaction and the end of the reaction. The end of the reaction was set as the minimum heat flow after the main reaction peak, and hence the baseline is sloped. A linear baseline accommodated measurement of the same heat of reaction for all tests, isothermal and dynamic, but is incorrect as will be discussed in the cure study done on T800H/3900-2 in Chapter 5. A horizontal baseline should have been used.
In Stage 4, a model was given to the participants to fit the data such that the fitting method could be compared across all groups. This stage was not pursued because of the difficulty for some participants to adjust their model fitting programs to accommodate the UBC model.

The anticipated duration of the Round Robin was 6-7 months, starting in November 2004 and ending in May 2005. Rather, the study continued until April 2007. 23 Laboratories were invited to participate, 8 agreed to be involved and started the study (including UBC), and 5 laboratories completed the study. ASTM E691 [1999] states that ideally an interlaboratory study on the precision of a test method should have 30 or more participants, but for practical purposes should have no less than 6 for a final statement of precision of a test method. ASTM E6631 [2005] states that a minimum of three and preferably at least 5 laboratories should participate in the evaluation of a test method. Although it is not entirely clear which ASTM rule should be applied to deem the number of tests to be adequate in our case, a conservative number of participants would have been six or higher. The number of participants in this work falls just below this rule.
Table 4.1 Final temperature for dynamic tests

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<th>Heating Rate (°C/min)</th>
<th>Final Temperature (°C)</th>
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Table 4.2 Isothermal temperatures and hold times

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<td>230</td>
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Table 4.3 Round Robin scheme for UBC study

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<th>Uncertainty Parameter</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
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<td>UBC Provided</td>
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Table 4.4 Test parameters for Round Robin data

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<th>Dynamic Heating Rate (°C/min)</th>
<th>Final Temperature (°C)</th>
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<td>250</td>
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Chapter 4: Experimental Methods

Figure 4.1 (a) Tetraglycidyl-4,4'-diaminodiphenylmethane, TGDDM  
(b) 4,4'-diaminodiphenyl sulfone, DDS

Figure 4.2 T800H/3900-2 prepreg system schematic
Figure 4.3 Toray Composites 3900-2 typical cure cycle

Figure 4.4 Changes in \( T_{g0} \) over a 2.5 year period; material received October 2004 and stored at -20°C
Figure 4.5  TA Instruments MDSC Q1000 [photo courtesy of TA Instruments, 2007]

Figure 4.6  Cross-sections of the sample and reference platforms and the automated lid [illustrations courtesy of TA Instruments, 2007]
Figure 4.7 Cross-section to illustrate furnace and cooling system
[illustration courtesy of TA Instruments, 2007]

Figure 4.8 Autosampler loading a sample on the sample platform
[photo courtesy of TA Instruments, 2007]
Figure 4.9 (a) Comparison of $K_{Cp}$ Total over 8 MDSC calibrations

Figure 4.9 (b) Comparison of $K_{Cp}$ Reversing over 8 MDSC calibrations
Chapter 4: Experimental Methods

Figure 4.10 Effect of 1-point versus 3-point temperature calibration on $C_p$ reversing signal

Figure 4.11 Comparison of DSC measured melting temperatures to standard values for indium, tin and lead
Chapter 4: Experimental Methods

Figure 4.12 Variation in appearance (striations of light and dark regions) across a strip of T800H/3900-2 prepreg

Figure 4.13 Effect of maximum temperature during a dynamic on $T_{g_{\text{final}}}$
Chapter 5. **RESULTS FOR T800H/3900-2 CURE KINETIC ANALYSIS AND ROUND ROBIN STUDY**

5.1. **T800H/3900-2 PREPREG MDSC MEASUREMENTS AND DATA REDUCTION**

5.1.1. Dynamic tests

Dynamic tests were performed with heating rates ranging from 0.2 to 10 °C/min to: 1) determine the ultimate heat of reaction and its reproducibility over a wide range of heating rates; and, 2) distinguish between different mechanisms, such as epoxide-amine versus epoxide-hydroxyl. For heating rates of 1.5 °C/min and below, diffusion effects were observed and probed by performing dynamics up to various intermediate temperatures, cooling quickly to preserve the state, and rescanning at 4 °C/min to determine the residual state of the partially cured material. For verification, a 4 °C/min test (without diffusion effects) was also probed with this method of partial cures. This section details the interpretation and data reduction decisions for dynamic tests.

5.1.1.1. Raw data and preliminary interpretation

Figure 5.1 (a) shows the nonreversing heat flow signal measured during modulated dynamic scans of 0.2 to 10 °C/min. Figure 5.1 (b) shows a subset of a), 0.2 to 2 °C/min dynamics, for ease of comparison. The nonreversing heat flow signal is the kinetic response and is equal to the total heat flow minus the reversing heat flow. The reversing heat flow is equal to the Cp multiplied by the heating rate (Section 2.2.2). Figure 5.2 (a) shows the Cp signal measured for all dynamic scans, and 5.2 (b) shows a subset of 0.2 to 2 °C/min. Figures 5.1 and 5.2 consider only one test for each heating rate. Figures 5.3 to 5.6 show the nonreversing heat flow and Cp signals for residual dynamics performed at 4 °C/min after heating to various temperatures at rates of 0.5, 1, 1.5 and 4 °C/min. The instantaneous Tg (traditionally the Tα transition, and in this work referred to as Tg i) was measured using the Cp signal during the devitrification transition.

There are several notable events in the nonreversing heat flow and Cp signals over the range of dynamic tests. The first four events listed here are labelled in Figure 5.7 for a 1 °C/min dynamic as a representative result. Not all events could be identified at this time, but are recorded here for the benefit of future work to understand this material system.
1) An endothermic peak appeared between -9 and -3 °C, also evident as a step change in the Cp signal. This is the initial Tg of the material, and was measured as the midpoint of the step transition in the Cp signal.

2) An endothermic plateau extended over a wide range of low temperatures, ending at roughly 80°C. Scanning to 75°C, cooling the sample and rescanning to higher temperatures showed that this endothermic trend could be removed and Tg increased by roughly 3°C, indicative of moisture removal as discussed in Section 4.1.3, Figure 4.4.

3) A small endothermic peak extending over 2 to 3 degrees at 80°C measuring 1.5 J/g, which was also notable as a distinct peak in the Cp signal. The peak did not appear during residuals of 150°C isothermals held at least 15 minutes, reaching a degree of cure of 0.1, but did remain for room temperature cure to 0.1 degree of cure. After the 80°C transition, there was a flattening of the heat flow signal before the main reaction kickoff, the Cp signal also rose and fell in this region.

4) The main exothermic peak which contains four peaks: i) one small peak (at 130°C for the 1°C/min test, Figure 5.7) rises after the reaction kickoff; there is also a low peak in Cp in this temperature region (Figure 5.2 (a)); ii) the main peak which shifted to higher temperatures with increased heating rate; iii) a shoulder after the main peak; and, iv) a peak rising at the tail of the curve at high temperatures which prevented the heat flow from returning to its starting position. The fourth peak (iv) was identified with the onset of degradation since Cp changes are already removed in the nonreversing heat flow signal, the instrument baseline is flat, and the degradation as measured by resin burnoff in a thermogravimetric analyzer (TGA) occurred over the same temperature range. A 2°C/min dynamic MDSC test was run to 400°C to observe the fourth peak, overlaid in Figure 5.8 with the weight loss measured by TGA. Running a DSC test in resin degradation temperature zones is generally not an advisable procedure because volatiles from the degrading polymer can contaminate the cell. The onset of the TGA peak occurred at lower temperatures than the local minimum at the end of the DSC exotherm profile (see TGA results in Appendix D for a closer view of this particular point). Table 5.1 records the onset temperature of the reaction (i), the peak temperature (ii), and the temperature of the local minimum at the end of the exotherm profile, with respect to heating rate. Table 5.2 records the onset temperature of degradation measured by TGA for several heating rates.

5) There are two events observed in the Cp signal for the low dynamic tests, 0.2 to 1.5 °C/min (Figure 5.2 (b)): i) a decrease in Cp at an intermediate temperature followed by ii) an increase in Cp at higher temperatures. A decrease in Cp is accepted in the literature as a measure of vitrification, and an increase as a measure of devitrification [Van Assche et al., 1996]. Otherwise the Cp signal increased with temperature.
6) A second softening transition (T_β) was noted around 150°C for partially cured samples. The samples which exhibited T_β had been interrupted at relatively high temperatures, towards the end of cure; for example a 4°C/min test stopped at 240°C, 0.5°C/min tests at 200 and 250°C, 1°C/min tests at 205 and 215°C, and a 1.5°C/min test at 225°C.

5.1.1.2. Baseline selection

The dynamic baseline developed in this work is bi-linear, see Figure 5.9: 1) a horizontal baseline starting at cure kickoff as suggested by MDSC theory that the nonreversing heat flow is solely the kinetic material response to cure (reaction onset temperatures are recorded in Table 5.1); 2) for simplicity, a straight line connects the horizontal baseline at the onset of degradation, recorded in Table 5.2, to the local minimum in heat flow at the end of the epoxy reactions, T_F (recorded in Table 5.1). Later in this Chapter in Section 5.2.3.2 various baseline decisions for this data set will be compared for their effect on cure rates.

5.1.1.3. Heats of reaction, degree and rate of cure

Integration of the nonreversing heat flow curves with time or temperature gives the heat of reaction, 

\[ Q(t) = \int_0^{t_f} \frac{dQ}{dt} \, dt = \int_{T_s}^{T_f} \frac{dQ}{dT} \cdot \frac{dT}{dt} \, dt \]  

where \( t_f \) is the time corresponding to the end of the reaction (or local minimum in heat flow for this case), \( T_s \) is the reaction start temperature, \( T_f \) is the final reaction temperature, and \( \frac{dT}{dt} \) is the heating rate. The heats of reaction for all of the dynamics are summarized in Figure 5.10 with respect to heating rate. There is a small trend of increasing heat of reaction with increasing heating rate. All tests except for 0.5, 8 and 10°C/min fall within the error bars established by the standard deviations for repeat tests. The average ultimate heat of reaction was calculated to be 157.04 J/g ± the standard deviation of 4.86 J/g using data between 2 and 5 °C/min. Two scenarios may be suggested to account for these trends in heat of reaction: i) vitrification has occurred and a slow heating rate is unable to devitrify the material before degradation complicates the signal; and ii) degradation has not been entirely removed by the baseline selection.

Accepting the assumption that \( H_{Total} \) for any process cycle should equal \( H_{Ultimate} \) (157 J/g for this work), Figures 5.11 to 5.14 show the heats of reaction calculated for partially cured dynamics based on the measured residual heats of reaction for each test, and the estimated heat of reaction from tests cured to completion for the same heating rate up to the temperature of interest. It is evident that there is missing heat of reaction, particularly for tests which were raised only above the moisture endotherm, 75 and
100°C, before the reaction kickoff. Apart from the tests interrupted at temperatures before the reaction kickoff, there does not appear to be a correlation with missing heat and higher temperatures of test interruption, except for the 0.5°C/min tests. However, the measured heat of reaction for the full cure 0.5°C/min test is lower than the other tests, and hence the estimates for heat of reaction at interrupted temperatures also underestimate \(H_{\text{Ultimate}}\) by a similar amount. For the other heating rates, heating to 75 and 100°C did not change the reaction kickoff temperature, but did increase the \(T_{\text{g0}}\) value as discussed in Section 2.1.3, indicative that moisture had been removed. With cure ruled out as a reason for a decrease in heat of reaction, other factors such as change in mass due to moisture or release of volatiles, or changes to the pan shape were investigated. A sample was weighed, crimped in a pan, and ramped to 75°C at 4°C/min, after which they were re-weighed and inspected for changes to the pan shape before re-scanning to capture the residual heat of reaction. No changes in weight or shape were observed. A second sample was tested in the same manner, except after the ramp to 75°C, the sample was removed from the pan and re-crimped in a new pan for the ramp to capture the residual heat of reaction. The measured heat of reaction was still lower than the \(H_{\text{Ultimate}}\). To date, this issue has not been resolved, whether it is a baseline issue or if some change in the material structure is causing the loss of reaction heat. The \(T_{\text{g}}\) and \(T_{\text{b}}\) measurements will be discussed in detail with the data for isothermal partial cure tests in Section 5.1.3.

Figures 5.15 and 5.16 illustrate the degrees and rates of cure for each heating rate, with repeat tests. Three tests were performed for heating rates 1 to 10°C/min and had differences less than 3% in degree of cure at any temperature. The degrees of cure associated with the onset of vitrification and devitrification transitions for low heating rates are recorded below in Table 5.4.

### 5.1.2. Isothermal tests

Isothermal temperatures ranging from 24 to 230°C were tested over various lengths of time. Residuals at 4°C/min were measured after all isothermals. Heat flow measured by MDSC during the hold between temperatures 130 and 230°C were chosen for analysis because a definitive end of reaction (steady state) could be reached and a baseline clearly drawn for degree of cure calculations. Temperatures below 130°C showed abnormal endotherms at long times, or the heat flow magnitude was indistinguishable from instrument noise. Isothermal holds at 100 and 110°C were analyzed to determine the trends in Arrhenius constants between room temperature tests and the isothermals used for kinetic analysis (130°C and above). Hold times less than those required to reach steady state could not be analyzed for the isothermal data because a baseline could not be determined. This section details the results, interpretation and data reduction decisions for isothermal tests.
5.1.2.1. Results

Figures 5.17 and 5.18 illustrate the total heat flow and Cp signals, respectively, measured during isothermal cure held for 400 min and longer. Figure 5.19 (a) overlays the residual nonreversing heat flow for each temperature, and Figure 5.19 (b) shows the nonreversible heat flow profiles for residuals with endotherms removed. An endotherm is a measure of the amount of heat required by the system to overcome a condensed free volume and/or chain packed state. Once the volume and mobility is recovered the reaction can proceed. The endotherm was removed according to the method outlined by Wisanrakkit and Gillham [1990]. In this method, the temperature was increased until the end of the endotherm, at which point the material is cooled rapidly to freeze the state of the material. A dynamic is then performed to measure the residual heat of reaction. Figure 5.20 overlays the Cp signal recorded during the residuals with the endotherm present, and after the endotherm has been removed by annealing. Figure 5.21 a) shows the nonreversing heat flow residual profiles for various room temperature cures over a 90 day period, and b) shows their respective Cp profiles. Partial cure tests were performed for temperatures 150, 160, 170, 180, 190 and 200°C, but representative plots are only shown here for 150 and 200°C. Figure 5.22 (a) shows the nonreversing heat flow profiles for 150°C partial cure residuals, and (b) the Cp profiles. Figure 5.23 shows the same plots for 180°C partial cure residuals. The Cp profiles were arranged to overlap consecutively with progress of cure; the Cp magnitude of the uncured dynamic profile was unchanged.

From these Figures, several kinetic and non-kinetic events were identified for the isothermal holds and residuals measurements which are worthy of note:

1) Only one peak was evident in the heat flow curves for isothermal holds, hence multiple mechanisms were not discernable from this view.

2) The shape of the low temperature profiles revealed that the initial reactions are part autocatalytic and nth order since the heat flow jumped quickly to a value greater than zero (relative to the overall profile), but still required time to reach a peak heat flow value.

3) In the Cp curves for isothermal holds, time to vitrification and the height of Cp drop during vitrification decreased with increasing temperature.

4) Cp on the hold also increased slightly at early cure times, perhaps an expression of delayed material expansion after the fast ramp from room temperature to the isothermal hold, Matsuoka [1981].

5) The endotherm measured during a residual was due to ageing [Wisanrakkit and Gillham, 1990]. When the endotherm was removed by annealing before performing a residual test, the result during
the residual was a broadening of the $T_g$ transition. The reaction kickoff temperature occurred earlier in the nonreversing heat flow signal and the $C_p$ transition broadened. The location of the peak temperature in the nonreversing signal was relatively constant, as was the $T_g$ measured at the midpoint of the transition in $C_p$. For some hold times (e.g. 180 min at 150°C), the nonreversing heat flow signal did not have an endotherm but did flatten prior to the reaction kickoff and had a steep slope at reaction kickoff, indicative that some aging had occurred.

6) When $T_g$ was less than 150°C, only one softening transition was evident during the residuals (e.g. 180°C, 20 minutes), that being $T_g$, Figure 5.23 (b). Not until the $T_g$ exceeded 150°C by 15°C or more did $T_\beta$ appear (e.g. 180°C, 50 to 80 minutes), and hence two softening transitions were evident. Once the $T_g$ reached or exceeded 150°C, the reaction kickoff in the nonreversing heat flow signal still appeared to occur around 150°C, or $T_\beta$ (e.g. 180°C, 40 to 80 minutes). This last statement was true except in the presence of an aging endotherm (e.g. 180°C, 400 minutes), Figure 5.23 (a).

7) With increasing cure, the peak temperature in residual nonreversing heat flow profiles shifted to the right.

8) Figure 5.24 correlates the $T_g$ measured during the heat-up of the residual after long hold times (400+ minutes), and the $T_g$ measured on the cool-down of the residual. For isothermal temperatures up to 170°C the $T_g$ was 220°C, and higher than $T_g$. At 180°C and above the $T_g$ is 211°C and lower than $T_g$. Both $T_g$ and $T_g$ begins to decrease after isothermal holds of 230°C, an indication of degradation (low $T_g$ and $T_g$ is also evident for individual tests as early as 210°C).

### 5.1.2.2. Phase separation as a mechanism to explain trends in $T_g$-$\alpha$

Using only the residual heats of reaction to determine the final degree of cure for isothermal tests, a $T_g$-$\alpha$ plot was constructed with $\alpha = 1 - \frac{H_{\text{Residual}}}{H_{\text{Ultimate}}}$ ($H_{\text{Ultimate}} = 157 \text{ J/g}$) and the measured $T_g$’s from residual $C_p$ signals. The $T_g$-$\alpha$ plot is shown in Figures 5.25 (a) and (b); other features in these plots will be explained below. This approach follows the work of Wisanrakkit and Gillham [1990] and Simon and Gillham [1992] who proposed that only the residual heats of reaction be used for cure analysis due to inaccuracies in isothermal measurements. The baseline for the residuals was the same as outlined for the dynamics in Section 5.1.1.2. Data for interrupted dynamic tests is also shown on this plot.

Towards the end of cure for each isothermal temperature, the $T_g$ continued to increase while degree of cure did not change considerably, thus creating a lower and upper $T_g$-$\alpha$ curve, as illustrated in Figure 5.25 (a). If two materials with different $T_g$’s are completely miscible an average $T_g$ will exist. If the two
Chapter 5: Results for T800H/3900-2 Cure Kinetic Analysis and Round Robin Study

phases are not mixed well, or separate during a process, their respective Tg’s will be exhibited. The lower curve was designated as the Tg-α relationship for the blend of thermoplastic and epoxy, and the upper curve for the epoxy alone. The appearance of Tβ in Cp profiles (likely a thermoplastic polyamide softening transition around 150°C, Muraki et al. [1986], Odigiri et al. [1988]) supports this phase separation mechanism concept in that Tβ was evident whenever the Tg moved to the upper curve. In Figure 5.25 (a) and (b), the open symbols refer to Cp profiles without Tβ, and filled symbols refer to the presence of Tβ. Tg for resin system 3900-2 can be defined as a path dependent measurement since for the same degree of cure the material undergoes phase separation depending on the temperature history. During cure, the Tg-α behaviour moves from a lower line, the blend relationship, to an upper line, the epoxy relationship. It was found that the Tg increased to the epoxy line at sequentially higher degrees of cure with increasing cure temperature. Figure 5.25 (b) shows this trend, the dynamics also coloured to match the appropriate isothermal temperatures. This implies that the blend was maintained until higher states of cure with increasing temperature, which fits with findings in the literature on phase separation that propose a high cure rate will not allow enough time for phase separation due to the immediate increase in viscosity. For high heating rates, during which the cure temperature stays above the Tg until nearly complete conversion (for example 4°C/min), the same logic can be applied: the rate of cure is delayed until higher temperatures due to the viscoelastic nature of the material, but occurs so quickly at those high temperatures that the thermoplastic modifier does not have the time to separate until very late stages of cure.

As a first test of the hypothesis that the upper and lower Tg-α lines are for a blend and separated system, the behaviour was modeled using the following relationship from copolymer theory [Gordon and Taylor, 1952],

$$Tg(\text{copolymer}) = \frac{w_1 Tg_1 + k w_2 Tg_2}{w_1 +kw_2}$$  \hspace{1cm} 5.2

where w is the percent weight and k is a fitted constant. When k = 1, the equation reduces to a linear relationship, and when k = Tg1/Tg2 the equation becomes the inverse rule of mixtures. The case when k = 1 was used to test the hypothesis since it is the simplest approximation, and given that there are several parameters that are difficult to define for this system. In the 1995 patent for T800H/3900-2 [Kishi et al., 1995], the percent weight of thermoplastic phase was suggested to be between 8 and 30%. Tg(copolymer) can be described by the DiBenedetto model [1987], Tg1 can be solved for the epoxy, and Tg2 is Tβ. Tβ measurements plotted against degree of cure, Figure 5.26 (a), showed an increasing relationship with degree of cure between 144 and 154°C, possibly starting around 120°C or lower. The fit of equation 5.2
in Figure 5.25 (a) used a $T_\beta$ of 122°C. The change in Cp during the $T_\beta$ transition was also measured to determine if the thermoplastic phase might be changing properties with cure or time, Figure 5.26 (b), but there was no obvious trend. Reasonable model parameters were found for the $T_g$(copolymer) and $T_g$(epoxy) relationships, as shown in Figure 5.25 (a), and listed and discussed below:

$$T_\beta = 122°C$$

$T_g_0$(copolymer) of 8.8°C

$T_g_\infty$(copolymer) 200°C

$T_g_\infty$(epoxy) 222°C

$\lambda$(copolymer) = 0.8

$w_1$(epoxy) = 0.7

$w_2$(thermoplastic) = 0.3

1) $T_g_0$(copolymer) of 8.8°C was based on i) the range of $T_g_0$’s measured for the material at the beginning of testing in 2004; and, ii) the value matched those measured after dynamic tests interrupted at temperatures before the reaction kickoff, which also remove the moisture endotherm.

2) The $T_g_\infty$(copolymer) was unknown, and hence became a variable for fitting. Recall that the $T_g_\infty$ was decreased for tests of 180°C and higher from 221 to 212°C. It is conceivable that the $T_g_\infty$ is influenced by the epoxy more than thermoplastic, and hence overestimates the blend $T_g_\infty$. A lower value of 200°C for $T_g_\infty$(copolymer) resulted in a better fit to data points at 0.7 degree of cure and higher that appear to form a blend $T_g$-$\alpha$ relationship.

3) The $T_g_\infty$(epoxy) was at least 220°C. It is possible that the measured $T_g_i$’s of the phase separated points at high temperature and degrees of cure and long hold times are subject to degradation, and hence are underestimated by a model solely based on cure. $T_g_i$’s for 190 and 200°C were equivalent, even though there were small residuals for both. The $T_g_i$’s started to decrease for 210 and 220°C, and then dramatically dropped for the 230°C isothermal.

4) $\lambda$(copolymer) = 0.8, in combination with the $T_g_\infty$(copolymer) fit the data below 0.5 degree of cure, and the lower $T_g_i$ data points at degrees of cure above 0.5.

5) A 0.3:0.7 weight ratio of thermoplastic-to-epoxy to match $T_g_\infty$(epoxy), and was within the limits of the weight ratio recommended in the 1995 patent [Kishi et al, 1995]. The $T_g$(epoxy) curve does not fit the dynamic data below the blend curve at degrees of cure less than 0.2, but it was difficult to assess if the degrees of cure were accurate for these tests due to issues with missing heat of reaction.

The epoxy curve fit by equation 5.2 (b) underestimates the rise in Tg. In order to have a better fit the value of $T_\beta$ would need to be roughly 120°C to match the onset of the rise in Tg. Given the trends
observed with temperature history, Figure 5.25 (b), this simple approach was not pursued further. Still, it offers insight that the behaviour observed for T800H/3900-2 follows expected trends of a multi-phase system. The estimation for the blend Tg was used in further analysis.

5.1.2.3. Heats of reaction

The measured heats of reaction are shown in Figure 5.27. The first estimate of the isothermal baseline was a horizontal line at the magnitude of heat flow experiencing negligible change. The total heat of reaction decreased from 147.6 J/g at 130°C to 140.5 J/g at 160°C and 170°C. Temperatures of 180°C and above had comparable magnitudes between 142 and 145 J/g. All temperatures are missing heat of reaction to match the H_Ultimate of 157J/g measured by dynamics. Part of the missing heat can be assigned to the ramp to the isothermal hold. This did not equate H_Total = H_Ultimate, and the rest of the missing heat was assigned to the isothermal hold by lowering the baseline, Figure 5.28.

To account for the heat of reaction lost during the ramp to the isothermal hold, samples were ramped at 100°C/min to the isothermal hold temperatures (130 to 200°C) and then rapidly cooled to maintain the state of that point. The samples was rescanned to measure the T_g. The maximum temperatures reached were recorded to be within 1.2°C below the hold temperatures. This method was inaccurate for isothermal temperatures above 200°C because the time spent at high temperatures during cool-down from the isothermal temperature allowed further cure (e.g. 50 seconds to reach 150°C from 200°C). The T_g's were then matched to the T_g-α curve for the blend (Figure 5.25 (b)) and the lost heat of reaction calculated by H_Lost = a*H_Ultimate. Figure 5.29 shows H_Lost and the DOC_i associated with the measured T_g. The lost heat of reaction is incorporated into the integral for calculating heat of reaction, and furthermore degree of cure, by the following equation,

\[ Q(t) = Q_i + \int_{t_0}^{t_f} \frac{dQ}{dt} dt \]

where \( Q_i \) is the lost heat of reaction, and \( t_f \) is the final time of the isothermal hold, or the time at which the baseline is chosen to end the heat of reaction calculation.

Given that there is likely a phase separation occurring during the later stages of isothermal cure, it was assumed this endothermic reaction may negate part of the exothermic heat flow profile. The decision was made to lower the baseline under the isothermal heat flow curve. At most, the baseline was lowered 0.0198 mW below the measured heat flow signal when negligible change is reached, as shown in Figure 5.28 for a 160°C test. The lowered baseline in this Figure encompasses a drop in the heat flow between
150 and 250 minutes. Such drops were not uncommon for this material at long hold times, and may be related to phase separation. On average, baselines were lowered 0.00774 ± 0.00483 mW, much greater than the instrument accuracy of 0.2 µW. Figure 5.30 shows the heats of reaction for 150°C isothermals of various hold times, the isothermal heat estimated from the tests held for 400 min and longer. Agreement was found between $H_{\text{Total}}$'s and $H_{\text{Ultimate}}$ for all isothermals (long and short hold times). At worst, a test at 190°C held for 20 minutes measured an $H_{\text{Total}}$ 8 J/g less than $H_{\text{Ultimate}}$ (5% difference). It may have been that for this test cure continued on the cool-down from the isothermal hold and hence the heat of reaction was underestimated.

5.1.2.4. Degree and rate of cure

Figure 5.31 (a) to (c) show the degree of cure versus time curves for isothermal temperatures 130 to 200°C, five tests for each temperature, and Figure 5.32 shows the cure rate. The isothermal results showed considerably more variability than the dynamics, at most 12% difference for degrees of cure between tests at the same isothermal temperature. High variability is also evident in the cure rate profiles and is most likely due to a combination of material, test method, and data reduction factors.

5.1.3. The effect of various baseline decisions on cure rate isoconversionals and the Tg-α relationships

Figures 5.33 to 5.37 show the cure rate isoconversionals for various baseline decisions. Standard deviations for Ln(cure rate) data are included as error bars. The baseline decisions and consequences are listed here:

1) Figure 5.33: Bi-linear dynamic baseline, estimated heat lost during heating ramp and isothermal baseline lowered to achieve $H_{\text{Total}} = H_{\text{Ultimate}} = 157$ J/g. This is the cure rate isoconversional plot for the data reduction described in this chapter. Isothermals and dynamic cure rates agree within 10% for degrees of cure below 0.5, but the difference increases to 20% at 0.7 degree of cure (between 180 and 200°C, where neither isothermals nor dynamics were showing signs of diffusion). It was found that the difference between the two at these intermediate temperatures could be eliminated if $H_{\text{Ultimate}}$ could equal 165 J/g (lowering both dynamic and isothermal baselines to obtain this heat of reaction), but no concrete evidence was available to assign the $H_{\text{Ultimate}}$ to such a high value for dynamic tests, and the isothermal cure rates would be lower than the dynamics at lower temperatures.
2) Figure 5.34: Bi-linear dynamic baselines, isothermal heats of reaction using original baseline (at point of negligible heat flow) with estimate of heat lost during heating ramp to the hold temperatures, $H_{\text{Total}} < H_{\text{Ultimate}} = 157 \text{ J/g}$. Most noticeable is a bend in the isothermal cure rates for temperatures 150 to 200°C, extending to low degrees of cure (e.g. 0.2).

3) Figure 5.35: Bi-linear dynamic baselines, isothermal heats of reaction using original baseline (at point of negligible heat flow) without the estimate of heat lost during heating ramp to the hold temperatures, $H_{\text{Total}} < H_{\text{Ultimate}} = 157 \text{ J/g}$. The trends observed for this case were the same as case 2, only exaggerated further by the lower $H_{\text{Total}}$ for isothermals.

4) Figure 5.36: Linear dynamic baselines between the kickoff and end reaction temperatures, measured heats of reaction using original baseline (at point of negligible heat flow) with estimate of heat lost during heating ramp to the hold temperatures, $H_{\text{Total}} = H_{\text{Ultimate}} = 145 \text{ J/g}$. The isothermal and dynamic heats of reaction were equal to 143.37 ± 2.84 J/g and 145.07 ± 4.13 J/g, respectively. Two artefacts are worthy of note in Figure 5.36 in the dynamic isoconversionals: a) for temperatures 150 to 200°C, dynamic cure rates create a bend in the curves and, b) the low heating rates (0.2 and 0.5°C/min) have a higher cure rate than the isothermals. For all isoconversionals the isothermal cure rates are higher than the dynamic cure rates (except for very low heating rates).

In light of the discussion thus far, the following list of guidelines for reducing DSC data can be proposed:

1) Choose appropriate baselines. Although a linear dynamic baseline provided a very satisfying balance of reaction heats between isothermal and dynamic tests, there was no physical basis for a linear dynamic baseline in light of the instrument choice and the fact that MDSC removes Cp changes during cure. This baseline choice also caused two distinct artefacts as discussed above. The horizontal baseline removed both of these artefacts for the dynamic tests, but left the $H_{\text{Isothermal}} < H_{\text{Dynamic}}$ by 8% (after heat lost during the heating ramp was accounted for).

2) Ensure $H_{\text{Total}} = H_{\text{Ultimate}}$. The total heats of reaction for all samples should be equal, no matter the test condition. Ensuring $H_{\text{Total}} = H_{\text{Ultimate}}$ was important in this work for minimizing differences between isothermal and dynamic cure rates, but only when the appropriate baseline decisions were made.

3) If $H_{\text{Total}} \neq H_{\text{Ultimate}}$, reasonable explanations must be offered. Isothermal tests are historically known to have less heat of reaction due to instrument sensitivity issues and lost heat of reaction during the ramp to the hold temperature. Methods in the literature which use only the residual heats of reaction by default assign missing heats of reaction to the isothermal. For the T800H/3900-2 system, the loss of isothermal heat of reaction due to phase separation appears to have been a
reasonable explanation for lowering the isothermal baseline to account for the missing heat of reaction.

4) Isothermal and dynamic cure rates should be equivalent. Lowering the baseline to recover the missing heat eliminated the differences between isothermal and dynamic cure rates at low degrees of cure, a cure zone which should be dominated by the chemical reactions. Differences between cure rates after gelation may be explainable on the basis of diffusion behaviour, or possibly the viscoelastic nature of the material.

5.2. **CURE KINETICS ANALYSIS AND MODELING**

5.2.1. **Kinetics interpretation based on cure rate isoconversionals**

Figure 5.37 shows the cure rate isoconversional chart for isothermals and dynamics given the baseline decisions of Section 5.1, divided into three zones of reaction behaviour which will be discussed in this section and used later for modeling. A straight isoconversional means that a single mechanism with constant activation energy exists at all temperatures. Deviations from this indicate changes in reaction mechanism or diffusion. Recalling the model features explored on the cure rate isoconversionals in the Introduction, the three zones were designated as follows:

1) **Zone 1** includes data at low degrees of cure at all temperatures, and intermediate degrees of cure and temperatures. These isoconversionals, and parts of isoconversionals, maintained a similar slope and were assigned as the epoxide-amine reaction dominated by the chemical reaction. The highest cure rates for any given temperature occur at 0.2 and 0.3 degree of cure (the two overlap), and the 0.1 curve is lower than both of these curves indicating that the reaction in this zone is a combination of autocatalytic and nth order behaviour, as would be expected according to the Horie model [Horie et al., 1970].

2) **Zone 2** includes data at high temperatures and degrees of cure. The slope of the isoconversionals increased in this region due to etherification. The high heating rates were helpful for determining this trend (appears as a shoulder in the cure rate versus temperature profiles at high temperatures).

3) **Zone 3** includes the rest of the data at low to high temperatures, intermediate to high degrees of cure, where the slope increased as an indication of diffusion. Dynamics were substantially lower than isothermals, but only for heating rates 0.2, 0.5, 1 and 1.5°C/min (the last four data points on each dynamic curve). The isothermal data for 0.9 and higher was skewed due to the difficulty in measuring cure rates when the reaction vitrified.
Figure 5.38 shows isoconversionals less than 0.1. The isothermals and dynamics overlap very well, except at 0.02 degree of cure which differ by 10%. It may be assumed an inaccuracy in the isothermal data since the reaction occurred so quickly and small changes to the baseline can alter the degree of cure considerably at this point. The slope becomes less steep with increasing cure. This may be an indication that the start of the reaction was inhibited, reflected also in the change in reaction start temperature between an uncured sample and one that is cured less than 0.2 degree of cure. Low heating rates, 0.2 and 0.5°C/min, create an even steeper slope (lower cure rate) at low temperatures. Isothermal tests at low temperatures are also steeper in slope, Figure 5.39. Again, this may be an indication of an inhibitor. Salla and Ramis [1997] showed an increasing slope with decreasing degree of cure on an isoconversional chart for an unsaturated polyester, and were able to relate the activation energy from their chart to that of thermal decomposition for the inhibitor benzoyle peroxide.

5.2.2. Activation energies

Activation energy is calculated by a model-free (see section 2.3.3.2) approach by the following equation,

\[
\ln \dot{\alpha} = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{5.4}
\]

where \(E/RT\) is the slope of the isoconversional, and \(\ln f(\alpha) + \ln A\) is the intercept. Avoiding data points affected by diffusion, activation energies for the chemical reactions were calculated using the temperature and heating rate ranges for isothermal and dynamic isoconversionals in Table 5.5.

Figure 5.40 shows the activation energies calculated from the data recorded in Figure 5.37 (also Figure 5.33), using the limits of temperature and degree of cure outlined in Table 5.5. These limits were chosen because the correlation coefficients (\(R^2\)) were greater than 0.99 for all slopes in Figure 5.37 except 0.75 and 0.8 degree of cure contours which had values greater than 0.98. There is good agreement between isothermal and dynamic tests. Isothermal activation energies are missing above 0.85 degree of cure because of the sparseness of isothermal temperatures which cure to such a high degree without being affected by diffusion. Values range from 61 to 70 kJ/mol up to 0.5 degree of cure, 93 kJ/mol at 0.8 degree of cure, and 105 kJ/mol at 0.95 degree of cure. These values are in very good agreement with those found by Cole [1991]: primary and secondary amine reactions were 61.4 and 72 kJ/mol, respectively, and etherification at 101 kJ/mol. At low degrees of cure the activation energy increases, to 75.9 kJ/mol at 0.05 and 92.6 kJ/mol at 0.02 dynamic isoconversionals. Again, this may be traceable to the activation energy of thermal degradation for an inhibitor, if the inhibitor for this system were known.
5.2.3. Framework for chemical model fitting using cure rate isoconversionals

In this section, the concept of fitting a model to the data of the cure rate isoconversional plot is explored. The strategy is to divide the plot into sections (refer to Figure 5.37), to build the model from the amine-epoxy reactions to the etherification reaction, and finally model diffusion. For fitting, data density was increased to 0.01 increments of cure.

The chemical model for epoxy and amine (primary and secondary), and etherification, was kept as broad as possible to account for the various behaviours encountered by phenomenological modellers. The only difference between our proposed model and that of previous authors is the flexibility to include an autocatalytic expression for the etherification reaction:

\[ \dot{\alpha} = K_1(1-\alpha)^{n_1} + K_2\alpha^{m_2}(1-\alpha)^{n_2} + K_3\alpha^{m_3}(1-\alpha)^{n_3} \]

where \( K_1, K_2 \) and \( K_3 \) refer to the Arrhenius constants for epoxy-primary amine, epoxy-secondary amine, and etherification. Separating the parameters \( K_1 \) and \( K_2 \) such that they may have different orders of reaction for the \( n \)th order term is a familiar practice in the literature, as discussed in the Section 2.3.3.1.

The first step in model fitting was to find appropriate parameter values for the epoxy-amine reactions,

\[ \dot{\alpha} = K_1(1-\alpha)^{n_1} + K_2\alpha^{m_2}(1-\alpha)^{n_2} \]

The activation energies and rate constants were fit by least squares to 1151 data points between 0.04 and 0.99 degrees of cure. Table 5.5 outlines the data used for this step. It was found necessary to allow \( n_2 \) to vary from the mechanistic value of 1. The parameter values were determined to be \( A_1 = 14240 \) /sec, \( E_1 = 66435 \) J/mol, \( m_1 = 0, n_1 = 1, A_2 = 453684 \) /sec, \( E_2 = 73063 \) J/mol, \( m_2 = 1, n_2 = 2.5 \). The epoxy-amine model is overlaid on the cure rate isoconversionals chart in Figures 5.41 (a) to (c). This model fits within 10% of the data used in the fit (see Figure 5.37, zone 1).

The total reaction for the secondary-amine and epoxy reaction, \( m + n \), is 3.5. Typical reaction orders are 3 or lower, although some authors have reported reaction orders greater than 3 to fit epoxy-amine reactions: Srinivasan et al. [1995] for PR500 (an RTM resin) found \( m + n = 4.18 \) for the Sourour and Kamal model; Salla and Ramis [1996] for an unsaturated polyester resin found \( m + n \) ranged from 3.31 to 3.96; Cole et al. [1991] for a TGDDM/DDS resin system found \( m + n = 4.18 \) for a fit to the Sourour and Kamal model, but opted to model the system mechanistically.

Below 0.035 degree of cure and roughly 124°C, the epoxy-amine model (equation 5.6 (b)) overestimates the measured cure rates. Figure 5.42 shows how the model fits to this range of data. In Section 5.1.1.1 it
was remarked that a rise in Cp and heat flow could be noted in this temperature region at reaction kick-off for the dynamic tests, both indications of passing through a transition which increases molecular mobility. A simpler representation of this cure rate behaviour was modeled as illustrated in Figure 5.43, with $E_1$ set to 66435 J/mol above 124°C, and 73300 J/mol below 124°C. The value for $A_1$ was found to equal a logarithmic function with cure below a degree of cure 0.035,

$$33278*\ln(\alpha) + 229563 \text{ /sec}$$

Above 0.035 degree of cure and below 124°C, $A_1$ was set to 113881 /sec. Above 0.035 degree of cure and above 124°C, $A_1$ was returned to the original value of 14240 /sec. Figure 5.44 shows the calculated values of $A_1$ with degree of cure for temperatures less than 124°C. Figure 5.45 shows the adjusted epoxy-amine model fit to the cure rate isoconversional data at low temperatures and degrees of cure. The adjusted model does not fit accurately between 119 and 124°C, but captures the behaviour well at room temperature as shown in Figure 5.46. Figure 5.47 shows how the adjusted model corrects the prediction of degree of cure for a 0.5°C/min dynamic.

For the etherification reaction fit (see Figure 5.37, zone 2), attempts were made to fit the orders of reaction recommended by Cole et al. [1990], but the fits were not as good as allowing $m_3$ and $n_3$ to vary. Parameters for etherification were fit by reducing the sum of least squares over 214 data points. Figure 5.48 shows the resulting model, including the amine-epoxy reactions, overlaid on the isoconversional data for degrees of cure 0.1 and greater, and the values for the etherification parameters were $A_3 = 1.5E9$ /sec, $E_3 = 115451$ J/mol, $m_3 = 2.91$, $n_3 = 0.83$. The total order of reaction is 3.74, which does not fall within general parameters for reaction orders of 3 or less [Cole et al. 1990]. The addition of etherification changes the model marginally at degrees of cure less than 0.4 (e.g. 6% increase in cure rate at 230°C at 0.4 degree of cure).

In summary, below is a list of the Arrhenius constants found to fit the chemical reactions:

**Primary-Amine and Epoxy:**

If $T < 124^\circ C$ and $\alpha < 0.035$, Then $A_1 = 34378*\ln(\alpha) + 229563 \text{ /sec}$ and $E_1 = 73300$ J/mol;

If $A_1 < 50000$ /sec, Then $A_1 = 50000$ /sec.

End If.

Else, If $T < 124^\circ C$ and $\alpha > 0.035$, Then $A_1 = 113881$ /sec and $E_1 = 73300$ J/mol;

Else, If $T > 124^\circ C$, Then $A_1 = 14240$ /sec and $E_1 = 66435$ J/mol.

End If.

$m_1 = 0, n_1 = 1$
Secondary-Amine and Epoxy: \[ A_2 = 473684 /\text{sec}, E_2 = 73063 \text{ J/mol}, m_2 = 1, n_2 = 2.5 \]
Etherification: \[ A_3 = 1.5E9 /\text{sec}, E_3 = 115624 \text{ J/mol}, m_3 = 2.91, n_3 = 0.83 \]

### 5.2.4. Modeling Tg behaviour

As observed in Figure 5.25, the Tg-\( \alpha \) behaviour moves from a lower line, the blend relationship, to an upper line, the epoxy relationship. In between it was found that the Tg increased to the epoxy line at sequentially higher degrees of cure with increasing temperature. To capture this behaviour, the DiBenedetto equation established for the blend line was combined with an S-shape curve used to describe the increase in Tg with cure and the trend of delayed departure from the blend line with respect to temperature,

\[
T_g = \frac{\lambda \alpha (T_g - T_g_0)}{1 - (1 - \lambda)\alpha} + T_g_0 + \frac{D}{1 + \exp[-F(\alpha - \alpha_{\text{critical}})]}
\]

where D is a multiplier with a value of 35 K, F is the breadth of the transition and a value of 25 was found to match the transition for all isothermal and dynamic cures, \( \alpha_{\text{critical}} \) is the mid-point of the S-shape transition and was found to change with temperature and heating rate by the equation and rules

If \( dT/dt < 0.0001 \text{ K/sec} \), Then \( \alpha_{\text{critical}} = (0.0025 / K) * T - 0.3329 \);  
\[
\text{Else, } \alpha_{\text{critical}} = (0.0025 / K) * T - 0.00017 / T(K/\text{sec}) - 0.3329.
\]

End If.

If \( \alpha_{\text{critical}} < 0.675 \), Then \( \alpha_{\text{critical}} = 0.675 \).

End If.

If \( \alpha_{\text{critical}} > 1 \), Then \( \alpha_{\text{critical}} = 1 \).

End If.

Figure 5.49 maps the change in \( \alpha_{\text{critical}} \) with degree of cure for isothermals and dynamics. Figure 5.50 shows the fit of the Tg model to isothermal data, Figure 5.51 to the dynamic data. In these plots the dynamic data points were colour coordinated with the isothermals. A dynamic interrupted at a given temperature will match that same isothermal temperature. Tg growth during a slow heating rate behaves like a low isothermal temperature. Figure 5.52 shows how the Tg model predicts a decreasing Tg as temperature increases during a residual dynamic, understandable output from the model given that higher isothermal cures were found to follow the blend line until higher degrees of cure. This suggests that the
material is changing back to the blend morphology, but this is likely an over-exaggerated behaviour. Future work should test the accuracy of this concept.

5.2.5. Modeling diffusion behaviour

The rate of diffusion was calculated by solving a quadratic equation for the primary and secondary amine reactions, stemming from the Rabinowitch relationship for chemical and diffusion rates of reaction.

\[
\frac{1}{k_{e,i}(\alpha, T)} = \frac{1}{k_{c,i}(T)} + \frac{1}{k_{d}(\alpha, T)}
\]

where \(e\) stands for effective, \(c\) for chemical, \(d\) for diffusion, and \(i\) can be 1, 2 or 3 for the primary amine and epoxide, secondary amine and epoxide, and etherification reactions. The etherification reaction was subtracted from the raw data,

\[
\dot{\alpha}_{E,A} = \dot{\alpha}_{\text{measured}} - \dot{\alpha}_{E-OFF \, \text{model}} = f_1(\alpha) \left[ \frac{1}{k_{c,1}(T)} + \frac{1}{k_{d,1-2}(\alpha, T)} \right]^{-1} + f_2(\alpha) \left[ \frac{1}{k_{c,2}(T)} + \frac{1}{k_{d,1-2}(\alpha, T)} \right]^{-1}
\]

and the quadratic root is the rate constant of diffusion,

\[
k_{d,1-2} = (k_{c,1} + k_{c,2})\alpha_{E,A} - (f_1 + f_2)(k_{c,1} \ast k_{c,2})
\]

The diffusion model developed was only applied to the amine reactions, not the etherification reaction. Figures 5.53 and 5.54 show the rate constant of diffusion plotted against T-Tg and degree of cure, respectively. Isothermal temperatures 130 to 200°C are shown, and dynamics 0.2 and 0.5°C/min. Higher heating rates did not show diffusion behaviour for modeling. On both plots, dynamic points which correspond with isothermal temperatures were coloured accordingly. It is evident that the diffusion behaviour of the 0.5°C/min dynamic corresponds well to the isothermal behaviour, but the 0.2°C/min dynamic has a slower diffusion rate for the same temperatures. The Macedo and Litovitz [1965] expression for diffusion rate, which combines the Doolittle and Arrhenius equations, was found to adequately fit the data,

\[
k_d = A_d \exp \left( -\frac{E_d}{RT} \frac{b}{f_v} \right)
\]

where \(A_d = 4E12 \, \text{/sec}, E_d = 60 \, \text{kJ/mol}, b = 0.52, \) and \(f_v = 0.00008(T\text{-Tg}) + 0.025.\) To prevent errors in program calculations due to very low values of \(K_d\) predicted at low T-Tg values by equation 5.14, a condition was placed on \(K_d:\)

If T-Tg < -50 K, Then \(K_d = 1E-99 \, \text{/sec}\)
Figure 5.55 shows the diffusion model fit to epoxide-amine Ln[k_{d1,2}] data. Lowering the free volume expansion coefficient, \( a_t \), to 0.00008 /K was necessary to capture the behaviour at high degrees of cure. The thermal component allows the necessary spread between 130 and 190°C diffusion data; a temperature dependent term for \( A_d \) would be needed to fit higher temperatures exactly. The influence of the Tg equation to decrease the diffusion rate is evident in the total model fit (chemical and diffusion) to low heating rates, particularly for the 0.2°C/min test at 160°C and 0.75 degree of cure. Figure 5.56 shows the total model fit at this point for a 180°C isothermal hold; that is, chemical models for epoxide-amine reactions and etherification (see summary of models in Section 5.2.3), and diffusion model for epoxide-amine reaction (equation 5.14). Diffusion on the epoxide-amine reactions alone is insufficient to slow the cure reaction at long times. A diffusion term on the etherification reaction was also needed.

The effective cure rate constant for etherification was calculated by subtracting the epoxide-amine model (chemical and diffusion) from the measured data, and dividing by the \( f(\alpha) \) the etherification reaction,

\[
k_{e,3} = \frac{\dot{\alpha}_{\text{measured}} - \dot{\alpha}_{1,2}}{f_3(\alpha)}
\]

The diffusion rate constant was calculated by rearranging the Rabinowitch relationship, equation 5.11. Equation 5.14 without the thermal component was used to model the diffusion rate constant for etherification,

\[
k_{d,3} = A_{d,3} \exp\left(\frac{-b}{f_v}\right)
\]

Figure 5.57, shows the \( k_{3,d} \) model fit to the data calculated by equations 5.15 and 5.16 with model parameters \( A_{d,3} = 1.5E9 \) /sec, \( b = 0.7 \), and \( f_v = 0.00008(T-T_g) + 0.025 \). Since the data does not follow a clear trend, the degree of cure versus time data for isothermal holds was also used to fit \( k_{3,d} \). Figure 5.58 shows the final comparison of data to total model (chemical and diffusion for both epoxide-amine and etherification reactions). The etherification reaction is slightly too low at very high degrees of cure, but this is in a temperature range that is considerably above the MRCC.

As noted in the Literature Review, Cp relationships are being used in diffusion factor models. Although this strategy was not pursued in this work, a Cp model was fitted to the isothermal and dynamic data. The Cp model was developed by Ali Shakarami of Convergent Manufacturing Technologies, Vancouver, British Columbia. An explanation of the model, how it was fitted to data, and Figures of the model and data fit are included in Appendix E. The equation for Cp has the form,
\[ Cp = Cp_r - \frac{Cp_r - Cp_g}{1 + \exp(K((T - T_g) - \Delta T_c))} \]  
5.17

where subscripts \( r \) and \( g \) refer to rubbery and glassy, respectively, \( K \) is a fitting parameter, \( T \) is the cure temperature, and \( \Delta T_c \) is the difference between \( T \) and \( T_g \) at vitrification. \( C_{pr} \) and \( C_{pg} \) are functions of degree of cure and temperature, with the form,

\[ C_{pr} = (1 - \alpha)C_{r0} + \alpha C_{r0} \]  
5.18

where subscripts \( \theta \) and \( \infty \) refer to the uncured and fully cured states of the material, and each is a linear function of temperature with slope \( s \) and constant \( c \). Equation 5.8 was used to describe \( T_g \). The parameters found to fit both the dynamic and isothermal data were as follows:

\[
\begin{align*}
C_{p_{r0}} &= 0.0025\times T + 0.00178 \\
C_{p_{r\infty}} &= 1.227\times T + 1.363 \\
C_{p_{g0}} &= 0.0423\times T + 0.903 \\
C_{p_{g\infty}} &= 0.00308\times T + 1.002 \\
K &= 0.124 \\
\Delta T_c &= 3.632 \text{ K}
\end{align*}
\]

5.2.6. Cure model summary and goodness of fit for T800H/3900-2

The final model fit is recorded below for the chemical, \( T_g - \alpha \), and diffusion behaviour of T800H/3900-2:

Total Model:

\[ \dot{\alpha} = K_{1\text{eff}} (1 - \alpha)^{n_1} + K_{2\text{eff}} \alpha^{m_2} (1 - \alpha)^{n_2} + K_{3\text{eff}} \alpha^{m_3} (1 - \alpha)^{n_3} \]  
5.19

Chemical Reaction:

\[ \dot{\alpha} = K_1 (1 - \alpha)^{n_1} + K_2 \alpha^{m_2} (1 - \alpha)^{n_2} + K_3 \alpha^{m_3} (1 - \alpha)^{n_3} \]

Primary-Amine and Epoxy:

If \( T < 124^\circ \text{C} \) and \( \alpha < 0.035 \), Then \( A_1 = 34378\times \ln(\alpha) + 229563 \text{ /sec and } E_1 = 73300 \text{ J/mol;}
\)

If \( A_1 < 50000 \text{ /sec, Then } A_1 = 50000 \text{ /sec.}
\)

End If.

Else, If \( T < 124^\circ \text{C} \) and \( \alpha > 0.035 \), Then \( A_1 = 113881 \text{ /sec and } E_1 = 73300 \text{ J/mol;}
\)

Else, If \( T > 124^\circ \text{C}, Then } A_1 = 14240 \text{ /sec and } E_1 = 66435 \text{ J/mol.}
\)
Secondary Amine and Epoxy: \( A_2 = 473684 \text{ /sec, } E_2 = 73063 \text{ J/mol} \)

Etherification: \( A_3 = 1.5E9 \text{ /sec, } E_3 = 115624 \text{ J/mol} \)

Reaction Orders:

\( m_1 = 0, n_1 = 1 \)
\( m_2 = 1, n_2 = 2.5 \)
\( m_3 = 2.91, n_3 = 0.83 \)

**Tg-\( \alpha \):**

\[
T_{g} = \frac{\lambda \alpha (T_{g_{e}} - T_{g_{0}})}{1 - (1 - \lambda)\alpha} + T_{g_{0}} + \frac{D}{1 + \exp[-F(\alpha - \alpha_{\text{critical}})]}
\]

\( \lambda \) (copolymer) = 0.8, \( T_{g_{0}} = 8.8 \text{°C} \), \( T_{g_{e}} \) (copolymer) = 200°C, \( D = 35, F = 25 \)

\( T_{g_{e}} \) (epoxy) \( \geq 222 \text{°C} \)

\( \alpha_{\text{critical}} \):

If \( \frac{dT}{dt} < 0.0001 \text{ K/sec} \), Then \( \alpha_{\text{critical}} = (0.0025 / K) \ast T - 0.3329 \);

Else, \( \alpha_{\text{critical}} = (0.0025 / K) \ast T - (0.00017K / \text{sec}) / \dot{\gamma} - 0.3329 \).

End If.

If \( \alpha_{\text{critical}} < 0.675 \), Then \( \alpha_{\text{critical}} = 0.675 \).

End If.

If \( \alpha_{\text{critical}} > 1 \), Then \( \alpha_{\text{critical}} = 1 \).

End If.

**Diffusion:**

Primary and secondary amine reactions with epoxide:

\[
k_{d,1,2} = A_{d,1,2} \exp \left( -\frac{E_{d,1,2}}{RT} - \frac{b_{1,2}}{f_v} \right)
\]
$A_{d_{1,2}} = 4E12 \text{ /sec}, \ E_{d_{1,2}} = 60 \text{ kJ/mol}, \ b_{1,2} = 0.52, \text{ and } f_v = a_j(T-T_g) + f_g, \ a_j = 0.00008 \text{ /°C}, \ f_g = 0.025$

If $T-T_g <-50 \text{ K}$, Then $K_{d_{1,2}} = 1E-99 \text{ /sec}$

End If.

Etherification:

$$k_d = A_d \exp \left( -\frac{b_d}{f_v} \right)$$

$A_d = 1.5E9 \text{ /sec}, \ b_d = 0.7, \text{ and } f_v = a_j(T-T_g) + f_g, \ a_j = 0.00008 \text{ /°C}, \ f_g = 0.025$

If $T-T_g <-50 \text{ K}$, Then $K_d = 1E-99 \text{ /sec}$

End If.

$k_{d_{1,2}}$ and $k_{d_3}$ are added to $k_1$, $k_2$ and $k_3$ chemical by the Rabinowitch equation:

$$\frac{1}{K_c} = \frac{1}{K_c} + \frac{1}{K_d}$$

Figures 5.59 a) and b) show the percent differences (Data – Model)/Data between the total model (chemical and diffusion behaviour) and the isothermal and dynamic cure rate data points from Figure 5.58, respectively. Lower degrees of cure measured for both isothermals and dynamics are also included, showing greater errors than the higher degrees of cure. The total model fit the cure rate data within ±10% for the majority of points considered (Figure 5.58), with the exception of some points at very low degrees of cure and at the end of cure in the diffusion range. Despite the apparently poor fit to data in the diffusion range, only one point in the diffusion zone did not lie within error bars for standard deviation, 160°C and 0.8 degree of cure, evident in Figure 5.58.

Figures 5.60 (a), (b) and (c) show the total model fit to the isothermal data with respect to time. The model fits within the data limits of all temperatures except 180°C where it lags the data by at most 1.2% between 75 and 160 minutes, but falls with the spread of data before and after that time period. Figure 5.61 shows the integral fit to the dynamics. At degree of cure less than 0.1, the model over-predicts the data by at most 3%. For 0.2 and 0.5°C/min, the fit is poor at high temperatures because the etherification reaction does not have a rate limiting diffusion term. At worst, if a 0.2°C/min ramp were applied up to 180°C, the degree of cure prediction would only be off by 3%. The 0.5°C/min test is over-predicted at most by 3% at 219°C. Figures 5.62 and 5.63 show the model fit to 4°C/min residuals performed after isothermal holds at 150°C and 180°C, respectively. At most, the degree of cure was overestimated by 2%
which could easily fall within testing variability. Variability between five residuals for the same isothermal hold temperature and time was at most 4%, for example the five 160°C tests shown in Figure 5.60 (a).

In summary, the model provides a good overall fit to isothermal and dynamic data (residuals included). Cure rates were fit within 10% with exception of those at very low degrees of cure and the 0.2°C/min test, and degrees of cure were fit within 3%. The final model and parameters are recorded in Table 5.6.

5.2.7. Robustness testing

Tests were performed to capture the degree of cure development during the MRCC limits to test against model predictions. These tests stopped the cure cycle at intermediate times and performed a residual to measure the degree of cure. Figures 5.64 and 5.65 illustrate the comparison on degree of cure versus time plots for 0.56 and 2.8 °C/min heating rates, the limits of the MRCC respectively. The model fit to these intermediate tests is very good, within 3% at the worst fit point which occurs during the change from chemical to diffusion control.

5.2.8. Process map for T800H/3900-2

Four process maps are presented in Figure 5.66, (a) to (d), and are explained here in detail:

1) Figure 5.66 (a) shows the isothermal contours (grey lines) overlaid with the Tg-α relationship (blue lines). The dotted isothermal lines progress from 1 to 9 minutes in 1 minute increments. The dashed isothermal lines move from 10 to 50 minutes in 10 minute increments. The solid isothermal lines move from 60 to 480 minute lines at 60 minute increments. The lower Tg-α relationship was calculated with a heating rate of 0.2°C/min, and corresponds with the lowest α_{critical} of 0.675. The upper Tg-α relationship was calculated with a heating rate of 4°C/min, and corresponds with the highest α_{critical} of 1. From this plot the following points are evident: (a) the transition at 124°C and low degree of cure shows as a discontinuity; recall that this is an approximation of the actual trend, but is a clear indication of a change in cure behaviour at this point, either by a change in viscosity due to the thermoplastic modifier, or perhaps the melting of an inhibitor; (b) the onset of diffusion also occurs at 124°C, at roughly 0.65 degree of cure; (c) the onset of phase separation bounds the onset of diffusion; it appears to occur at an earlier temperature due to the approximations made in Tg-α modeling (see Figure 5.50) whereas the onset of phase separation may be a sharper transition; (d) full
cure is reached at 200°C for the maximum time of 480 minutes in this plot; the model does not entirely arrest cure, but allows continued increase in degree of cure at long times; within the range of interest this model is acceptable, but should have an upper limit of 24 hours.

2) Figure 5.66 (b) shows the isothermal and Tg-α contours as in (a), overlaid with isorate contours which start at 0.001 degree of cure and range from 0.2 to 10 °C/min (0.2, 0.5, 1, 2, 3, 4, 5, 8, 10°C/min). For a 180°C isothermal hold (MRCC), heating rates of 0.2 and 0.5°C/min will pass gelation during the ramp, and it isn’t until 2°C/min and higher that the distance between the isorate contours decreases showing less cure sensitivity to heating rate. Heating rates of 2°C/min and higher do not overlap with the Tg-α curve, which is anticipated given lack of evidence of diffusion behaviour in the Cp data (Figure 5.2).

3) Figure 5.66 (c) and (d) show the isothermal and Tg-α contours as in (a), overlaid with 0.56°C/min contours (lower MRCC limit) and 2.8°C/min contours (upper MRCC limit), respectively, with initial degree of cure increments of 0.05. In comparing the two plots, it is clear that once cure enters the diffusion zone for the lower heating rate it will never fully devitrify, whereas the higher heating rate delays cure until higher temperatures beyond the limits of the Tg-α boundaries. Continuing cure at a lower heating rate will allow a higher final degree of cure at lower temperatures where it is sure to not degrade (below 200°C), but at the cost of time.

### 5.3. **ROUND ROBIN RESULTS**

#### 5.3.1. **Summary of the study**

The Round Robin study in this work explored the following three issues pertaining to cure measurement by DSC and modeling robustness:

1. Understanding and reducing uncertainty in the measurement-to-modeling decision-making process for DSC testing;
2. The impact of cure model variability on process and design decisions;
3. How to establish guidelines that promote cure model reproducibility for the process modeling community.

The study itself consisted of completing a series of experimental and modeling stages involving six participating laboratories, the strategy of which was to systematically reduce the variability between laboratories from measurement to model-fitting, as outlined in Table 5.7. In stage 1, participants made all measurement and modeling decisions on the same material (T800H/3900-2 provided by The Boeing
Company); in stage 2, participants were given a raw data set produced by UBC for T800H/3900-2 and asked to perform their data reduction, analysis and model fitting preferences; and, in stage 3, participants were given the same raw data set but with baselines applied for area measurements and the Tg-α curve, and were asked to analyze the data and fit a cure model of their choice. At each stage, participants were asked to report their measurements, analysis decisions, model parameters, and their measure for the goodness of model fit to data. The final step of the study will be to open the discussion reported herein to participants and partners, Table 5.8, and to create a procedure for a second Round Robin to test a developed strategy for reducing variability.

Equipment selection was not included as one of the stages, but could have been with the availability of remote control. Measurements were also required to establish the quality of each DSC instrument, referred to as stage 0. The sample preparation stage was also not found to be necessary, and was ignored in the interest of time. The study did not pursue the analysis or model selection/fitting stages due to time constraints, and the difficulty for some participants to adjust their model fitting programs to fit the proposed model.

Cure model variability was investigated by comparing a literature review of models for Hexcel 8552 (see Chapter 3) and the three formal stages of the Round Robin. The literature review provided a worst case scenario of batch-to-batch variability, resin and prepreg information, and a wide range of cure measurement and modelling complexity. Variability was tested on the basis of four critical points during standard manufacturer recommended cure cycles: 1) the time to reach gelation at the MRCC’s cure temperature; this is a value that is given in some product data sheets; 2) the degree of cure and Tg at the start of the isothermal hold; 3) the maximum cure rate at the end of the highest allowable heating ramp in the MRCC; and, 4) the final degree of cure and Tg after the isothermal hold. Ideally, all of these critical processing points would be provided by the manufacturer or an accepted database of test results. It was found that the greatest variability occurred for the literature study, followed by stages 1, 2 and 3 of the Round Robin, respectively. Therefore, at each stage of the decision-making process there are lessons to learn about reducing variability. Table 5.9 records the above measures of variability. The sources of uncertainty found in each stage will be discussed in the proceeding sections. Table 5.10 summarizes the experimental, reduction, analysis and modeling decisions made by all participants throughout the three stages of the Round Robin.
5.3.2. Stage 0: Instrument quality and material quality control

All instruments used in this study were heat flux devices with disk-type sample and reference cells, a sample volume of at least 25 mm$^3$, and a nitrogen atmosphere with a temperature range of at least -60 to 550°C (see Table 5.11 for a list of general instrument specifications for each laboratory). Three types of tests were performed by each laboratory to determine the quality of the heat flow signal in terms of noise, repeatability and reproducibility: 1) five dynamic zero-line tests (heat flow measurement without samples or sample containers), and two isothermal zero-lines, to determine noise and the repeatability of the instrument heat flow signal; 2) three dynamic tests on standard materials, tin and indium, to determine reproducibility and calibration accuracy; and, 3) three dynamic tests on the CFRP system T800H/3900-2 to determine reproducibility of the signal across a broad temperature range.

The peak-to-peak noise (pp) is the maximum variation of the measured signal in relation to the mean signal value for a given test [Hohne et al., 1996]. The ‘short-time’ noise was measured over a 1-minute period at the indicated temperatures for scanning rates of 2 and 5°C/min, recorded in Table 5.12. The pp noise was reported to be less than 1 µW in most cases. Resolution at the beginning and end of reaction will be most affected by noise, as well as slow heating rates. The isothermal noise is also less than 1 µW, recorded in Table 5.12, measured during 100 and 250°C holds after the signal had reached temperature equilibration.

The temperature-dependent range of the deviation from the ‘mean’ zero-line (absolute or in %) gives a measure of the repeatability [Hohne et al., 1996]. Table 5.13 reports the repeatability for five zero-lines from 5°C/min scans between 50 and 275°C. Repeatability for 2°C/min scans was also collected, but was not different from the 5°C/min scans.

Accuracy of temperature and enthalpy measurements was compared by measuring the onset temperature and heat of melting for indium and tin (see Table 5.14 for test results from each laboratory and standard values). ASTM E967 for DSC temperature calibration states that for an interlaboratory comparison reproduced measurements for melting temperatures should be suspect if they are different by 1.5°C (95% confidence interval). ASTM E793 for measurement of enthalpies of fusion recommends that reproduced measurements for the enthalpy of fusion should be considered suspect if they differ by more than 8.6% (95% confidence interval). Unlike the ASTM standards, duplicates were not performed, but given this guideline groups B and E measured melting temperatures beyond the deviation allowed by the standard for both materials and group C for tin, and groups C and E measured enthalpies lower than the standard for both materials. The greatest cause for concern is the low heats of melting measured by groups C and
E. It is advised that both laboratories perform their own calibration across a wide temperature range to assure that heat flows are not in error. All instruments used at least indium to calibrate temperature and enthalpy. Group B used cesium chloride, indium, tin, zinc and bismuth to calibrate for temperature and heatflow, and Group E used indium and tin to calibrate temperature.

Heat of reaction reproducibility for the CFRP T800H/3900-2 was compared from three 5°C/min dynamics submitted by each laboratory. The T_g of the prepreg before testing, \( T_{g0} \), ranged from -2.69 to 6.63°C with an average of 4.51 ± 3.75°C (Table 5.15). It is unclear why group E’s heat flow signal drops earlier than other instruments to pass through \( T_{g0} \). Group A did not measure the \( T_{g0} \) for stage 0, but measured a value of 7.93°C for stage 1. Unfortunately not all groups returned a piece of prepreg to the UBC lab for testing the \( T_{g0} \), nor did they consistently continue to test for the \( T_{g0} \) for the remainder of the stages. Group F did note a change in their material \( T_{g0} \) during the study and requested new material be sent to continue the study. If stored with desiccant, an increase in \( T_{g0} \) may be due to the evaporation of water molecules which plasticize the epoxy resin.

Baselines for heat of reaction measurement were drawn as straight lines between the start and end of the reaction for all groups except D and E. Group D (UBC) used a flat baseline up to the onset temperature of degradation, and then a straight line to a local minimum in heat flow. Group E used a sigmoidal baseline. The heat of reaction ranged from 115.09 to 159.89 J/g with an average of 144.96 ± 16.39 J/g (11.3%). Group D used modulated DSC (± 1°C per 60 seconds) to remove the effect of changes in \( C_p \), but the findings still lie within the range of measurements found by the other groups. The high variability within laboratory F may be due to the variability in resin fraction for small sample sizes, as discussed in Chapter 4.

Figure 5.67 (a) shows the heat flow signal with temperature for the 5°C/min test measured by each laboratory; laboratory C did not submit their data. Figure 5.67 (b) shows the degree of cure plotted against temperature. Also shown in Figure (b) is the error within a laboratory compared with the error between laboratories (with and without group B). The reaction timing measured by instrument B is in advance of the others, and hence is the most noteworthy contributor to variability between laboratories. By degree of cure of 0.2, the maximum error between the other four laboratories is roughly 1%. Without knowledge of the zerolines and the subtraction process from the measured signal for CFRP, it is difficult to comment further on this discrepancy.
In general, the quality of the instruments is good. Instrument E is the oldest instrument, and has the most zeroline variability. Instruments C and E showed considerable variation from the standard heat of melting for tin. Instrument C had the lowest value, which may also explain their low value for CFRP heat of reaction (Table 5.15). Yet the reduced data from these groups agreed well with others (Figure 5.67 (b)). Instrument B has an outstanding issue related to the reaction timing, which may be due to zero-line curvature, or a calibration artifact due to using several standards.

5.3.3. Stage 1: Participants perform cure measurements and develop cure models for T800H/3900-2 prepreg system

This section summarizes the experimental-to-modeling decisions made by each laboratory to produce cure models for T800H/3900-2. Table 5.16 records the experimental decisions for each group. Group D is UBC, and the experimental details and model development was outlined previously in this thesis and hence will not be repeated extensively here. Group B used dynamic tests to fit a model, Group D used both isothermal and dynamic tests, and all other groups used only isothermals apart from one dynamic to determine the ultimate heat of reaction. The ranges of isothermal temperatures used for fitting varied from 20°C (groups C and E), to 40°C (group A), 70°C (group D) and 80°C (group F). The mean temperatures for groups A, C, D and E were between 160 and 170°C, whereas for group C it was 205°C. Group C only intended to measure the chemical reaction, not diffusion, and hence decided to test above their measured Tg, of 193°C (measured during cooling from 320°C during a 5°C/min dynamic; according to Appendix D reaching 320°C would have caused degradation and hence lowered Tg,).

The following general data reduction decisions were made by all groups concerning baselines for heat of reaction calculations. Groups, except D (UBC), used a straight dynamic baseline between points on the heat flow curve at the reaction kickoff and end temperatures. All groups used a horizontal isothermal baseline. Figure 5.68 (a) shows the heats of reaction measured for all isothermal tests, and (b) for dynamic tests performed by groups B and D. Groups A and D back-calculated the magnitude of the isothermal baseline heat flow in order to equate $H_{\text{Ultimate}}$ and $H_{\text{Total}}$. All other groups set the isothermal baseline magnitude to match the heat flow at the end of the reaction (indicated by negligible change in heat flow), or when the test was stopped. The isothermals for group C were missing ~10J/g compared to their $H_{\text{Ultimate}}$, and did not correct for the difference. Group D reported up to 11% difference between isothermal and dynamic heats of reaction, and attributed some of the missing heat lost during the ramp to the isothermal hold, and the remaining was recovered by lowering the isothermal baseline. Group F reported missing ~20J/g from isothermal heat of reactions and attributed all heat lost to the ramp. In
contrast, group A did not report any missing heat of reaction and did not account for heat lost during the ramp to the isothermal hold. Dynamic heats of reaction for group B were lower than D due to the difference between using a straight-line baseline and flat baseline, respectively. Figure 5.69 shows the Tg-α curves from data provided by the participants. This data was not required of participants, but provided a comparison as to the influence of analysis decisions. Figure 5.69 shows that when \( H_{\text{Total}} = H_{\text{Ultimate}} \), no matter the exact value, the Tg-α relationships overlap.

Table 5.17 records the data analysis, model selection, and model fitting strategies reported by each group for stage 1. Secondary test methods were not employed to determine initial monomer content but group A did set an initial degree of cure to 1%. Nor were measurements taken to track the consumption of reactants, and hence all models were applied on a phenomenological basis. The models and values for parameters are recorded in Table 5.18. Most groups followed the assumption that the total heat measured by the DSC was analogous to the heat evolved by the consumption of epoxide, and their models were based on the consumption of epoxide (α) described by either an autocatalytic reaction or some variation of the Horie model. Group B did not follow the above assumption and proposed a two-term sequential reaction with the following design: in the first term the depletion of epoxide (A or α) is coupled with the formation of some product (B or β), which in turn is consumed by an nth order reaction to produce C. The normalized concentrations of α and β start at 0.99995 and 0.00003, respectively, and the degree of cure was defined as (1 – α), and the rate of cure by \( \alpha/\text{dt} \). This relationship implies that epoxide bonds are only participating in the first reaction, and hence their depletion will be faster than if they were limited by some proportion of reactant and were also a part of the second reaction. Only groups B and D showed fits to dynamic data.

Figures 5.70 (a) and (b) compare the model predictions for a 5°C/min dynamic in terms of degree of cure versus temperature and cure rate. In Figure (a) the data from Figure 5.67 (b) is also included, indicated by black circles. At this heating rate diffusion was not a factor. The percent error in Figure (a) between the six models is greater than 10% until the high degrees of cure. Given that degree of cure calculations for 5°C/min tests for at least five of the groups were under 10% after 170°C, differences have accrued during data analysis and model selection/fitting. Models B, E and F show the most deviation from the mean predictions (models A, C and D). Model F proposed a temperature dependent order of reaction, \( n \) over a (1-α) term, which increases with temperature and effectively delayed the reaction at higher temperatures and degrees of cure. Model E overestimated the progress of cure after 170°C, which perhaps is best explained by the limited isothermal temperature range used to fit the data and lack of diffusion control.
Chapter 5: Results for T800H/3900-2 Cure Kinetic Analysis and Round Robin Study

The timing of model B is in advance of all other models, which may be traced back to their decision to treat the second reaction separate from any epoxide interaction, reflected in Figure (b) as well.

Figures 5.71 (a) and (b) compare the degree of cure with respect to temperature predictions for the MRCC heating rate limits of 0.56°C/min and 2.86°C/min, respectively, followed by a 140 minute hold at 180°C. For the low MRCC limit the degree of cure predictions at the end of the ramp varied between 0.72 and 0.99 in degree of cure (±12.7% error), and 0.89 to 1 at the end of the hold (±4.9%). Given the Tg-α curve of Figure 5.69, the range of Tg’s at the end of the 0.56°C/min ramp would be 166 to 225°C, leading to a considerable difference in residual stress predictions. The heating rates required to assure that gelation is not reached by end of the ramp for each model were found to be: A: 0.9°C/min, B: 1.6°C/min, C: 1.5°C/min, D: 0.9°C/min, E: 1.15°C/min, F: 1°C/min. Also on these figures are three circles indicating the degree of cure calculated by interrupting the cure cycle at these points and measuring the residual heat of reaction. This is a ruggedness test. Models A, D and F have the most accurate cure profile up to the point where diffusion becomes dominant, and then groups A and D continue to have the best prediction of cure in the diffusion zone.

For the upper MRCC limit, models vary between 0.19 and 0.32 in degree of cure at the end of the ramp (±22.5%), and between 0.87 and 1 at the end of the hold (±6.1%). The degree of cure is sufficiently lower than gelation (i.e. 0.5) at the end of the ramp. The maximum heat flows ranged from 0.063 to 0.083 W/g.

5.3.4. Stage 2: Common data set, individual reduction-to-modeling decisions

In Stage 2, groups were given the same data set to analyze, provided by UBC. This data set was also different from the one used by group D (UBC) in stage 1. Most participants continued to perform area calculations to determine the degree of cure with time and temperature, and used the same baseline methodology as outlined for each group in Stage 1, as well as the same data reduction techniques. Group D used a straight line between the onset and end of the dynamic reaction curves rather than a flat baseline. Table 5.19 records the experiments used by each group to fit a model. Table 5.20 records the model and parameters chosen by each group. Groups A and F maintained the same model. Groups B added diffusion to the second reaction (B→C), and group E added a second autocatalytic reaction and a diffusion factor to their entire equation. Group D opted for a simpler chemical and diffusion model. Figure 5.72 shows the Tg-α models proposed by groups B and D, which differ considerably below 0.55 degree of cure. Group B used Tg in their diffusion model, but group D did not.
Figures 5.73 (a) and (b) compare the degree of cure predictions with respect to temperature for the MRCC limits, 0.56°C/min and 2.8°C/min ramps respectively, to 180°C for a 140 minute hold. For the slower heating rate, degree of cure varied from 0.78 to 0.89 at the end of the ramp (±6.5%), and 0.93 to 1 at the end of the hold (±3.1%). Given Figure 5.72, model D, the Tg range at the end of the ramp was 173 to 203°C. For the upper limit, degree of cure varied from 0.11 to 0.34 at the end of the ramp (±33.5% difference), and 0.91 to 1 at the end of the hold (±3.6%). Again, the model for group B would better match the timing of the others at high heating rates if the assumption of heat flow analogous to epoxide reaction were used. The model would over-estimate the cure at low heating rates, despite the change in fundamental assumptions. Otherwise, the timing is fairly consistent between the groups until the different diffusion definitions are active. The effect of group F’s rules for reaction orders (before and after 170°C) are apparent during the slow heating rate. Worthy of note is the complexity of the chemical models and how this may relate to variability. Models A and F use a single reaction and overlap up to the point of diffusion dominance. Comparatively, models D and E use at least two reaction mechanisms, and their rate of cure matches well up to the diffusion dominated zone. The ruggedness tests shows that models D and E follow the cure profile best up to the point of diffusion, after which model B predicts the most accurate final degree of cure.

5.3.5. Stage 3: Common data and reduction, individual model and fitting

In Stage 3, participants received data which had the areas and temperatures of interest (Tg’s, peak temperatures) measured. Baselines were provided with the raw data, and were the same as those used in Stage 2 for dynamic and isothermal data, respectively, as decided by the majority of participants. A diagonal baseline between the start and end points of the cure reaction were used for dynamics, which resulted in excellent agreement between isothermal and dynamic total heats of reaction (Hultimate = 133 J/g). Unfortunately this decision is incorrect, as discussed in Section 5.1.3, and leads to differences in dynamic and isothermal cure rates as shown in Figure 5.74. Only groups D and E noted the differences in cure rates between isothermals and dynamics. Participants chose the same data and models as in Stage 2. Group F changed their definition of final degree of cure to account for diffusion. Table 5.21 records the models and parameters proposed by each group. Figure 5.75 shows the Tg-α data and proposed models by groups B and D. Figures 5.76 (a) and (b) compare the model fits to the MRCC limits with degrees of cure calculated for interrupted tests throughout the cycle. For the lower heating rate, degree of cure varied between 0.77 and 0.92 at the end of the ramp (±6.7% error), and 0.88 to 1 at the end of the hold (±4.5%). For the higher heating ramp, degree of cure varied between 0.22 to 0.33 at the end of the ramp.
(±1.8%), and 0.88 to 1 at the end of the hold (±4.5%). The variability is roughly the same as that measured for stage 2, except for the decrease in variability at the end of the ramp during the highest heating rate by the MRCC standard, low degrees of cure and low temperatures. The same comment can be made for this stage regarding chemical model complexity: models A and F overlap and used a single reaction mechanism each, and models D and E overlap and used at least two reaction mechanisms each.

According to the ruggedness tests, for the slow heating rate all of the models (except B) perform very well up to the diffusion zone, and then model F predicts the most accurate final degree of cure. For the high heating rate, the best fit is for models D and E up to the diffusion zone, and thereafter

5.3.6. Summary of measurement and modeling uncertainty

Variability within the Round Robin study was clearly better than that of the 8552 literature review. Furthermore, variability decreased as the stages progressed. Below is a summary of the major sources of uncertainties identified between the levels of this study:

**Literature review:**

i. Material quality control. Batch-to-batch variability and possible changes to the chemistry (the findings span a decade). Also, the state of the material before cure testing was not reported, and hence the history of the material may have been an important factor.

ii. Unknown instrument and measurement quality, and a wide variety of instruments used.

iii. Range of experimental parameters. Those using dynamic data produced higher cure rates than the isothermal tests. Dynamic and isothermal data was not cross-compared for improved model fitting.

iv. Data reduction decisions were not consistently reported.

v. Comparing both resin and prepreg. Opalicki et al. [1996] showed a change in timing between the two.

vi. Chemical model accuracy. Some models could only be applied to isothermal or dynamic conditions, but not both. The choice of reactions to model, and the complexity of the chemical model, also varied.

**Stage 0:**

i. Heat flow accuracy over a wide range of temperatures. This was evident for both standard materials and CFRP.

**Stage 1:**
i. Range of experimental parameters. The use of higher temperatures and dynamics (excluding diffusion dominated zones) lead to overestimated cure rates at low temperatures and degrees of cure.

ii. Baseline selection within a data set. Although groups A and D used different baselines for their dynamic experiments, their cure predictions overlap very well for the MRCC limits. An artefact may be introduced, and modeled very well, but it would not be a true representation of the material behaviour.

iii. $H_{\text{Total}} = H_{\text{Ultimate}}$. This proved necessary for in order for $Tg_{\alpha}$ data to overlap between groups.

iv. Following the underlying assumption that heat flow is analogous to the reaction of epoxide. The underlying assumption may not be true, but it should be recognized that following it versus not will cause important differences in the interpretation of degree and rate of cure of epoxide.

v. Diffusion model accuracy.

**Stage 2:**

i. Diffusion model accuracy.

ii. Chemical model accuracy

**Stage 3:**

i. Baseline selection. A linear baseline created an artificial difference between dynamic and isothermal cure rates. A method of checking for consistency between isothermal and dynamic data is needed.

ii. Diffusion model accuracy.

iii. Chemical model accuracy.

In Chapter 6 the sources of uncertainty observed between the study on T800H/3900-2 in this thesis (Sections 5.1 and 5.2) and the results from the Round Robin (Section 5.3) are combined into a single list of best practices along with some proposed best practices for minimizing the uncertainty. Furthermore, the design for a second Round Robin to test the best practices will be presented.
Table 5.1 Identifying reaction temperatures in nonreversing heat flow signal

<table>
<thead>
<tr>
<th>dT/dt (°C/min)</th>
<th>T_s (°C)</th>
<th>T_p (°C)</th>
<th>T_f (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>88</td>
<td>140</td>
<td>237</td>
</tr>
<tr>
<td>0.5</td>
<td>83</td>
<td>160</td>
<td>237</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
<td>176</td>
<td>245</td>
</tr>
<tr>
<td>1.5</td>
<td>110</td>
<td>186</td>
<td>251</td>
</tr>
<tr>
<td>2</td>
<td>111</td>
<td>194</td>
<td>257</td>
</tr>
<tr>
<td>2.5</td>
<td>111</td>
<td>200</td>
<td>263</td>
</tr>
<tr>
<td>3</td>
<td>113</td>
<td>204</td>
<td>265</td>
</tr>
<tr>
<td>4</td>
<td>116</td>
<td>213</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>118</td>
<td>220</td>
<td>277</td>
</tr>
<tr>
<td>8</td>
<td>118</td>
<td>234</td>
<td>286</td>
</tr>
<tr>
<td>10</td>
<td>120</td>
<td>242</td>
<td>291</td>
</tr>
</tbody>
</table>

Table 5.2 Comparison of degradation and reaction end temperature for dynamics

<table>
<thead>
<tr>
<th>dT/dt (°C)/min</th>
<th>T_{onset} Degradation(°C)</th>
<th>T_f (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>217</td>
<td>237</td>
</tr>
<tr>
<td>0.5</td>
<td>220</td>
<td>237</td>
</tr>
<tr>
<td>1</td>
<td>224</td>
<td>245</td>
</tr>
<tr>
<td>2</td>
<td>245</td>
<td>257</td>
</tr>
<tr>
<td>3</td>
<td>252</td>
<td>265</td>
</tr>
<tr>
<td>4</td>
<td>259</td>
<td>270</td>
</tr>
<tr>
<td>10</td>
<td>276</td>
<td>291</td>
</tr>
</tbody>
</table>
Table 5.3 Measurement of vitrification in Cp signal for 0.2 to 1.5 °C/min dynamics

<table>
<thead>
<tr>
<th>dT/dt (°C/min)</th>
<th>T_{vit.} (°C)</th>
<th>ΔC_{P_{vit.}} (J/g°C)</th>
<th>T_{devit.} (°C)</th>
<th>ΔC_{P_{devit.}} (J/g°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>156</td>
<td>0.035</td>
<td>220</td>
<td>0.075</td>
</tr>
<tr>
<td>0.5</td>
<td>180</td>
<td>0.026</td>
<td>225</td>
<td>0.091</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>0.00001</td>
<td>225</td>
<td>0.067</td>
</tr>
<tr>
<td>1.5</td>
<td>218</td>
<td>&lt;0.00001</td>
<td>225</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 5.4 Degree of cure at vitrification/devitrification for slow dynamics

<table>
<thead>
<tr>
<th>dT/dt (°C/min)</th>
<th>DOC_{vit}</th>
<th>DOC_{devit}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.65</td>
<td>0.97</td>
</tr>
<tr>
<td>0.5</td>
<td>0.75</td>
<td>0.98</td>
</tr>
<tr>
<td>1</td>
<td>0.78</td>
<td>0.98</td>
</tr>
<tr>
<td>1.5</td>
<td>0.88</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 5.5 Temperature and heating rate ranges for activation energy calculations

<table>
<thead>
<tr>
<th>Experiment Type</th>
<th>Degree of Cure</th>
<th>Temperature/Heating Rate Range (°C, °C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>0.02</td>
<td>130 to 140</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>130 to 170</td>
</tr>
<tr>
<td></td>
<td>0.1 to 0.4</td>
<td>130 to 200</td>
</tr>
<tr>
<td></td>
<td>0.45 to 0.85</td>
<td>180 to 200</td>
</tr>
<tr>
<td>Dynamic</td>
<td>0.01 to 0.45</td>
<td>0.2 to 10</td>
</tr>
<tr>
<td></td>
<td>0.5 to 0.8</td>
<td>0.5 to 10</td>
</tr>
<tr>
<td></td>
<td>0.85 to 0.95</td>
<td>1.5 to 10</td>
</tr>
</tbody>
</table>
### Table 5.6 Record of cure and model constants

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Value for T800H/3900-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{c,1}, E_{c,1}$</td>
<td>$T&gt;124^\circ C$ Primary amine and epoxy reaction rate constant and activation energy</td>
<td>14239 /sec, 66435 J/mol</td>
</tr>
<tr>
<td>$A_{c,1}, E_{c,1}$</td>
<td>$T&lt;124^\circ C, DOC&lt;0.035$ Secondary amine and epoxy reaction rate constant and activation energy</td>
<td>34378*ln((\alpha)) + 229563 /sec, 73300 J/mol</td>
</tr>
<tr>
<td>$A_{c,1}, E_{c,1}$</td>
<td>$T&lt;124^\circ C, DOC&gt;0.035$ Etherification reaction rate constant and activation energy</td>
<td>150000 /sec, 73300 J/mol</td>
</tr>
<tr>
<td>$A_{c,2}, E_{c,2}$</td>
<td>Secondary amine and epoxy reaction rate constant and activation energy</td>
<td>473684 /sec, 73063 J/mol</td>
</tr>
<tr>
<td>$A_{c,3}, E_{c,3}$</td>
<td>Etherification reaction rate constant and activation energy</td>
<td>1.5E9 /sec, 115624 J/mol</td>
</tr>
<tr>
<td>$m_1, n_1$</td>
<td>Primary amine and epoxy orders of reaction</td>
<td>0, 1</td>
</tr>
<tr>
<td>$m_2, n_2$</td>
<td>Secondary amine and epoxy orders of reaction</td>
<td>1, 2.5</td>
</tr>
<tr>
<td>$m_3, n_3$</td>
<td>Etherification orders of reaction</td>
<td>2.91, 0.83</td>
</tr>
<tr>
<td>$\lambda_{Blend}$</td>
<td>Material constant</td>
<td>0.8</td>
</tr>
<tr>
<td>$T_{g0}$</td>
<td>Tg of B-staged prepreg</td>
<td>281.95 K</td>
</tr>
<tr>
<td>$T_{g\infty, Blend}$</td>
<td>Tg of fully cured resin in blend phase</td>
<td>473.15 K</td>
</tr>
<tr>
<td>$T_{g\infty, Epoxy}$</td>
<td>Tg of fully cured resin in epoxy phase (as measured)</td>
<td>493.15 K</td>
</tr>
<tr>
<td>$D$</td>
<td>Multiplier</td>
<td>35 /sec</td>
</tr>
<tr>
<td>$F$</td>
<td>Exponential shaping parameter</td>
<td>25</td>
</tr>
<tr>
<td>$\alpha_{critical}$</td>
<td>$dT/dt&lt;0.0001 \text{ K/sec}$ Transition point of an s-shape curve</td>
<td>(0.0025 /K)*T - 0.3329 - 0.00017/(dT/dt K/sec)</td>
</tr>
<tr>
<td>$\alpha_{critical}$</td>
<td>$dT/dt&gt;0.0001 \text{ K/sec}$ Transition point of an s-shape curve</td>
<td>(0.0025 /K)*T - 0.3329</td>
</tr>
<tr>
<td>$A_{d,1-2}, E_{d,1-2}$</td>
<td>Diffusion rate constant and activation energy</td>
<td>4E12 /sec, 60000 J/mol</td>
</tr>
<tr>
<td>$b_{1,2}$</td>
<td>Material constant</td>
<td>0.52</td>
</tr>
<tr>
<td>$A_{d,3}$</td>
<td>Diffusion rate constant and activation energy</td>
<td>1.5E9 /sec</td>
</tr>
<tr>
<td>$b_3$</td>
<td>Material constant</td>
<td>0.7</td>
</tr>
<tr>
<td>$a_f$</td>
<td>Free volume coefficient of expansion</td>
<td>0.00008 /K</td>
</tr>
<tr>
<td>$f_g$</td>
<td>Free volume at the glass transition</td>
<td>0.025</td>
</tr>
</tbody>
</table>
### Table 5.7 Outline of round robin stages

<table>
<thead>
<tr>
<th>Uncertainty Parameter</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Preparation</td>
<td>Individual Laboratory Decision</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Experiment Schedule</td>
<td>Individual</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Data Reduction (e.g. area measurement, peak temperature, $T_g$)</td>
<td>Individual</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Data Set Analysis / Model Fitting</td>
<td>Individual</td>
<td>Common</td>
<td>Common</td>
</tr>
</tbody>
</table>

### Table 5.8 Participants and partners

<table>
<thead>
<tr>
<th>Participants/Partners</th>
<th>Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Pascal Hubert, Dr. Martine Dubé</td>
<td>McGill University, Dept. of Mechanical Engineering, Montreal, Quebec, Canada</td>
</tr>
<tr>
<td>Dr. Nuri Ersoy¹, Dr. Nihan Ugay¹</td>
<td>¹Bogazici University, Polymer Research Centre, Istanbul, Turkey</td>
</tr>
<tr>
<td>Dr. Melih Papila²</td>
<td>²Sabanci University, Turkey</td>
</tr>
<tr>
<td>Dr. Michele Giordano, Dr. Vincenza Antonucci</td>
<td>National Research Council Italy, Institute of Composite Materials Technology, Napoli, Italy</td>
</tr>
<tr>
<td>Dr. Karl Nelson</td>
<td>Boeing Phantom Works, Seattle, Washington, United States</td>
</tr>
<tr>
<td>Prof. Ivanna Partridge, Thanos Dimopoulos</td>
<td>Composites Centre, Department of Materials, School of Applied Sciences, Cranfield University, Bedford, United Kingdom</td>
</tr>
<tr>
<td>Dr. Andrew Johnston³, Dr. Mehdi Hojjati⁴, Dr. Jihua (Alex) Chen⁴, Ghislain Chouinard⁴</td>
<td>³National Research Council Canada, Institute for Aerospace Research, Ottawa, Ontario, Canada ⁴Aerospace Manufacturing Technology Centre, Montreal, Quebec, Canada</td>
</tr>
<tr>
<td>Dr. Kenneth Cole⁵, Ngo Tri Dung⁶</td>
<td>⁵National Research Council Canada, Industrial Materials Institute, Boucherville, Quebec, Canada ⁶Concordia University, Dept. of Mechanical &amp; Industrial Engineering, Montreal, Quebec, Canada</td>
</tr>
<tr>
<td>Dr. Anoush Poursartip, Donna Dykeman</td>
<td>University of British Columbia, Dept. of Materials Engineering, Composites Group, Vancouver, British Columbia, Canada</td>
</tr>
</tbody>
</table>
### Table 5.9 Comparison of variability between 8852 literature survey and T800H/3900-2 Round Robin results

<table>
<thead>
<tr>
<th>Material</th>
<th>8552, AS4/8552&lt;sup&gt;1&lt;/sup&gt;</th>
<th>T800H/3900-2</th>
<th>T800H/3900-2</th>
<th>T800H/3900-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage</td>
<td>N/A</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Time to gel (min) 177°C/180°C</td>
<td>18.29 ± 6.97 (±38.1 %)</td>
<td>18.5 ± 3.57 (±19.3%)</td>
<td>20.8 ± 3.2 (±15.4%)</td>
<td>18.0 ± 3.9 (±21.2%)</td>
</tr>
<tr>
<td>DOC end of ramp, LMRCC&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.50 ± 0.24 (±46.7%)</td>
<td>0.83 ± 0.11 (±12.7%)</td>
<td>0.80 ± 0.04 (±4.8%)</td>
<td>0.82 ± 0.06 (±7.1%)</td>
</tr>
<tr>
<td>DOC end of hold, LMRCC</td>
<td>0.89 ± 0.08 (±8.8%)</td>
<td>0.96 ± 0.05 (±4.9%)</td>
<td>0.97 ± 0.03 (±2.8%)</td>
<td>0.94 ± 0.03 (±3.6%)</td>
</tr>
<tr>
<td>DOC end of ramp, HMRCC&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.35 ± 0.28 (±81.8%)</td>
<td>0.24 ± 0.05 (±22.5%)</td>
<td>0.22 ± 0.012 (±5.3%)</td>
<td>0.22 ± 0.02 (±8.1%)</td>
</tr>
<tr>
<td>DOC end of hold, HMRCC</td>
<td>0.89 ± 0.07 (±8.4%)</td>
<td>0.95 ± 0.06 (±6.1%)</td>
<td>0.97 ± 0.03 (±2.8%)</td>
<td>0.94 ± 0.03 (±3.6%)</td>
</tr>
<tr>
<td>$H_{\text{Ultimate}} (J/g)$</td>
<td>189.11 ± 12.27 (±6.5%)</td>
<td>144.96 ± 16.39 (±11.3%)</td>
<td>133.55 ± 1.26 (±0.9%)</td>
<td>134.54 ± 0.61 (±0.5%)</td>
</tr>
<tr>
<td>Max CR end of hold (/sec), HMRCC</td>
<td>9.00E-4 ± 7.78E-4 (±86.4%)</td>
<td>4.90E-4 ± 5.03E-5 (±10.3%)</td>
<td>4.99E-4 ± 4.19E-5 (±8.4%)</td>
<td>4.96E-4 ± 3.79E-5 (±7.7%)</td>
</tr>
</tbody>
</table>

1 Excluding models by Ng et al. for all measurements, and Costa et al. and Sun et al. (b) for measurements involving isothermal holds.

2 LMRCC refers to the lowest heating rate limit of the MRCC, 1.8°C/min for 8852 and 0.56°C/min for 3900-2.

3 HMRCC refers to the highest heating rate limit of the MRCC, 3°C/min for 8852 and 2.86°C/min for 3900-2.
Table 5.10 Decision process and results recorded during the Round Robin study

<table>
<thead>
<tr>
<th>Stage</th>
<th>Decision</th>
<th>Tests or options explored in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: Instrument quality</td>
<td>Zero-line repeatability</td>
<td>Repeat dynamic tests without sample or pans</td>
</tr>
<tr>
<td></td>
<td>Signal noise</td>
<td>Dynamic and isothermal tests</td>
</tr>
<tr>
<td></td>
<td>Calibration check</td>
<td>Enthalpy and onset temperature of melting for standard materials across a wide temperature range</td>
</tr>
<tr>
<td></td>
<td>Initial material state</td>
<td>Measured $T_g$</td>
</tr>
<tr>
<td></td>
<td>Repeatability and reproducibility of reaction heat flow</td>
<td>Repeat dynamic tests on CFRP, analyzed for degree and rate of cure and heat of reaction</td>
</tr>
<tr>
<td>1: All decisions made by individual laboratories</td>
<td>Process conditions to test</td>
<td>Isothermal temperatures and hold times, dynamic heating rates, combinations</td>
</tr>
<tr>
<td></td>
<td>Test methods</td>
<td>Programmed ramp to isothermal holds; modulation amplitude and period; heating rate to measure $T_g$’s, maximum temperatures, etc.</td>
</tr>
<tr>
<td></td>
<td>Data reduction</td>
<td>All used area calculations to measure degree and rate of cure. Decisions pertained to baseline selection and balancing $H_{Total} = H_{Ultimate} - T_g$, measured by heat flow and heat capacity signals.</td>
</tr>
<tr>
<td></td>
<td>Data analysis</td>
<td>Activation energy was calculated by 1. traditional isothermal kinetic method; 2. cure rate isocconversionals; 3. multivariable nonlinear regression programs.</td>
</tr>
<tr>
<td></td>
<td>Model selection</td>
<td>Phenomenological models with parameters based on the Horie model, versus a sequential model fit. Other behaviour and reactions modeled included diffusion and etherification.</td>
</tr>
<tr>
<td></td>
<td>Model fitting</td>
<td>a. Least squares; b. linear regression; c. multivariable nonlinear regression</td>
</tr>
<tr>
<td></td>
<td>Goodness of fit</td>
<td>Visual inspection of model fit to cure rate or heat flow</td>
</tr>
</tbody>
</table>

2: Raw data provided by UBC, individual laboratories reduce, analyze and model. Laboratories chose the same data reduction decisions as Stage 1 and only changed the model and parameter values.

3: Raw data and data reduction provided by UBC, individual laboratories analyzed the data, selected and fit a model. Participants chose the same analysis method and model, and only changed the parameter values.
### Table 5.11 General instrument information

<table>
<thead>
<tr>
<th>Group</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Type</th>
<th>Sample Volume (mm³)</th>
<th>Atmosphere</th>
<th>Scanning Range (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TA Instruments</td>
<td>Q100</td>
<td>Heat flux disk-type</td>
<td>133</td>
<td>Nitrogen</td>
<td>-90 to 750</td>
</tr>
<tr>
<td>B</td>
<td>Netzsch</td>
<td>204 Phoenix</td>
<td>Heat flux disk-type</td>
<td>25</td>
<td>Nitrogen</td>
<td>-170 to 700</td>
</tr>
<tr>
<td>C</td>
<td>TA Instruments</td>
<td>Q1000 MDSC</td>
<td>Heat flux disk-type</td>
<td>40</td>
<td>Nitrogen</td>
<td>-150 to 550</td>
</tr>
<tr>
<td>D</td>
<td>TA Instruments</td>
<td>Q1000 MDSC</td>
<td>Heat flux disk-type</td>
<td>40</td>
<td>Nitrogen</td>
<td>-90 to 550</td>
</tr>
<tr>
<td>E</td>
<td>TA Instruments</td>
<td>2920 MDSC</td>
<td>Heat flux disk-type</td>
<td>40</td>
<td>Nitrogen</td>
<td>-60 to 600</td>
</tr>
<tr>
<td>F</td>
<td>TA Instruments</td>
<td>Q1000 MDSC</td>
<td>Heat flux disk-type</td>
<td>40</td>
<td>Nitrogen</td>
<td>-180 to 725</td>
</tr>
</tbody>
</table>

#### 5.12 Scanning and isothermal noise

<table>
<thead>
<tr>
<th>Group</th>
<th>2°C/min at 100 °C (± µW)</th>
<th>2°C/min at 250 °C (± µW)</th>
<th>5°C/min at 100 °C (± µW)</th>
<th>5°C/min at 250 °C (± µW)</th>
<th>100°C (± µW)</th>
<th>250°C (± µW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>C</td>
<td>2.18</td>
<td>0.49</td>
<td>0.345</td>
<td>0.08</td>
<td>0.185</td>
<td>0.251</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>0.333</td>
<td>0.429</td>
<td>0.57</td>
<td>0.372</td>
<td>0.851</td>
<td>0.963</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.19</td>
<td>0.15</td>
</tr>
</tbody>
</table>

#### 5.13 5°C/min zero-line repeatability determined by five tests

<table>
<thead>
<tr>
<th>Group</th>
<th>at 50 °C (± µW)</th>
<th>at 125 °C (± µW)</th>
<th>at 200 °C (± µW)</th>
<th>at 275 °C (± µW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.344</td>
<td>1.329</td>
<td>1.062</td>
<td>2.181</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>C</td>
<td>3.86</td>
<td>0.74</td>
<td>7.03</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>37.18</td>
<td>23.307</td>
<td>13.36</td>
<td>8.33</td>
</tr>
<tr>
<td>E</td>
<td>12</td>
<td>11</td>
<td>12</td>
<td>12.5</td>
</tr>
<tr>
<td>F</td>
<td>9.4</td>
<td>6.73</td>
<td>6.09</td>
<td>5.06</td>
</tr>
</tbody>
</table>
Table 5.14 Calibration check

<table>
<thead>
<tr>
<th>Group</th>
<th>10°C/min scan on indium(^1) sample</th>
<th>10°C/min scan on tin(^2) sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (mg)</td>
<td>(T_m) onset (°C)</td>
</tr>
<tr>
<td>A</td>
<td>19.04</td>
<td>156.44</td>
</tr>
<tr>
<td>B</td>
<td>14.85</td>
<td>160.30</td>
</tr>
<tr>
<td>C</td>
<td>5.33</td>
<td>157.38</td>
</tr>
<tr>
<td>D</td>
<td>19.17</td>
<td>158.00</td>
</tr>
<tr>
<td>E</td>
<td>12.03</td>
<td>160.00</td>
</tr>
<tr>
<td>F</td>
<td>11.10</td>
<td>157.31</td>
</tr>
<tr>
<td>Average</td>
<td>157.53 ± 2.43 (±1.5%)</td>
<td>27.46 ± 2.72 (±9.9%)</td>
</tr>
<tr>
<td>Standard</td>
<td>156.6(^4)</td>
<td>28.43(^4)</td>
</tr>
</tbody>
</table>

\(^1\)Purity of indium 99.9999%

\(^2\)Purity of tin 99.99%

\(^3\)Considered an outlier observation and not used in subsequent calculations

\(^4\)Perkin Elmer Periodic Table, Version 2.02g

Table 5.15 Tests for material quality upon arrival at each laboratory, and reproducibility of heat of reaction

<table>
<thead>
<tr>
<th>Group</th>
<th>Temperature Scan Range (°C)</th>
<th>Time out of Freezer(^2) (hours)</th>
<th>Three Scans at 5°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mass (mg)</td>
</tr>
<tr>
<td>A</td>
<td>30 to 320</td>
<td>28</td>
<td>7.90 ± 0.84</td>
</tr>
<tr>
<td>B</td>
<td>-40 to 320</td>
<td>90</td>
<td>19.47 ± 1.76</td>
</tr>
<tr>
<td>C</td>
<td>-20 to 320</td>
<td>68</td>
<td>5.24 ± 1.17</td>
</tr>
<tr>
<td>D</td>
<td>-30 to 320</td>
<td>6</td>
<td>16.11 ± 0.98</td>
</tr>
<tr>
<td>E</td>
<td>-30 to 320</td>
<td>48</td>
<td>5.63 ± 3.30</td>
</tr>
<tr>
<td>F</td>
<td>-30 to 321</td>
<td>48</td>
<td>5.97 ± 0.06</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>144.96 ± 16.39 (±11.3%)</td>
</tr>
</tbody>
</table>

\(^1\)Group A did not start their tests for Stage 0 at low enough temperatures to measure \(T_g\). Rather, the Stage 1 value is reported here for a 5°C/min test.

\(^2\)Storage temperature requested of participants, and their reported temperature, was -18°C
Chapter 5: Results for T800H/3900-2 Cure Kinetic Analysis and Round Robin Study

Table 5.16 Experimental decisions for stage 1

<table>
<thead>
<tr>
<th>Group</th>
<th>Dynamic dT/dt (°C/min)</th>
<th>Modulation (± °C / seconds)</th>
<th>Isothermal temperature and time [°C (hours)]</th>
<th>Residual dT/dt (°C/min ± °C / seconds)</th>
<th>No. of repeat tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td></td>
<td>140 (6), 160 (6), 180 (6)</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>2, 5, 10</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>195 (2), 200 (1), 205 (1.3), 210 (1.3), 215 (1.3)</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>D</td>
<td>1 to 10</td>
<td>1 / 60</td>
<td>130 to 200 in 10°C intervals</td>
<td>4 ± 1 / 60</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td></td>
<td>150 (2), 170 (2)</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td></td>
<td>130 (7.7hr), 150 (6.7hr), 170 (6hr), 190 (5hrs), 210(4.7hrs)</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.17 Data reduction and analysis decisions

<table>
<thead>
<tr>
<th>Group</th>
<th>Model</th>
<th>Analysis to find Arrhenius constants</th>
<th>Model fitting strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>E-A: Autocatalytic [Prout-Tompkins, date] Diffusion: Chen and Poehlein [data], modified by Cole et al. [1990]</td>
<td>Cure rate isoconversional at 0.1 degree of cure</td>
<td>Weighted least squares fit to isothermal data. Visual goodness of fit to isothermals</td>
</tr>
<tr>
<td>D</td>
<td>E-A: modified Horie model by Wisanrakkit and Gillham [date] Diffusion: Doolittle [date]</td>
<td>Cure rate isoconversionals at 0.1 to 0.95 degree of cure</td>
<td>Least squares fit to isothermal and dynamic data</td>
</tr>
<tr>
<td>E</td>
<td>E-A: Autocatalytic</td>
<td>1) Plotted ln(da/dt) vs ln[1-α], linear regression to find n; 2) ln((da/dt)/(1-α)n) vs ln[α] calculate m and ln[K]</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>E-A: Autocatalytic</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.18 Models and parameters for Stage 1

<table>
<thead>
<tr>
<th>Group</th>
<th>Model</th>
<th>Parameters and values</th>
</tr>
</thead>
</table>
| A     | \[ \frac{d\alpha}{dt} = \frac{K\alpha^m(1-\alpha)^n}{1+e^{C[\alpha-(\alpha_{c0}+\alpha_{cT}T)]}} \] | A = 49571 /sec  
E = 65933 J/mol  
m = 0.40  
n = 1.62  
C = 17.60  
a_{c0} = -1.22, a_{cT} = 0.0044  
\alpha_0 = 0.01 |
| B     | \[ \frac{d\alpha_1}{dt} = \frac{d(A \rightarrow B)}{dt} = K_1\alpha^{m_1}\beta^{n_1} \]  
\[ \frac{d\alpha_2}{dt} = \frac{d(B \rightarrow C)}{dt} = K_2\beta^{m_2} \]  
\[ \frac{d\alpha}{dt} = fK_1\alpha^{m_1}\beta^{n_1} + (1-f)K_2\beta^{m_2} \] | log A_1 = 4.49 /sec  
E_1 = 63290 J/mol  
m_1 = 0.36  
n_1 = 0.87  
log A_2 = 7.64 /sec  
E_2 = 98269 J/mol  
m_2 = 0.58  
f = 0.65  
\alpha_0 = 0.00005  
\beta_0 = 0.00003 |
| C     | \[ \frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n \] | A_1 = 55599 /sec  
E_1 = 58383 J/mol  
A_2 = 72908 /sec  
E_2 = 51341 J/mol  
m = 0.58  
n = 1.43 |
| D     | \[ \frac{d\alpha}{dt} = k_1\alpha^{n_1}(1-\alpha)^{n_1} + k_2\alpha^{n_2}(1-\alpha)^{n_2} + k_3\alpha^{n_3}(1-\alpha)^{n_3} \]  
\[ T_g = \frac{\alpha\lambda(T_{g_n} - T_{g_0})}{1-(1-\lambda)\alpha} + T_{g_0} + \frac{D}{1+\exp(-F(\alpha-\alpha_c))} \]  
\[ k_d = A_d \exp\left(-\frac{E_d}{RT}\right) \exp\left(-\frac{b}{fv}\right) \]  
\[ fv = 0.00008(T - T_g) + 0.025 \] | If T < 124°C and \( \alpha < 0.035 \), then A_1 = 34378*\ln(\alpha) + 229563 /sec and E_1 = 73300 J/mol; If A_1 < 50000 /sec, then A_1 = 50000 /sec. Else, If T < 124°C and \( \alpha > 0.035 \), then A_1 = 113881 /sec and E_1 = 73300 J/mol; Else, If T > 124°C, then A_1 = 14240 /sec and E_1 = 66435 J/mol.  
A_2 = 473684 /sec, E_2 = 73063 J/mol  
A_3 = 1.5E9 /sec, E_3 = 115624 J/mol  
T_{g_0} = 8.8 °C, T_{g_n} = 200 °C, \( \lambda = 0.8 \)  
D = 35, F = -25, notes on \( \alpha_c \) in sec. 5.2.4  
A_{d,1-2} = 4E12 /sec, E_{d,1-2} = 60000 J/mol, b_{1-2} = 0.52, A_{d,3} = 1.5E9 /sec, b_3 = 0.7 |
| E     | \[ \frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n \] | A = 144879 /sec  
E = 71130 J/mol  
m = 0.19  
n = 0.98 |
| F     | \[ \frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n \] | A = 71167 /sec  
E = 66800 J/mol  
m = 0.42  
n = 0.015/K*T-5.53 |
### Table 5.19  Experimental decisions for stage 2 and 3

<table>
<thead>
<tr>
<th>Group</th>
<th>Dynamic $dT/dt$ ($^\circ$C/min)</th>
<th>Isothermal temperature and time [$^\circ$C (hours)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1, 2, 4, 5</td>
<td>140, 160, 180</td>
</tr>
<tr>
<td>B</td>
<td>0.5 to 0.5</td>
<td>120 to 190</td>
</tr>
<tr>
<td>D</td>
<td>1 to 10</td>
<td>130 to 200</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td>120 to 200</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>120 to 250</td>
</tr>
</tbody>
</table>
Table 5.20 Models and parameters for Stages 2

<table>
<thead>
<tr>
<th>Group</th>
<th>Model</th>
<th>Parameters and Values</th>
</tr>
</thead>
</table>
| A     | \[ \frac{d\alpha}{dt} = \frac{K\alpha^m(1-\alpha)^n}{1 + e^{C(\alpha - (a_{c0} + a_{CT} T))}} \] | A = 1.60E5 /sec  
E = 71177 J/mol  
m = 0.26, n = 1.01  
C = 21.57  
a_{c0} = -1.22, a_{CT} = 0.0046 |
| B     | \[ \frac{d\alpha}{dt} = fK_1\alpha^m_{b} \beta^n_{m} + (1 - f)K_2\beta^m_{z} \]  
\[ \frac{1}{K_2} = \frac{1}{K_{Chemical}} + \frac{1}{K_{Diffusion}} \]  
\[ K_{Diffusion} = k_d \exp \left( \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \right) \]  
\[ T_g(\alpha) = T_{g_0} \exp \left( \frac{g_1\alpha}{g_2 - \alpha} \right) \] | log A₁ = 3.95 /sec  
E₁ = 59537 J/mol  
m₁ = 0.33, n₁ = 0.68  
log A₂ = 9.11 /sec  
E₂ = 99549 J/mol  
m₂ = 0.93  
f = 0.89  
log k_d = -1.92  
C₁ = 0.14, C₂ = 1.70 K  
T_{g_0} = 322.26 K, g₁ = 3.19  
g₂ = 8.30 |
| D     | \[ \frac{d\alpha}{dt} = \frac{K(1-\alpha)(B-\alpha)(b + \alpha)}{1 + \exp[C(\alpha -(a_{c0} + a_{CT} T))] + K_3\alpha^m(1-\alpha)^n} \] | A = 59938 /sec  
E = 65000 J/mol  
b = 0.17, B = 1  
A₃ = 3E9 /sec, E₃ = 115000 J/mol  
m = 3, n = 1  
C = 20, a_{c0} = -1.88, a_{CT} = 0.0061  
T_g0 = 8.8 °C, T_g∞ = 228 °C, λ = 1  
T_g = 214.45α + 12.55 °C |
| E     | \[ \frac{d\alpha}{dt} = \frac{K_1\alpha^b(1-\alpha)^l + K_2\alpha^m(1-\alpha)^n}{1 + \exp[C(\alpha - (a_{c0} + a_{CT} T))]} \] | A₁ = 165497 /sec  
E₁ = 82183 J/mol  
A₂ = 31633 /sec  
E₂ = 64626 J/mol  
k = 0.84, l = 0.29  
m = 0.36, n = 1.49  
C = 9.92, a_{c0} = -1.32, a_{CT} = 0.0048 |
| F     | \[ \frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n \] | A = 18450 /sec  
E = 61300 J/mol  
m = 0.42  
n = 2.48 T<=170°C  
1.63 T>170°C |
Table 5.21 Models and parameters for Stages 3

<table>
<thead>
<tr>
<th>Group</th>
<th>Model</th>
<th>Parameters</th>
</tr>
</thead>
</table>
| A     | \[ \frac{d\alpha}{dt} = \frac{K\alpha^n (1-\alpha)^n}{1 + e^{C(\alpha - (a_{C0} + a_{CT}T))}} \] | A = 1.47E5 /sec  
E = 70919 J/mol  
m = 0.26, n = 0.94  
C = 17.19  
a_{C0} = -1.26, a_{CT} = 0.00452 |
| B     | \( \frac{d\alpha}{dt} = fK_1\alpha^n \beta^n + (1-f)K_2\beta^m \)  
\( K_2 = K_{\text{Chemical}} + K_{\text{Diffusion}} \)  
\( K_{\text{Diffusion}} = k_d \exp \left( \frac{C_1(T-T_g)}{C_2 + (T-T_g)} \right) \)  
\( T_g(\alpha) = T_{g_0} \exp \left( \frac{g_1\alpha}{g_2 - \alpha} \right) \) | log A_1 = 4.16 /sec  
E_1 = 59970 J/mol  
m_1 = 0.28  
n_1 = 0.13  
log A_2 = 4.49 /sec  
E_2 = 62113 J/mol  
m_2 = 0.33  
f = 0.54  
log k_p = -1.16  
C_1 = 0.86, C_2 = 28.77 K,  
T_{g_0} = 310.04 K, g_1 = 58.35,  
g_2 = 122.15 |
| D     | \[ \frac{d\alpha}{dt} = \frac{K(1-\alpha)(B-\alpha)(b+\alpha)}{1 + \exp(C(\alpha - (a_{C0} + a_{CT}T))}} + K_3\alpha^n (1-\alpha)^n \] | A = 59938 /sec, E = 65000 J/mol  
b = 0.17, B = 1  
A_3 = 3E9 /sec, E_3 = 115000 J/mol  
m = 3, n = 1  
C = 20, a_{C0} = -1.88, a_{CT} = 0.0061  
T_{g_0} = 8.8 °C, T_gx= = 228 °C, \lambda = 1  
T_g = 214.45α + 12.55 °C |
| E     | \[ \frac{d\alpha}{dt} = \frac{K_1\alpha^i (1-\alpha)^i + K_2\alpha^m (1-\alpha)^n}{1 + \exp[C(\alpha - (a_{C0} + a_{CT} * T))]} \] | A_1 = 47833 /sec  
E_1 = 65140 J/mol  
A_2 = 330523 /sec  
E_2 = 82184 J/mol  
k = 0.45, l = 1.77  
m = 2.06, n = 0.39  
C = 15.58, a_{C0} = -1.32,  
a_{CT} = 0.0048 |
| F     | \[ \frac{d\alpha}{dt} = K\alpha^m (\alpha_f - \alpha)^n \] | A_1 = 3.60E5 /sec  
E_1 = 79600 J/mol  
A_2 = 8.28E3 /sec  
E_2 = 59200 J/mol  
m = 0.47  
n = 0.79 T≤160°C  
0.015*T-1.67 T>170°C  
a_f = 0.0047*T+0.04 T≤210°C  
1 T > 210°C |
Figure 5.1 (a) Nonreversing heat flow for dynamic scans ranging from 0.2 to 10°C/min

Figure 5.1 (b) Nonreversing heat flow for dynamic scans ranging 0.2 to 2°C/min
Figure 5.2 (a)  $C_p$ for dynamic scans ranging from 0.2 to 10°C/min

Figure 5.2 (b)  $C_p$ for dynamic scans ranging 0.2 to 2°C/min
Figure 5.3 (a) Nonreversing heat flow from 4°C/min residuals for 0.5°C/min interrupted dynamics to maximum temperatures 0 to 200°C

Figure 5.3 (b) Cp from 4°C/min residuals for 0.5°C/min interrupted dynamics to maximum temperatures 0 to 175°C
Figure 5.4 (a) Nonreversing heat flow from 4°C/min residuals for 1°C/min interrupted dynamics to maximum temperatures 0 to 215°C

Figure 5.4 (b) Cp from 4°C/min residuals for 1°C/min interrupted dynamics to maximum temperatures 0 to 215°C
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Figure 5.5 (a) Nonreversing heat flow from 4°C/min residuals for 1.5°C/min interrupted dynamics to maximum temperatures 0 to 225°C

Figure 5.5 (b) Cp from 4°C/min residuals for 1.5°C/min interrupted dynamics to maximum temperatures 0 to 225°C
Figure 5.6 (a) Nonreversing heat flow from 4°C/min residuals for 4°C/min interrupted dynamics to maximum temperatures 0 to 240°C

Figure 5.6 (b) Cp from 4°C/min residuals for 4°C/min interrupted dynamics to maximum temperatures 0 to 240°C
Figure 5.7 General kinetic features during cure demonstrated using a 1°C/min dynamic, nonreversing heat flow and Cp signals

Figure 5.8 2°C/min MDSC and TGA results overlaid to show the temperature region of the resin degradation reaction
Figure 5.9 Dynamic baseline: horizontal line between reaction kickoff and onset of degradation followed by a diagonal line joining the local minimum in heat flow near the end of reaction.

Figure 5.10 Average dynamic heats of reaction with error bars of standard deviations (baseline as illustrated in Figure 5.9)
Figure 5.11 Heat of reaction for 0.5°C/min dynamics interrupted at maximum temperatures ranging from 75 to 250°C

Figure 5.12 Heat of reaction for 1°C/min dynamics interrupted at maximum temperatures ranging from 75 to 250°C
Figure 5.13 Heat of reaction for 1.5°C/min dynamics interrupted at maximum temperatures ranging from 75 to 250°C

Figure 5.14 Heat of reaction for 4°C/min dynamics interrupted at maximum temperatures ranging from 75 to 275°C
Figure 5.15 Degree of cure for all dynamics (dT/dt from left to right: 0.2, 0.5, 1, 1.5, 2, 3, 5, 8, 10 °C/min); three repeat tests each

Figure 5.16 Cure rate for all dynamics (dT/dt from left to right: 0.2, 0.5, 1, 1.5, 2, 3, 5, 8, 10 °C/min); three repeat tests each
Figure 5.17 (a) Total heat flow measured during isothermal cure for temperatures 130 to 230°C

Figure 5.17 (b) Total heat flow measured during isothermal cure for temperatures 130 to 180°C; smaller range for clarity
Figure 5.18 Cp measured during isothermal cure for temperatures 130 to 230°C (magnitudes unaltered from raw data)

Figure 5.19 (a) 4°C/min residuals for 130 to 180°C isothermals (400° minute holds), no annealing
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Figure 5.19 (b) 4°C/min residuals for isothermal holds (400+minute holds), endotherm removed by annealing

Figure 5.20 4°C/min residuals for isothermals (400+minute holds), dashed lines showing annealed sampled
Figure 5.21 (a) 4°C/min residuals for room temperature cure, 3 to 87 days, nonreversing heat flow data

Figure 5.21 (b) 4°C/min residuals for room temperature cure, 3 to 87 days, Cp data
Figure 5.22 (a) 4°C/min residuals for 150°C partial cures, 0 to 180 minute hold times, nonreversing heat flow data

Figure 5.22 (b) 4°C/min residuals for 150°C partial cures, 0 to 400 minutes, Cp data
Figure 5.23 (a) 4°C/min residuals for 180°C partial cures, 0 to 400 minutes, nonreversing heat flow data

Figure 5.23 (b) 4°C/min residuals for 180°C partial cures, 0 to 400 minutes, Cp data
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Figure 5.24 Comparison of $T_{gi}$ (Tg measured during residual) and $T_{gf}$ for isothermal tests (Tg measured after residual)

Figure 5.25 (a) $Tg$-$\alpha$ based on residuals of interrupted isothermals (25 to 230°C) and interrupted dynamics (0.2 to 4°C/min); comparison of $Tg$ for the blend and $Tg$ for the epoxy; closed symbols represent the presence of $T_{\beta}$ in the Cp signal
Figure 5.25 (b) History dependence of the Tg-α relationship; lines are drawn between tests performed at the same isothermal temperature, or interrupted at the same temperature during a dynamic ramp.

Figure 5.26 (a) Measured \( T_β \) during residuals of interrupted dynamic and isothermal tests.
Figure 5.26 (b) Change in $\Delta C_p$ during $T_\beta$ transition

Figure 5.27 Averaged heats of reaction for isothermal hold and residual with error bars of standard deviations; original isothermal baseline with magnitude equal to the steady state heat flow
Figure 5.28 160°C isothermal, original and lowered baseline

Figure 5.29 Heat and DOC lost during the ramp to isothermal holds
Figure 5.30 Heats of reaction for 150°C isothermals, lowered baseline

Figure 5.31 (a) Degree of cure for isothermals 130 to 160°C, 5 tests each
Figure 5.31 (b) Degree of cure for isothermals 170 to 200°C, 5 tests each

Figure 5.31 (c) Degree of cure for isothermals 170 to 200°C, 5 tests each; reduced time scale
Figure 5.32 (a) Cure rate for isothermals 130 to 160°C

Figure 5.32 (b) Cure rate for isothermals 170 to 200°C
Figure 5.33 Cure rate isoconversionals for case 1 where $H_{\text{Total}} = H_{\text{Ultimate}} = 157$ J/g; D stands for dynamic, and I for isothermal.

Figure 5.34 Cure rate isoconversionals for case 2 where $H_{\text{Total}} < H_{\text{Ultimate}}$
Figure 5.35 Cure rate isoconversionals for case 3 where $H_{\text{Total}} < H_{\text{Ultimate}} = 157$ J/g, $H_{\text{Isothermal}}$ does not include $H_{\text{Lost}}$ during heat-up.

Figure 5.36 Cure rate isoconversionals for case 4 where $H_{\text{Total}} < H_{\text{Ultimate}}$, $H_{\text{Isothermal}}$ does not include $H_{\text{Lost}}$ during heat-up, and the dynamic baseline is linear between the reaction kickoff and end temperatures.
Figure 5.37  Cure rate isoconversionals divided into three zones of reaction behaviour 1) epoxy-amine reaction, 2) etherification, 3) diffusion

Figure 5.38  Cure rate isoconversionals (0.02, 0.04, 0.06 and 0.08): D stands for dynamic, and I for isothermal
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Figure 5.39 Isoconversionals extended to low degrees of cure

Figure 5.40 Activation energies for chemical controlled reactions
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Figure 5.41 (a) Epoxy-amine chemical model fit to 0.1 to 0.95 isoconversional data

Figure 5.41 (b) Epoxy-amine chemical model fit to 0.1 to 0.4 isoconversional data
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Figure 5.41 (c) Epoxy-amine chemical model fit to 0.3 and 0.4 isoconversional data

Figure 5.42 Epoxy-amine model fit to degrees of cure < 0.1, and temperatures < 124°C
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Figure 5.43 Representation of the cure rate behaviour at degrees of cure <0.035

Figure 5.44 Value of $A_1$ for temperatures < 124°C
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Figure 5.45  Adjusted $A_1$ and $E_1$ of epoxy-amine model for $T<124^\circ$C and $\alpha <0.035$

Figure 5.46 Comparison of original epoxy-amine model and the adjusted model prediction of room temperature cure
Figure 5.47 Comparison of original epoxy-amine model and the adjusted model prediction for a 0.5°C/min test

Figure 5.48 Combined epoxy-amine and etherification model fit to isoconversional data
Figure 5.49 $\alpha_{\text{critical}}$ model trends with temperature and heating rate

Figure 5.50 Isothermal data and Tg model fit
Figure 5.51 Dynamic data and Tg model fit

Figure 5.52 Tg model predicting residual behaviour
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Figure 5.53  Diffusion rate versus $T-T_g$ for isothermals 130 to 200°C, and dynamics 0.2 and 0.5 °C/min

Figure 5.54  Diffusion rate versus degree of cure for isothermals 130 to 200°C, and dynamics 0.2 and 0.5 °C/min
Figure 5.55  Diffusion model for epoxy-amine reactions and fit to $\ln[k_{d_{1,2}}]$ data

Figure 5.56  Model overestimates final degree of cure for 180°C isothermal. Model includes epoxy-amine (chemical and diffusion), and etherification (chemical) reactions.
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Figure 5.57 Diffusion model for etherification reaction and fit to $\text{Ln}[k_d]$ data

Figure 5.58 Isoconversional contours, model compared to data. Model includes chemical and diffusion model behaviour for epoxy-amine and etherification reactions (isothermals are squares, dynamics are circles, the model has open symbols).
Figure 5.59 (a) Goodness of total model fit (chemical + diffusion) to isothermal isoconversional data

Figure 5.59 (b) Goodness of total model fit (chemical + diffusion) to dynamic isoconversional data
Figure 5.60  (a) Total model fit to isothermal degree of cure data, 130 to 160°C

Figure 5.60 (b) Total model fit to isothermal degree of cure data, 170 to 200°C
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Figure 5.60 (c) Total model fit to isothermal degree of cure data, 170 to 200°C, reduced time scale

Figure 5.61 Total model fit to dynamic degree of cure data (from left to right: 0.2, 0.5, 1, 1.5, 2, 3, 4, 5, 8, 10 °C/min)
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Figure 5.62 Total model fit to 4°C/min residual degree of cure data for 150°C isothermals (from left to right: 15, 30, 50, 70, 90, 120, 150, 180, 400 minutes)

Figure 5.63 Total model fit to 4°C/min residuals degree of cure data for 180°C isothermals (from right to left: 10, 20, 40, 50, 70, 400 minutes)
Figure 5.64 Ruggedness test for cure cycle 0.56°C/min to 180°C hold

Figure 5.65 Ruggedness test for cure cycle 2.8°C/min ramp to 180°C hold
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Cure Temperature, Tg (°C)

Degree of Cure

1 to 9 minutes
(1 minute increments)

10 to 50 minutes
(10 minute increments)

60 to 480 minutes
(60 minute increments)

Lower Tg-α limit
$\alpha_{\text{critical}} = 0.675$
(0.2°C/min)

Upper Tg-α limit
$\alpha_{\text{critical}} = 1$
(4°C/min)

Figure 5.66 (a) Process map with isothermal contours: solid, thin grey lines 1 to 9 min., 10 min. increments; dotted grey lines, 10 to 50 min., 10 min. increments; solid, thick grey lines, 60 to 480 min., 60 min. increments; lower Tg-α curve at $\alpha_{\text{critical}} = 0.675$ (0.2°C/min); upper Tg-α curve at $\alpha_{\text{critical}} = 1$
(4°C/min)
Figure 5.66 (b) Process map with isothermal and dynamic contours: isothermal and Tg-α contours have the same parameters as (a); dynamic contours start at 0.001 degree of cure and range from 0.2, 0.5, 1, 2, 3, 4, 5, 8, 10°C/min
Figure 5.66 (c) Process map with isothermal and 0.56°C/min dynamic contours: isothermal and Tg-α contours have the same parameters as (a); dynamic contours start have increments of 0.05 degree of cure.
Figure 5.66 (d) Process map with isothermal and 2.86°C/min dynamic contours: isothermal and Tg-α contours have the same parameters as (a); dynamic contours start have increments of 0.05 degree of cure.
Figure 5.67 (a) Heat flow for 5°C/min dynamic scans on T800H/3900-2

Figure 5.67 (b) Degree of Cure for 5°C/min dynamic scans on T800H/3900-2 with a comparison of % error for various data groups
Figure 5.68 (a) Stage 1 isothermal heats of reaction

Figure 5.68 (b) Stage 1 dynamic heats of reaction
Figure 5.69  Tg-α data, stage 1

Figure 5.70 (a)  Stage 1 model prediction of degree of cure for a 5°C/min dynamic
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Figure 5.70 (b) Stage 1 model prediction of cure rate for a 5°C/min dynamic

Figure 5.71 (a) Stage 1 model predictions for MRCC lower limit of 0.56°C/min ramp to 180°C
Figure 5.71 (b) Stage 1 model predictions for MRCC upper limit of 2.86°C/min ramp to 180°C

Figure 5.72 Tg-α models proposed in Stage 2
Figure 5.73 (a) Stage 2 model predictions for MRCC lower limit of 0.56°C/min ramp to 180°C

Figure 5.73 (b) Stage 2 model predictions for MRCC upper limit of 2.8°C/min ramp to 180°C
Figure 5.74 Cure rate isoconversional data supplied in Stage 3

Figure 5.75 Tg-α data and models proposed in Stage 3
Figure 5.76 (a) Stage 3 model predictions for MRCC lower limit of 0.56°C/min ramp to 180°C

Figure 5.76 (b) Stage 3 model predictions for MRCC upper limit of 2.8°C/min ramp to 180°C
Chapter 6. SUMMARY, CONCLUSIONS, AND FUTURE WORK

The goals of this work were to identify sources of uncertainty in the decision-making process (from cure measurement by DSC to cure kinetics modeling), and to recommend practices for minimizing uncertainty. Drawing from the literature review of Hexcel 8552 and the cure studies of Toray T800H/3900-2 recorded in Chapter 5, statements can be made about expected variability and sources of uncertainty for phenomenological cure models. The following measures of variability were recorded for the predictions of degree of cure development during MRCC conditions:

1) Unknown instrument quality, material consistency, measurement quality, data reduction and modeling best practices results in 50% variability between models;

2) Unknown measurement quality, data reduction and modeling best practices results in 20% variability between models;

3) Unknown data reduction and modeling best practices results in 10% variability between models;

4) Unknown modeling best practices results in 10% variability between models;

5) Within a laboratory, model fit to degree of cure data can be achieved to within 3% error.

In light of these findings, it is evident that updated guidelines are needed for measurement and data reduction quality, cure analysis and modeling practices based on DSC, and that measurements and models should undergo a qualification process to minimize uncertainty. To address these conclusions, Section 6.1 of this closing chapter contains an evaluation of the basic assumptions in cure kinetics analysis based on DSC measurements as explored in this work. Section 6.2 proposes a qualification process and presents a list of best measurement and modeling practices. It is the future goal of this work to have these best practices reviewed and added to by the broader process modeling community. A second Round Robin is also proposed to test the best practices. The final section in this Chapter, 6.3, shares further ideas for the cure characterization study on T800H/3900-2 in this thesis.

At the heart of the decision-making process for DSC-based cure kinetics analysis and modeling are four underlying assumptions regarding heat of reaction measurement and degree of cure calculation. These are well known assumptions in the literature and are evaluated here based on this thesis work and the Round Robin results for T800H/3900-2 cure studies:

1. **Heat measured by DSC is analogous to the heat released by reactions with epoxide:** True. To the best of our present knowledge this statement is true. In the studies presented herein, other test methods such as FTIR, NMR were not included to prove or challenge this assumption. Extensive works in the literature including DSC, FTIR, and NMR studies confirm that the above statement is reasonable, and several useful models have been proposed to capture the various epoxy reactions. Suggesting that only part of the heat evolved is due to epoxide consumption may be justifiable, but the user must show reasonable evidence for this decision. The result of allocating only part of the heat of reaction area to the epoxide reaction will be a cure rate for epoxide consumption that is faster than if the entire area were designated to the reactions, such as model B in the Round Robin.

2. **The cure rate is a unique function of degree of cure and temperature:** False. The history dependence of Tg (most likely due to morphology changes) was a strong indicator that cure rate is not always a unique function of degree of cure and temperature. This assumption may also be false in the diffusion zone as observed for the 0.2 and 0.5°C/min tests. However, the study in this thesis showed that cure rates dominated by chemical behaviour can be matched on the LnCR vs 1/T chart for isothermal and dynamic tests, justified on the grounds of baseline selection and appropriately allocated heat of reaction. These two factors, along with repeatability, proved to be important for achieving this assumption for chemically dominated behaviour. Data without the correct baselines showed different cure rates between isothermals and dynamics.

3. **$H_{\text{Ultimate}} = H_{\text{Total}}$, no matter the cure cycle:** True. As mentioned in (2), choosing the appropriate baselines and ensuring $H_{\text{Ultimate}} = H_{\text{Total}}$ was a necessary combination for matching cure rates between isothermal and dynamic tests when cure was dominated by chemical reactions. Application of this assumption was a precursor to achieving the correct $H_{\text{Ultimate}}$. Two important consequences of achieving this assumption are:
   a. **The Tg-$\alpha$ relationship can be built on residual heats of reaction and $H_{\text{Ultimate}}$ information.** This seems to be a reasonable method of calculating the degree of cure for
the Tg-α curve, particularly in light of the complications isothermal heats of reaction present. It was also found in the Round Robin, stage 1, that despite the magnitude for $H_{\text{Ultimate}}$ the various groups could achieve the same Tg-α relationship.

b. **The residual heat of reaction after intermediate stages of any cure cycle can be used to test the accuracy of a cure model.**

Sources of uncertainty for heat of reaction calculation included the heat lost during the ramps to isothermal temperatures, heat lost due to instrument sensitivity or a coincident endothermic reaction (e.g. potentially phase separation), and an incorrect dynamic baseline (diagonal versus flat).

4. **The Tg-α relationship is unique:** False. This was shown to not be true for the progression of phase separation during cure of T800H/3900-2. This behaviour could easily go unnoticed if intermediate cure cycle tests were not performed, as done for most of the Round Robin models. Compare the Tg-α curves from the study in this thesis which included intermediate tests of changing morphology from blend to epoxy, and the data from the Round Robin study for only phase separated conditions. The difference this knowledge contributes is in the prediction of residuals which require knowledge of the initial state (blend or phase separated) in order to predict the delay in reaction kickoff.

Apart from meeting these underlying assumptions, there were several aspects of calibration, model selection and fitting found to be sources of uncertainty in this work. The calibration error induced by the instrument’s fit of a polynomial through several temperature points (see Chapter 4 regarding the instrument used at UBC) was a costly error in terms of time and would have masked $T_\beta$ measurement. Data presented by Round Robin participants also brings into question the accuracy of calibration, particularly the measurement of enthalpy over a broad range of temperatures. More could be done on this subject to satisfy the needs of cure kinetic modellers of broad exothermic reactions. By the final stages of the Round Robin, the major discrepancies in models were on the basis of chemical and diffusion model accuracy. It was found that phenomenological models with an underlying mechanistic basis will capture the broadest range of cure behaviour. Following an appropriate model selection, goodness of fit tests should be performed for isothermal and dynamic tests (also residuals) over a wide range of conditions, including the MRCC. Without extensive testing for the goodness of model fit to data it is difficult to assess whether or not a model is adequate. Ultimately, comparative data for process modeling should be provided by the manufacturer, or a common database of characterized materials established by the process modeling community. The next section describes how a qualification scheme would serve to reduce the uncertainty in the decision-making process.
Chapter 6: Summary, Conclusions, and Future Work

6.2. A Qualification Process for Cure Measurements, Modeling, Monitoring and Reporting

6.2.1. Development of a qualification scheme

An example of such a scheme already in place for final part properties is NCAMP (National Center for Advanced Materials Performance, based at Wichita State University, Kansas, United States), funded by NASA with partners such as the FAA (US Federal Aviation Association), Boeing, and several universities (including UBC). The NCAMP program can be broken down into four categories: 1) standards for testing material properties (internationally accepted and have a review time-line); 2) design allowable standards for the aerospace industry; 3) materials and process database; 4) guidelines for continual monitoring of properties over time. The same scheme is appropriate for process parameters.

Considering cure measurement and modeling:

1. Standards for testing complex cure mechanisms are not currently available. There are those best practices in the literature and still being developed, as this work has pointed out. At this stage in the qualification scheme, the process modeling community should make reasonable guidelines and recommendations to standards’ agencies in order to share this information with the broadest community of users possible. Reasonable practices to accept for this purpose: i) the four underlying assumptions of DSC measurement and modeling discussed in section 6.1; ii) baselines; iii) experimental conditions of interest; iv) reaction mechanisms; v) cure models that are capable of capturing the material behaviour (may be a variety of models); vi) inclusion of other effective practices such as lookup tables, which still require a measure of certainty for their accuracy.

2. Required information for understanding and modeling cure behaviour. A wide range of process conditions should be tested. For DSC testing this means including isothermals, dynamics, and combinations thereof to probe partial cure conditions. In reporting the raw data, one should also include: 1) \(H_{\text{Ultimate}}\), and proof of balancing heats of reaction for all test conditions; 2) \(T_{g_0}\) changes over the time of the study; 3) \(T_{g_v}\); 4) \(T_{g-\alpha}\) relationship, with intermediate points showing the presence of phase separation or other complex factors; 5) time to gelation at the MRCC hold temperature, and the degree of cure at gelation; 6) degrees of cure measured along the limiting MRCC’s for robustness testing; and, 7) a secondary test method (e.g. FTIR, NMR) to investigate the interactions of reactants during cure. Furthermore, a model should be accompanied by a
measure of goodness of fit over an extensive range of data to clearly demonstrate the range of process conditions for which the model is valid.

3. Monitoring changes to the material system over time. Tests should be selected to monitor the changes in cure and cure behaviour over time as the underlying chemistry or system components (e.g. tougheners) may be altered between batches.

There are various levels of accuracy required of cure models. For example, a first approximation of material behaviour may only require a few measurements in a process zone of interest, versus a model used in a finite element prediction for part shape. A qualification scheme for measurements and models would reflect the range of final applications by stating minimum requirements for each stage of the decision-making process.

6.2.2. A framework for a process modeling guide to best practices for cure testing and modeling, and reporting the decision-making process

Based on the literature review (Chapter 2), methodologies developed (Chapter 3), and cure studies of T800H/3900-2 (Chapter 4 and 5), lists of best practices have been recorded in Tables 6.1 through to 6.6 pertaining to material knowledge, instrument quality, experimental procedure, data reduction, analysis, model selection, and model fitting. This list is certainly not exhaustive, but rather the concept behind its generation is to start the discussion amongst the process modeling community as to how we can provide the best information to modellers and how we can begin to qualify our measurement and models.

6.2.3. A Round Robin to evaluate the formalized decision-making process and qualification program, and achieve a measure of reproducibility

Two further concepts could be explored through Round Robin stages: 1) how well do models agree if participants generate their own data but follow a set of best practices for measurement-to-modeling decisions, as outlined in Section 6.2.2; and, 2) will agreement between models improve when a common database of information is provided for accuracy testing? In conjunction with these stages, the allowable accuracy of cure measurements and models needs to be documented. This should be investigated to address the impact of prediction accuracy for residual stress and deformation calculations.
6.3. **RECOMMENDATIONS FOR FUTURE WORK ON THE UBC CURE STUDY OF T800H/3900-2**

The material characterization of T800H/3900-2 should continue at UBC. Concerning the study of cure behaviour, four experimental/modeling investigations can be identified at this time as adding value to the cure model presented in this work: 1) to gain further insight to the changes in morphology and how they relate to cure properties, the study of morphology by transmission electron microscopy (TEM) or scanning electron microscopy (SEM), and/or measurement of the onset of phase separation (cloud point) by transmission optical microscopy (TOM); 2) testing the Tg-α model for residuals (Figure 5.52); 3) perform further aging tests between room temperature and 130°C to complete the spread of data; 4) as diffusion is an ongoing investigation in the literature, a ‘diffusion factor’ on the basis of T-Tg or Cp could be explored; and, 5) FTIR or NMR studies to improve the understanding of how the various reactants and system components interact during cure.
Table 6.1 Decision-making process to investigate material knowledge

<table>
<thead>
<tr>
<th>Decision and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>System components (reactant chemistry, catalysts, inhibitors, unreactive fillers, prepreg architecture)</td>
<td>Ideally provided by manufacturer; generally proprietary information. If unable to perform experiments (FTIR, NMR), search literature: Patents, journal articles, reviews on cure kinetics</td>
</tr>
<tr>
<td>Initial amine-to-epoxide ratio</td>
<td>Ideally provided by manufacturer. Unless etherification peak is substantially higher than amine-epoxide peak(s) to isolate heat of reaction by DSC, other methods are needed (FTIR, NMR).</td>
</tr>
<tr>
<td>Initial degree of cure</td>
<td>Ideally provided by manufacturer. i) Liquid chromatography. ii) Comparison to neat resin on basis of Tg, viscosity, HrXn (Tg is the most repeatable measurement); obtaining neat resin may be difficult.</td>
</tr>
<tr>
<td>Consistent resin-to-fibre volume or mass fraction within a batch, and between batches</td>
<td>i) Acid digestion: D 3171-99 ii) Matrix dissolution: D 3529-97 ii) Oven or TGA burn-off: ASTM D 3171-99 iii) Monitor sample location on prepreg and consistency of Tg and H measurements Batch repeatability studies to be provided by NCAMP</td>
</tr>
<tr>
<td>Effect of storage temperatures and times, and out temperatures and times and humidity on cure and moisture absorption</td>
<td>Monitor heat of reaction and Tg of resin over time. UBC confirmed that moisture absorbed by prepreg can cause plasticization and can be observed by a decreasing Tg; moisture can be removed by heating without cure.</td>
</tr>
<tr>
<td>Sample size has consistent components and will not cause a temperature gradient, nor self-heating. Preparation is consistent and does not add impurities</td>
<td>In general, follow DSC manufacturers’ guidelines. Size of reactive sample suggested as 1-2 mg in ASTM E2160, 1 to 10mg in 1 to 10mg in ASTM E2041. ASTM 2160 shows result of runaway reaction due to too much sample. Unless resin volume fraction can be measured for every sample, UBC showed that a prepreg sample size between 12-18mg is necessary to capture a nominal heat of reaction, indicative of a nominal resin volume fraction.</td>
</tr>
<tr>
<td>Sample preparation does not add impurities, and sample pan crimping and placement in cell is consistent</td>
<td>Follow DSC manufacturers’ guidelines for preparing samples (pan type, crimping technology). Pan placement and deformation investigated by Hohne et al., 1996</td>
</tr>
<tr>
<td>Onset of degradation; used to determine experimental limits (temperatures and times of onset)</td>
<td>i) Onset of mass loss (resin burnoff) by TGA with time and temperature ii) Decrease in Tg measured by DSC</td>
</tr>
</tbody>
</table>
Table 6.2 Instrument quality considerations

<table>
<thead>
<tr>
<th>Decisions and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument zeroline</td>
<td>Check for flatness and repeatability</td>
</tr>
<tr>
<td></td>
<td>Zeroline, if not flat, should be removed from heat flow measurements before calculation</td>
</tr>
<tr>
<td>Resolution</td>
<td>Report instrument specification</td>
</tr>
<tr>
<td>Signal noise</td>
<td>Report instrument specification</td>
</tr>
<tr>
<td></td>
<td>Test isothermally and dynamically across a range of temperatures of interest to a cure study</td>
</tr>
<tr>
<td>Accurate calibration (enthalpy,</td>
<td>ASTM E967, E968, E2069</td>
</tr>
<tr>
<td>temperature, Cp)</td>
<td></td>
</tr>
<tr>
<td>Repeatability of measurements</td>
<td>Perform repeat tests of standard materials for melting temperatures and heats of fusion.</td>
</tr>
<tr>
<td></td>
<td>See ASTM E967 and E973 for measures of repeatability. Test the repeatability of a resin system</td>
</tr>
<tr>
<td></td>
<td>with stable quantities of reactants and non-reacting components. Round Robin results show</td>
</tr>
<tr>
<td></td>
<td>repeatability can be attained to within 2% under consistent instrument and sample preparation</td>
</tr>
<tr>
<td>Reproducibility of measurements</td>
<td>Some measures exist for standard samples. See ASTM E967 and ASTM E973. A measure of reproducibility</td>
</tr>
<tr>
<td></td>
<td>between laboratories for CFRP from the Round Robin was roughly 16% (Table 5.14) given that the</td>
</tr>
<tr>
<td></td>
<td>baseline was not imposed.</td>
</tr>
</tbody>
</table>
Table 6.3  Best practices for selecting experimental parameters

<table>
<thead>
<tr>
<th>Decisions and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal temperatures</td>
<td>RT to above MRCC (20°C+)</td>
</tr>
<tr>
<td>Isothermal hold times</td>
<td>To measure area under a heat flow profile, heat flow should reach a point of negligible change at the end of reaction (usually 4 to 6 hours for MRCC cure temperature). Shorter times to fill-in Tg-α relationship, using only the residual heat of reaction.</td>
</tr>
<tr>
<td>Heating method to hold temperature</td>
<td>Heating to isothermal hold in DSC by dropping sample in preheated cell, or ramping sample in cell to isothermal temperature. Both methods lose heat during temperature equilibration. Heating sample and cell simultaneously advantageous for automation of experiments.</td>
</tr>
<tr>
<td>Lost heat of reaction during heating to isothermal hold</td>
<td>Repeat the heating ramp to the isothermal hold for a cured sample and subtract the heat flow curves (must be repeatable). Measure the Tg that coincides with the point at which the hold temperature is reached (UBC method).</td>
</tr>
<tr>
<td>MDSC modulation amplitude and period for quasi-isothermal experiments</td>
<td>Van Mele developed parameters [1994]</td>
</tr>
<tr>
<td>Heating rate selection for dynamics</td>
<td>Limits of MRCC; high heating rates to fill in high temperatures on cure rate isoconversational chart</td>
</tr>
<tr>
<td>MDSC modulation amplitude and period</td>
<td>MDSC manufacturers’ guidelines</td>
</tr>
<tr>
<td>Residual heating rate selection</td>
<td>High enough to devitrify material; low enough to not degrade material (PID controls considered); fast enough for testing efficiency. Becomes the heating rate for Tg-α relationship.</td>
</tr>
<tr>
<td>Annealing of endotherm found during a residual</td>
<td>Remove endotherm for cure rate analysis by heating up the sample until the endotherm is passed [Simon, 1992]. Not necessary for residual heat calculation and Tg measurement [UBC].</td>
</tr>
<tr>
<td>Calibration period</td>
<td>Track zeroline behaviour. Ideally all tests would be performed in one calibration period. If not, track changes to calibration parameters.</td>
</tr>
<tr>
<td>Test randomization</td>
<td>Perform repeat tests (at least 3) for each isothermal and dynamic condition. Randomize test sequence.</td>
</tr>
</tbody>
</table>
### Table 6.4 Best practices for data reduction

<table>
<thead>
<tr>
<th>Decisions and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
</table>
| Data to record before reduction: | i) Heat flow curves for isothermal and dynamic tests, normalized by mass: shape of isothermal curves indicates reaction type; presence of shoulders before or after main dynamic peak(s) indicate excess amine or epoxide, respectively.  
   ii) Cp versus time and temperature, drop in Cp indicates the onset of vitrification and an increase in Cp the onset of devitrification.  
   iii) Stability of initial state of material through testing: record Tg$_0$ to assess cure advancement and moisture absorption during storage.  
   iv) Effect of aging, degradation, and possibly morphology changes, on system during cure. |
| Dynamic baselines | Must remove instrument zeronline and changes in sample Cp from heat flow profile. With these two measurements removed, baseline should be flat, with a possible rise at the end to remove heat of degradation. Elimination of moisture endotherms at low temperatures for a clear indication kickoff temperature. Elimination of heat flow signal due to degradation to deconvolute the end of reaction. |
| Ultimate heat of reaction | Tests to measure H$_\text{Ultimate}$ should have heating rates high enough to avoid diffusion effects, and low enough to avoid degradation. If H$_\text{Ultimate}$ increases with dT/dt, the degradation exotherm at high temperatures was unsuccessfully removed. If H$_\text{Ultimate}$ decreases with decreasing dT/dt, vitrification effects at very low heating rates. |
| Tg-α | Relationship can be drawn from residual heat flow profiles. Include intermediate degrees of cure from interrupted isothermal and dynamic tests. |
| Isothermal baseline | With lost heat during the ramp accounted for, H$_\text{Total}$ must equal H$_\text{Ultimate}$. If it does not, attribute the error reasonably (instrument sensitivity, contribution of endothermic reaction, degradation) and calculate the isothermal baseline to equate the heats of reaction. |
| Alternative to balancing heats of reaction, TTS method by Gillham. Uncertainty lies in Tg measurement. | This method uses only dynamic tests, including residuals of isothermals. However, the Tg measurement may be a combination of cure, ageing, phase separation, degradation, etc. |
| Dynamic and isothermal cure rates are equivalent | Compare using a cure rate isoconversional chart [Ln(Cure Rate) vs 1/T] |

Practices for handling path dependence:  
- i) Assigning to various etherification cases [Cole, 1991]  
- ii) Differences between cure rates at low heating rates due to diffusion
Table 6.5 Best practices for data analysis

<table>
<thead>
<tr>
<th>Decisions and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determining number of reaction mechanism</td>
<td>Cure rate isoconversion chart will show a change in slope with temperature and degree of cure if the reaction has multiple mechanisms. Identified mechanisms: primary amine with epoxy, secondary amine with epoxy, etherification.</td>
</tr>
<tr>
<td>Activation energy and rate of reaction</td>
<td>Epoxy-amine reactions are multi-mechanism reaction. Activation energies and reaction type can be determined from the cure rate isoconversional chart. Very low temperatures may require adjustment to the activation energy.</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Diffusion rate calculated from the difference of the reduced isothermal data and the chemical model by the Rabinovitch equation.</td>
</tr>
</tbody>
</table>
Table 6.6 Best practices for model selection and fitting

<table>
<thead>
<tr>
<th>Decisions and Uncertainties</th>
<th>Best Practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model type for the epoxy-amine chemical reaction</td>
<td>i) Mechanistic: path dependent behaviour induced by various paths of etherification, e.g. Cole model ii) Phenomenological: Horie basis, adaptations to reaction orders (e.g. Kamal) iii) Empirical: not recommended as it will be extremely limited in range of process parameters and does not add to the understanding of material behaviour for process decision-making</td>
</tr>
<tr>
<td>Chemical Reaction order</td>
<td>i) Cure rate isoconversionals illustrate nth order vs autocatalytic dominance with temperature given the degree of cure associated with maximum cure rate; ASTM E2041, Appendix, illustrates standard behaviour for single mechanisms in heat flow versus time. ii) Variable reaction orders: chemical basis for reaction order up to 2; literature for epoxy-amine systems also shows modelers using up to 4 iii) In general, reaction orders for epoxy-amine reactions are first attempted with those laid out by Horie, but for complex behaviour become a variable for fitting by least squares or multi-variable analysis.</td>
</tr>
<tr>
<td>Other mechanisms affecting cure</td>
<td>i) Inhibitors ii) Catalysts iii) Morphology changes</td>
</tr>
<tr>
<td>Tg-α</td>
<td>DiBendetto, DiMazio, etc.</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Ideally a diffusion term could be resolved for each reaction mechanism. For a multi-mechanism reaction, Chern and Poehein equation (modified by Cole) applied as a rate limiting denominator. Higher order functions (e.g. quadratic, cubic) can also be solved to determine the rate of diffusion parameters for individual reactions. This is an ongoing area of investigation; diffusion factors using Cp models are currently being explored.</td>
</tr>
<tr>
<td>Goodness of model fit to data</td>
<td>Percent difference versus temperature for isoconversional contours calculated from model comparisons to isothermal and dynamic data (follows fitting to cure rate isoconversional plots).</td>
</tr>
<tr>
<td>Goodness of model fit to data</td>
<td>i) Comparison of intermediate times during the MRCC cure cycle ii) Model fit to residual data iii) Model fit to room temperature aging data ii) Process map to check limits of model applicability</td>
</tr>
<tr>
<td>Lookup Table – alternative to model fitting</td>
<td>Still requires a procedure for best practices for cure measurement, data reduction and analysis. Also requires robustness testing. This method may be more computationally efficient, but should not overlook the need to understand the underlying material behaviour.</td>
</tr>
</tbody>
</table>
References


ANSI, American National Standards Institute, (wwwansi.org).


ETSI, European Telecommunications Standards Institute, (www.etsi.org).


References


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SACMA, Suppliers of Advanced Composites Manufacturing Association.


References


Appendix A. Cure Model Development for Epoxy-Amine Reactions

This Appendix records the sequence of chemical balance equations used by Horie et al. [1970] and Cole et al. [1991] to establish reaction mechanisms for the epoxy-amine and etherification reactions, respectively. To begin, recall the balance of reactants from Section 2.1,

\[ A_i + E + (HX)_A \xrightarrow{k_i} A_2 + (HX)_A \]
\[ A_i + E + (HX)_0 \xrightarrow{k_i} A_2 + (HX)_0 \]
\[ A_2 + E + (HX)_A \xrightarrow{k_i} A_3 + (HX)_A \]
\[ A_2 + E + (HX)_0 \xrightarrow{k_i} A_3 + (HX)_0 \]
\[ E + mH + nA_j \xrightarrow{k_i} \text{ether} + mH + nA_j \]

The first four relations were mapped by Horie et al. [1970] based on the work by Schecter et al. [1956], and the fifth relationship was proposed by Cole [1991] based on work by Chiao [1990]. The kinetic equations for these reaction schemes are as follows [Cole, 1991]:

\[ \frac{dE}{dt} = -k_1(HX)A_iEA_1 - k_1'(HX)bEA_1 - k_2(HX)_AEA_2 - k_2'(HX)_bEA_2 - k_3E(OH)^mA_3^n \]  \hspace{1cm} A.1
\[ \frac{dA_1}{dt} = -k_1(HX)_AEA_1 - k_1'(HX)_bEA_1 \]  \hspace{1cm} A.2
\[ \frac{dA_2}{dt} = +k_1(HX)_AEA_1 + k_1'(HX)_bEA_1 - k_2(HX)_AEA_2 - k_2'(HX)_bEA_2 \]  \hspace{1cm} A.3
\[ \frac{dA_3}{dt} = +k_2(HX)_AEA_2 + k_2'(HX)_bEA_2 \]  \hspace{1cm} A.4
\[ \frac{dH}{dt} = +k_1(HX)_AEA_1 + k_1'(HX)_bEA_1 + k_2(HX)_AEA_2 + k_2'(HX)_bEA_2 \]  \hspace{1cm} A.5
\[ \frac{d[\text{ether}]}{dt} = +k_3EH^mA_3^n \]  \hspace{1cm} A.6

where E refers to epoxide, (HX) to either hydroxyl (OH) or impurities (X) formed during the reaction (subscript A) or initially present in the system (subscript 0), A_1 to primary amine, A_2 to secondary amine, and A_3 to tertiary amine. As outlined by Cole [1991], there are three material balance constraints within these equations. In the first, the loss of one N-H bond results in the formation of one O-H bond, such that the total number of O-H + N-H bonds remains constant. This can be expressed as \( 2A_1 + A_2 + H = \text{constant} = 2A_{10} + H_0 \), or

\[ A_2 = 2A_{10} + H_0 - 2A_1 - H \]  \hspace{1cm} A.7

The second material balance equation states that the total number of nitrogen atoms is constant, \( A_1 + A_2 + A_3 = \text{constant} = A_{10} + A_{30} \), or

\[ A_3 = A_{30} + A_{10} - A_1 - A_2 \]  \hspace{1cm} A.8

The third equation states that the total number of oxygen atoms is constant, \( E + H + [\text{ether}] = \text{constant} = E_0 + H_0 \), or
Appendix A: Cure Model Development for Epoxy-Amine Reactions

\[ \text{[ether]} = E_0 + H_0 - E - H \quad \text{A.9} \]

One of the earliest and most prominent chemical models was derived by Horie et al. [1970]. Horie only considered the consumption of epoxide by amine, equation A.1, without etherification,

\[
d\frac{dE}{dt} = -k_1(HX)_AE_1 - k'_1(HX)_bEA_1 - k_2(HX)_AE_2 - k'_2(HX)_bEA_2 \quad \text{A.10}
\]

Horie made the simplifying assumption that the amine hydrogen atoms have equal reactivity, no matter if they are found on a primary or secondary amine, such that \( \frac{k_2}{k_1} = \frac{k'_2}{k'_1} = n \), and that \( n \), or \( r \) as some authors notate, becomes 0.5 simply due to the fact that primary amine has twice the opportunity to react as does secondary amine (later noted by Cole in 1991 that this is not an exact solution for \( n \), although 0.5 is also used in his work). Prime [1997] suggests that the reactivity ratio may be equal to 1 rather than 0.5 for equal reactivity if the reaction model is written in terms of amine hydrogen atoms rather than amine groups. With this assumption, \( n = 0.5 \), the rate equation for rate of epoxide consumption reduces to,

\[
d\frac{dE}{dt} = (k_1(HX)_AE + k'_1(HX)_bE)(A_1 + nA_2) \quad \text{A.11}
\]

To reduce the number of reactants in the system, the N-H bonds available at any time during the reaction were related to epoxide consumed, \( x \), by the following relationship,

\[
A_0 - \frac{1}{2}x = A_1 + \frac{1}{2}A_2 \quad \text{A.12}
\]

where \( x = E_0 - E \) (without ether), \( k_3x = k_1(HX)_A \) because the amount of epoxide consumed is equal to the concentration of (OH) formed in the amine-epoxide reaction at time \( t \), such that equation (10) can be reduced to

\[
d\frac{dx}{dt} = (k_1x + k'_1(HX)_b(E_0 - x)(A_0 - \frac{1}{2}x) \quad \text{A.13}
\]

Setting the consumption of epoxide to a dimensionless unit, \( \alpha = 1 - \frac{E}{E_0} = x/E_0 \), each term in the equation can be rearranged as \( E_0(k_1\alpha + (1/E_0)k'_1(HX)_b) \), \( E_0(1 - \alpha) \), \( (1/2)E_0(B - \alpha) \), and the equation for rate of epoxide consumption further reduces to

\[
d\alpha/dt = (K_1 + K_2\alpha)(1 - \alpha)(B - \alpha) \quad \text{A.14}
\]

where \( K_1 = \frac{1}{2}k_1(HX)_bE_0 \), \( K_2 = \frac{1}{2}k_2E_0^2 \), \( B = 2A_0/E_0 \) is the initial ratio of amine hydrogen equivalents to epoxide equivalents. \( K_1 \) corresponds to catalysis by unknown impurities (X) and hydroxyl (OH) initially present (or primary amine and epoxy reaction), and \( K_2 \) corresponds to catalysis by hydroxyl groups formed in the reaction (secondary amine and epoxy reaction).
Appendix B: DEVELOPMENT OF DIFFUSION MODELS

B.1 Williams-Landel-Ferry Equation, Modified by Wisanrakkit

The Williams-Landel-Ferry (WLF) equation for diffusion-controlled relaxation behaviour of amorphous polymers [Williams et al., 1955] is commonly used to understand the diffusion phenomenon in crosslinked polymers during cure. The form of the WLF equation is as follows,

\[
\log(a_T) = \log \frac{\tau(T)}{\tau(T_0)} = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}
\]

or,

\[
\ln(a_T) = -\frac{2.303C_1(T - T_0)}{C_2 + (T - T_0)}
\]

where \(a_T\) is the time-temperature superposition factor, \(C_1\) and \(C_2\) are constants, and \(\tau(T)\) and \(\tau(T_0)\) are the polymer segmental relaxation times at temperature \(T\) and \(T_0\), respectively, where \(T_0\) is a reference temperature. The basis of the equation is time-temperature equivalence, which implies that the viscoelastic behaviour at one temperature can be related to that at another temperature by a change in the time-scale only, that is shifting by \(a_T\). The result of shifting the various relaxation curves is a single master curve over a greater length of time, typically having a backwards S-shape; material at low temperatures experience longer times to relax and are shifted to longer times on the master curve, and conversely for high temperature relaxation. This relation applies over a temperature range of \(T_0 + 50^\circ C\). \(C_1\) and \(C_2\) have universal values of 17.44 and 51.60\(^\circ C\), respectively, when \(T_0\) is taken to be \(T_g\), which implies that many materials have the same free volume fraction at their respective \(T_g\)’s.

Wisanrakkit and Gillham [1990] used the WLF equation to represent diffusion as follows,

\[
\log(a_T) = \log \frac{\tau(T)}{\tau(T_0)} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]

Or in terms of rate constants,

\[
\log \frac{K_d(T)}{K_d(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]

and in the natural logarithmic form is,

\[
\ln \frac{K_d(T)}{K_d(T_g)} = \frac{2.303C_1(T - T_0)}{C_2 + (T - T_0)}
\]
where 2.303 is used to convert from logarithmic to natural logarithmic scale. For network forming polymers, the glass transition temperature will change with conversion, and for a given conversion the relaxation times for segmental mobility can be related to temperature by the WLF equation. Hence, the WLF equation can describe behaviour when temperature is held constant and $T_g$ is changing, as the case for vitrification during an isothermal hold. Wisanrakkit and Gillham suggest a modified form of the WLF equation to model diffusion for an epoxy resin at constant temperature. The modification was to take the absolute value in the denominator,

$$\ln K_d(T) = \ln K_d(T_g) + \frac{2.303C_1(T - T_g)}{C_2 + |T - T_g|}$$

such that the equation could be extended to temperatures below $T_g - C_2$, after vitrification as mobility is increasingly inhibited. The value of $C_1$ was allowed to vary with the material. It was assumed that $K_d(T_g)$ is a constant and denoted as $K_{do}$, and $C_2$ was 51.6°C. The values of $K_{do}$ and $C_1$ were solved for by plotting $\ln K_d$ against $\frac{T - T_g}{C_2 + |T - T_g|}$, where $K_d = \frac{K_eK_c}{K_c - K_e}$ is the Rabinowitch equation rearranged and can be calculated using the cure rate data after the onset of vitrification and the estimated chemical cure rate from the Arrhenius relationship ($K_c$). Values for $K_c$ were determined by dividing the measured cure rate by the conversion function for a single reaction,

$$K_c = \frac{\alpha}{f(\alpha)}$$

The slope and intercept for a straight line on a plot of $\ln K_d$ versus $f_d(\alpha)$ will determine $C_1$ and $K_{do}$ respectively. Wisanrakkit and Gillham found that a single temperature could be used to determine WLF constants that were able to predict an overall diffusion coefficient for the entire range of temperatures of interest in their study.

The WLF equation stems from knowledge of temperature dependence viscosity behaviour of polymer melts, and the Eyring rate theory. The probability of molecular motion per unit of time, $P$, is described by $\exp(-E/RT)$ where $E$ is an Eyring activation energy and depends on the amount of free volume (more free volume means a lower energy barrier), $RT$ is thermal energy ($R$ is the universal gas constant), and $P$ increases with temperature. The total probability in time “t” is $Pt$, and $\ln Pt = -E/RT + \ln t$. When $\ln Pt$ reaches specified value for molecular movement, or flow, then $-E/RT + \ln t = C$, where $C$ is a constant relative to flow. Rearranging this expression, $\ln t = C + E/RT$, time become the inverse of temperature, as needed to construct time-temperature-superposition. The shift factor, $a_T$, compares the difference in $\ln$’s of two times, $t$ and $t_0$, associated with $T$ and $T_0$, $\ln a_T = \ln t - \ln t_0$. Viscosity is proportional to time in a flow experiment, and hence can be replaced for time, $\ln a_T = \ln(\eta/\eta_0)$. 

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The probability of molecular motion, $E/RT$, is proportional to $b/f_v$ of the Doolittle equation for viscosity (1951),

$$\eta = a \exp(b / f_v) \quad \text{B.8}$$

where $\eta$ is viscosity (Pa·sec = kg·m$^{-1}$·sec$^{-1}$), $a$ and $b$ are constants, and $f_v$ is the fractional free volume. This equation basically states that viscosity will increase exponentially with decreasing free volume, Figure B.1. Following diffusion theory, an increase in viscosity will result in an increased time for segmental movement to occur, or increased diffusion time. Setting $\eta_T / \eta_{T_g} = a_T$, and $T_b = T_g$,

$$\frac{\eta_T}{\eta_{T_g}} = \frac{a \exp(b / f_v)}{a \exp(b / f_g)} \quad \text{B.9}$$

$$a_T = \exp(b / f_v - b / f_g) \quad \text{B.10}$$

$$\ln(a_T) = b \left( \frac{1}{f_v} - \frac{1}{f_g} \right) \quad \text{B.11}$$

Substituting the free volume equation into the above relationship, $f_v = f_g + a_f(T - T_g)$,

$$\ln(a_T) = \left( \frac{1}{f_g + a_f(T - T_g)} - \frac{1}{f_g} \right) \quad \text{B.12}$$

$$\ln(a_T) = b \left( \frac{T - T_g}{f_g / a_f + (T - T_g)} \right) \quad \text{B.13}$$

where $\ln(a_T) = -K(T)/K(T_g)$, $C'_1 = b/f_g$ and $C_2 = f_g / a_f + (T - T_g)$ to achieve the WLF equation. $C'_1$ is equal to $2.303* C_1$, or 40.16, since the natural logarithm is used. When $b$ is equal to 1, the free volume at the glass transition temperature, $f_g$, is roughly 2.5% (0.025), and $a_f$, the linear expansivity of free volume above $T_g$ is 0.00048 °C$^{-1}$. As mentioned previously, $C_f$ is allowed to vary with material, which is really $b$ changing with material.
In order to apply WLF to cure data, the diffusion time distribution function and shape of the diffusion rate curves with $f_d(\alpha)$ do not change with temperature. Superimposed diffusion curves that overlap are considered to be thermorheologically simple and therefore can be modeled by the WLF expression. In contrast, curves that do not overlap are thermorheologically complex and may need to be characterized by more complex models.

Figure B.2 (a) shows the diffusion rate as described by the WLF-W equation with conversion. The S-shape has a maximum rate of diffusion when $K/B_e$ is equal to ½, and this is the point at which $T_g = T$; altering $C_l$ or $Kd_0$ does not change this behaviour. Figure B.2 (b) shows how the same isothermal contours overlap when plotted against $T-T_g$, with maximum rate of diffusion occurring at $T-T_g = 0$. By not taking the absolute of the temperature difference in the denominator as in the original WLF form, the behaviour changes to an exponential decrease in cure rate with increasing cure, Figure B.3 (a). Figure B.3 (b) shows the same isothermal contours plotted against $T-T_g$, illustrating the point that below $T-T_g = 0$, the WLF equation describes a cure rate which decreases exponentially with increasing $T_g$.

### B.2 Macedo-Litovitz Equation, Modified by Simon

Simon et al. [1992, 1993, 2000] used the Doolittle equation modified by adding a term to account for temperature dependence to find an overall diffusion rate expression,

$$K_d = A \exp\left(-\frac{E_d}{RT}\right) \exp(-b/f_v) = A \exp\left(-\frac{E_d}{RT} + \frac{-b}{f_v}\right) \quad \text{B.14}$$

where $A \exp\left(-\frac{E_d}{RT}\right)$ is a rate constant, $E_d$ is the activation energy for diffusion, $R$ is the gas constant, $T$ is the cure temperature, and $f_v = f_g + a_j (T - T_g)$. The Arrhenius equation is also designated as $K_{do}$, and the constants $K_{do}$ and $b$ are determined from plots of $\ln K_d$ (as determined by the Rabinowitch equation) versus $1/f_v$, using data in the diffusion-controlled region and calculating the intercept and slope, respectively

$$\ln K_d = \ln K_{do} - b/f_v \quad \text{B.15}$$

Figure B.4 (a) illustrates the diffusion rate constant for the ML-S equation when $Kd_0$ is taken as a constant. Figure B.4 (b) shows the same isothermal data plotted against $T-T_g$, showing an exponential decrease when $T_g$ increases beyond $T$, as does the WLF equation. In the 1992 work by Simon, the activation energy for diffusion for a high-$T_g$ epoxy-amine system was found to be 140 kJ/mol. Alternatively, $\ln K_{do}$ was taken as an ‘adjustable parameter’ to suit a material system, similar to the concept for $b$ [Simon and Gillham, 1992]. Furthermore, $f_g$, the free volume at the glass transition
temperature was taken as 2.5% (0.025), and \( a_f \) the linear expansion of free volume above Tg as 0.00048 \(^\circ\text{C}^{-1}\). The WLF constant \( C_2 \) is the ratio of \( f_v / a_f \), and is underestimated by the values quoted above. As explained in Simon and Gillham [1993], \( C_2 \) equated by the values above is 52\(^\circ\text{C}\) and predicts that the free volume in the non-equilibrium glassy polymer is zero at Kauzmann’s temperature, 52\(^\circ\text{C}\) below Tg. The authors cite that the advantage of using the fractional free volume is that the effects of physical aging after vitrification can be accounted for by allowing the fractional free volume to be time-dependent when the material is in the glassy state, Tg > T.

The concept of combining the two terms stems from the Macedo and Litovitz expression [1965]. These authors state that a molecule vibrates about an equilibrium position until: 1) the molecule attains sufficient energy to overcome the attractive forces holding it to its neighbors (enough to break bonds), and 2) an empty site (or hole) is available for the molecule to jump into. The probability that the first would occur was described by

\[
p_E \approx \exp\left(-E_v^*/RT\right) \tag{B.16}
\]

where \( E_v^* \) is the height of the potential barrier between equilibrium positions, \( R \) the gas constant, and \( T \) the absolute temperature. The probability of an available site is described by

\[
p_v \approx \exp\left(-\gamma \nu_0 / \nu_f \right) \tag{B.17}
\]

where \( \nu_f \) is the average free volume per molecule, \( \nu_0 \) is the close-packed molecular volume, and \( \gamma \) is a numerical factor to correct for the overlap of free volume and lies between 0.5 and 1. The probability for a molecule to attain sufficient energy to jump from one site to another, \( p_j = p_E p_v \). In turn, the viscosity of a liquid is presumed to be inversely proportional to the diffusional jump probability such that

\[
\eta = A / p_E p_v = A_0 \exp\left(\gamma \nu_0 / \nu_f + E_v^*/RT\right) \tag{B.18}
\]

where \( A_0 \) varies with temperature, but not to the same extent as the exponential term. Macedo and Litovitz suggest that the shear and volume relaxation times of liquids should also have the form,

\[
\tau = \tau_0 \exp\left(\gamma \nu_0 / \nu_f + E_v^*/RT\right) \tag{B.19}
\]

Furthermore, they employ the Einstein equation to relate the diffusion coefficient and shear viscosity,

\[
D = \frac{kT}{6\pi \eta} \tag{B.20}
\]

where \( k \) is a rate constant, and \( r \) is molecular radius. The diffusion coefficient has the form \( D = D_0 \exp[-(\gamma \nu_0 / \nu_f + E_v^*/RT)] \), which is the form of the ML-S equation.
The ML-S equation can be equated to the WLF-W equation through the meaning of the shift factor. In the WLF-W derivation, the shift factor was formed by the ratio of Doolittle equations at the cure temperature and reference temperature, or $T_g$,

$$\frac{\eta_T}{\eta_{T_g}} = \frac{a \exp(b/\alpha_f)}{a \exp(b/\gamma_f)}$$  \hspace{1cm} \text{B.21}

where viscosity is inversely proportional to the rate constant for diffusion,

$$K_d \propto \frac{1}{\eta(T)} \propto \exp(-b/\gamma_f)$$  \hspace{1cm} \text{B.22}

An expression for $K_d$ and $\exp(-b/\gamma_f)$ is possible by establishing a rate constant, $K_{d_0}$, such that $K_d = K_{d_0} \exp(-b/\gamma_f)$, and the ratio of $K_d / K_{d_0}$ is synonymous to the shift factor for the WLF equation. Recall that $f_v = f_g + \alpha_f (T - T_g)$, and when $T = T_g$, $f_v = f_g$, such that

$$K_d(T_g) = K_{d_0} \exp\left[-\frac{b}{\gamma_g}\right]$$  \hspace{1cm} \text{B.23}

Solving for $K_{d_0}$,

$$K_{d_0} = K_d(T_g) \exp\left[ \frac{b}{\gamma_g} \right]$$  \hspace{1cm} \text{B.24}

By substituting $K_{d_0}$ for $K_d$ in the ML-S equation, the WLF-W equation is achieved (with rearrangement and using the absolute of $T - T_g$ as appropriate),

$$K_d(T) = K_d(T_g) \exp\left[\frac{b}{\gamma_g}\right] \exp\left[-\frac{b}{\gamma_v}\right] = K_d(T_g) \exp\left[-b\left(\frac{1}{\gamma_v} - \frac{1}{\gamma_g}\right)\right]$$  \hspace{1cm} \text{B.25}

To resolve the equation into the ML-S form, $K_{d_0} = K_d(T_g) \exp(b/\gamma_g) = K_d(T_g) \exp(E_v/RT)$. Although the above equation can now be rearranged to find the WLF-W formula, there are no substitute values for $E_v/RT$ which will procure the same expression. To achieve equivalence with the WLF-W equation, the equation must be fully rearranged to the WLF-W form.

**B.3 Chern-Poehlein Equation, Modified by Cole**

Chern and Poehlein [1987] introduced a semi-empirical approach to modeling diffusion control which was modified by Cole et al. [1991], and used by others since [Hubert et al., 2001; Ersoy et al., 2004; Karayannidou et al, 2006; Tan et al., 2006; etc.]. The equation in present-day form is as follows,
\[ K_d = K_c \exp[-C(\alpha - \alpha_c)] \]  

where \( K_c \) is the chemical rate constant, \( C \) is a constant, and \( \alpha_c \) is the critical degree of cure at the onset of diffusion control. As noted by Cole et al. [1991], the onset to diffusion is generally a gradual transition from chemical to diffusion control, rather than abrupt transition at \( \alpha_c \). Substituting this diffusion rate into the Rabinowitch equation and rearranging, a diffusion factor was found, \( f(\alpha) \) which became the denominator to the overall cure rate equation,

\[ f(\alpha) = \frac{K_c}{K_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \]

Cole et al. found that \( \alpha_c \) was linearly dependent on temperature, taking the form \( \alpha_c = \alpha_{c_T} T - \alpha_{c_0} \), with values of 0.005376 and 0.1350 \( \alpha_{c_T} \) and \( \alpha_{c_0} \), respectively, for a high-Tg epoxy system. The temperature relationship was found by plotting \( K_c/K_e \) versus conversion and observing the point at which the ratio drops from a value of 1. In actual fact, Cole et al. plotted the experimental values for \( \frac{da/dt}{da/\delta t} \) divided by the values predicted by the chemical model, since there are two \( K_c \)’s for the epoxy-amine reaction. Figure B.5 (a) illustrates the linear behaviour of the diffusion rate as described by the CP-C equation. Figure B.5 (b) shows the same isothermal data plotted against \( T - T_g \). Unlike the previous equations, WLF-W and ML-S, the cure rate increases with increasing temperature.

Chern and Poehlein established this equation based on a relationship between diffusion rate and fractional free volume,

\[ K_i = a^* \exp \left( -\frac{V^*}{V_f} \right) \]

where \( K_i \) is the reaction rate constant at a given conversion, \( a^* \) is a material constant (defined in the present work), \( V^* \) is an adjustable constant, an index that is a measure of the degree of diffusion control of reactions, and \( V_f \) is fractional free volume. Although the above equation is not explicitly stated in the authors’ work, it is obviously the starting point considering the equations they do propose. It is essentially the Doolittle equation, where \( K_i \) has replaced viscosity, \( a^* \) replaces \( a \), \( V^* \) could be the same as \( b \), and \( V_f \) is a different notation for \( f_c \). Chern and Poehlein have defined a critical fractional free volume, \( V_{fc} \), when the three-dimensional cross-linking network is just formed. This is similar in concept to the WLF approach wherein the limiting value for fractional free volume was that at \( T_g \). As in the WLF approach, Chern and Poehlein take the ratio of the above general term for reaction rate with \( V_{fc} \) and divide by the same term expressed specifically for \( V_{fc} \).
\[
\frac{K_i}{K_{i_0}} = \frac{a^* \exp(-V^*/V_f)}{a^* \exp(-V/V_{f_c})}
\]

which reduces to,

\[
\frac{K_i}{K_{i_0}} = \exp[-V^* (1/V_f - 1/V_{f_c})]
\]

It is at this junction that Chern and Poehlein create a different expression from WLF by suggesting that fractional free volume can be related to conversion by a polynomial,

\[
\frac{V^*}{V_f} = A_0 + A_1 \alpha + A_2 \alpha^2 \ldots
\]

The authors specifically propose that the relationship can be linear,

\[
\frac{V^*}{V_f} = A_0 + A_1 \alpha
\]

and argue that this linear relationship for free volume and conversion is true when the relationship between Tg and conversion is linear, \((T_g - T_{g_0})/(T_{g_c} - T_{g_0})\); the latter expression is the DiBenedetto equation when \(\lambda = 1\). The evidence presented for a linear relationship is relatively weak as the data for a Tg versus \(\alpha\) has curvature evident of a \(\lambda\) less than 1 (this particular data was taken from another author’s work). Essentially, the authors propose that

\[
\frac{1}{A_1 \left(\frac{V^*}{V_f} - A_0\right)} = \frac{T_g - T_{g_0}}{T_{g_c} - T_{g_0}}
\]

Substituting the linear relationship back into the ratio for reaction rate, the final expression is,

\[
\frac{K_i}{K_{i_0}} = \exp[-C(\alpha - \alpha_c)]
\]

where \(\alpha_c\) is the critical degree of cure, and \(C\) is a material constant (exchanged for \(A_1\)). To rewrite this equation in terms of \(T - T_g\), first replace \(\alpha\) with the DiBenedetto equation for \(\lambda = 1\),

\[
\frac{K_i}{K_{i_0}} = \exp\left[-C\left(\frac{T_g - T_{g_0}}{T_{g_c} - T_{g_0}} - a_{c_y} T + a_{c_0}\right)\right]
\]

\[
= \exp\left[-C(C_1(T_g - T_{g_0}) - a_{c_y} T + a_{c_0})\right]
\]

\[
= \exp\left[-C(C_1 T_g - a_{c_y} T + a_{c_0} - C_1 T_{g_0})\right]
\]

\[
= \exp\left[C(a_{c_y} T - C_1 T_g) + C_2\right]
\]

\[
= \exp\left[C_3(T - T_g) + C_2\right]
\]
where $C_1 = \frac{1}{T_g - T_{g_0}}$, $C_2 = -C(a_e - C_1 T_g)$, $C_3 = C a_{c_r} = \frac{C}{T_g - T_{g_0}}$, and $a_{c_r} = \frac{1}{T_g - T_{g_0}}$.

When $T = T_g$, $K_i = K_i_0 \exp[C_2]$, and rearranged $K_i_0 = K_i(T_g) \exp[-C_2]$. Substituting $K_i_0$ back into the above equation,

$$K_i = K_i(T_g) \exp[-C_2] \exp[C_3(T - T_g) + C_2]$$

B.36

To equate the CP-C equation with the WLF-W equation, set $Kd_0 = K_i(T_g)$ and $C_3 = \frac{C_{1-WLF}}{C_{2-WLF} + |T - T_g|}$.

Since $C_3 = \frac{C}{T_g - T_{g_0}}$ for the CP-C equation, $C$ would need to be equal to $\frac{C_{1-WLF}(T_g - T_{g_0})}{C_{2-WLF} + |T - T_g|}$. Figure B.5 (c) shows how the WLF-W and CP-C equations can produce the same results when the above relationships are used for the CP-C equation.

An adaptation to the CP-C equation was proposed by Fournier et al. [1996]. Using the final degree of cure for an isothermal instead of the critical degree of cure, which is difficult to measure, was argued by the authors to be a more accurate method. The proposed $f_d(\alpha)$ is as follows,

$$f_d(\alpha) = 2 \left[ \frac{1}{1 + \exp((\alpha - \alpha_f)/b)} - \frac{1}{2} \right]$$

B.37

where $b$ is a fitting parameter, and $\alpha_f$ is the final degree of cure. Previously, when $\alpha = \alpha_c$, $f_d(\alpha)$ became 0.5, and hence the rate of reaction was reduced to half. Now, when $\alpha = \alpha_f$, the cure rate should be zero rather than half, hence the term is multiplied by 2 and $\frac{1}{2}$ is subtracted to drive the reaction to zero when the final degree of cure is reached. Final degree of cure was found to be a natural logarithmic function of temperature, specifically $\alpha_f = 1.354 \ln(T) - 7.127$ for a low temperature cure DGEBA/DDM epoxy-amine system.

**B.4 Summary**

Similarities between the three equations:

- Based on free volume behaviour with temperature.
- The diffusion rate is inversely proportional to the Doolittle equation for viscous behaviour at some point in their generation;
- $T - T_g$ can be used to define the state;
• All equations can be reduced to the WLF-W form. Table B.1 outlines the necessary substitutions to achieve the WLF-W equation. Note, the equations still need to be rearranged to the WLF-W $f_d(\alpha)$ format, with the absolute values of $|T-T_g|$ applied in the denominator, in order to match the diffusion rate trends of the WLF-W equation.

Differences:

• Each equation imposes a different shape for $K_d(\alpha, T)$. Figures B.2 to B.5 illustrate this point. WLF-W has an S-shape decreasing in diffusion rate with cure (Figure B.2 a), ML-S exhibits an exponential decrease in diffusion rate with cure (Figure B.4 a), and CP-C decreases the diffusion rate linearly with cure reflecting the decision to treat free volume as a linear change with degree of cure or $T_g$ (Figure B.5 a).

• The CP-C equation allows for critical degree of cure (or $T_g$) to be temperature dependent, whereas WLF-W and ML-S do not. WLF-W will maintain $T=T_g$ at the maximum rate of change (or at $\frac{1}{2}K_e/K_c$). ML-S allows $T=T_g$ to occur when diffusion has a subtle effect (low degrees of cure) or influential effect (high degrees of cure) on the reaction rate depending on the values of parameters.
Table B.1 Equivalent terms to achieve the WLF-W equation

<table>
<thead>
<tr>
<th>Model</th>
<th>$K_d$</th>
<th>$f_d(\alpha)$</th>
<th>WLF-W Equivalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>WLF-W</td>
<td>$K_{d_0}$</td>
<td>$\exp\left[ \frac{C_1(T - T_g)}{C_2 +</td>
<td>T - T_g</td>
</tr>
<tr>
<td>ML-S</td>
<td>$K_{d_0}$, $A_0 \exp(-E_d/RT)$</td>
<td>$\exp\left[ -\frac{b}{f_v} \right]$</td>
<td>$K_{d_0} = K_d(T_g) \exp\left[ -\frac{b}{f_g} \right]$</td>
</tr>
<tr>
<td>CP-C</td>
<td>$K_{d_0}$</td>
<td>$\exp\left[ -C(\alpha - \alpha_c) \right]$, $\exp\left[ C_3(T - T_g) + C_2 \right]$</td>
<td>$K_{d_0} = K_d(T_g) \exp\left[ -C_2 \right]$</td>
</tr>
</tbody>
</table>

$$C_3 = \frac{C}{T_g - T_{g_0}}$$

$$C = \frac{C_{1-WLF}(T_g - T_{g_0})}{C_{2-WLF} + |T - T_g|}$$
Appendix B: Diffusion Models

Figure B.1 Relationship between free volume and viscosity, $b = 0.2, a_f = 0.00048 \, ^\circ C, f_g = 0.025, T_g_0 = 5^\circ C, T_g_\infty = 225^\circ C, \lambda = 1$

![Fractional Free Volume vs. Tg (°C)](image)

Figure B.2 (a) WLF-W rate of diffusion with cure, $K_d_0 = 1E-13 /sec, C_f = 40, C_2 = 51.6^\circ C, T_g_0 = 5^\circ C, T_g_\infty = 225^\circ C, \lambda = 1$

![WLF-W Kd (sec)](image)
Appendix B: Diffusion Models

Figure B.2 (b) WLF-W rate of diffusion with cure, $K_{d0} = 1 \times 10^{-13}$ /sec, $C_1 = 40$, $C_2 = 51.6^\circ\text{C}$, $T_{g0} = 5^\circ\text{C}$, $T_{g\infty} = 225^\circ\text{C}$, $\lambda = 1$

Figure B.3 (a) WLF rate of diffusion with cure, $K_{d0} = 1 \times 10^{-13}$ /sec, $C_1 = 40$, $C_2 = 51.6^\circ\text{C}$, $T_{g0} = 5^\circ\text{C}$, $T_{g\infty} = 225^\circ\text{C}$, $\lambda = 1$
Appendix B: Diffusion Models

Figure B.3 (b) WLF rate of diffusion with cure,
\( Kd_0 = 1 \times 10^{-13} \text{/sec}, C_1 = 40, C_2 = 51.6^\circ\text{C}, Tg_0 = 5^\circ\text{C}, Tg_\infty = 225^\circ\text{C}, \lambda = 1 \)

Figure B.4 (a) ML-S rate of diffusion with cure,
\( Kd_0 = 1 \times 10^{26} \text{/sec}, b = 2, a_t = 0.00048 /^\circ\text{C}, f_g = 0.025, Tg_0 = 5^\circ\text{C}, Tg_\infty = 225^\circ\text{C}, \lambda = 1 \)
Appendix B: Diffusion Models

Figure B.5  (a) CP-C rate of diffusion with cure, $Kd_0 = 1/\text{sec}$, $C = 60$, $a_{CT} = C_1 = 0.005/\text{oC}$, $a_{C0} = 0.22$, $T_{g0} = 5\text{oC}$, $T_{g\infty} = 225\text{oC}$, $\lambda =1$

Figure B.4  (b) ML-S rate of diffusion with cure, $Kd_0 = 1E26/\text{sec}$, $b = 2$, $a_f = 0.00048/\text{oC}$, $f_g = 0.025$, $T_{g0} = 5\text{oC}$, $T_{g\infty} = 225\text{oC}$, $\lambda =1$
Figure B.5 (c) Rate of diffusion with cure comparison between CP-C and WLF-W.

**CP-C parameters:**
- \( K_{d0} = 1 \text{ /sec} \)
- \( C = 60 \)
- \( a_{CT} = C_1 = 0.005 \text{ /°C} \)
- \( a_{C0} = 0.22 \)
- \( T_{g0} = 5\text{°C} \)
- \( T_{g\infty} = 225\text{°C} \)
- \( \lambda = 1 \)

**WLF-W parameters:**
- \( K_{d0} = 1 \text{ /sec} \)
- \( C = 40 \)
- \( C_2 = 51.6 \text{°C} \)
- \( \lambda = 1 \)

**Degree of Cure**

Figure B.5 (c) Rate of diffusion with cure comparison between CP-C and WLF-W.

CP-C parameters:
- \( K_{d0} = 1 \times 10^{-13} \text{ /sec} \)
- \( C_1 = 0.0045455 \text{ /°C} \)
- \( a_{C0} = 0.15 \)
- \( C_1-WLF = 2.303\times40 \)
- \( C_2-WLF = 51.6 \text{°C} \)
- \( T_{g0} = 5\text{°C} \)
- \( T_{g\infty} = 225\text{°C} \)
- \( \lambda = 1 \)

WLF-W parameters:
- \( K_{d0} = 1 \times 10^{-13} \text{ /sec} \)
- \( C_1 = 40 \)
- \( C_2 = 51.6 \text{°C} \)
- \( \lambda = 1 \)
Appendix C. ROUND ROBIN DOCUMENTATION

C.1 Agreement Forms
The forms presented here are based on the recommended language and format from ASTM.

Laboratory Coordinator's Agreement:
This is to confirm that our laboratory is qualified in terms of facilities and testing experience, competent operators, familiarity with the test method, and time and interest to be a diligent participant of this Round Robin. If the laboratory experimentalist conducting the Round Robin has insufficient experience with the test methods for cure kinetic model development (or data analysis methods), I will ensure that the experimentalist receives appropriate familiarization before beginning the Round Robin. Data and reports will be returned to the Round Robin Coordinator by the times specified. Any questions or errors regarding the procedure will be reported immediately to the Round Robin Coordinator. All persons involved in the Round Robin study within my lab have read and understood the accompanying documentation. I understand all that is involved to complete the tests requested by the study within my laboratory, and agree to carry out its responsibility with diligence.

Signature of Laboratory Coordinator: _______________________________
Print Name Here: _______________________________
Date Signed: ________________________________ (YY/MM/DD)

Laboratory Participants’ Agreement:
I will adhere to: manufacturer's specifications for DSC calibration, proper handling and storage of materials, be familiar with testing and data analysis methods required to be a participant in this study, perform all tasks with due diligence, complete data reports clearly and to the fullest, check results with the Laboratory Coordinator for errors, return the results to the Round Robin Coordinator by the dates on the time-line, report any questions or errors regarding the procedure immediately to the Round Robin Coordinator.
C.2 Material Received Response Form

Please return the designated material to the UBC Composites Lab with your signature on this form immediately after receiving the material for the Round Robin.

Mail To:
(Round Robin Coordinator)

Mailing Address and Contact Information

This package should include CFRP for Round Robin testing, a sample of CFRP to be sent back to the Round Robin Coordinator immediately upon receiving the material, MSDS sheets for the CFRP, materials for calibration check tests, Preliminary Information Form to be completed, and instructions for preliminary tests. Please use gloves and tongues to handle the raw material to avoid contamination. See the enclosed MSDS sheets.

Time and Date material received: ______________ (YY/MM/DD), __________ (AM/PM)
Time and Date material was put in the freezer for storage: ________________ (YY/MM/DD),
____________ (AM/PM)

My signature ensures that the material was received, double bagged, and immediately stored at –20 ºC. Stage 0 of the Round Robin, including completion of the Preliminary Information Forms Part A and Part B and accompanying experimental data and analysis will be completed and returned to the UBC Composites Laboratory via E-mail by (Date Here), or when your laboratory begins testing.
### C.3 Preliminary Form Part A: DSC CFRP Measurement Uncertainty and Instrument Quality

Return the completed table below via E-mail to the Round Robin Coordinator by: (Date Here)

<table>
<thead>
<tr>
<th>Name of Manufacturer</th>
<th>Instrument Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of measuring instrument (highlight one)</th>
<th>Heat flux disk-type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heat flux cylinder type</td>
</tr>
<tr>
<td></td>
<td>Power compensation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample volume to be used during the Round Robin (standard crucible)</th>
<th>mm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atmosphere to be used during the Round Robin (vacuum?, gases?, pressure?)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature range (manufacturer’s information)</th>
<th>From . . . to . . . °C or K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Scanning rates (manufacturer’s information)</th>
<th>From . . . to . . . K/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Zero-line repeatability¹,² 2 °C/min Atmosphere: | From ± . . . μW (at 50 °C) |
|                                               | to ± . . . μW (at 125 °C)  |
|                                               | to ± . . . μW (at 200 °C)  |
|                                               | to ± . . . μW (at 275 °C)  |
|                                               |                            |

| Zero-line repeatability 5 °C/min Atmosphere: | From ± . . . μW (at 50 °C) |
|                                               | to ± . . . μW (at 125 °C)  |
|                                               | to ± . . . μW (at 200 °C)  |
|                                               | to ± . . . μW (at 275 °C)  |
|                                               |                            |

<table>
<thead>
<tr>
<th>Peak area repeatability³ Atmosphere:</th>
<th>± . . . % (Tin, average . . . J/g) mass . . . mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Extrapolated peak onset temperature repeatability⁴</th>
<th>± . . . °C (Tin, average . . . °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Scanning noise⁵ (pp) at 2 °C/min</th>
<th>From ± . . . μW (at 100 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to ± . . . μW (at 250 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Scanning noise (pp) at 5 °C/min</th>
<th>From ± . . . μW (at 100 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to ± . . . μW (at 250 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isothermal noise⁶ (pp) Atmosphere:</th>
<th>From ± . . . μW (at 100 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to ± . . . μW (at 250 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>


**Notes:**

1. Repeatability is a quantitative measure of the precision of the results by a single analyst in a given laboratory using a given apparatus (ASTM E 2161 Standard Terminology Relating to Performance Validation in Thermal Analysis). Please ask one instrument
operator to perform all DSC experiments for consistency, including these preliminary tests.

2. The zero-line is the curve measured with the instrument empty, i.e. without samples and without sample containers (crucibles), or without samples and with the sample containers (crucibles) empty. For this test the zero-line will be taken to mean the curve without samples and without sample containers. Zero-line repeatability is determined by measuring 4 or 5 zero-lines (over the whole temperature range at medium scanning rate and superimposing the curves. The temperature-dependent range of the deviation from the ‘mean’ zero-line (absolute or in %) gives the repeatability. Use the atmosphere that will be employed during Round Robin testing and report all necessary testing conditions. Perform two sets of tests, one set at each heating rate of 2 and 5 °C/min. Open the sample chamber/cell/furnace before each test and allow the instrument to equilibrate before starting the heating ramp.

3. Repeatability of the peak area is determined by measuring the peak area caused by the melting of a pure metal several times under the same condition (either only repeat measurements without moving the sample crucible or with replacing the crucible after each run). In this work, the participant will be given a sample of tin. The sample should be run through the temperature cycle first, and area measurements taken on the subsequent four tests. The sample should be removed and replaced before each test. The heating rate to be used is 5 °C/min to 260 °C. The repeatability of the peak area also intrinsically includes the repeatability of the baseline under the peak. Use the atmosphere that will be employed during the Round Robin and also report the mass of the sample. Take care to place the sample in the same position for each test.

4. The onset point refers to the intersection of two slopes. Repeatability of the onset temperature for a peak area is determined by measuring the onset temperature caused by the melting of a pure metal several times under the same condition. Measure the onset temperatures of the temperature ramp tests from (3) for Tin to obtain the onset temperature repeatability.

5. The peak-to-peak noise (pp) is the maximum variation of the measured signal in relation to the mean signal value. Use the zero-lines to measure the ‘short-time’ noise over a 1-minute period at the indicated temperatures.
6. Perform two tests using the atmosphere to be used during Round Robin testing, without samples or crucibles, at 100 and 250 °C. The ‘short term’ isothermal noise can be measured over a 1-minute period once the temperature has equilibrated.

Please provide a brief description or a scanned copy of the manufacturer’s calibration guidelines.

C.4 Preliminary Form Part B

Complete and return the following:

1. Completed Preliminary Information Form, Parts A and B
2. Description of manufacturer's DSC calibration procedures (may be a scanned copy of your instrument manual, or a brief written description)

1. Data for 3 calibration check tests:
   1 temperature ramp at 5 °C/min for indium to 200 °C,
   _ / / _ RR S0 T7, mass _ _ _ _ mg
   1 temperature ramp at 5 °C/min for tin to 260 °C,
   _ / / _ RR S0 T8, mass _ _ _ _ mg
   1 temperature ramp at 5 °C/min for zinc to 450 °C,
   _ / / _ RR S0 T9, mass _ _ _ _ mg

4. Spreadsheet data of 6 tests for CFRP material:
   3 temperature ramps from -30 to 320 °C at 5 °C/min
   Labels: _ / / _ RR S0 T1, mass _ _ _ _ mg, out of storage time ____ min
   _ / / _ RR S0 T2, mass _ _ _ _ mg, out of storage time ____ min
   _ / / _ RR S0 T3, mass _ _ _ _ mg, out of storage time ____ min
   where the date corresponds with YY/MM/DD, S stands for stage and T for test

   3 temperature ramps from -30 to 320 °C at 2 °C/min
   Labels: _ / / _ RR S0 T4, mass _ _ _ _ mg, out of storage time ____ min
   _ / / _ RR S0 T5, mass _ _ _ _ mg, out of storage time ____ min
   _ / / _ RR S0 T6, mass _ _ _ _ mg, out of storage time ____ min
6 calculated values for $T_g$ and $H_{\text{ultimate}}$, with accompanying baselines in the spreadsheets

$H_{\text{ultimate}}$ Values:

- $T_1 \quad J/g$, $T_g \quad ^\circ C$
- $T_2 \quad J/g$, $T_g \quad ^\circ C$
- $T_3 \quad J/g$, $T_g \quad ^\circ C$
- $T_4 \quad J/g$, $T_g \quad ^\circ C$
- $T_5 \quad J/g$, $T_g \quad ^\circ C$
- $T_6 \quad J/g$, $T_g \quad ^\circ C$

5. Return all tested samples, appropriately labelled to the UBC laboratory.

Notes:

1. Include 3 decimal places for all data and measurements
2. First perform a temperature scan on the metal sample through its melting point, and use a second temperature scan to obtain the melting endotherm
3. DSC samples of prepreg must not leak during the experiment to be considered a valid test
4. Please use gloves and tongues to handle the material to avoid contamination
5. Remove the material from the freezer for short as possible times and record the 'out of storage time' before testing

C.5 Stage 1 Instructions to Participants

Instructions for Stage 1:

1. Use gloves and tongues to handle the raw material at all times, see the MSDS sheets.
2. Perform a quality control test: temperature ramp at 5 $^\circ C$/min to 320 $^\circ C$, measure the $T_g$ and $H_{\text{ultimate}}$; if the value for $T_g$ and $H_{\text{ultimate}}$ differ greatly from the values found in Stage 0, repeat the test again to make sure there were no errors in the experiment; if the difference persists, contact the Round Robin Coordinator.
3. Plan the experimental method and number of tests to be performed as would normally be done in your laboratory, as well as repeatability test sets if a regular part of your laboratory cure kinetics protocol.
4. Randomize the test sequence before starting experimentation.
5. Label all data and samples appropriately starting with YY/MM/DD RR S1.
6. Record the test sequence, dates of each experiment, sample mass, time out of storage, and measurements (e.g. area, temperature).
7. Provide a clear/brief written description of the experimental method, data analysis, and
model fitting method.

8. Spreadsheet must include data analysis tools such as baselines or onset points. E.g. spreadsheet column titles should include Time, Temperature, Heat Flow (W/g), Baseline (W/g) as necessary.

9. Send to the Round Robin Coordinator via E-mail all data and analysis and record sheet(s). Properly label samples and ship to the UBC laboratory.

Example data record sheet to be sent to Round Robin Coordinator:

Quality Control Test Result: 5 ºC/min temperature ramp to 320 ºC
YY/MM/DD RR S1 T0, mass = _ _ _ _ _ _ mg, H_{ultimate} = _ _ _ _ _ _ J/g, Tg _ _ _ _ _ _ ºC

Example Experimental Method Details:
A series of isothermal tests at 130, 150, 170 ºC, held for 2 hours each, baseline selected as a straight line between two points, area under the curve calculated. Repeated 3 times each temperature.

Example Test Data and Measured Results:

<table>
<thead>
<tr>
<th>Sample/Test Label</th>
<th>Sample Mass</th>
<th>Test Condition</th>
<th>Measurement Type</th>
<th>Measured Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>YY/MM/DD RR S1 T1 Out of freezer time before testing: ____ min</td>
<td>8 mg</td>
<td>Isothermal 180ºC, 2 hours hold</td>
<td>Area under peak</td>
<td>130 J/g (prior to V_f adjustment)</td>
</tr>
<tr>
<td>YY/MM/DD RR S1 T1 Out of freezer time before testing: ____ min</td>
<td>8 mg</td>
<td>Residual Ramp at 5 ºC/min</td>
<td>Area under peak</td>
<td>50 J/g</td>
</tr>
<tr>
<td>YY/MM/DD RR S1 T2 Out of freezer time before testing: ____ min</td>
<td>100 mg</td>
<td>Ramp at 10 ºC/min</td>
<td>Peak temperature</td>
<td>210 ºC</td>
</tr>
</tbody>
</table>
Excel file name containing all data and analysis (including quality control test results):
_____________________________________. All data should be in SI units to three figures after the decimal place.

**Example Model:**

\[ \frac{d\alpha}{dt} = K\alpha^n (1-\alpha)^n \]

where \( K = _\ldots \ldots \), \( m = _\ldots \ldots \), \( n = _\ldots \ldots \)

**Example Model Fitting Details:**

Equations/plots used to find \( E_a \), \( A \) of the Arrhenius expression, solution methods for all model parameters, fitting methods used such as Least Squares, etc.

### C.6 Stage 2 Instructions

E-mail results to Round Robin Coordinator by (Date Here)

i. Perform a quality control check for the glass transition temperature and heat of reaction, \( 5 \) °C/min, from \( -30 \) to \( 320 \) °C.

ii. Based on analysis of the aggregate data submitted, the UBC laboratory will recommend a method of sample size and preparation. If the submitted data from participants in Stage 1 already complies with the recommendation for sample preparation, the study will progress to Stage 3 for those participants. If not, participants will be asked to perform a limited number of tests from Stage 1 to observe the difference sample size makes to the results. If there is no difference, participants will be asked to move onto Stage 3. If there is a large difference, participants will be asked to repeat the tests of Stage 1 using the recommended sample size and preparation. Variations in instrument sample size specifications will be taken into consideration. Subsequent Stages should use the recommended sample
size and preparation method. Details of the experimental preparation, measurement method, data reduction technique and model will be reported to the Round Robin coordinator, accompanied by the data, data reduction, analysis and model parameters. Refer to Stage 1 Form in Appendix A, for an example of how to report the findings.

C.7 Stage 3 Instructions

E-mail results to Round Robin Coordinator by (Date Here)

i. Based on analysis of the aggregate data submitted, the UBC laboratory will provide a raw DSC data set for each laboratory to reduce and fit a model to at the discretion of the participants. The data will be in the form of heat flow, time, and temperature values before the application of any data reduction techniques such as baselines. The participant is asked to complete the data reduction, data analysis and model fitting and return the results to the Round Robin Coordinator.

C.8 Stage 4 Instructions

E-mail results to Round Robin Coordinator by (Date Here)

i. Based on analysis of the aggregate data submitted, the UBC laboratory will provide an exact data set with the data reduction complete, e.g. baselines. The participant is asked to complete the data analysis and model fitting and return the results to the Round Robin Coordinator.
C.9 Stage 5 Instructions

E-mail results to Round Robin Coordinator by (Date Here)

i. Based on analysis of the aggregate data submitted, the UBC laboratory will recommend a specific model for fitting the data of Stage 4. The participant is asked to complete the data analysis and model fitting and return the results to the Round Robin Coordinator.
Appendix D. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) was used to measure the onset temperature of degradation during dynamic scans at heating rates matching MDSC dynamic tests. The onset temperature of degradation was used in this work to create a baseline capable of subtracting the degradation reaction from the nonreversing heat flow magnitude when cure and degradation peaks overlapped at the end of cure.

D.1 TGA Instrumentation and Operation

TGA measures the change in sample mass during a programmed temperature cycle. This instrument may be used in the degradation temperature region of the epoxy because a gas flow is capable of removing effluent and volatiles (an unadvisable practice for MDSC due to cell contamination issues). Heating the material to high temperatures, 600°C in this work, burns-off the resin and the remaining mass should be fibres, and hence one can calculate the mass fraction of the resin, and volume fraction if the densities of resin and fibers are known.

TA Instruments’ TGA Q500 was employed. This instrument claims an isothermal temperature accuracy of ± 1°C and precision of ± 0.1°C, and a continuous weighing capacity of 1.0 g, sensitivity of 0.1 µg and weighing precision of ± 0.01%. For T800H/3900-2, prepreg was placed with tongs in open, platinum pans and subsequently hung by an automated arm on one end of the TGA horizontal balance. The furnace was raised automatically to enclose the pan. Nitrogen gas was chosen to fill and purge the chamber to ensure that only the resin and not the carbon fibres would degrade, and to match the MDSC environment. The rate of nitrogen flow was 50ml/min, which enters the furnace and flows directly across the sample to remove decomposition products from the sample area. Temperature control and measurement was facilitated by a thermocouple positioned immediately adjacent to the sample. A second thermocouple is placed above the first such that if the difference between the two exceeds a set value, the furnace will be disabled. The mass loss was measured by the TGA balance during a dynamic heating schedule. Heating rates included 0.2, 0.5, 1, 2, 3, 4 and 10 °C/min, between room temperature and 600°C (0.2 and 0.5 °C/min tests were ramped between 60 and 40°C, respectively, and 400°C in the interest of time). The average sample mass was 17.29 ± 2.41 mg, one sample for each heating rate. The sample was laid on the pan as a single ply. Samples were uncured before testing.
D.2 Measuring the Onset Temperature of Degradation

Figure D.1 (a) shows the percent weight loss with temperature increase for the seven heating rates, and (b) a reduced scale to magnify the onset of degradation. Although it is evident from this view that the degradation temperatures increase with heating rate, the exact onset temperature was difficult to pinpoint using the percent weight measurement. To clarify the observed changes in percent weight, Figure D.2 (a) shows the derivative of the percent weight with temperature, and (b) the same plot with a reduced scale. Two peaks in the TGA derivative profiles were evident within the temperature region of cure, Figure D.2 (b). The onset temperature of the first peak occurred between 110 and 160°C across the range of heating rates tested. For heating rates 0.2 to 10°C/min, the onset temperatures of the main degradation peak were recorded as follows: 217, 220, 224, 245, 252, 259, 276°C. This first loss of mass is also evident in Figure D.1 (b), for which the loss is at most 0.5% for the highest heating rate, and plateaus after this decrease before continuing to degrade.

To further clarify the onset temperature of degradation, Figure D.3 shows a 2°C/min MDSC test ramped to 400°C to observe the degradation exotherm, overlaid with the 2°C/min TGA test. According to this illustration, the main degradation peak of the TGA test coincided very well with the second peak of the MDSC test which was thought to be due to degradation, starting at roughly 240°C. Hence, the onset temperature of resin degradation was designated as the onset to the main peak in the derivative of percent weight with respect to temperature signal (as recorded above), and the smaller peak was considered to be a negligible contribution to the main resin degradation process.
Appendix D: Thermogravimetric Analysis

Figure D.1 (a) TGA measured weight loss during degradation of T800H/3900-2 at various heating rates.

Figure D.1 (b) TGA measured weight loss during degradation of T800H/3900-2 at various heating rates, reduced scale.
Appendix D: Thermogravimetric Analysis

Figure D.2 (a) Derivative of weight loss with respect to temperature during degradation of T800H/3900-2 at various heating rates

Figure D.2 (b) Derivative of weight loss with respect to temperature during degradation of T800H/3900-2 at various heating rates, reduced scale
Figure D.3  Comparison of MDSC nonreversing heat flow and TGA derivative of % weight with respect to temperature during a 2°C/min ramp to 400°C
Appendix E. SPECIFIC HEAT CAPACITY MODEL

A model for specific heat capacity (Cp) of a thermosetting material was developed by Dr. Ali Shakarami of Convergent Manufacturing Technologies in September of 2007. The model considers the transition in Cp with increasing temperature from a rubbery to a glassy state (Cp_r versus Cp_g), in both the uncured and fully cured states (Cp_r0 versus Cp_r∞, and Cp_g0 versus Cp_g∞) by the following linear equations:

\[
Cp_r = s_r T + c_r \quad \text{E.1}
\]

\[
Cp_{r∞} = s_{r∞} T + c_{r∞} \quad \text{E.2}
\]

\[
Cp_g = s_g T + c_g \quad \text{E.3}
\]

\[
Cp_{g∞} = s_{g∞} T + c_{g∞} \quad \text{E.4}
\]

The rubbery and glassy Cp behaviour with changing degree of cure is described by adding the fractions of the uncured and cured Cp values, and is illustrated in Figure E.1:

\[
Cp_r = (1 - \alpha)Cp_r0 + \alpha Cp_{r∞} \quad \text{E.5}
\]

\[
Cp_g = (1 - \alpha)Cp_g0 + \alpha Cp_{g∞} \quad \text{E.6}
\]

The overall Cp behaviour transitions between these two straight line relationships for the rubbery and glassy states when the material vitrifies and devitrifies. The vitrification/devitrification transition follows the T-Tg relationship and its proximity to a value specific to a material (traditionally thought to be zero, but recently shown to be nonzero by Van Mele [Data] and Yang and Simon [2005]), referred to here as \(\Delta T_c\). The Cp transitions according to the proximity of T-Tg to \(\Delta T_c\) (Figure E.1), modeled here as an S-shape such that Cp has the form

\[
Cp = Cp_r - \frac{Cp_r - Cp_g}{1 + \exp(K((T - Tg) - \Delta T_c))} \quad \text{E.7}
\]

where \(K\) is a shaping parameter which sets the breadth of the transition. When \(T-Tg = \Delta T_c\) the Cp is at the midpoint of the vitrification/devitrification transition, \(\frac{1}{2}\Delta Cp\).

T800H/3900-2 Cp data was fit with equations E.1 to E.7 using the following tests: 0.2, 0.5, 1, 1.5, 2, 3, 4, 5, 8 10 °C/min; 130, 140, 150, 160, 170, 180, 190, 200 °C. The Tg model for was taken as equation 5.8, which accounts for increasing Tg with phase separation. The model was first fit to dynamic data which was shifted in Cp such that all of the data overlapped above the Tg0 transition, Figures E.2 to E.7. Parameters found by least squares regression are recorded in Table E.1. The model was then compared to the isothermal data, Figure E.8 to E.12. The model does not fit well to the initial rubbery isothermal and
dynamic data, although the timing of the dynamic $T_g_0$ transition matches the data well, as does the timing of the vitrification and devitrification transitions in both the isothermal and dynamic data. The most likely reason for the discrepancy is that the breadth of the transition is fixed in the model whereas it actually changes with cure. As shown in Figures E.6 and E.7, the $T_g_0$ transition is broader for the model than the data. The best fit of the model was found for the transition to, and behaviour within, the glassy state since it is this state that is of most concern for design purposes. The $C_p$ model fit to dynamic data is within ±2% error (Data-Model ÷ Data), except for the $T_g_0$ transition which is within 15%. The $C_p$ model fit to isothermals is within -2 to 1% error, the largest errors measured for the rubbery behaviour.
Figure E.1  Cp glassy and rubbery states, T800H/3900-2 Cp models for 0.2°C/min dynamic

Figure E.2  Cp transition between glassy and rubbery states (T800H/3900-2 model, 0.2°C/min dynamic)
Figure E.3 Cp model fit to T800H/3900-2 0.5°C/min dynamic

Figure E.4 Cp model fit to T800H/3900-2 1°C/min dynamic
Appendix E: 
Cp Model for T800H/3900-2

Figure E.5 Cp model fit to T800H/3900-2 1.5°C/min dynamic

Figure E.6 Cp model fit to T800H/3900-2 2°C/min dynamic
Appendix E: Cp Model for T800H/3900-2

Figure E.7 Cp model fit to T800H/3900-2 4°C/min dynamic

Figure E.8 Cp model fit to T800H/3900-2 10°C/min dynamic
Appendix E: Cp Model for T800H/3900-2

Figure E.9 Cp model fit to T800H/3900-2 130°C isothermal

Figure E.10 Cp model fit to T800H/3900-2 150°C isothermal
Appendix E: Cp Model for T800H/3900-2

Figure E.11 Cp model fit to T800H/3900-2 170°C isothermal

Figure E.12 Cp model fit to T800H/3900-2 190°C isothermal